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Activation and Reaction Volumes in Solution. 2

R. VAN ELDIK,*[†] T. ASANO,*[‡] and W. J. LE NOBLE*[§]

Institute for Inorganic Chemistry, University of Witten/Herdecke, 5810 Witten, FRG, Department of Chemistry, Faculty of Engineering, Oita University, Oita 870-11, Japan, and Department of Chemistry, State University of New York at Stony Brook, Stony Brook, New York 11794

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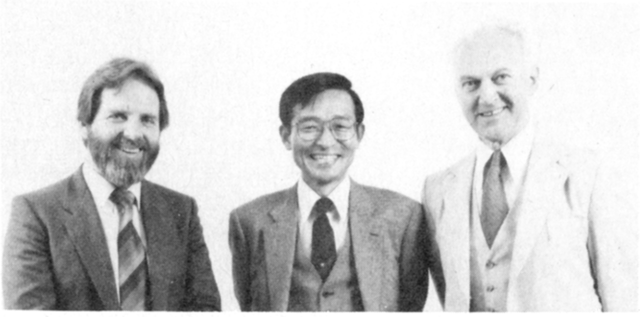

Rudi van Eldik (left) was born in Amsterdam, Holland, and grew up in South Africa, where he received his B.Sc., M.Sc., and Ph.D. (1971) degrees from Potchefstroom University. He spent 2 years (1972 and 1978) with Gordon M. Harris at SUNY at Buffalo and 1 year as an Alexander von Humboldt Fellow with Hartwig Kelm at the University of Frankfurt. He was appointed as Professor of Chemistry at Potchefstroom University (1979) and was awarded the Raikes Medal by the SA Chemical Institute in the same year. He took up the position of group leader at the Institute for Physical Chemistry, University of Frankfurt (1980), where he completed his Habilitation in Physical Chemistry (1982). He was appointed as Professor of Inorganic Chemistry at the University of Witten/Herdecke in 1987. His research interests are in mechanistic studies of inorganic, organometallic, and bioinorganic reactions, with special emphasis on the application of high-pressure techiques.

Tsutomu Asano (middle) was born in Osaka, Japan, in 1941. He obtained an undergraduate degree in chemistry at Kyoto University, followed by a Ph.D. at the same institute in 1969. He was introduced to high-pressure chemistry by the late Professor Ryozo Goto at the beginning of his graduate work. After postdoctoral work with Professor William J. le Noble, he returned to Kyoto and worked for Professor Jiro Osugi. He joined the faculty of Oita University in 1975, where he is now a Professor of Chemistry. His primary interests are in application of high-pressure kinetics to the elucidation of organic reaction mechanisms. His recent study is concentrated in thermal cis–trans type isomerizations about nitrogen–nitrogen and carbon–nitrogen double bonds.

Bill le Noble (right) is a native of Rotterdam, The Netherlands. He did undergraduate work in chemical engineering in Dordrecht and then moved to the U.S. in 1949. After a stint in the U.S. Army, which included wartime service in Korea, he attended the University of Chicago and received a Ph.D. degree in organic chemistry with Professor G. Wheland. Postdoctoral work at Purdue University was followed in 1959 by an appointment at the State University of New York at Stony Brook, where he has stayed ever since. He has held Visiting Professorships at the Free University of Amsterdam and the University of Groningen, received Humboldt Senior Scientist and Mombusho Special Professorship Awards, and serves as Senior Editor of the *Journal of Organic Chemistry* and *Recueil*. His research interests include, besides high-pressure organic chemistry, stereoelectronic control of stereochemistry.

[†] University of Witten/Herdecke.
[‡] Oita University.
[§] State University of New York at Stony Brook.

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1. Introduction

A. Scope

Two of us reviewed the activation and reaction volumes of chemical reactions in solution 10 years ago. We covered the literature to the end of 1976.[1] The main part of that review concerned reactions of organic systems. Due to the veritable data explosion in the area of inorganic/coordination chemistry, an additional author is now included to take responsibility for that section of the data. Our objective here has been to present a listing as complete as possible of the activation and reaction volumes for all chemical reactions in solution published during the period from January 1977 to the end of 1986; some 1987 data have become available and were also incorporated. This review therefore covers 10 years of activity in this field.

The organization of the data follows that of the earlier review; i.e., they are organized in tabular form according to the type of reaction studied. In the accompanying text the mechanistic implication of the data is discussed and detailed analyses are presented. Several reviews have appeared since 1977 that are more limited in scope (though perhaps also more critical); among these there are accounts dealing with chemistry and biochemistry,[2-6] organic synthesis,[7,8] inorganic reactions,[9-24] photochemical and photophysical aspects,[25,26] and the dynamic structure of solvents.[27] We note that the Proceedings of the NATO ASI on High Pressure Chemistry and Biochemistry[6] held in Corfu 1986 is an update of the earlier proceedings published on the ASI held in 1977. Those interested in becoming actively involved in high-pressure research should consult these Proceedings.

B. The Basic Concepts

In general, the kinetic approach to elucidate the mechanism of a chemical reaction involves the measurement of reaction rates and rate constants as a function of many chemical and physical variables. Much emphasis is usually placed on the activation parameters obtained from the temperature dependence of the reaction. The accuracy of the suggested reaction mechanism is likely to increase with increasing number of variables covered during such investigations. This is one of the reasons why pressure has been included as a kinetic (or thermodynamic) variable in an increasing number of studies over the past decade. Such additional information may assist not only in the elucidation of the intimate reaction mechanism, but it may also reveal new fundamental aspects of the studied systems, and thus add to the comprehension of reaction kinetics.

Pressure is a fundamental physical property that influences the values of different thermodynamic and kinetic parameters. In the same way as temperature-dependence studies tell us something about the energetics of the process, pressure-dependence studies reveal information on the volume profile of the process. For any reaction in solution (1), the reaction volume $\Delta\bar{V}$ is

$$\mathrm{A} + \mathrm{B} \rightleftharpoons [\mathrm{A}\text{---}\mathrm{B}]^{\ddagger} \rightarrow \mathrm{AB} \tag{1}$$

$$\Delta\bar{V} = \bar{V}_{\mathrm{AB}} - \bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{B}} \tag{2}$$

defined by (2) and the activation volume $\Delta V^{\ddagger}$ by (3),

$$\Delta V^{\ddagger} = \bar{V}_{\ddagger} - \bar{V}_{\mathrm{A}} - \bar{V}_{\mathrm{B}} \tag{3}$$

where $\bar{V}$ denotes the partial molar volume of the reactant or product species. The relationships between $\Delta\bar{V}$ and $\Delta V^{\ddagger}$ and the pressure dependence of equilibrium and rate constants, respectively, find their origin in the fundamental thermodynamic equations (4) that describe the pressure dependence of the chemical potential μ_i of a solute species i in an ideal solution.

$$\left(\frac{\partial\mu_i}{\partial P}\right)_T = \bar{V}_i \tag{4}$$

The chemical potential can be expressed in terms of mole fraction (x), molality (m), and molarity (M), as shown in (5). Since x and m are pressure-independent

$$\begin{aligned}\mu_i &= \mu_i^{\circ}(x) + RT\ln x_i\\ &= \mu_i^{\circ}(m) + RT\ln m_i\\ &= \mu_i^{\circ}(M) + RT\ln M_i\end{aligned} \tag{5}$$

concentration scales, differentiation with respect to pressure results in (6). In the case of the molarity

$$\left(\frac{\partial\mu_i^{\circ}(x)}{\partial P}\right)_T = \left(\frac{\partial\mu_i^{\circ}(m)}{\partial P}\right)_T = \left(\frac{\partial\mu_i}{\partial P}\right)_T = \bar{V}_i \tag{6}$$

concentration scale, M_i changes with pressure in the same way as the density of the solution; eq 7 then applies, where κ is the compressibility of the solution.

$$\left(\frac{\partial\mu_i^{\circ}(M)}{\partial P}\right)_T = \left(\frac{\partial\mu_i}{\partial P}\right)_T - RT\left(\frac{\partial\ln\rho}{\partial P}\right)_T = \bar{V}_i - RT\kappa \tag{7}$$

For a general chemical reaction (8), the chemical potential at equilibrium should be zero, and the pressure dependence of K_x (or K_m) is given by eq 9, where

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons r\mathrm{R} + s\mathrm{S} \tag{8}$$

$$-RT\left(\frac{\partial\ln K_x}{\partial P}\right)_T = r\bar{V}_{\mathrm{R}} + s\bar{V}_{\mathrm{s}} - a\bar{V}_{\mathrm{A}} - b\bar{V}_{\mathrm{B}} = \Delta\bar{V} = \sum\bar{V}_{\mathrm{products}} - \sum\bar{V}_{\mathrm{reactants}} \tag{9}$$

$K = x_{\mathrm{R}}{}^{r}x_{\mathrm{S}}{}^{s}/x_{\mathrm{A}}{}^{a}x_{\mathrm{B}}{}^{b}$, if the overall equilibrium constant is expressed in terms of mole fraction (or molality for K_m). In the case of the molarity concentration scale, eq 7 must be applied, and the appropriate expression for the pressure dependence of K_M ($=M_{\mathrm{R}}{}^{r}M_{\mathrm{S}}{}^{s}/M_{\mathrm{A}}{}^{a}M_{\mathrm{B}}{}^{b}$) is given in (10). These thermodynamic relationships

$$-RT\left(\frac{\partial\ln K_M}{\partial P}\right)_T = \Delta\bar{V} - RT\kappa(r + s - a - b) \tag{10}$$

can be extended to rate constants by adopting the transition-state theory, according to which it is assumed that reaction 8 proceeds through a transition state that exists in equilibrium with the reactant species. This is formulated in eq 11, where $K^{\ddagger}$ obeys the thermody-

$$a\mathrm{A} + b\mathrm{B} \overset{K^{\ddagger}}{\rightleftharpoons} [a\mathrm{A}\text{---}b\mathrm{B}]^{\ddagger} \rightarrow r\mathrm{R} + s\mathrm{S} \tag{11}$$

namic relationships given above, and the experimentally measured rate constant k is assumed to be proportional to $K^{\ddagger}T$. Since k has then the same concentration dimensions as $K^{\ddagger}$, eq 9 and 10 can be used to describe the pressure dependence of k in terms of the activation volume $\Delta V^{\ddagger}$ as given in (12) and (13), where $\Delta V^{\ddagger} = \bar{V}_{\ddagger} - a\bar{V}_{A} - b\bar{V}_{B}$.

$$-RT\left(\frac{\partial \ln k_x}{\partial P}\right)_T = -RT\left(\frac{\partial \ln k_m}{\partial P}\right)_T = \Delta V^{\ddagger} \quad (12)$$

$$-RT\left(\frac{\partial \ln k_M}{\partial P}\right)_T = \Delta V^{\ddagger} - RT\kappa(1 - a - b) \quad (13)$$

It follows that in the case of a first-order process, the expressions for the pressure dependence of k_x, k_m, and k_M are identical. However, for reactions of a higher order the additional term in eq 13 should be taken into account, which could vary between 1 and 6 cm^3 mol^{-1}, depending on the solvent used.[5,28] It is important to note that this term has caused much misunderstanding in the literature and that it has led to many incorrectly applied "corrections" of rate constants higher than first order. This situation has come about because many workers have failed to realize that moles/liter *at 1 atm* is a pressure-independent unit just as much as mole fraction or molality; if, as is usually the case, the concentrations are known in this unit (of moles/liter *at 1 atm*), no correction must be applied, and to do so leads to wrong results. A correction is needed only *if* the concentrations are only known as moles/liter at the pressures at which they are used, *and if* one wishes to calculate an activation (or reaction) volume from these data.

Of course, *if* one wishes to record the rate or equilibrium constants simply in terms of moles/liter, without specifying the pressure, then one needs to know the compressions that have occurred at the pressures at which these constants were measured. This is done by calculating M_i indirectly by correcting the normal-pressure value M_i^* for the increase in pressure by means of relationship 14, where ρ is the density of the solution at the elevated pressure and ρ^* the value at ambient pressure.

$$M_i = M_i^*\rho/\rho^* \quad (14)$$

In the case of a second-order rate constant, i.e., where $1 - a - b = -1$, an uncorrected rate constant k_M^* is usually calculated by using the concentration M_i^* at atmospheric pressure. To obtain k_M in terms of the actual concentration at elevated pressure, k_M^* must be corrected, by converting M_i^* to M_i using eq 14.

$$k_M = k_M^* M_i^*/M_i = k_M^*\rho^*/\rho \quad (15)$$

Differentiation with respect to pressure results in (16), since ρ^* is a constant and $(\partial \ln \rho/\partial P)_T = \kappa$. From a comparison of (13) and (16) with $1 - a - b = -1$, one obtains eq 17.

$$-RT\left(\frac{\partial \ln k_M}{\partial P}\right)_T = -RT\left(\frac{\partial \ln k_M^*}{\partial P}\right)_T - RT\left(\frac{\partial \ln \rho^*/\rho}{\partial P}\right)_T = -RT\left(\frac{\partial \ln k_M^*}{\partial P}\right)_T + RT\kappa \quad (16)$$

Thus the uncorrected rate constants k_M^* (calculated with atmospheric molarities M_i^*) can be used to determine $\Delta V^{\ddagger}$: the correction term in eq 13 is canceled by a similar term in (16).

$$-RT\left(\frac{\partial \ln k_M^*}{\partial P}\right)_T = \Delta V^{\ddagger} \quad (17)$$

Similar arguments can be applied to eq 10; i.e., an uncorrected K_M value can be used to estimate $\Delta\bar{V}$.[28] We conclude that molarity concentration units *at 1 atm* are just as valid (and usually more convenient) for high-pressure work as mole fractions and molalities.

The choice of pressure units in the literature is gradually changing, from bars and kilobars to pascals. Most of the articles quoted made use of kbar, and we therefore do also, but MPa and GPa are seen with increasing frequency, and we recommend their future use (1 kbar = 100 MPa). It follows from eq 10 and 17 and the above discussion that $\Delta\bar{V}$ and $\Delta V^{\ddagger}$ can be determined from the pressure dependence of K and k, respectively, whether they are expressed as mole fraction, molality, or molarity. The instrumentation used to determine these dependencies will be treated in the following section. Important to note, however, is the fact that plots of ln k (or ln K) versus pressure need not be, and generally are not, linear. A few typical examples of such plots are given in Figure 1. For cycloaddition, the rate constant increases with increasing pressure: the negative volume of activation decreases in absolute magnitude with increasing pressure. In homolytic scission, the rate constant decreases with increasing pressure, corresponding to a positive volume of activation; this also decreases with increasing pressure. Curves A and C are markedly curved, and various mathematical treatments have been suggested to calculate the volume of activation at zero (atmospheric) pressure, $\Delta V^{\ddagger}_0$, and the compressibility coefficient of activation, $\Delta\beta^{\ddagger}$, defined by eq 18. Among these treatments, perhaps the most popular one is the parabolic function (19), for which $\Delta V^{\ddagger}_0 = -bRT$ and $\Delta\beta^{\ddagger} = 2cRT$.[1]

$$\Delta\beta^{\ddagger} = -(\partial\Delta V^{\ddagger}/\partial P)_T \quad (18)$$

Equilibrium constants can exhibit similar curved pressure dependencies, and these are treated in the same way.

$$\ln k = a + bP + cP^2 \quad (19)$$

During the period covered by this review, several new equations were employed to account for the pressure dependence of $\Delta\bar{V}$ (or $\Delta V^{\ddagger}$) and k (or K), and these can be summarized as follows:

$$\Delta\bar{V}_P/\Delta\bar{V}_0 = 1 - a \ln(1 + bP) \quad \text{(ref 29)} \quad (20)$$

$$\int_0^P (\Delta\bar{V}_P/\Delta\bar{V}_0)\, dP = (1 + a)P - a(1 - bP)\ln(1 + bP)/b \quad \text{(ref 30)} \quad (21)$$

$$\begin{aligned} \ln k &= \ln k_0 + aP + bP/(1 + cP) \\ \Delta V^{\ddagger}_0 &= -(a + b)RT \quad \text{(ref 31)} \end{aligned} \quad (22)$$

$$\begin{aligned} \ln k &= \ln k_0 + aP + b \ln(1 + cP) \\ \Delta V^{\ddagger}_0 &= -(a + bc)RT \quad \text{(ref 31)} \end{aligned} \quad (23)$$

In general, some of the various equations used (for a complete summary, see ref 24) will result in slightly different values for $\Delta V^{\ddagger}_0$ and $\Delta\beta^{\ddagger}$, as illustrated by the typical example in Figure 2.[32] It is difficult to distinguish between the validity of these data-fitting procedures based on the deviations (ΔF) from the fitted line. The trend in ΔF is caused more by the statistical scatter of the data points than by the specific equation adopted. However, the mechanistic interpretation of

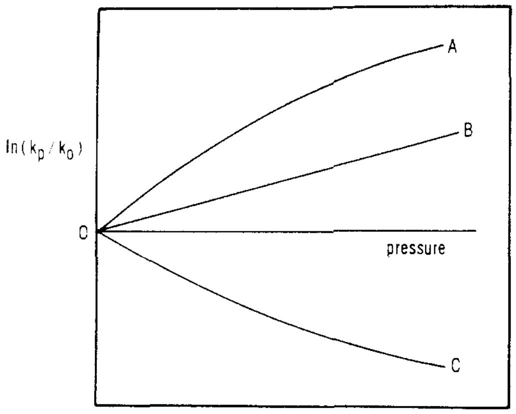


Figure 1. Typical plots of ln (k_P/k_0) vs pressure: (A) cycloaddition reaction; (B) ligand substitution reaction; (C) homolytic scission reaction.

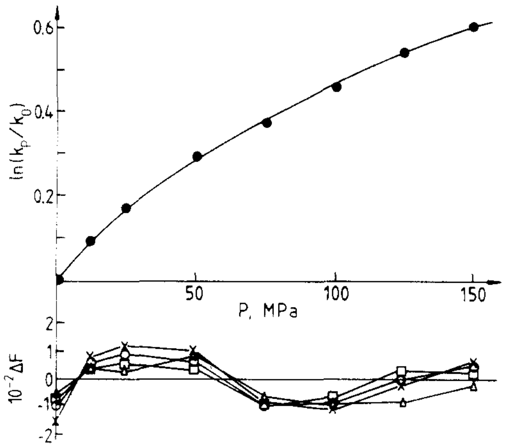


Figure 2. Treatment of data for the ligand substitution reaction involving Pt(dien)Cl$^+$ and OH$^-$ in aqueous solution:[32] (×) $F = a + bP + cP^2$, $\Delta V^{\ddagger}_0 = -14.7 \pm 0.8$ cm^3 mol^{-1}; (○) $F = a + bP + cP^2 + dP^3$, $\Delta V^{\ddagger}_0 = -17.9 \pm 1.0$ cm^3 mol^{-1}; (□) $F = a + b[1 - \exp(-cP)]$, $\Delta V^{\ddagger}_0 = -16.2 \pm 2.0$ cm^3 mol^{-1}; (△) $F = a + bP/(c + P)$, $\Delta V^{\ddagger}_0 = -17.3 \pm 0.5$ cm^3 mol^{-1}.

$\Delta V^{\ddagger}_0$ will not be affected by the relatively small differences indicated in Figure 2.

It is the general objective to combine activation, reaction, and partial molar volume data to construct a reaction volume profile that describes the reaction in terms of volume changes that occur along the reaction coordinate. Such a profile (see Figure 3 for the volume profile of reaction 1) is a pictorial view of the chemical reaction on the basis of volume changes, which may contribute to the understanding and/or elucidation of the underlying reaction mechanism. Thus, the relationship between $\Delta V^{\ddagger}$ and $\Delta \bar{V}$ can reveal information concerning the "early" or "late" nature of the transition state,[3] as demonstrated schematically in Figure 4. We emphasize that $\Delta \bar{V}$ and $\Delta V^{\ddagger}$ need not have the same sign; the transition state often represents a volume extremum.

Three factors determine the partial molar volume of a dissolved species in solution:[33] (i) the intrinsic size of the species as determined by its van der Waals radius; (ii) the interaction of the species with the solvent to cause electrostriction; (iii) the interaction of the species with all the solute species, including itself. In general, the contribution from (iii) is unimportant in dilute solutions, and the contribution from (i) is usually accepted to be independent of the solvent and the concentration. The contribution from (ii) is a complex one: the solute molecules or ions exert repulsive forces on the solvent molecules at close separations and attractive forces at longer distances, such that the orientation and packing of the solvent molecules vary significantly. If the solute is ionic, the attractive forces are overwhelming and the solvent molecules are contracted by electrostriction. This contribution is important and often so large that it completely overrides the intrinsic volume component, so that some ions actually have negative net partial molar volumes in solution.

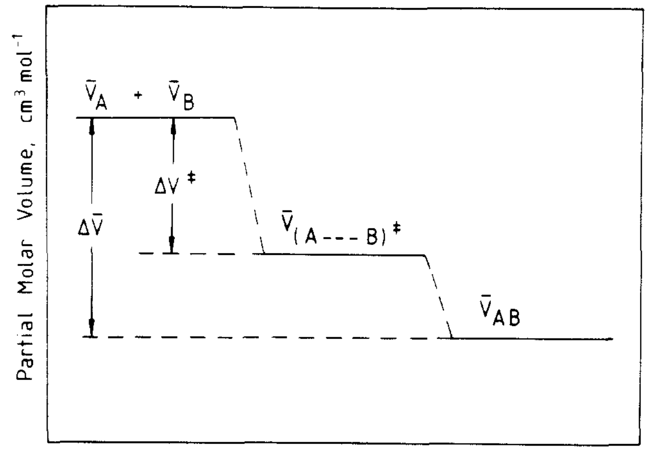


Figure 3. Volume profile for reaction 1.

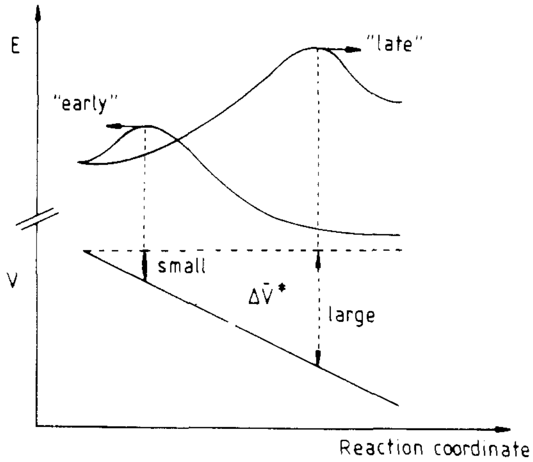


Figure 4. Energy and volume profiles to illustrate the effect of "early" and "late" transition states.[3]

On the basis of these factors it became advantageous and valid to a first approximation to consider reaction and activation volumes as the sum of an intrinsic and a solvational component as shown in (24). The intrinsic

$$\Delta \bar{V} = \Delta \bar{V}_{\text{intr}} + \Delta \bar{V}_{\text{solv}} \quad (24)$$

part results from the net motion of the nuclei of the reacting species, i.e., changes in bond lengths and angles during the formation of the products. The solvation part represents all volume changes associated with changes in polarity, electrostriction, and dipole interactions during the reaction. The validity of this relationship can easily be seen from typical reaction volume data. For instance, $\Delta \bar{V}$ for a series of neutralization reactions of the type shown in (25), where MA^z is an

$$\text{MA}^z + \text{OH}^- \rightarrow \text{MB}^{z-1} + \text{H}_2\text{O} \quad (25)$$

octahedral transition-metal complex, is expected to correlate with Δz^2 ($=z^2$(product) $- z^2$(reactant)) since

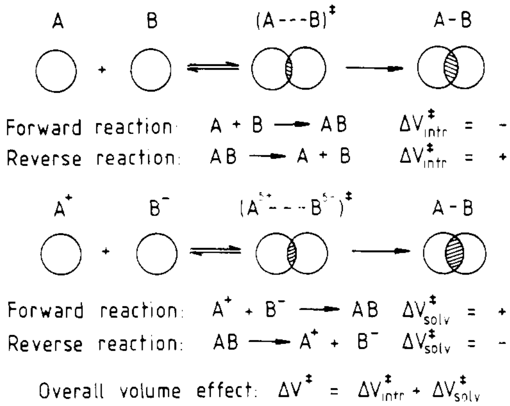


Figure 5. Schematic representation to illustrate the sign of the components of $\Delta V^{\ddagger}$.

$\Delta \bar{V}_{\mathrm{solv}}$ will vary with Δz^2.[34] Experimental data for a series of 21 different complexes demonstrate the validity of these expectations, and $\Delta \bar{V}$ varies between 3 and 35 $cm^3\ mol^{-1}$, depending on the size of Δz^2.

In a similar way, $\Delta V^{\ddagger}$ may be considered as the sum of two components: an intrinsic part ($\Delta V^{\ddagger}_{\mathrm{intr}}$), which represents the change in volume due to changes in bond lengths and angles, and a solvation part ($\Delta V^{\ddagger}_{\mathrm{solv}}$), which represents the volume changes due to electrostriction and other effects acting on the surrounding solvent molecules during the activation process. It is principally the intrinsic contribution that is the mechanistic indicator. A schematic representation of these components for a typical bond formation or bond cleavage process, during which partial charge neutralization or creation may occur, is given in Figure 5. The mechanistic assignments for processes in which no major solvational changes occur are, in fact, straightforward, since bond formation should result in a negative $\Delta V^{\ddagger}_{\mathrm{intr}}$ and bond cleavage in a positive one. In reactions with large polarity changes, $\Delta V^{\ddagger}_{\mathrm{solv}}$ may be larger than $\Delta V^{\ddagger}_{\mathrm{intr}}$, and it can in fact counteract and swamp the $\Delta V^{\ddagger}_{\mathrm{intr}}$ term. Various ways to describe the solvent dependence of $\Delta V^{\ddagger}$ have been suggested.[3,33] It is therefore not surprising that good correlations between $\Delta V^{\ddagger}$ and some solvent-characterizing parameters have been observed.[3,33,35] In such correlations the intercept at $\Delta V^{\ddagger}_{\mathrm{solv}} = 0$ represents $\Delta V^{\ddagger}_{\mathrm{intr}}$, and this is one way to separate the two contributions. Asano[36] suggested a different method to estimate $\Delta V^{\ddagger}_{\mathrm{intr}}$ directly from the pressure dependence of k according to eq 26, where B is a characteristic solvent parameter and the pressure is in bars.

$$-\frac{RT}{P-1}\ln\frac{k_P}{k_1} = \Delta V^{\ddagger}_{\mathrm{intr}} - \frac{K}{P-1}\ln\frac{B+P}{B+1} \qquad (26)$$

Much of the discussion concerning the interpretation of $\Delta V^{\ddagger}$ is based on our acceptance of the validity of the transition-state theory (TST). In view of the general simplicity of this theory, it is quite remarkable that it can be used in so many cases to account for the observed activation parameters. On the other hand, one must be aware of its shortcomings and should consider alternative treatments to account for the observed data. In the usual TST treatment it is assumed that the activity coefficients are close to unity (dilute solutions) and that the transmission coefficient $\bar{\kappa} = 1$. In that case, TST overestimates the rate of a reaction since $\bar{\kappa}$ must often be smaller than one. It follows that the experimental and TST rate constants are related through eq 27. Stochastic models have been introduced to account

$$k_{\mathrm{exptl}} = \bar{\kappa} k_{\mathrm{TST}} \qquad (27)$$

for the deviation of $\bar{\kappa}$ from unity.[37-39] Frictional effects (i.e., solvent dynamics) are contained in $\bar{\kappa}$ and can force a system to reverse its reaction mode at the transition state; reactants may cross the transition state back and forth before reacting to give the product.[40] This coupling of the reaction coordinate with the surrounding medium brings about that at low friction, $\bar{\kappa}$ is proportional, and at high friction inversely proportional to the collision frequency, which in turn is proportional to viscosity.[27,40,41] In the low-friction (damping) region, collision activation is rate determining, whereas in the high-friction region, the process is diffusion controlled. In terms of the pressure dependence of the experimental rate constant, eq 27 results in (28), where

$$\Delta V^{\ddagger}_{\mathrm{exptl}} = \Delta V^{\ddagger}_{\mathrm{coll}} + \Delta V^{\ddagger}_{\mathrm{TST}} \qquad (28)$$

$\Delta V^{\ddagger}_{\mathrm{exptl}} = -RT(\partial \ln k_{\mathrm{exptl}}/\partial P)_T$, $\Delta V^{\ddagger}_{\mathrm{TST}} = -RT(\partial \ln k_{\mathrm{TST}}/\partial P)_T$, and $\Delta V^{\ddagger}_{\mathrm{coll}} = -RT(\partial \ln \bar{\kappa}/\partial P)_T$. The latter term can be positive or negative, depending on whether $\bar{\kappa}$ increases or decreases with increasing collision frequency, i.e., viscosity. $\Delta V^{\ddagger}_{\mathrm{exptl}}$ is the only measurable quantity, and $\Delta V^{\ddagger}_{\mathrm{TST}}$ must be estimated theoretically in order to obtain values for $\Delta V^{\ddagger}_{\mathrm{coll}}$ and $\bar{\kappa}$ as a function of pressure. Jonas et al.[27,41] studied the pressure dependence of the chair-to-chair isomerization of cyclohexane in various solvents and estimated $\Delta V^{\ddagger}_{\mathrm{TST}}$ to be -1.5 $cm^3\ mol^{-1}$, which results in $\Delta V^{\ddagger}_{\mathrm{coll}}$ values of between -3.4 and $+0.5$ $cm^3\ mol^{-1}$, depending on the solvent employed.

Troe and co-workers[42-44] have followed an alternative approach. They recognize that the interpretation of $\Delta V^{\ddagger}$ in the spirit of the TST neglects the "transport" aspect of the reaction, which is a flow in a viscous medium. Under conditions where the transport property, i.e., interaction with the medium, enters the rate constant as a factor, $\Delta V^{\ddagger}_{\mathrm{exptl}}$ can be expressed as in (29),

$$\Delta V^{\ddagger}_{\mathrm{exptl}} = \Delta V^{\ddagger}_{\mathrm{TST}} + \Delta V^{\ddagger}_{\mathrm{transport}} \qquad (29)$$

where $\Delta V^{\ddagger}_{\mathrm{transport}} = RT(\partial \ln \eta/\partial P)_T$. To study the transport contribution in dissociation and recombination reactions, they investigated the pressure dependence of reactions over a range of densities from the gas phase (collision energy transfer controlled) to the dense fluid phase (diffusion controlled). The experimental data can be fitted with a model in which cluster- and cage-solvent shifts of the threshold energy are taken into account.

The discussed modifications of TST treatment are first efforts to account for the observed experimental data, but the good agreement between theoretically expected and experimentally observed trends is very encouraging and more developments are surely forthcoming. The nature of the processes studied up to now is more physical than chemical, and because of that collision, friction, and transport phenomena are bound to play an important role.

C. Experimental Techniques

Detailed accounts of experimental techniques are given elsewhere.[2,5,6,24,45] During the past decade UV-vis spectral measurements were increasingly made with the "pillbox" quartz cell[46] using a typical two-window high-pressure cell. A modification of this cell enables one to do pulsed laser flash photolysis and to make excited-state lifetime mesaurements[47,48] at pressures up to 300 MPa using a three- or four-window high-pressure cell. Considerable development of instrumentation to perform kinetic measurements under pressure on a milli-, micro-, or nanosecond time scale has led to a remarkable increase in activity in this area. A mixing system was developed for moderately fast reactions with a half-life of a few seconds or longer.[49] Various groups have developed high-pressure stopped-flow instrumentation for which the deadtime varies between 10 and 40 ms at pressures up to 200 MPa.[50-59] Two groups have constructed Joule-heating T-jump instruments for pressures up to 200 MPa and heating times of about 10 μs.[60,61] Inoue and co-workers[62] have reported technical information on a high-pressure pressure-jump system in which a jump of 13 MPa was used for pressures up to 100 MPa. High-pressure NMR techniques have contributed significantly to the study of fast reactions at pressures up to 300 MPa.[63-69] Equipment originally designed for spectrometers with electromagnets has been modified for use with superconducting magnets. Similar instrumentation has been used for ESR and EPR measurements at elevated pressure.[4,70,71] Processes in the nanosecond time range can be studied with the aid of pulsed-laser techniques, and various instruments have been developed to perform such measurements at elevated pressure.[47,48,72-76] In addition, Whalley et al. developed two techniques to study chemical kinetics at extremely high pressures of up to 10^4 MPa.[77]

As discussed before, $\Delta V^{\ddagger}$ measurements should be complemented by $\Delta\bar{V}$ data, which can be obtained from partial molar volume measurements via density data or measured directly with the aid of a dilatometer (and, when practical of course, by measuring the effect of pressure on the equilibrium constant). Special dilatometers have been constructed to measure $\Delta\bar{V}$ for fast reactions in which two chambers are used to separate the reactants prior to mixing. A new design for such an instrument was recently reported by Hashitani et al.[78]

D. Correlation with Other Parameters

In the previous sections, we have referred to the pressure and solvent dependence of $\Delta V^{\ddagger}$ and $\Delta\bar{V}$. The temperature dependence of these quantities can be obtained by considering the temperature dependence of the chemical potential μ_i as done in eq 30. Since it

$$(\partial\mu_i/\partial T)_P = -S_i \qquad (30)$$

is a property of partial differentials that the order of successive differentiations of a continuous function $\mu_i(T,P)$ is immaterial, it follows that

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial\mu_i}{\partial T}\right)_P\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial\mu_i}{\partial P}\right)_T\right]_P \qquad (31)$$

or

$$(\partial\bar{V}_i/\partial T)_P = -(\partial S_i/\partial P)_T \qquad (32)$$

Application of eq 32 (one of the Maxwell relations) to an equilibrium or a reaction results in the expressions given in (33). A number of groups have measured these

$$(\partial\Delta\bar{V}/\partial T)_P = -(\partial\Delta S/\partial P)_T$$

$$(\partial\Delta V^{\ddagger}/\partial T)_P = -(\partial\Delta S^{\ddagger}/\partial P)_T \qquad (33)$$

quantities and found the data to conform quite well to the relationships in (33). Some of these authors used this equality to prove the assumption made in the TST, namely, that a thermodynamic equilibrium exists between the reactant and transition state;[10,11,79] however, Hamann[80] recently pointed out that such conclusions are unfounded since the relationship (33) is merely a mathematical consequence of the definitions of $\Delta\bar{V}$ (or $\Delta V^{\ddagger}$) and ΔS (or $\Delta S^{\ddagger}$).

Many studies of the effects of pressure on the rate and equilibrium constants of chemical processes in solution have been carried out under conditions where the concentrations of the reactants are known, but their activity coefficients were not. Partial molar volumes are related thermodynamically to the pressure dependence of the mean activity coefficient $\gamma_{\pm}$ by eq 34,

$$(\partial \ln \gamma_{\pm}/\partial P)_T = (\bar{V} - \bar{V}^{\circ})/vRT \qquad (34)$$

where v is the stoichiometric number of ions produced by dissociation of the electrolyte and $\bar{V}$ and $\bar{V}^{\circ}$ are the partial molar volumes at the ionic strength of the solution and at infinite dilution, respectively. Experimental data for some 1:1 and 1:2 electrolytes[81] indicate that $\gamma_{\pm}$ increases with increasing pressure, particularly at higher ionic strengths. For very dilute solutions the effect of pressure on $\gamma_{\pm}$ can be predicted accurately from the Debye–Hückel limiting law. In less dilute solutions, to $\mu \approx 0.2$ M, it would be expected that $\gamma_{\pm}$ will be described well by the complete Debye–Hückel relationship. The results, however, show that the pressure dependence can be described by the limiting Debye–Hückel treatment, and it is surprising that the complete expression cannot describe it in a quantitatively satisfactory way.[81] In any event, these effects may partly account for the pressure dependence of $\Delta\bar{V}$ and $\Delta V^{\ddagger}$.

Finally, much emphasis has been placed on the possible correlation between $\Delta\bar{V}$ (and $\Delta V^{\ddagger}$) and ΔS (and $\Delta S^{\ddagger}$). The relationships (33) indicate that there is no thermodynamic or quasi-thermodynamic equation that links the derivatives of these quantities directly. However, since these quantities stem from the same source in a thermodynamic and kinetic sense, some correlation is expected. This has been realized by a number of investigators; they have reported plots of $\Delta\bar{V}$ versus ΔS, or $\Delta V^{\ddagger}$ versus $\Delta S^{\ddagger}$.[10,82-85] Much of their interpretation of $\Delta V^{\ddagger}$ data has focused on their correlation with $\Delta S^{\ddagger}$. However, it is misleading to use such a generalized correlation since there are numerous exceptions. It should be noted that ΔS and $\Delta S^{\ddagger}$ are usually subject to large error limits since they are determined by extrapolating the experimental data (K and k as a function of temperature) to $1/T \rightarrow 0$. In contrast, $\Delta\bar{V}$ and $\Delta V^{\ddagger}$ result from the slope of ln K or ln k versus P plots, respectively, and can therefore usually be determined more accurately. All in all, it is quite safe to conclude that a large positive $\Delta S^{\ddagger}$ value will correspond to a clearly positive $\Delta V^{\ddagger}$ value and vice versa, and similarly for large negative values. Data in the intermediate range may exhibit all kinds of trends and do not correlate well.[86]

2. Activation and Reaction Volumes of Inorganic Reactions

A. General Remarks

In contrast to the longstanding application of high-pressure techniques in the study of organic reaction mechanisms, it was only in the mid-1950s that this method was first applied to the study of inorganic and organometallic systems. However, the activity in this area has increased exponentially since then: ca. 170 volumes of activation had been determined by 1978,[1] an additional 360 data sets were available by the end of 1983, and a further 200 data sets were published by 1985.[23] This increased activity is partly due to the general availability of equipment allowing kinetic measurements in the milli-, micro-, and nanosecond time ranges at pressures up to 300 MPa.

The data in the tables are arranged according to the different types of reactions and the atomic number of the central metal atom, going from the highest to the lowest oxidation state for a particular atom. Reaction volume data ($\Delta\bar{V}$) are included in the tables where available, and the methods employed to determine $\Delta\bar{V}$ are (a) from the pressure dependence of the equilibrium constant, (b) from dilatometric or partial molar volume (density) measurements, and (c) from theoretical extrapolations. Other general remarks are as follows: $\Delta V^\ddagger$ data are quoted at ambient pressure; in case of significant curvature in the ln *k* versus *P* plot, $\Delta\beta^\ddagger$ is also given. The number of data refers to the number of pressures at which kinetic measurements (usually three to five kinetic runs) were performed. The maximum applied pressure is quoted in the fifth column, the concentration is given in mol L^{-1} (M) or mol kg^{-1} (*m*), and the anions quoted in parentheses refer to the ionic strength controlling medium employed; ClO_4^- usually refers to a mixture of $HClO_4$ and $NaClO_4$. A list of abbreviations follows the tabulated data. Reactions for which no reaction products are specified in detail are indicated in this way since the original papers do not state a definite product assignment.

B. Solvent- and Ligand-Exchange Reactions

This and the following section C deal with ligand substitution processes, i.e., processes in which coordinated ligand or solvent molecules are substituted by identical or other molecules. The two sections differ in that this section presents systems in which no net chemical reaction occurs—i.e., solvent and ligand molecules are substituted (exchanged) by identical uncoordinated molecules—whereas section C presents systems with a net chemical reaction.

Most substitution reactions are still discussed in terms of the Langford and Gray classification[322] introduced more than 20 years ago. For a general ligand substitution reaction (34a), where X is the leaving

$$ML_nX + Y \rightarrow ML_nY + X \qquad (34a)$$

group, Y is the entering ligand, and L is the nonparticipating ligands, there are three simple pathways: (i) the dissociative (D) process, with an intermediate of lower coordination number; (ii) the associative (A) process, with an intermediate of higher coordination number; (iii) the interchange (I) process, in which no intermediate of lower or higher coordination number is involved. The latter possibility is further subdivided into two types: associative interchange (I_a) or dissociative interchange (I_d). A schematic presentation of these mechanisms is given in Figure 6. A comparison of this notation can be made with Ingold's nomenclature introduced for nucleophilic substitution (S_N), with a D mechanism corresponding to limiting S_N1, an A mechanism corresponding to limiting S_N2, and the interchange mechanisms I_d and I_a corresponding to S_N1 and S_N2, respectively. The outlined classification can best be understood on the basis of energy profiles, in which the formation of an intermediate of higher or lower coordination number is characterized by a minimum in the profile.[323] For the purpose of this review, such cases will be referred to as limiting associative (A) or limiting dissociative (D), respectively, whereas the interchange notation will be adopted for cases in which both bond formation and bond cleavage occur simultaneously.

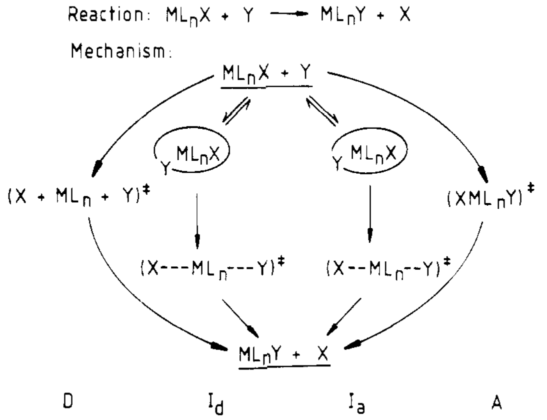


Figure 6. Schematic representation of the possible ligand substitution mechanisms.

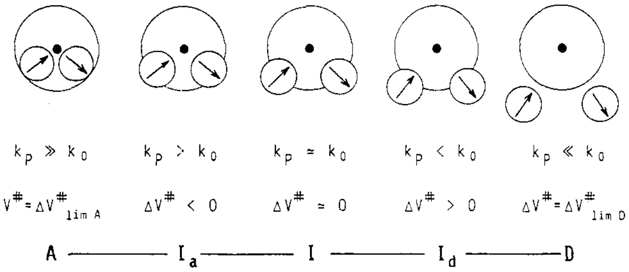


Figure 7. Schematic representation of the transition state at crucial points in the spectrum of solvent-exchange mechanisms.[324]

For the solvent- and ligand-exchange reactions reported in this section, electrostriction is assumed to be constant throughout the reaction coordinate, and the volume of activation is given by the intrinsic contribution, $\Delta V^\ddagger_{\text{intr}}$. With this assumption the sign of $\Delta V^\ddagger$ gives immediate insight into the intimate nature of the activation process. The volume changes associated with the various possible substitution mechanisms are schematically presented in Figure 7. A continuous spectrum of transition-state configurations can be envisaged, ranging from very compact with a large negative $\Delta V^\ddagger$ value to very expanded with a large positive $\Delta V^\ddagger$ value.

According to the data collected in Table I, 115 data sets became available during the time covered. These have allowed a systematic analysis of the data,[15,16,324] which resulted in the formulation of a number of important mechanistic trends along the elements in the periodic table. Most of the solvent- and ligand-ex-

TABLE I. Activation and Reaction Volumes of Inorganic Reactions[a]

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
	Solvent/Ligand Exchange Reactions									
1	$Al(H_2O)_6^{3+} + H_2O$	H_2O	0–120	2.0	14 × 12	+5.7 ± 0.2			87	$[H^+] = 0.3–3\ m$ $\mu = 4.3–7.5\ m\ (ClO_4^-)$
2	$Al(DMSO)_6^{3+}$ + DMSO	CH_3NO_2	85	2.0	12	+15.6 ± 1.4	+4.8 ± 1.4		88	
3	$Al(DMF)_6^{3+}$ + DMF	CH_3NO_2	82	2.0	12	+13.7 ± 1.2	+5.4 ± 1.2		88	
4	$Al(tmp)_6^{3+}$ + tmp	CD_3NO_2	68			+22.5 ± 0.6			15	
5	$Al(acac)_3 + acac^-$	Hacac	25	2.4	7	+10.2 ± 1.8			89	spontaneous reaction
6						+5.0 ± 0.4			89	H_2O catalyzed reaction
7	$Sc(tmp)_6^{3+}$ + tmp	CD_3NO_2	26			−18.7 ± 1.1	−2.4 ± 1.2		15	
8		CD_3NO_2	−33 to +77			−23.8 ± 2.7			15	
	cis-$TiCl_4{\cdot}2L + L$			2.3	ca. 10				90	
9	L = Me_2S	CH_2Cl_2	−55			+24.4 ± 1.0	+7.0 ± 0.9			
10	L = Me_2Se	CH_2Cl_2	−45			+26.1 ± 1.2	+8.5 ± 0.9			
11	L = tmp	$CHCl_3$	12			+17.5 ± 1.2	+2.6 ± 1.1			
12	$Ti(H_2O)_6^{3+} + H_2O$	H_2O	0–25	2.4	3 × 10	−12.1 ± 0.4	−1.9 ± 0.4		91	2–3 m CF_3SO_3H
13	$VO(DMSO)_5^{2+}$ + DMSO	CD_3NO_2	13	1.4	15	−5.3 ± 0.4			92	$\mu = 0.03$ M (ClO_4^-)
14	$V(H_2O)_6^{3-} + H_2O$	H_2O		2.5		−9.3 ± 0.5			93	Cl^- medium
15		H_2O		2.5		−10.1 ± 0.5			93	Br^- medium
16		H_2O	63–85	2.5	4 × 11	−8.9 ± 0.4	−1.1 ± 0.3		94	2m CF_3SO_3H, $\mu = 2–9\ m\ (CF_3SO_3^-)$
	mer-$VCl_3(CH_3CN)_3 + CH_3CN$	CH_3NO_2							18	
17	mutually *trans*-CH_3CN					+6.1				
18	CH_3CN trans to Cl^-					+15.5				
19	$V(H_2O)_6^{2+} + H_2O$	H_2O	77	2.5	13	−4.1 ± 0.1			93, 95	$\mu \sim 2$ M (Cl^-)
20	$Cr(H_2O)_6^{3+} + H_2O$	H_2O	45	4.0	6	−9.6 ± 0.1	+0.2 ± 0.2		96	$\mu = 0.7\ m\ (ClO_4^-)$
21	$Cr(H_2O)_5OH^{2+} + H_2O$	H_2O	45	4.0	6	+2.7 ± 0.5			96	$\mu = 0.7\ m\ (ClO_4^-)$
22	$Mn(H_2O)_6^{2+} + H_2O$	H_2O	5–6	2.5	20	−6.2 ± 0.2			97	0.06–0.1 m $HClO_4$
23		H_2O	5	2.5	>10	−6.0 ± 0.6			98	0.06–0.1 m $HClO_4$
24		H_2O	6	2.5	>10	−6.3 ± 0.5			98	0.06–0.1 m $HClO_4$
25		H_2O	103	2.5	>10	−4.3 ± 0.4			98	0.06–0.1 m $HClO_4$
26	$Mn(CH_3OH)_6^{2+} + CH_3OH$	CH_3OH	4	2.0	9	−5.0 ± 0.2			99	
27	$Mn(CH_3CN)_6^{2+} + CH_3CN$	CH_3CN	−20 to −13	1.1	~10	−7.0 ± 0.4			66	
28	$Mn(DMF)_6^{2+}$ + DMF	DMF	36	3.0	7	+1.6 ± 0.5			100	
29		DMF	−3 and −10	2.0	9	+2.4 ± 0.2			101	
30	$Mn(Me_6(tren))DMF^{2+}$ + DMF	DMF	−10 and 59	2.5	13	−6 ± 2			102	
31	$Fe(H_2O)_6^{3+} + H_2O$	H_2O	110	2.4	13	−5.4 ± 0.4			103	$\mu = 6\ m\ (ClO_4^-)$
32	$Fe(H_2O)_5OH^{2+} + H_2O$	H_2O	110	2.4	13	+7.0 ± 0.2			103	$\mu = 6\ m\ (ClO_4^-)$
33	$Fe(DMSO)_6^{3+}$ + DMSO	DMSO	5–35	2.0	10	−3.1 ± 0.3			104	
34	$Fe(DMF)_6^{3+}$ + DMF	DMF	−18 to +127	2.0	10	−0.9 ± 0.2			104	
35	$Fe(CH_3OH)_5(OCH_3)^{2+} + CH_3OH$	CH_3OH	42–43	2.0	6	+6.4 ± 0.2			104	
36	$Fe(H_2O)_6^{2+} + H_2O$	H_2O	−5 to +19	2.5	>15	+3.8 ± 0.2			98	$\mu = 0.2–1\ m\ (ClO_4^-)$
37	$Fe(CH_3OH)_6^{2+} + CH_3OH$	CH_3OH	−23	2.0	9	+0.4 ± 0.3			99	
38	$Fe(CH_3CN)_6^{2+} + CH_3CN$	CH_3CN	−15 to −10	1.4	~10	+3.0 ± 0.5			66	
39	$Fe(DMF)_6^{2+}$ + DMF	DMF	2 and 19	2.0	9	+8.5 ± 0.4			101, 105	
40	$Co(NH_3)_5DMF^{3+}$ + DMF	DMF	55	4.0	5	+3.2 ± 0.1			106	0.24 M acid
41	$Co(H_2O)_6^{2+} + H_2O$	H_2O	−10 to +34	2.5	>15	+6.1 ± 0.2			98	$\mu = 0.1–0.8\ m\ (ClO_4^-)$
42		H_2O	83	2.4	14	+5.5 ± 0.6			107	
43		H_2O	72	2.4	14	+5.2 ± 0.7			107	
44	$Co(CH_3CN)_6^{2+} + CH_3CN$	CH_3CN	13	2.0	11	+7.7 ± 1.7			67	
45		CH_3CN	−0.8	1.5	~12	+6.7 ± 0.4			108	
46	$Co(tmc)(CH_3CN)^{2+} + CH_3CN$	CH_3CN	−25	1.5	9	−9.6 ± 0.5			109	
47	$Co(CH_3OH)_6^{2+} + CH_3OH$	CH_3OH	6	2.0	~13	+8.9 ± 0.3			110	
48	$Co(DMF)_6^{2+}$ + DMF	DMF	23	2.0	~14	+6.7 ± 0.3			110	
49	$Co(Me_6(tren))DMF^{2+}$ + DMF	DMF	99 and 100	2.5	13	−2.7 ± 0.2			102	
50	$Co(Me_6(tren))DEF^{2+}$ + DEF	DEF	92	2.5	13	−1.3 ± 0.2			111	

	$Co(CH_3)(dmg)_2L + L$		25					18	
51	L = MeOH	$CDCl_3$				+6.8			
52	L = Me_2NCHO	$CDCl_3$/ CD_3NO_2				+7.9			
53	L = $(PhCH_2)_3Sb$	CD_3NO_2				+12.9			
54	L = Me_2NCHS	CD_3NO_2				+13.6			
55	L = Me_2S	CD_3NO_2				+15.6			
56	L = $(MeO)_3P$	CD_3NO_2				+16.8			
57	$Co(PPh_3)_2Br_2 + PPh_3$	$CDCl_3$	30	2.6	7	−12.1 ± 0.6	−3.3 ± 0.5	112	
58	$Ni(H_2O)_6^{2+} + H_2O$	H_2O	36–41	2.5		+7.2 ± 0.3		98	
59		H_2O	35–44	2.2	10	+7.1 ± 0.2		113	μ = 0.1–0.3 *m* (ClO_4^-)
60	$Ni(CH_3CN)_6^{2+} + CH_3CN$	CH_3CN	35	1.5	~12	+7.3 ± 0.3		108	
61	$Ni(tmc)(CH_3CN)^{2+} + CH_3CN$	CH_3CN	−25	1.5	9	−9.6 ± 0.5		109	
62	$Ni(NH_3)_6^{2+} + NH_3$	NH_3	10–30	2.0	8	+5.9 ± 0.4		114	
63	$Ni(CH_3OH)_6^{2+} + CH_3OH$	CH_3OH	34	2.0	~10	+11.4 ± 0.6		110	
64	$Ni(DMF)_6^{2+}$ + DMF	DMF	24	2.0	~13	+9.1 ± 0.3		110	
65	$Cu(Me_6(tren))DMF^{2+}$ + DMF	DMF	77 and 92	2.5	13	+6.5 ± 0.2		102	
66	$Cu(Me_6(tren))DEF^{2+}$ + DEF	DEF	92	2.0	11	+5.3 ± 0.3		111	
67	$Cu(CH_3OH)_6^{2+} + CH_3OH$	CH_3OH	−62	2.0	11	+8.3 ± 0.4		115	
68	$Ga(H_2O)_6^{3+} + H_2O$	H_2O	22–70	2.0	10 × 9	+5.0 ± 0.5		116	$[H^+] \leq 3$ *m* ($HClO_4$)
69	$Ga(H_2O)_5OH^{2+} + H_2O$	H_2O	22–70	2.0	10 × 9	+6.2 ± 1.4		116	$[H^+] \leq 3$ *m* ($HClO_4$)
70	$Ga(DMSO)_6^{3+}$ + DMSO	CH_3NO_2	62	2.0	12	+13.1 ± 1.0	+5.5 ± 0.9	88	
71	$Ga(DMF)_6^{3+}$ + DMF	CH_3NO_2	40	1.2	9	+7.9 ± 1.6	+2.6 ± 2.7	88	
72	$Ga(tmp)_6^{3+}$ + tmp	CD_3NO_2	46			+20.7 ± 0.3		15	
	$NbCl_5{\cdot}L + L$			2.5	6–8			117	
73	L = Me_2O	CH_2Cl_2	22			+28.7 ± 1.1	+6.6 ± 1.2		
74	L = MeCN	$CHCl_3$	13			+19.5 ± 1.6	+0.7 ± 1.6		
75	L = Me_3CCN	$CHCl_3$	14			+15.2 ± 1.7	+2.0 ± 1.5		
76	L = $(MeO)Cl_2PO$	$CHCl_3$	18			+20.5 ± 0.7	+3.7 ± 0.7		
77	L = $(Me_2N)_3PS$	CH_2Cl_2	35			+17.7 ± 1.4			
78	$NbBr_5{\cdot}Me_2S + Me_2S$	CH_2Cl_2	7	2.5	8	−12.1 ± 1.0	−4.2 ± 1.0	117, 118	
79	$Ru(NH_3)_5H_2O^{3+} + H_2O$	H_2O	12	4.0	5	−4.0 ± 0.1		119	0.012 M CF_3SO_3H
80	$Rh(NH_3)_5DMF^{3+}$ + DMF	DMF	45	4.0	7	−1.4		106	0.05 M acid
81	$Pd(H_2O)_4^{2+} + H_2O$	H_2O	51	2.6	11	−2.2 ± 0.2		120	0.8–1.7 *m* $HClO_4$, μ = 2.0–2.6 *m* (ClO_4^-)
82	*trans*-$Pd(DMS)_2Cl_2$ + DMS	$CHCl_3$	35	2.0	10	−7.1 ± 0.5		121	
83		CH_2Cl_2	23	2.0	10	−8.4 ± 0.3		121	
84		*o*-$C_6H_4Cl_2$	14	2.0	10	−7.2 ± 0.6		121	
85		C_6H_5CN	25	2.0	10	−5.4 ± 0.1		121	
86	$[Pd(2\text{-methallyl})Cl]_2$ + $Pd(2\text{-methallyl})Cl(PPh_3)$, 2-methallyl exchange	$CHCl_3$	56	2.3		+11 ± 2		122	
87	$In(tmp)_6^{3+}$ + tmp	CD_3NO_3	50			−22.8 ± 1.1	−3.9 ± 1.1	15	
88			62			−20.0 ± 1.7	−5.9 ± 1.0	15	
89	*cis*-$SnCl_4{\cdot}2Me_2S + Me_2S$	CH_2Cl_2	−48 and −50	2.5	10	+38.4 ± 0.7	+13.9 ± 0.6	123	
	$SbCl_5{\cdot}L + L$	CH_2Cl_2		2.0	~10			15, 124	
90	L = MeCN		−20			+24.7 ± 1.7	+4.1 ± 1.8		
91	L = Me_3CCN		−37			+18.2 ± 0.9	+3.2 ± 0.6		
92	L = Me_2O		0			+27.2 ± 1.4	+5.9 ± 1.0		
93	L = Et_2O		−10			+30.0 ± 1.5	+3.8 ± 1.4		
94	L = Me_2CO		−8.5			+28.1 ± 2.0	+8.1 ± 1.9		
95	L = $(Me_2N)Cl_2PO$		1.1			+23.0 ± 0.6			
96	$Tb(H_2O)_9^{3+} + H_2O$	H_2O	−4	2.5	12	−5.7 ± 0.5		125	2 *m* $HClO_4$
97	$Tb(DMF)_8^{3+}$ + DMF	CD_3NO_2	−38	2.0		+5.2 ± 0.2		68	
98	$Dy(H_2O)_9^{3+} + H_2O$	H_2O	−4	2.5	9	−6.0 ± 0.4		125	2 *m* $HClO_4$
99	$Dy(DMF)_8^{3+}$ + DMF	CD_3NO_2	−37 to −33	2.0		+6.1 ± 0.2		68	
100	$Ho(H_2O)_9^{3+} + H_2O$	H_2O	−4	2.5	16	−6.6 ± 0.4		125	2 *m* $HClO_4$
101	$Ho(DMF)_8^{3+}$ + DMF	CD_3NO_2	−39 to −34	2.0		+5.2 ± 0.5		68	
102	$Er(H_2O)_9^{3+} + H_2O$	H_2O	−4	2.5	17	−6.9 ± 0.4		125	2 *m* $HClO_4$

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
103	$Er(DMF)_8^{3+} + DMF$	CD_3NO_2	-37 to -32	2.0		+5.4 ± 0.3			68	
104	$Tm(H_2O)_9^{3+} + H_2O$	H_2O	-4	2.5	10	-6.0 ± 0.8			125	2 *m* $HClO_4$
105	$Tm(DMF)_8^{3+} + DMF$	CD_3NO_2	-18	2.0		+7.4 ± 0.3			68	
106	$Yb(DMF)_8^{3+} + DMF$	CD_3NO_2	-38 to -33	2.0		+11.8 ± 0.4	+2.0 ± 0.9		68	
	$TaCl_5{\cdot}L + L$	CH_2Cl_2		2.5	6-8				117	
107	L = Me_2O		37			+27.8 ± 1.2	+8.3 ± 1.3			
108	L = Me_2S		11			-19.8 ± 0.9	-5.3 ± 0.8			
109	L = Me_2Se		15			-18.7 ± 1.0	-5.9 ± 1.0			
110	L = Me_2Te		12			-10.7 ± 0.8				
	$TaBr_5{\cdot}L + L$	CH_2Cl_2		2.5	6.8				117	
111	L = Me_2O		11			+30.5 ± 0.8	+6.5 ± 0.7			
112	L = Me_2S		17			-12.6 ± 0.8	-0.3 ± 0.7			
113	L = Me_2Se		12			-13.6 ± 0.8				
114	L = Me_2Te		34			-16.4 ± 0.7	-3.1 ± 0.7			
115	$Pt(H_2O)_4^{2+} + H_2O$	H_2O	24	2.3	6	-4.6 ± 0.2			126	1.5 *m* $HClO_4$, μ = 2.3 *m* (ClO_4^-)
	Ligand Substitution Reactions									
116	$Al^{3+} + Hipt \rightarrow Al(ipt)^{2+} + H^+$	DMSO	40	1.2	6	+12.2 ± 1.0			127	μ = 0.19 *m* (ClO_4^-)
117	$V_{10}O_{28}^{6-} \xrightarrow{H^+} VO_2^+$	H_2O	25	2.0	5	+16.3 ± 1.4 +14.5 ± 0.2			128	in water in buffer
118	$V_{10}O_{28}^{6-} \xrightarrow{OH^-} HVO_4^{2-} + VO_4^{3-}$					-4.1 ± 0.6			128	
119	$V(H_2O)_6^{2+} + SCN^- \rightarrow V(H_2O)_5SCN^+ + H_2O$	H_2O	25	1.5	9	-2.1 ± 0.8			52	μ = 0.5 M (ClO_4^-)
120	$V(H_2O)_5SCN^+ + H_2O \rightarrow V(H_2O)_6^{2+} + SCN^-$	H_2O	25	1.5	9	-11.5 ± 0.9			52	μ = 0.5 M (ClO_4^-)
	$Cr_2O_7^{2-} + B \rightarrow BCrO_3 + CrO_4^{2-}$	H_2O	25						129	μ = 0.1 M (KNO_3)
121	B = OH^-			1.75	17	-17.9 ± 0.6				
122	B = NH_3			1.3	13	-19.2 ± 0.9				
123	B = H_2O			1.75	10	-24.9 ± 0.9				
124	B = 2,6-lutidine			1.75	10	-26.9 ± 0.7				
125	$Cr(NH_3)_5H_2O^{3+} + SCN^- \rightarrow Cr(NH_3)_5NCS^{2+} + H_2O$	H_2O	50	1.5	4	-4.9 ± 0.6			130	μ = 1.0 M (ClO_4^-)
126			50	1.5	4	-2.4 ± 1.3			130	μ = 0.3 M (ClO_4^-)
127	$Cr(tpps)(H_2O)_2^{3-} + SCN^- \rightarrow Cr(tpps)(H_2O)NCS^{4-} + H_2O$	H_2O	15	1.0	5	+7.4 ± 0.1			131	[H^+] = 0.1 M, μ = 1.0 M
	$Cr(NH_3)_5L^{3+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + L$	H_2O							132	
128	L = DMSO					-3.2				
129	L = $OCHNH_2$					-4.8				
130	L = $OCHN(CH_3)_2$					-7.4				
131	L = $OC(NH_2)_2$					-8.2				
132	L = $OC(NHCH_3)_2$					-3.8				
133	$Cr(NH_3)_5Br^{2+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + Br^-$	H_2O	25	2.0		-9.3 ± 2.0			133	0.1 M $HClO_4$
134						-7			133	0.1 M $HClO_4$, 10^{-3} M NaPES
135						-4			133	0.1 M $HClO_4$, 5 × 10^{-3} M NaPES
136						-4			133	0.1 M $HClO_4$, 10^{-3} M $(C_4H_9)_4$NPES
137						-9			133	0.1 M$HClO_4$, 10^{-3} M NaPSS
138	$Cr(NH_2CH_3)_5Cl^{2+} + H_2O \rightarrow Cr(NH_2CH_3)_5H_2O^{3+} + Cl^-$	H_2O	70	1.5	4	+0.5 ± 0.6			134	μ = 0.1 M (ClO_4^-)
139	$Cr(NCS)_6^{3-} + H_2O \rightarrow Cr(NCS)_5H_5O^{2-} + SCN^-$	H_2O	25	1.5	7	+2.9 ± 0.8			135	0.1 M NaOH

140	$Cr(tpps)(H_2O)NCS^{4-} + H_2O \rightarrow Cr(tpps)(H_2O)_2^{3-} + SCN^-$	H_2O	15	1.0	5	+8.2 ± 0.4		131	$[H^+] = 0.1$ M, $\mu = 1.0$ M
141	$Cr(C_2O_4)_3^{3-} + H_2O \rightarrow$ *cis*-$Cr(C_2O_4)_2(H_2O)_2^- + C_2O_4^{2-}$	H_2O	50	1.7	8	−6.3 ± 0.4		136	1 M $HClO_4$
142	*cis*-$Cr(C_2O_4)_2(H_2O)_2^- + H_2O \rightarrow Cr(C_2O_4)(H_2O)_4^+ + C_2O_4^{2-}$	H_2O	45	1.4	3	+1.7 ± 0.7		137	3 M $HClO_4$
143	*cis*-$Cr(CH_2C_2O_4)_2(H_2O)_2^- + H_2O \rightarrow Cr(CH_2C_2O_4)(H_2O)_4^+ + CH_2C_2O_4^{2-}$	H_2O	65	1.4	3	+2.4 ± 0.6		137	0.5 M $HClO_4$
144	*trans*-$Cr(en)_2Br_2^+ + H_2O \rightarrow$ *trans*-$Cr(en)_2(H_2O)Br^{2+} + Br^-$	H_2O	15	2.0	5	+2.1		138	
145			20			+2.2			
146			25			+2.2			
147			30			+2.3			
148	*trans*-$Cr(tn)_2Br_2^+ + H_2O \rightarrow$ *trans*-$Cr(tn)_2(H_2O)Br^{2+} + Br$	H_2O	15	2.0	5	+1.4		138	
149			20			+1.7			
150			25			+1.8			
151			30			+1.9			
152	$Cr(NH_3)_5Cl^{2+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + Cl^-$	H_2O	15	1.0	5	−1.7 ± 1.0		139	$[H^+] = 0.3$ M, $\mu = 0.6$ M
153	$Cr(CO)_4dto + P(OEt)_3 \rightarrow Cr(CO)_4(P(OEt)_3)_2 + dto$	$(CH_2Cl)_2$	55	1.5	5	+14.7 ± 0.7		140	
154	$Cr(CO)_4BTE + P(OEt)_3 \rightarrow Cr(CO)_4(P(OEt)_3)_2 + BTE$	$(CH_2Cl)_2$	45	1.5	5	+14.0 ± 0.6		140	
155	$Mn(H_2O)_6^{2+} + bpy \rightarrow Mn(bpy)(H_2O)_4^{2+} + H_2O$	H_2O	21	2.0	5	−1.2 ± 0.2	+3.0 ± 0.4 (a)	141	$\mu = 0.3$ M (ClO_4^-)
156	$Mn(H_2O)_6^{2+} + terpy \rightarrow Mn(terpy)(H_2O)_3^{2+} + H_2O$	H_2O	15	1.0	5	−3.4 ± 0.7	+4.7 ± 0.3 (a)	142, 143	$\mu = 0.1$ M (ClO_4^-), $[M] \gg [L]$
157						−1.3 ± 0.3		143	$\mu = 0.1$ M (ClO_4^-), $[L] \gg [M]$
158	$Mn(H_2O)_6^{2+} + edta^{4-} \rightarrow Mn(edta)^{2-} + H_2O$	H_2O	25				+32.8 (b)	144	$\mu \rightarrow 0$
159	$Mn(H_2O)_6^{2+} + Hedta^{3-} \rightarrow Mn(Hedta)H_2O^- + H_2O$	H_2O	25				+25.2 (b)	144	$\mu \rightarrow 0$
160	$Mn^{2+} + H(mtpp) \rightarrow Mn(mtpp)^+ + H^+$	DMF	25	1.5	7	+12.9 ± 0.8		145	$\mu \leq 0.15$ *m*
161	$Mn(bpy)(H_2O)_4^{2+} + H_2O \rightarrow Mn(H_2O)_6^{2+} + bpy$	H_2O	21	2.0	5	−4.1 ± 0.4		141	$\mu = 0.3$ *m* (ClO_4^-)
162	$Mn(terpy)(H_2O)_3^{2+} + H_2O \rightarrow Mn(H_2O)_6^{2+} + terpy$	H_2O	15	1.0	5	−7.7 ± 2.2		142, 143	$\mu = 0.1$ M (ClO_4^-)
163	$Mn(terpy)(H_2O)_3^{2+} + Co(H_2O)_6^{2+} \rightarrow Mn(H_2O)_6^{2+} + Co(terpy)(H_2O)_3^{2+}$	H_2O	25	2.0	11	−10.1 ± 0.4		142	$\mu = 0.01$ M (ClO_4^-)
164	$Fe(H_2O)_6^{3+} + SCN^- \rightarrow Fe(H_2O)_5SCN^{2+} + H_2O$	H_2O	25	1.5	~8	−6.1 ± 1.0		146	$\mu = 1.5$ *m* (ClO_4^-)
165			20	2.0	5	+6.7 ± 0.4	+8.3 ± 0.3 (a)	147	$\mu = 0.2$ M (NO_3^-)
166			25	1.2	4		+10.0 ± 0.3 (c)	148	$\mu = 0$
167			25	1.2	4	+4.3 ± 0.6	+8.2 ± 0.4 (a)	148, 149	$\mu = 0.1$ M (ClO_4^-)
168			25	1.2	4		+7.8 ± 0.2 (a)	148	$\mu = 0.5$ M (ClO_4^-)
169			25	1.2	4		+7.6 ± 0.3 (a)	148	$\mu = 1.0$ M (ClO_4^-)
170			25	1.2	4		+7.5 ± 0.2 (a)	148	$\mu = 1.5$ M (ClO_4^-)
171			25	1.5	~8	−6.1 ± 1.0 −12	 +7.5	146 150	$\mu = 1.5$ *m* (ClO_4^-)
172	$Fe(H_2O)_6^{3+} + Cl^- \rightarrow Fe(H_2O)_5Cl^{2+} + H_2O$	H_2O	25	2.8	5	−4.5 ± 1.1		151	$\mu = 1.5$ M (ClO_4^-)
173	$Fe(H_2O)_6^{3+} + Br^- \rightleftarrows Fe(H_2O)_6^{3+}, Br^-$	H_2O	25	2.8	5		+11 ± 1 (c)	152	$\mu = 2.0$ M (ClO_4^-)
174	$Fe(H_2O)_6^{3+} + Br^- \rightarrow Fe(H_2O)_5Br^{2+} + H_2O$	H_2O	25	2.8	5	−19 ± 4		152	$\mu = 2.0$ M (ClO_4^-)
175	$Fe(H_2O)_6^{3+} + Br^- \rightarrow Fe(H_2O)_5Br^{2+} + H_2O$	H_2O	25	2.8	5		+8.1 ± 0.2 (a)	152	$\mu = 2.0$ M (ClO_4^-)
176	$Fe(H_2O)_6^{3+} + Hipt \rightarrow Fe(H_2O)_5ipt^{2+} + H^+$	H_2O	25	1.5	~10	−8.7 ± 0.8		153	$\mu = 1.0$ *m* (ClO_4^-)
177	$Fe(H_2O)_6^{3+} + Hahx \rightarrow Fe(H_2O)_5ahx^{2+} + H^+$	H_2O	25	1.5	~8	−10.0 ± 1.4		153	$\mu = 1.0$ *m* (ClO_4^-)

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
178	$Fe(H_2O)_6^{3+} \rightleftarrows Fe(H_2O)_5OH^{2+} + H^+$	H_2O	25	1.2	4			+4.8 ± 0.3 (c)	154	$\mu = 0$
179								+2.9 ± 0.1 (a)		μ = 0.1 M (ClO_4^-)
180								+2.7 ± 0.1 (a)		μ = 0.2 M (ClO_4^-)
181								+2.2 ± 0.1 (a)		μ = 0.5 M (ClO_4^-)
182								+1.9 ± 0.1 (a)		μ = 1.0 M (ClO_4^-)
183								+1.6 ± 0.1 (a)		μ = 2.0 M (ClO_4^-)
184	$Fe(H_2O)_5OH^{2+} + SCN^- \rightarrow Fe(H_2O)_4(SCN)OH^+ + H_2O$	H_2O	25	1.5	~8	+8.5 ± 1.2			146	μ = 1.5 *m* (ClO_4^-)
185		H_2O	20	2.0	5	~0			147	μ = 0.2 M (NO_3^-)
186		H_2O	25	1.2	4			+17.1 ± 1.0 (c)	148	$\mu = 0$
187		H_2O	25	1.2	4	+5.4 ± 1.5		+17.0 ± 0.9 (c)	148, 149	μ = 0.1 M (ClO_4^-)
188		H_2O	25	1.2	4			+16.4 ± 0.5 (c)	148	μ = 0.5 M (ClO_4^-)
189		H_2O	25	1.2	4			+16.6 ± 0.6 (c)	148	μ = 1.0 M (ClO_4^-)
190		H_2O	25	1.2	4			+16.6 ± 0.5 (c)	148	μ = 1.5 M (ClO_4^-)
191		H_2O	25			+8.8			150	
192	$Fe(H_2O)_5OH^{2+} + Cl^- \rightarrow Fe(H_2O)_4(Cl)OH^+ + H_2O$	H_2O	25	2.8	5	+7.8 ± 1.0			151	μ = 1.5 M (ClO_4^-)
193	$Fe(H_2O)_5OH^{2+}$ + Hipt $\rightarrow Fe(H_2O)_5ipt^{2+} + H_2O$	H_2O	25	1.5	~10	+4.1 ± 0.6			153	μ = 1.0 *m* (ClO_4^-)
194	$Fe(H_2O)_5OH^{2+} + H_2ipt^+ \rightarrow Fe(H_2O)_5ipt^{2+} + H_3O^+$	H_2O	25	1.5	~10	−10.0 ± 1.2			153	μ = 1.0 *m* (ClO_4^-)
195	$Fe(H_2O)_5OH^{2+}$ + Hahx $\rightarrow Fe(H_2O)_5ahx^{2+} + H_2O$	H_2O	25	1.5	~8	+7.7 ± 0.6			153	μ = 1.0 *m* (ClO_4^-)
196	$Fe^{3+} + SCN^- \rightarrow Fe(SCN)^{2+}$	DMSO	25	2.0	6	+3.3 ± 0.6			155	μ = 0.2 *m* (ClO_4^-)
197	Fe^{3+} + Hipt $\rightarrow Fe(ipt)^{2+}$	DMSO	25	2.0	6	+10.9 ± 1.7			155	μ = 0.2 *m* (ClO_4^-)
198		DMF	25	2.0	6	+5.0 ± 0.4			155	μ = 0.2 *m* (ClO_4^-)
199	Fe^{3+} + Hahx $\rightarrow Fe(ahx)^{2+}$	DMSO	25	2.0	6	+3.0 ± 0.3			155	μ = 0.2 *m* (ClO_4^-)
200		DMF	25	2.0	6	−0.8 ± 0.2			155	μ = 0.2 *m* (ClO_4^-)
201	$Fe(SCN)^{2+} \rightarrow Fe^{3+} + SCN^-$	H_2O	25	2.0	6	−15.0 ± 1.2			155	μ = 0.2 *m* (ClO_4^-)
202		DMSO	25	2.0	6	−8.5 ± 1.4			155	μ = 0.2 *m* (ClO_4^-)
203	$FeBr^{2+} \rightarrow Fe^{3+}{}_3Br^-$	H_2O	25	2.8	5	−2 ± 4			152	μ = 2.0 M (ClO_4^-)
204	$Fe(H_2O)_5SCN^{2+} \rightleftarrows Fe(H_2O)_4(SCN)OH^+ + H^+$	H_2O	25	1.2	4			+11.9 ± 0.4 (c)	148	$\mu = 0$
205								+11.7 ± 0.4 (a)		μ = 0.1 M (ClO_4^-)
206								+11.3 ± 0.2 (a)		μ = 0.5 M (ClO_4^-)
207								+11.2 ± 0.2 (a)		μ = 1.0 M (ClO_4^-)
208								+11.0 ± 0.2 (a)		μ = 1.5 M (ClO_4^-)
209	$Fe(H_2O)_6^{2+}$ + terpy $\rightarrow$ Fe(terpy)$(H_2O)_3^{2+} + H_2O$	H_2O	25	1.0	5	+3.4 ± 0.6			143, 156	μ = 0.1 M (ClO_4^-), [L] ≫ [M]
210						+3.7 ± 0.8			143	μ = 0.1 M (ClO_4^-), [M] ≫ [L]
211	$Fe(CN)_5H_2O^{3-} + CN^- \rightarrow Fe(CN)_6^{4-} + H_2O$	H_2O	23	4.5	6	+13.5 ± 1.5			157	
212	Fe(tptdt)$(CH_3CN)_2^{2+}$ + Im $\rightarrow$ Fe(tptdt)(Im)$CH_3CN^{2+} + CH_3CN$	CH_3CN	25	2.0	9	+13.7 ± 0.9			158	
213	Fe(tptdt)$(CH_3CN)_2^{2+} + SCN^- \rightarrow$ Fe(tptdt)(SCN)$CH_3CN^+ + CH_3CN$	CH_3CN	25	2.0	9	+10.1 ± 0.2			158	
214	Fe(tptdt)$(DMSO)_2^{2+}$ + Im $\rightarrow$ Fe(tptdt)(Im)$DMSO^{2+}$ + DMSO	DMSO	30	0.8	10	+27.2 ± 1.5			159	
215	Fe(tptdt)(Im)$DMSO^{2+}$ + Im $\rightarrow$ Fe(tptdt)$(Im)_2^{2+}$ + DMSO	DMSO	35	1.2	6	+21.8 ± 0.9			159	
216	$Fe(bpy)_3^{2+} + H_2O \rightarrow$ products	H_2O	30	2.1	6	+12.3 ± 0.5			160	1.0 M HCl
217		H_2O	35	1.4	5	+14.8 ± 0.7			160	0.01 M HCl
218		D_2O	35	1.4	5	+13.3 ± 0.4			160	1.0 M DCl
219		D_2O	35	1.4	5	+16.3 ± 0.5			160	0.01 M DCl

	$Fe(R_2bpy)_3^{2+} + H_2O \rightarrow$ products	H_2O	25					161	
220	R_2 = 4,4′-Me_2			1.4	5	+15.5 ± 0.5			0.01 M HCl
221				1.4	5	+12.5 ± 0.7			1.0 M HCl
222	R_2 = 4,4′-Et_2			1.4	5	+16.9 ± 0.6			0.01 M HCl
223				1.4	5	+12.7 ± 0.6			1.0 M HCl
224	R_2 = 5,5′-Me_2			1.4	5	+17.4 ± 0.8			0.01 M HCl
225				1.4	5	+13.7 ± 0.5			1.0 M HCl
226	$Fe(phen)_3^{2+}$ + MeOH → products	MeOH	36.8	1.4	5	+14.1 ± 0.2		161	0.1 M CF_3SO_3H
227	$Fe(bpy)_3^{2+} + OH^- \rightarrow$ products	H_2O	20	1.4	5	+19.7 ± 0.3		162	μ = 0.1 M
228	$Fe(phen)_3^{2+} + OH^- \rightarrow$ products	H_2O	20	1.4	5	+21.5 ± 0.4		162	μ = 0.1 M
229	$Fe(sb)_3^{2+} + OH^- \rightarrow$ products	H_2O	25	1.34	6	+11.1 ± 1.6		163, 164	$[OH^-]$ = 0.07 M, μ = 0.33 M
230		30% MeOH	25	1.01	3	+19.9 ± 1.0		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
231		50% MeOH	25	1.18	4	+22.8 ± 1.8		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
232		75% MeOH	25	1.34	4	+25 ± 2		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
233		85% MeOH	25	1.34	3	+27 ± 3		163, 164	$[OH^-]$ = 0.07 M, μ = 0.33 M
234		94% MeOH	25	1.34	2	+29		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
235		17% *t*-BuOH	25	1.34	4	+27 ± 4		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
236		17% DMSO	25	1.18	3	+15 ± 3		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
237		25% DMSO	25	0.68	3	+18 ± 3		164	$[OH^-]$ = 0.07 M, μ = 0.33 M
238	$Fe(hxsb)^{2+} + OH^- \rightarrow$ products	H_2O	25	1.34	4	+13.4 ± 1.9		163, 164	$[OH^-] = \mu$ = 0.33 M
239		50% MeOH	25	1.34	4	+14.0		164	$[OH^-] = \mu$ = 0.33 M
240		75% MeOH	25	1.34	4	+6.2 ± 0.6		164	$[OH^-] = \mu$ = 0.33 M
241		75% MeOH	25	1.34	2	+5.5 ± 1.2		163, 164	$[OH^-]$ = 0.1 M, μ = 0.33 M
242		85% MeOH	25	1.34	3	+6.8		164	$[OH^-] = \mu$ = 0.33 M
243		17% *t*-BuOH	25	1.34	3	+14.1 ± 1.1		164	$[OH^-] = \mu$ = 0.33 M
244		20% DMSO	25	1.34	2	+14		164	$[OH^-] = \mu$ = 0.33 M
245		30% DMSO	25	1.34	3	+21 ± 3		164	$[OH^-] = \mu$ = 0.33 M
246		30% DMSO	25	1.34	4	+11.8 ± 1.6		164	$[OH^-]$ = 0.1 M, μ = 0.33 M
247	$Fe(fz)_3^{4-} + OH^- \rightarrow$ products	33% MeOH	25	1.1		−2 ± 2	0 ± 2 (a)	165, 166	
248	$Fe(4\text{-}Mephen)_3^{2+} + CN^- \rightarrow$ products	H_2O	25	1.4	2	+10		167, 168	
249		33% MeOH	25	1.4	2	+13		167, 168	
250	$Fe(bpy)_3^{2+} + CN^- \rightarrow$ products	H_2O	20	1.4	5	+20.9 ± 1.6		162	μ = 0.1 M
251	$Fe(phen)_3^{2+} + CN^- \rightarrow$ products	H_2O	25	1.4	5	+19.8 ± 1.0		162	μ = 0.1 M
252	$Fe(CN)_5(3,5\text{-}Me_2py)^{3-} + CN^- \rightarrow Fe(CN)_6^{4-} + 3,5\text{-}Me_2py$	H_2O	25	1.4	5	+20.5 ± 0.8		169	μ = 0.5 M (ClO_4^-)
253	$Fe(CN)_5(3,5\text{-}Me_2py)^{3-} + pz \rightarrow Fe(CN)_5pz^{3-} + 3,5\text{-}Me_2py$	H_2O	25	1.4	5	+21.2 ± 1.0		169	μ = 0.5 M (ClO_4^-)
254	$Fe(CN)_5(3,5\text{-}Me_2py)^{3-} + imH \rightarrow Fe(CN)_5imH^{3-} + 3,5\text{-}Me_2py$	H_2O	25	1.4	5	+20.3 ± 1.0		169	μ = 0.5 M (ClO_4^-)
255	$Fe(CN)_5(3\text{-}CNpy)^{3-} + CN^- \rightarrow Fe(CN)_6^{4-} + 3\text{-}CNpy$	H_2O	25	1.4	5	+20.6 ± 0.5		169	μ = 0.5 M (ClO_4^-)
256	$Fe(CN)_5(4\text{-}CNpy)^{3-} + CN^- \rightarrow Fe(CN)_6^{4-} + 4\text{-}CNpy$	H_2O	25	1.0	4	+20.6		170	
257	$Fe(CN)_5(2\text{-}Mepz)^{3-} + CN^- \rightarrow Fe(CN)_6^{4-} + 2\text{-}Mepz$	H_2O	25	1.4	4	+19.4		170	
258	$Co(NH_3)_5H_2O^{3+} + Cl^- \rightarrow Co(NH_3)_5Cl^{2+} + H_2O$	H_2O	60	1.8	8	+1.4 ± 0.8	+11.6 (b)	130, 171	μ = 2 M (ClO_4^-)
259	$Co(NH_3)_5H_2O^{3+} + SO_4^{2-} \rightarrow Co(NH_3)_5SO_4^+ + H_2O$	H_2O	60	1.5	4	+2.3 ± 1.8	+19.2 (b)	130	μ = 2 M (ClO_4^-)

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^\ddagger$, cm^3 mol^{-1}	$\Delta\beta^\ddagger$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
260	$Co(NH_3)_5OH^{2+} + SO_3^{2-} \rightarrow Co(NH_3)_5SO_3^{+} + OH^-$	H_2O	35	1.2	6	+18.6 ± 1.5			172	pH = 9.4, μ = 0.5 M
261	*cis*-$Co(en)_2(H_2O)_2^{3+} + H_2C_2O_4 \rightarrow Co(en)_2C_2O_4^{+} + 2H_3O^+$	H_2O	60	1.5	4	+4.8 ± 0.2			173	μ = 2 M (NO_3^-)
262		H_2O	70	1.5	4	+1.1 ± 0.2			174	2 M $HClO_4$
263		H_2O	60	1.5	4	+3.5 ± 0.8			174	2 M HNO_3
264	*cis*-$Co(en)_2(H_2O)_2^{3+} + HC_2O_4^- \rightarrow Co(en)_2C_2O_4^+ + H_2O + H^+$	H_2O	60	1.5	4	+14.8 ± 0.2			173	μ = 2 M (NO_3^-)
265	*cis*-$Co(en)_2(H_2O)OH^{2+} + C_2O_4^{2-} \rightarrow Co(en)_2(OH)C_2O_4 + H_2O$	H_2O	30	1.5	4	+3.6 ± 1.9			173	μ = 2 M (NO_3^-)
266	$Co(en)_2(OH)C_2O_4 + H^+ \rightarrow Co(en)_2C_2O_4^+ + H_2O$	H_2O	50	1.4	5	0 ± 1			173	μ = 0.4 M (NO_3^-)
	$Co(CN)_5H_2O^{2-} + L^- \rightarrow Co(CN)_5L^{3-} + H_2O$	H_2O	40	1.5	7				175	μ = 1.0 M (ClO_4^-)
267	$L^- = Br^-$					+8.4 ± 1.0				
268	$L^- = I^-$					+9.4 ± 1.6				
269	$L^- = SCN^-$					+8.2 ± 0.9				
270	$Co(tpps)(H_2O)_2^{3-} + SCN^- \rightarrow Co(tpps)(H_2O)NCS^{4-} + H_2O$	H_2O	20	1.0	5	+15.4 ± 0.6			131	[H^+] = 0.1 M, μ = 1.0 M
271	$Co(tmpp)(H_2O)_2^{5+} + SCN^- \rightarrow Co(tmpp)(H_2O)NCS^{4+} + H_2O$	H_2O	25	1.2	6	+14 ± 4			176	[H^+] = 0.1 *m*, μ = 2.2 *m*
272	$Co(tmpp)(H_2O)_2^{5+} + SC(NH_2)_2 \rightarrow Co(tmpp)(H_2O)SC(NH_2)_2^{5+} + H_2O$	H_2O	22	1.4	5	+12.6 ± 0.6			177	[H^+] = 0.1 M, μ = 1.0 M
	$Co(NH_3)_5X^{(3-n)+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + X^{n-}$									
273	$X^{n-} = OHCH_3$	H_2O	38	1.7	4	+2.2 ± 0.2		+1.6 (b)	178, 179	0.01 M CF_3SO_3H
274	$X^{n-} = OHCH_2CH_3$	H_2O	38	1.7	4	+2.9 ± 0.3		+2.2 (b)	178, 179	0.01 M CF_3SO_3H
275	$X^{n-} = OHCH(CH_3)_2$	H_2O	25	1.7	4	+3.8 ± 0.2		+2.9 (b)	178, 179	0.01 M CF_3SO_3H
276	$X^{n-} = OC(NH_2)_2$	H_2O	34	1.7	4	+1.3 ± 0.5		+1.2 (b)	178, 180	$\mu \sim 0$
277	$X^{n-} = OC(NH_2)(NHCH_3)$	H_2O	35	1.7	4	+0.3 ± 0.3		−1.6 (b)	178	$\mu \sim 0$
278	$X^{n-} = OC(NHCH_3)_2$	H_2O	34	1.7	4	+1.5 ± 0.3		−0.6 (b)	178	$\mu \sim 0$
279	$X^{n-} = OCH(NH_2)$	H_2O	48	1.7	4	+1.1 ± 0.3		+0.5 (b)	178	0.01 M CF_3SO_3H
280	$X^{n-} = OCH(NHCH_3)$	H_2O	48	1.7	4	+1.7 ± 0.3		+1.5 (b)	178	0.01 M CF_3SO_3H
281	$X^{n-} = OCH(N(CH_3)_2)$	H_2O	49	1.7	4	+2.6 ± 0.4		+2.9 (b)	178	0.01 M CF_3SO_3H
282	X^{n-} = DMSO	H_2O	41	1.7	4	+2.0 ± 0.4		+3.1 (b)	178	0.01 M CF_3SO_3H
283		H_2O	25	1.5	7	−1.7 ± 0.7			181	μ = 0.1 M (ClO_4^-)
284	$X^{n-} = Br^-$	H_2O	25	2.0		−8.7 ± 2			182	0.01 M $HClO_4$
285		H_2O	25	2.0		−0.2			182	0.01 M $HClO_4$, 10^{-4} M NaPES
286		H_2O	25	2.0		+1.3			182	0.01 M $HClO_4$, 3×10^{-4} M NaPES
287		H_2O	25	2.0		+12			182	0.01 M $HClO_4$, 8×10^{-4} M NaPES
288	$X^{n-} = SO_4^{2-}$ spontaneous reaction	H_2O	35	1.5	6	−18.3 ± 0.4		−26 ± 3 (b)	183	μ = 1.0 *m* (ClO_4^-)
289		H_2O	55	1.0	5	−19.7 ± 0.8			183	μ = 1.0 *m* (ClO_4^-)
290	$X^{n-} = SO_4^{2-}$ acid-catalyzed reaction	H_2O	35	1.5	6	−3.5 ± 0.6			183	μ = 1.0 *m* (ClO_4^-)
291		H_2O	55	1.0	5	−3.9 ± 0.5			183	μ = 1.0 *m* (ClO_4^-)
292	$Co(NH_3)_5SO_3^+ + H_3O^+ \rightarrow$ *trans*-$Co(NH_3)_4(SO_3)H_2O^+ + NH_4^+$	H_2O	25	1.0	5	+6.0 ± 1.2			172	[H^+] = 1.5 M, μ = 2 M
293	*trans*-$Co(NH_3)_4(NH_2CH_3)Cl^{2+} + H_2O \rightarrow$ *trans*-$Co(NH_3)_4(NH_2CH_3)H_2O^{3+} + Cl^-$	H_2O	49	1.7	6	−4.6 ± 0.5	−0.5 ± 0.2		184	μ = 0.1 M (ClO_4^-)

294	$Co(NH_2CH_3)_5Cl^{2+} + H_2O \rightarrow Co(NH_2CH_3)_5H_2O^{3+} + Cl^-$	H_2O	39	1.7	6	−2.3 ± 0.4		184	$\mu = 0.1$ M (ClO_4^-)
	$Co(NH_2CH_3)_5L^{3+} + H_2O \rightarrow Co(NH_2CH_3)_5H_2O^{3+} + L$	H_2O		1.7	4			185	0.1 M $HClO_4$
295	L = DMSO		23			+5.9 ± 0.2			
296	L = DMF		38			+6.3 ± 0.3			
297	L = CH_3CN		45			+6.0 ± 0.5			
298	$Co(NH_3)_4(NH_2)Cl^+ + H_2O \rightarrow Co(NH_3)_5OH^{2+} + Cl^-$	H_2O	35			+15.0	−9.4 (b)	186	$\mu \sim 0$
299	$Co(NH_3)_4(NH_2)Br^+ + H_2O \rightarrow Co(NH_3)_5OH^{2+} + Br^-$	H_2O	25			+13.6	−8.6 (b)	186	$\mu \sim 0$
	trans-$Co(NH_3)_4(CN)X^{(2-n)+} + H_2O \rightarrow$ *trans*-$Co(NH_3)_4(CN)H_2O^{2+} + X^{n-}$								
300	$X^{n-} = Cl^-$	H_2O	40	1.5	7	−7.3 ± 0.4	−12.5 ± 0.9 (b)	187	$\mu = 0.1$ M (ClO_4^-)
301	$X^{n-} = Br^-$	H_2O	40	1.5	7	−6.2 ± 0.6	−12.3 ± 1.6 (b)	187	$\mu = 0.1$ M (ClO_4^-)
302	$X^{n-} = I^-$	H_2O	30	1.5	7	−3.3 ± 0.9	−10.8 ± 3.5 (b)	187	$\mu = 0.1$ M (ClO_4^-)
303	$X^{n-} = N_3^-$	H_2O	40	1.5	7	+5.7 ± 0.2		187	0.1 M HNO_3
304	X^{n-} = DMSO	H_2O	20	1.5	7	+0.6 ± 0.3		187	$\mu = 0.1$ M (ClO_4^-)
	cis-$Co(NH_3)_4(H_2O)X^{2+} + H_2O \rightarrow$ *cis*-$Co(NH_3)_4(H_2O)_2^{3+} + X^-$	H_2O						188	
305	$X^- = Cl^-$		55	2.0	5	−4.3 ± 0.2	−11.2 (b)		$\mu = 0.5$ M (ClO_4^-)
306							−12.1 (b)		$\mu = 0.03$ M (ClO_4^-)
307	$X^- = Br^-$		43	2.0	5	−3.5 ± 0.6	−12.4 (b)		$\mu = 0.5$ M (ClO_4^-)
308							−11.8 (b)		$\mu = 0.04$ M (ClO_4^-)
309	$X^- = NO_3^-$		37	1.6	5	−2.1 ± 0.1	−9.7 (b)		$\mu = 0.5$ M (ClO_4^-)
310							−9.0 (b)		$\mu = 0.01$ M (ClO_4^-)
	cis-$Co(NH_3)_4(OH)X^+ + H_2O \rightarrow$ *cis*-$Co(NH_3)_4(H_2O)OH^{2+} + X^-$	H_2O						188	
311	$X^- = Cl^-$		55	2.0	5	+3.3 ± 0.3			
312	$X^- = Br^-$		43	2.0	5	+4.9 ± 0.7			
313	$X^- = NO_3^-$		37	1.6	5	+5.4 ± 0.5			
	trans-$Co(N_4)Cl_2^+ + H_2O \rightarrow$ *trans*-$Co(N_4)(Cl)H_2O^{2+} + Cl^-$								
314	$N_4 = (NH_3)_4$	H_2O	25	1.5	7	−1.3 ± 0.3	−15.5 ± 2.1 (b)	10, 187	$\mu \sim 0$
315		H_2O	10	1.5	7	−1.7 ± 0.7		10, 187	$\mu = 0.1$ M (ClO_4^-)
316	$N_4 = (en)_2$	H_2O	25	1.5	7	−1.7 ± 1.1	−13.9 ± 1.7 (b)	10, 187	$\mu \sim 0$
317		H_2O	30	1.5	7	−1.1 ± 0.9		10, 187	$\mu = 0.1$ M (ClO_4^-)
318		H_2O	25	2.0	5	+0.8		189	
319	$N_4 = (pn)_2$	H_2O	31	2.0	5	+14.4		190	pH = 2.5
320		H_2O	40	2.0	5	+10.5		190	pH = 2.5
321		H_2O	50	2.0	5	+6.3		190	pH = 2.5
322		H_2O	61	2.0	5	+1.5		190	pH = 2.5
323	N_4 = (Me en)$_2$	H_2O	30	1.5	7	−3.1 ± 0.5	−13.1 ± 0.8 (b)	10, 187	$\mu = 0.1$ M (ClO_4^-)
324		H_2O	40	1.5	4	+6.0		189	
325	N_4 = (Et en)$_2$	H_2O	30	1.5	7	−0.3 ± 0.9	−11.7 ± 1.8 (b)	10, 187	$\mu = 0.1$ M (ClO_4^-)
326		H_2O	25	1.5	4	+0.3		189	
327	N_4 = (Pr en)$_2$	H_2O	30	1.5	7	+0.3 ± 0.6	−14.9 ± 1.6 (b)	10, 187	$\mu = 0.1$ M (ClO_4^-)
328	$N_4 = (tn)_2$	H_2O	5	1.5	4	+7.3		189	
329	N_4 = 3,2,3-tet	H_2O	30	1.5	7	−2.8 ± 1.5	−14.9 ± 2.7 (b)	10, 187	$\mu = 0.1$ M (ClO_4^-)
330	N_4 = (*R*,*S*)-2,3,2-tet	H_2O	25	1.5	7	−0.8 ± 1.7		10, 187	0.01 M HNO_3
331		H_2O	50	1.5	7	−1.3 ± 0.4	−13.1 ± 2.1 (b)	10, 187	$\mu \sim 0$
332		H_2O	50	1.5	7	−1.9 ± 0.4		10, 187	$\mu = 1.0$ M (ClO_4^-)
333		H_2O	30	1.5	7	−1.0 ± 0.4		10, 187	$\mu = 0.1$ M (ClO_4^-)
334	N_4 = (*RR*,*SS*)-2,3,2-tet	H_2O	25	1.5	7	+1.0 ± 0.4		10, 187	$\mu = 0.01$ M HNO_3
335	N_4 = cyclam	H_2O	50	1.5	7	−2.0 ± 0.9	−14.3 ± 1.2 (b)	10, 187	0.1 M HNO_3
	trans-$Co(N_4)Br_2^+ + H_2O \rightarrow$ *trans*-$Co(N_4)(Br)H_2O^{2+} + Br^-$								
336	$N_4 = (en)_2$	H_2O	30	1.5	7	+1.4 ± 0.6	−14.5 ± 1.7 (b)	187	$\mu = 0.1$ M (ClO_4^-)
337	N_4 = 2,3,2-tet	H_2O	30	1.5	7	+3.4 ± 0.6	−13.1 ± 2.3 (b)	187	$\mu = 0.1$ M (ClO_4^-)
	trans-$Co(en)_2(X)Y^+ + H_2O \rightarrow$ *trans*-$Co(en)_2(X)H_2O^{2+} + Y^-$								

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	$\Delta\beta^{\ddagger}$, $cm^3\ mol^{-1}\ kbar^{-1}$	$\Delta\bar{V}$, $cm^3\ mol^{-1}$ (method)	ref	remarks
338	$X^- = NO_2^-$, $Y^- = Cl^-$	H_2O	10	2.0	6	−0.3			186	$\mu \sim 0$
339		H_2O	15	2.0	6	+0.1		−10.4 (b)	186	$\mu \sim 0$
340		H_2O	20	2.0	6	+0.3			186	$\mu \sim 0$
341	$X^- = NO_2^-$, $Y^- = Br^-$	H_2O	10	2.0	6	+0.3 ± 0.2			191	
342		H_2O	10	2.0	6	+0.2 ± 0.2		−10.4 ± 0.1 (b)	191	0.01 M $HClO_4$
343	$X^- = CN^-$, $Y^- = Cl^-$	H_2O	35	1.4	5	−2.0 ± 0.4			192	0.1 M $HClO_4$
344	$X^- = N_3^-$, $Y^- = Cl^-$	H_2O	30	2.0	6	+0.7 ± 0.2		−11.0 ± 0.6 (b)	191	0.01 M $HClO_4$
345	*trans*-$Co(dtcd)(N_3)Cl^+ + H_2O \rightarrow$ *trans*-$Co(dtcd)(N_3)H_2O^{2+} + Cl^-$	H_2O	25	1.4	5	+8.3 ± 0.5			193	0.1 M HNO_3
346	*trans*-$Co(dtcd)(N_3)Br^+ + H_2O \rightarrow$ *trans*-$Co(dtcd)(N_3)H_2O^{2+} + Br^-$	H_2O	20	1.4	4	+5.3 ± 0.7			193	0.1 M HNO_3
	cis-$Co(N_4)Cl_2^+ + H_2O \rightarrow$ *cis*-$Co(N_4)(Cl)H_2O^{2+} + Cl^-$									
347	$N_4 = (en)_2$	H_2O	30	1.5	7	−0.3 ± 0.4		−14.2 ± 1.8 (b)	10, 187	$\mu = 0.1\ M\ (ClO_4^-)$
348	N_4 = tren	H_2O	14	1.4	5	+7.3 ± 0.4			194	
349	N_4 = α-trien	H_2O	27	1.4	5	−5.0 ± 0.4			192	0.1 M $HClO_4$
350	N_4 = β-trien	H_2O	25	1.4	5	−2.0 ± 0.6			192	0.1 M $HClO_4$
351		H_2O	25	1.4	5	+3.0 ± 0.6			194	
	cis-$Co(N_4)(NO_2)X^+ + H_2O \rightarrow$ *cis*-$Co(N_4)(NO_2)H_2O^{2+} + X^-$									
352	$N_4 = (en)_2$, $X^- = Cl^-$	H_2O	30	2.0	6	+0.9		−9.3 (b)	186	$\mu \sim 0$
353		H_2O	35	1.4	5	−2.9 ± 0.3			192	0.1 M $HClO_4$
354	$N_4 = (bpy)_2$, $X^- = Cl^-$	H_2O	30	2.0	6	+2.9		−9.1 (b)	186	$\mu \sim 0$
355	$N_4 = (bpy)_2$, $X^- = Br^-$	H_2O	30	2.0	5	+11.3		−6.7 (b)	186	$\mu \sim 0$
356	$N_4 = (phen)_2$, $X^- = Br^-$	H_2O	35	2.0	6	+3.3		−12.5 (b)	186	$\mu \sim 0$
357	$Co(dmg)_2(Cl)OC(NH_2)_2 + H_2O \rightarrow Co(dmg)_2(OC(NH_2)_2)H_2O^+ + Cl^-$	H_2O				+3.5 ± 0.3			180	$\mu \sim 0$
	$Co(CN)_5X^{3-} + H_2O \rightarrow Co(CN)_5H_2O^{2-} + X^-$			1.5	7				175	
358	$X^- = Cl^-$	H_2O	40			+7.8 ± 0.5				$\mu = 1.0\ M\ (ClO_4^-)$
359		H_2O	40			+10.0 ± 0.6				$\mu = 0.1\ M\ (ClO_4^-)$
360		H_2O	25			+9.1 ± 0.3				$\mu = 0.1\ M\ (ClO_4^-)$
361	$X^- = Br^-$	H_2O	40			+7.6 ± 0.6				$\mu = 1.0\ M\ (ClO_4^-)$
362	$X^- = I^-$	H_2O	40			+14.0 ± 0.7				0.9 M NaOH, $\mu = 1.0\ M$
363	$X^- = N_3^-$	H_2O	40			+16.8 ± 0.5				0.1 M $HClO_4$
364	$Co(C_2O_4)_3^{3-} + H_2O \rightarrow Co(C_2O_4)_2(H_2O)_2^- + C_2O_4^{2-}$	H_2O	50	1.5	7	+10.8 ± 0.4			136	1 M $HClO_4$
365	$Co(en)_2CO_3^+ + H_2O \rightarrow$ *cis*-$Co(en)_2(H_2O)OCO_2^+$	H_2O	25	1.5	4	−6.1 ± 0.3			137	pH = 5, $\mu = 0.5\ M$
366	$Co(en)_2CO_3^+ + H_3O^+ \rightarrow$ *cis*-$Co(en)_2(H_2O)OCO_2H^{2+}$	H_2O	25	1.0	5	−7.1 ± 0.9			137	$[H^+] = 0.2\ M$, $\mu = 2\ M$
367	α-$Co(edda)CO_3^- + H_2O \rightarrow$ α-$Co(edda)(H_2O)OCO_2^-$	H_2O	25	1.5	4	−14.0 ± 0.9			137	pH = 5, $\mu = 0.5\ M$
368	α-$Co(edda)CO_3^- + H_3O^+ \rightarrow$ α-$Co(edda)(H_2O)OCO_2H$	H_2O	25	1.0	5	−4.2 ± 0.4			137	$[H^+] = 0.05\ M$, $\mu = 2\ M$
369	β-$Co(edda)CO_3^- + H_2O \rightarrow$ β-$Co(edda)(H_2O)OCO_2^-$	H_2O	25	1.5	4	−14.5 ± 2.5			137	pH = 5, $\mu = 0.5\ M$
370	β-$Co(edda)CO_3^- + H_3O^+ \rightarrow$ β-$Co(edda)(H_2O)OCO_2H$	H_2O	25	1.0	5	−3.8 ± 0.4			137	$[H^+] = 0.05\ M$, $\mu = 2\ M$
371	$Co(nta)CO_3^{2-} + H_2O \rightarrow Co(nta)(H_2O)OCO_2^{2-}$	H_2O	25	1.5	4	−9.4 ± 1.1			137	pH = 5, $\mu = 0.5\ M$
372	$Co(nta)CO_3^{2-} + H_3O^+ \rightarrow Co(nta)(H_2O)OCO_2H^-$	H_2O	25	1.0	5	+0.2 ± 1.2			137	$[H^+] = 0.05\ M$, $\mu = 2\ M$
	$Co(NH_3)_5X^{(3-n)+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + X^{n-}$									

373	X^{n-} = DMSO	H_2O	25	1.0	5	+40.2 ± 0.5	+21.2 ± 0.3 (b)	195	μ = 0.016 M (ClO_4^-)
374	$X^{n-} = F^-$	H_2O	25	1.5	7	+26.4 ± 1.0	+7.4 ± 1.0 (b)	195	μ = 0.011 M (ClO_4^-)
375	$X^{n-} = Cl^-$	H_2O	25	1.5	7	+33.6 ± 0.6		195	μ = 0.001 M (ClO_4^-)
376		H_2O	25	1.5	7	+33.0 ± 1.1	+9.9 ± 0.2 (b)	195	μ = 0.01 M (ClO_4^-)
377		H_2O	25	1.5	7	+33.8 ± 1.0		195	μ = 0.1 M (ClO_4^-)
378		H_2O	35	1.5	4	+33.4		196	carbonate buffer
379	$X^{n-} = Br^-$	H_2O	25	1.0	5	+32.5 ± 1.4	+11.1 ± 0.2 (b)	195	μ = 0.013 M (ClO_4^-)
380		H_2O	25	3.0	4	+32 ± 2		197	
381		H_2O	25	3.0	4	+30		197	10^{-5} M NaPES
382		H_2O	25	3.0	4	+23		197	5 × 10^{-5} M NaPES
383		H_2O	25	3.0	4	+10		197	10^{-4} M NaPES
384		H_2O	25	2.0	4	+30		197	4 × 10^{-5} M polybrene
385		H_2O	25	2.0	4	+30		197	4 × 10^{-4} M polybrene
386		H_2O	25	2.0	4	+34		197	4 × 10^{-3} M polybrene
387	$X^{n-} = I^-$	H_2O	25	1.0	5	+33.6 ± 1.0	+15.5 ± 0.3 (b)	195	μ = 0.011 M (ClO_4^-)
388	$X^{n-} = NO_3^-$	H_2O	25	1.0	5	+31.0 ± 0.8	+13.2 ± 0.4 (b)	195	μ = 0.013 M (ClO_4^-)
389	$X^{n-} = SO_4^{2-}$	H_2O	25	1.0	5	+22.2 ± 0.7	−3.9 ± 0.4 (b)	195	μ = 0.01 M (ClO_4^-)
	$Co(NH_3)_4(NH_2X)Cl^{2+} + OH^- \rightarrow Co(NH_3)_4(NH_2X)OH^{2+} + Cl^-$	H_2O	25	1.0	5			198	μ = 0.013 M (ClO_4^-)
390	X = cis, Me					+29.4 ± 0.4	+9.8 (b)		
391	X = trans, Me					+28.6 ± 1.3	+10.4 (b)		
392	X = trans, Et					+28.3 ± 1.4	+10.1 (b)		
393	X = cis, *n*-Pr					+26.4 ± 1.5	+11.4 (b)		
394	X = trans, *n*-Pr					+29.9 ± 1.2			
395	X = trans, *n*-Bu					+28.7 ± 0.7	+11.9 (b)		
396	X = trans, *i*-Bu					+28.5 ± 1.2	+12.0 (b)		
397	α-$Co(edda)(NH_3)_2^+ + OH^- \rightarrow$ α-$Co(edda)(NH_3)OH + NH_3$	H_2O	66	1.5	4	+16.6		199	pH = 9.4, buffer
398	β-$Co(edda)(NH_3)_2^+ + OH^- \rightarrow$ β-$Co(edda)(NH_3)OH + NH_3$	H_2O	43	1.5	4	+22.3		199	pH = 9.5, buffer
399	α-$Co(edda)(NO_2)_2^- + OH^- \rightarrow$ α-$Co(edda)(NO_2)OH^- + NO_2^-$	H_2O	66	1.5	4	+11.9		199	pH = 9.9, buffer
	$MA^z + OH^- \rightarrow MA^{z-1} + H_2O$	H_2O	25					34	$\mu \rightarrow 0$
400	$MA^z = Co(NH_3)_5H_2O^{3+}$						+25.5 ± 0.1 (b)		
401	MA^z = *trans*-$Co(NH_3)_4(CN)H_2O^{2+}$						+20.5 ± 0.5 (b)		
402	$MA^z = Co(NH_3)_5C_2O_4H^{2+}$						+19.5 ± 0.1 (b)		
403	MA^z = *trans*-$Co(en)_2(NO_2)H_2O^{2+}$						+19.9 ± 0.1 (b)		
404	MA^z = *cis*-$Co(en)_2(NO_2)H_2O^{2+}$						+18.9 ± 0.2 (b)		
405	MA^z = *cis*-$Co(bpy)_2(NO_2)H_2O^{2+}$						+17.6 ± 0.3 (b)		
406	MA^z = α-$Co(edda)(H_2O)_2^+$						+14.9 ± 0.4 (b)		
407	MA^z = α-$Co(edda)(H_2O)OH$						+13.6 ± 1.3 (b)		
408	MA^z = β-$Co(edda)(H_2O)_2^+$						+17.9 ± 0.6 (b)		
409	MA^z = β-$Co(edda)(H_2O)OH$						+10.7 ± 1.3 (b)		
410	$MA^z = Co(nta)(H_2O)_2$						+15.7 ± 0.3 (b)		
411	$MA^z = Co(nta)(H_2O)OH^-$						+9.0 ± 0.7 (b)		
412	$MA^z = Co(CN)_5H_2O^{2-}$						+2.4 ± 0.3 (b)		
413	$Co(NH_3)_5Cl^{2+} + H_2O \xrightarrow{Hg^{2+}} Co(NH_3)_5H_2O^{3+} + Cl^-$	H_2O	15	1.0	6	+0.7 ± 0.4		139	$[H^+]$ = 0.3 M, μ = 0.6 M
414	$Co(NH_3)_5Br^{2+} + H_2O \xrightarrow{Hg^{2+}} Co(NH_3)_5H_2O^{3+} + Br^-$	H_2O	15	1.0	5	+0.8 ± 0.5		139	$[H^+]$ = 0.3 M, μ = 0.6 M
415	$Co(NH_3)_5Br^{2+} + H_2O \xrightarrow{Ag^+} Co(NH_3)_5H_2O^{3+} + Br^-$	H_2O	25	2.0	4	−5.3 ± 0.2		182	
416		H_2O	25	2.0	4	−2.3		182	10^{-6} M NaPSS
417		H_2O	25	2.0	4	+16		182	10^{-5} M NaPSS
418		H_2O	25	2.0	4	+30		182	5 × 10^{-5} M NaPSS
419	$Co(NH_3)_5Cl^{2+} + NH_3 \rightarrow Co(NH_3)_6^{3+} + Cl^-$	NH_3	0.5	4.0	~16	−30 ± 4		200	μ = 0.2 *m* (ClO_4^-)
420	$Co(NH_3)_5N_3^{2+} + NH_3 \rightarrow Co(NH_3)_6^{3+} + N_3^-$	NH_3	24.4	4.0	~16	−20 ± 3		200	μ = 0.2 *m* (ClO_4^-)

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
421	$Co(NH_3)_5SO_3^+ + SO_3^{2-} \rightarrow$ *trans*-$Co(NH_3)_4(SO_3)_2^- + NH_3$	H_2O	25	1.0	10	+13.7 ± 0.7			172	pH = 9.4, μ = 0.5 M
422	Co^{2+} + pada $\rightarrow$ Co(pada)$^{2+}$	H_2O	25	2.0	5	+11.2 ± 2.5			201	ClO_4^- salt
423		H_2O	25	2.0	5	+5.3 ± 0.5		+3.7 ± 0.2 (a)	61	μ = 0.1 M (NO_3^-)
424		DMSO	50	2.0	6	+8.3 ± 0.5			201	ClO_4^- salt
425		DMSO	50	2.0	6	+6.8 ± 0.5			201	BPh_4^- salt
426		DMF	50	2.0	6	+10.1 ± 0.8			201	BPh_4^- salt
427	$Co(H_2O)_6^{2+}$ + bpy $\rightarrow$ Co(bpy)$(H_2O)_4^{2+} + H_2O$	H_2O	25	1.0	5	+4.3 ± 1.0			143	μ = 0.1 M (ClO_4^-), [L] ≫ [M]
428		H_2O	25	1.0	5	+7.5 ± 1.4			143	μ = 0.1 M (ClO_4^-), [M] ≫ [L]
429	$Co(H_2O)_6^{2+}$ + terpy $\rightarrow$ Co(terpy)$(H_2O)_3^{2+} + H_2O$	H_2O	25	1.0	5	+4.5 ± 0.8			143	μ = 0.1 M (ClO_4^-), [L] ≫ [M]
430		H_2O	25	1.0	5	+3.8 ± 0.8			143	μ = 0.1 M (ClO_4^-), [M] ≫ [L]
431	Co^{2+} + Hmtpp $\rightarrow$ Co(mtpp)$^+ + H^+$	H_2O	25	2.0	9	+8.0 ± 0.3			202	0.28 M $Co(NO_3)_2$
432		DMF	25	2.0	9	+8.0 ± 0.3			145	μ ≤ 0.15 m
433	$Co(H_2O)_6^{2+}$ + edta^{4-} $\rightarrow$ Co(edta)$^{2-}$ + $6H_2O$	H_2O	25					+44.1 (b)	144	$\mu \rightarrow 0$
434	$Co(H_2O)_6^{2+}$ + Hedta^{3-} $\rightarrow$ Co(Hedta)$(H_2O)^-$ + $5H_2O$	H_2O	25					+34.4 (b)	144	$\mu \rightarrow 0$
435	Co(edta)$^{2-}$ + H^+ $\rightarrow$ Co(edtaH)$^-$	H_2O	25					+3.5 ± 0.2 (b)	203	
436	Co(terpy)$_2^{2+}$(low spin) $\rightleftarrows$ Co(terpy)$_2^{2+}$(high spin)	H_2O	25	1.4	5			+10.1 ± 0.4 (a)	204	
	Co(py)$_2X_2$ + 2py $\rightleftarrows$ Co(py)$_4X_2$									
437	X = Cl	H_2O	25	3.0	7			−41 (a)	205	
438	X = Br	H_2O	20	3.0	7			−30 (a)	205	
439	X = I	H_2O		3.0				−6 (a)	206	
	Co(3-Mepy)$_2X_2$ + 2(3-Mepy) $\rightleftarrows$ Co(3-Mepy)$_4X_2$									
440	X = Cl	H_2O	17	3.0				−18 (a)	207	
441	X = Br	H_2O	18.5	3.0				−19 (a)	207	
	$Ni^{2+} + L^{n-} \rightarrow NiL^{(2-n)+}$									
442	L^{n-} = bpy	H_2O	25	1.0	5	+5.5 ± 0.3			143, 156	μ = 0.1 M (ClO_4^-), [L] ≫ [M]
443		H_2O	25	1.0	5	+5.1 ± 0.4			143	μ = 0.1 M (ClO_4^-), [M] ≫ [L]
444	L^{n-} = terpy	H_2O	25	1.0	5	+6.7 ± 0.2			143, 156	μ = 0.1 M (ClO_4^-), [L] ≫ [M]
445		H_2O	25	1.0	5	+4.5 ± 0.6			143	μ = 0.1 M (ClO_4^-), [M] ≫ [L]
446	L^{n-} = pada	H_2O	25	1.7	5	+8.2 ± 2.1			201	ClO_4^- salt
447		DMSO	50	2.0	6	+11.3 ± 1.0			201	ClO_4^- salt
448		DMSO	50	2.0	5	+12.4 ± 0.8			201	BPh_4^- salt
449		DMF	35	2.0	6	+11.5 ± 1.5			201	ClO_4^- salt
450		DMF	25	2.0	5	+9.2 ± 1.4			201	BPh_4^- salt
451		DMF	35	2.0	5	+6.4 ± 1.3			201	BPh_4^- salt
452		DMF	50	2.0	5	+9.5 ± 0.4			201	BPh_4^- salt
453	L^{n-} = isoquinoline	H_2O	25	2.0	9	+7.4 ± 1.3			208	μ = 0.1 M (ClO_4^-)
454		DMF	25	2.0	9	+9.3 ± 0.3			208	μ = 0.1 M (ClO_4^-)
455		CH_3CN	25	2.0	9	+9.4 ± 0.1			208	μ = 0.1 M (ClO_4^-)
456		CH_3OH	25	2.0	9	+12.8 ± 0.6			208	μ = 0.1 M (ClO_4^-)
457		C_2H_5OH	25	2.0	9	+12.6 ± 0.5		+1.1 ± 0.1 (b)	208	μ = 0.1 M (ClO_4^-)
458	L^{n-} = malate	H_2O	20	1.0	6	+13.8 ± 0.6		+17.8 ± 0.6 (a)	209	$\mu \rightarrow 0$
459	L^{n-} = maleate	H_2O	10	1.0	6	+13.5 ± 0.6		+14.9 ± 0.4 (a)	210	pH ~ 7.3, μ ~ 0

460	L^{n-} = malonate	H_2O	20	1.0	6	+16.0 ± 2.1		62	$\mu \sim 0$
461	L^{n-} = glycolate	H_2O	20	1.0	6	+14.7 ± 0.5	+17.3 ± 1.0 (a)	211	pH ~ 6, $\mu \sim 0$
462	L^{n-} = lactate	H_2O	20	1.0	6	+13.5 ± 0.4	+17.6 ± 0.9 (a)	211	pH ~ 6, $\mu \sim 0$
463	L^{n-} = succinate	H_2O	10	1.0	6	+14.1 ± 0.8	+11.1 ± 0.9 (a)	210	pH ~ 6.8, $\mu \sim 0$
464	L^{n-} = tartrate	H_2O	20	1.0	6	+13.7 ± 1.2	+17.8 ± 0.5 (a)	209	$\mu \to 0$
465	L^{n-} = mtpp	DMF	25	2.0	9	+9.0 ± 0.9		145	$\mu \le 0.15\ m$
466	L^{n-} = SCN^-	DMF	-9	1.8	10	+8.8 ± 0.5		212	μ = 0.2 M (ClO_4^-)
467	L^{n-} = Et_2DTC^-	DMF	25	2.0	15	+12.4 ± 0.2		212	μ = 0.1 M (ClO_4^-)
468	L^{n-} = $edta^{4-}$	H_2O	25				+44.4 (b)	144	$\mu \to 0$
469	L^{n-} = $Hedta^{3-}$	H_2O	25				+33.7 (b)	144	$\mu \to 0$
	$NiL^{(2-n)+} \to Ni^{2+} + L^{n-}$								
470	L^{n-} = isoquinoline	H_2O	25	2.0	9	+8.9 ± 0.8		208	μ = 0.1 M (ClO_4^-)
471		DMF	25	2.0	9	+12.2 ± 0.3		208	μ = 0.1 M (ClO_4^-)
472		CH_3OH	25	2.0	9	+9.9 ± 0.5		208	μ = 0.1 M (ClO_4^-)
473		C_2H_5OH	25	2.9	9	+15.7 ± 1.1		208	μ = 0.1 M (ClO_4^-)
474	L^{n-} = malate	H_2O	20	1.0		-4.0 ± 0.5		209	calculated
475	L^{n-} = maleate	H_2O	10	1.0	6	-1.4 ± 0.4		210	pH ~ 7.3, $\mu \sim 0$
476	L^{n-} = glycolate	H_2O	20	1.0	6	-2.6 ± 0.7		211	pH ~ 6, $\mu \sim 0$
477	L^{n-} = lactate	H_2O	20	1.0	6	-4.1 ± 0.6		211	pH ~ 6, $\mu \sim 0$
478	L^{n-} = succinate	H_2O	10	1.0	6	+3.0 ± 0.9		210	pH ~ 6.8, $\mu \sim 0$
479	L^{n-} = tartrate	H_2O	20	1.0		-4.1 ± 0.7		209	calculated
480	L^{n-} = $edta^{4-}$	H_2O	25				+3.3 ± 0.3 (b)	203	
	NiL_2 + pan $\to$ Ni(pan)$L^+ + L^-$	CH_3COOH	25	0.5					[Ni] ≫ [pan]
481	L^- = NO_3^-				11	+23.4 ± 2.4		213	
482	L^- = CH_3COO^-				10	+15.5 ± 2.6		213, 214	
483	L^- = Cl^-				10	+35.4 ± 5.5		213	
	$Ni(L)^{2+} + 2H_2O \rightleftarrows Ni(L)(H_2O)_2^{2+}$								
484	L = 2,3,2-tet	H_2O	57				-3.1 ± 0.3 (b)	107	μ = 0.25 M (ClO_4^-)
485		H_2O	62				-2.5 ± 0.1 (b)	107	μ = 4.2 M (ClO_4^-)
486		H_2O	45				-2.1 ± 0.1 (b)	107	μ = 4.2 M (ClO_4^-)
487	L = cyclam	H_2O		1.5	5		-3.5 ± 0.1 (a)	215	μ = 0.05 M
488		H_2O	20	3.5	8		-1.2 ± 0.1 (a)	216	μ = 0.1 M (ClO_4^-)
489	L = Me_4cyclam	H_2O	10–35	1.5			-10.1 ± 0.2 (a)	215	
490		H_2O		1.5	5		-9.8 ± 0.3 (a)	215	μ = 0.3 M (ClO_4^-)
491		D_2O	-3 to +87	1.4	9		-10.0 ± 0.1 (a)	217	
492	L = $N_4$7	H_2O	20	3.5	9		-5.0 ± 0.2 (a)	216	μ = 0.1 M (ClO_4^-)
493	L = $N_4$8	H_2O	20	3.5	9		-3.0 ± 0.2 (a)	216	μ = 0.1 M (ClO_4^-)
494	L = $N_4$9	H_2O	20	3.5	4		-3.4 ± 0.2 (a)	216	μ = 0.1 M (ClO_4^-)
495	L = DTHP	H_2O	20	3.5	5		-1.4 ± 0.1 (a)	216	μ = 0.1 M (ClO_4^-)
496	$Cu(H_2O)_6^{2+} + edta^{4-} \to Cu(edta)^{2-} + 6H_2O$	H_2O	25				+45.8 (b)	144	$\mu \to 0$
497	$Cu(H_2O)_6^{2+} + Hedta^{3-} \to Cu(Hedta)(H_2O)^- + 5H_2O$	H_2O	25				+36.5 (b)	144	$\mu \to 0$
498	$Cu(edta)^{2-} + H^+ \to Cu(Hedta)^-$	H_2O	25				+4.8 ± 0.2 (b)	203	
499	$Cu(Hedta)^- + H^+ \to Cu(H_2edta)$	H_2O	25				+8 ± 1	203	
500	$Zn(H_2O)_6^{2+} + edta^{4-} \to Zn(edta)^{2-} + 6H_2O$	H_2O	25				+44.4 (b)	144	$\mu \to 0$
501	$Zn(H_2O)_6^{2+} + Hedta^{3-} \to Zn(Hedta)(H_2O)^- + 5H_2O$	H_2O	25				+33.6 (b)	144	$\mu \to 0$
502	Zn^{2+} + Hmtpp $\to$ Zn(mtpp)$^+ + H^+$	DMF	25	2.0	8	+7.0 ± 0.6		145	$\mu \le 0.15$ m
503	Ga^{3+} + HTROP $\to$ Ga(TROP)$^{2+} + H^+$	H_2O	25	1.2	6	+4.0 ± 1.3		218	μ = 0.5–1.0 M (ClO_4^-)
504	$GaOH^{2+}$ + HTROP $\to$ Ga(TROP)$^{2+} + H_2O$	H_2O	25	1.2	6	+5.1 ± 0.7		218	μ = 0.5–1.0 M (ClO_4^-)
505	Ga^{3+} + Hipt $\to$ Ga(ipt)$^{2+} + H^+$	DMSO	35	1.2	7	+10.6 ± 0.6		127, 219	μ = 0.27 m (ClO_4^-)
506	MoO(tmpyp)$H_2O^{5+} + H_2O_2 \to$ MoO(O_2)(tmpyp)$^{3+} + 2H^+ + H_2O$	H_2O	25	1.8	7	-0.2 ± 0.3		220	μ = 1.05 m (NO_3^-)
507	$Mo(H_2O)_6^{3+} + SCN^- \to Mo(H_2O)_5SCN^{2+} + H_2O$	H_2O	12	1.4	8	-11.4 ± 0.5		221	[H^+] = 0.98 M, μ = 1 M

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
508	$Mo(CO)_5py + phen \rightarrow Mo(CO)_4phen + CO + py$	$PhCH_3$	50	1.5	4	+0.5 ± 0.5			222	
	$Mo(CO)_5(4\text{-}Mepy) + L \rightarrow Mo(CO)_4L + 4\text{-}Mepy + CO$									
509	L = bpy	$PhCH_3$	40	1.0	3	+0.9 ± 0.5			222	
510		$PhCH_3$	50	1.0	3	−0.3 ± 0.7			222	
511	L = phen	$PhCH_3$	40	1.0	3	+0.1 ± 0.5			222	
512	L = dab	$PhCH_3$	50	1.5	4	+0.7 ± 0.8			223	
513	$Mo(CO)_4bpy + CN^- \rightarrow$ products	DMSO	25	1.4	3	−9			167, 224	
514		CH_3OH	25	1.4	3	+4			167, 224	
	cis-$Mo(CO)_4(py)_2 + L \rightarrow Mo(CO)_4L + 2py$									
515	L = dab	$PhCH_3$	17	1.5	4	+3.6 ± 0.8			223	
516	L = bpy	$PhCH_3$	17	1.5	4	+3.9 ± 0.8			223	
517		$(CH_2Cl)_2$	15	2.0	5	+4.5 ± 0.6			222	
518	L = phen	$(CH_2Cl)_2$	15	2.0	5	+4.1 ± 0.5			222	
519	$MoO(O_2)(tmpyp)^{3+} + H^+ + H_2O \rightarrow MoO(tmpyp)H_2O^{5+} + H_2O_2$	H_2O	25	1.8	7	+5.2 ± 1.6			220	μ = 1.05 *m* (NO_3^-)
520	$Mo_3O_4(H_2O)_9^{4+} + SCN^- \rightarrow Mo_3O_4(H_2O)_8NCS^{3+} + H_2O$	H_2O	15	1.5	4	+6.1 ± 0.4			225	
521			20	1.5	4	+5.5 ± 0.1			225	
522			25	1.5	4	+5.4 ± 0.2			225	
523	$Ru(NH_3)_5H_2O^{3+} + Cl^- \rightarrow Ru(NH_3)_5Cl^{2+} + H_2O$	H_2O	60	1.2	6	−20 ± 1.4			226	μ = 0.11 M
524	$Ru(NH_3)_5Cl^{2+} + H_2O \rightarrow Ru(NH_3)_5H_2O^{3+} + Cl^-$	H_2O	60	2.9	18	−30.2 ± 2.4		−9 ± 1 (25 °C) (b)	226	μ ~ 0.01 M
525								−10 ± 3 (60 °C) (b)	226	
526	$HRu_3(CO)_{11}^- + PPh_3 \rightarrow HRu_3(CO)_{10}PPh_3^- + CO$	THF	25	1.0	5	+21.2 ± 1.4			227	
527	$Ru_3(CO)_{10}CO_2CH_3^- + P(OCH_3)_3 \rightarrow Ru_3(CO)_9(P(OCH_3)_3)CO_2CH_3^- + CO$	10% CH_3OH/THF	25	0.8	4	+16 ± 2			227	
528	$Ru_3(CO)_9(P(OCH_3)_3)CO_2CH_3^- + P(OCH_3)_3 \rightarrow Ru_3(CO)_{10}(P(OCH_3)_3)_2 + CH_3O^-$	10% CH_3OH/THF	25	1.0	5	+24.5 ± 2			227	
529	$Rh(NH_3)_5H_2O^{3+} + Cl^- \rightarrow Rh(NH_3)_5Cl^{2+} + H_2O$	H_2O	60	1.8	8	+3.0 ± 0.7		+18.3 (a)	130	μ = 2 M (ClO_4^-)
530	$RhCl_5H_2O^{2-} + Cl^- \rightarrow RhCl_6^{3-} + H_2O$	H_2O	20	1.5	7	+15.7 ± 6.5			228	4 M $HClO_4$
531	*cis*-$RhCl_4(H_2O)_2^- + Cl^- \rightarrow RhCl_5H_2O^{2-} + H_2O$	H_2O	20	1.5	7	+14.7 ± 1.6			228	3.8 M $HClO_4$, 0.2 M HCl
532	$Rh(tpps)(H_2O)_2^{3-} + SCN^- \rightarrow Rh(tpps)(H_2O)NCS^{4-} + H_2O$	H_2O	15	1.0	5	+8.8 ± 0.4			131	$[H^+]$ = 0.1 M, μ = 1 M
533	$Rh(tpps)(H_2O)_2^{3-} + SC(NH_2)_2 \rightarrow Rh(tpps)(H_2O)SC(NH_2)_2^{3-} + H_2O$	H_2O	22	1.4	4	+11.1 ± 0.5			177	$[H^+]$ = 0.1 M, μ = 1 M
534	$Rh(NH_3)_5NO_3^{2+} + H_2O \rightarrow Rh(NH_3)_5H_2O^{3+} + NO_3^-$	H_2O	40	1.5	7	−6.9 ± 0.4			229	
535	$RhCl_6^{3-} + H_2O \rightarrow RhCl_5H_2O^{2-} + Cl^-$	H_2O	20	1.5	7	+21.5 ± 0.6			228	4 M $HClO_4$
536		H_2O	20	1.5	6	+24.5 ± 0.3			228	1 M $HClO_4$
537	$RhCl_5H_2O^{2-} + H_2O \rightarrow RhCl_4(H_2O)_2^- + Cl^-$	H_2O	20	1.5	7	+14.3 ± 0.5			228	4 M $HClO_4$
538	$Rh(C_2O_4)_3^{3-} + H_2O \rightarrow Rh(C_2O_4)_2(H_2O)_2^- + C_2O_4^{2-}$	H_2O	60	1.5	7	−7.9 ± 0.6			136	1 M $HClO_4$
	$Rh(NH_3)_5X^{2+} + OH^- \rightarrow Rh(NH_3)_5OH^{2+} + X^-$	H_2O	40	1.5					229	
539	$X^- = Cl^-$				9	+18.7 ± 0.7				μ = 1.0 M (OH^-)
540					7	+19.9 ± 0.2				μ = 1.0 M (ClO_4^-)
541	$X^- = Br^-$				7	+20.2 ± 0.5				μ = 1.0 M (ClO_4^-)
542					7	+20.3 ± 0.9				μ = 0.1 M (OH^-)
543	$X^- = I^-$				7	+20.4 ± 0.5				μ = 1.0 M (OH^-)

544	$X^- = NO_3^-$				7	+22.3 ± 0.9			μ = 1.0 M (ClO_4^-)
545	*trans*-$Rh(en)_2(H_2O)_2^{3+} + OH^- \rightarrow$ *trans*-$Rh(en)_2(H_2O)OH^{2+} + H_2O$	H_2O	25				+26.7 ± 0.5 (b)	34	$\mu \rightarrow 0$
546	*trans*-$Rh(en)_2(H_2O)OH^{2+} + OH^- \rightarrow$ *trans*-$Rh(en)_2(OH)_2^+ + H_2O$	H_2O	25				+18.4 ± 1.0 (b)	34	$\mu \rightarrow 0$
547	$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow{Hg^{2+}} Rh(NH_3)_5H_2O^{3+} + Cl^-$	H_2O	15	1.5	7	−1.0 ± 0.4		139	$[H^+]$ = 0.3 M, μ = 0.6 M
548	$Rh(NH_3)_5I^{2+} + H_2O \xrightarrow{Hg^{2+}} Rh(NH_3)_5H_2O^{3+} + I^-$	H_2O	12	1.5	7	+1.2 ± 0.3		230	μ = 0.3 M (ClO_4^-)
549	*mer*-$RhCl_3(H_2O)_3 + H_2O \xrightarrow{Hg^{2+}} RhCl_2(H_2O)_4^+ + Cl^-$	H_2O	23	1.5	7	+8.1 ± 0.4		231	μ = 2 M ($HClO_4$)
550	$Pd(H_2O)_4^{2+} + DMSO \rightarrow Pd(H_2O)_3DMSO^{2+} + H_2O$	H_2O	25	1.7	8	−10.4 ± 0.5		53	
551		H_2O	25	1.7	8	−9.2 ± 0.6	−7.5 ± 0.3 (a)	232	1 M $HClO_4$
	$Pd(dien)H_2O^{2+} + L \rightarrow Pd(dien)L^{2+} + H_2O$	H_2O	12	1.0	5			233	μ = 0.1 M (ClO_4^-)
552	L = adenosine					−2.0 ± 0.4			
553	L = cytidine					+1.5 ± 0.7			
554	L = thymidine					−0.6 ± 2.2			
555	L = uridine					−0.8 ± 2.2			
	$Pd(L)H_2O^{2+} + X^- \rightarrow Pd(L)X^+ + H_2O$								
556	L = 1,1,7,7-Me_4dien, $X^- = Cl^-$	H_2O	25	1.0	5	−7.2 ± 0.2		234	μ = 0.1 M (ClO_4^-)
557	L = 1,1,7,7-Me_4dien, $X^- = Br^-$	H_2O	25	1.0	5	−7.6 ± 0.3		234	μ = 0.1 M (ClO_4^-)
558	L = 1,1,7,7-Me_4dien, $X^- = I^-$	H_2O	25	1.0	5	−9.3 ± 0.8		234	μ = 0.1 M (ClO_4^-)
559	L = 1,1,4-Et_3dien, $X^- = Cl^-$	H_2O	25	1.0	5	−2.7 ± 0.2		51	μ = 0.1 M (ClO_4^-)
560	L = 1,1,4,7,7-Me_5dien, $X^- = Cl^-$	H_2O	25	1.0	5	−4.9 ± 0.4		234	μ = 0.1 M (ClO_4^-)
561	L = 1,1,4,7,7-Me_5dien, $X^- = Br^-$	H_2O	25	1.0	5	−7.3 ± 0.4		234	μ = 0.1 M (ClO_4^-)
562	L = 1,1,4,7,7-Me_5dien, $X^- = I^-$	H_2O	25	1.0	5	−9.9 ± 1.2		234	μ = 0.1 M (ClO_4^-)
563	L = 1,1,4,7,7-Me_5dien, $X^- = N_3^-$	H_2O	25	1.0	5	−11.7 ± 1.2		234	μ = 0.1 M (ClO_4^-)
564	L = 1,1,7,7-Et_4dien, $X^- = Cl^-$	H_2O	25	1.0	5	−3.0 ± 0.2		51	μ = 0.1 M (ClO_4^-)
565	L = 4-Me-1,1,7,7-Et_4dien, $X^- = Cl^-$	H_2O	25	1.0	5	−7.7 ± 0.5		49	μ = 0.1 M (ClO_4^-)
566	$Pd(H_2O)_3DMSO^{2+} + H_2O \rightarrow Pd(H_2O)_4^{2+} + DMSO$	H_2O	25	1.7	8	−0.9 ± 0.2		53	
567		H_2O	25	1.7	8	−1.7 ± 0.6		232	1 M $HClO_4$
	$Pd(dien)L^{2+} + H_2O \rightarrow Pd(dien)H_2O^{2+} + L$	H_2O	12	1.0	5			233	μ = 0.1 M (ClO_4^-)
568	L = thymidine					−0.8 ± 1.1			
569	L = uridine					−6.3 ± 4.6			
	$Pd(L)X^{(2-n)+} + H_2O \rightarrow Pd(L)H_2O^{2+} + X^{n-}$								
570	L = dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−12.2 ± 0.8		234	μ = 0.1 M (ClO_4^-)
571						−10.0 ± 0.6			
572	L = dien, $X^{n-} = CO_3^{2-}$	H_2O	25	1.0	5	−9.7 ± 0.4		235	μ = 1.0 M (ClO_4^-)
573	L = 1,4,7-Me_3dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−12.2 ± 0.6		236	μ = 0.1 M (ClO_4^-)
574						−9.2 ± 0.6			
575	L = 1,4,7-Et_3dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−10.8 ± 0.7		234	μ = 0.1 M (ClO_4^-)
576						−10.8 ± 1.0			
577	L = 1,1,7,7-Me_4dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−15.5 ± 0.6		236	μ = 0.1 M (ClO_4^-)
278						−13.4 ± 1.9			
579	L = 1,1,7,7-Me_4dien, $X^{n-} = CO_3^{2-}$	H_2O	25	1.0	5	−8.6 ± 0.4		235	μ = 1.0 M (ClO_4^-)
580	L = 1,1,4-Et_3dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−14.2 ± 0.6		234	μ = 0.1 M (ClO_4^-)
581						−14.5 ± 1.2			
582	L = 1,1,4,7,7-Me_5dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−11.6 ± 0.5		236	μ = 0.1 M (ClO_4^-)
583						−10.9 ± 0.3			
584	L = 1,1,7,7-Et_4dien, $X^{n-} = Cl^-$	H_2O	25	1.0	5	−13.0 ± 0.6		234	μ = 0.1 M (ClO_4^-)
585		H_2O	25	1.5	7	−14.9 ± 0.2		237	μ = 0.05 M (ClO_4^-)
586		H_2O	25	1.5	7	−15.4 ± 0.3		237	μ = 0.05 M (ClO_4^-)
587		H_2O	25	1.0	6	−16 ± 1		237	μ = 0.5 M (ClO_4^-)
588		H_2O	25	1.5	7	−14 ± 1		237	μ = 0.5 M (ClO_4^-)
589	L = 1,1,7,7-Et_4dien, $X^{n-} = Br^-$	H_2O	25	1.5	7	−12.5 ± 0.2		237	μ = 0.05 M (ClO_4^-)
590						−13.3 ± 0.2		237	μ = 0.05 M (ClO_4^-)
591	L = 1,1,7,7-Et_4dien, $X^{n-} = N_3^-$	H_2O	25	1.5	7	−13.9 ± 0.5		237	μ = 0.05 M (ClO_4^-)
592	L = 1,1,7,7-Et_4dien, $X^{n-} = I^-$	H_2O	25	1.5	7	−11.5 ± 0.2		237	μ = 0.05 M (ClO_4^-)

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
593						−11.8 ± 0.2			237	μ = 0.05 M (ClO_4^-)
594	L = 1,1,7,7-Et_4dien, X^{n-} = SCN^-	H_2O	40	1.5	7	−10.3 ± 0.2			237	μ = 0.2 M (ClO_4^-)
595		H_2O	30	1.5	5	−10.6 ± 0.4			238	μ = 0.5 M (ClO_4^-)
596	L = 1,1,7,7-Et_4dien, X^{n-} = NH_3	H_2O	40	1.5	7	−3.0 ± 0.9			237	μ = 0.2 M (ClO_4^-)
597	L = 1,1,7,7-Et_4dien, X^{n-} = CO_3^{2-}	H_2O	25	1.5	7	−6.7 ± 0.5			235	μ = 1.0 M (ClO_4^-)
598	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = Cl^-	H_2O	25	1.7	7	−12.2 ± 0.6			239	μ = 0.1 M (ClO_4^-)
599		H_2O	30	1.2	7	−14.3 ± 0.6			234	μ = 0.05 M (ClO_4^-)
600		H_2O	30	1.5	7	−13.5 ± 1.8			239	μ = 1.0 M (ClO_4^-)
601		H_2O	40	1.0	5	−13.2 ± 1.0			239	μ = 0.1 M (ClO_4^-)
602	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = I^-	H_2O	30	1.5	7	−7.8 ± 0.2			234	μ = 0.05 M (ClO_4^-)
603		H_2O	30	1.5	7	−8.4 ± 0.6			239	μ = 0.1 M (ClO_4^-)
604	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = Br^-	H_2O	25	1.5	7	−11.9 ± 0.5			239	μ = 0.1 M (ClO_4^-)
605	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = SCN^-	H_2O	30	1.5	5	−10.5 ± 0.6			238	μ = 0.5 M (ClO_4^-)
606	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = py	H_2O	50	1.5	4	−3.7 ± 0.4			239	μ = 0.1 M (ClO_4^-)
607	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = NH_3	H_2O	50	1.5	6	−3.0 ± 0.4			239	μ = 0.1 M (ClO_4^-)
608	L = 4-Me-1,1,7,7-Et_4dien, X^{n-} = $C_2O_4^{2-}$	H_2O	14	1.5	6	−10.6 ± 0.2			239	μ = 0.1 M (ClO_4^-)
609	L = 1,1,4,7,7-Et_5dien, X^{n-} = Cl^-	H_2O	25	1.5	7	−12.8 ± 0.8			234	μ = 0.05 M (ClO_4^-)
610		H_2O	25	1.5	7	−11.6 ± 0.2			239	μ = 0.1 M (ClO_4^-)
611	L = 1,1,4,7,7-Et_5dien, X^{n-} = I^-	H_2O	30	1.2	6	−8.2 ± 0.3			234	μ = 0.05 M (ClO_4^-)
612	Pd(Et_4dien)I^+ + solvent → Pd(Et_4dien)solvent^{2+} + I^-	CH_3OH	40	1.5	7	−13.4 ± 0.5			240	μ = 0.05 M
613		C_2H_5OH	40	1.5	7	−12.9 ± 0.4			240	μ = 0.05 M
614		DMSO	40	1.5	7	−10.1 ± 0.2			240	μ = 0.05 M
615		DMF	40	1.5	7	−9.3 ± 0.3			240	μ = 0.05 M
616		CH_3CN	40	1.5	7	−7.9 ± 0.5			240	μ = 0.05 M
	Pd(L)Cl^+ + Y^- → Pd(L)Y^+ + Cl^-									
617	L = dien, Y^- = I^-	H_2O	25	1.0	5	−10.3 ± 1.0			234	μ = 0.1 M (ClO_4^-)
618	L = 1,4,7-Me_3dien, Y^- = OH^-	H_2O	25	1.0	5	+21.2 ± 1.6			236	μ = 0.1 M (ClO_4^-)
619	L = 1,4,7-Me_3dien, Y^- = I^-	H_2O	25	1.0	5	−18.9 ± 0.3			236	μ = 0.1 M (ClO_4^-)
620	L = 1,4,7-Et_3dien, Y^- = I^-	H_2O	25	1.0	5	−11.1 ± 0.8			234	μ = 0.1 M (ClO_4^-)
621	L = 1,1,4-Et_3dien, Y^- = I^-	H_2O	25	1.0	5	−11.3 ± 1.3			234	μ = 0.1 M (ClO_4^-)
622	L = 1,1,7,7-Me_4dien, Y^- = OH^-	H_2O	25	1.0	5	+25.2 ± 3.6			236	μ = 0.1 M (ClO_4^-)
623	L = 1,1,7,7-Et_4dien, Y^- = OH^-	H_2O	25	1.0	5	+6.4 ± 0.9			234	μ = 0.1 M (ClO_4^-)
624	L = 1,1,7,7-Et_4dien, Y^- = N_3^-	H_2O	25	1.5	7	−15.5 ± 0.8			237	μ = 0.5 M (ClO_4^-)
625	L = 1,1,7,7-Et_4dien, Y^- = SCN^-	H_2O	25	1.5	7	−2.6 ± 0.5			237	μ = 0.5 M (ClO_4^-)
626	Pd(Et_4dien)Br^+ + SCN^- → Pd(Et_4dien)SCN^+ + Br^-	H_2O	25	1.0	6	−10.1 ± 0.1			237	μ = 0.5 M (ClO_4^-)
627	Pd(Et_4dien)SO_3 + HSO_3^- → Pd$(SO_3)_2^{2-}$ + Et_4dien	H_2O	25	1.0	5	~0			241	[H^+] = 0.01 M, μ = 0.5 M
628	Cd$(H_2O)_6^{2+}$ + bpy → Cd(bpy)$(H_2O)_4^{2+}$ + H_2O	H_2O	0	2.0	5	−5.5 ± 1.0		+2.0 ± 0.8 (a)	242	
629	Cd^{2+} + Hmtpp → Cd(mtpp)$^+$ + H^+	DMF	25	2.0	8	+8.9 ± 1.6			145	$\mu \leq 0.15$ *m*
630	Cd(bpy)$(H_2O)_4^{2+}$ + $2H_2O$ → Cd$(H_2O)_6^{2+}$ + bpy	H_2O	0	2.0	5	−6.9 ± 1.2			242	
631	In^{3+} + Hipt → In(ipt)$^{2+}$ + H^+	DMSO	35	1.2	6	−0.1 ± 0.6			127	μ = 0.05 *m* (ClO_4^-)
632		DMF	16	2.0	9	+0.3 ± 0.3			127	μ = 0.05 *m* (ClO_4^-)
633	WO$(H_2O)(CN)_4^{2-}$ + N_3^- → WO$(N_3)(CN)_4^{3-}$ + H_2O	H_2O	25	1.0	5	+10.6 ± 0.5			243	μ = 1.0 M (NO_3^-), pH = 5.8
634	*cis*-W$(CO)_4$(4-Mepy)$_2$ + phen → W$(CO)_4$phen + 4-Mepy	$PhCH_3$	25	0.7	2	+8			244	
	Pt(dien)X^+ + H_2O → Pt(dien)H_2O^{2+} + X^-	H_2O	25						245	
635	X^- = Br^-			1.5	7	−10.0 ± 0.3				μ ~ 0, Br^- salt
636				1.5	7	−9.8 ± 0.3				μ = 0.2 M $LiClO_4$
637				1.8	9	−9.3 ± 0.1				μ = 0.2 M $NaClO_4$
638				1.5	7	−9.0 ± 0.2				μ = 0.2 M NaBr

639				1.5	7	-9.7 ± 0.1			$\mu \sim 0$, ClO_4^- salt
640				1.8	10	-9.2 ± 0.2			$\mu = 0.2$ M, ClO_4^- salt
641	$X^- = Cl^-$			1.8	8	-10.5 ± 0.3			$\mu \sim 0$
642				1.5	8	-9.9 ± 0.3			$\mu = 0.2$ M $NaClO_4$
643				1.5	8	-9.3 ± 0.4			$\mu = 1.0$ M $NaClO_4$
644	$PtCl_4^{2-} + H_2O \rightarrow PtCl_3H_2O^- + Cl^-$	H_2O	40				$+1.3 \pm 0.1$ (b)	246	
645	*cis*-$Pt(NH_3)_2Cl_2 + H_2O \rightarrow$ *cis*-$Pt(NH_3)_2(Cl)H_2O^+ + Cl^-$	H_2O	45	2.0	6	-9.5 ± 1.2		246	10^{-3} M HNO_3
646	$Pt(en)Cl_2 + H_2O \rightarrow Pt(en)(Cl)H_2O^+ + Cl^-$	H_2O	41	2.0	6	-9.2 ± 1.0		246	10^{-3} M HNO_3
	cis-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)Br + S \rightarrow$ *cis*-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)S^+ + Br^-$								
647	$S = CH_3OH$	CH_3OH	30	1.5	8	-14.1 ± 0.5		247	
648		CH_3OH	30	1.0	5	-17.0 ± 0.7		247	
649	$S = C_2H_5OH$	C_2H_5OH	30	1.0	5	-13.0 ± 1.0		248	
650	S = DMSO	DMSO	35	1.0	5	-13.5 ± 1.5		248	
	trans-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)Br + S \rightarrow$ *trans*-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)S^+ + Br^-$								
651	$S = CH_3OH$	CH_3OH	30	1.5	7	-15.8 ± 0.4		247	
652		CH_3OH	30	1.0	5	-11.0 ± 5.7		247	
653	S = DMSO	DMSO	35	1.0	5	-6 ± 8		248	
	cis-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)Br + X^{n-} \rightarrow$ *cis*-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)X^{(2-n)+} + Br^-$								
654	$X^{n-} = SC(NH_2)_2$	CH_3OH	30	1.0	5	-13.3 ± 2.6		247	
655		C_2H_5OH	30	1.0	5	-16.9 ± 1.0		248	
656		DMSO	30	1.0	5	-22 ± 3		248	
	trans-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)Br + X^{n-} \rightarrow$ *trans*-$Pt(PEt_3)_2(2,4,6\text{-}Me_3Ph)X^{(2-n)+} + Br^-$								
657	$X^{n-} = SC(NH_2)_2$	CH_3OH	15	1.0	5	-12.5 ± 2.0		247	
658		C_2H_5OH	15	1.0	5	-12.2 ± 0.6		248	
659		DMSO	35	1.0	5	-14.1 ± 1.8		248	
660	$X^{n-} = I^-$	CH_3OH	30	1.5	7	-16.4 ± 5.4		247	
661	*trans*-$Pt(py)_2(Cl)NO_2 + py \rightarrow Pt(py)_3NO_2^+ + Cl^-$	CH_3NO_2	10	1.5	7	-8.5 ± 0.4		35	
662		CH_3OH	10	1.5	7	-11.6 ± 0.3		35	
663			25	1.5	7	-11.9 ± 0.6		35	
664			40	1.5	7	-12.6 ± 0.6		35	
665		C_2H_5OH	25	1.5	7	-15.9 ± 0.8		35	
666		CH_2Cl_2	25	1.5	7	-22.2 ± 1.7		35	
667	*cis*-$Pt(py)_2(Cl)NO_2 + py \rightarrow Pt(py)_3NO_2^+ + Cl^-$	CH_3OH	25	1.5	7	-8.6 ± 0.5		35	
668	*trans*-$Pt(PEt_3)_2Cl_2 + py \rightarrow$ *trans*-$Pt(PEt_3)_2(py)Cl^+ + Cl^-$	CH_3OH	25	1.5	7	-16.7 ± 0.8		35	
	$MA^z + OH^- \rightarrow MA^{z-1} + H_2O$	H_2O	25					34	$\mu \sim 0$
669	$MA^z = Pt(NH_3)_6^{4+}$						$+35.5 \pm 0.4$ (b)		
670	$MA^z = Pt(NH_3)_5NH_2^{3+}$						$+29.1 \pm 0.4$ (b)		
671	$MA^z = Pt(NH_3)_5Cl^{3+}$						$+32.2 \pm 0.5$ (b)		
672	$MA^z = Pt(NH_3)_5OH^{3+}$						$+33.4 \pm 0.7$ (b)		
673	$Nd(DMF)_8^{3+} + DMF \rightarrow Nd(DMF)_9^{3+}$	DMF	−42 and −17				-9.8 ± 1.1 (a)	249	
674	$Nd(tmp)_8^{3+} + tmp \rightarrow Nd(tmp)_9^{3+}$	tmp	25				-23.8 ± 1.5 (a)	249	
675	$Hg^{2+} + Hmtpp \rightarrow Hg(mtpp)^+ + H^+$	DMF	25	2.0	9	$+4.3 \pm 0.8$		145	
			Isomerization: Racemization Reactions						
676	$Cr(C_2O_4)_3^{3-}$	H_2O	15	1.4	5	-16.3 ± 0.4		250	0.05 M HCl
677	$Cr(C_2O_4)_2(phen)^-$	H_2O	25	1.4	5	-12.3 ± 0.3		250	
678	$Cr(C_2O_4)_2(bpy)^-$	H_2O	25	1.4	5	-12.0 ± 0.3		250	
679	$Cr(C_2O_4)(phen)_2^+$	H_2O	45	2.1	4	-1.5 ± 0.3		250	
680	$Cr(C_2O_4)(bpy)_2^+$	H_2O	45	2.1	4	-1.0 ± 0.2		250	
681	$Cr(phen)_3^{3+}$	H_2O	75	2.1	4	$+3.3 \pm 0.3$		250	
682	$Cr(bpy)_3^{3+}$	H_2O	75	2.1	4	$+3.4 \pm 0.3$		250	0.05 M HCl

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
683	$Co(Ph_2dtc)_3$	DMF	50	2.6	3	−2.0			251	
684			70	2.6	2	−5.7			251	
685		$CHCl_3$	55	2.6	2	−6.6			251	
686		PhCl	63	2.6	2	−9.3			251	
687		CCl_4	69	2.6	2	−5.2			251	
688		$(CH_3)_2CO$	50	2.6	2	−6.8			251	
689	$Co(pyrdtc)_3$	C_2H_5OH	43	1.4	5	+9.8 ± 0.5	+4.0 ± 0.9		251	
690		DMF	43	1.4	5	+5.2 ± 0.7	+2.2 ± 1.0		251	
691		CH_3CN	41	1.4	5	+5.4 ± 0.5	+2.5 ± 0.8		251	
692		$PhCH_3$	55	1.4	5	+7.8 ± 0.6	+3.1 ± 0.9		251	
693	$Ni(phen)_2(bpy)^{2+}$	H_2O	20	2.8	3	−0.1 ± 0.1			252	1 M HCl
694		H_2O	20	2.8	5	+0.6 ± 0.2			252	0.01 M HCl
695	$Ni(phen)(bpy)_2^{2+}$	H_2O	10	2.1	4	−5.2 ± 0.5			252	1 M HCl
696		H_2O	20	2.8	5	−1.9 ± 0.2			252	0.01 M HCl
697	$Ge(acac)_3^+$	TCE	60	2.8	7	+15.1 ± 0.8			253	
698		PC	60	2.8	7	+5.4 ± 0.3			253	
699		CH_3CN	50–60	2.8	4	0.0 ± 0.2			253	
700		DMF	50	2.8	7	−4.1 ± 0.6			253	
				Geometrical Isomerization Reactions						
701	*cis* → *trans*-$TiCl_4 \cdot 2TMPA$	$CHCl_3$	68	2.3	10	+6.2 ± 1.8		−1.3 ± 0.8 (a)	90, 254	
702	*trans* → *cis*-$Cr(C_2O_4)_2(H_2O)_2^-$	H_2O	30	1.7	6	−16.6 ± 0.5	−1.8 ± 0.6		137	pH = 3.1, μ = 1.0 M (ClO_4^-)
703	*trans* → *cis*-$Cr(CH_2C_2O_4)_2(H_2O)_2^-$	H_2O	60	1.7	6	+8.9 ± 0.3			137	pH = 3.0, μ = 1.0 M (ClO_4^-)
704	*trans* → *cis*-$Co(en)_2(H_2O)_2^{3+}$	H_2O	46	1.4	5	+12.4 ± 0.4	+5 ± 0.5		255	0.05 M $HClO_4$, μ = 1 M
705		D_2O	48	1.4	5	+10.6 ± 0.2			255	0.05 M $DClO_4$
706		D_2O	46	1.4	5	+11.9 ± 0.2			255	0.05 M $DClO_4$, μ = 1 M
707	*trans* → *cis*-$Co(en)_2(H_2O)OH^{2+}$	H_2O				+14.5 ± 1.1			9, 256	
708	*trans* → *cis*-$Co(en)_2(CH_3COO)H_2O^{2+}$	H_2O	45	1.4	5	+7.9 ± 0.3			257	0.05 M $HClO_4$
709		H_2O	45	1.4	5	+6.5 ± 0.4			257	0.05 M $HClO_4$, μ = 1 M
710		H_2O	45	1.4	5	+5.6 ± 0.6			257	1 M $HClO_4$
711		D_2O	45	1.4	5	+3.7 ± 0.3			255	0.05 M $DClO_4$
712		D_2O	45	1.4	5	+2.5 ± 0.3			255	0.05 M $DClO_4$, μ = 1 M
713	*trans* → *cis*-$Co(en)_2(SeO_3)H_2O^+$	H_2O				+7.2 ± 0.4			9, 256	
714	*trans* → *cis*-$Co(en)_2(SeO_3H)H_2O^{2+}$	H_2O				+7.5 ± 0.2			9, 256	
715		D_2O	40	1.4	5	0.0 ± 0.4			255	pD = 1.4, 0.5 M Na_2SeO_3
716	*trans* → *cis*-$Co(en)_2(Cl)H_2O^{2+}$	H_2O	25	2.0	6	+5.9 ± 0.5		−3.3 ± 0.4 (b)	258	0.01 M $HClO_4$
717		H_2O	31.5	2.0	6	+5.2 ± 0.4		−2.2 ± 0.4 (a)	258	0.01 M $HClO_4$, μ = 0.5 M
718		H_2O	31.5					−2.9 ± 0.2 (b)	258	0.04 M $HClO_4$
719		H_2O	31.5	2.0	6	+5.1 ± 0.3		−1.9 ± 0.4 (a)	258	0.01 M $HClO_4$
720		H_2O	38	2.0	6	+5.6 ± 0.3		−2.6 ± 0.4 (a)	258	0.01 M $HClO_4$
721		H_2O	38	2.0	6	+4.7 ± 0.3		−0.9 ± 0.8 (a)	258	0.01 M HNO_3
722	β → α-$Co(edda)(tn)^+$	H_2O	59			+19.9 ± 0.4			83	0.2 M buffer
723	β → α-$Co(edda)(en)^+$	H_2O	64			+25.2 ± 0.5			83	0.2 M buffer
724	*trans* → *cis*-$SnCl_4 \cdot 2Me_2S$	CH_2Cl_2	10	2.5	8	+12.2 ± 0.7	+1.5 ± 0.6	+3.2 ± 0.4 (a)	123	
	cis → *trans*-$Pt(PEt_3)_2(R)X$									
725	R = Ph, X^- = Cl^-	CH_3OH	30	1.5	6	+6.4 ± 0.4			259	μ = 0.01 M (ClO_4^-)
726	R = Ph, X^- = Br^-	CH_3OH	30	1.5	6	+5.2 ± 0.3			259	μ = 0.01 M (ClO_4^-)
727	R = Ph, X^- = I^-	CH_3OH	30	1.5	6	+7.2 ± 0.8			259	μ = 0.01 M (ClO_4^-)

728	R = 2,4,6-Me_3Ph, X^- = Br^-	CH_3OH	30	1.8	8	−12.0 ± 0.5			260	$\mu < 10^{-6}$ M
729		CH_3OH	30	1.5	4	−10.0 ± 0.3			260	μ = 0.01 M (ClO_4^-)
	Linkage Isomerization Reactions									
730	$Co(NH_3)_5ONO^{2+} \rightarrow Co(NH_3)_5NO_2^{2+}$	H_2O	30	2.5	8	−6.7 ± 0.4		−12.9 ± 1.5 (b)	261	μ = 0.1 M
731		H_2O	20	1.4	4	−6.5 ± 0.2			262	$\mu \sim 0$
732		H_2O	20	1.7	7	+27 ± 1.4	+5 ± 2		263	0.1 M NaOH
733		MFA	35	1.4	5	−5.7 ± 0.5			262	$\mu \sim 0$
734		DMSO	36	1.4	5	−3.6 ± 0.3			262	$\mu \sim 0$
735		SFL	54	1.4	5	−6.8 ± 0.7			262	$\mu \sim 0$
736		NH_3	5	4.0	7	−16 ± 2			264	0.001 M NH_4NO_3, μ = 0.2 M (NO_3^-)
737		NH_3	11	4.0	~12	−12 ± 2			200	μ = 0.2 *m* (ClO_4^-)
738	$Co(NH_3)_5SCN^{2+} \rightarrow Co(NH_3)_5NCS^{2+}$	H_2O	50	1.5	7	−5.3 ± 0.8			265	μ = 1.0 M (ClO_4^-)
739		DMSO	50	1.5	7	−1.0 ± 1.2			265	μ = 1.0 M (ClO_4^-)
740	*cis*-$Co(en)_2(ONO)_2^+ \rightarrow$ *cis*-$Co(en)_2(NO_2)ONO^+$	H_2O	25	1.0	6	−5.6 ± 0.6			266	μ = 0.5 M (ClO_4^-)
741	*cis*-$Co(en)_2(NO_2)ONO^+ \rightarrow$ *cis*-$Co(en)_2(NO_2)_2^+$	H_2O	35	1.5	4	−6.9 ± 0.6			266	μ = 0.5 M (ClO_4^-)
742		H_2O	35	1.5	4	−3.4 ± 0.2			266	μ = 0.5 M (ClO_4^-)
743	*trans*-$Co(en)_2(ONO)_2^+ \rightarrow$ *trans*-$Co(en)_2(NO_2)_2^+$	H_2O	35	1.7	8	−3.6 ± 0.4			266	μ = 0.5 M (ClO_4^-)
744	*cis*-$Co(en)_2(ONO)_2^+ \xrightarrow{OH^-}$ *cis*-$Co(en)_2(NO_2)_2^+$	H_2O	25	1.0	6	+19.7 ± 1.1			267	μ = 0.5 M (ClO_4^-)
745	*trans*-$Co(en)_2(ONO)_2^+ \xrightarrow{OH^-}$ *trans*-$Co(en)_2(NO_2)_2^+$	H_2O	25	1.0	6	+13.6 ± 1.2			267	μ = 0.5 M (ClO_4^-)
746	$Co(en)_2(OS(O)CH_2CH_2NH_2)^{2+} \rightarrow$ $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$	H_2O	60	1.5	4	−9.0 ± 0.7			268	0.01 M $HClO_4$
747	Ni(1,4-Et_2en)$_2(ONO)_2 \rightarrow$ Ni(1,4-Et_2en)$_2(NO_2)_2$	$CHCl_3$	25	1.4	5			−7.2 ± 1.0 (a)	269	
748	Ni(1,4-Me_2en)$_2(ONO)_2 \rightarrow$ Ni(1,4-Me_2en)$_2(NO_2)_2$	$CHCl_3$	25	1.7	6			−4.5 ± 0.8 (a)	269	
749	$Rh(NH_3)_5ONO^{2+} \rightarrow Rh(NH_3)_5NO_2^{2+}$	H_2O	20	1.3	6	−7.4 ± 0.4			261	μ = 0.1 M
	$Pd(L)SCN^+ \rightarrow Pd(L)NCS^+$									
750	L = 1,1,7,7-Et_4dien	H_2O	30	1.5	6	−10.1 ± 0.3			238	μ = 0.1 M
751		DMF	30	2.0	8	−9.5 ± 0.5			238	μ = 0.1 M
752	L = 4-Me-1,1,7,7-Et_4dien	H_2O	30	1.5	6	−10.8 ± 0.3			238	μ = 0.5 M
753	*trans*-Pd($\overline{SCH_2CMe_2CH_2}$)$_2Br_2$ i.a.S	$CHCl_3$	18	2.2		0 ± 2			270	
754	*trans*-Pd($\overline{SCH_2CH_2CH_2}$)$_2Cl_2$ i.a.S	$CHCl_3$	26	2.2		0 ± 2			270	
755	*trans*-Pd($\overline{S(CH_2)_5}$)$_2Cl_2$ i.a.S	$CHCl_3$	−3	2.2		0 ± 2			270	
756	*trans*-Pd($\overline{SCH_2CMe_2CH_2}$)$_2Cl_2$ i.a.S	CH_2Cl_2		2.2		small pos			270	
757	$Ir(NH_3)_5ONO^{2+} \rightarrow Ir(NH_3)_5NO_2^{2+}$	H_2O	30	1.5	7	−5.9 ± 0.6			261	μ = 0.1 M
	Addition Reactions									
758	$TiO^{2+} + H_2O_2 \rightarrow Ti(O_2)^{2+} + H_2O$	H_2O	25	1.2	6	−6.0 ± 0.4			271	μ = 3.0 *m* (ClO_4^-)
759	$TiO^{2+} + H_2O_2 \xrightarrow{H^+} Ti(O_2)^{2+} + H_2O$	H_2O	25	1.2	6	−0.1 ± 0.3			271	μ = 3.0 *m* (ClO_4^-)
760	$TiO(nta)(H_2O) + H_2O_2 \rightarrow$ $Ti(O_2)(nta)(H_2O)^- + H_2O$	H_2O	25	1.2	6	−19 ± 2			271	μ = 1.0 *m* (ClO_4^-)
761	$TiO(nta)(H_2O) + H_2O_2 \xrightarrow{H^+}$ $Ti(O_2)(nta)(H_2O)^- + H_2O$	H_2O	25	1.2	6	+13 ± 1			271	μ = 1.0 *m* (ClO_4^-)
762	$TiO(tpypH_4)^{4+} + H_2O_2 \rightarrow$ $Ti(O_2)(tpypH_4)^{4+} + H_2O$	H_2O	25	1.2	6	−3.3 ± 0.2			271, 272	μ = 1.0 *m* (ClO_4^-)
763	$TiO(tmpyp)^{4+} + H_2O_2 \rightarrow$ $Ti(O_2)(tmpyp)^{4+} + H_2O$	H_2O	25	1.2	7	−18.6 ± 0.3			273	μ = 1.0 M (NO_3^-)
764	$TiO(tmpyp)^{4+} + H_2O_2 \xrightarrow{H^+}$ $Ti(O_2)(tmpyp)^{4+} + H_3O^+$	H_2O	25	1.2	7	−3.9 ± 0.2			273	μ = 1.0 M (NO_3^-)

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta\bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
765	$VO_2(nta)^{2-} + H_2O_2 \rightarrow VO(O_2)(nta)^{2-} + H_2O$	H_2O	25	1.5	~10	-3.4 ± 0.5			56	μ = 1.0 m (ClO_4^-)
766	$VO_2(nta)^{2-} + H_2O_2 \xrightarrow{H^+} VO(O_2)(nta)^{2-} + H_2O$	H_2O	25	1.5	~10	+1.5 ± 0.5			56	μ = 1.0 m (ClO_4^-)
767	$Fe(CO)_3HTE$ + TCNE → cycloaddition	CH_2Cl_2	25	0.7	5	-29 ± 3			274	
768		Me_2CO	25	0.5	4	-33 ± 3			274	
769		CH_3CN	25	0.7	3	-31 ± 5			274	
770	$Co(NH_3)_5OH^{2+} + NO^+ \rightarrow Co(NH_3)_5ONO^{2+} + H^+$	H_2O	25	1.5	7	-1.8 ± 0.7			275	pH = 3.7, μ = 2 M
771	$Co(NH_3)_5OH^{2+} + CO_2 \rightarrow Co(NH_3)_5OCO_2^+ + H^+$	H_2O	25	1.0	5	-10.1 ± 0.6			276	pH = 8.5, μ = 0.5 M
772	$Co(en)_2(hfac)^{2+} + OH^- \rightarrow Co(en)_2(hfac{\cdot}OH)^+$	H_2O	25	1.9	5	+9.2 ± 2.3			277	μ = 1.1 M (ClO_4^-)
773	$Co(en)_2(hfac)^{2+} + H_2O \rightarrow Co(en)_2(hfac{\cdot}OH)^+ + H^+$	H_2O	25	1.9	5	-4.2 ± 2.1			277	μ = 1.1 M (ClO_4^-)
	$Co(L)hfac^{z+} + OH^- \rightarrow Co(L)(hfac{\cdot}OH)^{(z-1)+}$	H_2O	25						278	
774	L = $(NH_3)_4$							+11.2 ± 0.4 (b)		
775	L = $(en)_2$							+10.7 ± 0.1 (b)		
776	L = α-trien							+8.9 ± 0.4 (b)		
777	L = β-trien							+11.1 ± 0.3 (b)		
778	L = i-dtma							+1.6 ± 0.5 (b)		
779	L = α-edda							-8.3 ± 0.9 (b)		
780	L = β-edda							-3.9 ± 0.3 (b)		
781	$Rh(NH_3)_5OH^{2+} + CO_2 \rightarrow Rh(NH_3)_5OCO_2^+ + H^+$	H_2O	25	1.0	5	-4.7 ± 0.8			276	pH = 8.5, μ = 0.5 M
782	$Ir(NH_3)_5OH^{2+} + CO_2 \rightarrow Ir(NH_3)_5OCO_2^+ + H^+$	H_2O	25	1.0	5	-4.0 ± 1.0			276	pH = 8.5, μ = 0.5 M
783	$Ir(P(OPh)_3)_2(CO)Cl + HCl \rightarrow Ir(P(OPh)_3)_2(CO)(H)Cl_2$	$PhCH_3$	25	1.0	5	-20.5 ± 1.4			279	
784	$Ir(cod)(phen)^+ + O_2 \rightarrow Ir(cod)(phen)O_2^+$	CH_3OH	40	1.5	4	-31.1 ± 1.7			280	0.01 M LiCl
785	$Ir(cod)(phen)I + O_2 \rightarrow Ir(cod)(phen)O_2^+ + I^-$	CH_3OH	25	0.7	4	-44.4 ± 1.6			280	0.5 M LiCl
	Elimination Reactions									
	$Cr(H_2O)_5R^{2+} + H_2O \rightarrow Cr(H_2O)_6^{2+} + R$									
786	R = $C(CH_3)_2OH$	H_2O	25	1.0	5	+15.1 ± 1.6			281	μ = 1.1 M (ClO_4^-)
787	R = $C(CH_3)_2H$	H_2O	25	3.0	11	+26 ± 2			281	μ = 0.22 M (ClO_4^-)
788	R = $CH_2C_5H_4NH$	H_2O	63	3.5	10	+20.0 ± 0.9	+0.7 ± 0.6		282	0.026 M $HClO_4$
	$Cr(H_2O)_5R^{2+} + H_2O \rightarrow Cr(H_2O)_5OH^{2+} + RH$									
789	R = $C(CH_3)_2OH$	H_2O	15	1.0	7	+0.3 ± 0.2			281	μ = 1.1 M (ClO_4^-)
790	L = $C(CH_3)_2H$	H_2O	25	3.0	5	-0.2 ± 0.2			281	μ = 1.0 M (ClO_4^-)
791	$Co(NH_3)_5OCO_2H^{2+} \rightarrow Co(NH_3)_5OH^{2+} + CO_2$	H_2O	25	1.0	5	+6.8 ± 0.3			276	[H^+] = 0.1 M, μ = 0.5 M
792	cis-$Co(en)_2(H_2O)OCO_2H^{2+} \rightarrow$ cis-$Co(en)_2(H_2O)OH^{2+} + CO_2$	H_2O	25	1.0	5	-1.1 ± 1.2			283	[H^+] = 2 M, μ = 3 M
793	α-$Co(edda)(H_2O)OCO_2H \rightarrow$ α-$Co(edda)(H_2O)OH + CO_2$	H_2O	25	1.0	5	-0.7 ± 2.4			283	[H^+] = 1 M, μ = 2 M
794	β-$Co(edda)(H_2O)OCO_2H \rightarrow$ β-$Co(edda)(H_2O)OH + CO_2$	H_2O	25	1.0	5	+0.3 ± 1.4			283	[H^+] = 2 M, μ = 3 M
795	$Co(nta)(H_2O)OCO_2H^- \rightarrow Co(nta)(H_2O)OH^- + CO_2$	H_2O	25	1.0	5	-1.5 ± 1.7			283	[H^+] = 2 M, μ = 3 M
796	$Co(en)_2(hfac{\cdot}OH)^+ \rightarrow Co(en)_2(hfac)^{2+} + OH^-$	H_2O	25	1.9	5	+2.9 ± 2.3			277	μ = 1.1 M (ClO_4^-)

797	Co(en)$_2$(hfac·OH)$^+$ + H$^+$ → Co(en)$_2$(hfac)$^{2+}$ + H$_2$O	H$_2$O	25	1.9	5	+9.4 ± 2.1			277	μ = 1.1 M (ClO$_4^-$)
798	Rh(NH$_3$)$_5$OCO$_2$H^{2+} → Rh(NH$_3$)$_5$OH^{2+} + CO$_2$	H$_2$O	25	1.0	5	+5.2 ± 0.3			276	[H$^+$] = 0.1 M, μ = 0.5 M
799	Ir(NH$_3$)$_5$OCO$_2$H^{2+} → Ir(NH$_3$)$_5$OH^{2+} + CO$_2$	H$_2$O	25	1.0	5	+2.5 ± 0.4			276	[H$^+$] = 0.1 M, μ = 0.5 M
			Electron-Transfer Reactions							
800	VO(nta)H$_2$O$^-$ + H$_2$O$_2$ → VO(O$_2$)(nta)$^{2-}$ + H$_3$O$^+$	H$_2$O	25	1.2	6	−10.5 ± 0.3			284	μ = 1 M (ClO$_4^-$)
801	VO(pda)H$_2$O$^-$ + H$_2$O$_2$ → VO(O$_2$)(pda)$^{2-}$ + H$_3$O$^+$	H$_2$O	25	1.2	6	−13.0 ± 0.5			284	μ = 1 M (ClO$_4^-$)
802	MnO$_4^-$ + MnO$_4^{2-}$ → products	H$_2$O	45	2.0	10	−21.1 ± 0.9			285	K$^+$ medium, μ = 1.1 M
803		H$_2$O	45	2.0	10	−21.3 ± 1.3			285	Na$^+$ medium, μ = 1.1 M
804		H$_2$O	45	2.0	10	−22.8 ± 1.2	−6 ± 3		286	μ = 1.1 M
805	MnO$_4^-$ + MnO$_4^{2-}$ → Na$^+$ catalyzed	H$_2$O	45	2.0	10	+3.3 ± 1.0			286	μ = 1.1 M
806	MoO$_4^-$ + MnO$_4^{2-}$ → K$^+$ catalyzed	H$_2$O	45	2.0	10	−1.1 ± 0.3			286	μ = 1.1 M
	Mn(CNR)$_6^+$ + Mn(CNR)$_6^{2+}$ → products	CH$_3$CN		2.2	6–10				287	
807	R = CH$_3$		0			−2.4 ± 0.8				
808			9			−2.1 ± 0.8				
809	R = C$_2$H$_5$		6			−5.5 ± 0.5				
810	R = *t*-C$_4$H$_9$		6			−10.2 ± 0.5				
811			25			−13.3 ± 0.9	−4.5 ± 0.6			
812	R = C$_6$H$_{11}$		6			−17.4 ± 1.3				
813			12			−20.2 ± 1.6	−8.2 ± 1.4			
814	R = *n*-C$_4$H$_9$		6			−19.7 ± 2.4	−8.1 ± 2.0			
815	Fe(CN)$_6^{3-}$ + Fe(CN)$_6^{4-}$ → products	H$_2$O	25	1.0	3	+13			288	1 M KCl
816		H$_2$O	25	1.0	3	+30			288	1 M NaCl
817		H$_2$O	25	1.0	3	+41			288	1 M LiCl
818	Co(terpy)$_2^{2+}$ + Co(bpy)$_3^{3+}$ → Co(terpy)$_2^{3+}$ + Co(bpy)$_3^{2+}$	H$_2$O	25	1.0	6	−9.4 ± 0.9			289, 290	
819		HCONH$_2$	25	1.0	6	−13.8 ± 1.1				
820		CH$_3$CN	25	1.0	7	−5.1 ± 1.4				
821	Fe(4-Mephen)$_3^{2+}$ + S$_2$O$_8^{2-}$ → products	H$_2$O	25	1.4	2	~0			167, 166	
	Co(NH$_3$)$_5$X^{2+} + Fe^{2+} → Co^{2+} + Fe(III)									
822	X = F	H$_2$O	25			+10.7 ± 0.1			291	recalcd from lit.
823		DMSO	35	1.0	6	+10.3 ± 0.4			292	μ = 0.5 M (ClO$_4^-$)
824	X = Cl	H$_2$O	35			+8.7 ± 0.3			291	recalcd from lit.
825		DMSO	35	1.4	8	+3.8 ± 0.7			292	μ = 0.5 M (ClO$_4^-$)
826	X = Br	H$_2$O	35			+6.4 ± 1.1			291	recalcd from lit.
827		DMSO	35	1.7	9	+0.0 ± 0.4			292	μ = 0.5 M (ClO$_4^-$)
828	X = N$_3$	H$_2$O	40	1.5	4	+12.1 ± 0.5			291	[H$^+$] = 0.1 M, μ = 0.3 M
829		DMSO	40	1.5	4	+6.5 ± 0.2			291	[H$^+$] = 0.1 M, μ = 0.3 M
830	*cis*-Co(en)$_2$Cl$_2^+$ + Fe^{2+} → Co^{2+} + Fe(III)	DMSO	30	1.2	4	−9.2 ± 5.5		+10.9 ± 5.6^b	293	[H$^+$] = 0.02 M, μ = 0.3 M
	Co(NH$_3$)$_5$X$^{(3-n)+}$ + Fe(CN$_6$)$^{4-}$ → Co^{2+} + Fe(III)									
831	X^{n-} = H$_2$O	H$_2$O	25	1.0	5	+26.5 ± 2.4		−15.4 ± 7.9^b	294	pH = 4.7, μ = 0.5 M
832		H$_2$O	25	1.0	5	+37.6 ± 1.2		+3.5 ± 0.6^b	295	μ = 0.5 M (ClO$_4^-$)
833	X^{n-} = py	H$_2$O	15	1.2	7	+30.7 ± 1.3			289, 296	μ = 1.0 M (ClO$_4^-$)
834		H$_2$O	15	1.0	5	+28.9 ± 1.4			289, 296	μ = 1.0 M (ClO$_4^-$)
835		H$_2$O				+23.9 ± 1.0		+23.4 ± 3.3^b	297	μ = 1.0 M
836	X^{n-} = DMSO	H$_2$O	25	1.0	6	+34.4 ± 1.1		−11 ± 3^b	289, 296	μ = 1.0 M (ClO$_4^-$)
837	X^{n-} = Cl$^-$	H$_2$O	35			+26.1 ± 1.3		+2 ± 1^b	289	μ = 1.0 M (ClO$_4^-$)
838	Co(edta)$^-$ + Fe(CN)$_6^{4-}$ → Co^{2+} + Fe(III)	H$_2$O	25			+13.4 ± 0.5			297	μ = 1.0 M

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	$\Delta\beta^{\ddagger}$, $cm^3\ mol^{-1}\ kbar^{-1}$	$\Delta\bar{V}$, $cm^3\ mol^{-1}$ (method)	ref	remarks
839	$Co(NH_3)_5OSO_2^+ \xrightarrow{H^+} Co^{2+} + 5NH_4^+ + SO_3^-$	H_2O	25	1.0	5	+34.4 ± 2.9			298	pH = 6.2 μ = 1 M
840		H_2O	14.4	1.0	5	+34.6 ± 0.5			298	pH = 6.2, μ = 1 M
841	$Co_2(\mu\text{-}O_2,NH_2)(en)_4^{4+} + Mo_2O_4(OH)(hedta)^{2-} \rightarrow$ products	H_2O	25			+11.8 ± 0.8		+7.8 ± 3.7[b]	297	μ = 0.1 M
842	$Co_2(\mu\text{-}O_2)(NH_3)_{10}^{5+} + Mo_2O_4(edta)^{2-} \rightarrow$ products	H_2O	41	2.9	10	+12.1 ± 1.9	−6.2 ± 2.2	+23.7 ± 3.0[b]	299	μ = 0.1 M
843	$Co_2(\mu\text{-}O_2)(en)_4(NH_3)_2^{4+} \rightarrow$ products	H_2O	20			+23.8 ± 0.3			297	μ = 0.1 M
844	$Co_2(\mu\text{-}O_2)(dien)_2(en)_2^{4+} \rightarrow$ products	H_2O	45			+18.8 ± 0.3			297	μ = 0.1 M
845	$Co_2(\mu\text{-}O_2)(dien)_2(R\text{-}pn)_2^{4+} \rightarrow$ products	H_2O	45			+21.3 ± 0.6			297	μ = 0.1 M
846	$Co_2(\mu\text{-}O_2,NH_2)(en)_4^{4+}$ + TMPNO $\rightarrow Co_2(\mu\text{-}O_2,NH_2)(en)_4^{3+}$ + TMPNO$^+$	H_2O	15	2.0		+0.2 ± 0.5			300	μ = 0.1 M
847		H_2O	15	1.0		−1.4 ± 1.3			300	μ = 0.5 M
848	$(NH_3)_5Co^{III}(\mu\text{-}pz)Fe^{II}(CN)_5 \rightarrow Co^{2+}$ + Fe(III)	H_2O	25	0.7		+38 ± 1			301	pH = 5, μ = 0.1 M
849	$(en)_2Co^{III}(pzc)Fe^{II}(CN)_5^- \rightarrow Co^{2+}$ + Fe(III)	H_2O	25	0.7	3	+24			302	
850		60% MeOH/ H_2O	25	0.7	3	+7			302	
	$MoO(L)H_2O^{5+} + H_2O_2 \xrightarrow{H^+} Mo(O_2)(L)H_2O^{6+}$ + OH	H_2O	35	1.2	6				220	
851	L = tmpyp					+1.3 ± 0.3				
852	L = tpyp					+4.7 ± 0.4				
853	$Mo_2O_4(OH)(hedta)^{2-} + IrCl_6^{2-} \rightarrow$ products	H_2O	25			−12.3 ± 1.4			297	μ = 0.1 M
	Photochemical Substitution Reactions									
854	$Cr(NH_3)_5Cl^{2+} + H_2O$ $\rightarrow cis\text{-}Cr(NH_3)_4(Cl)H_2O^{2+} + NH_3$	H_2O	20	1.5	4	−9.4 ± 0.4			303	[H^+] = 0.01 M, μ = 0.5 M
855	$\rightarrow Cr(NH_3)_5H_2O^{3+} + Cl^-$	H_2O	20	1.5	4	−13.0 ± 0.5			303	[H^+] = 0.01 M, μ = 0.5 M
856	$Cr(NH_3)_5Br^{2+}$ $\rightarrow cis\text{-}Cr(NH_3)_4(Br)H_2O^{2+} + NH_3$	H_2O	5	1.5	4	−10.2 ± 0.1			303	[H^+] = 0.01 M, μ = 0.5 M
857	$\rightarrow Cr(NH_3)_5H_2O^{3+} + Br^-$	H_2O	5	1.5	4	−12.2 ± 0.3			303	[H^+] = 0.01 M, μ = 0.5 M
858	$Cr(NH_3)_5NCS^{2+}$ $\rightarrow cis\text{-}Cr(NH_3)_4(NCS)H_2O^{2+} + NH_3$	H_2O	15	1.5	4	−11.4 ± 0.1			303	[H^+] = 0.01 M, μ = 0.5 M
859	$\rightarrow Cr(NH_3)_5H_2O^{3+} + SCN^-$	H_2O	15	1.5	4	−9.8 ± 0.2			303	[H^+] = 0.01 M, μ = 0.5 M
860	$Cr(bpy)_3^{2+} + 2H_2O \rightarrow Cr(bpy)_2(OH)_2^+ + 2H^+$ + bpy	H_2O	22	2.3	4	+2.9 ± 1.2			304	pH = 10, μ = 1 M (NaCl)
861	$Cr(NH_3)_6^{3+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + NH_3$	H_2O	15	1.0	5	−12.6 ± 0.5			305	[H^+] = 0.01 M, μ = 0.015 M
862	$Cr(NCS)_6^{3-} + H_2O \rightarrow Cr(NCS)_5H_2O^{2-} + SCN^-$	H_2O	15	1.0	5	+2.9 ± 0.6			305	[H^+] = 0.1 M, μ = 0.5 M
863	$Cr(CN)_6^{3-} + H_2O \rightarrow Cr(CN)_5H_2O^{2-} + CN^-$	H_2O	15	1.5	7	+3.0 ± 0.2			305	pH = 8.9, μ = 0.3 M
864	$Fe(CN)_6^{4-} + H_2O \rightarrow Fe(CN)_5H_2O^{3-} + CN^-$	H_2O	23	5.5	8	+6.2 ± 0.4			157	
		20% EtOH	23	5.0	9	+5.1 ± 0.4			157	
865	$Co(NH_3)_5Br^{2+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + Br^-$	H_2O	20	2.8	2	−0.4 ± 3.2			306	pH = 4, buffer
866	$Co(CN)_6^{3-} + H_2O \rightarrow Co(CN)_5H_2O^{2-} + CN^-$	H_2O	15	1.5	7	+2.0 ± 0.2			305	pH = 6, μ ~ 0
	$Ru(bpy)_3^{2+}$ + S $\rightarrow$ products								307	

867	S = CH_3CN, Cl^- salt	CH_3CN	15	3.0		+12		
868		CH_3CN	25	3.0		+14		
869		CH_3CN	60	3.0		+22		
870	S = CH_3CN, PF_6^- salt	CH_3CN	25	3.0		+8		
871		CH_3CN	60	3.0		+10		
872	S = H_2O, Cl^- salt	H_2O	60	3.0		+9.5		
873		H_2O	60	3.0		+12		9 M LiCl
874	S = CH_2Cl_2, Cl^- salt	CH_2Cl_2	25	3.0		+17		
875	$Ru(phen)_3^{2+} + CH_3CN \rightarrow$ products	CH_3CN	15	3.0		+9	307	
876		CH_3CN	25	3.0		+18	307	
877		CH_3CN	60	3.0		+27	307	
878	$Ru(\eta^6\text{-}C_6H_6)(H_2O)_3^{2+} + 3H_2O \rightarrow$ $Ru(H_2O)_6^{2+} + C_6H_6$	H_2O	25	2.0		+1.1 ± 0.4	308	
879	$Rh(NH_3)_6^{3+} + H_2O \rightarrow$ $Rh(NH_3)_5H_2O^{3+} + NH_3$	H_2O	25	2.0	5	+3.9 ± 0.5	74	10^{-3}–10^{-2} M $HClO_4$
880	$Rh(NH_3)_5py^{3+} + H_2O \rightarrow$ $Rh(NH_3)_5H_2O^{3+}$ + py	H_2O	25	2.0		+3.8 ± 0.4	309	
	$Rh(NH_3)_5Cl^{2+} + S \rightarrow Rh(NH_3)_5S^{3+} + Cl^-$							
881	S = H_2O	H_2O	25	2.0	9	−8.6 ± 1.6	47	10^{-3}–10^{-2} M $HClO_4$
882	S = FMA	FMA	25	2.0	9	−4.9 ± 1.1	310	
883	S = DMSO	DMSO	30	1.0	5	−8.9 ± 2.7	310	
	$Rh(NH_3)_5Cl^{2+} + S \rightarrow$ *trans*-$Rh(NH_3)_4(S)Cl^{2+} + NH_3$							
884	S = H_2O	H_2O	25	2.0	9	+9.3 ± 1.9	47	10^{-3}–10^{-2} M $HClO_4$
885	S = FMA	FMA	25	2.0	9	+3.9 ± 1.3	310	
886	S = DMSO	DMSO	30	1.0	5	+3.3 ± 1.8	310	
887	S = DMF	DMF	25	2.0	9	+7.6 ± 1.1	310	
888	$Rh(ND_3)_5Cl^{2+} + D_2O$ $\rightarrow Rh(ND_3)_5D_2O^{3+} + Cl^-$	D_2O	25	2.0	9	−7.7 ± 1.6	47	10^{-3}–10^{-2} M $DClO_4$
889	$\rightarrow$ *trans*-$Rh(ND_3)_4(D_2O)Cl^{2+} + ND_3$	D_2O	25	2.0	9	+6.0 ± 2.2	47	10^{-3}–10^{-2} M $DClO_4$
890	$Rh(NH_3)_5Br^{2+} + H_2O$ $\rightarrow Rh(NH_3)_5H_2O^{3+} + Br^-$	H_2O	25	2.0	9	−6.8 ± 1.6	47	10^{-3}–10^{-2} M $HClO_4$
891	$\rightarrow$ *trans*-$Rh(NH_3)_4(H_2O)Br^{2+} + NH_3$	H_2O	25	2.0	9	+8.1 ± 1.2	47	10^{-3}–10^{-2} M $HClO_4$
892	$Rh(ND_3)_5Br^{2+} + D_2O$ $\rightarrow Rh(ND_3)_5D_2O^{3+} + Br^-$	D_2O	25	2.0	8	−5.3 ± 1.8	47	10^{-3}–10^{-2} M $DClO_4$
893	$\rightarrow$ *trans*-$Rh(ND_3)_4(D_2O)Br^{2+} + ND_3$	D_2O	25	2.0	8	+7.5 ± 1.1	47	10^{-3}–10^{-2} M $DClO_4$
894	$Rh(NH_3)_5I^{2+} + H_2O \rightarrow$ *trans*-$Rh(NH_3)_4(I)H_2O^{2+} + NH_3$	H_2O	25	2.0	5	+1.4 ± 0.9	74	10^{-3}–10^{-2} M $HClO_4$
895	$Rh(NH_3)_5SO_4^+ + H_2O \rightarrow$ $Rh(NH_3)_5H_2O^{3+} + SO_4^{2-}$	H_2O	25	2.0	5	−3.9 ± 0.6	74	10^{-3}–10^{-2} M $HClO_4$
896	*cis*-$Rh(bpy)_2Cl_2^+ + H_2O \rightarrow$ *cis*-$Rh(bpy)_2(H_2O)Cl^{2+} + Cl^-$	H_2O	25	2.0	5	−9.7 ± 0.8	311	pH = 2.7 (ClO_4^-)
897	*cis*-$Rh(NH_3)_4Br_2^+ + H_2O \rightarrow$ $Rh(NH_3)_3(H_2O)Br_2^+ + NH_3$	H_2O	25	2.0	5	+9.3 ± 0.8	312	10^{-3} M $HClO_4$
898	*trans*-$Rh(NH_3)_4Cl_2^+ + H_2O \rightarrow$ *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^-$	H_2O	25	2.0	5	+2.8 ± 0.6	312	10^{-3} M $HClO_4$
899	*trans*-$Rh(NH_3)_4Br_2^+ + H_2O \rightarrow$ *trans*-$Rh(NH_3)_4(H_2O)Br^{2+} + Br^-$	H_2O	25	2.0	5	+2.9 ± 0.7	312	10^{-3} M $HClO_4$
	Photochemical Isomerization Reactions							
900	$(Co)en_2(SO_2CH_2CH_2NH_2)^{2+} \rightarrow$ $Co(en)_2(OS(O)CH_2CH_2NH_2)^{2+}$	H_2O	25	2.0	9	+6.5 ± 0.6	268	0.01 M $HClO_4$
901	*cis*-$Rh(NH_3)_4Cl_2^+ + H_2O \rightarrow$ *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+} + Cl^-$	H_2O	25	2.0	5	−3.5 ± 0.3	312	10^{-3}–10^{-2} M $HClO_4$
902	*cis*-$Rh(NH_3)_4(H_2O)Cl^{2+} \rightarrow$ *trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	H_2O	25	2.0	5	0.0 ± 0.4	312	10^{-3} M $HClO_4$
903	*cis*-$Rh(NH_3)_4Br_2^+ + H_2O \rightarrow$ *trans*-$Rh(NH_3)_4(H_2O)Br^{2+} + Br^-$	H_2O	25	2.0	5	−2.3 ± 0.3	312	10^{-3} M $HClO_4$

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, $cm^3\ mol^{-1}$	$\Delta\beta^{\ddagger}$, $cm^3\ mol^{-1}\ kbar^{-1}$	$\Delta\bar{V}$, $cm^3\ mol^{-1}$ (method)	ref	remarks
904	*cis*-$Rh(NH_3)_4(H_2O)Br^{2+}$ → *trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	H_2O	25	2.0	5	−1.0 ± 0.4			312	10^{-3} M $HClO_4$
905	*trans*-$Rh(NH_3)_4(OH)Cl^+$ → *cis*-$Rh(NH_3)_4(OH)_2^+ + Cl^-$	H_2O	25	2.0	5	−8.8 ± 0.7			312	0.1 M NaOH
	Photochemical Electron-Transfer Reactions									
	$Fe(CN)_5NO^{2-} + S \rightarrow Fe(CN)_5S^{2-} + NO$		25	2.0	5				313	
906	S = H_2O	H_2O				+8.8 ± 0.4				λ_{irr} = 436 nm
907						+7.8 ± 1.0				λ_{irr} = 313 nm
908	S = CH_3OH	CH_3OH				+10.3 ± 0.6				λ_{irr} = 436 nm
909						+13.0 ± 1.9				λ_{irr} = 313 nm
910	S = DMSO					+11.1 ± 0.4				λ_{irr} = 436 nm
911						+11.4 ± 1.6				λ_{irr} = 405 nm
912						+14.1 ± 1.0				λ_{irr} = 313 nm
913	$Co(NH_3)_5Br^{2+} \rightarrow Co^{2+} + 5NH_3 + Br^-$	H_2O	20	2.8	2	+6.0 ± 0.6			306	pH = 4, buffer
914		H_2O	20	2.8	2	+4.8 ± 0.3			306	pH = 4, buffer
915	$[Mo_6Cl_{14}^{2-}]^* + Ir^{IV}Cl_6^{2-} \rightarrow Mo_6Cl_{14}^{2-} + Ir^{III}Cl_6^{3-}$	CH_3CN	25	2.5	4	−8 ± 2			314	
	$[Ru(bpy)_3^{2+}]^* + Q \rightarrow Ru(bpy)_3^{3+} + Q^-$	H_2O	25	3.0					315	
916	Q = $Fe(CN)_6^{3-}$					0.0 ± 0.1				0.1 M HCl, μ = 0.25 M
917	Q = $(en)_2Co(\mu\text{-}NH_2, O_2)Co(en)_2^{4+}$					0 to +1.0				0.05 M H_2SO_4, μ = 0.25 M
918	Q = $(NH_3)_5Co(\mu\text{-}O_2)Co(NH_3)_5^{5+}$					+1 ± 2				0.05 M H_2SO_4, μ = 0.25 M
919	Q = $(CN)_5Co(\mu\text{-}O_2)Co(CN)_5^{5-}$					0 to +1.2				0.1 M HCl, μ = 0.25 M
920	Q = Tl^{3+}					+0.2 ± 0.1				4.75 M $HClO_4$
	$[Ru(bpy)_3^{2+}]^* + Q \rightarrow Ru(bpy)_3^+ + Q^+$	H_2O	25	3.0					315	
921	Q = $Fe(CN)_6^{4-}$					0.0 ± 0.5				pH = 5.2, μ = 0.5 M
922	Q = $Mo(CN)_6^{4-}$					+24.7 ± 0.6				0.1 M HCl, μ = 0.25 M
923	Q = $Os(CN)_6^{4-}$					+6.8 ± 2.0				0.1 M HCl, μ = 0.25 M
924	Q = $IrCl_6^{3-}$					+1.1 ± 0.5				0.1 M HCl, μ = 0.25 M
925	Q = $Eu(aq)^{2+}$					−11.0 ± 1.0				0.5 M $HClO_4$
926	Q = $Fe(H_2O)_6^{2+}$					−0.6 ± 0.6				0.05 M H_2SO_4, μ = 0.25 M
927	$[Ru(bpy)_3^{2+}]^* + Q \rightarrow Ru(bpy)_3^{2+} + Q^*$	H_2O	25	3.0					315	
	Q = $Co(NH_3)_5H_2O^{3+}$					−2.6 ± 0.6				0.05 M H_2SO_4, μ = 0.25 M
928	*trans*-$Pt(CN)_4(N_3)_2^{2-} \rightarrow Pt(CN)_4^{2-} + 3N_2$	H_2O	25	2.0	9	+8.1 ± 0.4			316	
929		C_2H_5OH	25	2.0	9	+14.3 ± 0.9			316	
	Photophysical Processes: Lifetime Data									
930	$Cr(bpy)_3^{3+}$	H_2O		2.3		−0.7 ± 0.2			73	
931	$Cr(en)_3^{3+}$	H_2O		2.3		−0.9 ± 0.2			73	
932		H_2O	15–34	2.1	5 × 4	+3.3 ± 0.2			317	pH = 1.8–2.8
933	$Cr(NH_3)_6^{3+}$	H_2O	15–34	2.1	9 × 4	+4.2 ± 0.2			317	pH = 1.8–2.8
934	$Cr(ND_3)_6^{3+}$	H_2O	23	2.1	4	+4.2 ± 0.2			317	pH = 2.0
935	$Cr(NH_3)_5CN^{2+}$	H_2O	25	2.1	4	+3.4 ± 0.1			317	pH = 3.3
936	$Cr(NH_3)_5NCS^{2+}$	H_2O	25	2.1	4 × 4	+6.9 ± 0.1			317	pH = 2.0–3.3
937	*trans*-$Cr(en)_2(NCS)_2^+$	H_2O	25	2.1	4	+0.4 ± 0.1			317	pH = 3.3
938	*trans*-$Cr(en)_2(F)_2^+$	H_2O	25	2.1	3 × 4	+1.2 ± 0.2			317	pH = 1.8–2.8

939	*trans*-Cr(cyclam)$(CN)_2^+$	H_2O	23	2.1	4	+0.1 ± 0.2		317	pH ~ 1
	$[FeL_n]_{LS}^{2+} \rightarrow [FeL_n]_{HS}^{2+}$								
940	L = pyim (n = 3)	Me_2CO	25	3.0		+5.2 ± 2.0	+8.1 (a)	75	
941		Me_2CO	25	1.2		+4.9 ± 0.3	+10.3 ± 0.4 (a)	74	
942		CH_3CN	25	1.2		+8.9 ± 0.4	+14.3 ± 0.5 (a)	74	
943		CH_3OH/20% CH_3CN	25	1.2		0.0 ± 0.2	+5.3 ± 0.2 (a)	74	
944	L = pybim (n = 3)	CH_3CN	25	1.2		+5.9 ± 0.4	+12.4 ± 0.5 (a)	74	
945		Me_2CO	25	1.2		+4.7 ± 0.4	+9.6 ± 0.4 (a)	74	
946		CH_3OH/20% CH_3CN	25	1.2		+0.2 ± 0.3	+4.3 ± 0.4 (a)	74	
947	L = phenmethoxa (n = 2)	Me_2CO	25	3.0		+3.9 ± 1.0	+12.3 (a)	75	
	$[FeL_n]_{HS}^{2+} \rightarrow [FeL_n]_{LS}^{2+}$								
948	L = pyim (n = 3)	Me_2CO	25	3.0		−2.9 ± 1.5		75	
949		Me_2CO	25	1.2		−5.4 ± 0.3		74	
950		MeCN	25	1.2		−5.4 ± 0.3		74	
951		CH_3OH/20% CH_3CN	25	1.2		−5.3 ± 0.3		74	
952	L = pybim (n = 3)	CH_3CN	25	1.2		−6.4 ± 0.4		74	
953		Me_2CO	25	1.2		−4.9 ± 0.4		74	
954		CH_3OH/20% CH_3CN	25	1.2		−4.1 ± 0.4		74	
955	L = phenmethoxa (n = 2)	Me_2CO	25	3.0		−8.4 ± 2.0		75	
956	$Ru(bpy)_3^{2+}$	H_2O		2.3		−1.6 ± 1.0		73	
957		H_2O	2	3.0	6	−1.5		318	
958		H_2O	15	3.0	6	−1.0		318	
959		H_2O	15	3.0	6	−1.0		318	9.6 M LiCl
960		H_2O	15	3.0	6	−0.4		318	5.0 M urea
961		H_2O	25	3.0	6	−1.0		318	
962		H_2O	25	2.1	4	−0.6 ± 0.1		317	pH ~ 7
963		H_2O	40	3.0	6	+2.5		318	
964		H_2O	60	3.0	6	+4.2		318	
965		H_2O	60	3.0	6	+3.1		318	9.6 M LiCl
966		H_2O	60	3.0	6	+6.6		318	5.0 M urea
967		H_2O	70	3.0	6	+7.5		318	
968		D_2O	3.5	3.0	6	0.0		318	
969		D_2O	25	3.0	6	+0.9		318	
970		D_2O	40	3.0	6	+3.7		318	
971		D_2O	60	3.0	6	+5.9		318	
972		D_2O	70	3.0	6	+8.9		318	
973		CH_3CN	15	3.0	5	+2.9		76	
974		CH_3CN	25	3.0	5	+4.7		76	
975		CH_3CN	45	3.0	5	+8.7		317	
976	$Ru(bpy)_3^{2+}$ CT → GS	H_2O				−2.2 ± 0.2		318	calculated
977		D_2O				−1.0 ± 0.2		318	calculated
978		CH_3CN				−1.7 ± 0.2		318	calculated
979	$Ru(bpy)_3^{2+}$ CT → LF	H_2O				+9.7 ± 1.0		318	calculated
980		D_2O				+9.1 ± .0		318	calculated
981		CH_3CN				+12.5 ± 1.0		318	calculated
982		CH_3CN	15	3.0	5	+10.5		76	
983		CH_3CN	25	3.0	5	+10.5		76	
984		CH_3CN	45	3.0	5	+11.6		76	
985	$Ru(phen)_3^{2+}$	H_2O	2			+2.0		318	
986		H_2O	25			+5.6		318	
987		H_2O	40			+8.0		318	
988		H_2O	60			+8.3		318	
989		H_2O	70			+10.6		318	
990		D_2O	3.5			+2.9		318	
991		D_2O	25			+6.4		318	
992		D_2O	40			+9.4		318	

TABLE I (Continued)

no.	reaction	solvent	T, °C	P, kbar	no. of data	$\Delta V^{\ddagger}$, cm^3 mol^{-1}	$\Delta\beta^{\ddagger}$, cm^3 mol^{-1} kbar^{-1}	$\Delta \bar{V}$, cm^3 mol^{-1} (method)	ref	remarks
993		D_2O	60			+10.0			318	
994		D_2O	70			+11.7			318	
995		CH_3CN	15	3.0	5	+8.8			76	
996			25	3.0	5	+8.2			76	
997			45	3.0	5	+9.9			76	
998	$Ru(phen)_3^{2+}$ CT → GS	H_2O				−2.2 ± 0.2			318	calculated
999		D_2O				−1.1 ± 0.2			318	calculated
1000	CT → LF	H_2O				+10.4 ± 1.0			318	calculated
1001		D_2O				+11.5 ± 1.0			318	calculated
1002		CH_3CN	15	3.0	5	+10.9			76	
1003			25	3.0	5	+8.9			76	
1004			45	3.0	5	+10.5			76	
1005	$Rh(NH_3)_5Cl^{2+}$	FMA	25	3.0		−0.3 ± 0.4			319	
1006		DMF	25	3.0		+1.3 ± 0.2			319	
1007		DMSO	25	1.0		−1 ± 1			319	
1008	$Rh(ND_3)_5Cl^{2+}$	D_2O	25	2.8	6	−3.5 ± 1.1			47	10^{-3} M DCl
1009	$Rh(ND_3)_5Br^{2+}$	D_2O	25	2.0	6	+4.1 ± 0.6			47	10^{-3} M DCl
1010	*cis*-$Rh(bpy)_2Cl_2^+$	H_2O	23	3.3	7–10	−2.2 ± 0.3			311	
1011		FMA	23	3.3	7–10	+0.2 ± 0.2			311	
1012		CH_3OH	23	3.3	7–10	+0.6 ± 0.6			311	
1013		CH_3CN	23	3.3	7–10	+0.9 ± 0.2			311	
1014	$Os(bpy)_3^{2+}$	CH_3CN	25	3.0	5	−0.2			76	
1015		CH_3CN	45	3.0	5	−1.9			76	
1016	$Ir(bpy)_2Cl_2^+$	DMF	25	3.0		+4.0 ± 0.2		−4.2 ± 0.5 (a)	320	
1017	$Ir(Me_2phen)_2Cl_2^+$	DMF	25	3.0		+0.3 ± 0.1		−4.1 ± 0.8 (a)	320	
			Photophysical Processes: Nonradiative Deactivation							
1018	$Cr(bpy)_3^{2+}$	H_2O	22	2.3		−1.6 ± 0.2			304	
1019	$Ni(dpe)Cl_2$	CH_2Cl_2		1.2	11	−9.6 ± 0.5			321	
1020		C_2H_5Br		1.2	11	−12 ± 2			321	
1021	$Ni(dpe)Br_2$	CH_2Cl_2		1.2	11	−9.1 ± 0.4			321	
1022		C_2H_5Br		1.2	11	−11 ± 2			321	
1023	$Ni(vpp)Br_2$	CH_2Cl_2		1.2	11	−8.3 ± 0.4			321	
1024		C_2H_5Br		1.2	11	−10 ± 2			321	
1025	$Rh(NH_3)_5Cl^{2+}$	FMA	25	2.0		+0.2 ± 0.5			319	calculated
1026		DMF	25	2.0		+0.7 ± 0.3			319	calculated
1027		DMSO	30	1.0		−1 ± 1			319	calculated
1028	$Rh(ND_3)_5Cl^{2+}$	D_2O	25	2.0		−2.6 ± 1.0			47	calculated
1029	$Rh(ND_3)_5Br^{2+}$	D_2O	25	2.0		+2.5 ± 1.2			47	calculated

[a] Abbreviations: Ac, acetate; acac, acetylacetonate; bpy, 2,2′-bipyridine; BTE, 1,2-bis(*tert*-butylthio)ethane; cod, cycloocta-1,5-diene; cyclam, 1,4,8,11-tetraazacyclotetradecane; dab, biacetylbis(phenylimine); DCTA, 1,2-diaminocyclohexanetetraacetate; DTHP, 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene; dien, diethylenetriamine; dmg, dimethylglyoxime; dpe, 1,2-bis(diphenylphosphino)ethane; DTC, dithiocarbamate; dtcd, *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; dto, 3,6-dithiaoctane; edda, ethylenediaminediacetate; edta, ethylenediaminetetraacetate; en, ethylenediamine; Et, ethyl; fz, ferrozine (3-(2-pyridyl)-5,6-bis(4-sulfophenyl)-1,2,4-triazine); gly, glycinate; glyco, glycolate; Hahx, acetohydroxamic acid; Hame, 2-aminoethanol; hfac, hexafluoroacetylacetonate; Hipt, 4-isopropyltropolone; HTE, heptatrienone; hxsb, 1,8-bis[(2-pyridylmethylene)amino]-3,6-diazaoctane; i.a.S, inversion about S; i-dtma, *N*,*N*-bis(2-aminoethyl)glycinate; imid, imidazole; isoq, isoquinoline; lac, lactate; malo, malonate; male, maleate; Me, methyl; MFA, *N*-methylformamide; mtpp, *N*-methyl-5,10,15,20-tetraphenylporphine; mur, murexide; $N_4$7, 1,4,7,10-tetraazacyclotetradecane; $N_4$8, 1,4,7,10-tetraazacyclopentadecane; $N_4$9, 1,4,7,10-tetraazacyclohexadecane; nta, nitrilotriacetate; ox, oxalate; pada, pyridyl-2-azo-4-dimethylaniline; pan, 1-(2-pyridylazo)-2-naphthol; PC, propylene carbonate; pda, 2,6-pyridinedicarboxylate; PES, poly(ethylenesulfonate); Ph, phenyl; phen, 1,10-phenanthroline; pn, propylenediamine; Pr, propyl; PSS, poly(styrenesulfonate); py, pyridine; pybim, 2-(2-pyridyl)benzimidazole; pyrim, 2-(2-pyridyl)imidazole; pyrdtc, pyrrolidinecarbodithionate; pz, pyrazine; pzc, pyrazine carboxylate; sb, [(3,4-dimethylphenyl)imino]phenyl-2-pyridylmethane; suc, succinate; TCNE, tetracyanoethane; terpy, 2,2′:6′,2″-terpyridine; 2,3,2-tet, 1,3-bis(2′-(aminoethyl)amino)propane; 3,2,3-tet, *N*,*N*′-bis(3-aminopropyl); tmc, 1,4,8,11-tetramethylcyclam; tmp, trimethyl phosphate; TMPNO, 2,2,6,6-tetramethyl-1-piperidinyloxyl; tmpp, *meso*-tetrakis(4-*N*-methylpyridyl)porphine; tmpyp, 5,10,15,20-tetrakis(4-*N*-methylpyridiniumyl)porphine; tn, trimethylenediamine; tpps, *meso*-tetrakis(*p*-sulfonatophenyl)porphine; tptdt, 2,3,9,10-tetraphenyl-1,4,8,11-tetraaza-1,3,8,10-cyclotetradecatetraene; tpyp, 5,10,15,20-tetra-4-pyridylporphine; tren, 2,2′,2″-triaminotriethylamine; trien, triethylenetetramine; TROP, tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one); vpp, *cis*-1,2-bis(diphenylphosphino)ethylene. [b] $\Delta\bar{V}$ for precursor/ion-pair formation.

TABLE II. $\Delta V^{\ddagger}$ for Solvent Exchange on MS_6^{2+}[a]

M^{2+}	V	Mn	Fe	Co	Ni	Cu
r_i, pm	79	83	78	74	69	73
e_d^-	t_{2g}^3	$t_{2g}^3e_g^2$	$t_{2g}^4e_g^2$	$t_{2g}^5e_g^2$	$t_{2g}^6e_g^2$	$t_{2g}^6e_g^3$
S = H_2O	−4.1	−5.4	+3.8	+6.1	+7.2	
S = CH_3OH		−5.0	+0.4	+8.9	+11.4	+8.3
S = CH_3CN		−7.0	+3.0	+8.1	+8.5	
S = DMF		+2.0	+8.5	+6.7	+9.1	
S = NH_3					+5.9	

[a] From ref 16. Data in $cm^3\ mol^{-1}$.

change data were obtained by employing NMR techniques and are restricted to diamagnetic metal ions. For trivalent octahedral metal ions, $\Delta V^{\ddagger}$ varies from +22 for Al^{3+} and Ga^{3+} to −23 $cm^3\ mol^{-1}$ for Sc^{3+} and In^{3+}. The large positive values are typical for a limiting dissociative activation mode and the large negative values for an associative activation mode. The smaller cations tend to expel a solvent molecule, whereas the larger cations tend to host a seventh molecule in their coordination sphere. Theoretical semiempirical calculations by Swaddle[184,325–327] suggest $\Delta V^{\ddagger}$ values for Ga^{3+} of −13.6 and +13.1 $cm^3\ mol^{-1}$ for a limiting A and D mechanism, respectively. Other trivalent metal ions give significantly smaller absolute values of $\Delta V^{\ddagger}$, for instance Co^{3+}, Cr^{3+}, and V^{3+}, and an I_a or I_d mechanism becomes plausible. Similar trends are observed in different solvents and small mechanistic changes from I_a to A or I_d to D, and vice versa, may occur for a given metal ion in different solvents. The spectrum of $\Delta V^{\ddagger}$ data for MS_6^{3+} systems demonstrates the sensitivity of this parameter to the size of the central metal ion and the coordinated solvent/ligand molecules. For Cr^{3+}, Fe^{3+}, and Ga^{3+} in water, the conjugate base species $M(H_2O)_5OH^{2+}$ (entries 21, 32, and 69) exhibit dissociative behavior, most probably I_d, which represents a changeover in mechanism for the hexaaqua species of Cr^{3+} and Fe^{3+}, which react associatively, most probably I_a. A similar behavior is observed for Fe^{3+} in methanol (entry 35), where only exchange of the methoxy species occurs. This mechanistic changeover is probably due to the strong-electron-donating capability of HO^- or MeO^-, causing a weakening of the remaining metal–solvent bonds, most probably the trans solvent molecule.

Volumes of activation for solvent exchange of octahedral divalent metal ions are presently available for almost every member of the first-row transition-metal elements. A summary of the available data is presented in Table II (taken from ref 16), from which it follows that a gradual changeover in mechanism is occurring along the series. The earlier members are associatively activated and the later members dissociatively activated. In terms of the mean limiting value of 13.1 cm^3 mol^{-1} calculated from Swaddle's model for a limiting D (or A) mechanism, the data in Table II suggest the operation of interchange processes varying from I_a for V^{2+} and Mn^{2+} to I_d for Co^{2+} and Ni^{2+}. The data for Fe^{2+} could be considered a borderline case, and a pure interchange mechanism (I) has been suggested. These trends are especially clear for H_2O, CH_3OH, and CH_3CN as solvents. The results for DMF are significantly more positive for Mn^{2+} and Fe^{2+}, and it was suggested that steric hindrance may account for a more dissociatively activated transition state.[100] The good agreement between the $\Delta V^{\ddagger}$ data reported for DMF exchange on Mn^{2+} by two independent groups is quite remarkable (entries 28 and 29) and demonstrates the accuracy with which such data can be determined. Surely not only the size of the metal ion but also that of the coordinated solvent molecules will affect the intimate nature of the substitution process.

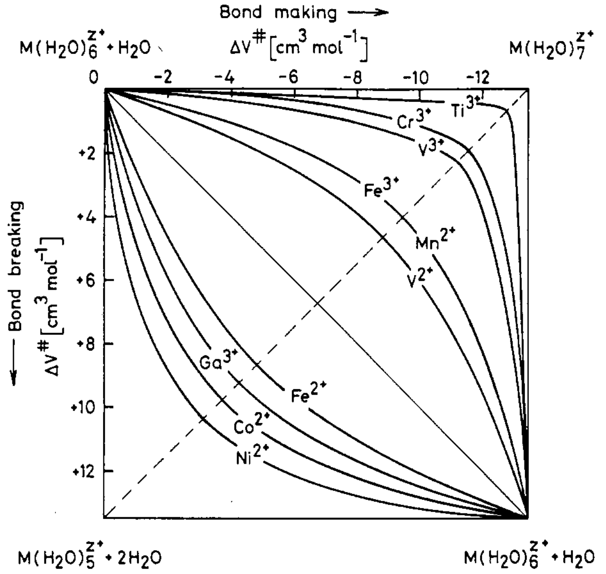


Figure 8. Bond-making and bond-breaking contributions to the volumes of activation for water exchange on $M(H_2O)_6^{z+}$.[324]

It has been suggested that the interpretation of the above data may be complicated by important changes in the bond lengths between the central metal ion and the nonexchanging ligands.[328] It was shown that this contribution is small and can be neglected for divalent and trivalent metal ions.[325,329] The systematic trend observed along the first-row transition-metal series can be visualized with the aid of a two-dimensional More O'Ferral plot[14,16] presented in Figure 8. The sum of the coordinates of each point along a trajectory represents the change in volume to reach that point. The $\Delta V^{\ddagger}$ value is obtained at the intersection with the dashed line. The limiting $|\Delta V^{\ddagger}|$ value of 13.1 $cm^3\ mol^{-1}$, as predicted by Swaddle's model, was chosen in Figure 8. The observed changeover can be explained in terms of the cation size and the electron configuration in the valence shell of the metal ion. For a σ-bonded octahedral complex, the t_{2g} orbitals are nonbonding, whereas the e_g orbitals are antibonding. The gradual filling of the t_{2g} orbitals will electrostatically disfavor the approach of a seventh ligand and therefore decrease the ease and extent of bond making. Similarly, an increased occupancy of the e_g orbitals will enhance bond breaking. These effects along with the steric effects mentioned above can account for the sequence of the $\Delta V^{\ddagger}$ data in Table II.

The determination of $\bar{V}$ for complexes of the type $M(H_2O)_6^{2+}$ and $M(NH_3)_5H_2O^{3+}$ has allowed the evaluation of the partial molar volume of the transition state, $\bar{V}_{\ddagger}$, for the solvent-exchange process through eq 35.[119,184,326] The calculations show rather surprisingly

$$\bar{V}_{\ddagger} = \bar{V} + \Delta V^{\ddagger} \tag{35}$$

that $\bar{V}_{\ddagger}$ is independent of the size of the central metal ion, which means that the lengthening of the metal–ligand bonds at the transition state with respect to the reactant state increases with decreasing ionic radius. This lengthening mainly affects the exchanging solvent molecules and implies that for a large cation the transition state is more compact than for a small cation, where the exchanging molecules are further away from the central atom.

Quite a number of studies have been performed on ligand-exchange reactions of metal halide adducts.[117] The kinetic facts available suggest the operation of a D mechanism when L = RCN, R_2O, or R_3PO and of an I_a mechanism when L = Me_2S, Me_2Se, and Me_2Te; i.e., there is a ligand-controlled crossover in mechanism. Once again electrostriction effects can be neglected for these reactions, and the reported $\Delta V^{\ddagger}$ mainly represents the intrinsic volume changes. The large positive $\Delta V^{\ddagger}$ values for the first set of ligands and the large negative $\Delta V^{\ddagger}$ values for the second set of ligands (see Table I, entries 73–77, 90–95, and 107–115) clearly confirm the ligand-controlled crossover from dissociative to associative. $\Delta V^{\ddagger}$ data for solvent exchange on five-coordinate complexes of the type $M(Me_6(tren))S^{2+}$ (S = DMF, DEF) and $M(tmc)CH_3CN^{2+}$ range between -9.6 and +6.5 $cm^3\ mol^{-1}$, depending on the central metal ion; they are typical of I_a and I_d processes, respectively.

A few results have become available for solvent- and ligand-exchange reactions of four-coordinate complexes in recent years. $\Delta V^{\ddagger}$ for the exchange of PPh_3 on the labile pseudotetrahedral complex $Co(PPh_3)_2Br_2$ (entry 57) is significantly negative, demonstrating the associative nature (I_a or A) of the process. Water exchange of $Pd(H_2O)_4^{2+}$ and $Pt(H_2O)_4^{2+}$ exhibits small negative $\Delta V^{\ddagger}$ values, indicating an I_a type of mechanism. However, other kinetic parameters suggest that square-planar substitution reactions usually proceed according to an A mechanism. The formation of the metal–solvent bond may well be accompanied by the lengthening of the two axial metal–solvent bonds during the formation of a trigonal-bipyramidal transition state, which will decrease the overall volume collapse associated with bond formation and account for the relatively small negative $\Delta V^{\ddagger}$ data. In a similar way, the $\Delta V^{\ddagger}$ data for exchange of DMS on $Pd(DMS)_2Cl_2$ (entries 82–85) in different solvents can be interpreted in terms of either an I_a or A mechanism.[121] If the Kirkwood parameter q_p is used to describe solvent electrostriction, a plot of $\Delta V^{\ddagger}$ versus q_p results in an intercept ($\Delta V^{\ddagger}_{intr}$) of -5.9 $cm^3\ mol^{-1}$, which could be a characteristic number for an associative substitution reaction of square-planar complexes (see further discussion and ref 35).

Data for DMF exchange on $Ln(DMF)_8^{3+}$ suggest a gradual changeover from I_d to D along the series of elements.[68] The positive $\Delta V^{\ddagger}$ values are thought to arise from the sum of two opposite effects: a volume decrease due to penetration of the ninth ligand into the coordination sphere and a dominant volume increase due to lengthening of the leaving and nonexchanging ligand bonds. Recently published data[125] for water exchange on $Ln(H_2O)_9^{3+}$ clearly underline the associative nature of the exchange process in the case of this less bulky solvent. The mechanistic trends described in this section are of fundamental importance to the interpretation of the $\Delta V^{\ddagger}$ data for ligand substitution reactions in general.

C. Ligand Substitution Reactions

In this section we discuss the data reported for nondegenerate ligand substitution reactions in which the product species differ from the reactant species, i.e., a nonsymmetrical substitution process (entries 116–675). It follows that the largest number of data were reported in this area, demonstrating the importance of ligand substitution processes in the understanding of chemical reactions. Various types of ligand substitution reactions may occur, and the data in Table I for a particular metal ion in a particular oxidation state have been ordered as follows: complex formation reactions, aquation or solvolysis, base hydrolysis, metal ion catalyzed aquation, and general ligand for ligand substitution processes.

The fundamental aspects of ligand substitution reactions were treated in the previous section, and the mechanisms outlined in Figures 6 and 7 will be adopted in this section. Mechanistic similarities are expected to occur for solvent-exchange and complex formation reactions involving these solvated metal ions. Due to the microscopic reversibility of complex formation reactions, the reverse aquation or solvolysis processes are expected to pass through the same transition state. The data discussed in the previous section clearly demonstrate the occurrence of mechanistic changeovers along particular series of metal complexes and ligands. A logical question is whether similar trends will show up in complex formation reactions of these solvated metal ions.

Complex Formation Reactions

In general, complex formation reactions, i.e., anation when the solvent is water, of transition-metal ions follow an interchange mechanism in which rapid precursor (ion pair) formation is followed by rate-determining ligand interchange, as outlined in (36). Under pseudo-first-order conditions, i.e., excess of L, the first-order rate constant can be expressed by (37). When L is

$$MS_6 + L \overset{K}{\rightleftharpoons} \{MS_6{\cdot}L\} \xrightarrow{k} MS_xL + (6-x)S \quad (36)$$

$$k_{obsd} = kK[L]/\{1 + K[L]\} \quad (37)$$

neutral, K is expected to be small and (37) reduces to $k_{obsd} = kK[L]$, the normal second-order behavior expected for such a substitution process. Important, however, is the fact that the second-order rate constant kK is a composite quantity with the result that $\Delta V^{\ddagger} = \Delta \bar{V}(K) + \Delta V^{\ddagger}(k)$. This means that the experimentally determined volume of activation must be corrected for the volume change arising from the precursor (ion pair) formation step in order to obtain the value for the actual interchange step. This is not always possible since in many cases K and k cannot be separated kinetically, and $\Delta \bar{V}(K)$ must be predicted theoretically by using the Fuoss theory. A summary of the data available for complex formation reactions of the divalent first-row transition-metal elements in Table III clearly demonstrates that complex formation reactions exhibit the same trend in $\Delta V^{\ddagger}$ as do the corresponding water-exchange reactions. Similar results are observed for such processes in other solvents, which supports the generality of a mechanistic changeover along the first-row transition elements from I_a to I_d. A typical volume profile for a complex formation reaction of Mn^{2+}, demonstrating the I_a nature of the process, is given in Figure 9. In this case, $\Delta \bar{V}(K)$ is assumed to be close to zero since the entering ligand is neutral. An example of a

TABLE III. $\Delta V^{\ddagger}$ for the Interchange of Neutral and Uninegative Ligands on M^{2+} Ions in Water[a]

ligand	V^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
H_2O	−4.1	−5.4	+3.8	+6.1	+7.2		
NH_3				+4.8	+6.0		
imidazole					+11.0		
isoquinoline					+7.4		
pada				+7.9	+7.1		
bpy		−1.2		+5.9	+5.3		
terpy		−3.4	+3.6	+4.1	+5.6		
SCN^-	−5.3						
glycinate(1−)				+5	+7	+9	+4
murexide(1−)					+8.7		

[a] From ref 16. Data in $cm^3\ mol^{-1}$.

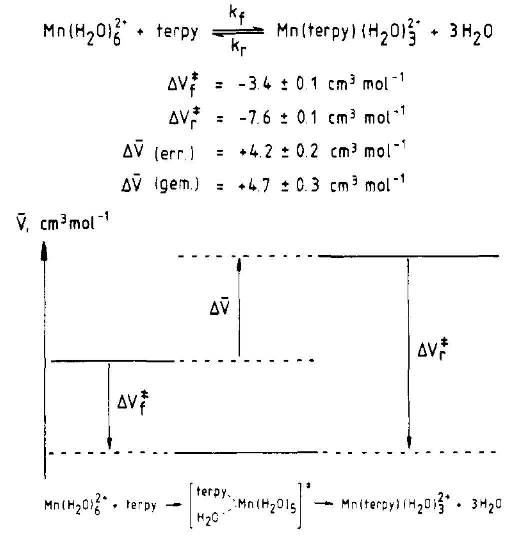


Figure 9. Volume profile for the complex formation reaction of Mn(II).[142]

volume profile where this is not the case is presented in Figure 10.

A mechanistic changeover has also been observed for the complex formation reactions of Fe^{3+} and $FeOH^{2+}$. It parallels that reported for the solvent-exchange reactions. In comparison, $\Delta V^{\ddagger}$ for complex formation of Fe^{3+} with neutral ligands should be more negative than for complexation by anionic ligands. This is indeed the case for ligands such as Hipt and Hahx, for which $\Delta V^{\ddagger}$ is significantly more negative than for SCN^-, Cl^-, and Br^-. Changing to other solvents sometimes results in a change in sign of $\Delta V^{\ddagger}$ for complex formation. This may be explained in terms of the relative bulkiness of the solvent molecules, in terms of which the metal–solvent bonds may have to lengthen in order to accommodate a larger entering ligand. $\Delta V^{\ddagger}$ therefore increases in the order H_2O < DMF < DMSO in which steric crowding increases. It is, therefore, reasonable to expect a mechanistic changeover along the series of solvents studied from I_a to I_d for the more bulky ones.

In many cases the interpretation of $\Delta V^{\ddagger}$ data for complex formation reactions is complicated by the fact that electrostriction effects, arising from charge neutralization, may dominate the intrinsic volume changes. This is especially noticed for anation reactions of trivalent metal complexes of the type $M^{III}L_5H_2O$, where L = NH_3, CN^-, and Cl^- and M = Co(III), Rh(III), Cr(III), and Ru(III). In two cases (entries 125 and 523) the anation process is accompanied by a negative $\Delta V^{\ddagger}$, and since both reactions involve neutralization of charge, the actual intrinsic component will be more negative than these values. This then suggests an I_a mechanism for the Cr(III) system and a limiting A mechanism for the Ru(III) system. The anation reactions of $Co(CN)_5H_2O^{2-}$ (entries 358–363) have a long-standing reputation of being typical of a limiting D mechanism. However, recent studies[330] have indicated that the original evidence supporting a D mechanism is in error and that an I_d mechanism is operative. The values of $\Delta V^{\ddagger}$ are such that they do not allow a distinct differentiation between these possibilities, but they do underline the dissociative nature of the process. Evidence in favor of a limiting D mechanism was also reported for anation reactions of $Rh(H_2O)_6^{3+}$, $Rh(H_2O)_5Cl^{2+}$, cis-$RhCl_4(H_2O)_2^-$, and $RhCl_5(H_2O)^{2-}$ (entries 530 and 531). The large positive values of $\Delta V^{\ddagger}$ were ascribed to the dissociation of coordinated water to produce a five-coordinate intermediate. In contrast, anation of $Rh(NH_3)_5H_2O^{3+}$ by chloride proceeds according to an interchange mechanism, for which differentiation between I_a and I_d is difficult on the basis of the $\Delta V^{\ddagger}$ value (entry 529). Similar results are reported for the other pentaammine complexes referred to above, for which a mechanistic assignment based on $\Delta V^{\ddagger}$ is also difficult.

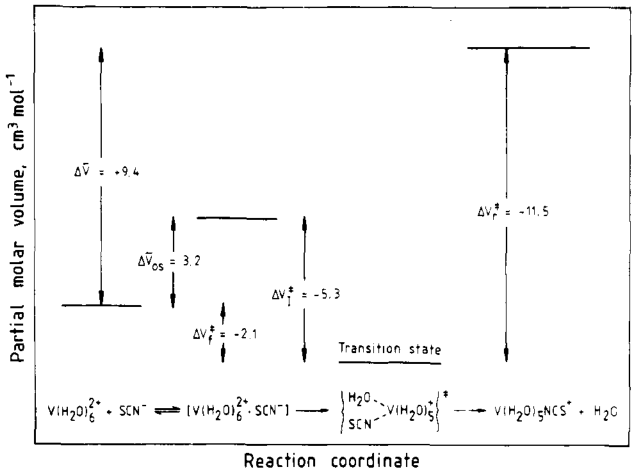


Figure 10. Volume profile for the formation of $V(H_2O)_5NCS^+$.[52]

The results for anation reactions of porphyrin complexes of Co(III), Rh(III), and Cr(III) indicate that $\Delta V^{\ddagger}$ is large and positive in all cases (entries 127, 270–272, 532, and 533). The data for the Co(III) complexes are in line with a limiting D mechanism, whereas those for Rh(III) and Cr(III) are somewhat smaller in magnitude and could point to an I_d mechanism. The trend clearly demonstrates the labilization effect of the porphyrin ligands in these complexes.

The interpretation of $\Delta V^{\ddagger}$ data for anation reactions is in many cases limited by our inability to estimate $\Delta \bar{V}(K)$ accurately. The anation reactions are in some cases slow and must be studied at high-temperature and high-concentration conditions, where K tends to be small and $\Delta \bar{V}(K)$ is difficult to determine. In addition, ion-pair formation with inert electrolyte ions, added to control the ionic strength of the medium, may also affect the interpretation of the data. It follows that differentiation between I_a and I_d mechanisms, especially for anation reactions involving oppositely charged reactants where significant ion-pair formation is present, remains speculative and must be treated with care.

Anation reactions of square-planar complexes of Pd(II) (entries 550–565) are generally accepted to proceed

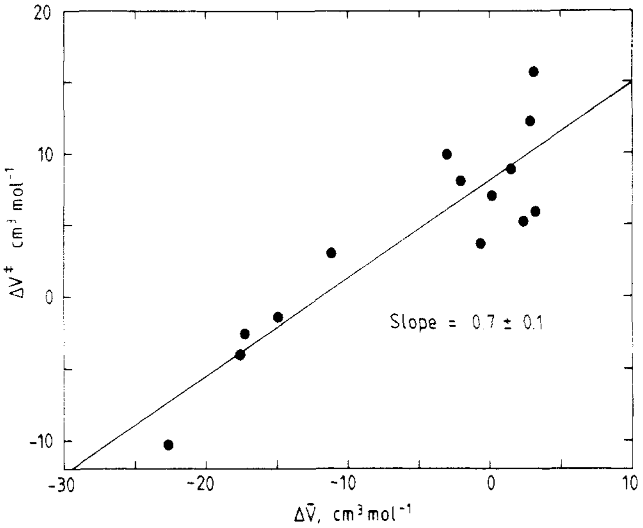


Figure 11. Plot of $\Delta V^{\ddagger}$ versus $\Delta\bar{V}$ for the solvolysis of a series of Ni(II) complexes.[331]

according to an associative mechanism, typical for such systems. Anation of $Pd(L)H_2O^{2+}$ exhibits in most cases negative values for $\Delta V^{\ddagger}$, except for anation by the very bulky ligands such as adenosine, cytidine, thymidine, and uridine, where $\Delta V^{\ddagger}$ is approximately zero. For the anation by the anionic halides and azide, charge neutralization during bond formation will result in a positive contribution from $\Delta V^{\ddagger}_{solv}$, which will partly counterbalance the negative $\Delta V^{\ddagger}_{intr}$ contribution arising from bond formation. The steric hindrance on L, the size of the entering ligand, and the overlap of the molecular orbitals in the transition state will determine the magnitude of $\Delta V^{\ddagger}_{intr}$ and therefore $\Delta V^{\ddagger}$. There seems to be a good correlation between the magnitude of $\Delta V^{\ddagger}$ and the size of the entering group down the series Cl^-, Br^-, I^-, and N_3^-, up to the point where the overlap with very large ligands (entries 552–555) becomes negligible. For the anation of $Pd(H_2O)_4^{2+}$ by DMSO (entries 550 and 551), the reported $\Delta V^{\ddagger}$ should only represent $\Delta V^{\ddagger}_{intr}$, such that these data confirm a limiting A mechanism.

Aquation and Solvolysis Reactions

The majority of high-pressure data deal with the reverse reactions of the processes discussed in the previous section, and only in a few cases were such reactions investigated in solvents other than water. We first consider the data for the spontaneous aquation reactions of complexes of divalent first-row transition-metal ions, i.e., the reverse of the reactions reported in Table II. For neutral leaving groups, $\Delta V^{\ddagger}$ is in general negative for V(II) and Mn(II), compared to positive for the other members of the series. In the case of anionic leaving groups, $\Delta V^{\ddagger}$ is in general more negative due to partial charge creation during bond cleavage in the transition state. The change in sign of $\Delta V^{\ddagger}$ fits the trend discussed for the complex formation reactions and indicates a changeover from I_a to I_d along the series, expected on the basis of microscopic reversibility of ligand substitution processes. Figures 9 and 10 illustrate that the volume of the transition state is significantly smaller than that of the reactant and product species, underlining the associative nature of reactions in these cases. The majority of data for the aquation/solvolysis of Ni(II) complexes (entries 470–480) exhibit positive volumes of activation, in agreement with the data reported for the complex formation reactions (entries 442–469). The transition state has a significantly larger volume than either the reactant or product states. The slightly negative $\Delta V^{\ddagger}$ values found for anionic leaving groups must be due to negative contributions from $\Delta V^{\ddagger}_{solv}$ arising from charge creation during bond cleavage. Notwithstanding these differences, the available data for the solvolysis of Ni(II) complexes exhibit a good correlation between $\Delta V^{\ddagger}$ and $\Delta\bar{V}$, with a slope of 0.7 ± 0.1 (see Figure 11), which is in line with the concept of an I_d mechanism since bond breakage is considerably advanced in the transition state.

The aquation reactions of amine complexes of Cr(III) and Co(III) (entries 128–152 and 273–372) have received considerable attention from high-pressure kineticists. The mechanistic assignments cover the whole spectrum of D, I_d, I_a, and A, which has led to quite some controversy in the literature. For instance, aquation reactions of the type in (38) all exhibit negative volumes

$$Cr(NH_3)_5X^{2+} + H_2O \rightarrow Cr(NH_3)_5H_2O^{3+} + X^- \quad (38)$$

of activation (including data reported in ref 1); but these can be interpreted either in terms of an associative process (due to bond formation) or in terms of a dissociative process during which Cr–X bond cleavage is accompanied by a strong increase in electrostriction due to charge creation. A plot of $\Delta V^{\ddagger}$ versus $\Delta\bar{V}$[332] results in a slope of 0.6, from which it was concluded that bond stretching is half advanced in the transition state. However, this can be the case for I_a as well as I_d, demonstrating the difficulty of interpretation. Unambiguous mechanistic information can be obtained for such reactions only when the leaving group is neutral so that no major solvational changes occur. Data reported recently[132] for the aquation of a series of complexes of the type $Cr(NH_3)_5X^{3+}$ (entries 128–132) demonstrate that $\Delta V^{\ddagger}$ is throughout negative, in line with an I_a mechanism.

An increase in steric hindrance (entry 138) results in a significantly more positive $\Delta V^{\ddagger}$, in line with an increasing importance of bond breakage and a possible changeover from I_a to I_d. Even more positive $\Delta V^{\ddagger}$ values are reported for the aquation of $Cr(NCS)_6^{3-}$ and $Cr(tpps)(H_2O)NCS^{4-}$, demonstrating the dissociative nature of these reactions, most probably I_d. The $\Delta V^{\ddagger}$ data reported for the aquation of the bis(oxalato) and bis(malonato) complexes of Cr(III) are too difficult to interpret, due to various contributions arising from ring opening and charge creation that may influence $\Delta V^{\ddagger}$.

Aquation reactions of the type outlined in (39) usually exhibit negative $\Delta V^{\ddagger}$ values when the leaving group is anionic (see data reported in ref 1). Again the negative

$$Co(NH_3)_5X^{(3-n)+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + X^{n-} \quad (39)$$

contribution of $\Delta V^{\ddagger}_{solv}$ arising from the charge creation during Co–X bond breakage is suggested to overrule $\Delta V^{\ddagger}_{intr}$. A plot of $\Delta V^{\ddagger}$ versus $\Delta\bar{V}$ is linear with unit slope,[331] indicating that the leaving group must be almost fully dissociated in the transition state, which is in line with an I_d mechanism. Even more convincing is the observation that $\Delta V^{\ddagger}$ is small and positive for a series of complexes where X is a neutral ligand (entries

273–283), for which $\Delta V^\ddagger$ will mainly represent $\Delta V^\ddagger_{intr}$ and so underlines the validity of an I_d mechanism. An increase in steric hindrance on the amine ligand (entries 293–297) results in a significant increase in $\Delta V^\ddagger$, demonstrating a more dissociative nature of the process.

Data for the pentaammine complexes have been used to perform some quantitative calculations concerning the partial molar volumes of intermediate and transition-state species.[178,181,183,333] Detailed analyses of the data have led to the suggestion that the partial molar volumes of $Co(NH_3)_5^{3+}$ and $Co(NH_3)_6^{3+}$ are either equal or differ by 17–20 $cm^3\ mol^{-1}$. This aspect is presently still unsettled, and more work is required before a definite conclusion regarding the partial molar volumes of 5- and 6-coordinate species can be reached.

At this point we should refer to Asano's approach[36] to obtain $\Delta V^\ddagger_{intr}$ of aquation reactions of Co(III) and Cr(III) complexes in which large solvational changes affect the sign and value of $\Delta V^\ddagger$. His calculations result in $\Delta V^\ddagger_{intr}$ values of +0.2 ($X^{n-} = NO_3^-$), +4.6 ($X^{n-} = Cl^-$), +4.0 ($X^{n-} = Br^-$), and +5.4 ($X^{n-} = SO_4^{2-}$) for the aquation of $Co(NH_3)_5X^{(3-n)+}$ compared to values of −4.9 ($X^{n-} = Cl^-$), −4.1 ($X^{n-} = Br^-$), and −4.2 ($X^{n-} = I^-$) cm^3 mol^{-1} for the aquation of $Cr(NH_3)_5X^{(3-n)+}$.

A large proportion of the data in Table I concern aquation reactions of *trans*- and *cis*-Co(L)XY, where L represents a wide range of mono- and multidentate (mainly amine) ligands and X and Y are Cl^-, Br^-, I^-, N_3^-, CN^-, NO_2^-, etc. For many of the systems, $\Delta V^\ddagger$ has a small (positive or negative) value, whereas $\Delta \bar{V}$ is substantially negative in all cases. Despite a few exceptions, most of these data can be interpreted in terms of a dissociatively activated (I_d or D) process in which the positive intrinsic contribution is partially or totally canceled by the negative solvational contribution arising form charge creation during bond cleavage. The large difference between $\Delta V^\ddagger$ and $\Delta \bar{V}$ indicates that we are dealing with an "early" transition state followed by a volume collapse during bond formation with the entering solvent molecule. The mean value of $\Delta V^\ddagger - \Delta \bar{V}$ is 12 ± 3 $cm^3\ mol^{-1}$, in good agreement with that expected for the entrance of a water molecule into the coordination sphere. The fact that these complexes aquate with retention requires that the entering solvent molecule be preassociated to some extent, supporting an I_d mechanism.

The aquation reactions of Co(III) oxalato and carbonato complexes proceed via the formation of ring-opened species followed by aquation or decarboxylation, respectively. The corresponding $\Delta V^\ddagger$ data can be interpreted in terms of volume increases during ring opening, accompanied by volume decreases due to an increase in electrostriction around the free end of the ligand. This also accounts for the more negative $\Delta V^\ddagger$ of the spontaneous (water assisted) ring-opening process than of the acid-catalyzed path for anionic carbonato complexes; the ring-opened species is a bicarbonate complex in the acid-catalyzed path, and no significant solvent electrostriction occurs around this free end of the ligand.

The aquation reactions of Fe(II) complexes all exhibit large positive $\Delta V^\ddagger$ values that underline the dissociative nature of the process. In a similar way, the substantially positive values reported for the aquation of $RhCl_6^{3-}$ and $RhCl_5H_2O^{2-}$ are clearly in line with a limiting D mechanism. In contrast to these extreme positive values found for the aquation of octahedral complexes, $\Delta V^\ddagger$ for the aquation/solvolysis reactions of square-planar Pd(II) and Pt(II) complexes are significantly negative, in line with an associative mechanism (entries 566–616 and 635–653). Very significant is the observation that an increase in steric hindrance on L for reaction 40 is

$$Pd(L)X^{(2-n)+} + H_2O \rightarrow Pd(L)H_2O^{2+} + X^{n-} \quad (40)$$

not accompanied by a change in $\Delta V^\ddagger$ for a particular leaving group (X^{n-}). Although the aquation rate constant decreases by 6 orders of magnitude with increasing steric hindrance, the constancy of $\Delta V^\ddagger$ underlines the validity of an associative process throughout the series. The data for the more hindered Et_4(dien) and $MeEt_4$(dien) complexes do exhibit a special dependence on the nature of the leaving group, viz., significantly more positive $\Delta V^\ddagger$ values for neutral leaving group such as NH_3 and py. It is possible that this may indicate a change in mechanism, since a dissociative reaction mode could be favored under certain circumstances for these highly sterically crowded complexes. Alternatively, the observed variation in $\Delta V^\ddagger$ of −3 to −13 $cm^3\ mol^{-1}$ could indicate a gradual changeover in mechanism from A to I_a. The solvolysis reaction of $Pd(H_2O)_3DMSO^{2+}$ and the solvent-exchange reactions of $Pt(H_2O)_4^{2+}$ and $Pd(H_2O)_4^{2+}$ also exhibit small negative $\Delta V^\ddagger$ values, in close agreement with those reported for the NH_3 and py aquation reactions. It follows that such small values can surely not result from a dissociative component due to steric hindrance. It is more likely that a $\Delta V^\ddagger$ of ca. −3 $cm^3\ mol^{-1}$ probably represents the pure intrinsic component for the associative entrance of a water molecule into the coordination sphere of a square-planar complex. The additional negative contribution toward $\Delta V^\ddagger$ when the leaving group is anionic may result from changes in dipole interaction when the square-planar complex is converted to a trigonal-bipyramidal transition state accompanied by the lengthening of the axial bonds and an increase in electrostriction. These effects may also partly account for the small magnitude of $\Delta V^\ddagger$ (for neutral leaving groups), since lengthening of the axial bond lengths will increase the volume of the five-coordinate species, which will partially balance the volume decrease due to bond formation. With the available $\Delta V^\ddagger$ for both anation and the reverse aquation reactions, it is possible to construct a relative reaction volume profile for the overall process. Two representative examples are given in Figure 12, from which it follows that the transition state has a significantly lower partial molar volume than either the reactant or product species, demonstrating the associative character of the substitution process.

Aquation reactions of Pt(II) amine complexes are all characterized by $\Delta V^\ddagger$ values of ca. −9.5 $cm^3\ mol^{-1}$, which is in close agreement with those reported for the corresponding Pd(II) complexes, i.e., where the leaving group is anionic. Massive steric hindrance was generally thought to force the substitution mode of such complexes into a dissociative one. In this respect it was reported in the literature that solvolysis reactions of *cis*-$Pt(PEt_3)_2(R)Br$, where R = Ph, *p*-MeC_6H_4, *o*-MeC_6H_4, and *o*-EtC_6H_4, proceed via an associative mechanism, but the more crowded complex with R = 2,4,6-$Me_3C_6H_2$ follows a dissociative mechanism (see ref 247 for more details). The pressure dependence of this reaction (entries 647–653), however, suggests the asso-

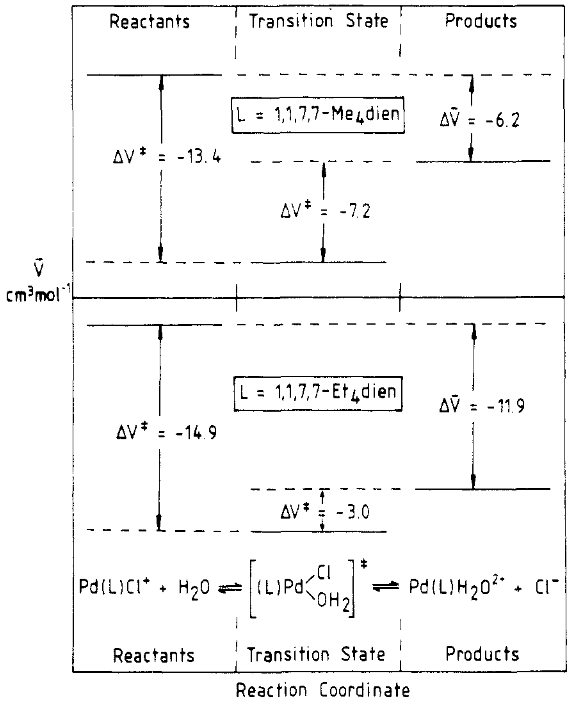


Figure 12. Volume profiles for the reaction $Pd(L)Cl^+ + H_2O \rightleftharpoons Pd(L)H_2O^{2+} + Cl^-$.

ciative nature of the process[247,248] and that a similar transition state is reached from either the cis or the trans complex.

Base-Catalyzed Aquation

The spontaneous aquation reactions discussed in the previous section are usually very slow for the inert complexes of Co(III), Cr(III), and Rh(III). In contrast, these reactions are orders of magnitude faster in basic medium and hence are generally referred to as base-catalyzed aquation or base hydrolysis. The increased reactivity is ascribed to the formation of a labile conjugate base (CB) species.

Base hydrolysis of $Cr_2O_7^{2-}$ (entries 121–124) is characterized by strongly negative volumes of activation, which is ascribed to the volume contraction arising from bond formation and an increase in electrostriction due to charge concentration on the chromate end on going to the transition state. For the reaction with OH^-, the mechanism can be outlined as in (41). During the

$$Cr_2O_7^{2-} + OH^- \rightarrow [CrO_4^- \cdots CrO_3OH^{3-}]^\ddagger \rightarrow CrO_4^{2-} + HCrO_4^- \quad (41)$$

dissociation of the transition state a volume increase of ca. 16 cm^3 mol^{-1} occurs. Base hydrolysis of Fe(II) complexes (entries 227–247) is usually characterized by large positive values of $\Delta V^\ddagger$ that vary significantly with the nature and composition of the solvent. The sign and magnitude of $\Delta V^\ddagger$ underline the dissociative nature of the process. A more detailed interpretation of these data is restricted by insufficient information on the nature of the rate-determining step and of the associated reaction products.

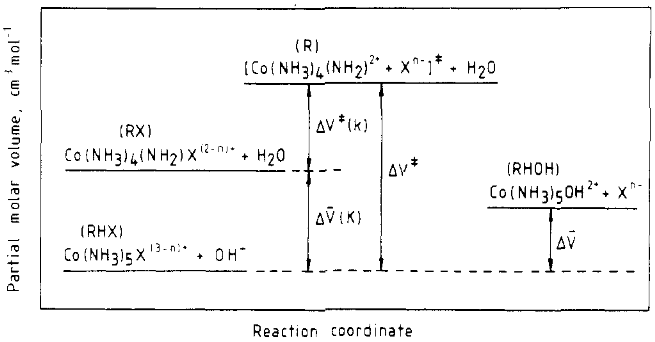


Figure 13. Volume profile for the base hydrolysis of $Co(NH_3)_5X^{(3-n)+}$ according to a S_N1cb mechanism.[195]

Base hydrolysis reactions of Co(III) amine complexes have received considerable attention in recent years (entries 373–399), with special focus on the $Co(NH_3)_5X^{(3-n)+}$ and $Co(NH_3)_4(NH_2X)Cl^{2+}$ systems. The base hydrolysis reactions of the pentaamminecobalt(III) complexes are generally accepted to react according to a S_N1cb mechanism as outlined in (42).[334] In the

$$Co(NH_3)_5X^{(3-n)+} + OH^- \overset{K}{\rightleftharpoons} Co(NH_3)_4(NH_2)X^{(2-n)+} + H_2O$$

$$Co(NH_3)_4(NH_2)X^{(2-n)+} \xrightarrow{k} Co(NH_3)_4NH_2^{2+} + X^{n-}$$

$$Co(NH_3)_4NH_2^{2+} + H_2O \xrightarrow{\text{fast}} Co(NH_3)_5OH^{2+} \quad (42)$$

rate-determining step the conjugate base species dissociates to produce the five-coordinate $Co(NH_3)_4NH_2^{2+}$ intermediate, which rapidly picks up a solvent molecule to produce the final product. The volume profile expected for such a reaction scheme is shown in Figure 13. The quantities $\Delta V^\ddagger$ $(=\Delta\bar{V}(K) + \Delta V^\ddagger(k))$ and $\Delta\bar{V}$ are expected to depend strongly on the nature of the leaving group, since an increase in electrostriction due to charge creation will occur when X is an anion. The experimental data support these expectations: the most positive $\Delta V^\ddagger$ and $\Delta\bar{V}$ values are reported for DMSO as leaving group, and the most negative values for SO_4^{2-} as leaving group, i.e., where the largest volume decrease due to electrostriction will occur. It is also possible to estimate the partial molar volume of the five-coordinate intermediate (denoted by R in Figure 13) with eq 43,

$$\bar{V}(R) = \Delta V^\ddagger + \bar{V}(RHX) + \bar{V}(OH^-) - \bar{V}(H_2O) - \bar{V}(X^{n-}) \quad (43)$$

and the available data[195] indicate that this value is independent of the nature of X^{n-}, with an average of 71 ± 4 cm^3 mol^{-1}. This is indeed close to the partial molar volume of 68 cm^3 mol^{-1} estimated for the six-coordinate $Co(NH_3)_5OH^{2+}$ species and significantly larger than the 60.3 and 61.3 cm^3 mol^{-1} values reported for the partial molar volumes of $Co(NH_3)_5H_2O^{3+}$ and $Co(NH_3)_6^{3+}$, respectively. From these results one may conclude that these five- and six-coordinate species of similar charge (2+) have approximately the same partial molar volume. Another interesting aspect of the data is that $\Delta V^\ddagger - \Delta\bar{V}$ should be independent of the nature of X^{n-}, since this difference involves the reaction of $Co(NH_3)_4NH_2^{2+}$ with H_2O to produce $Co(NH_3)_5OH^{2+}$. This difference is indeed constant for the investigated systems,[195] with an average value of +20 ± 2 cm^3 mol^{-1}; this almost equals the ionization volume of water, i.e., the collapse in volume on forming the H^+ and OH^- species.

The base hydrolysis reactions of a series of monoalkyl-substituted chloropentaamminecobalt(III) complexes revealed very similar results. In this case it is possible to gradually increase the size of the five-coor-

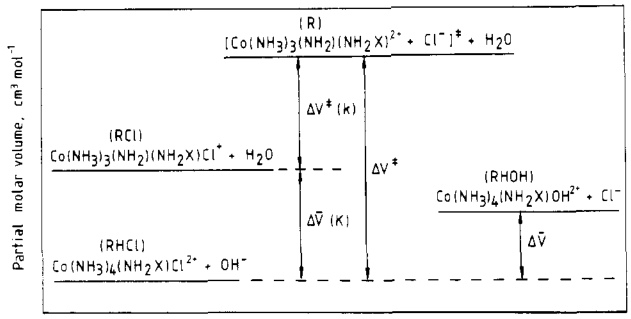


Figure 14. Volume profile for the base hydrolysis of $Co(NH_3)_4(NH_2X)Cl^{2+}$ according to a S_N1cb mechanism.[198]

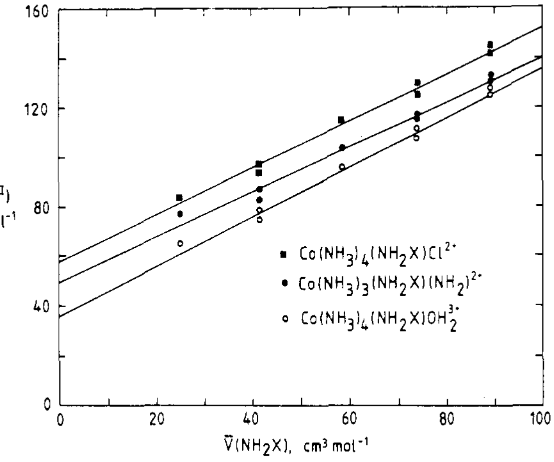


Figure 15. Plot of $\bar{V}(Co^{III})$ versus $\bar{V}(NH_2X)$ for a series of monoalkyl-substituted ammine complexes.[198]

dinate intermediate by increasing the size of the substituent X. The suggested mechanism is similar to that outlined in (42); the corresponding volume profile is given in Figure 14. Partial molar volume calculations were carried out in the way described above. The partial molar volume of $Co(NH_3)_3(NH_2)(NH_2X)^{2+}$ increases linearly with increasing X, as demonstrated in Figure 15. Furthermore, these values equal those for the corresponding $Co(NH_3)_4(NH_2X)OH^{2+}$ species; they are lower than those for $Co(NH_3)_4(NH_2X)Cl^{2+}$ and larger than those for $Co(NH_3)_4(NH_2X)H_2O^{3+}$. Thus, five- and six-coordinate species do seem to have similar partial molar volumes when the sixth ligand is indeed small such as OH^- or H_2O. For this series of complexes, the value of $\Delta V^\ddagger - \Delta\bar{V}$ is once again fairly constant, with an average value of 18 ± 2 $cm^3\ mol^{-1}$. This would also suggest that the volume of a water molecule completely disappears during the final step of the reaction and that the ionization process may account for this volume collapse.

In these systems $\Delta V^\ddagger$ is a composite quantity, and neutralization volume data (entries 400–412) were used to estimate the magnitude of $\Delta\bar{V}(K)$. The resulting $\Delta V^\ddagger(k)$ is strongly dependent on the nature and size of the leaving group[195] and consists of intrinsic and solvational contributions. Alternative base hydrolysis mechanisms A, S_N2cb, and E2, were considered[198] and found to be unsuitable to account for the reported data. It follows that a S_N1cb mechanism presents the most realistic description of the observed data. The base hydrolysis reactions of a series of $Rh(NH_3)_5X^{2+}$ complexes (entries 539–546) are characterized by $\Delta V^\ddagger$ values of ca. +20 $cm^3\ mol^{-1}$. These are substantially lower than those for the corresponding Co(III) complexes, with the result that $\Delta V^\ddagger(k) \approx 0$, after correction has been made for the contribution of $\Delta\bar{V}(K)$. This suggests that the intimate nature of the substitution process on the conjugate base species may be of the I_d type, during which partial bond breakage is accompanied by a volume decrease due to charge creation (i.e., increasing electrostriction). However, further investigations with differently charged leaving groups are needed before a more definite assignment can be made.

Metal Ion Catalyzed Aquation

Some metal ion catalyzed aquation reactions have been studied under pressure (entries 152, 413–418, and 547–549). In general, the reaction sequence involves a preassociation equilibrium during which Hg^{2+} or Ag^+ is attached to the halide ligand, followed by rate-determining dissociation of the bridged species. This reaction sequence can be summarized as in (44), from

$$M_1(NH_3)_5X^{2+} + M_2^{n+} \overset{K}{\rightleftharpoons} (NH_3)_5M_1\text{–}X\text{–}M_2^{(n-2)+} \xrightarrow{k}$$
$$M_1(NH_3)_5^{3+} + M_2X^{(n-1)+} \xrightarrow[\text{fast}]{H_2O} M_1(NH_3)_5H_2O^{3+} \quad (44)$$

which it follows that $\Delta V^\ddagger$ is once again a composite quantity, viz., $\Delta\bar{V}(K) + \Delta V^\ddagger(k)$. The Hg^{2+}-catalyzed aquation reactions of $M(NH_3)_5X^{2+}$, where M = Cr(III), Co(III), and Rh(III) and X = Cl and Br, all exhibit near-zero values for $\Delta V^\ddagger$. This means that the volume decrease expected for the formation of the bridged species is evidently canceled by the volume increase during the rate-determining bond-cleavage process.[139] For the Hg^{2+}-catalyzed aquation of $Rh(NH_3)_5I^{2+}$ and *mer*-$RhCl_3(H_2O)_3$, it was possible to separate K and k, and obtain $\Delta\bar{V}(K)$ and $\Delta V^\ddagger(k)$, kinetically. Surprisingly, $\Delta\bar{V}(K) = -1.7 \pm 1.0\ cm^3\ mol^{-1}$ for the iodo system, indicating that bridge formation is presumably accompanied by release of solvent molecules around the Hg^{2+} ion. The value is even slightly positive in the case of the trichloro complex.[231] It follows that $\Delta V^\ddagger(k)$ itself is also small, and an interchange mechanism is likely to account for the observed data. The Ag^+-catalyzed aquation of $Co(NH_3)_5Br^{2+}$ is significantly affected by the presence of polyelectrolyte (NaPSS) species, and desolvation of the reactant and transition-state species was suggested to account for the observed effects.

Ligand for Ligand Substitution Reactions

In the previous sections we have concentrated on ligand substitution processes that involve solvent molecules either as entering or as leaving groups. This section focuses on substitution reactions involving ligands other than solvent molecules. These usually occur in noncoordinating solvents or in the presence of strong nucleophiles for which the competition by solvent molecules is negligible.

Mechanistic uncertainties regarding chelate-ring replacement reactions of $Cr(CO)_4(S\frown S)$ complexes resulting from large differences in values for $\Delta S^\ddagger$ were solved with the help of the large positive $\Delta V^\ddagger$ data (entries 153 and 154) that underline the operation of a D mechanism. Substitution reactions of Fe(II) complexes (entries 248–257) all exhibit large positive $\Delta V^\ddagger$ values characteristic of a D mechanism. Departure of the leaving group accounts for the large increase in

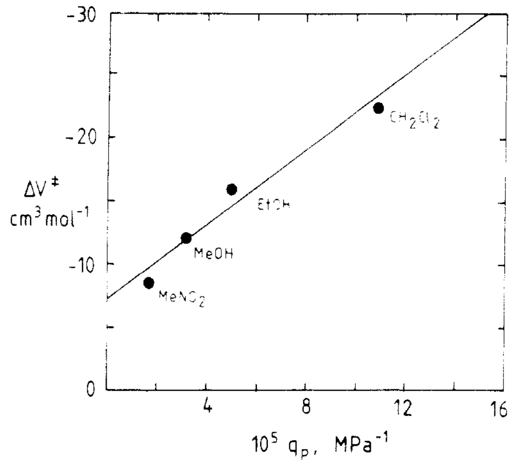


Figure 16. Relationship between $\Delta V^{\ddagger}$ and q_p for the substitution of *trans*-Pt(py)$_2$(Cl)NO$_2$ by pyridine in different solvents.[338]

volume in the transition state. For the substitution of the Fe(4-Mephen)$_3^{2+}$ complex (entries 248 and 249), the authors suggest that the $\Delta V^{\ddagger}$ value may arise from extensive desolvation of CN$^-$ during an associative binding of CN$^-$. The formation of *trans*-Co(NH$_3$)$_4$(SO$_3$)$_2^-$ from Co(NH$_3$)$_5$SO$_3^+$ (entry 421) is characterized by an independence of the entering-ligand concentration and a positive $\Delta V^{\ddagger}$. These observations point toward a limiting D mechanism enhanced by the strong trans labilization effect of the sulfite ligand. The Co–NH$_3$ bond lengthening in the transition state was estimated to be 140 pm, which is remarkably close to the 120 pm predicted on the basis of a simple harmonic oscillator model.[335] A similar mechanism was suggested for the substitution of NiL$_2$ (entries 481–483) by pan in acetic acid as solvent.

Ligand substitution reactions of tetra- and pentacarbonyl complexes of Mo are in many cases characterized by small positive or near-zero volumes of activation (entries 508–518). Although these were generally interpreted in terms of a dissociative mechanism, recent observations have suggested the possible operation of an interchange mechanism, and more work is required to reach a definite conclusion. This is a typical problem of interpreting kinetic data for a multistep mechanism such as the one outlined in (45), where several reaction

$$cis\text{-Mo(CO)}_4(\text{py})_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Mo(CO)}_4(\text{py}) + \text{py}$$

$$\text{Mo(CO)}_4(\text{py}) + \text{N}\frown\text{N} \xrightarrow{k_2} \text{Mo(CO)}_4(\text{py})\text{N}\frown\text{N} \xrightarrow{\text{fast}} \text{Mo(CO)}_4(\text{N}\frown\text{N}) + \text{py} \quad (45)$$

steps will contribute to the overall value of $\Delta V^{\ddagger}$ and complicate its interpretation. The $\Delta V^{\ddagger}$ data reported for substitution reactions of triruthenium carbonyl clusters (entries 526–528) are significantly positive to underline the operation of a dissociative mechanism involving the release of CO. Here again the determination of $\Delta V^{\ddagger}$ helped to resolve the apparent discrepancy based on the reported values of $\Delta S^{\ddagger}$.[336,337] Substitution reactions of W (entries 633 and 634) also exhibit significantly positive $\Delta V^{\ddagger}$ values, which are in agreement with the suggested D mechanism.

Ligand substitution reactions of Pd(II) and Pt(II) complexes (entries 617–627 and 654–668) are all characterized by negative volumes of activation, except for three cases where OH$^-$ is the entering ligand and a conjugate base mechanism is presumably operating. The negative values are typical for limiting A mechanisms that operate under all conditions, even where significant steric hindrance could affect the nature of the mechanism. The $\Delta V^{\ddagger}$ values show a remarkable solvent dependence resulting from varying degrees of electrostriction in the transition state when the leaving group is anionic. For the substitution of *trans*-Pt(py)$_2$(NO$_2$)Cl by py, the $\Delta V^{\ddagger}$ data show a good correlation with the q_p solvent parameter (Figure 16); the intercept of this plot gives a $\Delta V^{\ddagger}_{\text{intr}}$ value of -7 ± 1 cm^3 mol^{-1}. This value is quite realistic for the associative process since the volume decrease associated with bond formation will partly be compensated by the volume increase due to the lengthening of the axial bonds in reaching a trigonal-bipyramidal transition state, as mentioned before.

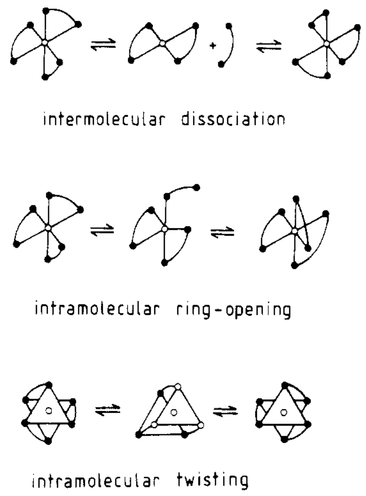


Figure 17. Schematic representation of different racemization mechanisms of octahedral complexes.[9]

D. Isomerization Reactions

Volumes of activation for three types of isomerization reactions, viz., racemization, geometrical, and linkage isomerization, have been determined (entries 676–757) and will be discussed in this sequence. The interpretation of the data in many cases strongly relies on our understanding of closely related substitution processes treated in the previous section, since these often form the basis of the isomerization process.

Racemization reactions can occur according to intermolecular dissociation, intramolecular ring opening, and intramolecular twisting, schematically presented in Figure 17. Some of these mechanisms exhibit characteristic pressure dependencies, although the overall reaction volume is zero for such processes. In the case of the one-ended dissociation mechanism, ring opening should result in a positive $\Delta V^{\ddagger}_{\text{intr}}$ contribution. However, when the ring-opened moiety is charged, solvent electrostriction could dominate the overall effect. This is the case, for instance, for the series of Cr(III) complexes (entries 676–678) in which ring opening of the oxalate ligand is accompanied by charge creation and an overall negative $\Delta V^{\ddagger}$. The small negative and positive values reported for the other Cr(III) complexes are more consistent with a twist mechanism. Similarly, the data for the racemization of the Co-

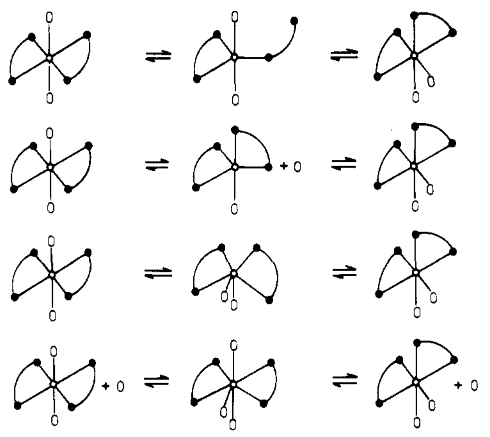
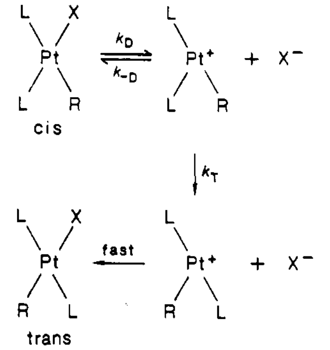


Figure 18. Schematic representation of the possible geometrical isomerization mechanisms of octahedral complexes.[9]

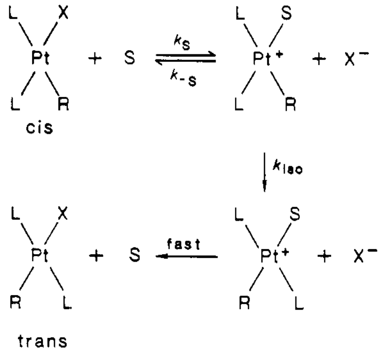
$(Ph_2dtc)_3$ and $Co(pyrdtc)_3$ complexes are considered to be evidence for one-ended ring opening and intramolecular twisting, respectively. The ring-opening mechanism is also suggested to account for the data reported for the Ni(II) and Ge(IV) complexes. In the latter case, $\Delta V^\ddagger$ correlates with the donor number of the solvent, indicating that the one-ended opening of the acac chelate is accompanied by a negative volume contribution due to an increase in electrostriction.

Similar mechanisms have been suggested to account for the geometrical isomerization reactions, and these are summarized schematically in Figure 18, namely, one-ended dissociation of a chelate ligand, dissociation of a monodentate ligand, twisting without bond rupture, and an associative reaction with a nucleophile (usually a solvent or OH^- species). The large negative $\Delta V^\ddagger$ for the trans-to-cis isomerization of $Cr(C_2O_4)_2(H_2O)_2^-$ is consistent with one-ended dissociation of the oxalate ligand. An associative reaction mode could also account for this value, but the rate of water exchange is known to be 2 orders of magnitude slower than isomerization, thus eliminating this possibility. In addition, a more positive value of -5.5 cm^3 mol^{-1} was found for the reaction in 0.2 M $HClO_4$, which is associated with a smaller electrostriction contribution when the ring-opened ligand is protonated.[339] In contrast, the corresponding malonate complex isomerizes more slowly; the positive volume of activation suggests a dissociative (most probably I_d) release of coordinated water. The positive $\Delta V^\ddagger$ data for the isomerization reactions of the bis(ethylenediamine) complexes of Co(III) (entries 704–721) are all in agreement with dissociatively activated processes, ranging from D for the more positive to I_d for the less positive values. The $\beta \rightarrow \alpha$ isomerization of the edda complexes depends strongly on the $[OH^-]$, which along with the large positive $\Delta V^\ddagger$ values suggests the operation of a S_N1cb mechanism similar to that outlined in eq 42. Ring opening of the diamine ligand is suggested to account for the observed isomerization process.[83] The substantially positive $\Delta V^\ddagger$ reported for the isomerization of $SnCl_4{\cdot}2Me_2S$ is interpreted in terms of an intramolecular twist mechanism. This value is significantly smaller than the +38.4 cm^3 mol^{-1} reported for the exchange of Me_2S (entry 89) and rules out the possibility of a limiting D mechanism. In a similar way, the $\Delta V^\ddagger$ data for the isomerization of *cis*-$Pt(PEt_3)_2(Ph)X$ (entries 725–727) can be interpreted in terms of an intramolecular twist mechanism, although the operation of a dissociative mechanism can probably not be ruled out completely. However, the more sterically hindered mesityl complex (entry 728) isomerizes with rate-determining solvolysis, which is an associative process. There is a longstanding contradiction in the literature concerning the dissociative nature of such isomerization processes, since the two possible mechanisms outlined in (46) and (48) exhibit similar rate laws (47) and (49), respectively.[247,259,260,340-342]



(46)

$$k_{obsd} = k_D k_T/\{k_{-D}[X^-] + k_T\} = k_D \text{ (at low } [X^-]) \qquad (47)$$



(48)

$$k_{obsd} = k_{iso}K_s/\{[X^-] + K_s\} = k_{iso} \text{ (at low } [X^-]) \qquad (49)$$

In the latter case (eq 48), increasing steric hindrance on R may decrease k_S and k_{-S} to the point that the preequilibrium treatment is invalid, and the steady-state treatment will modify eq 49 to eq 50. This means

$$k_{obsd} = k_{iso}k_S/\{k_{-S}[X^-] + k_{iso}\} = k_S \text{ (at low } [X^-]) \qquad (50)$$

that on increasing the steric hindrance a changeover in rate-determining step may occur (from k_{iso} to k_S), exactly as observed in the $\Delta V^\ddagger$ data. This is a typical example of how high-pressure kinetic studies sometimes lead to a complete reconsideration of a generally accepted mechanism.

A number of linkage isomerization reactions of M–ONO and M–SCN species have been studied under pressure (entries 730–757). For complexes of the type $M(NH_3)_5ONO^{2+}$ (M = Co(III), Rh(III), and Ir(III)), $\Delta V^\ddagger$ is negative and the transition state lies approximately halfway between the reactant and product states (see Figure 19). Similar results were reported for the bis(ethylenediamine) complexes. No specific solvent dependence was observed, except for the catalysis by base, in which case the reaction proceeds via a conjugate base mechanism as supported by the large positive $\Delta V^\ddagger$ values (entries 732, 744, and 745). The isomerization reactions of $Pd(L)SCN^+$ (entries 750–752) are suggested to proceed via a solvento intermediate. The reported $\Delta V^\ddagger$ values are therefore in good agreement with those observed for solvolysis of such complexes (entries 566–616). Finally, no significant pressure effects were

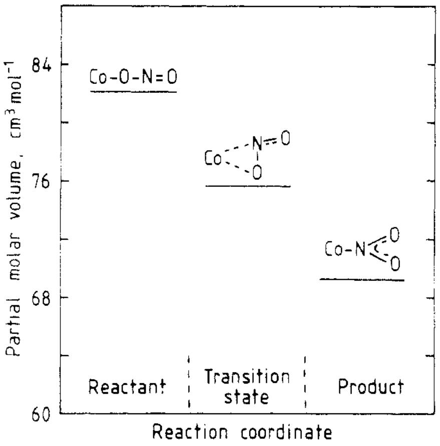


Figure 19. Volume profile for the linkage isomerization of $Co(NH_3)_5ONO^{2+}$.[261]

reported for inversion at the sulfur atom for the series of cyclic sulfide complexes of the type $\textit{trans}\text{-}MX_2[S(CR_2)_n]_2$ (entries 753–756). This suggests that the inversion reaction is evidently a simple intramolecular process in which solvation changes are small and no significant volume changes are observed.

E. Addition and Elimination Reactions

The data for addition reactions summarized in Table I (entries 758–785) represent systems in which addition to a coordinate ligand or oxidative addition to the central metal ion occurs. The latter is accompanied by a change in coordination number and geometry, usually from square-planar to octahedral. Oxotitanium(IV) complexes react with H_2O_2 to produce peroxotitanium(IV) species. This process can be considered either as a substitution reaction or as an addition reaction. The negative $\Delta V^\ddagger$ values reported for the uncatalyzed path support a mechanism in which bond formation with H_2O_2 occurs, i.e., an associative reaction mode. In the case of the acid-catalyzed path, protonation of the oxo group is expected to make a small positive contribution and so account for the more positive $\Delta V^\ddagger$ values. A similar trend is observed for the reaction of $VO_2(nta)^{2-}$ with H_2O_2, and the suggested mechanism is outlined in Figure 20. Both reaction paths involve a seven-coordinate intermediate, and the rate-determining step is the rearrangement of the associated complex to the distorted pentagonal bipyramid. Thus, the proton actually assists the rearrangement step. There is no direct evidence to distinguish between the release of the oxo or H_2O_2 oxygen as water in the final step, but it is likely that the peroxo product results from the oxo group and an oxygen atom of the H_2O_2 molecule.

Additions of NO^+ and CO_2 to metal hydroxo complexes are generally referred to as uptake processes.[343,344] A general example of such an uptake mechanism, combined with the reverse decarboxylation step, is given in (51). Such uptake reactions are characterized by

$$\begin{tikzcd} ML_5OH^{(n-1)+} + CO_2 \arrow[r, shift left] \arrow[d, shift left, "+H^+"] & ML_5OCO_2H^{(n-1)+} \arrow[l, shift left] \arrow[d, shift left] \\ ML_5H_2O^{n+} \arrow[u, shift left, "-H^+"] & ML_5OCO_2^{(n-2)+} + H^+ \arrow[u, shift left] \end{tikzcd} \quad (51)$$

negative $\Delta V^\ddagger$ values, and these are ascribed to the intrinsic volume decrease associated with O–C bond formation. A similar effect was observed for the hydrolysis of CO_2, for which $\Delta V^\ddagger$ has a value of -9.9 ± 1.9 $cm^3\ mol^{-1}$.[345]

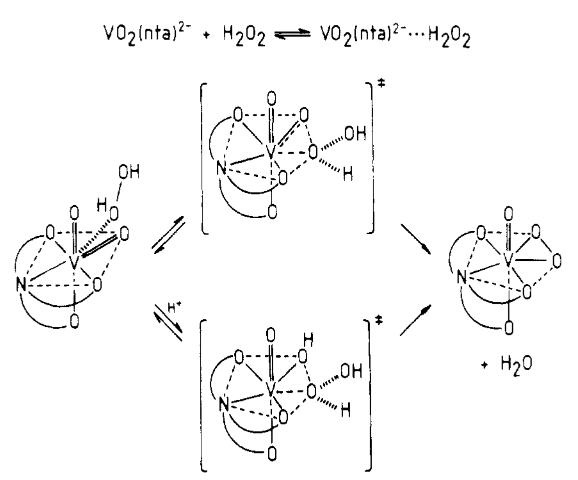


Figure 20. Proposed mechanism for the reaction of H_2O_2 with $VO_2(nta)^{2-}$ to produce $VO(O_2)(nta)^{2-}$.[56]

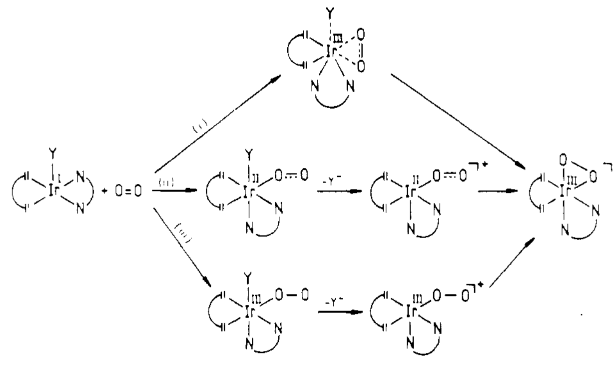


Figure 21. Possible pathways for dioxygen activation by a coordinatively saturated Ir(I) complex.[280]

Addition of OH^- to complexes of the type $Co^{III}(L)(hfac)$ proceeds through addition to the hfac ligand[346,347] and is characterized by a $\Delta \bar{V}$ value of between -8 and $+11$ $cm^3\ mol^{-1}$, depending on the nature of L. Solvational effects due to charge neutralization will result in volume increases for the cationic complexes, whereas charge concentration will cause volume decreases. Thus, $\Delta V^\ddagger$ for the addition of OH^- is also positive due to the decrease in electrostriction, compared to a negative $\Delta V^\ddagger$ for the reaction with H_2O ascribed to the bond formation component.

Cycloaddition reactions of tricarbonyl(cycloheptatrienone)iron with tetracyanoethene (entries 767–769) exhibit remarkably negative volumes of activation, in agreement with the type of data usually observed for organic cycloaddition reactions. The authors[274] suggest the operation of a concerted mechanism.

Oxidative-addition reactions are in general characterized by strongly negative volumes of activation (entries 783–785), which arise partly from intrinsic volume changes due to bond formation and partly from an increase in electrostriction since the transition state is expected to exhibit polar properties. The values of $\Delta V^\ddagger$ for instance favor two of the possible reaction paths (ii and iii) outlined for the oxidative addition of O_2 to Ir(cod)(phen)I in Figure 21. It should be kept in mind that part of the volume collapse observed during oxidative addition must arise from the formal oxidation of the metal ion.

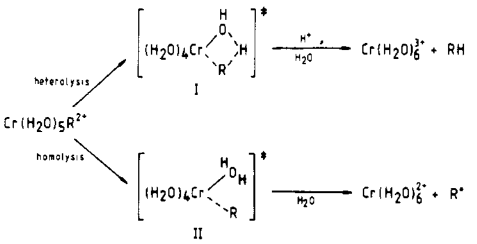


Figure 22. Heterolysis and homolysis reactions of organochromium(III) species.[281]

Elimination reactions are in the majority of cases characterized by positive $\Delta V^{\ddagger}$ values (entries 786–799). The first couple of entries demonstrate substantially different $\Delta V^{\ddagger}$ data for homolytic and heterolytic bond scission reactions of organochromium(III) complexes. These data can be interpreted in terms of the mechanism outlined in Figure 22. Heterolytic cleavage exhibits almost zero $\Delta V^{\ddagger}$ values, which point to a transition state (I) that involves no net development of charge or major net changes in bond lengths. On the contrary, $\Delta V^{\ddagger}$ for homolytic bond cleavage is significantly positive, which has been ascribed to massive desolvation, i.e., breakup of the solvent cage, as the organic radicals separate from Cr^{2+} in the transition state (II). Decarboxylation reactions of complexes of the type $M(NH_3)_5OCO_2H^{2+}$ (see eq 51) are characterized by small positive $\Delta V^{\ddagger}$ values that are in close agreement with a value of +6.4 ± 0.4 cm^3 mol^{-1} reported[345] for the decarboxylation of HCO_3^-. The near-zero values found for the decarboxylation of the en, edda, and nta carbonato complexes are partly ascribed to the high ionic strength (2–3 M) employed during such measurements. Hydrogen-bonding effects in such strongly acidic medium could also partly account for the low values. The elimination of OH^- from $Co(en)_2(hfacOH)^+$ exhibits a positive volume of activation, which is even more profound in the base-catalyzed path.

A few reaction volume data have become available for the change in coordination number of Ni(II) complexes. A series of data for the addition of water molecules to square-planar Ni(II) complexes (entries 484–495) demonstrate an overall volume decrease during such reactions. One can assume that these $\Delta\bar{V}$ values mainly represent the intrinsic component, since no change in electrostriction is expected. The volume decrease can be ascribed to the transfer of two solvent molecules from the bulk solvent into the coordination sphere, which is partially canceled by a volume increase due to the expansion of the macrocyclic molecular aperture associated with the change in spin state.

F. Electron-Transfer Reactions

Electron-transfer reactions can in general be classified as outer sphere or as inner sphere, depending on the nature of the precursor intermediate species, Ox//Red, in (52), which can be either an ion pair or encounter

$$\mathrm{Ox + Red} \overset{K}{\rightleftharpoons} \mathrm{Ox//Red}$$

$$\mathrm{Ox//Red} \xrightarrow{k} \mathrm{Ox^-//Red^+} \qquad (52)$$

$$\mathrm{Ox^-//Red^+} \rightleftharpoons \mathrm{Ox^- + Red^+}$$

complex, or a bridged intermediate, respectively. This means that the coordination sphere of the reactants remains intact in the former case and is modified by substitution processes in the latter. It is, therefore, reasonable on the basis of these two mechanisms to expect significantly different pressure dependencies not only when the electron-transfer step is rate determining but also when precursor formation or successor dissociation is rate determining. Preliminary studies reviewed before[1] indicated that $\Delta V^{\ddagger}$ was invariably positive (+2 to +11 cm^3 mol^{-1}) for an inner-sphere mechanism, presumably due to the expulsion of a ligand during precursor formation, and significantly negative for an outer-sphere mechanism. In fact, the apparent agreement between experimentally observed and theoretically predicted $\Delta V^{\ddagger}$ values for a series of outer-sphere self-exchange reactions was so good that it probably discouraged further experimental studies of such processes.[348] However, as we will see later, the agreement is not at all good and in many cases highly questionable.

A general difficulty encountered in kinetic studies of electron-transfer processes concerns the separation of K and k in (52). In the majority of cases precursor formation is a fast step, followed by rate-determining electron transfer. In the presence of an excess of Red the rate expression is given by (53). K is usually small,

$$k_{\mathrm{obsd}} = kK[\mathrm{Red}]/\{1 + K[\mathrm{Red}]\} \qquad (53)$$

such that (53) reduces to $k_{\mathrm{obsd}} = kK[\mathrm{Red}]$, which means that the observed second-order rate constant (kK) is a composite quantity and $\Delta V^{\ddagger}(k_{\mathrm{obsd}}) = \Delta\bar{V}(K) + \Delta V^{\ddagger}(k)$. In some cases it is indeed possible to separate k and K kinetically by the use of the doubly reciprocal plotting procedure. A detailed account on the effect of pressure on inner-sphere and outer-sphere processes was recently presented by Swaddle.[349]

The recent interest in $\Delta V^{\ddagger}$ studies of outer-sphere electron-transfer (OSET) reactions was partly aroused by the possibility to use such data to test the applicability of theories of the Marcus–Hush type. Pressures up to 300 MPa have a marked effect on the intermolecular distances and interactions and can therefore reveal intermolecular phenomena. In the case of self-exchange and closely related reactions, $\Delta\bar{V}$ is zero and does not have to be considered in the overall interpretation of $\Delta V^{\ddagger}$. This is not the case for nonsymmetrical ET reactions.[350] In the earlier work referred to above,[348] $\Delta V^{\ddagger}$ for the self-exchange reactions $Fe(H_2O)_6^{2+/3+}$, $Co(en)_3^{2+/3+}$, and $Tl(H_2O)_6^{+/3+}$ varies between −12 and −20 cm^3 mol^{-1}. Stranks used the Marcus–Hush theory to calculate $\Delta V^{\ddagger}$ in terms of internal reorganization (IR), solvent reorganization (SR), Coulombic interaction (Coul), and Debye–Hückel contributions (DH) according to eq 54. But as Wherland[351] pointed out, the sign

$$\Delta V^{\ddagger} = \Delta V^{\ddagger}_{\mathrm{IR}} + \Delta V^{\ddagger}_{\mathrm{SR}} + \Delta V^{\ddagger}_{\mathrm{Coul}} + \Delta V^{\ddagger}_{\mathrm{DH}} \qquad (54)$$

of $\Delta V^{\ddagger}_{\mathrm{DH}}$ in Stranks' original article was in error, so that the calculated values did not come close to the observed values. In a recent study of the $MnO_4^{-/2-}$ system (entries 802–806), a detailed theoretical treatment was presented in an effort to improve the understanding and to resolve the apparent discrepancy. Each of the terms in (54) was reanalyzed[286,349] by varying the metal–metal internuclear separation and by considering possible contributions arising from the nonadiabaticity of the

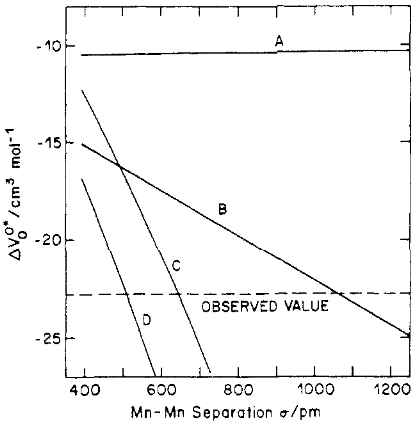


Figure 23. Calculated dependence of $\Delta V^\ddagger$ for the cation-independent ET reaction on the Mn–Mn distance: (A) adiabatic two-sphere model; (B) nonadiabatic two-sphere model; (C) adiabatic ellipsoidal-cavity model; (D) nonadiabatic ellipsoidal-cavity model.[286]

process. $\Delta V^\ddagger$ was predicted by the use of an adiabatic two-sphere model, a nonadiabatic two-sphere model, an adiabatic ellipsoidal-cavity model, and a nonadiabatic ellipsoidal-cavity model, for which the results are presented as a function of the Mn–Mn separation in Figure 23. It can be concluded from these calculations that $\Delta V^\ddagger$ can be predicted by a modified Marcus–Hush type model in which the pressure dependence of the most favorable Mn–Mn separation is acknowledged and the reactants are considered to be enclosed in a common cavity in the solvent. It is concluded that an adiabatic or slightly nonadiabatic ellipsoidal-cavity model accounts for the experimental data.

Theoretical calculations for OSET in the systems $Mn(CNR)_6^{+/2+}$ (entries 807–814) cannot account for the experimentally observed $\Delta V^\ddagger$, and it is concluded that it is the flexibility of the ligands and not their size that contributes most to the observed trends. Quite surprising is the fact that the simple Marcus–Hush treatment does predict a value of −7.3 cm^3 mol^{-1} for the OSET reaction of $Co(terpy)_2^{2+}$ and $Co(bpy)_3^{3+}$ in aqueous solution, in good agreement with the experimental value (entry 818). However, this reaction is not strictly speaking a true self-exchange reaction, and the apparent agreement could be fortuitous.[349] The strongly positive $\Delta V^\ddagger$ values reported for the $Fe(CN)_6^{3-/4-}$ system (entries 815–817) clearly fall out of line with the other data for such processes, and it has been suggested[349] that the involvement of alkali-metal cations in the transition state may account for these results.

Quite an extensive series of data is presently available for nonsymmetrical OSET reactions (entries 822–838). In many of these cases it was possible to resolve $\Delta V^\ddagger$ into $\Delta\bar{V}(K)$ and $\Delta V^\ddagger(k)$. For closely related systems, the values of $\Delta\bar{V}(K)$ exhibit tremendous fluctuations. Although we generally expect a substantial increase in volume due to partial charge neutralization during ion-pair formation, this has only been found in two cases (entries 835 and 842). It is surprising that $\Delta\bar{V}(K)$ is usually very small (almost zero) and in some cases even slightly negative. It must be kept in mind that such data are subjected to large error limits due to the indirect way in which the pressure dependence of K is obtained. Furthermore, since many of these studies are performed at high ionic strength, ion association with other counterions must take place and could account for the observed deviations. However, the nature of the ion pair produced as precursor species is unknown, and it is therefore difficult to predict volume changes based on partial molecular overlap and partial charge neutralization. On the contrary, the $\Delta V^\ddagger(k)$ values are all substantially positive and do not exhibit a clear trend with the nature of the substituents on the Co(III) center. Two explanations were offered to account for these values. The Sendai group argued that the expansion of the cobalt complex on going from low-spin Co(III) to high-spin Co(II) can contribute substantially (20–30 cm^3 mol^{-1}) to $\Delta V^\ddagger(k)$; the Frankfurt group suggested that the increase in molar volume of ca. 43 cm^3 mol^{-1} in going from $Fe(CN)_6^{4-}$ to $Fe(CN)_6^{3-}$ largely accounts for the observed data. Recent theoretical calculations[352] underline the important contribution arising from the overall increase in volume of ca. 65 cm^3 mol^{-1} during the ET step.

The remaining data concern inner-sphere electron-transfer (ISET) reactions. The series of data reported for the reduction of $Co(NH_3)_5X^{2+}$ by Fe^{2+} in H_2O and DMSO (entries 822–829) can be accounted for in terms of changes in solvation and steric crowding. They definitely rule out the possible formation of a tetrahedral $Fe(solvent)_4^{2+}$ species rather than the predominant hexacoordinate solvent species, a suggestion made in the literature.[353] The results for the reduction of *cis*-$Co(en)_2Cl_2^+$ (entry 800) are the first data reported for an ISET reaction in which the precursor formation step can be separated from the electron-transfer step. The negative $\Delta V^\ddagger$ for the latter step is in good agreement with that usually found for OSET reactions. Intramolecular electron-transfer reactions (entries 839, 843–845, and 848–850) are all characterized by large positive $\Delta V^\ddagger$ values. The value of +35 cm^3 mol^{-1} for the $Co(NH_3)_5OSO_2^+$ reaction was ascribed to the formation of Co(II) and a SO_3^- radical. Alternatively, the release of the trans ammine ligand or the breakup of the solvent cage surrounding the sulfite radical (see homolysis) could also account for this large value. The extreme value of +38 cm^3 mol^{-1} reported for the μ-pyrazine complex (entry 848) cannot be accounted for in terms of the sum of intrinsic and solvational volume changes. Hydrogen-bonding interactions were suggested to play a significant role in determining the magnitude of $\Delta V^\ddagger$.

G. Photochemical and Photophysical Processes

The reactions reported in the earlier sections originate from the electronic ground state of the molecule and occur at rates for which transition-state theory is applicable. In this section, we focus on the effect of pressure on chemical and physical processes that occur in the electronic excited state of a molecule. The overall photochemical process is the result of a sequence of events, some of which cannot be treated by transition-state theory. These events include initial electronic excitation, vibrational relaxation, internal conversion and intersystem crossing, reactive, radiative, and nonradiative deactivation, and further reactions of transient intermediates to the final products.[354] It follows that any of these events can be influenced by pressure, and mechanistic information on such events can only be obtained when the excited-state or transient species has a sufficient lifetime to be vibrationally relaxed with

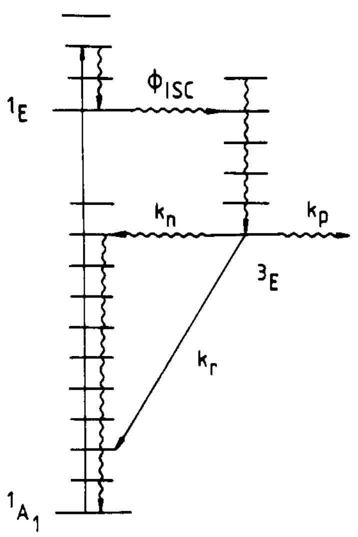


Figure 24. Jablonski diagram for the ligand field photolysis of Rh(III) ammine complexes.

respect to the medium.[25,26,354,355] Although the treatment and interpretation of such data are usually much more complicated than for thermally induced reactions, the obtained information may be unique since high-pressure studies are one of only a few methods available to obtain mechanistic information on excited-state processes.

The presentation of the data in Table I has been subdivided into photochemical and photophysical processes. To understand the effect of pressure on a photochemical reaction, it is of fundamental importance to have sufficient information on all the deactivation processes that affect the overall reaction. If we consider a sequence of events in which excitation of a single ground state is followed by internal conversion and intersystem crossing to the lowest excited triplet state, it can then be followed by the photoreaction (k_p), nonradiative (k_n), and radiative (k_r) deactivation. The Jablonski diagram for such a series of events is given in Figure 24. The photochemical quantum yield can then be expressed by (55), where τ is the lifetime of the

$$\phi_p = \phi_{ISC}k_p/(k_p + k_n + k_r) = \phi_{ISC}k_p\tau \qquad (55)$$

lowest excited triplet state. A similar expression can be written for the quantum yield for phosphorescence ϕ_r, and both these can be rewritten in the form given in (56). Thus, the pressure dependence of k_p (or k_r)

$$k_p = \phi_p/\phi_{ISC}\tau$$
$$k_r = \phi_r/\phi_{ISC}\tau \qquad (56)$$

can only be obtained when the pressure dependencies of ϕ_p (or ϕ_r), ϕ_{ISC}, and τ are known. In terms of volumes of activation, this results in (57). The nonradiative

$$\Delta V^*(k_p) = \Delta V^*(\phi_p) - \Delta V^*(\phi_{ISC}) - \Delta V^*(\tau)$$
$$\Delta V^*(k_r) = \Delta V^*(\phi_r) - \Delta V^*(\phi_{ISC}) - \Delta V^*(\tau) \qquad (57)$$

deactivation rate constant k_n (and its pressure dependence) can be calculated from eq 58. Equations 56 and

$$k_n = \tau^{-1} - k_p - k_r \qquad (58)$$

58 clearly demonstrate the type of measurements that must be performed in order to obtain the effect of pressure on a single rate constant (k_p, k_n, or k_r) from which mechanistic conclusions are to be drawn in a similar way as reported in the earlier sections. Another complication originates from the fact that partial molar volumes of short-lived excited states cannot be as readily determined as those for ground-state species; they must be obtained in indirect ways. Despite these difficulties, the growing use of pressure effects in the study of photochemical and photophysical properties[25,26,354,355] has provided valuable new insight into the mechanisms of excited-state processes.

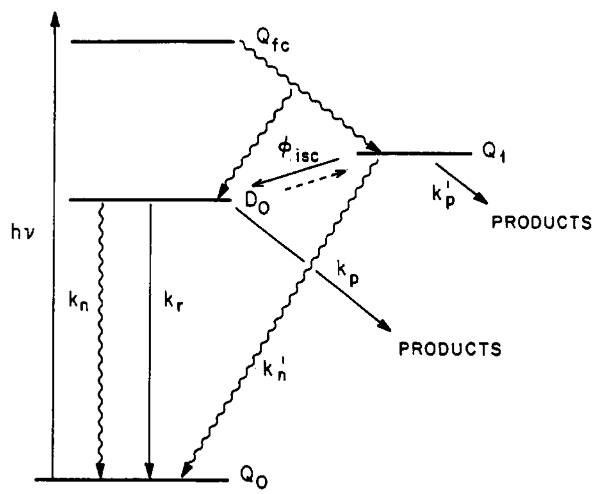
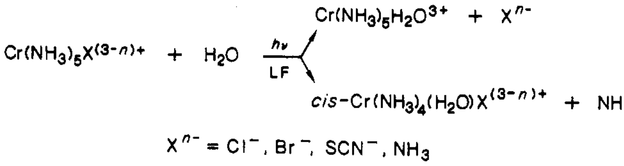


Figure 25. A simplified state diagram for the photoreactions of Cr(III) complexes: Q_{fc} is the Franck–Condon quartet state formed by vertical excitation; Q_1 and D_0 are the thermally equilibrated quartet and doublet excited states.[354]

Substitution Reactions

Entries 854–899 represent the photoinduced substitution reactions studied over the past decade. The first quantitative studies of pressure effects on such reactions were reported for a series of Cr(III) complexes, for which the two ligand-exchange processes are thought to occur via different electronic excited states. The



$$Cr(NH_3)_5X^{(3-n)+} + H_2O \xrightarrow[LF]{h\nu} \begin{cases} Cr(NH_3)_5H_2O^{3+} + X^{n-} \\ cis\text{-}Cr(NH_3)_4(H_2O)X^{(3-n)+} + NH_3 \end{cases}$$

$$X^{n-} = Cl^-, Br^-, SCN^-, NH_3$$

pressure dependence of ϕ_p resulted in significantly negative apparent ΔV^* values, viz., an average value of -6 cm^3 mol^{-1} for aquation of NH$_3$ and of -10 to -13 cm^3 mol^{-1} for aquation of X^{n-}. Since little was known about the pressure dependence of the other deactivation processes, it was assumed that these apparent values represent those for the primary photoreactions. Accordingly, the data were interpreted in terms of an associative (most probably I_a) substitution process. The more negative values found for the aquation of X^{n-} as compared to NH$_3$ can be ascribed to solvational contributions originating from charge creation (i.e., electrostriction) in the transition state. A recent detailed reanalysis of the data[26] also supports the associative nature of the substitution process. However, it must be kept in mind that the doublet emission lifetimes of Cr(III) ammine complexes exhibit nonnegligible pressure dependencies (entries 930–939), which could affect the above given interpretation. Furthermore, the complex state diagram suggested for the photoreactions of Cr(III) complexes (Figure 25) offers a series of possible

TABLE IV. $\Delta V^‡$ from Photochemical and Photophysical Measurements for the Solvolysis Reactions of Rh(III) Ammine Complexes[355]

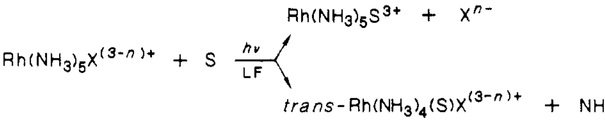
solvent	complex	photosolvolysis product	$\Delta V^‡(\phi_p)$	$\Delta V^‡(\tau^{-1})$	$\Delta V^‡(k_p)$
H_2O	$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5(H_2O)^{3+}$	−5.2 ± 0.4	(−3.4)[a]	−8.6 ± 1.6
		trans-$Rh(NH_3)_4(H_2O)Cl^{2+}$	+12.7 ± 1.2		+9.3 ± 1.9
D_2O	$Rh(ND_3)_5Cl^{2+}$	$Rh(ND_3)_5(D_2O)^{3+}$	−4.2 ± 0.5	−3.5 ± 1.1	−7.7 ± 1.6
		trans-$Rh(ND_3)_4(D_2O)Cl^{2+}$	+9.5 ± 1.6		+6.0 ± 2.2
H_2O	$Rh(NH_3)_5Br^{2+}$	$Rh(NH_3)_5(H_2O)^{3+}$	−10.3 ± 1.2	(+3.5)[a]	−6.8 ± 1.6
		trans-$Rh(NH_3)_4(H_2O)Br^{2+}$	+4.6 ± 0.6		+8.1 ± 1.2
D_2O	$Rh(ND_3)_5Br^{2+}$	$Rh(ND_3)_5(D_2O)^{3+}$	−9.4 ± 1.5	+4.1 ± 0.6	−5.3 ± 1.8
		trans-$Rh(ND_3)_4(D_2O)Br^{2+}$	+3.4 ± 0.5		+7.5 ± 1.1
H_2O	*trans*-$Rh(NH_3)_4Cl_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Cl^{2+}$	+2.5 ± 0.5	*b*	+2.8 ± 0.6
H_2O	*trans*-$Rh(NH_3)_4Br_2^+$	*trans*-$Rh(NH_3)_4(H_2O)Br^{2+}$	+3.4 ± 0.7	*b*	+2.9 ± 0.7
H_2O	$Rh(NH_3)_6^{3+}$	$Rh(NH_3)_5(H_2O)^{3+}$	+3.7 ± 0.5	*b*	+3.9 ± 0.5
H_2O	$Rh(NH_3)_5I^{2+}$	*trans*-$Rh(NH_3)_4(H_2O)I^{2+}$	+0.3 ± 0.1	*b*	+1.4 ± 0.9
H_2O	$Rh(NH_3)_5SO_4^+$	$Rh(NH_3)_5(H_2O)^{3+}$	−2.7 ± 0.4	*b*	−3.9 ± 0.6
FMA	$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5(FMA)^{3+}$	−4.6 ± 0.7	−0.3 ± 0.4	−4.9 ± 1.1
		trans-$Rh(NH_3)_4(FMA)Cl^{2+}$	+4.2 ± 0.9		+3.9 ± 1.3
DMF	$Rh(NH_3)_5Cl^{2+}$	*trans*-$Rh(NH_3)_4(DMF)Cl^{2+}$	+6.3 ± 0.9	+1.3 ± 0.2	+7.6 ± 1.1
DMSO	$Rh(NH_3)_5Cl^{2+}$	$Rh(NH_3)_5(DMSO)^{3+}$	−7.8 ± 1.8	−1 ± 1	−8.9 ± 2.7
		trans-$Rh(NH_3)_4(DMSO)Cl^{2+}$	+4.4 ± 0.9		+3.3 ± 1.8

[a] Assumed value. [b] Not measured. Data in $cm^3\ mol^{-1}$.

reaction routes that can account for the spectrum of photochemical effects reported in the literature.[354]

The positive value of $\Delta V^‡$ reported for the photoaquation of $Cr(bpy)_3^{3+}$ (entry 860) was interpreted in terms of possible mechanisms for the formation of $Cr(bpy)_3(H_2O)^{3+}$, in which coordination of the "pocket" water molecules appears to be most likely. All in all, the interpretation of the data for Cr(III) ammine complexes is limited by the fact that pressure effects have been determined for ϕ_p and τ, but not for two other key excited-state processes, viz., intersystem crossing efficiency and the yield of the "prompt" reaction from the quartet state.[354]

Significantly more progress has been made in the study of photosolvolysis reactions of Rh(III) amine complexes (entries 879–899). For complexes of the type $Rh(NH_3)_5X^{(3-n)+}$, the photosolvolysis reactions can be summarized by (59), where S = solvent. These reactions are generally accepted to follow the sequence of steps outlined in Figure 24 (see literature cited in ref 47). Since $\phi_{ISC} = 1$ for these reactions, eq 56 simplifies to $k_p = \phi_p/\tau$, which means that $\Delta V^‡(k_p)$ can be determined from $\Delta V^‡(\phi_p) - \Delta V^‡(\tau)$. It was generally found that the two photosolvolysis reactions in (59) exhibit opposite pressure effects; a typical example for the photoaquation of $Rh(NH_3)_5Cl^{2+}$ is given in Figure 26. Similarly, the pressure dependence of the excited-state lifetime, measured by using pulsed laser techniques, also exhibits different trends depending on the major photochemical reaction observed (see entries 1005–1009). Combining these data results in the $\Delta V^‡(k_p)$ values summarized in Table IV, from which it follows that the primary photochemical reactions exhibit the same pressure dependencies as ϕ_p. Throughout the series of complexes, solvolysis of NH_3 is accompanied by a positive $\Delta V^‡(k_p)$ value, whereas the solvolysis of X^{n-} exhibits negative values. Both these values can be interpreted in a qualitative way in terms of a D mechanism. The substantial difference in $\Delta V^‡(k_p)$ for the halide and ammine labilizations can be ascribed to a negative contribution from $\Delta V^‡_{solv}$ due to charge creation when the halide dissociates from the dipositive complex to form a tripositive cation and X^-. No appreciable charge creation is expected for the dissociation of NH_3. This difference also shows up in the overall $\Delta \bar{V}$ for the ground-state process of +3.9 and −17.8 $cm^3\ mol^{-1}$, respectively, in the case of the $Rh(NH_3)_5Cl^{2+}$ complex,[47] demonstrating the important contribution of charge creation when the leaving group is anionic. A volume profile for this system is given in Figure 27, in which it is assumed that the ligand field excited triplet state has a partial molar volume of ca. 10 $cm^3\ mol^{-1}$ larger than the ground-state molecule based on an expected increase in bond length of 0.1 Å.[356,357] According to this profile it is quite possible that the excess volume of the excited state is focused along the axis of the bond-cleavage process to produce a "ground-state-like" five-coordinate intermediate. The other data in Table IV can be interpreted in a similar way. It is interesting to note that the complexes showing larger $\Delta V^‡(k_p)$ values are those undergoing the excited-state reaction with slower rates, i.e., with lower ϕ_p. This can probably be attributed to the later transition states of the slower reactions. Photoaquation of *cis*-$Rh(bpy)_2Cl_2^+$ exhibits a much more negative $\Delta V^‡(k_p)$ value (entry 896) compared to the values reported



$$Rh(NH_3)_5X^{(3-n)+} + S \xrightarrow[LF]{h\nu} \begin{cases} Rh(NH_3)_5S^{3+} + X^{n-} \\ trans\text{-}Rh(NH_3)_4(S)X^{(3-n)+} + NH_3 \end{cases} \quad (59)$$

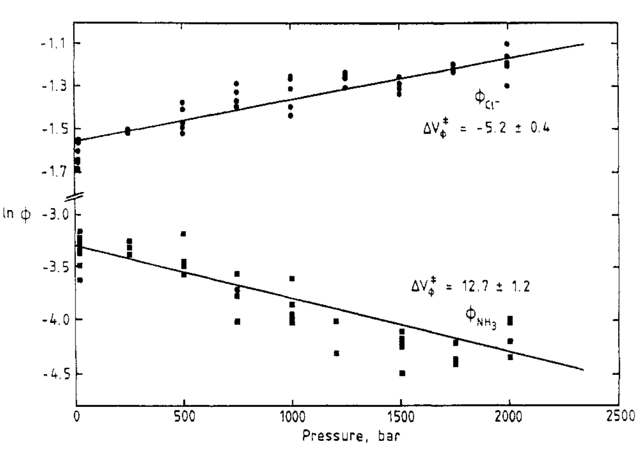
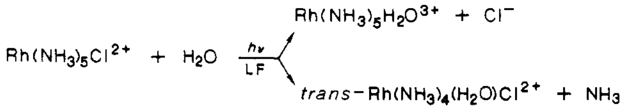


Figure 26. Pressure dependence of the reaction[355]



$$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow[LF]{h\nu} \begin{cases} Rh(NH_3)_5H_2O^{3+} + Cl^- \\ trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + NH_3 \end{cases}$$

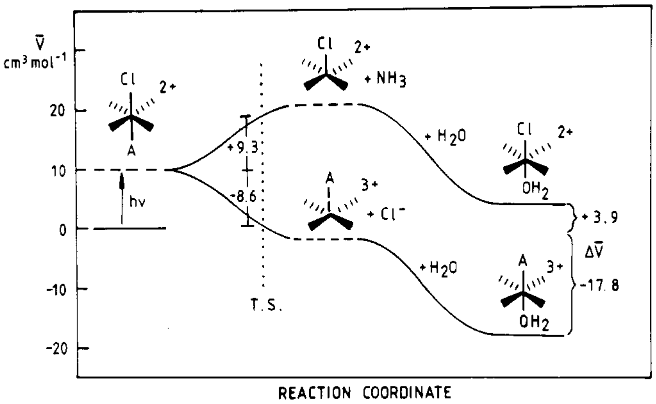


Figure 27. Volume profile for the reaction[25]

$$Rh(NH_3)_5Cl^{2+} + H_2O \xrightarrow[LF]{h\nu} \begin{cases} trans\text{-}Rh(NH_3)_4(H_2O)Cl^{2+} + NH_3 \\ Rh(NH_3)_5H_2O^{3+} + Cl^- \end{cases}$$

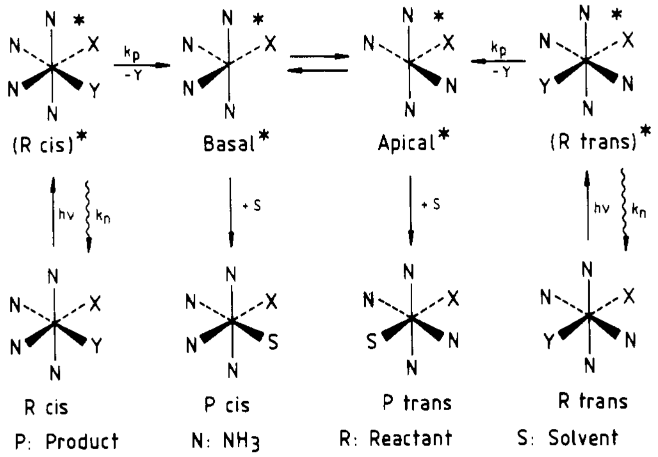


Figure 28. General scheme for the photochemical cis/trans isomerization of Rh(III) amine complexes.[312]

for the dichloro and dibromo ammine complexes (entries 898 and 899). This could signify the operation of an A mechanism involving the "pocket" water molecules as suggested for the $Cr(bpy)_3^{3+}$ complex.

A few data sets have also been reported for the photosolvolysis of other metal complexes. Aquation of $Fe(CN)_6^{4-}$ (entry 864) exhibits significantly positive $\Delta V^\ddagger$ values, which are in the light of the other reported data in good agreement with a D mechanism. The thermal back reaction exhibits a $\Delta V^\ddagger$ value of +13.5 cm^3 mol^{-1}, which underlines the dissociative nature of that process. The data for the Co(III) complexes can be interpreted in a similar way. Charge creation during release of Br^- can account for the slightly negative $\Delta V^\ddagger$ value (entry 865). The photosolvolysis reactions of the series of Ru(II) complexes all exhibit positive $\Delta V^\ddagger$, once again supporting a D mechanism.

Isomerization Reactions

A number of photoisomerization reactions have been studied as a function of pressure (entries 900–905). On ligand field excitation of the Rh(III) ammine complexes, dissociation of a ligand occurs prior to rearrangement, as indicated in Figure 28. The values of $\Delta V^\ddagger(k_p)$ are such that they do not provide a definitive description of the mechanism, but support the dissociative (I_d or D) nature of the process when a general mechanism is operable. The linkage isomerization of $Co(en)_2(SO_2CH_2CH_2NH_2)^{2+}$ (entry 900) proceeds via charge-transfer (CT) excitation and exhibits a clearly positive $\Delta V^\ddagger(k_p)$ value, compared to that of −9.0 ± 0.7 cm^3 mol^{-1} for the thermal back reaction. Both these values are interpreted in terms of ring-opening reactions, which can be visualized as homolysis for the ring opening of the CT state and dissociation accompanied by significant charge creation for the thermal process. A volume profile for the overall process was constructed on the assumption that the partial molar volume of the CT state is very close to that of the ground state (see Figure 29). The volume profile shows a difference of at least 13 cm^3 mol^{-1} between the two transition states, which is due to the increase in electrostriction and the smaller volume of the Co(III) ring-opened species.

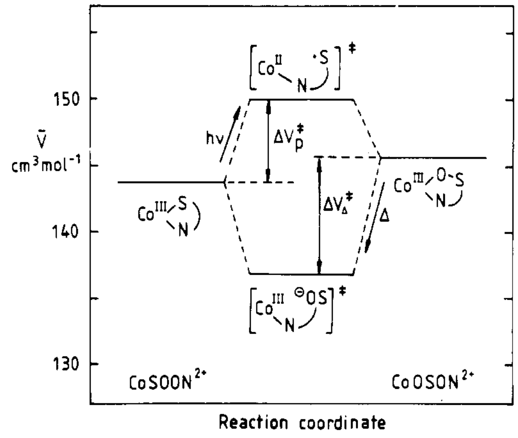


Figure 29. Volume profile for the system[268]

$$(en)_2Co(SOON)^{2+} \underset{\Delta}{\overset{h\nu,\ CT}{\rightleftharpoons}} (en)_2Co(OSON)^{2+}$$

Electron-Transfer Reactions

Charge-transfer excitation can in principle lead to the formation of redox products. Photooxidation of $Fe(CN)_5NO^{2-}$ (entries 906–912) has been studied by numerous investigators, and oxidation of Fe(II) accompanied by solvation of the NO ligand was reported to be the major reaction mode in aqueous and nonaqueous solvents. In these studies (see literature cited in ref 313), arguments were presented in favor of associative and dissociative reaction modes. The process is significantly affected by the properties of the solvent and the viscosity of the medium. The clearly positive values of $\Delta V^\ddagger(k_p)$ are in line with a dissociative mechanism in which a cage recombination step accounts for the observed medium effects. The formation of a caged radical pair $Co^{II}(Br^\bullet)$ from the LMCT state was suggested to account for the pressure dependence of the CT photolysis of $Co(NH_3)_5Br^{2+}$ (entry 913). Several data were reported for electronic and electron-transfer quenching of the long-lived MLCT excited state of $Ru(bpy)_3^{2+}$ (entries 916–927). Some quenchers exhibit remarkably large $\Delta V^\ddagger$ values, although there does not appear to be a satisfactory explanation for these observations at present. The reductive elimination reaction of *trans*-$Pt(CN)_4(N_3)_2^{2-}$ exhibits significantly positive volumes of activation, which are in agreement with the dissociative nature of the decay of the LMCT state to produce Pt(III) and N_3 radicals. Dissociation of the caged radical pair is expected to exhibit large solvent-dependent pressure effects (entries 928 and 929).

Photophysical Processes

The remainder of the data in Table I concern the pressure dependence of photophysical processes, viz., radiative deactivation, nonradiative deactivation, and electronic transitions. Information on these processes is usually obtained in an indirect manner by measuring the pressure dependence of the excited-state lifetime (τ) and combining this with quantum yields and spectral data as a function of pressure. For most of the studied systems, radiative deactivation (k_r) is only a minor component of the overall mechanism. Nevertheless, this property is an important probe for the dynamics of the excited state since it enables the measurement of τ even when the emission is weak since it can usually be determined very accurately. Entries 930–1017 present the data in terms of the pressure dependence, i.e., the volume of activation, of the lifetime of the excited state expressed as τ^{-1} (i.e., the sum of all the deactivation rate constants). Information on the pressure dependence of the nonradiative deactivation process (in terms of k_n) is given in entries 1018–1029.

The emission lifetimes of $Cr(bpy)_3^{3+}$, $Cr(en)_3^{3+}$, and related compounds exhibit relatively small pressure dependencies, the largest effect being found for $Cr(NH_3)_5NCS^{2+}$. The latter value is such that it must be taken into account in the interpretation of $\Delta V^‡(\phi_p)$. Low-spin/high-spin transitions and equilibria of Fe(II) complexes exhibit very significant $\Delta V^‡$ and $\Delta\bar{V}$ values (entries 940–955). The high-spin complex has a partial molar volume of up to 14 cm^3 mol^{-1} larger than the low-spin configuration, depending on the nature of the solvent. Values of $\Delta V^‡$ are throughout positive for the low-spin/high-spin conversion and negative for the reverse process, indicating that the transition state must be between the two spin states on a volume basis. The $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes exhibit remarkably temperature-dependent $\Delta V^‡(\tau^{-1})$ values. These complexes show little or no unimolecular photochemistry and the emission quantum yield is small, so that the dominant deactivation process is nonradiative. The temperature dependence was explained in terms of two competing deactivation processes, one involving slow deactivation from the MLCT state, and the second via a thermally activated LF state from which nonradiative deactivation is extremely rapid. Such a mechanism is presented schematically in Figure 30. From the available data is was possible to calculate $\Delta V^‡(k_n)$ for the CT → GS and CT → LF transitions (entries 976–984 and 998–1004), from which it follows that the ca. 10 cm^3 mol^{-1} more positive value for the deactivation via the LF state originates from the larger partial molar volume of this state.

The lifetimes of the lowest excited state of the Rh(III) ammine complexes (entries 1005–1009) show small pressure dependencies. Combination of these data with $\Delta V^‡(\phi_p)$ results in $\Delta V^‡(k_n)$ (see entries 1025–1029). Remarkable is the observation that both $\Delta V^‡(\tau^{-1})$ and $\Delta V^‡(k_n)$ parallel the $\Delta V^‡(\phi_p)$ values found for the major photochemical process; this correlation is presented quantitatively in Figure 31. It follows that nonradiative deactivation exhibits the same mechanistic properties as the photochemical process, which points at the so-called "strong coupling" of k_p and k_n.

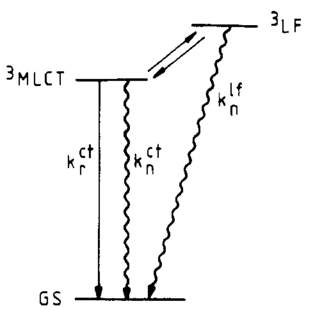


Figure 30. Model describing the proposed mechanism for decay of the MLCT state of $Ru(bpy)_3^{3+}$ and related complexes.[354]

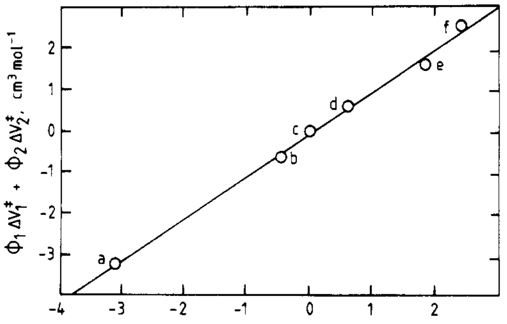


Figure 31. Plot of $\phi_1\Delta V^‡_1 + \phi_2\Delta V^‡_2$ vs $\Delta V^‡(k_n)$ for the photosolvolysis of $Rh(NH_3)_5Cl^{2+}$ and $Rh(NH_3)_5Br^{2+}$ in various solvents.[25] Cl: (a) D_2O; (b) formamide; (c) DMSO; (d) DMF. Br: (e) H_2O; (f) D_2O.

The emission spectra and lifetimes of the Ir(III) complexes (entries 1016 and 1017) exhibit characteristic pressure dependencies, from which it was concluded that the MLCT and LF states have a volume difference of ca. 4 cm^3 mol^{-1}. Finally, the $\Delta V^‡$ data reported for the nonradiative deactivation of a series of Ni(II) complexes (entries 1019–1024) are all significantly negative. The lowest excited state is tetrahedral for these complexes; it has a larger partial molar volume than the more tightly solvated square-planar ground state. It follows that the transition state for the nonradiative decay resembles the ground state in geometry.

We conclude from the discussion in this section by stating the expectation that pressure effects can be used to study the dynamics of excited-state species and that they will contribute to the mechanistic understanding of photoreactions. It is not surprising that in some cases such effects have introduced ambiguities into the existing understanding of the systems, and alternative possibilities must be considered. Naturally it should be kept in mind that $\Delta V^‡$ data alone cannot provide a definite description of an excited-state mechanism. Some of the difficulties lie in the unknown partial molar volume of excited-state species and the separation of intrinsic and solvational contributions toward $\Delta V^‡$.

H. Bioinorganic Reactions

A number of reviews have been published on the effect of pressure on biophysical and biochemical processes.[4,358–365] In this section we will review the work performed on bioinorganic systems, with the emphasis on those where a chemical reaction or process occurs.

It is a well-known fact that the structure and dynamic properties of biochemical systems can be modified by pressure. In general, oligomeric proteins tend to dissociate under pressure.[360] Relevant for this review are the heme proteins, since covalent bonds are formed and broken during the reaction of ligand binding. In addition, the electronic configuration of the central ion atom plays an important role in spin equilibrations and redox reactions. All the mentioned processes should exhibit characteristic pressure dependencies that can once again be expressed in terms of the thermodynamic and kinetic volume parameters, viz., $\Delta \bar{V}$ and $\Delta V^{\ddagger}$, respectively.

Pressure Effects on Proteins

The quaternary structure of many proteins is very sensitive to pressure.[362-365] In general, the volume of a protein consists of three contributions arising from the constitutive volume of the atoms, the void volume that is due to imperfect packing of the atoms, and the decrease in volume due to the hydration of the peptide bonds and the amino acid residues. The partial specific volume of a protein can be calculated from the constitutive atomic volumes, which indicates that the last two contributions are small or partially cancel each other. The compressibility of a globular protein is smaller than that usually observed for liquids and solid polymers, but larger than those of metals and covalent solids. This has been interpreted in terms of the solid-like interior of a protein. In addition, pressure can induce protein denaturation, which is accompanied by a small volume change usually less than 1% of the protein volume (ranging between 1×10^4 and 2×10^4 cm^3 mol^{-1}). Pressure may also induce localized conformational changes, and these will be discussed separately. In many cases, pressure disrupts protein–protein interaction, and this is then accompanied by large reaction volumes;[364,365] for instance, $\Delta \bar{V}$ for the ribosome subunit interaction is 250 cm^3 mol^{-1}.[366] The main effects in the pressure range up to 2 kbar are to be expected on small localized conformational changes in proteins and protein–protein interactions.[358]

Iron Spin Equilibria

Changes in the spin state of iron centers in biological molecules have in general been suggested to account for specific binding properties of such molecular units.[358,361] In principle, such spin changes should be accompanied by significant volume changes, and so have stimulated the application of high-pressure techniques. For instance, the Fe(II) center in deoxyhemoglobin is in the high-spin state (designated as tense), whereas in oxyhemoglobin it is in the low-spin state (designated as relaxed). In the Fe(III) derivatives of these compounds (methemoglobin), the high-spin and low-spin states may be in a true thermal equilibrium under certain conditions.[358]

Measurements on model systems indicate that the spin-state change of Ni(II) complexes from high spin to low spin during an increase in coordination number from 4 to 6 is accompanied by a volume decrease (entries 484–495). A series of Fe(II) complexes (entries 940–955) exhibits a significant increase in volume for the low-spin/high-spin transition. Similar effects are therefore expected to show up in the spin equilibria of heme proteins. Reaction 60 was studied by several

$$\text{metmyoglobin-L (HS)} \rightleftharpoons \text{metmyoglobin-L (LS)} \quad (60)$$

groups for sperm whale metmyoglobin and L = H_2O, OH^-, N_3^-, imidazole, and CN^-. Values of $\Delta \bar{V}$ for L = N_3^- are −12.5,[367] −15,[368] and −9 cm^3 mol^{-1}.[369] Other values reported are[369] −3 (L = H_2O), −5 (L = OH^-), and −12 (L = imidazole) cm^3 mol^{-1}. These values correlate with the general trend observed in the entropy changes and are attributable to stereochemical changes of the protein during the spin change. Experimental evidence also suggests that core compression of the porphyrin ring occurs during the spin change as written in (60).[370] A reaction volume of −7 cm^3 mol^{-1} was found for human metmyoglobin.[371] Similar results were reported for the spin change on methemoglobin, viz., −13.3 cm^3 mol^{-1} for carp methemoglobin with L = N_3^-.[367]

TABLE V. Activation and Reaction Volumes (in cm^3 mol^{-1}) for the Binding of Ligands to Heme Proteins

reaction	$\Delta V^{\ddagger}$	$\Delta \bar{V}$	ref
heme + CO	+2.0		375
sperm whale myoglobin + O_2	+7.8	−2.9	376
sperm whale myoglobin + CO	−8.9		376
bovine hemoglobin + O_2	+5.2		376
bovine hemoglobin + CO (fast)	−0.9		376
bovine hemoglobin + CO (slow)	−22.1		376
sperm whale metmyoglobin + N_3^-	+4	−9.6	369, 377
sperm whale metmyoglobin + F^-		−3.3	377
sperm whale metmyoglobin + $HCOO^-$		+7.5	377
sperm whale metmyoglobin + imidazole	+8	0	369, 377
sperm whale metmyoglobin + OH^-		+11.0	377
horse metmyoglobin + N_3^-	+11	−5	369
horse metmyoglobin + imidazole	+14	+10	369

A number of studies have been done on spin equilibria of other heme proteins. In ferric cytochrome P-450, the low-spin to high-spin transition is accompanied by a volume increase of 16–75 cm^3 mol^{-1}, depending on the conditions employed.[372] The range of values strongly depends on the pH and reduces to between 35 and 75 cm^3 mol^{-1} for neutral pH. The activation volume for the high-spin to low-spin conversion is close to zero. It was recently shown that the large increase in volume is partly due to the dissociation of the camphor substrate from the active site.[373] A value of 8 cm^3 mol^{-1} was reported for the reaction volume of the LS/HS equilibrium of cytochrome oxidase.[374]

Ligand Binding

The binding of oxygen and other ligands to heme proteins and model systems has been studied also, in view of the physiological functions of such proteins. A summary of the available data is given in Table V. The value reported for the binding of CO to heme iron was interpreted in terms of an I_d mechanism.[375] In glycerol, $\Delta V^{\ddagger}$ increases to 14 cm^3 mol^{-1}, which points at a diffusion-controlled process. Surprising is the large difference for the binding of CO and O_2 to myoglobin, and no simple interpretation can be offered.[376] Similar differences were observed for the reactions of hemoglobin. The biphasic nature of the reaction with CO is attributed to the various quaternary conformations. The data for the metmyoglobin reactions should be interpreted in terms of ligand substitution during which H_2O is the leaving group. This is not the case for the

TABLE VI. Activation and Reaction Volumes (in cm^3 mol^{-1}) for the Redox Reactions of Horse Heart Cytochrome *c*[350]

reaction	$\Delta V^{\ddagger}$ exptl	$\Delta V^{\ddagger}$ theor	$\Delta \bar{V}$
Cyt-Fe(III) + $Fe(CN)_6^{4-}$	+13	+17	+37
Cyt-Fe(II) + $Co(phen)_3^{2+}$	+8.5	+5.1	+20
Cyt-Fe(III) + ascorbate^{2-}	−11	−1	+6.5

earlier data in Table V, since there is no sixth ligand present prior to the binding of CO and O_2. The interpretation of such data is further complicated by the fact that ligand binding or substitution is usually accompanied by a change in spin state. A complete account of the various arguments for the interpretation of the data is given elsewhere.[358] Important in determining the sign and magnitude of $\Delta V^{\ddagger}$ seems to be the subtle role of the amino side chains packed around the heme.

During the binding of ligands to cytochrome *c*, the Fe–S bond is broken and iron remains in the low-spin state. $\Delta V^{\ddagger}$ for the binding of imidazole and N_3^- to horse heart cytochrome *c* is +20 cm^3 mol^{-1} compared to $\Delta \bar{V}$ values of +7 and −13 cm^3 mol^{-1}, respectively. The positive $\Delta V^{\ddagger}$ is interpreted in terms of the breakage of the Fe–S bond prior to binding of the ligand.[358] Binding of HCN to horseradish peroxidase Fe(III) exhibits a $\Delta V^{\ddagger}$ of +1.7 cm^3 mol^{-1}, and compensation effects for the ionization of the substrate and transfer of the proton are discussed to account for this small pressure effect.[378] In contrast, recombination of CO with the reduced enzyme following photodissociation is characterized by a $\Delta V^{\ddagger}$ of −16 cm^3 mol^{-1}, which is in good agreement with the reaction of CO with myoglobin.[379] The binding of cyanide to chloroperoxidase exhibits $\Delta V^{\ddagger}$ and $\Delta \bar{V}$ values of −2.5 and −17 cm^3 mol^{-1}, respectively.[380] The volume profile is largely determined by the spin transition in this case.

Redox Reactions of Heme Proteins

Heremans and co-workers[50,381] have studied the pressure dependence of a series of OSET reactions. Their results are summarized in Table VI. They clearly demonstrate that the trend in $\Delta V^{\ddagger}$ parallels that in $\Delta \bar{V}$, from which the important conclusion is reached that $\Delta V^{\ddagger}$ for electron-transfer processes can only be interpreted more meaningfully when the reaction volume is known. The theoretically predicted $\Delta V^{\ddagger}$ values are remarkably close to the experimental values for the first two entries. The positive sign of these values is in agreement with that for related inorganic systems in Table I. The data for the reduction by ascorbate is more difficult to interpret due to the interference of a deprotonation equilibrium.

Redox reactions of horseradish peroxidase (HRP) can be summarized as in (61), where R* represents a free

$$\mathrm{HRP\ (Fe^{III})} + H_2O_2 \rightleftharpoons \mathrm{compound\ I\ (Fe^{IV} + R^*)} + H_2O$$

$$\mathrm{compound\ I} + \mathrm{A} \rightleftharpoons \mathrm{compound\ II\ (Fe^{IV})} + \mathrm{A^+}$$

$$\mathrm{compound\ II\ (Fe^{IV})} + \mathrm{A} \rightleftharpoons \mathrm{HRP\ (Fe^{III})} + \mathrm{A^+} \qquad (61)$$

radical species and A a reducing agent. The formation of compound I exhibits a $\Delta V^{\ddagger}$ of −1.5 cm^3 mol^{-1},[378] compared to a series of positive and negative values for the reaction of compound II with several reductants.[382] The value of +6.7 cm^3 mol^{-1} for the reaction with $Fe(CN)_6^{4-}$ is in close agreement with that reported in Table VI and is probably determined by the same factors as the reaction volume. Balny et al.[58] reported a two-phase behavior for the reaction of cytochrome *c* peroxidase with EtOH; the fast reaction with $\Delta V^{\ddagger}$ = +9 cm^3 mol^{-1} is ascribed to the formation of compound I, and the slow reaction with $\Delta V^{\ddagger}$ = +14 cm^3 mol^{-1} is attributed to the change in spin state of the protein. In a recent study,[383] the fast reaction was studied in more detail. $\Delta V^{\ddagger}$ values ranging from +3 to +15 cm^3 mol^{-1} were found for the reaction in H_2O, and values of +18 to +30 cm^3 mol^{-1} were found for the reaction in 60% DMSO, depending on the temperature employed. The largest $\Delta V^{\ddagger}$ of +30 cm^3 mol^{-1} at −23 °C could be split into a reaction volume of +11 cm^3 mol^{-1} for the formation of the precursor complex and an activation volume of +19 cm^3 mol^{-1} for the rate-determining step. Such large values suggest extensive structural rearrangements that need not be limited to the neighborhood of the heme alone.

3. Activation Volumes of Organic Reactions

A. General Remarks

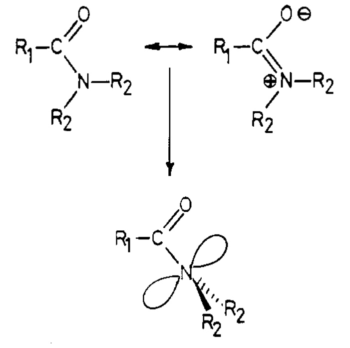
As in the previous section, the references in the three main Tables VII–IX are numbered consecutively, followed by further numbers in the text. Investigators in inorganic laboratories have in many instances measured both activation and reaction volumes of the same reactions, so that it made sense to tabulate them in side-by-side columns. In the present section, this correlation is often not available, and hence reaction volumes (of all types) have been grouped separately as section 5.

B. The Data in Tabular Form

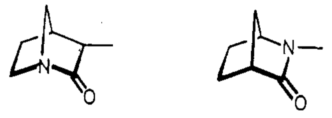
Activation volumes for reactions of organic compounds are listed in Table VII.

C. Bond Rotations (Entries 1–295)

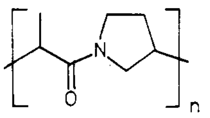
A large number of data have been reported concerning the C–N bond rotation in amides; especially Lüdemann and his co-workers deserve credit for this. The activation volumes are invariably positive: the coalescence temperatures are raised by increasing the pressure. $\Delta V^{\ddagger}_0$ varies between about +2 and +10 cm^3 mol^{-1}. Two possible reasons for this effect have been advanced. Lüdemann himself favors the opinion[65] that the molecule needs some open space if it is going to carry out a rotation; in other words, such a motion cannot be totally coordinated with surrounding molecules such as would be necessary to avoid expansion. We have noted[1] that the perpendicular transition state has a reduced dipole moment since the zwitterionic structure no longer can make a contribution, and a less dipolar structure will allow nearby molecules greater freedom to expand ("electrorelaxation", as opposed to "electrostriction"). It has not been possible ro reach



a clear conclusion in this matter. It should in principle be possible to make a direct comparison of the partial volumes of the two states, planar and perpendicular, by comparing isomeric bicyclic amides with the nitrogen atom either adjacent to or at the bridgehead atom position, respectively, as in



Unfortunately, the former type of compound is represented by only very few examples,[720] exactly because the absence of resonance makes it very unstable, for example, to polyamide formation, which generates planar amido functions:



The absence of any measurable pressure effect on the rotation rate of the C–CO bond in α-naphthoic acid amides would seem to support the argument that no great volume changes occur if the rotation is not accompanied by a large change in dipole (entries 116–119). On the other hand, however, Lüdemann's argument has gained strength from studies of the pressure effect on conformational equilibrium (entries 120–128 and part 5A). It has been found that pressure tends to favor the more crowded gauche forms and eclipsed conformations; by analogy, in the amides it should disfavor the perpendicular transition states. But the conformational cases show volume changes that tend to be smaller than the activation volumes seen in amide rotations, and at present our opinion is that both effects play roles that can probably not be quantitatively dissected in the near future.

A large number of data have been accumulated for the *Z–E* isomerization rates of azo compounds, and these data, too, have generated some controversy. It is generally believed[398] that the reaction of symmetrical azobenzenes proceeds via an inversion mechanism in which one of the nitrogen atoms becomes sp hybridized. The polarity should remain essentially unchanged during activation, and the pressure effect should be small, as is observed. As has been stated,[721] the polarity must decrease slightly, but $\Delta V^{\ddagger}$ is found to be negative; only the azobenzene capped crown ether has a positive value. This probably reflects the expansion of the crown ether cavity during activation.

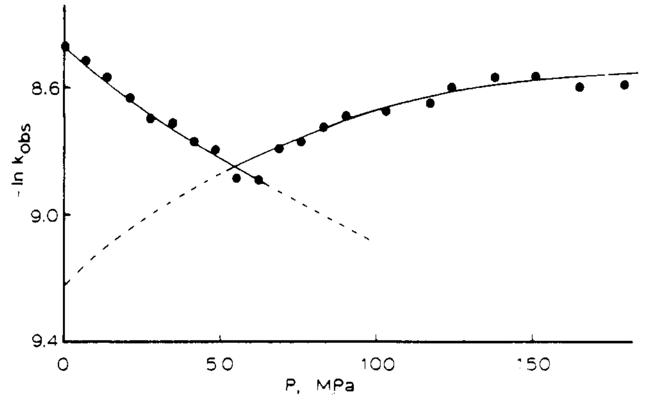


Figure 32. Effect of pressure on the rate of displacement of a pyridine by piperidine from the *p*-methoxybenzyl derivative.

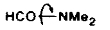
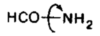
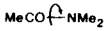
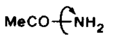
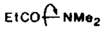
A more serious disagreement concerns the 4-donor-4′-acceptor substituted azobenzenes such as 4-(dimethylamino)-4′-nitroazobenzene. In that case, pressure enhances the reaction only slightly in some solvents such as hexane, but much more strongly in others such as benzene and *p*-dioxane; the rate constants at ambient pressure are also faster in such solvents. One of us[397] has interpreted these findings as indications of the onset of the rotational mechanism in which the N=N π bond breaks to form an essentially zwitterionic transition state. This view is supported by an unusual temperature dependence of the activation volume and by curved Arrhenius plots.[399,403] On the other hand, Nishimura[402] has interpreted the results by assuming an inversion transition state alone, but with a variable polarity, and supported this view with the allegation that the reaction volume was even more negative than the activation volume (in other words, that the latter simply foreshadowed the former). But the measurements do not inspire confidence. The dilatometric one is based on evidently unstated assumptions, and in any case, the results show unacceptably wide error limits; in the other, the pressure dependence of the photostationary state composition is equated to the equilibrium dependence.

This same compound has also been found to be a rare example of a maximum in an ln *k* vs *P* plot (Figure 32); this is observed when the solvent is triacetin. A *minimum* can be accommodated as a result of two competing mechanisms: a fast one that is retarded by pressure, and a slow one that is enhanced by it (section 3G). To date, a *maximum* has been observed in solution only in a *bimolecular* displacement reaction that was thought to become diffusion-limited at extreme pressure.[722] The incursion of a viscosity restriction of a *unimolecular* reaction in the slow-rate domain and at moderate pressures is bound to have important repercussions (see also section 3D).

The olefins studied by Sueishi[409] represent another interesting group. *Z–E* isomerization in this case might be expected to involve bond extension in the transition state. Indeed, small positive activation volumes and small solvent effects are found.

In entries 296–310, both the ring closures and openings are retarded by pressure. The large, positive value of $\Delta V^{\ddagger}$ for closure is clearly related to the neutralization of charge. The apparent fact that the ring opening of the carboxylic acid is also retarded by pressure is remarkable and deserves further study.[411]

TABLE VII. Activation Volumes for Reactions of Organic Compounds

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
1	 HCO–NMe$_2$	*al*	127	2.0	5	+9.6	384	
2		*bl*	121–128^{cl}	1.5	4	+7.8	385	
3		80 vol % C_6D_6^{dl}	127–136^{cl}	1.5	4	+9.8	385	
4		*el*	125–134^{cl}	2.0	5	+9.4	385	
5		80 vol % CD_3CN^{dl}	124–131^{cl}	1.5	4	+9.1	385	
6		80 vol % CD_3OD^{dl}	138–146^{cl}	1.5	4	+9.6	385	
7		80 vol % D_2O^{dl}	149–153^{cl}	1.5	4	+6.0	385	
8		99 wt % D_2O^{dl}	137–152^{cl}			+1.6	65	
9		98.3 wt % D_2O^{dl}	137–152^{cl}			+2.0	65	
10		95.7 wt % D_2O^{dl}	137–152^{cl}			+3.0	65	
11		91.2 wt % D_2O^{dl}	137–152^{cl}			+6.4	65	
12		81.6 wt % D_2O^{dl}	137–152^{cl}			+7.1	65	
13		53.2 wt % D_2O^{dl}	137–152^{cl}			+8.3	65	
14		10.5 wt % D_2O^{dl}	137–152^{cl}			+8.4	65	
15	 HCO–NH$_2$	*fl*	37	1.5	4	+2.3	386	
16		*gl*	59	1.5	4	+3.0	387	
17		*gl*	66	1.5	4	+3.0	387	
18		*gl*	73	1.5	4	+3.5	387	
19		*gl*	79	1.5	4	+4.1	387	
20	 MeCO–NMe$_2$	*al*	77	2.0	5	+10.3	384	
21		neat	78–84^{cl}	1.5	4	+7.6	385	
22		*bl*	67–71^{cl}	1.5	4	+5.5	385	
23		80 vol % C_6D_6^{dl}	69–78^{cl}	1.5	4	+9.0	385	
24		*el*	74–83^{cl}	2.0	5	+10.0	385	
25		80 vol % $(CD_3)_2SO$^{dl}	82–87^{cl}	1.5	4	+6.8	385	
26		80 vol % CD_3CN^{dl}	74–81^{cl}	1.5	4	+9.3	385	
27		80 vol % CD_3OD^{dl}	91–97^{cl}	1.5	4	+7.6	385	
28		80 vol % D_2O^{dl}	99–101^{cl}	1.5	4	+1.6	385	
29		95.6 wt % D_2O^{dl}	77–102^{cl}	1.5	4	+0.3	65	
30		82.0 wt % D_2O^{dl}	77–102^{cl}	1.5	4	+1.5	65	
31		53.5 wt % D_2O^{dl}	77–102^{cl}	1.5	4	+5.0	65	
32		43.4 wt % D_2O^{dl}	77–102^{cl}	1.5	4	+5.9	65	
33		22.4 wt % D_2O^{dl}	77–102^{cl}	1.5	4	+7.0	65	
34		neat	77–102^{cl}	1.5	4	+7.6	65	
35		98 wt % acetone^{dl}	77–102^{cl}			+10.0	65	
36		95 wt % acetone^{dl}	77–102^{cl}			+10.2	65	
37		79 wt % acetone^{dl}	77–102^{cl}			+10.0	65	
38		58.5 wt % acetone^{dl}	77–102^{cl}			+10.3	65	
39		38.5 wt % acetone^{dl}	77–102^{cl}			+10.3	65	
40		6.8 wt % acetone^{dl}	77–102^{cl}			+8.5	65	
41		98 wt % MeOH^{dl}	77–102^{cl}			+7.4	65	
42		79.2 wt % MeOH^{dl}	77–102^{cl}			+7.6	65	
43		95 wt % D_2O^{dl}	97–107^{cl}			+5.6	388^{hl}	[NaBr] = 0.14 mol/kg
44		95 wt % D_2O^{dl}	97–107^{cl}			+3.8	388^{hl}	x_{NaBr} = 0.0003
45	 MeCO–NH$_2$	*il*	67	1.5	4	+2.2	386	
46	 EtCO–NMe$_2$	99 wt % D_2O^{dl}	67–92^{cl}			+2.1	65	
47		98.2 wt % D_2O^{dl}	67–92^{cl}			+2.3	65	
48		95.8 wt % D_2O^{dl}	67–92^{cl}			+6.3	65	
49		82.6 wt % D_2O^{dl}	67–92^{cl}			+7.6	65	
50		58.3 wt % D_2O^{dl}	67–92^{cl}			+8.6	65	
51		32.9 wt % D_2O^{dl}	67–92^{cl}			+9.4	65	

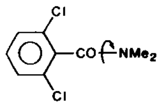
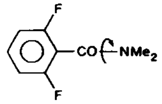
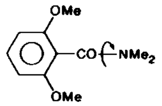
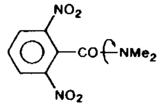
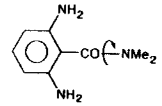
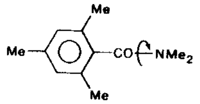
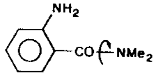
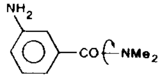
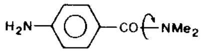
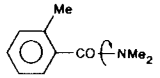
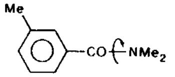
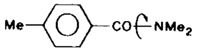
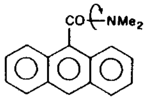
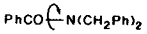
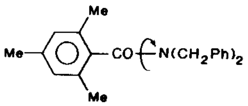
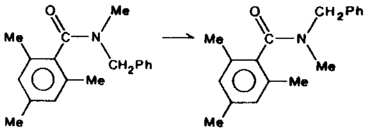
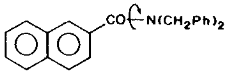
52		10.8 wt % D_2O^{dl}	67–92^{cl}			+9.2	65	
53		neat	67–92^{cl}			+8.6	65	5 wt % HMDSiO
54	$i\text{-PrCO}\frown\text{NMe}_2$	98 wt % D_2O^{dl}	52–92^{cl}			+2.5	65	
55		95 wt % D_2O^{dl}	52–92^{cl}			+3.2	65	
56		90 wt % D_2O^{dl}	52–92^{cl}			+6.0	65	
57		80.1 wt % D_2O^{dl}	52–92^{cl}			+7.0	65	
58		41.1 wt % D_2O^{dl}	52–92^{cl}			+8.2	65	
59		5 wt % D_2O^{dl}	52–92^{cl}			+8.1	65	
60		neat	52–92^{cl}			+8.3	65	
61	$n\text{-BuCO}\frown\text{NMe}_2$	99 wt % D_2O^{dl}	62–97^{cl}			+4.0	65	
62		97.7 wt % D_2O^{dl}	62–97^{cl}			+5.1	65	
63		95 wt % D_2O^{dl}	62–97^{cl}			+6.5	65	
64		80.1 wt % D_2O^{dl}	62–97^{cl}			+7.5	65	
65		60.5 wt % D_2O^{dl}	62–97^{cl}			+8.4	65	
66		13.4 wt % D_2O^{dl}	62–97^{cl}			+8.7	65	
66b		neat	62–97^{cl}			+8.9	65	5 wt % HMDSiO
67	$\text{MeCO}\frown\text{N}(i\text{-Pr})\text{Me}$	*k1*	38–55^{cl}	1.5	4	+10.6	386	
68	$\text{PhCO}\frown\text{NMe}_2$	*a1*	27	2.0	5	+8.5	384	
69		*b1*	4–7^{cl}	1.5	4	+9.6	385	
70		*j1*	23–29^{cl}	1.5	4	+8.1	385	
71		*e1*	13–20^{cl}	2.0	5	+8.6	385	
72		78.2 wt % acetone-d_6^{dl}	13	1.5	4	+7.5	389	
73		80 vol % CD_3CN^{dl}	25–30^{cl}	1.5	4	+9.5	385	
74		80 vol % CD_3OD^{dl}	38–45^{cl}	1.5	4	+12.9	385	
75		99.4 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+3.0	65	
76		97.2 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+4.5	65	
77		95.4 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+5.5	65	
78		90.7 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+6.8	65	
79		80.7 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+8.9	65	
80		80 vol % D_2O^{dl}	64–70^{cl}	1.5	4	+8.9	385	
81		59.9 wt % D_2O^{dl}	32–77^{cl}	1.0	3	+8.9	65	
82		21 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+9.0	65	
83		11.4 wt % D_2O^{dl}	32–77^{cl}	1.5	4	+8.9	65	
84	$\text{PhCO}\frown\text{NEt}_2$	*l1*	−1 to 16^{cl}	1.5	4	+7.7	386	
85	$\text{PhCO}\frown\text{N}(i\text{-Pr})_2$	*m1*	−14 to 24^{cl}	1.5	4	+5.4	386	
86		80.1 wt % acetone-d_6^{dl}	161	1.5	4	+4	389	
87		77.2 wt % acetone-d_6^{dl}	111	1.5	4	+7.5	389	
88		67 wt % acetone-d_6^{dl}	115	1.5	4	+7.5	389	
89		77.6 wt % acetone-d_6^{dl}	178	1.5	4	+5.5	389	

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	ΔV^{*}/ (cm^3 mol^{-1})	ref	remarks
90		*n1*	−20	1.5	4	+5	389	
91		*o1*	176	1.5	4	+3	389	
92		*p1*	−22	1.5	4	+6	389	
93		*p1*	17	1.5	4	+7	389	
94		*q1*	−19	1.5	4	+5	389	
95		50.3 wt % acetone^{d1}	13	1.5	4	+6	389	
96		78.9 wt % acetone^{d1}	72	1.5	4	+7.5	389	
97		80.6 wt % acetone^{d1}	11	1.5	4	+9	389	
98		*r1*	192	1.5	4	+5	389	
99		*s1*	33	1.5	4	+12.5	390	
100		*t1*	211	1.5	4	+4.5	390	
101		*u1*	186	1.5	4	+3	390	
102		*v1*	22	1.5	4	+11.5	390	

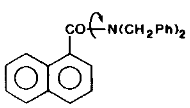
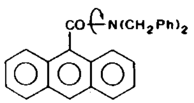
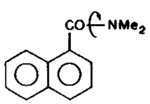
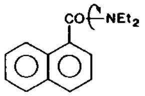
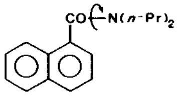
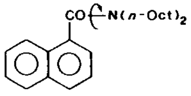
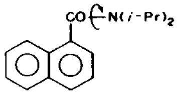
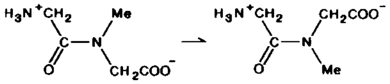
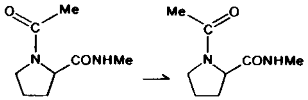
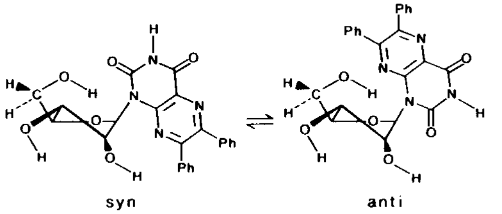
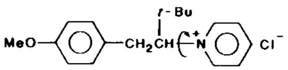
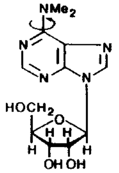
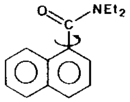
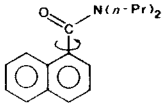
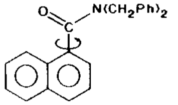
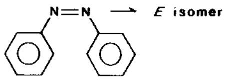
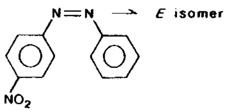
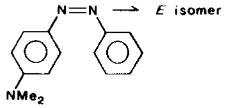
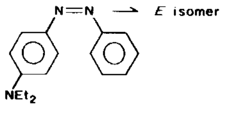
103		*w1*	83	1.5	4	+8.5	390	
104		80 wt % $CHCl_3$[d1]	225	1.5	4	+6.5	390	in the presence of HMDSiO
105		*x1*	79	1.5	4	+7.5	390	in the presence of HMDSiO
106		*y1*	66	1.5	4	+6.5	390	
107		*z1*	82	1.5	4	+6.5	390	in the presence of HMDSiO
108		*a2*	81	1.5	4	+6.5	390	in the presence of HMDSiO and acetone-d_6
109		90 wt % $CHCl_3$[d1]	72	1.5	4	+4.8	390	in the presence of HMDSiO
110		*b2*	97	1.5	4	+4	391	$\Delta V \leq +0.5$ cm^3 mol^{-1}
111		*c2*	62, 59	1.5	4	+7	391	$\Delta V \leq +0.5$ cm^3 mol^{-1}
112		*d2*	−44	1.5	4	+5[e2]	392	
113		*f2*	26, 28	2	5	−3	393	

TABLE VII (Continued)

no.	reaction	solvent	$T/°C$	$P/$ kbar	no. of k	$\Delta V^{\ddagger}/$ (cm^3 mol^{-1})	ref	remarks
114		*g2*	−12 to −4^{cl}	2	5	+8.9	394	
115		*h2*	−15 to −8^{cl}	2	5	+7.7	394	
116		71 wt % CHCl$_3$^{dl}	20	1.5	4	0	395	in the presence of HMDSiO
117		*i2*	20	1.5	4	0	395	
118		*j2*	19	1.5	4	0	395	in the presence of HMDSiO
119		90 wt % CHCl$_3$^{dl}	31	1.5	4	0	395	in the presence of HMDSiO
120		$C_6D_{11}CD_3$	−48	4.7	10	−1.3	41	
121		$C_6D_{11}CD_3$	−55	4.4	10	−1.0	41	
122		$C_6D_{11}CD_3$	−60	4.0	9	−1.0	41	
123		CS_2	−48	4.7	10	−3.1	41	
124		CS_2	−55	4.4	10	−3.4	41	
125		CS_2	−60	3.5	8	−3.2	41	
126		acetone-d_6	−48	3.3	8	−4.8	41	
127		acetone-d_6	−55	2.4	5	−4.0	41	
128		acetone-d_6	−60	1.6	5	−4.9	41	
129		hexane	60	2.1	8	−3.3	396	
130		PhH	60	2.1	5	−1.2	396	
131		cyclohexanone	50	2.1	8	−0.8	397	
132		MeOH	65	2.1	5	−0.7	398	
133		hexane	25	2.1	8	−3.7	399	
134		MeOH	25	2.1	8	−3.5	399	
135		CCl_4	70			−2.5	400	*k2*
136		PhMe	70	1.2	5	−0.1	401	*k2*
137		$CHCl_3$	57			−1.9	401	*k2*
138		MeOH	50			−3.6	401	*k2*
139		hexane	25	2.1	8	−1.7	399	*k2*
140		PhH	25	0.7	5	−1.7	399	*k2*
141		acetone	25	0.9	4	−3.1	399	*k2*
142		EtOH	20	2.1	8	−1.6	399	*k2*
143		MeOH	20	2.1	8	−17.6	399	*k2*

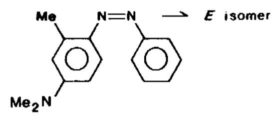
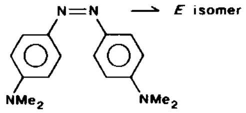
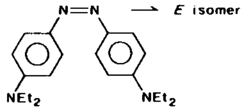
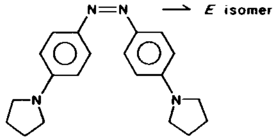
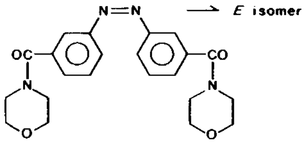
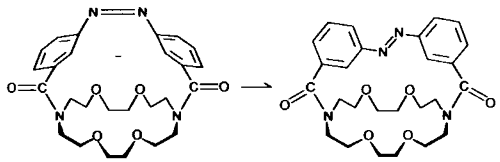
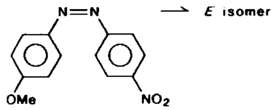
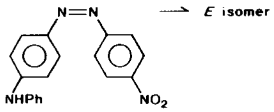
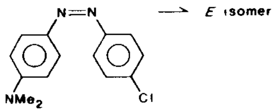
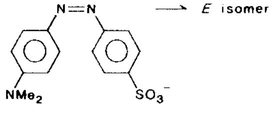
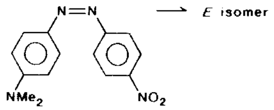
144		PhMe	70	1.2	5	−4.2	401	*k2*
145		PhCl	70			−3.7	401	*k2*
146		hexane	40			−4.8	402	*k2*
147		CCl_4	40			−1.2	402	*k2*
148		PhMe	40			−3.7	402	*k2*
149		CH_2ClCH_2Cl	40			−5.6	402	*k2*
150		MeCN	40			−4.7	402	*k2*
151		DMSO	40			−3.1	402	*k2*
152		hexane	40			−5.9	402	*k2*
153		hexane	50			−2.9	401	*k2*
154		CCl_4	40			−1.9	402	*k2*
155		PhMe	40			−3.5	402	*k2*
156		PhMe	50	1.2	5	−5.7	401	*k2*
157		$CHCl_3$	40			−6.8	401	*k2*
158		CH_2ClCH_2Cl	40			−5.7	402	*k2*
159		MeCN	40			−5.7	402	*k2*
160		DMSO	40			−4.7	402	*k2*
161		MeOH	15			−5.0	401	*k2*
162		hexane	40	1.2	4	−2.2	402	*k2*
163		CCl_4	40	1.2	4	−1.5	402	*k2*
164		PhMe	40	1.2	4	−2.2	402	*k2*
165		CH_2ClCH_2Cl	40	1.2	4	−3.9	402	*k2*
166		MeCN	40	1.2	4	−2.5	402	*k2*
167		DMSO	40	1.2	4	−1.2	402	*k2*
168		MeOH	55	2.1	8	−0.4	398	
169		MeOH	50	2.1	8	+2.0	398	
170		hexane	25	2.1	8	−1.2	397	
171		PhH	25	0.7	5	−2.6	397	
172		CH_2Cl_2	25	2.1	8	−5.3	397, 399	
173		CH_2ClCH_2Cl	25	2.1	8	−6.4	397, 399	
174		acetone	25	2.1	8	−7.9	397	
175		MeOH	20	2.1	8	−4.6	397, 399	
176		PhH	40	1.5	6	−6.5	397	
177		acetone	25	2.1	8	−17.9	397	
178		hexane	20	2.1	8	−1.1	399	*k2*
179		EtOH	20	2.1	8	−0.7	399	*k2*
180		MeOH	20	2.1	8	−10.5	399	*k2*

TABLE VII (Continued)

no.	reaction	solvent	$T/°C$	$P/$ kbar	no. of k	$\Delta V^{\ddagger}/$ (cm^3 mol^{-1})	ref	remarks
181		EtOH	25	2.1	8	−2.7	399	[EtONa] = 0.02–0.1 mol/L
182		MeOH	25	2.1	8	−17.2	399	[MeONa] = 0.02–0.1 mol/L
183		H_2O	25	2.1	8	−18.0	399	[NaOH] = 0.1 mol/L
184		H_2O	25	2.1	8	−17.3	399	[NaOH] = 0.2 mol/L
185		H_2O	25	2.1	8	−21.1	399	[NaOH] = 0.02 mol/L
186		hexane	40	2.1	8	−3.0	399	*k2*
187		hexane	50	1.2	5	−7.7	401	*k2*
188		hexane	55	2.4	9	−3.7	399	*k2*
189		hexane	70	2.1	8	−7.7	399, 403	*k2*
190		CCl_4	25	1.0	4	−10.2	402	*k2*, $\Delta V = -12.2$
191		CCl_4	40	1.8	7	−9.5	397	*k2*
192		CCl_4	40	1.2	5	−10.3	401	*k2*
193		PhH	25	0.6	4	−22.8	402	*k2*, $\Delta V = -26.0$
194		PhH	30	0.8	5	−23.8	399	*k2*
195		PhH	40	1.5	6	−22.0	399	*k2*
196		PhH	50	2.1	8	−19.9	403	*k2*
197		PhH	60	2.4	9	−19.5	403	*k2*
198		PhH	70	2.1	8	−19.4	399	*k2*
199		PhMe	25	1.0	5	−22.1	402	*k2*, $\Delta V = -24.3$
200		PhMe	25	1.2	5	−22.0	401	*k2*
201		*p*-dioxane	25	0.6	5	−25.3	402	*k2*, $\Delta V = -26.9$
202		*p*-dioxane	40	1.5	6	−17.5	403	*k2*
203		*p*-dioxane	50	2.1	8	−19.9	403	*k2*
204		*p*-dioxane	60	2.4	9	−17.6	403	*k2*
205		*p*-dioxane	70	2.4	9	−19.1	403	*k2*
206		$CHCl_3$	15	2.1	8	−25.9	397, 399	*k2*
207		$CHCl_3$	15	1.2	5	−30.4	401	*k2*
208		$CHCl_3$	25	3.9	14	−25.1	31	*k2*
209		$CHCl_3$	25	1.0	4	−29.5	402	*k2*, $\Delta V = -32.2$
210		CH_2Cl_2	25	2.1	8	−28.6	397, 399	*k2*
211		CH_2ClCH_2Cl	25	2.1	8	−27.7	397, 399	*k2*
212		PhCl	25	1.0	4	−31.9	402	*k2*, $\Delta V = -33.8$
213		THF	10	2.4	9	−23.7	403	*k2*
214		THF	25	2.4	9	−28.1	403	*k2*
215		THF	40	2.4	9	−29.4	403	*k2*
216		THF	50	2.4	9	−31.7	403	*k2*
217		THF	60	2.4	9	−33.5	403	*k2*
218		*o*-$C_6H_4Cl_2$	10	1.8	7	−20.6	403	*k2*
219		*o*-$C_6H_4Cl_2$	25	2.4	9	−21.7	403	*k2*
220		*o*-$C_6H_4Cl_2$	40	2.4	9	−22.3	403	*k2*
221		cyclohexanone	25	1.8	7	−18.2	397	*k2*
222		acetone	25	2.1	8	−25.3	397	*k2*
223		*i*-PrOH	25	2.1	8	−20.3	397	*k2*
224		EtOH	10	2.4	9	−21.2	403	*k2*
225		EtOH	15	8.0	17	-21.3^{l2}	404	*k2*
226		EtOH	25	2.4	9	−22.9	403	*k2*
227		EtOH	40	2.4	9	−25.6	403	*k2*
228		EtOH	60	2.4	9	−28.5	403	*k2*
229		EtOH	70	2.4	9	−31.2	403	*k2*
230		MeOH	10	2.4	9	−23.0	403	*k2*
231		MeOH	25	2.4	9	−25.5	403	*k2*

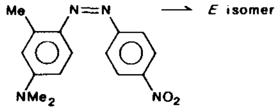
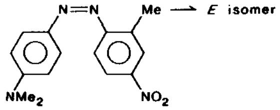
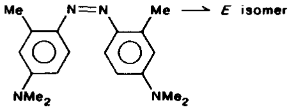
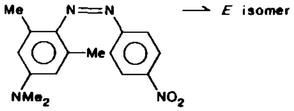
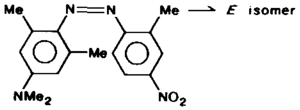
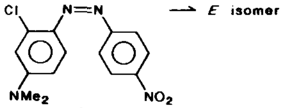
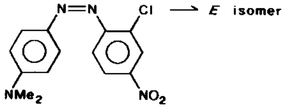
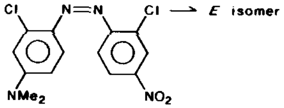
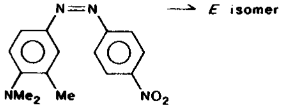
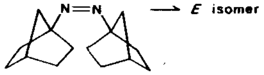
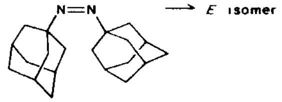
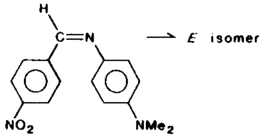
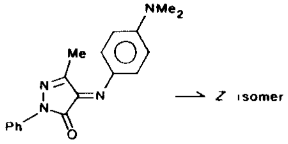
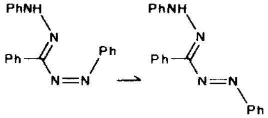
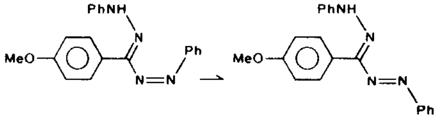
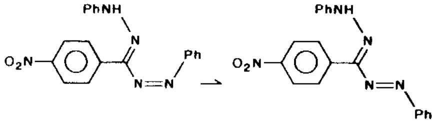
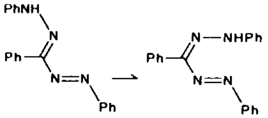
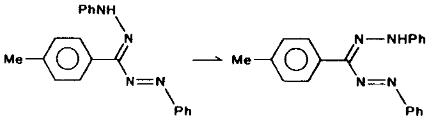
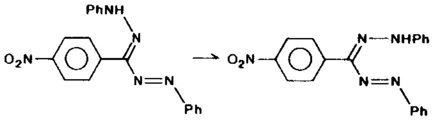
232		MeOH	30	2.4	9	−26.7	403	$k2$
233		MeOH	40	2.4	9	−27.6	403	$k2$
234		MeOH	60	2.4	9	−30.4	403	$k2$
235		triacetin	25	8.0	17	-19.8^{m2}	404	$k2$, $\Delta V^{\ddagger} > 0$ at $P > 5$ kbar
236		triacetin	40	8.0	17	-20.9^{m2}	404	$k2$, $\Delta V^{\ddagger} > 0$ at $P > 6$ kbar
237		hexane	40	1.2	5	−13.0	401	$k2$
238		CCl_4	40	1.2	5	−12.1	401	$k2$
239		PhMe	16	0.9	4	−24.0	401	$k2$
240		hexane	50	1.2	5	−3.2	401	$k2$
241		CCl_4	40	1.2	5	−7.1	401	$k2$
242		PhMe	25	1.2	5	−12.0	401	$k2$
243		$CHCl_3$	16			−22.1	401	$k2$
244		hexane	40	1.2	5	−11.2	401	$k2$
245		CCl_4	40	1.2	5	−8.8	401	$k2$
246		PhMe	25	1.2	5	−24.3	401	$k2$
247		hexane	50	1.2	5	−16.9	401	$k2$
248		CCl_4	40	1.2	5	−17.8	401	$k2$
249		PhMe	15	1.2	5	−23.6	401	$k2$
250		hexane	40	1.2	5	−13.7	401	$k2$
251		CCl_4	25	1.2	5	−17.6	401	$k2$
252		PhMe	15	1.2	5	−21.9	401	$k2$
253		hexane	50	1.2	5	−6.4	401	$k2$
254		CCl_4	50	1.2	5	−8.2	401	$k2$
255		PhMe	50	1.2	5	−12.0	401	$k2$
256		hexane	25	1.2	5	−8.8	401	$k2$
257		CCl_4	25	1.2	5	−9.6	401	$k2$
258		PhMe	15	1.2	5	−17.6	401	$k2$
259		hexane	35	1.2	5	−11.3	401	$k2$
260		CCl_4	40	1.2	5	−12.0	401	$k2$
261		PhMe	25	1.2	5	−21.9	401	$k2$
262		hexane	50			−8.6	401	$k2$
263		PhMe	50			−11.8	401	$k2$
264		$CHCl_3$	25			−30.8	401	$k2$
265		heptane	85	2.0	5	+6.1	405	$\Delta V = +11.5$ (25 °C)

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
266		hexane	21	2.0	6	+7	406	
267		EtOH	35.7			+6	406	
268		hexane	25	2.1	8	+0.3	407	
269		benzene	25	0.7	5	+1.5	407	
270		acetone	25	2.4	9	+1.2	407	
271		MeOH	25	2.4	9	+3.1	407	
272		hexane	25	2.4	9	+2.3	407	
273		benzene	25	0.7	5	+4.2	407	
274		acetone	25	2.4	9	+3.7	407	
275		MeOH	25	2.4	9	+3.6	407	
276		PhMe	15	1.2	4	−5.0	408	
277		PhMe	15	1.2	4	−4.5	408	
278		PhMe	15	1.2	4	−4.7	408	
279		PhMe	20	0.8	5	−8.7	408	
280		hexane	45	1.2	4	−11.7	408	
281		hexane	45	1.2	4	−10.9	408	
282		hexane	45	1.2	4	−8.6	408	

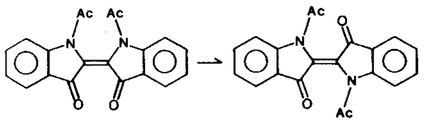
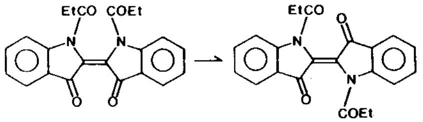
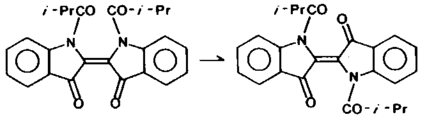
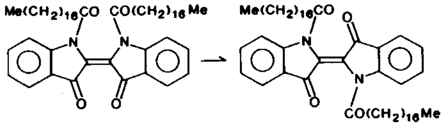
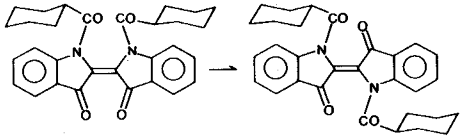
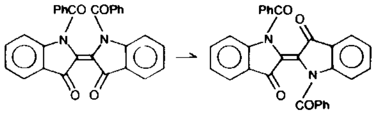
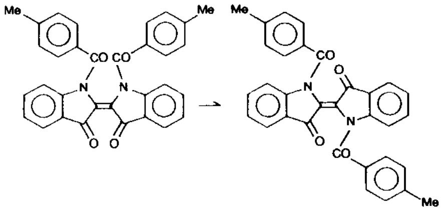
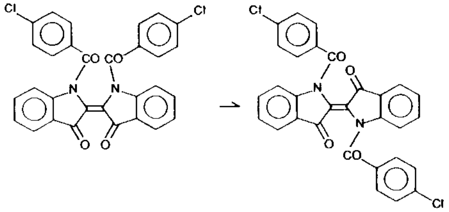
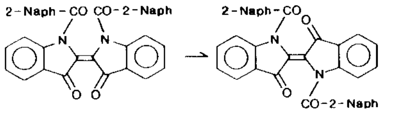
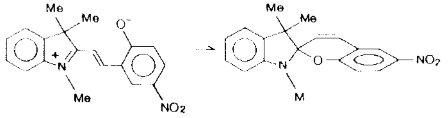
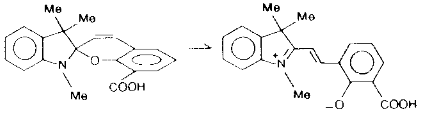
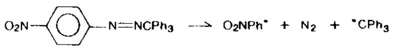
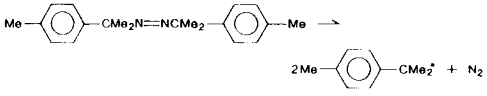
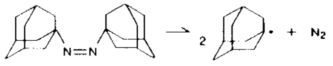
283 284 285		PhMe acetone MeCN	50 50 50	1.2 1.2 1.2	4 4 4	+1.9 +2.2 +3.6	409 409 409
286		PhMe	50	1.2	4	+3.1	409
287		PhMe	50	1.2	4	+3.5	409
288		PhMe	50	1.2	4	+3.0	409
289 290		PhMe MeCN	50 50	1.2 1.2	4 4	−0.6 +3.3	409 409
291 292		PhMe acetone	50 50	1.2 1.2	4 4	+8.0 +9.3	409 409
293		acetone	50	1.2	4	+6.6	409
294		acetone	50	1.2	4	+7.9	409
295		PhMe	50	1.2	4	+6.4	409

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
296		hexane	30	1.2	4	+12.8	410	
297		cyclohexane	30	0.4	4	+9.4	410	
298		p-dioxane	30	1.2	4	+9.8	410	
299		PhH	30	0.8	4	+6.5	410	
300		$CHCl_3$	30	1.2	4	+15.1	410	
301		acetone	30	1.2	4	+19.5	410	
302		DMF	30	1.2	4	+17.5	410	
303		MeCN	30	1.2	4	+21.2	410	
304		DMSO	30	1.2	4	+15.6	410	
305		$CHCl_3$	30	1.2	4	+1.2	411	
306		AcOEt	30	1.2	4	+4.7	411	
307		CH_2Cl_2	30	1.2	4	+2.1	411	
308		acetone	30	1.2	4	+1.4	411	
309		MeCN	30	1.2	4	+0.8	411	
310		DMSO	30	1.2	4	+4.6	411	
311	$(t\text{-BuO})_2 \rightarrow 2t\text{-BuO}^{\bullet}$		130	10.1	5	+5.7^{n2}	412	$o2$
312		PhCl	130	10.1	5	+10.0	413	$p2$
313		PhCl	130	10.1	5	+10.8	413	$q2$
314		2-isopropyl-1,3-dioxolane	130	9.8	4	+11	414	
315		2-(cyclohexyloxy)-tetrahydropyran	130	5	4	+21	415	
316		heptane	140	2.3	5	+10.5^{n2}	416	
317		heptane	160	2.3	6	+7.9^{n2}	416	
318		heptane	180	2.3	6	+11.1^{n2}	416	
319		heptane	190	2.3	6	+8.6^{n2}	416	
320		heptane	200	2.3	5	+10.1^{n2}	416	
321	$(t\text{-BuNO})_2 \rightarrow 2t\text{-BuNO}^{\bullet}$	CO_2	25	0.5	21	+60	417	$\Delta V = +33$, at $P > 0.2$ kbar, $\Delta V^{\ddagger} = +9$
322	$PhN{=}NCPh_3 \rightarrow Ph^{\bullet} + N_2 + {}^{\bullet}CPh_3$	octane	50	4.3	5	+16.4	418	
323		i-PrPh	50	4.3	5	+18.8	418	
324		t-BuPh	50	4.3	5	+16.5	418	
325		octane	60	3.9	5	+17.8	418	
326		i-PrPh	60	3.9	5	+19.0	418	
327		t-BuPh	60	3.9	5	+21.1	418	
328	$PhCMe_2N{=}NCMe_2Ph \rightarrow 2PhCMe_2^{\bullet} + N_2$	i-PrPh	55	6.2	9	+5.0	419	
329		PhCl	55	4.2	8	+4.3	419	
330		i-PrPh	55	4.2	4	+4.6	419	
331	$Me_2C(CN)N{=}NC(CN)Me_2 \rightarrow 2Me_2CCN^{\bullet}$ (free) $+ N_2$	styrene	50	2.9	4	+8.3	420	
332		$CH_2{=}C(Me)COOMe$	30	0.9	5	+7.0	420	
333		$CH_2{=}C(Me)COOMe$	50	0.9	5	+8.1	420	
334		hexane	21	2	6	+18	406	

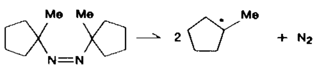
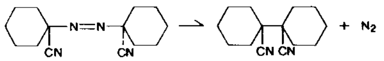
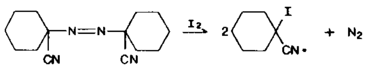
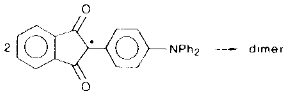
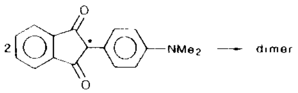
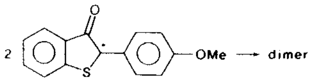
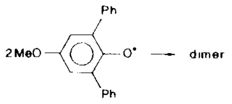
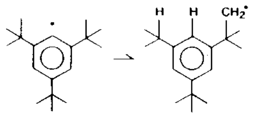
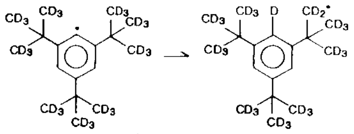
335		EtOH	9			+17	406	
336		PhMe	78	3	3	+5.4	421	$r2$
337		PhCN	88	3	3	+5.5	421	
338		PhMe	64	3	3	+8.5	421	$r2$
339		PhCN	64	3	4	+7.5	421	
340		PhCHO	64	2	3	+6.9	421	
341	MeOCO(CH$_2$)$_3$COOOCO(CH$_2$)$_3$COOMe → 2MeOCO(CH$_2$)$_3$$^\bullet$ + 2CO$_2$	PhMe	70	9.8	4	+1.6	422	
342		MeCN	50	5.9	7	+10.9	423	
343		PhH	50	2	5	+11.5	423	
344		PhMe	50	5.9	7	+10.9	423	
345	PhCOOOCOMe → [PhCOO$^{\bullet\bullet}$OCOMe]$_{\mathrm{cage}}$	PhCl	96	1.9	4	+4	424	[CCl$_4$] = 3.11 mol/L
346	t-BuCOOO-t-Bu → t-Bu$^\bullet$ + CO$_2$ + t-BuO$^\bullet$	heptane	70	2	5	$+1.7^{n2}$	425	
347		heptane	80	2	5	$+2.8^{n2}$	425	
348		heptane	90	2	5	$+3.4^{n2}$	425	
349		heptane	105	2	5	$+1.2^{n2}$	425	
350		isododecane	80	3	4	$+5.9^{n2}$	426	
351		isododecane	120	3	3	$+4.2^{n2}$	426	
352		isododecane	140	3	4	$+6.2^{n2}$	426	
353		isododecane	200	3	3	$+4.4^{n2}$	426	
354	t-BuCOOOCMe$_2$Et → t-Bu$^\bullet$ + CO$_2$ + Me$_2$EtCO$^\bullet$	isododecane	120	3	3	$+9.2^{n2}$	426	
355		isododecane	150	3	3	$+15.2^{n2}$	426	
356		isododecane	200	3	3	$+11.6^{n2}$	426	
357	t-BuCOOOCMe(n-Pr)(n-Bu) →	isododecane	120	3	3	$+10.1^{n2}$	426	
358	t-Bu$^\bullet$ + CO$_2$ + Me(n-Pr)(n-Bu)CO$^\bullet$	isododecane	140	3	3	$+14.6^{n2}$	426	
359		isododecane	180	3	3	$+6.2^{n2}$	426	
360		isododecane	200	3	3	$+7.6^{n2}$	426	
361	t-BuCOOOCMe$_2$(i-Pent) →	isododecane	120	3	2	$+10.7^{n2}$	426	
362	t-Bu$^\bullet$ + CO$_2$ + (i-Pent)Me2CO$^\bullet$	isododecane	140	3	3	$+9.2^{n2}$	426	
363		isododecane	200	3	3	$+8.6^{n2}$	426	
364	Me(Et)(n-Pent)CCOOOCMe$_3$ →	isododecane	100	3	2	$+5.2^{n2}$	426	
365	Me(Et)(n-Pent)C$^\bullet$ + CO$_2$ + t-BuO$^\bullet$	isododecane	130	3	2	$+7.1^{n2}$	426	
366		isododecane	200	3	2	$+6.4^{n2}$	426	
367	Me(Et)(n-Pent)CCOOOCMe$_2$(Et) →	isododecane	100	3	3	$+6.3^{n2}$	426	
368	Me(Et)(n-Pent)C$^\bullet$ + CO$_2$ + Me$_2$(Et)CO$^\bullet$	isododecane	130	3	3	$+7.5^{n2}$	426	
369		isododecane	200	3	3	$+6.7^{n2}$	426	
370	Me(Et)(n-Pent)CCOOOCMe$_2$(i-Pent) →	isododecane	100	3	3	$+9.3^{n2}$	426	
371	Me(Et)(n-Pent)C$^\bullet$ + CO$_2$ + Me$_2$(i-Pent)CO$^\bullet$	isododecane	120	3	3	$+13.0^{n2}$	426	
372		isododecane	200	3	3	$+5.5^{n2}$	426	
373	decomposition of dicyclohexyl peroxydicarbonate	isododecane	95–200	3	4	+4.3	427	
374	decomposition of n-C$_7$H$_{15}$COOOCO-n-C$_7$H$_{15}$	isododecane	80–200	3	3	+5.9	427	
375	decomposition of *tert*-butyl perneodecanoate	isododecane	100–200	3	3	+6.1	427	
376	decomposition of *tert*-amyl perneodecanoate	isododecane	100–200	3	3	+7.0	427	
377	decomposition of t-BuCOOO-t-Bu	isododecane	80–200	3	4	+6.1	427	
378	decomposition of t-BuCOOOC(Et)Me$_2$	isododecane	120–200	3	3	+9.4	427	
378b	decomposition of t-BuOO-t-Bu	isododecane	143–230	3	3	+13.4	427	
378c	decomposition of MeC(OO-t-Bu)$_2$Et	isododecane	200	2	6	+22.3	429	
379	Me$_3$SiOOCPh$_3$ → MeOSiMe$_2$OCPh$_3$ + Me$_3$SiO$^\bullet$ + $^\bullet$OCPh$_3$	PhOMe	170	10	6	-3.5^{n2}	430	$s2$
380	Ph$_2$C=C=NCH$_2$Ph → Ph$_2$C(CN)CH$_2$Ph	PhCl	60	3	5	+9.9	431	
381	PhCH$_2$CH$_2$Ph → 2PhMe + PhCH=CHPh	neat	395	0.9	5	+31	432	
382	H$_2$CO$_3$ → H$_2$O + CO$_2$	H$_2$O	25	1	5	+6.4	345	ionic strength 0.5 mol/L, $\Delta V^{\ddagger} = -9.9$ for the reverse reaction

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
383	$MeCOCH_2C(OH)Me_2 \rightarrow 2MeCOMe$	H_2O	25	4	8	+6.9	433	[NaOH] = 0.1 mol/L
384	$\sim CH_2CH_2^{\bullet} + CH_2{=}CH_2 \rightarrow$ propagation	neat	132–189	1.8	6	-25.5	434, 435	
385	$-CH_2CHPh^{\bullet} + CH_2{=}CHPh \rightarrow$ propagation	neat	22	2.1	4	-18.6	436	
386		H_2O	25	2.7	5	-18.7	437	*t2*
387		H_2O	25	2.7	5	-17.9	437	*u2*
388		H_2O	25	2.7	5	-18.3	437	*v2*
389		H_2O	25	2.7	5	-18.7	438	*w2*
390	recombination of $(t\text{-Bu})_2C{=}N^{\bullet}$	isopentane	-79	0.3	2	-18.0	439	
391		hexane	20	2.4	5	+15.5	440	
392		PhMe	20	2.6	5	+16.0	440	
393		$CHCl_3$	20	2.4	6	+17.2	440	
394		PhMe	20	2.9	7	+5.1	440	$\Delta V^{\ddagger}$ = -8.1 for the reverse reaction, *x2*
395		$CHCl_3$	20	3	7	0	440	$\Delta V^{\ddagger}$ = -8.0 for the reverse reaction, *x2*
396		PhMe	23	2.5	9	+9.0	441	
397		$CHCl_3$	23	2.5	7	+7.0	441	
398		n-PrOH	23	2.5	6	+14.5	441	
399		PhCl	20	2.6	5	+15.0	440	ΔV = +15.0 for the reverse reaction
400	$2{\sim}CH_2CH_2^{\bullet} \rightarrow$ termination	neat	132–189	1.8	6	+7	434, 435	
401	$2{\sim}CH_2CHPh^{\bullet} \rightarrow$ termination	neat	22	2.1	4	+5.8	436	
402		isopentane	-129 to -63	0.3	2	+5.3	439	
403		t-BuPh	-22 to +16	0.3	2	-1.2	439	
404	$(t\text{-Bu})_2C{=}N^{\bullet} \rightarrow t\text{-Bu}^{\bullet} + t\text{-BuC}{\equiv}N$	isopentane	-22 to +10	0.3	2	+3	439	
405	$t\text{-BuO}\dot{P}(OEt)_3 \rightarrow t\text{-Bu}^{\bullet} + OP(OEt)_3$	isopentane	-92 to -68	0.3	2	+0.2	439	
406	$PhCH_2Si(Me)_2OOSi(Me)_2CH_2Ph \rightarrow PhCH_2OSi(Me)_2OSi(Me)_2CH_2Ph$	PhOMe	90	9.8	4	-8	442	
407	$Me_3SiOOSiMe_3 \rightarrow MeOSiMe_2OSiMe_3$	PhOMe	135	9.8	4	-10	442	
408	$PhSiMe_2OOSiMe_2Ph \rightarrow PhOSiMe_2OSiMe_2Ph$	PhOMe	80	5.9	4	-7.9	443	

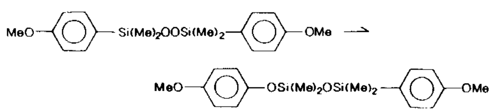
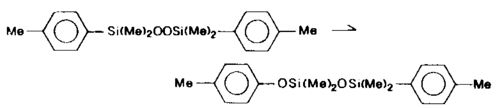
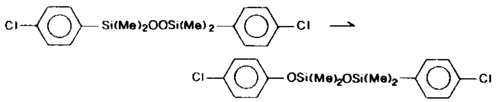
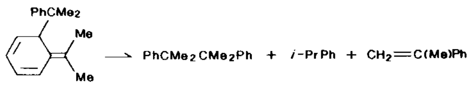
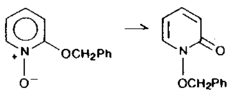
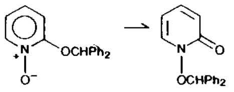
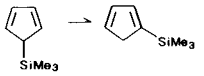
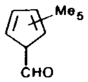
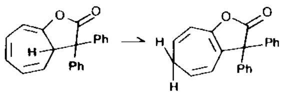
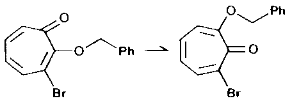
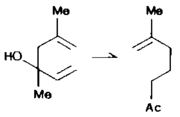
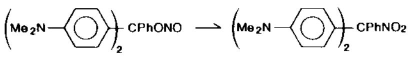
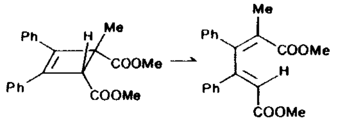
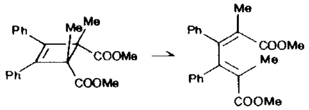
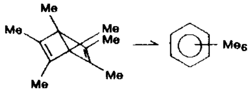
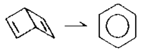
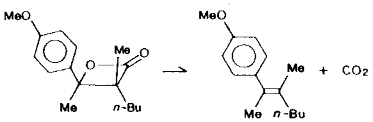
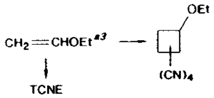
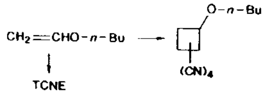
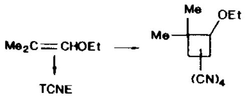
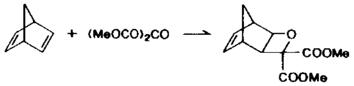
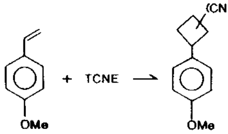
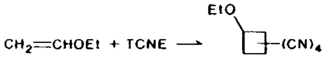
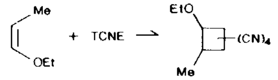
409		PhOMe	80	5.9	4	−9.6	443	
410		PhOMe	80	5.9	4	−7.4	443	
411		PhOMe	80	5.9	4	−8.0	443	
412		cyclohexane	20	1.5	5	+6	419	
413		diglyme	100	4.2	5	−30	444	
414		diglyme	100	4.2	5	+10	444	
415		$CDCl_3$	30	1.5	6	−26	445	$\Delta V^\ddagger = -26$ for the reverse reaction
416	degenerate isomerization of 	neat	68	2.5	12	−12.5	445	
417	degenerate isomerization of 	neat?	−4			−4	445	
418		Bu_2O	130	1.6	5	−2.2	446	$\Delta V = +3.0$ (60 °C)
419		*i*-PrPh	130	1.6	5	−11.1	447	
420		$1\text{-}C_6H_{13}OH$	130	1.6	5	−10.1	447	
421		*N*-methylpyrrolidone	180	10	8	−9.7	448	
422	degenerate isomerization of 	CS_2	20	5.0	7	−0.5	445	
423		AcOEt	25			−15	449	$\Delta V = +37$
424		acetone	25			−6	449	$\Delta V = +9$

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
425		y2	70	9.2	9	-12.7^{z2}	450	$\Delta V = +25$ (70 °C)
426		y2	70	9.4	10	-6.9^{z2}	450	
427		PhBr	140	1.4	3	−12	451	$\Delta V = -22$ (20 °C)
428		pyridine	42	2.2	4	+5	451	
429		DMSO	56	0.9	6	−28.5	452	$\Delta V = +52$
430		EtOH	60	0.7	4	−30	452	
431		$CHCl_3$	25	1.5	5	−28.0	453	b3, $\Delta V = -10.3$ for EDAC formation
432		$CHCl_3$	25	1.5	5	−30.8	454	b3, $\Delta V = -11.0$ for EDAC formation
433		$CHCl_3$	25	1.5	5	−41.8	454	b3, $\Delta V = -5.8$ for EDAC formation
434		CH_2Cl_2	79	2.4	7	−29	455	$\Delta V = -31.8$ (25 °C)^{c3}
435		$CHCl_3$–CCl_4	25	1	5	−49	456	d3, $CHCl_3$ 50 vol %
436		CH_2Cl_2	25	0.9	8	−55	457	$\Delta V = -31.9^{c3}$
437		CH_2Cl_2	25	1	9	−50	457	$\Delta V = -30.3^{c3}$

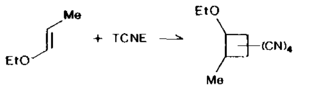
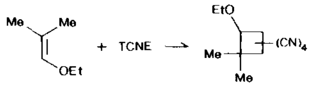
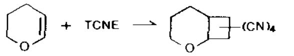
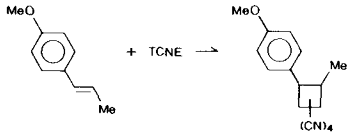
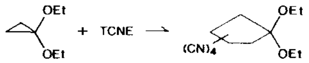
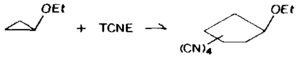
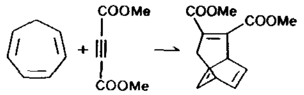
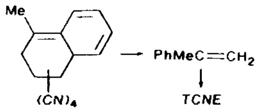
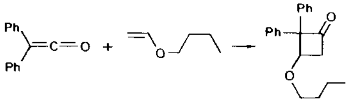
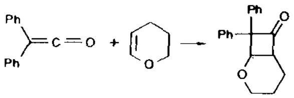
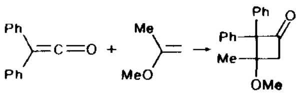
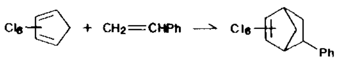
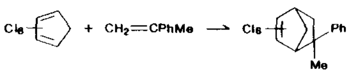
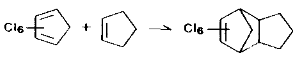
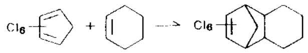
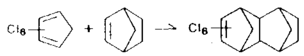
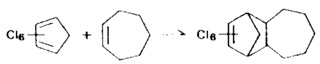
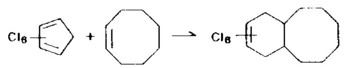
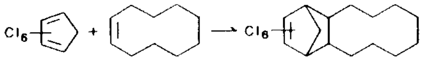
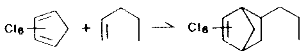
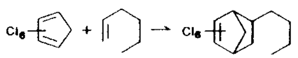
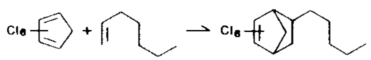
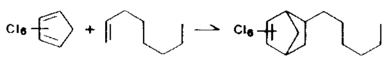
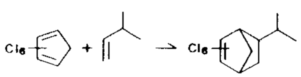
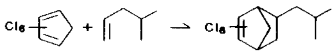
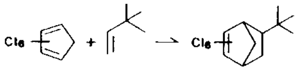
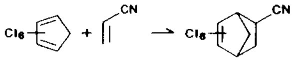
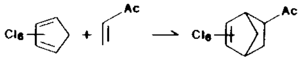
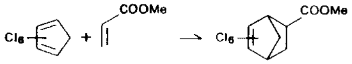
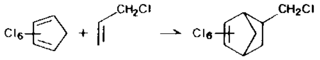
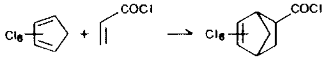
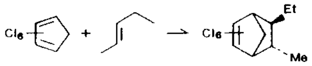
438		CH_2Cl_2	25	1	11	−55	457	$\Delta V = -29.7^{c3}$
439		CH_2Cl_2	25	1	9	−55	457	$\Delta V = -29.5^{c3}$
440		CH_2Cl_2	25	1	8	−36	457	$\Delta V = -36.1^{c3}$
441		CH_2Cl_2	25	0.3	6	−44	457	$\Delta V = -26.7^{c3}$
442		CH_2Cl_2	34	2	5	−20.9	458	$\Delta V = -29.5^{c3}$
443		MeCN	34	2	4	−24.5	458	$\Delta V = -30.9^{c3}$
444		1,4-dioxane	60	0.8	3	−33.7	459	$\Delta V = -28.1^{c3}$
445		MeCN	60	2	6	−29.2	459	$\Delta V = -33.6^{c3}$
446		PhMe	97	1.2		−28.8	460	
447		CCl_4	25	0.8	5	−11	461	$\Delta V = +19$
448		$CHCl_3$	25	1.5	7	−7	461	$\Delta V = +22$
449		CH_2ClCH_2Cl	25	1	5	−7	461	$\Delta V = +23$
450		MeCN	25	0.8	5	−9	461	
451		hexane	25	1	6	−28	462	
452		cy-C_6H_{12}	25	0.5	5	−26	462	$\Delta V = -31.3^{c3}$
453		PhMe	25	1.3	8	−52	462	$\Delta V = -29.0^{c3}$
454		PhH	25	1	8	−44	462	$\Delta V = -23.0^{c3}$
455		CH_2Cl_2	25	1.3	8	−29	462	$\Delta V = -26.2^{c3}$
456		PhCl	25	1	7	−30	462	$\Delta V = -26.4^{c3}$
457		CCl_4	25	1	6	−32	462	
458		PhCN	25	1	7	−22	462	$\Delta V = -10.4^{c3}$
459		PhMe	25	1,3	7	−50	462	$\Delta V = -31.1^{c3}$
460		CH_2Cl_2	25	1.3	7	−32	462	$\Delta V = -25.2^{c3}$
461		PhMe	25	1	7	−43	462	
462		CH_2Cl_2	25	1	7	−31	462	
463		decane–heptane	80	0.9	7	−38.5	463	$\Delta V = -30.0$ (25 °C)^{c3}
464		decane–heptane	100	2.3	8	−40	463	$\Delta V = -31.0$ (25 °C)^{c3}
465		decane^{e3}	91	1.4	6	−45	464	$\Delta V = -33.2$ (25 °C, heptane)^{c3}

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
466		decane^{e3}	91	1.4	6	−43	464	ΔV = −34.3 (25 °C, heptane)^{c3}
467		decane^{e3}	100	1	6	−38	464	ΔV = −33.3 (25 °C, heptane)^{c3}
468		decane^{e3}	91	1.4	6	−35	464	ΔV = −35.6 (25 °C, heptane)^{c3}
469		decane^{e3}	80	1	6	−32	464	ΔV = −34.5 (25 °C, heptane)^{c3}
470		decane^{e3}	100	1.4	5	−30	464	
471		heptane^{e3}	100	1.2	5	−37	465	ΔV = −33.0 (25 °C)^{c3}
472		heptane^{e3}	100	1.4	6	−39	465	ΔV = −33.2 (25 °C)^{c3}
473		heptane^{e3}	100	1	7	−39	465	ΔV = −33.5 (25 °C)^{c3}
474		heptane^{e3}	100	1	6	−38	465	ΔV = −33.1 (25 °C)^{c3}
475		heptane^{e3}	100	0.9	6	−41	465	ΔV = −33.5 (25 °C)^{c3}
476		heptane^{e3}	100	1.4	5	−37	465	ΔV = −33.0 (25 °C)^{c3}
477		heptane^{e3}	110	1.9	5	−36	465	ΔV = −32.5 (25 °C)^{c3}
478		heptane^{e3}	100	0.9	7	−31.5	465	
479		heptane^{e3}	49	0.9	5	−27.5	465	
480		heptane^{e3}	70	0.9	5	−30	465	ΔV = −30.6 (25 °C)^{c3}
481		heptane^{e3}	100	0.9	5	−39	465	ΔV = −28.0 (25 °C)^{c3}
482		heptane^{e3}	50	0.9	6	−27	465	ΔV = −28.5 (25 °C)^{c3}
483		heptane^{e3}	100	1	6	−45	465	ΔV = −34.6 (25 °C)^{c3}

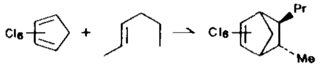
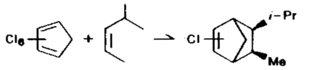
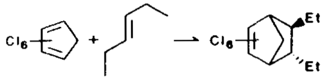
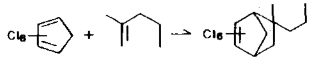
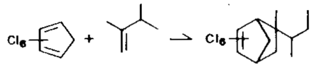
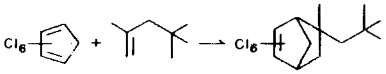
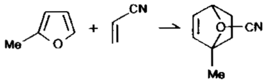
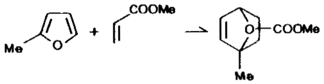
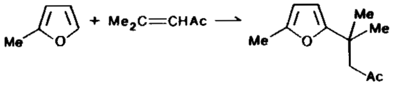
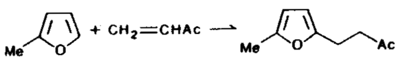
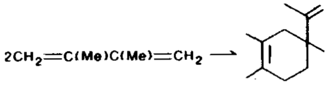
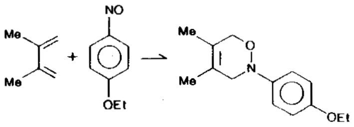
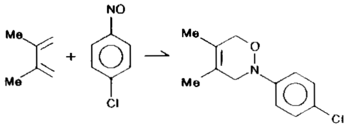
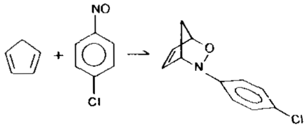
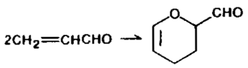
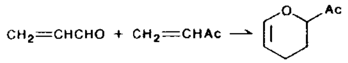
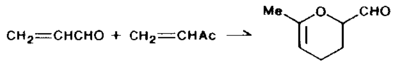
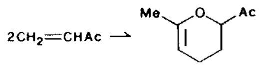
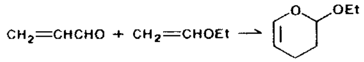
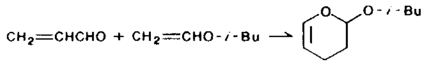
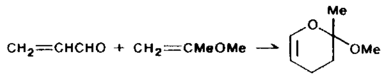
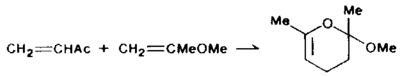
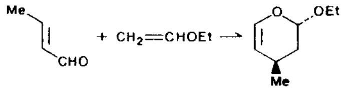
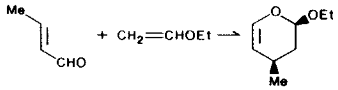
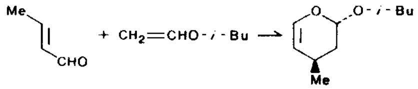
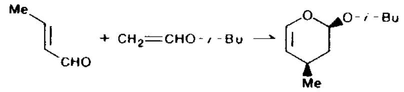
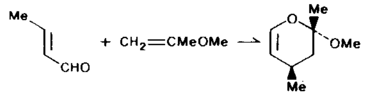
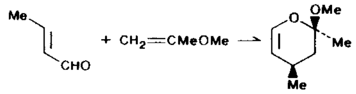
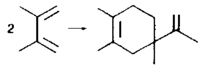
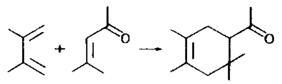
484		heptane^{e3}	100	1.9	5	−42	465	$\Delta V = -32.9$ (25 °C)^{c3}
485		heptane^{e3}	100	1.3	5	−47	465	$\Delta V = -33.5$ (25 °C)^{c3}
485b		heptane^{e3}	72		2	−43	465	
486		heptane^{e3}	72		2	−38	465	$\Delta V = -33.3$ (25 °C)^{c3}
487		heptane^{e3}	72		2	−35	465	
488		heptane^{e3}	72		2	−28	465	
489		CH_2Cl_2	37	7.5	5	−30.3	466	
490		CH_2Cl_2	37	10	6	−32.2	466	
491		heptane	117	1	3	−46	467	
492		Et_2O	117	1	3	−49	467	
493		CH_2Cl_2	117	3	5	−50	467	
494		MeCN	117	1	3	−50	467	
495		CH_2Cl_2	106	1.5	4	−46	467	
496		*n*-BuBr	70	5	9	−34.5	468	$\Delta V = -44.9^{c3}$
497		PhMe	25	1	7	−39.7	469	$\Delta V = -32.5^{c3}$
498		EtOH	25	1	7	−37.0	469	$\Delta V = -32.2^{c3}$
499		CH_2Cl_2	25	1	7	−28.8	469	$\Delta V = -30.9^{c3}$
500		PhCl	25	1	7	−26.8	469	$\Delta V = -30.6^{c3}$
501		$PhNO_2$	25	1	7	−22.8	469	$\Delta V = -31.2^{c3}$
502		CH_2ClCH_2Cl	25	1	7	−30.0	469	$\Delta V = -32.6^{c3}$
503		CCl_4	25	1	7	−29.3	469	$\Delta V = -33.5^{c3}$
504		PhMe	25	1	7	−39.2	469	$\Delta V = -38.2^{c3}$
505		CCl_4	25	1	7	−32.0	469	$\Delta V = -40.5^{c3}$
506		PhCl	25	1	7	−26.7	469	$\Delta V = -35.3^{c3}$
507		CH_2Cl_2	25	1	7	−27.8	469	$\Delta V = -36.6^{c3}$
508		CH_2ClCH_2Cl	25	1	7	−27.5	469	$\Delta V = -38.4^{c3}$
509		EtOH	25	1	7	−29.1	469	$\Delta V = -40.8^{c3}$
510		$PhNO_2$	25	1	7	−26.6	469	$\Delta V = -33.7^{c3}$
511		PhMe	25	1	7	−33.9	469	$\Delta V = -41$
512		PhCl	25	1	7	−37.1	469	$\Delta V = -52$
513		CH_2Cl_2	25	1	7	−25.7	469	$\Delta V = -36$
514		EtOH	25	1	7	−39.5	469	$\Delta V = -40$
515		heptane	70	11.3	6	−37.0	470	$\Delta V = -28.6^{c3}$

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
516		heptane	70	11.3	6	−36.5	470	$\Delta V = -29.7^{c3}$
517		heptane	70	11.3	6	−35.0	470	$\Delta V = -29.7^{c3}$
518		heptane	70	11.3	6	−37.0	470	$\Delta V = -32.3^{c3}$
519		heptane	120	2	4	−42	471	
520		heptane	120	2	3	−45	471	
521		heptane	120	1	4	−47	471	
522		heptane	120	2	4	−50	471	
523		heptane	120	2	4	−42	471	
524		heptane	120	2	4	−45	471	
525		heptane	120	2	4	−44	471	
526		heptane	120	2	4	−39	471	
527		heptane	120	2	4	−43	471	
528		heptane	120	2	4	−43	471	
529		neat	120	3		−33	472	
530		neat	120	3		−39	472	

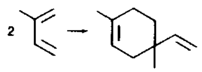
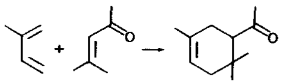
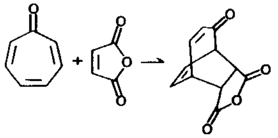
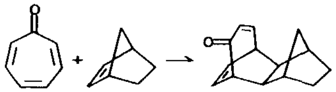
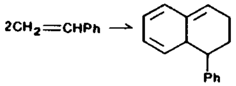
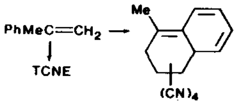
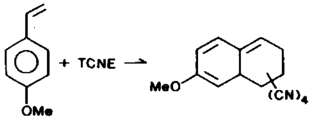
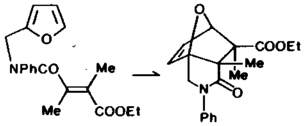
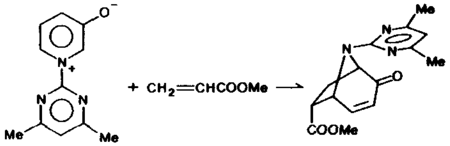
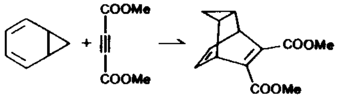
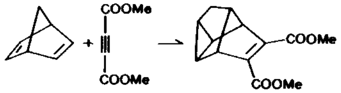
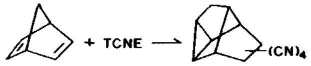
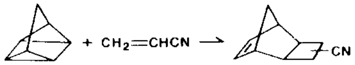
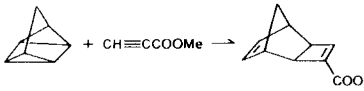
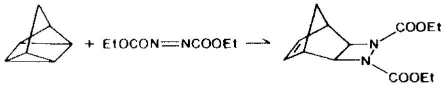
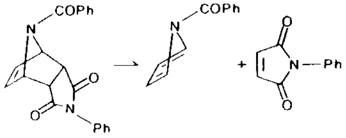
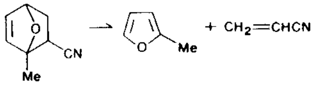
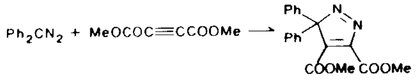
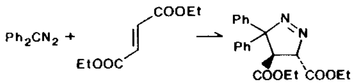
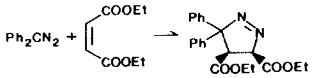
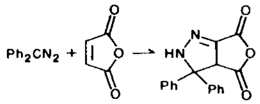
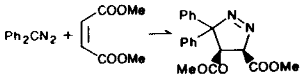
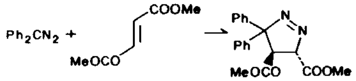
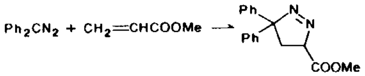
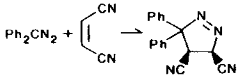
531		neat	120	3		−39	472	
532		neat	120	3		−36	472	
533		*i*-PrPh	105	2	5	−21.4	473	
534		DMF	105	2	5	−16.8	473	Δ*V* = −25.5 (60 °C)[c3]
535		*i*-PrPh	135	2	5	−30.0	473	Δ*V* = −33.5 (60 °C)[c3]
536		DMF	135	2	5	−27.8	473	Δ*V* = −32.1 (60 °C)[c3]
537		neat	80	2.0	6	−36.7	474	*f3*
538		CCl_4	25	0.8	5	−30	461	*b3*
539		$CHCl_3$	25	1.5	7	−29	461	*b3*, Δ*V* = −4.0 for EDAC formation
540		CH_2ClCH_2Cl	25	1	5	−30	461	*b3*, Δ*V* = −6.9 for EDAC formation
541		$CHCl_3$–CCl_4	25	1	5	−38	456	*d3*, $CHCl_3$ 50 vol %
542		EtOH		1	7	−25	475	Δ*V* = −23
543		EtOH	25	1	8	−36.0	476	Δ*V* = −37.0[c3]
544		PhMe	97	1.2		−33.8	460	
545		PhH	90	1.9	7	−40.5	477	Δ*V* = −35.5 (25 °C)[c3]
546		PhMe	40	1.1	6	−30.0	477	Δ*V* = −32.9 (25 °C)[c3]
547		MeCN	40	0.8	6	−32.8	477	Δ*V* = −36.2 (25 °C)[c3]

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^‡$/ (cm^3 mol^{-1})	ref	remarks
548	 + $CH_2{=}CHCN$ →	$CHCl_3$	90	0.9	6	−32.0	478	ΔV = −29.1 (25 °C)^{c3}
549	 + $CH{\equiv}CCOOMe$ →	$CHCl_3$	90	0.9	5	−43.5	478	ΔV = −38.8 (25 °C)^{c3}
550	 + EtOCON=NCOOEt →	$CHCl_3$	50	0.9	5	−28.2	478	ΔV = −29.6 (25 °C)^{c3}
551		$CHCl_3$	38	1.3	5	−8.3	479	ΔV = +22.4 (25 °C)^{c3}
552	 + $CH_2{=}CHCN$	cyclohexane	80	0.9	5	−2.0	480	
553		CH_2Cl_2	80	0.9	5	−1.0	480	
554		MeCN	80	1.9	6	−3.4	480	
555	 Ph_2CN_2 + $MeOCOC{\equiv}CCOOMe$ →	hexane	25	1	7	−24	481	ΔV = −34.9^{c3}
556		PhMe	25	1	7	−23.2	481	ΔV = −26.8^{c3}
557		PhCl	25	1	7	−17.8	481	ΔV = −26.4^{c3}
558		MeCN	25	1	7	−15.3	481	ΔV = −27.8^{c3}
559	 Ph_2CN_2 +	PhCl	25	1	6	−20.9	481	ΔV = −27.0^{c3,g3,h3}
560	 Ph_2CN_2 +	PhCl	25	1	8	−23.6	481	ΔV = −25.1^{c3,g3,h3}
561	 Ph_2CN_2 +	MeCN	25	1	6	−16.7	481	
562	 Ph_2CN_2 +	PhMe	25	1.5	4	−23.4	482	ΔV = −24.5^{i3}
563	 Ph_2CN_2 +	PhMe	25	1.5	4	−22.3	482	$g3$
564	 Ph_2CN_2 + $CH_2{=}CHCOOMe$ →	PhMe	25	1.5	4	−19.8	482	$g3$
565	 Ph_2CN_2 +	PhMe	25	1.4	4	−21.5	482	$g3$

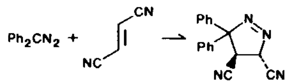
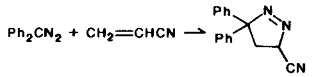
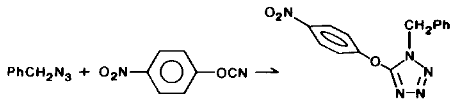
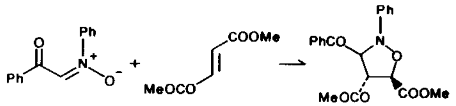
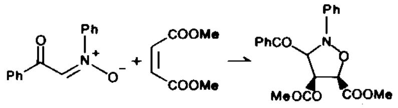
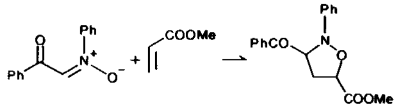
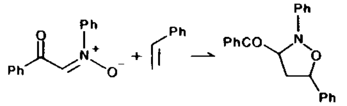
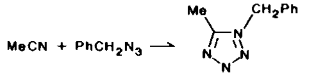
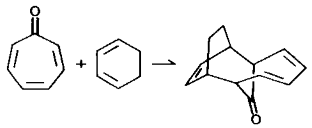
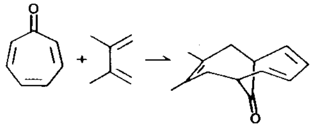
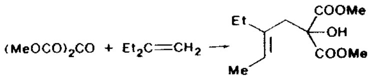
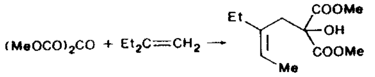
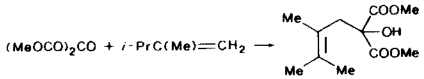
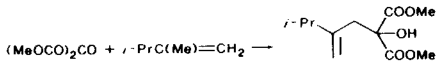
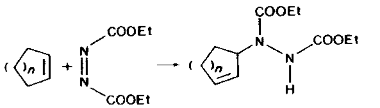
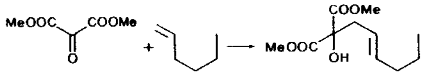
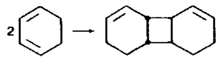
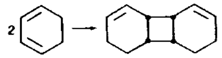
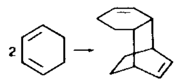
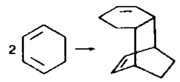
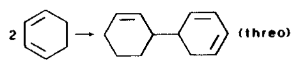
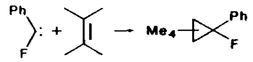
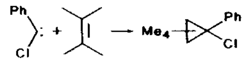
566		PhMe	25	1.5	4	−21.0	482	*g3*
567		PhMe	25	1.5	4	−23.9	482	*g3*
568		MeCN	80	6	6	−21	483	
569		PhMe	25			−21.7	484	$\Delta V = -22.7^{i3}$
570		$CHCl_3$	25			−24.3	484	
571		MeCN	25			−18	484	
572		PhMe	25			−19.9	484	
573		PhMe	25			−22.9	484	
574		PhMe	25			−19.5	484	
575		none	130	9.7	4	−18.3	485	MeCN 89 mol %, $P \geq 3.9$ kbar
576		none	139	9.7	4	−20.5	485	MeCN 89 mol %, $P \geq 3.9$ kbar
577		none	149	9.7	4	−21.3	485	MeCN 89 mol %, $P \geq 3.9$ kbar
578		none	158	9.7	4	−24.4	485	MeCN 89 mol %, $P \geq 3.9$ kbar
579		*i*-PrPh	80	2	5	−37.6	486	$\Delta V = -36.1$ (60 °C)^{c3}
580		1,4-dioxane	80	2	5	−28.2	486	$\Delta V = -31.8$ (60 °C)^{c3}
581		DMF	80	2	5	−32.6	486	$\Delta V = -34.2$ (60 °C)^{c3}
582		*i*-PrPh	80	2	5	−33.1	487	$\Delta V = -34.9$ (60 °C)^{c3}
583		1,4-dioxane	80	2	5	−30.5	487	$\Delta V = -35.0$ (60 °C)^{c3}
584		DMF	80	2	5	−30.1	487	$\Delta V = -34.0$ (60 °C)^{c3}
585	$(MeOCO)_2CO + n\text{-}BuCH{=}CH_2 \rightarrow n\text{-}PrCH{=}CHCH_2C(OH)(COOMe)_2$	CCl_4	110	1.3	7	−39	488	$\Delta V = -27.0$ (25 °C)^{c3}
586	$(MeOCO)_2CO + s\text{-}BuCH{=}CH_2 \rightarrow Et(Me)C{=}CHCH_2C(OH)(COOMe)_2$	CCl_4	110	1.3	9	−36	488	$\Delta V = -26.5$ (25 °C)^{c3}
587	$(MeOCO)_2CO + t\text{-}BuCH_2C(Me){=}CH_2 \rightarrow CH_2{=}C(CH_2\text{-}t\text{-}Bu)CH_2C(OH)(COOMe)_2$	CCl_4	110	1	7	−44	488	$\Delta V = -30.9$ (25 °C)^{c3}

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
588		CCl$_4$	110	1.3	7	-48	488	ΔV = -31.3 (25 °C)^{c3}
589		CCl$_4$	110	1.3	7	-45	488	ΔV = -31.3 (25 °C)^{c3}
590		CCl$_4$	110	1.3	6	-45	488	ΔV = -31.9 (25 °C)^{c3}
591		CCl$_4$	110	1.3	6	-46	488	ΔV = -31.9 (25 °C)^{c3}
592	$(EtOCO)_2CO + Me_2CO \rightarrow MeCOCH_2C(OH)(COOEt)_2$	acetone	97	1.4	5	-34.7^{n2}	489	ΔV = -33.9 (20 °C)^{c3}
								
593	$n = 1$	PhMe	75	1.5		-28.7	490	ΔV = -33.9 (20 °C)
594	$n = 2$	PhMe	75	1.5		-24.5	490	
595	$n = 3$	PhMe	75	1.5		-32.1	490	
596	$n = 4$	PhMe	75	1.5		-33.4	490	
597	$n = 6$	PhMe	75	1.5		-32.9	490	
598		CCl$_4$	110	1.3	5	-37.8^{z3}	491	ΔV = -27 (25 °C)
599			70	7	3	-18	492	
600			70	7	3	-22	492	
601			70	7	3	-22	492	
602			70	7	3	-28	492	
603			70	7	3	-32	492	
604		cy-C$_6$H$_{11}$Me		2		-22	493	
605		cy-C$_6$H$_{11}$Me		2		-18	493	

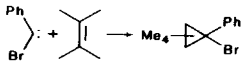
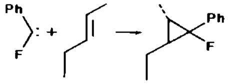
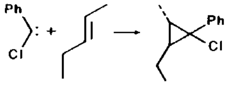
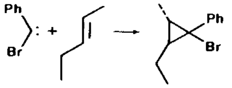
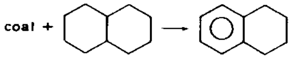
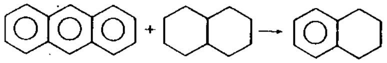
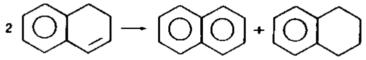
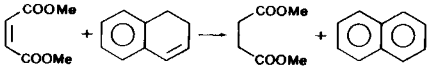
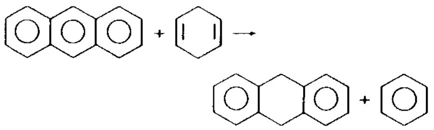
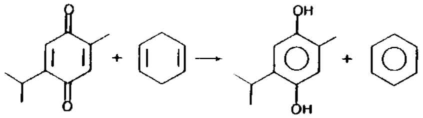
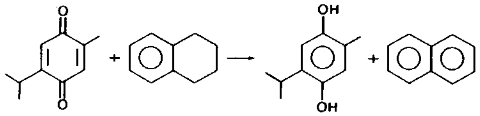
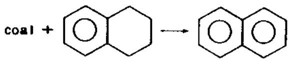
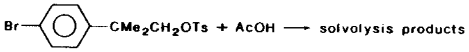
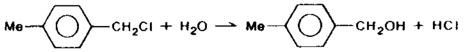
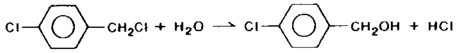
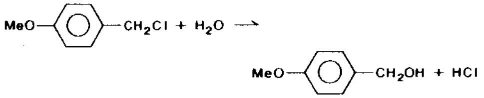
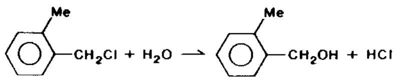
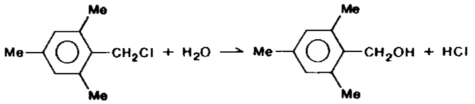
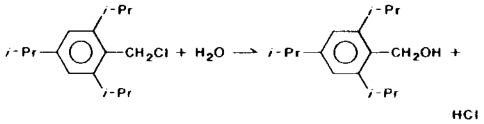
606		cy-$C_6H_{11}Me$		2		−13	493
607		cy-$C_6H_{11}Me$		2		−18	493
608		cy-$C_6H_{11}Me$		2		−15	493
609		cy-$C_6H_{11}Me$		2		−12	493
610		neat	400	0.6	3	−70	494
611		neat	400	0.6	3	−55	494
612		neat	260	1.1	4	−25	495
613		neat	220	1	3	−29	495
614		neat	220	1	3	−23	495
615		neat	200	1	3	−31	495
616		neat	75	0.7	3	−33	495
617		neat	175	0.7	3	−28	496
618		neat	344	0.7	3	−27	496
621		AcOH	75	1	6	−24.5	497

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	ΔV^{*}/ (cm^3 mol^{-1})	ref	remarks
622		H_2O	30	1.6	6	−7.3	498	
623		aq EtOH	30	1.6	6	−13.0	498	EtOH 10 mol %
624		aq EtOH	30	1.6	6	−19.5	498	EtOH 20 mol %
625		aq EtOH	30	1.6	6	−23.4	498	EtOH 30 mol %
626		aq EtOH	30	1.6	6	−16.4	498	EtOH 40 mol %
627		H_2O	40	1.6	6	−8.3	498	
628		aq EtOH	40	1.6	6	−13.8	498	EtOH 10 mol %
629		aq EtOH	40	1.6	6	−20.3	498	EtOH 20 mol %
630		aq EtOH	40	1.6	6	−23.0	498	EtOH 30 mol %
631		aq EtOH	40	1.6	6	−17.5	498	EtOH 40 mol %
632		H_2O	30	1.6	6	−11.6	499	
633		aq EtOH	30	1.6	6	−17.6	499	EtOH 10 mol %
634		aq EtOH	30	1.6	6	−21.2	499	EtOH 20 mol %
635		aq EtOH	30	1.6	6	−15.0	499	EtOH 30 mol %
636		aq EtOH	30	1.6	6	−15.3	499	EtOH 40 mol %
637		H_2O	40	1.6	6	−11.2	499	
638		aq EtOH	40	1.6	6	−17.4	499	EtOH 10 mol %
639		aq EtOH	40	1.6	6	−21.4	499	EtOH 20 mol %
640		aq EtOH	40	1.6	6	−15.7	499	EtOH 30 mol %
641		aq EtOH	40	1.6	6	−15.3	499	EtOH 40 mol %
642		H_2O	2	1.6	6	−6.9	500	
643		aq EtOH	2	1.6	6	−10.8	500	EtOH 10 mol %
644		aq EtOH	2	1.6	6	−19.0	500	EtOH 20 mol %
645		aq EtOH	2	1.6	6	−20.5	500	EtOH 30 mol %
646		aq EtOH	2	1.6	6	−15.4	500	EtOH 40 mol %
647		H_2O	10	1.6	6	−7.5	500	
648		aq EtOH	10	1.6	6	−11.2	500	EtOH 10 mol %
649		aq EtOH	10	1.6	6	−20.0	500	EtOH 20 mol %
650		aq EtOH	10	1.6	6	−21.6	500	EtOH 30 mol %
651		aq EtOH	10	1.6	6	−16.2	500	EtOH 40 mol %
652		H_2O	30	1.6	6	−7.9	501	
653		aq EtOH	30	1.6	6	−14.4	501	EtOH 10 mol %
654		aq EtOH	30	1.6	6	−18.7	501	EtOH 20 mol %
655		aq EtOH	30	1.6	6	−21.7	501	EtOH 30 mol %
656		aq EtOH	30	1.6	6	−16.1	501	EtOH 40 mol %
657		H_2O	40	1.6	6	−8.4	501	
658		aq EtOH	40	1.6	6	−14.8	501	EtOH 10 mol %
659		aq EtOH	40	1.6	6	−19.3	501	EtOH 20 mol %
660		aq EtOH	40	1.6	6	−22.8	501	EtOH 30 mol %
661		aq EtOH	40	1.6	6	−16.7	501	EtOH 40 mol %
662		aq EtOH	25	1.5	7	−17.3	502	EtOH 80 vol %
663		aq EtOH	25	1.5	7	−18.4	502	EtOH 80 vol %

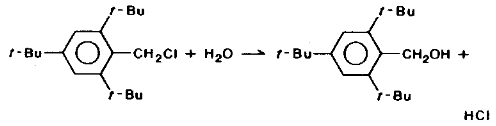
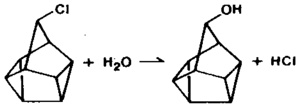
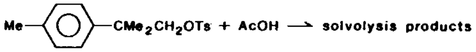
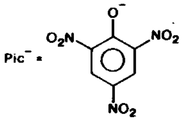
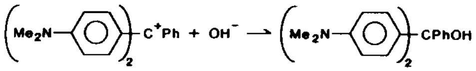
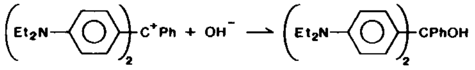
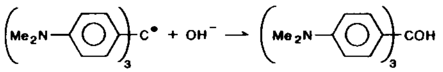
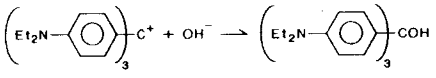
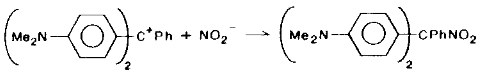
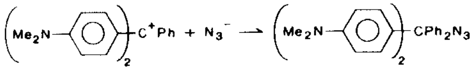
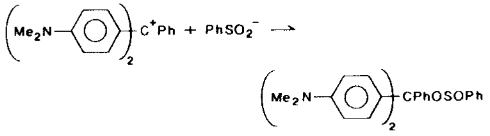
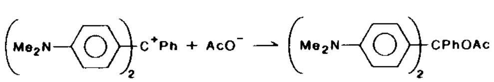
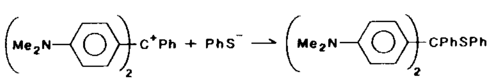
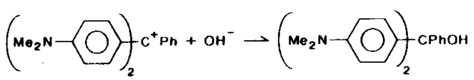
664		aq EtOH	25	1.5	7	−15.7	502	EtOH 80 vol %
665	$PhCH_2Cl + H_2O \rightarrow PhCH_2OH + HCl$	H_2O	30	6.9	20	−8.3	503	
666		aq EtOH	30	1	6	−19	504	EtOH 80 vol %
666b	*t*-BuCl + H_2O → solvolysis products	aq EtOH	30	1.1	6	−40	504	EtOH 80 vol %
667	*t*-BuCl + *t*-BuOH → solvolysis products	*t*-BuOH	40	0.5	5	−5	505	
668		*t*-BuOH	50	0.9	9	−5	505	
669	*t*-BuBr + *t*-BuOH → solvolysis products	*t*-BuOH	50	0.9	8	−23	505	
670	*i*-PrBr + ROH → solvolysis products	MeOH–EtOH	46	81	9	−30	506	$\Delta V^{\ddagger}$ = +0.9 at 70 kbar, EtOH 80 vol %
671	$PhC(Me)_2CH_2OTs$ + AcOH → solvolysis products	AcOH	65	1	6	−36.8	507	
672		AcOH	75	1	6	−31.5	497	
673		AcOH	85	1	6	−21.4	507	
674		AcOH	65	1	6	−26.9	507	
675		AcOH	75	1	6	−39.3	497	
676		AcOH	85	1	6	−21.6	507	
677	*n*-Bu_4N^+ + Pic^- → *n*-$Bu_4N^+Pic^-$	PhCl–PhH	25	0.7	6	+19.7	508	PhCl 30 vol %; for dissociation, $\Delta V^{\ddagger}$ = −32.3
678		PhCl–PhH	25	0.7	6	+18.0	508	PhCl 40 vol %; for dissociation, $\Delta V^{\ddagger}$ = −30.8
679		PhCl–PhH	25	0.7	6	+20.5	508	PhCl 50 vol %; for dissociation, $\Delta V^{\ddagger}$ = −30.6
680		H_2O	25	2.1	4	+30	509	in Dabco buffer
681		H_2O	25			−1	510	in Tris buffer (pH 8.0); uncorrected for ionization of water
682		H_2O	25	1	4	+4	510	in Tris buffer (pH 8.0), *j3*, *k3*
683		H_2O	25	1.5	5	+10	510	in Tris buffer (pH 8.0), *k3*, *l3*
684		H_2O	25			−1	510	in Tris buffer (pH 8.0); uncorrected for ionization of water
685		H_2O	25	1	4	+7	510	in Tris buffer (pH 8.0), *j3*, *m3*
686		H_2O	25	1	4	+8	510	in Tris buffer (pH 8.0), *l3*, *m3*
687		H_2O	25			0	510	in Tris buffer (pH 9.5); uncorrected for ionization of water
688		H_2O	25			−0.9	511	$[OH^-]$ = 0.0909 mol/L
689		H_2O	25	2	6	−6	510	in Tris buffer (pH 9.5), *j3*, *k3*

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/kbar	no. of k	$\Delta V^{\ddagger}$/(cm^3 mol^{-1})	ref	remarks
690		H_2O	25	1	4	+4	510	in Tris buffer (pH 9.5), *l3*, *n3*
691		H_2O	25			+2.9	511	*o3*
692		H_2O	25			+1.3	511	*o3*
693		H_2O	25	1.5	5	0	510	in Tris buffer (pH 9.5), *j3*, *p3*
694		H_2O	25	1.5	5	+3	510	in Tris buffer (pH 9.5), *l3*, *m3*
695		MeCN	51	1	3	−13.7	449	
696		$MeNO_2$	30	0.6	3	−12	449	
697		DMSO	30	0.9	3	−8	449	$\Delta V = +13$
698		$MeOCH_2CH_2OH$	50	0.8	3	0	449	$\Delta V = +10$ (40 °C)
699		MeOH	26	0.6	2	−16	449	$\Delta V = +28$ (24 °C)
700		aq MeOH	31	0.9	3	−8.4	449	MeOH 95% $\Delta V = +28$ (26 °C)
701		aq MeOH	35	0.9	3	−8.3	449	MeOH 90%, $\Delta V = +18$
702		aq MeOH	26	0.9	3	−11	449	MeOH 82.5%, $\Delta V = +30$
703		aq MeOH	26	0.9	3	−16	449	MeOH 80%, $\Delta V = +25$
704		MeOH	25	0.6	2	−20	449	$\Delta V = +18$
705		DMSO	43	0.8	2	−6	449	
706		MeOH	22	0.6	3	−4	449	$\Delta V = +20$ (20 °C)
707		DMSO	23	0.8	2	−4	449	
708		$MeOCH_2CH_2OH$	38	0.9	3	−5.6	449	
709		MeOH	22			0	449	$\Delta V = +15$ (21 °C)
710		MeOH	26			−7		$\Delta V = +12$
711		$MeOCH_2CH_2OH$	43			−18	449	
712		H_2O	24			−8.5	449	
713	$PhN_2^+ + N_3^- \rightarrow PhN{=}NN_3$	H_2O	25	1	5	+2.2	512	
714	$PhN_2^+ + HSO_3^- \rightarrow PhN{=}NSO_3H$	H_2O	25	1	5	−9.1	512	
715	$PhN_2^+ + SO_3^{2-} \rightarrow PhN{=}NSO_3^-$	H_2O	25	1	5	−8.9	512	
716	$p\text{-}O_2NC_6H_4N{=}N^+ + PhSO_2^- \rightarrow p\text{-}O_2NC_6H_4N{=}NSO_2Ph$	H_2O	25	1	5	−1.7	512	
717	$p\text{-}MeOC_6H_4N{=}N^+ + p\text{-}O_2NC_6H_4COO^- \rightarrow MeOC_6H_4N{=}NOCOC_6H_4NO_2$	DMSO	30	0.9	4	−15.0	512	
718	$n\text{-}PrBr + I^- \rightarrow n\text{-}PrI + Br^-$	$MeCOCH_2\text{-}i\text{-}Pr$	25	1.7	8	+14	513	$\Delta V = -5.6$, *c3*, *q3*
719		acetone	25	2.8	8	−3.8	513	$\Delta V = +3.3$, *c3*, *q3*
720		MeCN	25	1	3	−6.2	513	$\Delta V = +2.1$, *c3*, *q3*
721		sulfolane	40	0.6	5	−11.6	513	$\Delta V = -3.7$, *c3*, *q3*
722		propylene carbonate	25	1.7	8	−10.4	513	$\Delta V = -4.0$, *c3*, *q3*

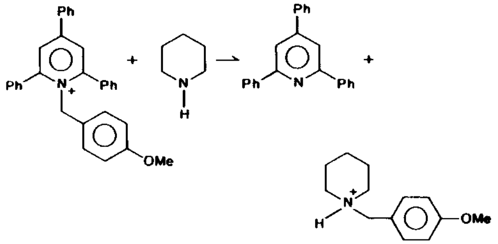
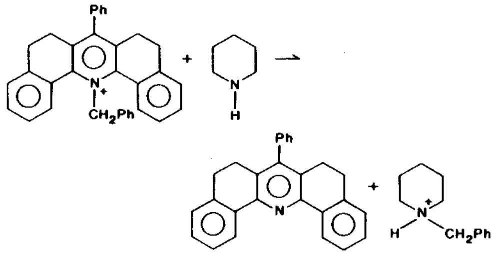
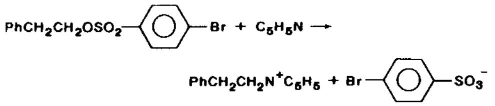
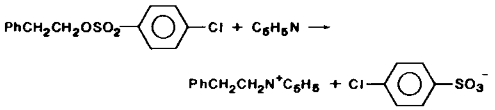
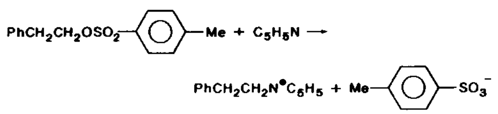
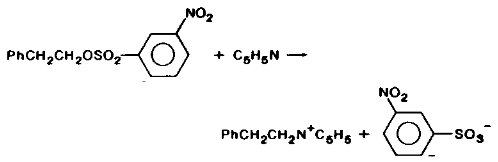
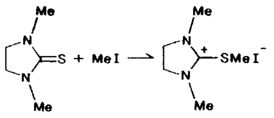
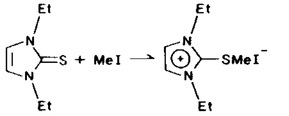
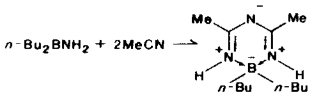
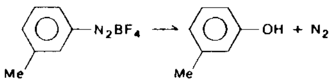
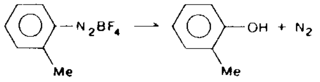
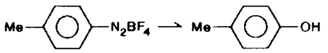
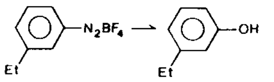
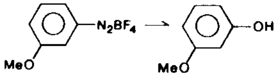
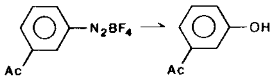
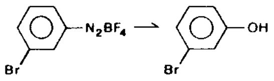
723		EtOH	50	6.3	10	−18	513	$\Delta V = -3.5$ (25 °C), *c3*, *q3*
724		MeOH	50	2.6	8	−14	513	$\Delta V = -1.7$ (25 °C), *c3*, *q3*
725		HCONHMe	50	2.1	6	−17	513	$\Delta V = -3.5$ (25 °C), *c3*, *q3*
726		PhCl	30			+18.9	514	
727		PhCl	30	1.8	21	+22	514	$\Delta V^{\ddagger} = -20$ at 1 kbar
728	$PhCOCH_2Br + C_5H_5N \rightarrow PhCOCH_2NC_5H_5^+ + Br^-$	acetone	25	2.5	6	−15.4	515	
729		acetone	30	2.5	6	−16.6	515	
730		acetone	35	2.5	6	−20.5	515	
731		acetone	40	2.5	6	−21.9	515	
732		MeCN	40	1	3	−12.3	516	
733		MeCN	50	1.5	4	−10.3	516	
734		MeCN	60	1.5	4	−9.6	516	
735		MeCN	50	2	5	-9.2^{n2}	517	
736	$PhCH_2CH_2OSO_2Ph + C_5H_5N \rightarrow PhCH_2CH_2NC_5H_5^+ + PhSO_3^-$	MeCN	50	2	5	-11.4^{n2}	517	
737		MeCN	50	2	5	-12.8^{n2}	517	
738		MeCN	40	2	5	−13.9	518	
739		MeCN	50	2	5	−12.8	518	
740		MeCN	60	2	5	−12.6	518	
741	$PhCH_2OSO_2Ph + C_5H_5N \rightarrow PhCH_2NC_5H_5^+ + PhSO_3^-$	acetone	20	2	4	−20.9	519	
742		acetone	25	2	4	−16.9	519	
743		acetone	30	2	4	−14.4	519	
744		acetone	40	2	4	−13.0	519	

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
745	$Et_3N + MeI \rightarrow Et_3NMe^+I^-$	MeCN	30			-28.2	520	ΔV = -63.1[c3]
746		propylene carbonate	30			-25.8	520	ΔV = -36.2[c3]
747	$Ph_3P + MeI \rightarrow Ph_3PMe^+I^-$	MeCN	30			-28.0	520	ΔV = -49.8[c3]
748		propylene carbonate	30			-17.6	520	ΔV = -28.2[c3]
749		DMF	30			-21.7	520	ΔV = -39.3[c3]
750		DMA	30			-21.8	520	ΔV = -41.4[c3]
751	$Me_2NCSNMe_2 + MeI \rightarrow (Me_2N)_2CSMe^+I^-$	MeCN	30			-22.0	521	ΔV = -37.4[c3]
752		propylene carbonate	30			-17.4	521	ΔV = -21.1[c3]
753		MeCN	30			-23.6	522	ΔV = -42.7[c3]
754		propylene carbonate	30			-16.9	522	ΔV = -22.3[c3]
755		MeCN	30			-21.8	523	ΔV = -40.3[c3]
756		propylene carbonate	30			-16.4	523	ΔV = -21.9[c3]
757		DMA	30			-16.7	523	ΔV = -30.7[c3]
758		none	160	9.8	7	-30	524	P > 1 kbar
759	$PhN_2BF_4 \rightarrow PhOH + N_2$	H_2O	25	2	5	+10.6	525	[HCl] = 0.001 mol/L
760		H_2O	40	2	5	+10.9	525	[HCl] = 0.001 mol/L
761		H_2O	25	2	5	+10.8	525	[HCl] = 0.001 mol/L
762		H_2O	25	2	5	+10.9	525	[HCl] = 0.001 mol/L
763		H_2O	40	2	5	+10.8	525	[HCl] = 0.001 mol/L
764		H_2O	55	2	5	+11.0	525	[HCl] = 0.001 mol/L
765		H_2O	25	2	5	+10.5	525	[HCl] = 0.001 mol/L
766		H_2O	25	2	5	+10.9	525	[HCl] = 0.001 mol/L
767		H_2O	35	2	5	+11.0	525	[HCl] = 0.001 mol/L
768		H_2O	45	2	5	+10.7	525	[HCl] = 0.001 mol/L
769		H_2O	55	2	5	+10.8	525	[HCl] = 0.001 mol/L

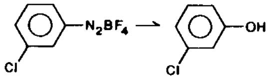
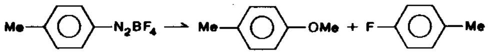
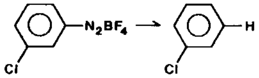
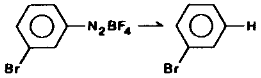
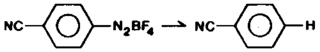
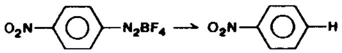
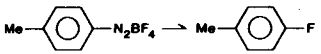
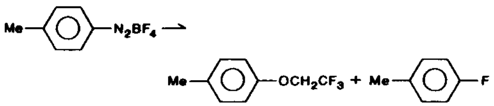
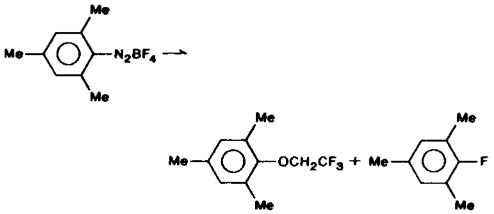
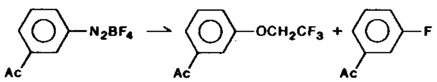
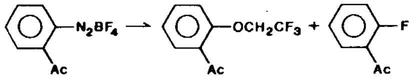
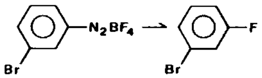
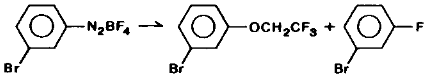
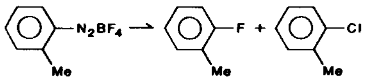
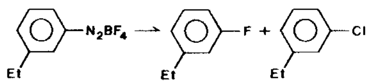
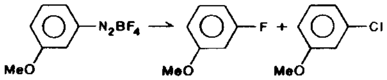
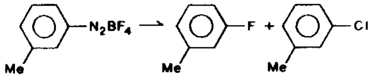
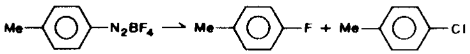
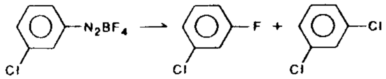
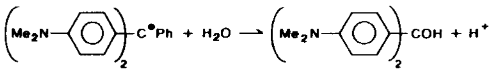
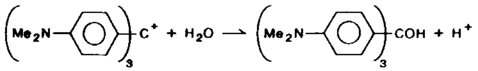
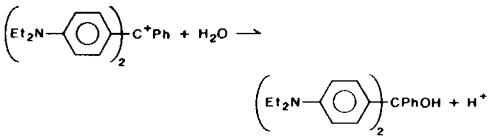
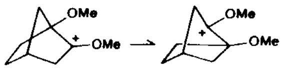
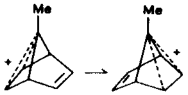
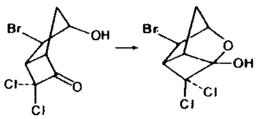
770		H_2O	55	2	5	+10.8	525	[HCl] = 0.001 mol/L
771	$PhN_2BF_4 \rightarrow PhOMe + PhF + N_2$	MeOH	30	2	5	+12.9	526	$[H_2SO_4]$ = 0.001 mol/L
772		MeOH	45	2	5	+13.2	526	$[H_2SO_4]$ = 0.001 mol/L
773		MeOH	50	2	5	+5.3	527	$[H_2SO_4]$ = 0.001 mol/L
774		MeOH	45	2	5	+4.7	527	$[H_2SO_4]$ = 0.001 mol/L
775		MeOH	50	2	5	+6.0	527	$[H_2SO_4]$ = 0.001 mol/L
776		MeOH	50	2	5	+5.4	527	$[H_2SO_4]$ = 0.001 mol/L
777	$PhN_2BF_4 \rightarrow PhOCH_2CF_3 + PhF + N_2$	CF_3CH_2OH	30	2	5	+16.1	526	
778		1,4-dioxane	55	2	5	+9.2	526	
779		CF_3CH_2OH	45	2	5	+16.9	526	
780		CF_3CH_2OH	25	0.3	5	+11.1	528	
781		CF_3CH_2OH	30	2	5	+16.8	526	
782		CF_3CH_2OH	55	2	5	+16.3	526	
783		1,4-dioxane	60	2	5	+8.5	526	
784		CF_3CH_2OH	45	2	5	+16.8	526	
785		CH_2ClCH_2Cl	22	2	5	+8.3	529	

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
786		CH_2ClCH_2Cl	22	2	5	+8.2	529	
787		CH_2ClCH_2Cl	22	2	5	+8.2	529	
788		CH_2ClCH_2Cl	25	2	5	+8.3	529	
789	$PhN_2BF_4 \rightarrow PhF + PhCl$	CH_2ClCH_2Cl	35	2	5	+8.4	529	
790		CH_2ClCH_2Cl	40	2	5	+8.8	529	
791		CH_2ClCH_2Cl	50	2	5	+8.8	529	
792		CH_2ClCH_2Cl	55	2	5	+8.6	529	
793		CH_2ClCH_2Cl	55	2	5	+8.2	529	
794	$PhNN^+BF_4^- \rightarrow PhH + PhF + PhCl$	CH_2ClCH_2Cl	50	2	5	$+15.3^{r3}$	530	in the presence of pentaglyme
795		CH_2ClCH_2Cl	50	2	5	$+15.8^{r3}$	530	in the presence of PEG 1000
796		CH_2ClCH_2Cl	50	2	5	$+15.6^{r3}$	530	in the presence of PEG 2000
797		CH_2ClCH_2Cl	60	2	5	$+15.2^{r3}$	530	in the presence of 18-crown-6
798		H_2O	25	2.1	4	-12	509	in Dabco buffer
799		H_2O	25			-11	510	in Tris buffer (pH 8.0)
800		H_2O	25			-15	510	in Tris buffer (pH 9.5)
801		H_2O	25			-12	510	in Tris buffer (pH 9.5)
802		FSO_3H	4	2	9	+8.7	531	
803		FSO_3H	-23	2		0	532	
804		DMSO–$CDCl_3$	28	2	3		533	DMSO 20 wt % ΔV = -3.2

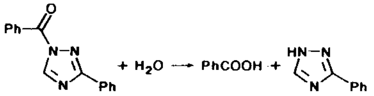
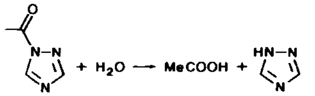
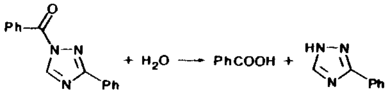
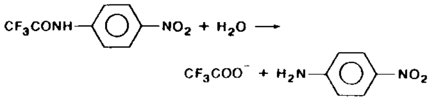
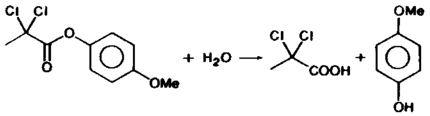
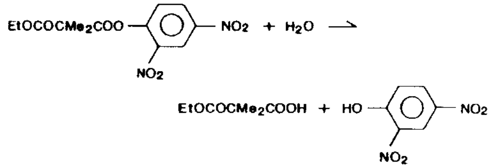
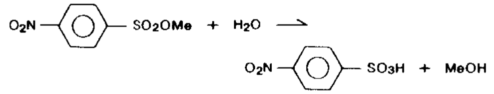
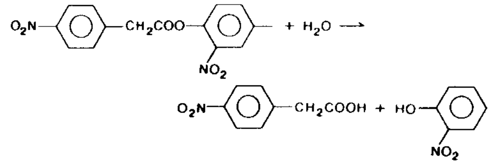
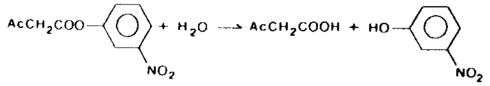
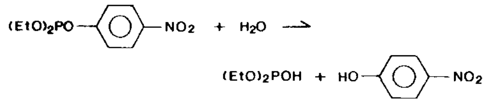
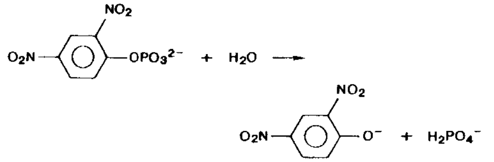
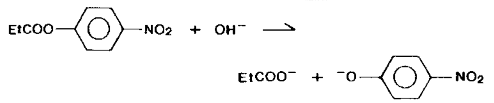
805	MeCOCN + $PhCH_2SH \rightarrow$ MeC(OH)(CN)SCH_2Ph	$CDCl_3$	30	1.2	5		533	$\Delta V = -13.0$
806	PhCOCl + $H_2O \rightarrow$ PhCOOH + HCl	aq acetone	15	2.5	6	−17.4	534	acetone 95 wt %
807		aq acetone	15	2.5	6	−18.2	534	acetone 90 wt %
808		aq acetone	20	2.5	6	−17.2	534	acetone 95 wt %
809		aq acetone	20	2.5	6	−17.7	534	acetone 90 wt %
810		aq acetone	25	2.5	6	−16.8	534	acetone 95 wt %
811		aq acetone	25	2.5	6	−17.0	534	acetone 90 wt %
812		aq acetone	30	2.5	6	−16.7	534	acetone 95 wt %
813		aq acetone	30	2.5	6	−16.8	534	acetone 90 wt %
814		H_2O	25			−17.2	535	4 mol % D-glucose
815		H_2O	25	2		−17.9	536	
816		aq *t*-BuOH	25	2		−17.5	536	H_2O 95 mol %
817		aq MeCN	25	2		−20.5	536	H_2O 85 mol %
818		H_2O	25	2		−15.8	536	
819		aq *t*-BuOH	25	2		−30.3	536	H_2O 95 mol %
820		aq MeCN	25	2		−28.1	536	H_2O 85 mol %
821		H_2O	25	2	5	−25	537	*s3*, *t3*
822		H_2O	25	2	5	−18	537	*u3*, *v3*
823		H_2O	25	2	7	−32	538	
824		aq *t*-BuOH	25	2	7	−63	538	H_2O 95 mol %
825		aq *t*-BuOH	25	2	6	−69	538	H_2O 92.5 mol %
826		aq *n*-butyl-cellosolve	25	2	7	−77	538	H_2O 98 mol %
827	AcOMe + $H_2O \rightarrow$ AcOH + MeOH	H_2O	40	1.6	4	−9.3	539	HCl catalyzed
828		H_2O	40	2.1	4	−5.9	539	catalyzed by fully sulfonated polystyrene
829		H_2O	40	2.1	3	−2.7	539	catalyzed by 60% sulfonated polystyrene
830		H_2O	40	1.1	3	−32	539	*w3*
831		H_2O	40	1.1	3	−41	539	*x3*
832		H_2O	40	2	5	−5.3	540	*y3*
833	AcOEt + $H_2O \rightarrow$ AcOH + EtOH	H_2O	40	1.6	4	−9.4	539	HCl catalyzed
834		H_2O	40	2.1	5	−0.8	539	catalyzed by fully sulfonated polystyrene
835		H_2O	40	2.1	5	+3.7	539	catalyzed by 60% sulfonated polystyrene
836		H_2O	40	1.1	3	−28	539	*w3*
837		H_2O	40	1.1	3	−37	539	*x3*
838		H_2O	40	2	5	+0.4	540	*y3*, $\Delta V^{\ddagger} < 0$ at $P > 1$ kbar
839	AcO-*n*-Pr + $H_2O \rightarrow$ AcOH + *n*-PrOH	H_2O	40			−9.0	540	HCl catalyzed
840		H_2O	40	2	5	+9.7	540	*y3*, $\Delta V^{\ddagger} < 0$ at $P > 1$ kbar
841	AcO-*n*-Bu + $H_2O \rightarrow$ AcOH + *n*-BuOH	H_2O	40	1.6	5	−7.9	539	HCl catalyzed

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
842		H_2O	40	1.8	5	+2.1	539	catalyzed by fully sulfonated polystyrene
843		H_2O	40	1.8	5	+7.6	539	catalyzed by 60% sulfonated polystyrene
844		H_2O	40	1.1	3	−15	539	*w3*
845		H_2O	40	1.1	3	−30	539	*x3*
846		H_2O	40	2	5	+20	540	*y3*, $\Delta V^{\ddagger} < 0$ at $P > 1$ kbar
847		H_2O	40	2	5	−4	541	catalyzed by Dowex 50W-X2
848	$CCl_3COOEt + H_2O \rightarrow CCl_3COOH + EtOH$	H_2O	25	2.1	7	−33	542	no catalyst used, [MeCN] = 0.02 mol/L, [NaClO$_4$] = 0.2 mol/L
849			23	0.6	4	−21.4	543	
850		H_2O	25	2.1	7	−24	542	$\Delta V^{\ddagger}$ = −6.3 at above 0.15 kbar [NaClO$_4$] = 0.2 mol/L
851		aq acetone	24	0.7	4	−20.7	543	acetone 43 vol %, pH 7.5
852		aq acetone	30	0.7	4	+8.7	543	acetone 86 vol %, pH 4.6
853		aq EtOH	25	1	6	−16	544	EtOH 50 vol %
854		H_2O	43	4	19	−4.8	545	pH 12
855		H_2O	25	2	5	−13.1^{z3}	546	*a4*, *b4*

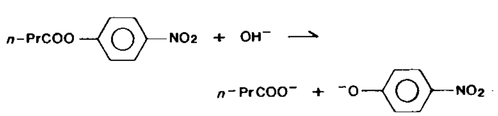
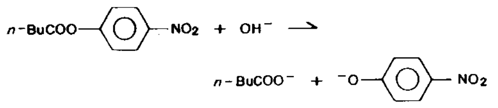
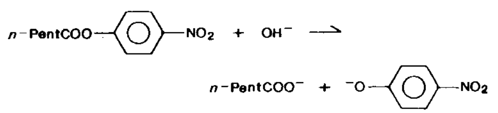
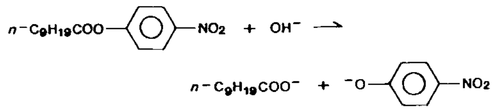
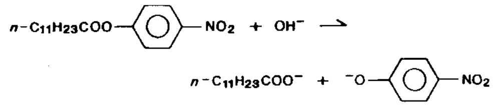
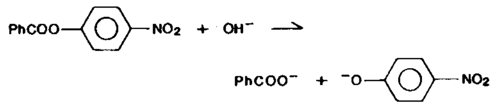
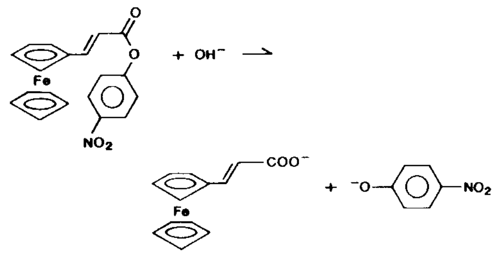
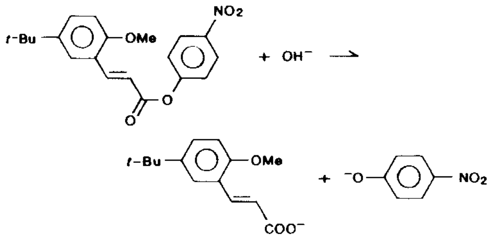
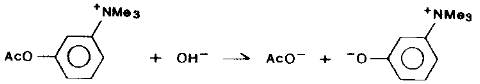
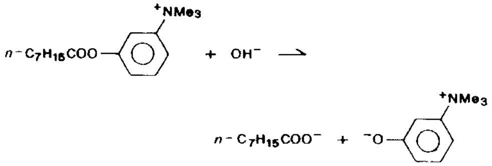
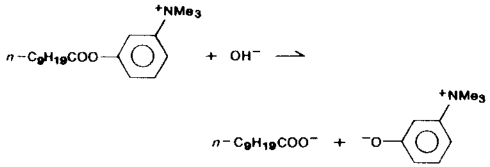
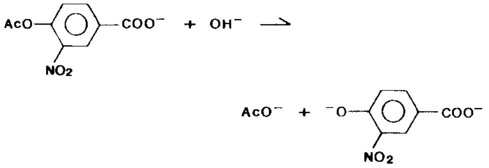
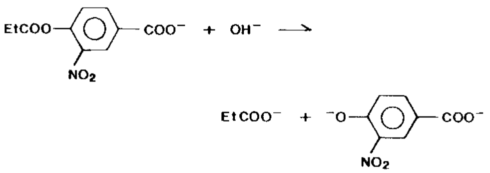
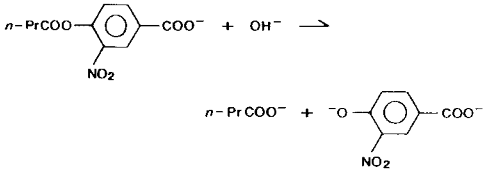
856		H_2O	25	2	5	−3	546	in Tris buffer (pH 8.3) hydroxide ion catalyzed
857		H_2O	25	2	5	−18	546	in Tris buffer (pH 8.3) Tris catalyzed
858		H_2O	25	2	5	-18.2^{z3}	546	*a4*, *c4*, *d4*
859		H_2O	25	1.8	7	−5	547	*e4*
860		H_2O	25	1.8	7	−8	547	*e4*, *f4*
861		H_2O	25	1.8	7	−2	547	*e4*, *g4*
862		H_2O	25	2	5	-21.6^{z3}	546	*a4*, *h4*
863		H_2O	25	1.5	4	−24.5	548	*i4*
864		H_2O	25	1.5	4	−23	548	*j4*
865		H_2O	25	1.5	4	−11	548	*k4*
866		H_2O	25	1.5	4	−29	548	*l4*
867		H_2O	25	1.5	4	−8	548	*m4*
868		H_2O	25	1	3	−27	548	*n4*
869		H_2O	25	1	3	−5	548	*o4*
870		H_2O	25	2	5	-17.0^{z3}	546	*a4*, *p4*
871		H_2O	25			0	548	*i4*
872		H_2O	25	1.5	4	−24		*j4*
873		H_2O	25	1.5	4	−20	548	*k4*
874		H_2O	25	1.5	4	−12	548	*l4*
875		H_2O	25	1.5	4	−35	548	*m4*
876		H_2O	25	1.5	4	−19	548	*q4*
877		H_2O	25	1	3	−12	548	*n4*
878		H_2O	25	1	3	−70	548	*o4*
879		H_2O	25	1	3	−18	548	*r4*
880		aq EtOH	25			−11	547	*e4*, EtOH 10%
881		aq EtOH	25			−13	547	*e4*, *f4*, EtOH 10%
882		aq EtOH	25			−7	547	*e4*, *g4*, EtOH 10%
883		aq acetone	30	0.9	4	−21.4	543	acetone 43 vol %, pH 10.1
884		aq $CH_2(OH)CH_2OH$	30	1.8	6	−12.8	549	ethylene glycol 50 vol %, *s4*
885		aq $CH_2(OH)CH_2OH$	30	1.8	6	+1	549	ethylene glycol 50 vol %, *s4*, *t4*

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^\ddagger$/ (cm^3 mol^{-1})	ref	remarks
886		aq $CH_2(OH)CH_2OH$	30	1.8	9	+21	549	ethylene glycol 50 vol %, *u4*
887		H_2O	25			−5	547	*e4*
888		H_2O	25			−9	547	*e4*, *f4*
889		H_2O	25			−4	547	*e4*, *g4*
890		H_2O	25			−7	547	*e4*
891		H_2O	25			−8	547	*e4*, *f4*
892		H_2O	25			−3	547	*e4*, *g4*
893		H_2O	25			−7	547	*e4*
894		H_2O	25			−10	547	*e4*, *f4*
895		H_2O	25			−5	547	*e4*, *g4*
896		H_2O	25	2	5	−5	550	in Tris buffer (pH 8.7) hydroxide ion catalyzed
897		H_2O	25	2	5	−16	550	in Tris buffer (pH 8.7) Tris catalyzed
898		H_2O	25	2	5	-20.6^{n2}	550	*v4*, *w4*, *x4*
899		H_2O	25	2	5	-21.7^{n2}	550	*y4*
900		H_2O	25	2	5	-22.5^{n2}	550	*v4*, *z4*
901		H_2O	25	2	5	-22.8^{n2}	550	*y4*
902		H_2O	25	2	5	-22.0^{n2}	550	*v4*, *a5*

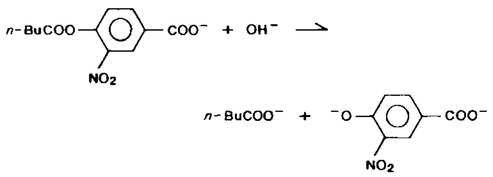
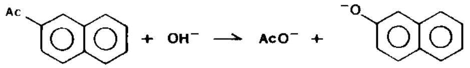
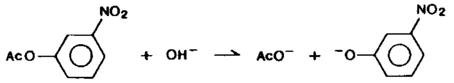
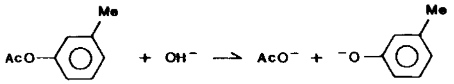
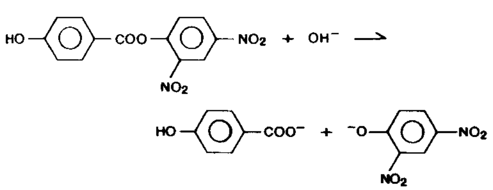
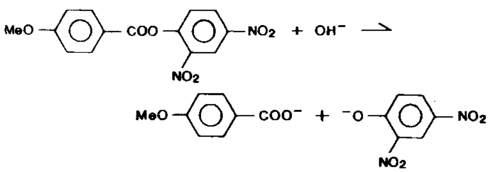
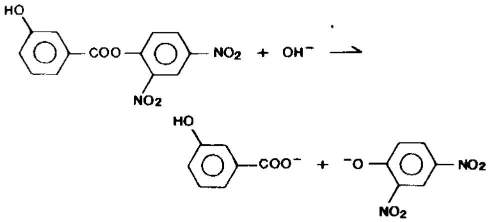
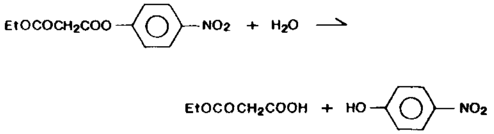
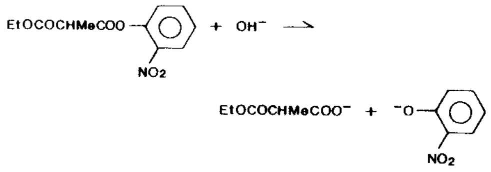
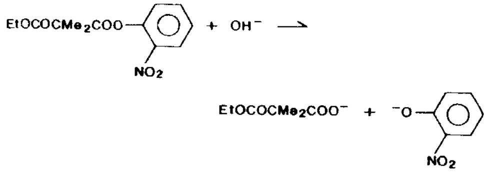
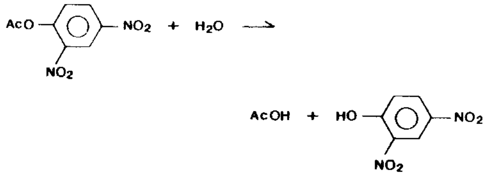
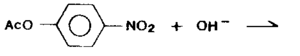
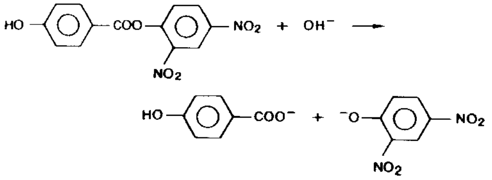
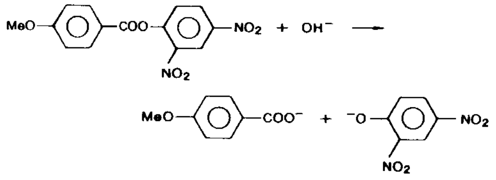
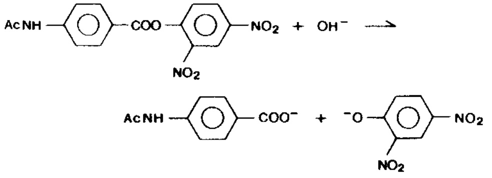
903		H_2O	25	2	5	-21.9^{n2}	550	*y4*
904		H_2O	25	2	5	-24.2^{n2}	550	*v4*, *b5*
905		H_2O	25	1.3	4	−17.5	551	*c5*, *d5*
906		H_2O	25	2	5	−13	551	*e5*, *f5*
907		H_2O	25	1.5	5	−4	552	in Tris buffer (pH 7.0)
908		H_2O	25	1.5	5	−9	552	*g5*, *h5*
909		H_2O	25	2	5	−5	552	in Tris buffer (pH 8.3)
910		H_2O	25	2	5	−12	552	*i5*, *j5*
911		H_2O	25	2	5	−4	552	in Tris buffer (pH 9)
912		H_2O	25	2	5	−17	552	*k5*, *l5*
913		H_2O	29	0.9	4	+16.5	543	pH 8.0
914		aq acetone	30	0.9	4	+7.1	543	acetone 43 vol %, pH 10.1
915		aq acetone	30	0.9	4	−17.9	543	acetone 43 vol %, pH 12.5
916		aq acetone	30	0.9	4	−19.2	543	acetone 43 vol %, pH 10.3
917		aq acetone	29	0.9	4	−14.8	543	acetone 43 vol %, pH 10.7
918		H_2O	31	0.9	4	+10.0	543	pH 5.8

TABLE VII (Continued)

no.	reaction	solvent	$T/°C$	$P/$ kbar	no. of k	$\Delta V^{\ddagger}/$ (cm^3 mol^{-1})	ref	remarks
919		H_2O	23	0.9	4	+9.7	543	pH 8.0
920		aq acetone	30	0.9	4	−19.6	543	acetone 43 vol %, pH 11.3
921		H_2O	28	0.9	4	−19.7	543	pH 4.75
922		H_2O	25			−3	547	*e4*
923		H_2O	25			−8	547	*e4*, *f4*
924		H_2O	25			−3	547	*e4*, *g4*
925		H_2O	25	2	5	-18.7^{z3}	546	*a4*, *m5*
926		H_2O	25	2	5	−16	551	*i5*, *n5*
927		H_2O	25	2	7	−13	551	*n5*, *o5*
928		aq acetone	28	0.9	4	+12	553	pH 8.0, acetone:H_2O = 4:5 v/v
929		aq acetone	30	0.9	4	−14	553	pH 10.3, acetone:H_2O = 4:5 v/v
930		aq acetone	27	0.7	4	−17.3	543	acetone 43 vol %, pH 9.8

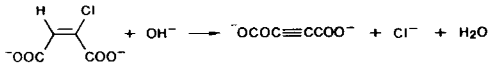
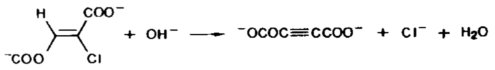
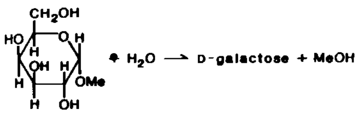
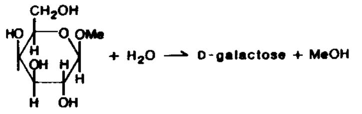
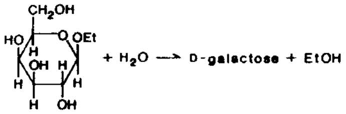
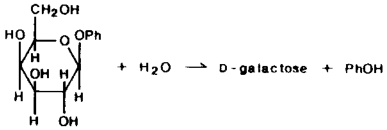
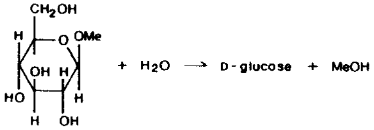
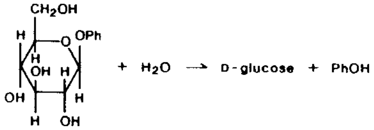
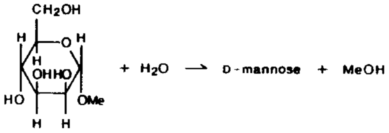
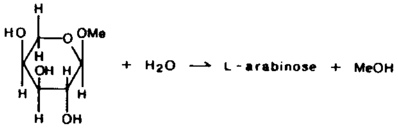
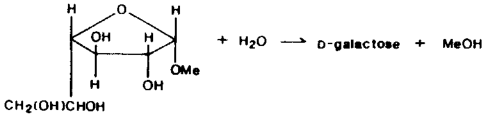
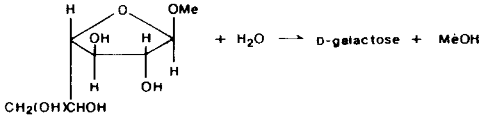
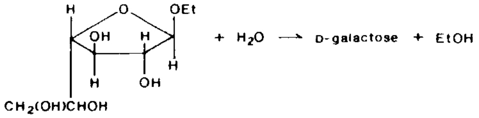
931	$PhCH_2COOEt + MeO^- \rightarrow PhCH_2COOMe + EtO^-$	MeOH	24	1.1	4	−12	554	
932	$BrCH_2CH_2SO_3^- + OH^- \rightarrow CH_2{=}CHSO_3^- + Br^- + H_2O$	H_2O	10	1	5	−6.3	555	
933		H_2O	25	1	5	−5.3	555	
934		aq MeOH	25	1	5	−3.6	555	MeOH 60 wt %
935		H_2O	70			−2.5	556	ionic strength 0.218 mol/L
936		H_2O	80	2.1	3	−4.0	556	ionic strength 0.138 mol/L
937		H_2O	90	2.1	3	−3.8	556	ionic strength 0.138 mol/L
938		H_2O	60	1.4	5	−6.8	556	ionic strength 0.138 mol/L
939		H_2O	70	1.4	5	−6.0	556	ionic strength 0.138 mol/L
940		H_2O	70			−7.5	556	ionic strength 0.218 mol/L
941		H_2O	80	1.4	5	−8.3	556	ionic strength 0.138 mol/L
942	$CH_2{=}CHCN + CH_3CHO \rightarrow CH_2{=}C(CN)CH(Me)OH$	none		0.7	4	−79	557	Et_3N catalyzed
943	$Ph_2CN_2 + PhCOOH \rightarrow Ph_2CHOCOPh + N_2$	Bu_2O	27.5	1.1	5	−13	558	
944	$Ph_2CN_2 + PhCOOD \rightarrow Ph_2CDOCOPh + N_2$	Bu_2O	27.5	1.1	5	−13	558	
945	α-D-glucopyranose → β-D-glucopyranose	H_2O	25	1.1	3	−11.7	559	in acetate buffer (pH 4.75)
946	β-D-glucopyranose → α-D-glucopyranose	H_2O	25	1.1	3	−10.8	559	in acetate buffer (pH 4.75)
947	α-D-glucopyranose → β-D-glucopyranose	H_2O	20	1.5	3	−10.7	560	$[NaClO_4] = 2$ mol/L (pH 4.4)
948	β-D-glucopyranose → α-D-glucopyranose	H_2O	20	1.5	3	−10.0	560	$[NaClO_4] = 2$ mol/L (pH 4.4)
949	α-D-glucopyranose → β-D-glucopyranose	H_2O	20[p5]	2.1	6	−0.9	560	$[NaClO_4] = 2$ mol/L, $[Cu(ClO_4)_2] = 0.05$ mol/L (pH 2.95); Cu^{2+}-catalyzed route[q5]
950	α-D-glucopyranose → β-D-glucopyranose	H_2O	1	2	2	−1.4	560	$[NaClO_4] = 2$ mol/L, $[Cu(ClO_4)_2] = 0.05$ mol/L (pH 2.95); Cu^{2+}-catalyzed route[q5]
951	α-D-glucopyranose → β-D-glucopyranose	H_2O	20[p5]	2.1	4	+3.4	560	$[NaClO_4] = 2$ mol/L, $[Cu(ClO_4)_2] = 0.05$ mol/L (pH 4.4);[q5] $Cu[Cu(OH)_2]_2{}^+$-catalyzed route
952		H_2O			2	+5.4	561	$[HClO_4] = 2$ mol/L
953		H_2O			2	+4.9	561	$[HClO_4] = 2$ mol/L

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^\ddagger$/ (cm^3 mol^{-1})	ref	remarks
954	 + H_2O → D-galactose + EtOH	H_2O			2	+5.0	561	[$HClO_4$] = 2 mol/L
955	 + H_2O → D-galactose + PhOH	H_2O			2	0	561	[$HClO_4$] = 2 mol/L
956	 + H_2O → D-glucose + MeOH	H_2O			2	+6.2	561	[$HClO_4$] = 2 mol/L
957	 + H_2O → D-glucose + PhOH	H_2O			2	+2.9	561	[$HClO_4$] = 2 mol/L
958	 + H_2O → D-mannose + MeOH	H_2O			2	+3.6	561	[$HClO_4$] = 2 mol/L
959	 + H_2O → L-arabinose + MeOH	H_2O			2	+6.1	561	[$HClO_4$] = 2 mol/L
960	 + H_2O → D-galactose + MeOH	H_2O			2	−3.6	561	[$HClO_4$] = 2 mol/L
961	 + H_2O → D-galactose + MeOH	H_2O	39	2.1	9	−3.9	561	[$HClO_4$] = 2 mol/L
962	 + H_2O → D-galactose + EtOH	H_2O			2	−4.4	561	[$HClO_4$] = 2 mol/L

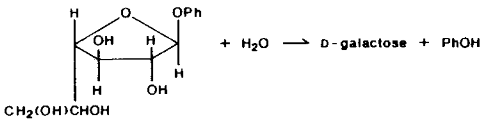
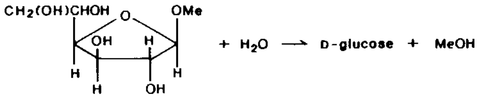
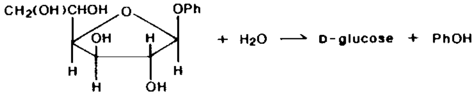
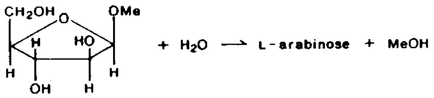
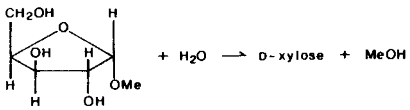
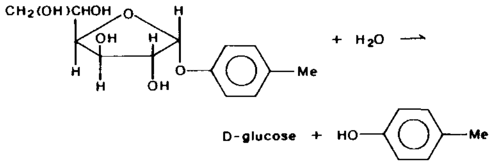
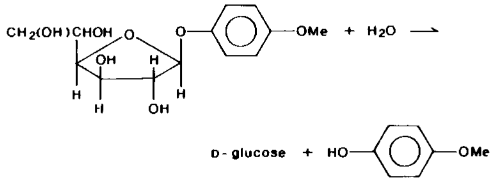
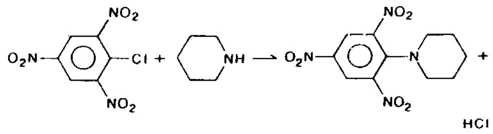
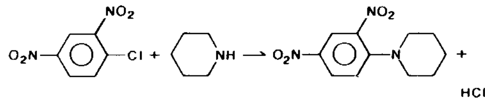
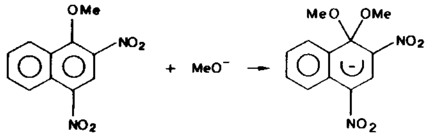
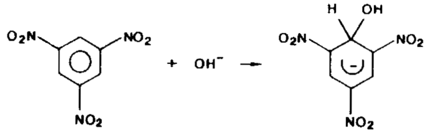
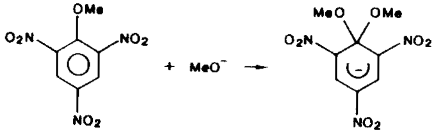
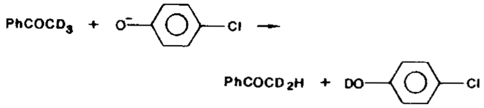
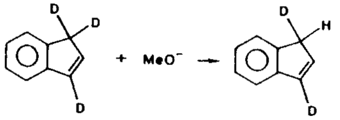
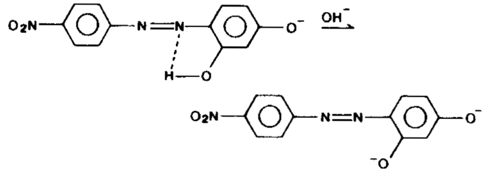
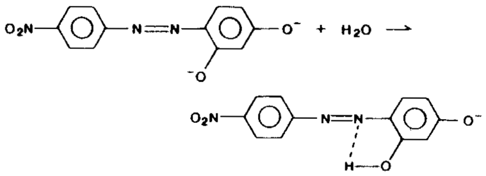
963		H_2O			2	+1.3	561	$[HClO_4]$ = 2 mol/L
964		H_2O			2	−3.5	561	$[HClO_4]$ = 2 mol/L
965		H_2O			2	+3.8	581	$[HClO_4]$ = 2 mol/L
966		H_2O			2	−2.0	581	$[HClO_4]$ = 2 mol/L
967		H_2O			2	−4.6	581	$[HClO_4]$ = 2 mol/L
968		H_2O			2	+3.4	561	$[HClO_4]$ = 2 mol/L
969		H_2O			2	+3.5	561	$[HClO_4]$ = 2 mol/L
970		aq EtOH	25	1.7	6	−20.7	562	EtOH 80 vol %
971		aq EtOH	30	1.7	6	−35.0	562	EtOH 80 vol %
973		MeOH	25	1.5	4	−13.2	563	$\Delta V = -4.3$ from $\Delta V^{\ddagger}$ for the reverse reaction

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
974		H_2O	25		4	+1.1	563	ΔV = +10.0 from $\Delta V^{\ddagger}$ for the reverse reaction
975		MeOH	25	1	5	−7.2	54, 563	ΔV = −5.2
976	$CDCl_3 + OH^- \rightarrow CHCl_3 + DOH$	H_2O	26	1.3	5	+9	554	
977	$CDF_3 + OH^- \rightarrow CHF_3 + DOH$	H_2O	65	1.3	5	+3	554	
978	$PhCOCD_3 + OH^- \rightarrow PhCOCD_2H + DOH$	H_2O	27	1.2	2	−1	554	
979	$PhCOCD_3 + EtO^- \rightarrow PhCOCD_2H + EtOD$	EtOH	20	1.1	2	−1	554	
980		aq MeOH	101	1.1	3	−5	554	
981	$PhCD_2CN + AcO^- \rightarrow PhCHDCN + AcOD$	MeOH	49	1.3	3	−4	554	
982	$PhCD_2COOMe + MeO^- \rightarrow PhCHDCOOMe + MeOD$	MeOH	28	1.2	3	−3	554	
983	$CD_3SOCD_3 + OH^- \rightarrow CHD_2SOCD_3 + DOH$	H_2O	71	1.3	2	+2	554	
984		MeOH	30	1.3	4	−4	554	
985	$PhC{\equiv}CD + OH^- \rightarrow PhC{\equiv}CH + HOD$	aq MeOH	27	1.3	4	−1	554	MeOH 60%, Tris buffer
986	$Ph_2CD_2 + MeO^- \rightarrow Ph_2CHD + MeOD$	MeOH–DMSO	109	1.3	2	−3	554	MeOH 75%
987	$Me_2CDNO_2 + AcO^- \rightarrow Me_2CHNO_2 + AcOD$	H_2O	65	1.3	2	−1	554	
988	$PhCH_2CN + MeOD \rightarrow PhCHDCN + MeOH$	MeOD	30	2.9	4	+24	564	MeO^- catalyzed
989	$PhCH_2CN + MeOH \rightarrow PhCH_2C(OMe){=}NH$	MeOH	40	2.9	4	−13.1	564	MeO^- catalyzed
990		H_2O	10	2	5	−3.9	565	ΔV = +0.3
991		H_2O	10	2	5	−3.1	565	

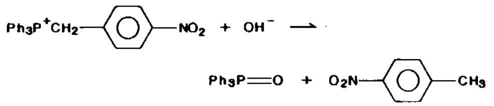
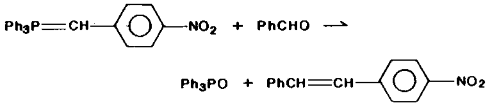
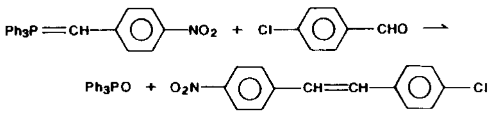
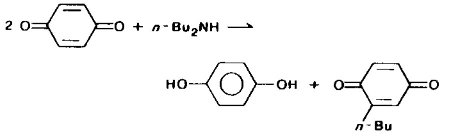
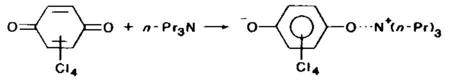
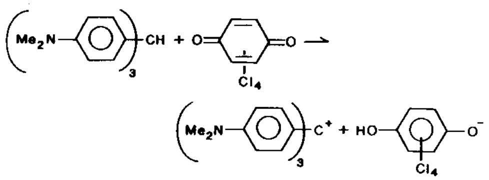
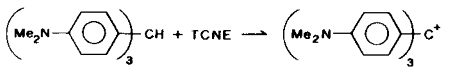
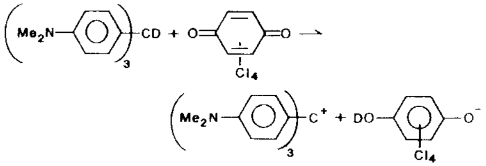
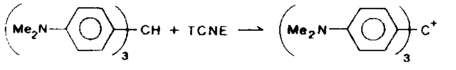
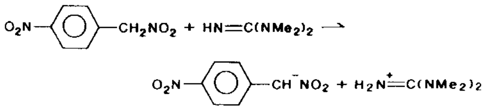
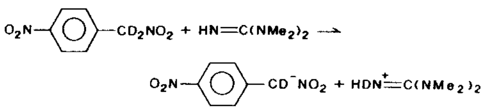
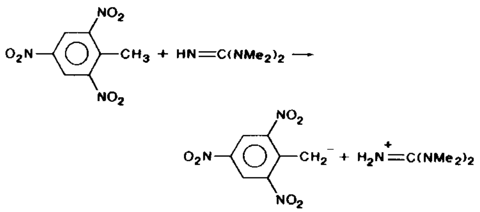
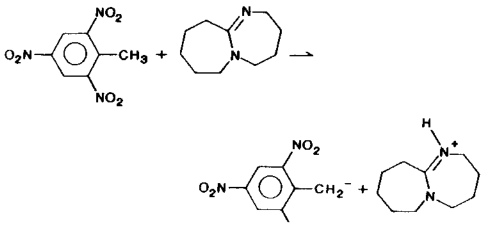
992	$HCOO^- + D_2O \rightarrow DCOO^- + HDO$	D_2O	180	8	4	−2.8	566	
993		D_2O	190	8	4	−2.6	566	
994		D_2O	200	8	3	−2.0	566	
995	$MeCOO^- + D_2O \rightarrow CH_2DCOO^- + HDO$	D_2O	160	8	4	−10.5	566	
996	$MeC(OH){=}CHCOMe \rightarrow MeCOCH_2COMe$	CCl_4	30	1	4	−19	567	[DAP][r5] = 2.6 mmol/kg
997		CCl_4	30	1	4	−20	567	[DAP] = 5.1 mmol/kg
998		CCl_4	30	1	4	−31	567	[DAP] = 6.4 mmol/kg
999		CCl_4	30	1	4	−24	567	[DAP] = 9.6 mmol/kg
1000		CCl_4	30	1	4	−8.5	567	[DAP] = 12.2 mmol/kg
1001		CCl_4	30	1	4	−4.7	567	[DAP] = 14.1 mmol/kg
1002		CCl_4	30	1	4	−3.6	567	[DAP] = 16.7 mmol/kg
1003		CCl_4	30	1	4	−2.9	567	[DAP] = 19.3 mmol/kg
1004		CCl_4	30	1	4	−15	567	[DAB][s5] = 1.9 mmol/kg
1005		CCl_4	30	1	4	−20	567	[DAB] = 3.2 mmol/kg
1006		CCl_4	30	1	4	−26	567	[DAB] = 6.4 mmol/kg
1007		CCl_4	30	1	4	−17	567	[DAB] = 9.6 mmol/kg
1008		CCl_4	30	1	4	−7.6	567	[DAB] = 12.9 mmol/kg
1009		CCl_4	30	1	4	−6.6	567	[DAB] = 16.1 mmol/kg
1010		CCl_4	30	1	4	−4.5	567	[DAB] = 19.3 mmol/kg
1011	$Ph_3(PhCH_2)P^+ + OH^- \rightarrow Ph_3P{=}O + PhCH_3$	aq EtOH	45	1	10	+31	544	EtOH 50 vol %
1012		aq EtOH	25	0.9	9	+32	544	EtOH 50 vol %
1013		*p*-dioxane	25	0.9	6	−21	568	Δ*V* = −19
1014		CH_2Cl_2	25	1	8	−19	568	
1015		MeCN	25	0.8	6	−25	568	Δ*V* = −18
1016		*p*-dioxane	25	0.8	5	−29	568	
1017		CH_2Cl_2	25	2.5	6	−63	569	
1018		CH_2ClCH_2Cl	25	3	4	−54	569, 570	
1019		MeCN	25	2.5	6	−67	569, 570	
1020		CH_2Cl_2	25	0.8	4	−44	569	
1021		CH_2ClCH_2Cl	25	0.8	4	−35	569	
1021b		$CHCl_3$	25	0.8	4	−31	569	
1022		MeCN	21	1.9	6	−25[z3]	558	
1023		MeCN	29	2.1	12	−26[z3]	558	
1024		MeCN	40	1.6	5	−28[z3]	558	
1025		*i*-PrCN	29	2	5	−22	558	
1026		$CHCl_3$	20	1.2	5	−25.4	571	
1027		$CHCl_3$	25	1.2	5	−29.6	571	
1028		$CHCl_3$	30	1.2	5	−28.6	571	
1029		$CHCl_3$	35	1.2	5	−33.7	571	
1030		$CHCl_3$	40	1.2	5	−32.0	571	

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
1031		MeCN	21	1.8	6	-29^{z3}	558	
1032		MeCN	29	2.1	14	-37^{z3}	558	
1033		MeCN	40	1.6	5	-33^{z3}	558	
1034		i-PrCN	29	2.1	5	−29	558	
1035		$CHCl_3$	20	1.2	5	−31.4	571	
1036		$CHCl_3$	25	1.2	5	−35.7	571	
1037		$CHCl_3$	30	1.2	5	−29.2	571	
1038		$CHCl_3$	35	1.2	5	−37.0	571	
1039		$CHCl_3$	40	1.2	5	−34.1	571	
1040	$Me_2CHNO_2 + I_2 \rightarrow Me_2CINO_2 + HI$	aq t-BuOH	25	1.3	7	−31.4	572	t-BuOH 60 wt %, $t5$
1041		aq t-BuOH	25	1.3	7	−28.1	572	t-BuOH 50 wt %, $t5$
1042		H_2O	21	1.3	4	−1	554	catalyzed by AcO^-
1043	$Me_2CDNO_2 + I_2 \rightarrow Me_2CINO_2 + HI$	aq t-BuOH	25	1.3	7	−40.4	572	t-BuOH 60 wt %, $t5$
1044		aq t-BuOH	25	1.3	7	−34.7	572	t-BuOH 50 wt %, $t5$
1045	$Ph_2CHOH + OH^- + MnO_4^- \rightarrow Ph_2CO + HMnO_4^{2-}$	H_2O	25	1		−7	573	
1046	$Ph_2CDOH + OH^- + MnO_4^- \rightarrow Ph_2CO + DMnO_4^{2-}$	H_2O	25	1		−7	573	
1047	$PhCOCH_3 + BH_4^- \rightarrow PhCH(OH)Me$	i-PrOH	22	1.3	5	−11	554	
1048	$2PhCHO \rightarrow PhCH_2OH + PhCOO^-$	aq MeOH	100	1	4	−27	554	
1049	$Me_4Sn + I_2 \rightarrow SnMe_3I + MeI$	n-Bu_2O	29	1.1	12	−50	574	
1050	$Et_4Sn + Br_2 \rightarrow Et_3SnBr + EtBr$	cyclohexane	25	0.8	7	−56	575	$\Delta V = +20$
1051	n-$Bu_4Sn + Br_2 \rightarrow n$-$Bu_3SnBr + n$-$BuBr$	cyclohexane	25	0.7	7	−65	575	$\Delta V = +23$
1052	sec-$Bu_4Sn + Br_2 \rightarrow sec$-$Bu_3SnBr + sec$-$BuBr$	cyclohexane	25	0.7	8	−47	575	$\Delta V = +36$
1053		PhMe	25	1	5	−18.8	576, 577	$\Delta V = -25.6$
1054		CH_2Cl_2	25	1	5	−15.3	576, 577	$\Delta V = -15.3$
1055		PhMe	25	1	5	−24.3	577	
1056		CH_2Cl_2	25	1	5	−14.6	577	
1057		CH_2Cl_2	25	1	5	−19.0	578	$\Delta V = -36.1$
1058		MeCN	25	1	5	−12.7	578	
1059		CH_2Cl_2	25	1	5	−10.8	578	$\Delta V = -22.7$
1060		MeCN	10	1	5	−5.7	579	
1061		MeCN	20	1	5	-6.8^{z3}	579	
1062		MeCN	25	1	5	−9.0	578	
1063		MeCN	40	1	5	−13.0	579	
1064		PhCN	25	1	5	−7.4	580	
1065		CH_2ClCH_2Cl	25	1	5	−10.0	580	

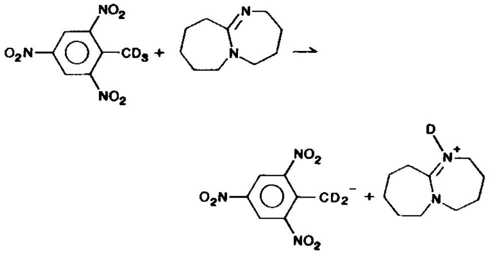
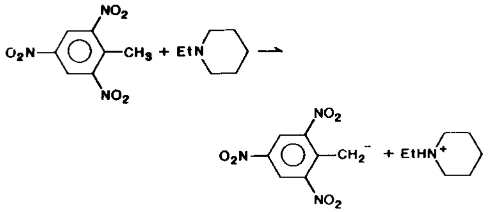
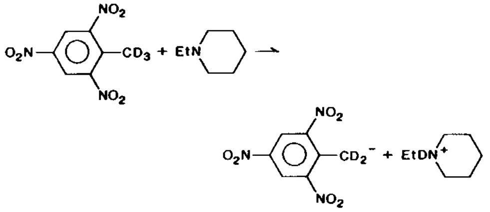
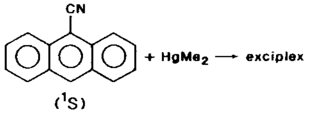
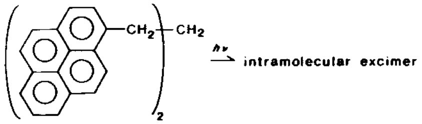
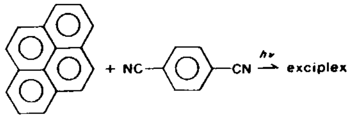
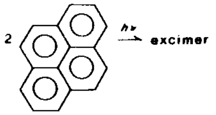
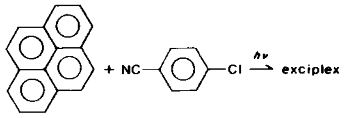
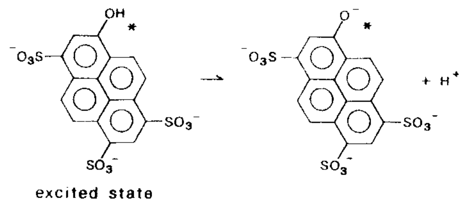
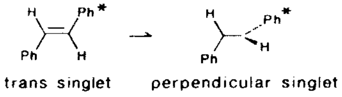
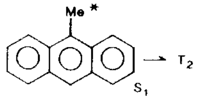
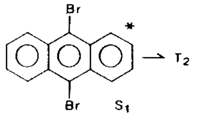
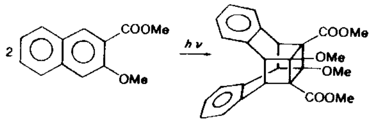
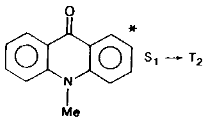
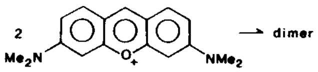
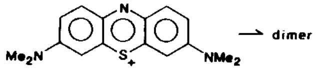
1066		MeCN	10	1	5	−11.3	579	
1067		MeCN	25	1	5	−12.1	579	
1068		MeCN	30	1	3	-10.8^{z3}	579	
1069		MeCN	40	1	5	−14.4	579	
1070		PhCN	25	1	5	−8.0	580	
1071		CH_2ClCH_2Cl	25	1	5	−15.6	580	
1072		MeCN	15	1	3	−6.5	581	*w3*
1073		MeCN	20	1	3	−7.0	581	*w3*
1074		MeCN	25	1	3	−7.2	581	*w3*
1075		MeCN	30	1	3	−7.7	581	*w3, x3*
1076		MeCN	15	1	3	−7.2	581	
1077		MeCN	20	1	3	−7.6	581	
1078		MeCN	25	1	3	−7.9	581	
1079		MeCN	30	1	3	−8.4	581	
1080		MeCN	25	3.5	8	−9	582	based on fluorescence quenching
1081		*u5*	25	2.5	11	+24.8	583	
1082		PhMe	25	3.5	8	+8.1	584	for the reverse reaction, $\Delta V^{\ddagger} = +46.8$
1083		AcOEt	25	3.5	8	+7.7	584	for the reverse reaction, $\Delta V^{\ddagger} = +26.0$
1084		THF	25	3.5	8	+5.7	584	
1085		CH_2ClCH_2Cl	25	1.5	7	+7.7	584	
1086		*v5*	25	2	5	+19	585	
1087		*w5*	25	2	5	+16	585	
1088		PhMe		3.5	11	−5.8	586	
1089		THF		3.5	8	−3.3	586	
1090		acetone		3.5	9	−2.2	586	
1091		EtOH		3.7	10	−1.4	586	
1092		MeCN		3.5	10	+0.9	586	

TABLE VII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
1093	$Ph_2CO + SH \xrightarrow{h\nu} Ph_2\dot{C}OH + \dot{S}$	i-PrOH	25	2.5	6	−10.6	587	
1094		$(CD_3)_2CDOD$	25	3	7	−9.6	587	
1095		MeOH	25	3	7	−9.7	587	
1096		CD_3OD	25	3	7	−6.9	587	
1097		PhMe	25	3	7	−12.6	587	
1098		$C_6D_5CD_3$	25	3	7	−11.8	587	
1099		n-hexane	25	3	7	−9.7	587	
1100		cy-$C_6H_{11}Me$	25	3	7	−13.1	587	
1101		H_2O	ambient	8	10	−6	588	
1102		D_2O	ambient	8	8	−6	588	
1103		n-hexane	ambient			+3.5	589	
1104		cy-$C_6H_{11}Me$	ambient			+3.7	589	
1105		$x5$	ambient			+9.5	589	
1106		paraffin oil	ambient			+13.2	589	
1107		i-BuOH	ambient			+5.2	589	
1108		MeOH	ambient			+2.2	589	
1109		glycerol	ambient			+12.9	589	
1110		heptane	20	1	6	+15.7	590	
1111		heptane	30	1	6	+15.2	590	
1112		heptane	40	1	6	+15.0	590	
1113		heptane	50	1	6	+14.5	590	
1114		PhMe	20	1	6	+9.0	590	
1115		PhMe	30	1	6	+9.6	590	
1116		PhMe	40	1	6	+9.5	590	
1117		PhMe	50	1	6	+10.1	590	
1118		PhMe	60	1	6	+10.6	590	
1119		PhMe	20	2	2	−9.1	591	
1120		MeOH	20	2	2	−10	591	
1121		PhMe	10	2.5	7	+16.3	592	
1122		PhMe	20	2.5	7	+19.5	592	
1123		PhMe	30	2.5	7	+18.7	592	
1124		PhMe	40	1.5	5	+20.3	592	
1125		PhCN	20	2.5		+6.5	593	
1126		PhBr	20	2.5		+9.4	593	
1127		Me_2CO	20	2.5		+11.2	593	
1128		THF	20	2.5		+13.2	593	
1129		p-dioxane	20	2.5		+15.0	593	
1130		PhMe	20	2.5		+17.1	593	
1131		hexane	20	2.5		+14.9	593	

1132		H_2O	20	1.5	4	0	594	[NaCl] = 1 mol/kg; for dissociation, $\Delta V^{\ddagger} = +8.9$
1133		aq MeOH	20	1.5	4	−1.1	594	MeOH 5%; [NaCl] = 1 mol/kg; for dissociation, $\Delta V^{\ddagger} = +6.9$
1134		aq MeOH	20	1.5	4	−5.3	594	MeOH 10%; [NaCl] = 1 mol/kg; for dissociation, $\Delta V^{\ddagger} = +4.3$
1135		H_2O	30	1.5	4	−4.4	594	[NaCl] = 1 mol/kg; for dissociation, $\Delta V^{\ddagger} = +7.1$
1136		H_2O	20	1.5	4	−0.7	594	[KNO_3] = 1.5 mol/kg; for dissociation, $\Delta V^{\ddagger} = +13.3$
1137	$Gd^{3+}{}_{(0)}$ + vesicle → $Gd^{3+}{}_{(i)}$	H_2O	25	1	4	+140	595	y5

[a1] 40% acetone-d_6, 20% TMS, 40% amide. [b1] 60 vol % CCl_4, 20 vol % hexamethyldisiloxane (HMDSiO), 20 vol % amide. [c1] Coalescence temperature range. Activation volumes were independent of temperatures in the vicinity of T_c. [d1] The rest is amide. [e1] 60 vol % acetone-d_6, 20 vol % TMS, 20 vol % amide. [f1] 77.5 wt % acetone-d_6, 12.7 wt % acetone, 9.8 wt % amide. [g1] 70.8 wt % acetone-d_6, 23.9 wt % acetone, 5.3 wt % amide. [h1] Other activation volumes in aq NaBr and urea solutions are given in figures. [i1] 14.3 wt % acetone-d_6, 14.3 wt % acetone, 51.1 wt % DMF-d_7, 20.3 wt % amide. [j1] 40 vol % benzene-d_6, 40 vol % toluene-d_8, 20 vol % amide. [k1] 69.3 wt % acetone-d_6, 10.3 wt % HMDSiO, 20.4 wt % amide. [l1] 72.3 wt % acetone-d_6, 9.2 wt % HMDSiO, 18.5 wt % amide. [m1] 69.8 wt % acetone-d_6, 9.9 wt % HMDSiO, 20.3 wt % amide. [n1] 20.4 wt % acetone-d_6, 10.2 wt % acetone, 65.5 wt % toluene-d_8, 3.9 wt % amide. [o1] 52.7 wt % acetone, 4.1 wt % HMDSiO, 43.2 wt % amide. [p1] 10 wt % acetone-d_6, 30 wt % acetone, 40 wt % toluene-d_8, 20 wt % amide. [q1] 69 wt % $CHCl_3$, 27 wt % pyridine-d_5, 4 wt % amide. [r1] 40 wt % pyridine-d_5, 40 wt % acetone, 20 wt % amide. [s1] 50 wt % DMF-d_7, 30 wt % acetone, 20 wt % amide. [t1] 45.3 wt % acetone, 1.7 wt % HMDSiO, 53 wt % amide. [u1] 48.2 wt % acetone, 2.3 wt % HMDSiO, 49.5 wt % amide. [v1] 46.7 wt % pyridine-d_5, 39.4 wt % toluene-d_8, 10.1 wt % acetone, 3.8 wt % amide. [w1] 28.3 wt % pyridine-d_5, 53.2 wt % toluene-d_8, 9.3 wt % acetone, 9.2 wt % amide. [x1] 19.9 wt % acetone, 69.7 wt % CD_2Cl_2. [y1] 20 wt % toluene-d_8, 30 wt % benzene, 30 wt % acetone-d_6, 20 wt % amide. [z1] 40 wt % CD_2Cl_2, 20 wt % CH_2Cl_2, 20 wt % acetone-d_6. [a2] 40 wt % CD_2Cl_2, 20 wt % CH_2Cl_2. [b2] 80 wt % D_2O, 20 wt % H_2O. [c2] 50 wt % benzene, 43 wt % acetone-d_6, 2 wt % HMDSiO, 5 wt % amide. [d2] 30 vol % methanol-d_4, 45 vol % ND_3, 25 vol % NH_3. [e2] Same value for both directions. [f2] 96 wt % D_2O, 4 wt % H_2O. [g2] 80 wt % D_2O, 20 wt % methanol-d_4. [h2] 70 wt % acetone-d_6, 20 wt % methanol-d_4, 10 wt % D_2O. [i2] 30 wt % acetone-d_6, 30 wt % benzene, 20 wt % toluene-d_8, 20 wt % amide. [j2] 40 wt % CD_2Cl_2, 20 wt % CH_2Cl_2, 20 wt % acetone-d_6, 20 wt % amide. [k2] In the presence of piperidine. [l2] −22.6 cm³ mol⁻¹ ($P \leq 2.5$ kbar). [m2] Activation volume was calculated on the basis of the rate constants at $P \leq 3$ kbar. [n2] Calculated by T.A. by means of $\ln k = a + bP$. [o2] In the presence of diisobutoxymethane (2 mol/L) and 1,1-diisobutoxyethane (2 mol/L). The solvent may be chlorobenzene. [p2] In the presence of *N*-propyl-1,3-oxaazacyclopentane (4 mol/L). [q2] In the presence of 2-ethyl-*N*-propyl-1,3-oxaazacyclopentane (4 mol/L). [r2] Pressure effects on the photolysis are also studied. [s2] Although the rates for $Me_3SiOOCMe_2Ph$ and $Ph_3SiOOCMe_3$ in several solvents were also measured, ln *k* was found to increase in stepwise fashion. [t2] Styrene is emulsified by sodium lauryl sulfate. [u2] Styrene is emulsified by sodium dodecyl sulfate. [v2] Styrene is emulsified by "Aerosol OT". [w2] Styrene is emulsified by "Teric GX13". [x2] $\Delta V^{\ddagger}$ for the reverse reaction becomes positive at ca. 1.4 kbar. [y2] 90% pentane–10% acetone. [z2] Estimated from the initial slope. [a3] Electron donor–acceptor complex (EDA complex). [b3] Formation of EDA complex is assumed to be the preequilibrium of the cycloaddition. [c3] From (partial) molar volumes. [d3] Calculated on the assumption that ΔV for EDA complex formation is −6 cm³ mol⁻¹ and $\Delta V^{\ddagger}$ for cycloreversion of the 4+2 adduct is −10 cm³ mol⁻¹. [e3] Contains ca. 15 vol % heptane or decane as an internal standard for GC analysis. [f3] The adduct reacts with 2,2,6,6-tetramethylpiperidin-1-oxyl forming 1-hydroxy-2,2,6,6-tetramethylpiperidin, and the adduct formation is followed by measuring the hydroxylamine concentration in the reaction mixture. [g3] The initial product isomerizes under the reaction condition to a 2-pyrazoline derivative. [h3] ΔV is the partial molar volume difference between the final product and the reactants. ΔV in other solvents are also given. [i3] Determined dilatometrically. [j3] Catalyzed by cetyltrimethylammonium bromide micelles. The activation volume given is the one for the second step in eq A.

$$\mathrm{M + D \overset{K}{\rightleftharpoons} MD \xrightarrow{k_m} M + DOH} \tag{A}$$

[k3] ΔV for MD formation is +4 cm³ mol⁻¹. [l3] Catalyzed by myristyltrimethylammonium bromide micelles. The activation volume given is the one for the second step in eq A. [m3] ΔV for MD formation is +15 cm³ mol⁻¹. [n3] ΔV for MD formation is +3 cm³ mol⁻¹. [o3] In the presence of styrene–acrylic acid copolymer latex. For detail, see the original. [p3] ΔV for MD formation is +14 cm³ mol⁻¹. [q3] Equilibrium constants at various pressures are given. [r3] For the overall decomposition of benzenediazonium tetrafluoroborate. The total yield of the listed products amounts only to 34–74%. [s3] Catalyzed by α-cyclodextrin in Tris buffer (pH 6.9). Activation volume given is the one for the second step in eq B.

$$\mathrm{CD + S \overset{K}{\rightleftharpoons} CD{-}S \xrightarrow{k_2} acyl{-}CD \xrightarrow{k_3} CD + P} \tag{B}$$

[t3] ΔV for CD–S formation is −3 cm³ mol⁻¹. [u3] Catalyzed by β-cyclodextrin in Tris buffer (pH 6.9). Activation volume given is the one for the second step in eq B. [v3] ΔV for CD–S formation is −2 cm³ mol⁻¹. [w3] Catalyzed by poly(vinyl alcohol) 30% acetalyzed with *o*-formylbenzenesulfonic acid. [x3] Catalyzed by poly(vinyl alcohol) 23% acetalyzed with *o*-formylbenzenesulfonic acid. [y3] Catalyzed by dodecyl hydrogen sulfate micelles. [z3] Calculated by T.A. by means of $\ln k = a + bP + cP^2$. [a4] Catalyzed

TABLE VII (Footnotes Continued)

by CTAB micelles in Tris buffer (pH 8.3). Activation volume given is the one for the second step in eq C.

$$\mathrm{M + S \underset{}{\overset{K}{\rightleftharpoons}} MS \xrightarrow{k_m} M + P} \qquad \text{(C)}$$

[b4] ΔV for MS formation is +4 cm^3 mol^{-1}. [c4] ΔV for MS formation is +9 cm^3 mol^{-1}. [d4] k_m is divided into hydroxide ion catalyzed and Tris-catalyzed rates, and the activation volumes are estimated to be −6 and −19, respectively. [e4] [OH$^-$] = 1 × 10^{-3} mol/L. [f4] In the presence of poly[(trimethylvinyl)benzylammonium chloride]. [g4] In the presence of sodium poly(styrene sulfonate). [h4] ΔV for MS formation is +14 cm^3 mol^{-1}. [i4] Tris buffer, pH 9; from pressure dependence of k_0; $k_0 = k_{OH}[OH^-] + k_T[Tris]$. [j4] Tris buffer, pH 9; in the presence of pentylamine, zero order in the amine. [k4] Tris buffer, pH 9; in the presence of pentylamine; first order in the amine. [l4] Tris buffer, pH 9; in the presence of heptylamine; zero order in the amine. [m4] Tris buffer, pH 9; in the presence of heptylamine; first order in the amine. [n4] Tris buffer, pH 9; in the presence of nonylamine; zero order in the amine. [o4] Tris buffer, pH 9; in the presence of nonylamine; first order in the amine. [p4] ΔV for MS formation is +18 cm^3 mol^{-1}. [q4] Tris buffer, pH 9; in the presence of heptylamine; second order in the amine. [r4] Tris buffer, pH 9; in the presence of nonylamine; second order in the amine. [s4] $KOH-KH_2PO_4$ buffer. [t4] Catalyzed by β-cyclodextrin. Activation volume given is the one for the second step in eq B. [u4] Derived from the apparent rate constants in the presence of β-cyclodextrin. The presure effect reverses at about 50 MPa. [v4] Catalyzed by hexadecyltrimethylammonium bromide micelles in Tris buffer (pH 8.7). Activation volume given is the one for the second step in eq C. [w4] ΔV for MS formation is +11 cm^3 mol^{-1}. [x4] k_m is divided into hydroxide ion catalyzed and Tris-catalyzed rates, and the activation volumes are estimated to be −6 and −16, respectively. [y4] In Tris buffer (pH 8.7). ΔV^{*} is calculated from apparent rate constant $k_0 = k_{OH}[OH^-] + k_T[Tris]$. [z4] ΔV for MS formation is +13 cm^3 mol^{-1}. [a5] ΔV for MS formation is +18 cm^3 mol^{-1}. [b5] ΔV for MS formation is +23 cm^3 mol^{-1}. [c5] Catalyzed by β-cyclodextrin in Tris buffer (pH 9.0). Activation volume given is the one for the second step in eq B. [d5] ΔV for CD–S formation is +10 cm^3 mol^{-1}. [e5] Catalyzed by γ-cyclodextrin in Tris buffer (pH 8.3). Activation volume given is the one for the second step in eq B. [f5] ΔV for CD–S formation is 0 cm^3 mol^{-1}. [g5] Catalyzed by α-cyclodextrin in Tris buffer (pH 7.0). Activation volume given is the one for the second step in eq B. [h5] ΔV for CD–S formation is −16 cm^3 mol^{-1}. [i5] Catalyzed by α-cyclodextrin in Tris buffer (pH 8.3). Activation volume given is the one for the second step in eq B. [j5] ΔV for CD–S formation is −10 cm^3 mol^{-1}. [k5] Catalyzed by α-cyclodextrin in Tris buffer (pH 9.0). Activation volume given is the one for the second step in eq B. [l5] ΔV for CD–S formation is −1 cm^3 mol^{-1}. [m5] ΔV for MS formation is 0 cm^3 mol^{-1}. [n5] ΔV for CD–S formation is 0 cm^3 mol^{-1}. [o5] Catalyzed by β-cyclodextrin in Tris buffer (pH 8.3). Activation volume given is the one for the second step in eq B. [p5] k's at 293 K are estimated from the rates at lower temperatures by means of Arrhenius equation. [q5] For pressure effects on enzyme-catalyzed mutarotation, see: Andersen, B. *Acta Chem. Scand. B* **1984**, *38*, 415. [r5] Dodecylammonium propionate. [s5] Dodecylammonium butyrate. [t5] Catalyzed by 2,4,6-trimethylpyridine. Proton transfer to the base is rate-determining. [u5] 2,6,10,14-Tetramethylpentadecane. [v5] In sodium dodecyl sulfate micelles. [w5] In hexadecyltrimethylammonium chloride micelles. [x5] 2,2,4,4,6,8,8-Heptamethylnonane. [y5] By means of 2,2,6,6-tetramethyl-4-piperidone (TEMPONE) spin label and ESR.

D. Bond Cleavage and Formation (Entries 311–405)

It is expected that volume expansion should characterize this process, and all the available data bear it out; simple radical decompositions generally have activation volumes near +10 cm^3 mol^{-1}. The very large value for $(t\text{-BuNO})_2$ is a consequence of the use of carbon dioxide as the medium at temperatures and pressures near the critical values;[417] variations in the size of the critical aggregates are likely to be responsible for the large positive value (+60 cm^3 mol^{-1}) and for the large compressibility of the transition state.

A complex situation arises in the many substrates studied that can potentially generate three particles by a two-bond scission process. It is now generally assumed that such reactions may be concerted but not synchronous; certainly, microscopic reversibility should then require that the trimolecular recombination also occur synchronously—an unlikely event. In fact, evidence for stepwise decompositions has now been found in many instances.[723]

As Neuman has often pointed out,[418] the possibility of return greatly complicates analysis of the high-pressure effect in these reactions; he concludes that small ΔV^{*}_0 values (<+5 cm^3 mol^{-1}) suggest concerted cleavage and large ones hint at stepwise decompositions. It may at first seem strange that the more extensive breakup of molecules in concerted reactions would exhibit the smaller expansion; however, it should be realized that this is most likely to happen in strongly exothermic reactions with "early" transition states.

Other reactions involving cleavage of neutral molecules into neutral fragments include the decomposition of carbonic acid to give carbon dioxide and water[338] and that of diacetone alcohol into acetone.[433] Both are inhibited by the application of pressure.

Extending these argments, one would now logically expect that bond formation between neutral particles to give neutral products will be characterized by contraction. In free radical polymerization, the propagation step is indeed accelerated by pressure, as attested to by several data in Table VII; surprisingly, however, the dimerization of radicals such as occurs in the termination step of such polymerizations is almost always *inhibited* by pressure. Formally, the activation volume is thus positive. The reason is that these reactions have little or no activation energy barriers, and they are usually diffusion controlled. Since pressure is known to increase the viscosity of liquids, diffusion is inhibited. These reactions provide perhaps the clearest example that the uncritical application of absolute rate formalisms to very fast reactions may lead to nonsensical conclusions—such as the possibility of substantial volume increases accompanying bond formation from neutral radicals.

Kuzmin's data[440] should be interpreted with knowledge of how they were obtained; the radicals were prepared by laser flash irradiation, meaning that the initial state is probably represented by a radical pair, and not by free radicals, in some of his examples. The warnings by Neuman mentioned earlier apply here as well.

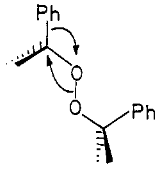
The isotope dependence of the pressure effect on the internal atom abstractions occurring in the 2,4,6-tri-*tert*-butylphenyl radical (+5.3 cm^3 mol^{-1} for H transfer,

-1.2 cm^3 mol^{-1} for D transfer) is an indication of the occurrence of tunneling in this reaction, as noted by Griller;[439] however, the need for measuring these effects in different regions of temperature complicates more detailed interpretation. The extremely small value for the fission of the phosphoranyl radical (0.2 cm^3 mol^{-1} entry 405) may not be an indication of an early transition state alone, as suggested;[439] the polar nature of the phosphate ester product may also in part be responsible.

E. Pericyclic Reactions (Entries 406–620)

The effect of pressure on pericyclic reactions has proved to be an enormously fertile area of research for two reasons. The first is that it furnishes one of the most reliable criteria about the concertedness of reactions involving multiple-bond reorganizations. Thus, as noted, one of the more easily recognized features of bond formation is the volume contraction that accompanies it; with multiple bonds, the correspondingly larger volume diminution is quite characteristic. The volume criterion is often the one of choice. Of the alternatives, stereoselectivity may be high even in diradicals if these are short-lived, and isotope effects are difficult to study to the degree of accuracy required to make a distinction. As we shall see below in several examples, the volume is useful as a criterion in essentially all types of pericyclic reactions. The second reason for the massive research effort lavished on pericyclic reactions is that the large contraction at very high pressure translates into several kcal/mol that can be subtracted from the free energy of activation, and in that way pressure becomes eminently useful for the synthetic chemist. Indeed, numerous laboratories have in recent years acquired 10- and 20-kbar presses for that very purpose.

The first group we discuss here is that of the dyotropic reactions. In view of the know proclivity of RO–OR single bonds to break into radicals, it seems surprising that the positive activation volumes normally seen in those reactions are not observed in the present cases,[442] and it can only be concluded that they must occur concertedly:

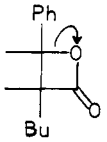


A second category in this group is that of the sigmatropic shifts, which may occur in concert or in stepwise fashion. The dicumyl isomer of entry 412 appears to undergo a "forbidden" thermal 1,3-shift, but this is certainly occurring via a radical pathway: it is retarded by pressure, and it yields side products resulting from radical disproportionation.

The two benzylic and benzhydrylic 1,4-shifts known clearly tell a story.[444] The former of these two occurs with retention (chiral PhCHD group used) and it has a large negative activation volume; the reaction is clearly concerted. In the second one, although the concerted pathway is obviously also allowed, the diradical mechanism becomes the preferred mechanism, perhaps for steric reasons. The activation volume is now indeed positive, and this conclusion derives further support from the complete racemization observed with one p-chlorophenyl group and from the CIDNP displayed by the product as it is formed.[724] The 1,5-shift examples are all concerted as allowed by virtue of orbital symmetry and as demonstrated by the transition-state contractions; however, quite a bit of variation is seen in the magnitude of the $\Delta V^{\ddagger}_0$ values. Presumably variable degrees of charge separation occur in these processes. The value of -10 cm^3 mol^{-1} observed in the oxy-Cope rearrangement is typical for Cope and Claisen rearrangements; the very small negative value for bullvalene was therefore disappointing to those of us who hoped to use this pressure effect to squeeze semibullvalene into a homoaromatic state.[445] It appears that with these superfast 3,3-shifts, the early stretching of the cyclopropyl bond is an important characteristic of the reaction, as foreseen by computational chemists.[725] Finally, the 1,3-shift of the triphenylmethyl nitride to give the nitro isomer is a stepwise reaction in spite of the negative activation volume; ionization and ion solvation are surely responsible for the contraction in that case.

A few electrocyclic ring openings have been studied under pressure. Cyclic structures generally have higher densities, as one can readily verify from handbook data on isomeric hydrocarbons, and indeed, as Plieninger[450] showed in one case (entry 425), the reaction volume for the opening of a cyclobutene is positive. The transition state is at a minimum in volume, however; presumably, the act of bringing all substituents together in one plane is responsible. This fact is also behind the difference in sign between the $\Delta V^{\ddagger}_0$ values for aromatization of Dewar benzene and of the hexamethyl homologue.[451]

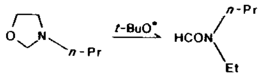
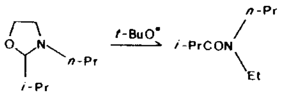
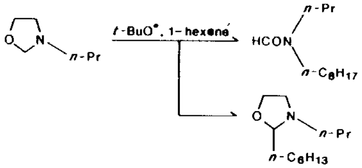
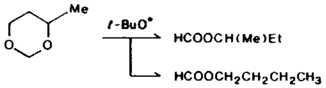
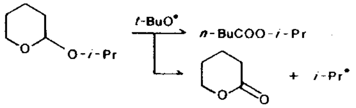
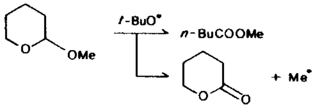
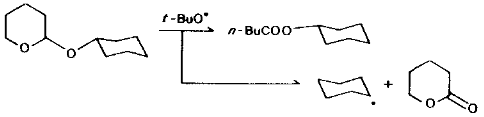
A large amount of information has been accumulated on cycloadditions. The decarboxylation of the β-lactone[452] of entry 429 almost certainly begins by rate-controlling ionization; there is no other way to explain the deep minimum in the volume profile.



The very large negative activation volumes in [2 + 2] cycloadditions of TCNE had previously been noted.[1] The reason is the formation of a zwitterionic intermediate. This is foreshadowed in the contraction occurring in the preliminary charge-transfer step;[453] in many cases, the formation of the second bond leads to expansion as the zwitterion charges are neutralized. In this case, the volume profile has a quite deep minimum, the more so the less polar is the solvent. This means that the reverse reaction is also accelerated by pressure.[461]

New examples of the powerful pressure-induced acceleration of Diels–Alder reactions continue to be reported; invariably the transition-state volumes are close to or even smaller than the product volumes. The phenomenon, its mechanistic implications, and the synthetic applications are well-known, and the new cases that have been reported all appear similar. They include Jenner's extensive examination of hexachlorocyclopentadiene as the diene.[465] In view of the well-known tendency of chlorine to stabilize radicals,[725,726]

TABLE VIII. Activation Volume Differences

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\delta\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
1	$[PhCOO^{\bullet}\,{}^{\bullet}Me]_{cage} \rightarrow PhCOOMe$	PhCl	96	1.9	4	0	424	
	$\rightarrow PhCOO^{\bullet} + {}^{\bullet}Me$					+8		
2	$[MeOCOCH_2CH_2CH_2^{\bullet}\,{}^{\bullet}CH_2CH_2CH_2COOMe]_{cage}$	PhMe	70	9.8	4	0	422	
	$\rightarrow 2MeOCOCH_2CH_2CH_2^{\bullet}$							
	$\rightarrow MeOCO(CH_2)_6COOMe$					+2		
3	$PhCOO^{\bullet} + PhCH{=}CH_2 \rightarrow PhCOOCH_2CHPh^{\bullet}$	PhMe	60	4	6	0	596	
	$\rightarrow Ph^{\bullet} + CO_2$					+21		
4	$PhCOO^{\bullet} + CH_2{=}CMeCOOMe \rightarrow PhCOOCH_2\dot{C}MeCOOMe$	PhMe	60	2	6	0	596	
	$\rightarrow Ph^{\bullet} + CO_2$					+15		
5	$PhCMe_2O^{\bullet} \rightarrow PhCOMe + Me^{\bullet}$	PhOMe	170		6	0	597	
	$PhCMe_2O^{\bullet} + PhOMe \rightarrow PhCMe_2OH + PhOCH_2^{\bullet}$					−21.1		
6	$CH_2(O\text{-}i\text{-}Bu)_2 + t\text{-}BuO^{\bullet} \rightarrow {}^{\bullet}CH(O\text{-}i\text{-}Bu)_2 + t\text{-}BuOH$	none	130	10.1	5	0	412	1:1 mixture of the two acetals
	$CHMe(O\text{-}i\text{-}Bu)_2 + t\text{-}BuO^{\bullet} \rightarrow {}^{\bullet}CMe(O\text{-}i\text{-}Bu)_2 + t\text{-}BuOH$					-2.6^{a}		
7	$PhCMe_2O^{\bullet} + PhMe \rightarrow PhCMe_2COH$	none	126	7	5	0	598	
	$PhCMe_2O^{\bullet} + C_6D_5CD_3 \rightarrow PhCMe_2COD$					−4.1		
8		PhCl	130	2.5	4	0	599	
						-8.9^{a}		
9		PhCl	150	10	6	0	599	
						−4.5		
10		none	130	10.1	5	0	600	
						−3.0		
11		none	130	9.8	4	0	601	
						−7		
12		none	130	9.8	5	0	601	
						−26		
13		none	130	5	4	0	415	
						−11		

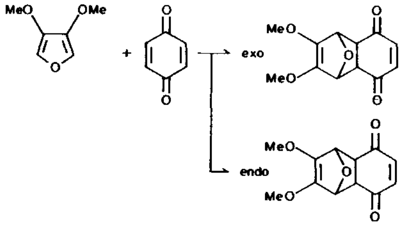
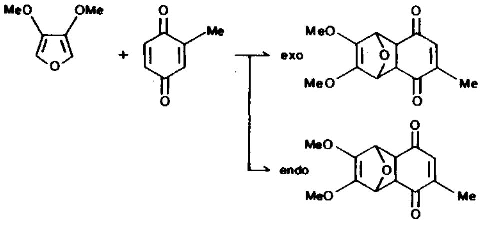
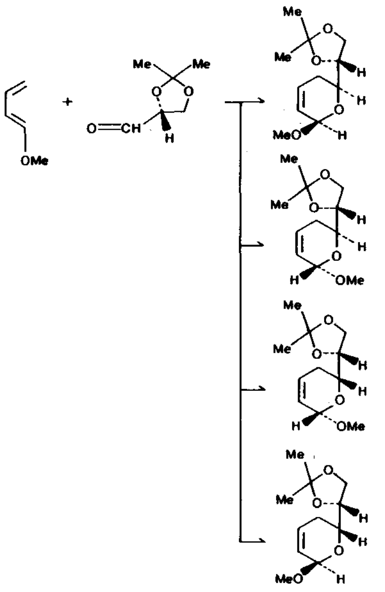
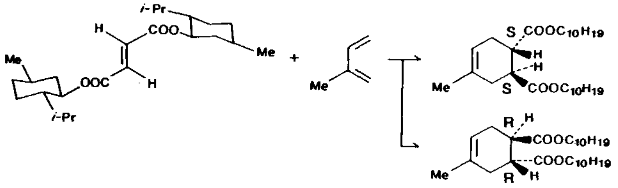
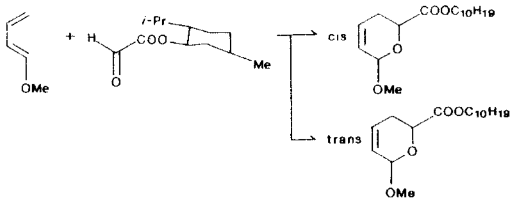
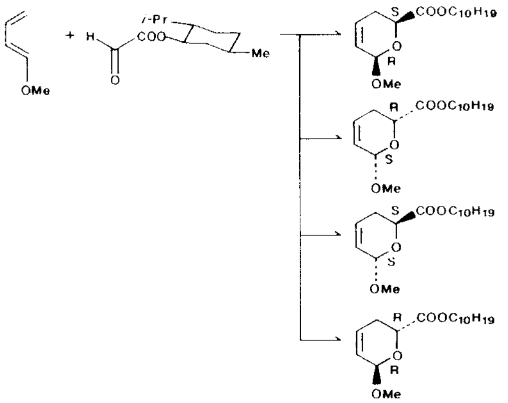
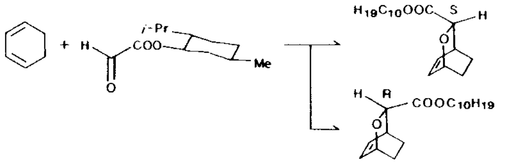
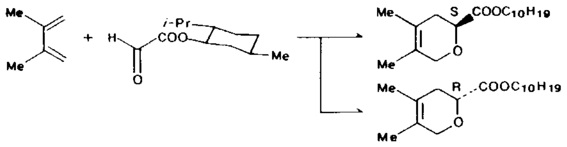
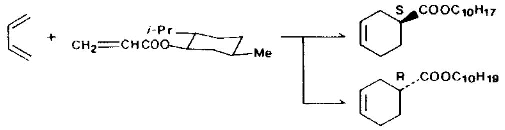
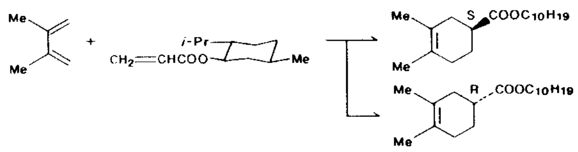
14		PhMe	25	19	3	0	602	$P \geq 7$ kbar
						$+4.0^a$		
15		PhMe	25	19	3	0	602	$P \geq 7$ kbar
						$+2.5^a$		
16			50	22	3	0	603	$P \geq 14.5$ kbar
		Et_2O PhMe–PhH CH_2Cl_2				$+0.5^a$ $+0.8^a$ $+1.1^a$		PhMe 70 vol %
		Et_2O PhMe–PhH CH_2Cl_2				$+0.6^a$ $+0.8^a$ $+1.1^a$		PhMe 70 vol %
		Et_2O PhMe–PhH CH_2Cl_2				$+1.1^a$ $+1.5^a$ $+1.8^a$		PhMe 70 vol %
17						0	604	
		PhMe	25	8.4	4	$+0.7^a$		$P \geq 4$ kbar
		CH_2ClCH_2Cl	25	7.8	4	$+0.7^a$		$P \geq 4.5$ kbar

TABLE VIII (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\delta\Delta V^\ddagger$/ (cm^3 mol^{-1})	ref	remarks
18						0	605	
		hexane	20	11.1	8	$+0.8^a$		
		PhMe	20	8.7	7	$+1.0^a$		
		Et$_2$O	20	15.5	4	$+0.7^a$		
		CH$_2$Cl$_2$	20	7.9	5	$+1.2^a$		
19		PhMe	20	8.4	2	0	605	
						-0.3^a		
20		PhMe	20	8.4	2	0	605	
						-0.3^a		
21						0	606	
		PhMe–PhH	20	12.4	4	-0.9^a		PhMe 70 vol %, $P \geq 8$ kbar
22						0	606	
		hexane	20	10.2	4	-0.8^a		$P \geq 6.2$ kbar
		PhMe	20	8.9	3	-0.9^a		$P \geq 7.1$ kbar
		CH$_2$Cl$_2$	20	8.3	4	-1.3^a		$P \geq 6.4$ kbar
23		PhMe–PhH	ambient	11.2	4	0	607	$P \geq 5$ kbar, PhMe 70 vol %
						$-0.2^{a,b}$		
24						0	607	
		PhMe–PhH	ambient	10.3	4	$-0.2^{a,b}$		$P \geq 5.5$ kbar
		CH$_2$Cl$_2$	ambient	7.9	4	$-0.3^{a,b}$		$P \geq 5.1$ kbar

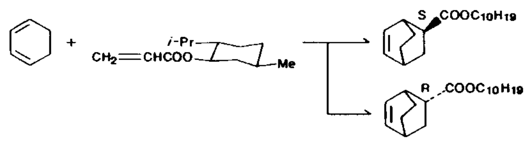
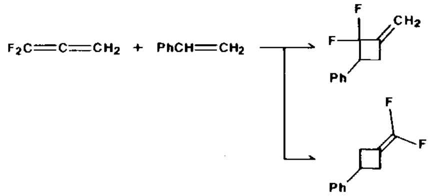
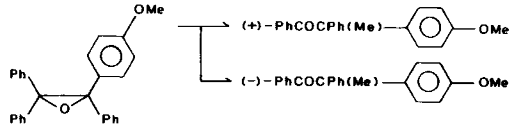
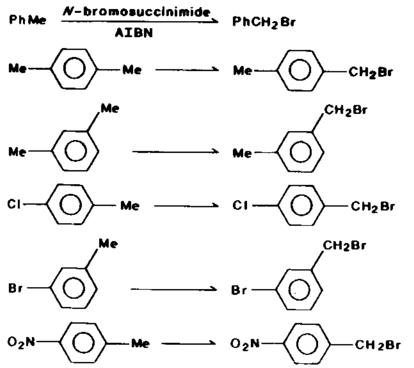
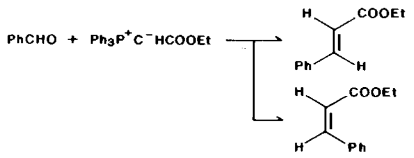
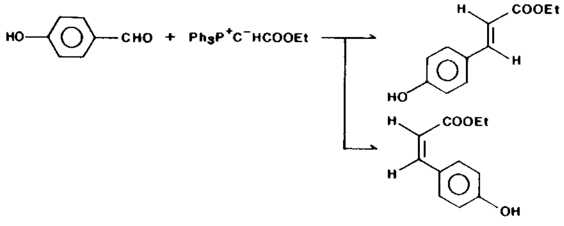
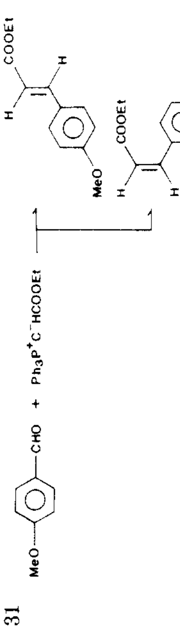
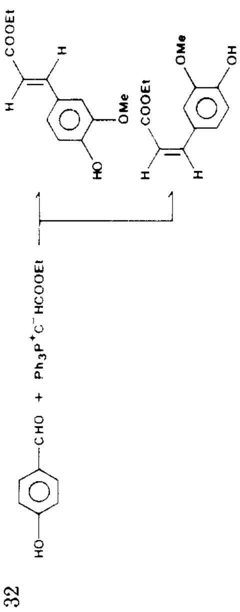
25						0	607	
		PhMe–PhH	ambient	12.5	4	$-0.4^{a,b}$		$P \geq 8.2$ kbar, PhMe 70 vol %
		hexane	ambient	12	3	$-0.3^{a,b}$		$P \geq 7.9$ kbar
26		pentane	25	6.2	6	0	608	$P \geq 2.95$ kbar
						-3.0^{a}		
27		*c*	100	10.1	2	0	609	$FeCl_3$ catalyzed
						-0.8^{a}		
28		CH_2Cl_2	70	5.9	4	0	610	
						+3.0		
						+1.5		
						−1.2		
						−3.0		
						−6.4		
29		CH_2Cl_2	50	10	2	0	611	
						+2.0		
30		CH_2Cl_2	50	10	2	0	611	
						+1.2		

TABLE VIII (Continued)

no.	reaction	solvent	T/°C	P/kbar	no. of k	$\delta\Delta V^{\ddagger}$/(cm^3 mol^{-1})	ref	remarks
31		CH$_2$Cl$_2$	50	10	2	0 +1.0	611	
32		CH$_2$Cl$_2$	50	10	—	0 +1.2	611	

[a] Calculated by T.A. by means of ln $k = a + bP$. [b] Temperature is assumed to be 20 °C. [c] Toluene 20 mL, 1-menthol 12 g.

this would seem to be an example particularly well suited to accommodate a diradical pathway, as Bartlett had found while using chloroethylenes as dienophiles.[727] We recall here also that Stewart[728] had found chloroprene to be subject to both a diradical and a concerted dimerization pathway and that the latter was accelerated much more by pressure than the former. But no evidence for competing pathways was found by Jenner; furthermore, (E)- and (Z)-olefins gave adducts with complete retention. The new examples include the reactions of furans and of nitroso compounds.

The reactions of TCNE with styrenes appear to be zwitterionic [2 + 8] cycloadditions, as judged by the large negative activation volumes and by the sensitivity of the rates to solvent polarity.[461] A number of additional variants may be found among entries 543–550. Entry 542 is a rare example of a species capable of undergoing an internal Diels–Alder reaction.[475] Its volume profile appears similar to that of the intermolecular type, although both activation and reaction volumes are somewhat less than average; indeed, synthetic chemists have found that the intramolecular variety does not respond to pressure quite as favorably. A few examples are now also known of retro-Diels–Alder reactions in which the negative activation volume of the forward reaction is larger than the reaction volume. As required then, the reaction in the opposite direction is also accelerated by pressure. This is valuable proof that this minimum cannot be dismissed as due to imprecise measurements.[480]

In dipolar [2 + 3] cycloadditions, the activation volume once again approaches the overall contraction in magnitude, and thus this evidence complements the extensive work of Huisgen showing the concerted nature of the reaction.[729] These contractions tend to be somewhat smaller than in Diels–Alder reactions, presumably due to the loss of the dipole.

The [4 + 6] cycloaddition of tropone, previously reported[730] to be characterized by similar but small volume contractions in both product and transition state, has been extensively reinvestigated by Takeshita,[473,486,487] who finds these contractions to have essentially normal values (thus, the mechanistic conclusions remain the same).

Ene reactions have made their appearance among the pericyclic reactions that have been investigated at high pressures; once again, the large accelerations suggest a concerted pathway.[488] Klärner examined the competition among the five dimers formed in the reaction of 1,3-cyclohexadiene; in a study reminiscent of Stewart's,[728] he concludes that the endo-Diels–Alder and [4 + 6] ene product form concertedly, while the other products arise via a common diradical.

The study by Turro and Moss[493] is the first report of a pressure effect in the cheletropic addition of flash-generated carbenes to olefins. The additions are stereospecific. The volumes of activation are somewhat less negative than those of Diels–Alder reactions, and these workers were cautious in their conclusions. It seems to the present authors that the reaction volumes will in all likelihood also be less than those in [4 + 2] cycloadditions; thus, most schemes to calculate molar volumes include a special correction for the cyclopropane moiety.[731] When this knowledge becomes available, the $\Delta V^{\ddagger}/\Delta V$ ratio may prove to be as high as those of concerted cycloadditions.

Brower has reported[495] the oxidation of hydronaphthalenes by various species, including coal. The large negative values rule out initial homolytic reactions of the substrates. The author mentioned that the mechanism might be ionic. Concerted hydrogen transfer such as is known with diazene[732] would probably also have a large negative volume, but the use of the rather high temperatures required makes the further pursuit of this question difficult at present.

F. Heterolysis and Neutralization (Entries 621–717)

The generation of electrically charged species in solution by heterolytic bond cleavage is a process well-known to be characterized by a large volume contraction due to tight solvation of the ions, a phenomenon first referred to as electrostriction by Drude and Nernst.[733] This chemistry has been reviewed extensively before,[1] and relatively little has been added in the intervening years. Solvolysis of Coates' chloride (entry 666) was found to have an activation volume less negative than that of *tert*-butyl chloride under the same conditions, and this was attributed to charge delocalization in the pentacyclic cation.[504] The reversal of sign in $\Delta V^{\ddagger}$ of entry 670 was observed by Whalley.[506] Additional examples were recently reported by him;[734] his interpretation rests on the fact that at extreme pressures, solvent compressibilities and hence electrostriction are small, so that the expansion due to bond cleavage in S_N1 heterolysis becomes dominant. Indeed, the reversal does not appear in S_N2 solvolyses, in which covalent solvent bonding to the incipient carbocation compensates for the cleavage. The expansion upon pairing of ammonium and picrate ions[508] is also noteworthy.

Charge neutralization of cationic organic dyes such as Malachite Green and Crystal Violet has a long history in high-pressure chemistry; this began with the report by Laidler in 1959 that this neutralization is strongly accelerated by pressure.[735] It was quite an unexpected finding. In one reinvestigation, it was noted[509] that the actual direct neutralization was retarded and that a competing indirect one via rate-controlling addition of neutral water to the cation was the reaction that Laidler had really observed (see also entries 798–801). Further work by Isaacs[449,512] has shown, however, that the matter is not completely resolved: in several nonaqueous solvents in which this complication cannot play the same role, the cation–anion reactions are also accelerated. It may be that the approach of the ions tends to focus charges more disperse in the separate ions, and hence increase electrostriction rather than diminish it.

G. Displacement Reactions (Entries 718–758)

Since bond formation and cleavage occur simultaneously in this type of reaction, the volume change is usually small in the transition state; futhermore, charge dispersal between attacking and departing anions may offset the small volume decreases that are usually observed. Eckert has reported[513] such a case (entry 718). Positive activation volumes were also observed[514] in two instances in which the substrate is a cation and the nucleophile and leaving group are neutral. These results are apparently cases of incursion of Sneen displacement mechanisms,[736] in which the substrate heterolyzes initially to a cation–molecule pair, which is then captured in the rate-controlling step. In the second case, the incipient cation is less able to accommodate charge, and the reaction reverts to its normal direct-displacement mode at high pressure; this changeover is graphically visible in a deep minimum in the ln *k* vs *P* plot (Figure 33).

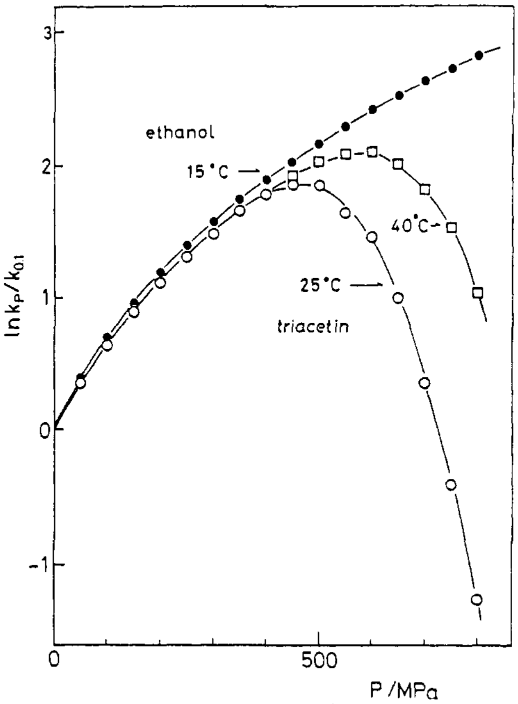


Figure 33. Effect of pressure on the isomerization rate of an azobenzene in triacetin.

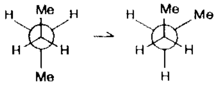
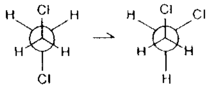
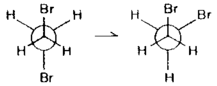
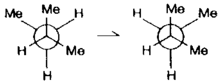
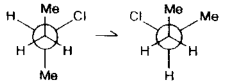
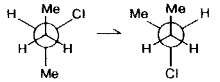
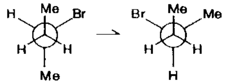
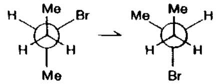
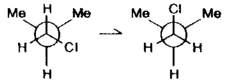
The remaining entries in this group are all Menschutkin reactions: displacements involving neutral substrates and nucleophiles with ion-pair products. Negative activation volumes are then expected and obtained in all instances.

H. Cationic Reactions (Entries 759–803)

Many phenyldiazonium cation decompositions have been studied at high pressure; all activation volumes are positive, with an average $\Delta V^{\ddagger}_0 \simeq +11 \pm 3$ cm^3 mol^{-1} in about 40 cases. Such a large expansion can only be reconciled with complete and unassisted bond cleavage. This conclusion has later also been reached by means of studies of the heavy isotope effects involved.[737] It is of interest that the results are compatible with the further finding by Zollinger[528] that nitrogen isotope scrambling in the cation occurs during the reaction; evidently a cation–nitrogen pair forms that is subject to return to some degree.

Entries 802 and 803 represent the only two cases so far of degenerate cation reactions studied at high pressure; the needs for NMR analysis, superacid media, and, often, low temperatures make this chemistry rather inaccessible to the high-pressure investigator. The Wagner–Meerwein equilibration must occur via the so-called nonclassical ion as transition state, and the expansion observed[531] lends strength to the interpretation offered[738] earlier for the small pressure sensitivity of *exo*-2-norbornyl substrates as compared to *endo*-2-norbornyl substrates; it involved the charge delocali-

TABLE IX. Reaction Volumes for Chemical Processes

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
1		neat	25	3	2	−1		612	by Raman spectra
2		neat	ambient	2.3	8	−2.7		613	by Raman spectra
3		hexane	22	4	6	−3.8		614	by Raman spectra, $C_2H_4Cl_2$ 20 vol %
4		hexane	22	5	9	−3.5		614	by Raman spectra, $C_2H_4Cl_2$ 30 vol %
5		Me_2CHEt	22	10	12	−2.9		615	by IR spectra, $C_2H_2Cl_2$ 5, 10 vol %
6		neat	50			−5.2		613	by Raman spectra
7		Me_2CHEt	22	2.5	5	−4.5		614	by Raman spectra, $C_2H_4Br_2$ 10 vol %
8		Me_2CHEt	22			−4.5		614	by Raman spectra, $C_2H_4Br_2$ 20 vol %
9		MeCN	22	3.6	6	−2.0		614	by Raman spectra, $C_2H_4Br_2$ 10 vol %
10		MeCN	22			−1.8		614	by Raman spectra, $C_2H_4Br_2$ 20 vol %
11		neat	25	3	2	−1.3		612	by Raman spectra
12		neat	ambient	2.1	10	−1.5		616	by Raman spectra
13		hexane	ambient			−1.8		617	by Raman spectra, BuCl 40 mol %
14		MeOH	ambient			−0.1		617	by Raman spectra, BuCl 40 mol %
15		neat	ambient	2.1	10	−0.8		616	by Raman spectra
16		hexane	ambient			−0.5		617	by Raman spectra, BuCl 40 mol %
17		MeOH	ambient			0		617	by Raman spectra, BuCl 40 mol %
18		neat	ambient			+2.0		616	by Raman spectra
19		hexane	ambient			−1.5		617	by Raman spectra, BuBr 40 mol %
20		MeOH	ambient			+0.8		617	by Raman spectra, BuBr 40 mol %
21		neat	ambient			+0.6		616	by Raman spectra
22		hexane	ambient			−0.9		617	by Raman spectra, BuBr 40 mol %
23		MeOH	ambient			+0.2		617	by Raman spectra, BuBr 40 mol %
24		neat	ambient			+0.5		616	by Raman spectra
25		hexane	ambient	2.5	11	+0.1		617	by Raman spectra, BuCl 80 mol %
26		hexane	ambient			−0.4		617	by Raman spectra, BuCl 60 mol %
27		hexane	ambient			−0.6		617	by Raman spectra, BuCl 40 mol %

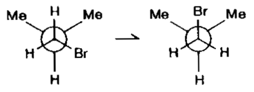
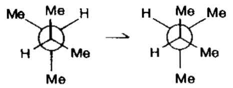
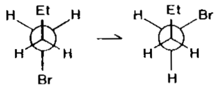
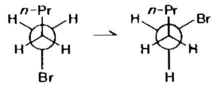
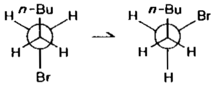
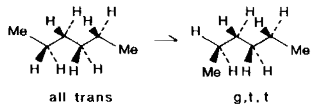
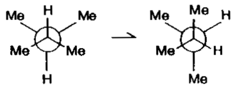
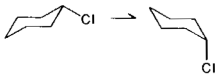
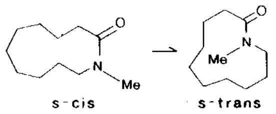
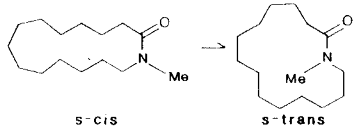
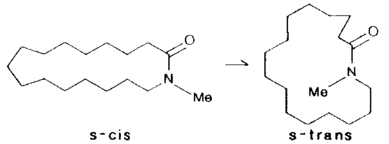
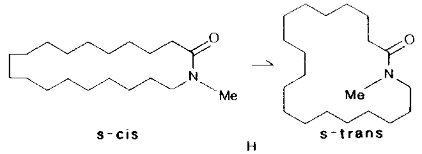
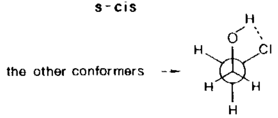
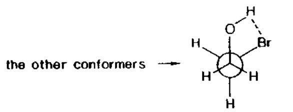
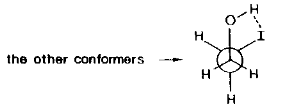
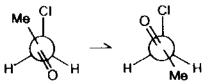
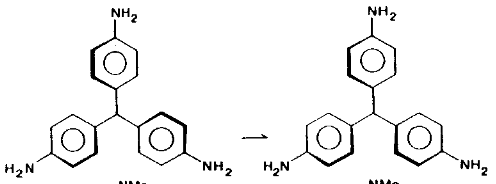
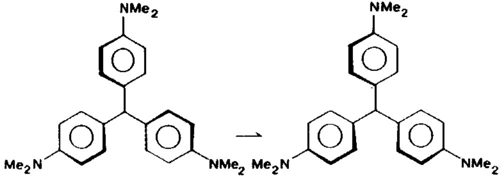
28		MeOH	ambient			−0.5	617	by Raman spectra, BuCl 40 mol %
29		neat	ambient			−1.7	616	by Raman spectra
30		hexane	ambient			−0.8	617	by Raman spectra, BuBr 80 mol %
31		hexane	ambient			−0.3	617	by Raman spectra, BuBr 60 mol %
32		hexane	ambient			−0.5	617	by Raman spectra, BuBr 40 mol %
33		MeOH	ambient			−0.7	617	by Raman spectra, BuBr 40 mol %
34		neat	25	3	2	−0.9	612	by Raman spectra
35		neat	ambient	5.5	12	−0.8	618	by Raman spectra
36		neat	ambient	5	10	−1.0	618	by Raman spectra
37		neat	ambient	6	13	−0.5	618	by Raman spectra
38		neat	30	7.4	10	−1.1	619	by Raman spectra
39		neat	−30	1	6	−3	620	from sound velocity measurements
40		neat	−34	1	6	−4	620	from sound velocity measurements
41		neat	−37	1	6	−4	620	from sound velocity measurements
42		neat	−40	1	6	−5	620	from sound velocity measurements
43		neat	−43	1	6	−5	620	from sound velocity measurements
44		neat	−46	1	6	−6	620	from sound velocity measurements
45		neat	−49	1	6	−6	620	from sound velocity measurements
46		neat	−52	1	6	−7	620	from sound velocity measurements
47		neat	−56	1	6	−7	620	from sound velocity measurements
48		neat	−60	1	6	−8	620	from sound velocity measurements
49		neat	25	5.6	9	−2.3	621	by Raman spectra

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
50		$CHCl_3$	35			−0.6		622	by ^{1}H NMR spectra, lactam 10 mol %
51		$CHCl_3$	35	1.9	8	+1.2		622	by ^{1}H NMR spectra, lactam 10 mol %
52		$CHCl_3$	35			+1.6		622	by ^{1}H NMR spectra, lactam 10 mol %
53		$CHCl_3$	29			+1.5		622	by ^{1}H NMR spectra, lactam 10 mol %
54		CS_2	25	2	3	−1.2		623	by IR spectra
55		CS_2	25	2.5	4	+0.5		623	by IR spectra
56		CS_2	25	2.1	5	+1.3		623	by IR spectra
57		CS_2	25	10	7	−1.5		624	by IR spectra, from C=O stretching
58		CS_2	25	12	9	−1.6		624	by IR spectra, from C–Cl stretching
59		H_2O	ambient	6	7	+0.2		625	[KCl] = 1 mol/L, 0.1 mol/L acetate buffer, by visible spectra
60		*c*	22	115	25	+0.2		626	by visible spectra
61		H_2O	ambient	9	10	+0.8		625	[KCl] = 1 mol/L, 0.1 mol/L acetate buffer, by visible spectra, *d*
62		*c*	22	144	27	+0.2		626	by visible spectra
63		*d*	22	125	31	+0.3		626	by visible spectra

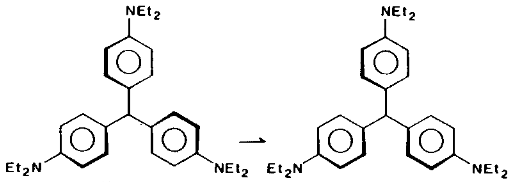
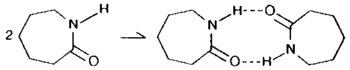
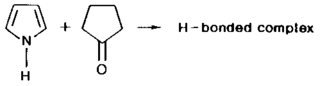
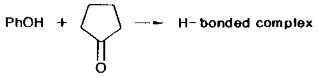
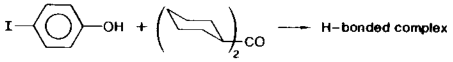
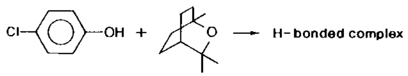
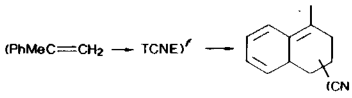
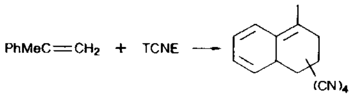
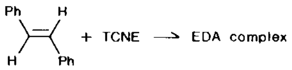
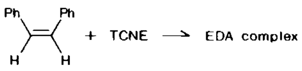
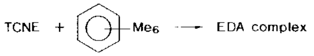
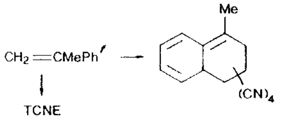
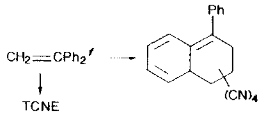
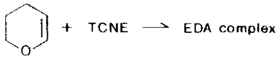
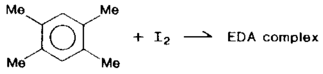
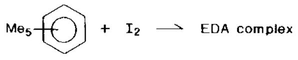
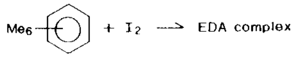
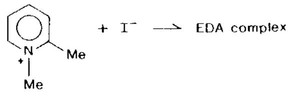
64		H_2O	ambient	3	6	+3.9		625	[KCl] = 1 mol/L, 0.1 mol/L acetate buffer, by visible spectra
65		*c*	22	130	20	+0.1		626	by visible spectra
66		*d*	22	144	23	+0.5		626	by visible spectra
67		CCl_4	20	1	3	−1.3		628	by IR spectra
68		CCl_4	60	2	5	−1.3		628	by IR spectra
69	2PhCOOH → dimer	heptane	25	6.4	6	+0.4		629	by UV spectra
70	2PhOH → dimer	CCl_4	20	1	6	−2.4		630	by IR spectra
71		CCl_4	60	1	4	−1.8		630	by IR spectra
72	$PhOH + Et_2O \rightarrow PhOH\cdots OEt_2$	hexane	25	6.4	6	−6.1		631	by UV spectra
73	$PhOH + n\text{-}Pr_2O \rightarrow PhOH\cdots OPr_2$	hexane	25	6.4	6	−6.4		631	by UV spectra
74	$PhOH + n\text{-}Bu_2O \rightarrow PhOH\cdots OBu_2$	hexane	25	6.4	6	−5.1		631	by UV spectra
75	$PhOH + PhNO_2$ → H-bonded complex	CCl_4	26			−1		632	by IR spectra
76		CCl_4	25			−1		632	by IR spectra
77		CCl_4	24			−3		632	by IR spectra
78		CCl_4	25			−3		632	by IR spectra
79		CCl_4	30			−5		632	by IR spectra
80	$CH_2{=}CHCH_2OCH_2CH_2OH + H_2O$ → association	H_2O	25				−0.6	633	by ultrasonic absorption
81	$n\text{-}PrOCH_2CH_2OH + H_2O$ → association	H_2O	25				−0.3	634	by ultrasonic absorption
82	$n\text{-}BuOCH_2CH_2OH + H_2O$ → association	H_2O	25				−0.7	634	by ultrasonic absorption
83	$i\text{-}BuOCH_2CH_2OH + H_2O$ → association	H_2O	25				−0.4	634	by ultrasonic absorption
84	$n\text{-}BuOCH_2CH_2OCH_2CH_2OH + H_2O$ → association	H_2O	25				−0.3	635	by ultrasonic absorption
85		CH_2ClCH_2Cl	25	1.5	6	−22.3		636	
86	$PhMeC{=}CH_2$ + TCNE → EDA complex	CH_2ClCH_2Cl	25	1.5	6	−6.9		636	
87		CH_2ClCH_2Cl	25	1.5	6	−29.2		636	
88	$CH_2{=}CPhMe$ + TCNE → EDA complex	$CHCl_3$	25	1.5	4	−4.0		637	
89		CH_2ClCH_2Cl	25	1.5	6	−6.9		637	
90	$CH_2{=}CPh_2$ + TCNE → EDA complex	$CHCl_3$	25	1.5	4	−5.2		637	
91		CH_2ClCH_2Cl	25	1.5	6	−5.1		637	
92		$CHCl_3$	25	1.5	4	−5.8		637	
93		$CHCl_3$	25	1.5	4	−5.4		637	

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
94		CH_2ClCH_2Cl	25	1.6	5	-11.4		638	by UV spectra
95		$CHCl_3$	25	2	6	-9.0		638	by UV spectra
96		hexane	25	1.6	5	-4.3		638	by UV spectra
97		$CHCl_3$	25	1.5	4	-20		637	
98		CH_2ClCH_2Cl	25	1.5	6	-21		637	
99		$CHCl_3$	25	1.5	4	-18		637	
100		CH_2ClCH_2Cl	25	1.5	6	-25		637	
101	$CH_2{=}CHOEt + TCNE \rightarrow$ EDA complex	$CHCl_3$	25	1.5	5	-10.3		453	
102	$CH_2{=}CHO\text{-}n\text{-}Bu + TCNE \rightarrow$ EDA complex	$CHCl_3$	25	1.5	5	-11.0		454	
103	$Me_2C{=}CHOEt + TCNE \rightarrow$ EDA complex	$CHCl_3$	25	1	4	-5.8		454	
104	$CH_2{=}CHOPh + TCNE \rightarrow$ EDA complex	CH_2Cl_2	25			-5.7		457	
105		CH_2Cl_2	25			-3.5		457	
106	$PhCH_2OH + TCNE \rightarrow$ EDA complex	$CHCl_3$	25	4.1	5	-1.9		639	
107	$Et_2O + I_2 \rightarrow$ EDA complex	heptane	25	3.3	4	-6.7		640	by means of visible I_2 absorption band
108		heptane	25	3.3	4	-7.5		641	by means of CT absorption band
109	$Et_2S + I_2 \rightarrow$ EDA complex	heptane	25	3.3	4	-8.1		640	by means of visible I_2 absorption band
110		heptane	25	3	4	-10.0		641	by means of CT absorption band
111	$Et_2Se + I_2 \rightarrow$ EDA complex	heptane	25	3	4	-14.6		640	by means of visible I_2 absorption band
112		heptane	25	3	4	-13.5		641	by means of CT absorption band
113	$PhH + I_2 \rightarrow$ EDA complex	hexane	25	1.6	5	-5.9		642	
114		hexane	40	1.6	5	-5.3		642	
115		hexane	60	1.6	5	-4.0		642	
116		hexane	25	1.6	5	-10.5		643	
117		hexane	40	1.6	5	-8.9		643	
118		hexane	60	1.6	5	-6.8		643	
119		hexane	25	1.6	5	-12.9		644	
120		hexane	40	1.6	5	-11.4		644	
121		hexane	60	1.6	5	-9.7		644	
122		hexane	25	1.6	5	-14.5		645	
123		hexane	40	1.6	5	-12.3		645	
124		hexane	60	1.6	5	-10.1		645	
125		aq EtOH	20	2	5	-7.5		646	EtOH 95 vol %
126		aq EtOH	30	2	5	-5.6		646	EtOH 95 vol %
127		aq EtOH	40	2	5	-5.4		646	EtOH 95 vol %
128		aq EtOH	50	2	5	-4.3		646	EtOH 95 vol %

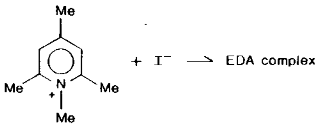
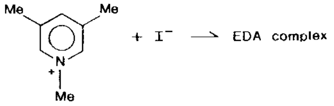
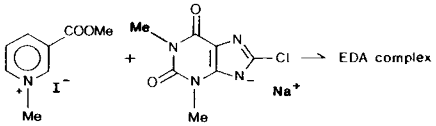
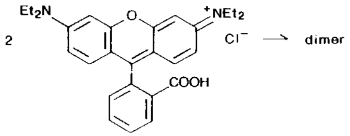
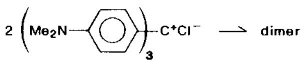
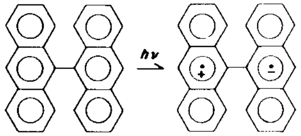
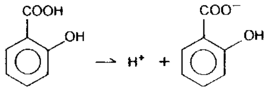
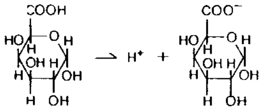
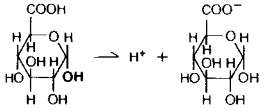
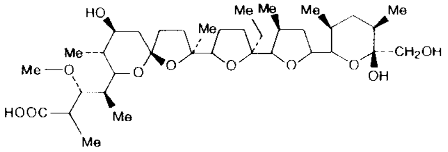
129		aq EtOH	25	2	5	−5.2		647	EtOH 95 vol %
130		aq EtOH	30	2	5	−3.7		647	EtOH 95 vol %
131		aq EtOH	40	2	5	−1.2		647	EtOH 95 vol %
132		aq EtOH	50	2	5	−2.6		647	EtOH 95 vol %
133		aq EtOH	25	2	5	−7.9		648	EtOH 95 vol %
134		aq EtOH	30	2	5	−7.0		648	EtOH 95 vol %
135		aq EtOH	40	2	5	−4.4		648	EtOH 95 vol %
136		aq EtOH	50	2	5	−3.5		648	EtOH 95 vol %
137		H_2O	25	2.1	6	−4.0		649	ionic strength 0.5 mol/L
138		H_2O	10	3.5	10	−6.2		650	ionic strength 0.2 mol/L
139		H_2O	25	3.5	10	−6.5		650	ionic strength 0.2 mol/L
140		H_2O	ambient	10	12	−4.2		651	[KCl] = 1 mol/L, 0.1 mol/L acetate buffer, *d* at 6 kbar $\Delta V = -5.1$
141		H_2O	ambient	10	8	−17.7		627	[KCl] = 1 mol/L, 0.1 mol/L acetate buffer, *d*
142	ribosomes → 2 subunits	H_2O	25	2	4	−250		366	pH 7.5
143	$Et(OCH_2CH_2)_{5-8}OC_{12}H_{15}$ → micelles	H_2O	25	1.6	9	+15		652	
144	cytochrome P-450 isozyme LM_2·cytochrome b_5 → P-450 + b_5	H_2O		1.1	10	−23		653	pH 7.4
145	pyrene + EtI $\xrightarrow{h\nu}$ exciplex	hexane	15	3.4	8	−6.5		654	
146		*i*-BuOH	15	10	7	−1.9		655	
147		Et_2O	15	10	7	−1.9		655	
148		hexane	15	10	6	−1.9		655	
149		*i*-BuOH	15	10	11	−2.3		656	
150		$MeEtCHCH_2OH$	15	10	11	−1.7		656	
151	$H_2O \rightarrow H^+ + OH^-$	H_2O	25	5.9	7	−22.4[g]		657	*h*
152		H_2O	25				−21.0	658	ionic strength 0.02 mol/L
153		H_2O	25				−22.1	34	by dilatometry
154		H_2O	25				−22.2	659	by dilatometry
155		H_2O	50	5.9	7	−20.9[g]		657	
156		H_2O	75	5.9	7	−21.4[g]		657	
157		H_2O	100	5.9	7	−26.1[g]		657	
158		H_2O	150	5.9	7	−42.1[g]		657	
159	$H_2S \rightarrow H^+ + SH^-$	H_2O	25	3	7	−12.5		660	
160		H_2O	40	3	7	−13.1		660	
161		H_2O	55	3	7	−13.7		660	
162		H_2O	75	3	7	−15.1		660	
163		H_2O	90	3	7	−16.6		660	
164	$H_2S + OH^- \rightarrow HS^- + H_2O$	H_2O	10				+8.2	661	
165		H_2O	25				+8.1	661	
166		H_2O	40				+6.8	661	
167	$H_3PO_4 \rightarrow H^+ + H_2PO_4^-$	H_2O	25	2	7	−23		662	
168		H_2O	25	1.9	6	−18		662	at 0.1 mol/L, by Raman spectroscopy

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
169		H_2O	25	2	6	−8		662	at 0.5 mol/L, by Raman spectroscopy
170		H_2O	25				−16.8	663	
171		H_2O	25				−16.3	664	
172	$H_2PO_4^- \rightarrow H^+ + HPO_4^{2-}$	H_2O	25				−26.1	663	
173		H_2O	25				−25.9	664	
174	$HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$	H_2O	25				−24.0	663	
175		H_2O	25				−36.0	664	
176	$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^-$	H_2O	25	2	8	+12		662	at 0.1 mol/L, by Raman spectroscopy
177	$^-HO_3POPO_3H_2 \rightarrow {}^-HO_3POPO_3H^- + H^+$	H_2O	25				−16.0	659	by dilatometry
178	$^-HO_3POPO_3H^- \rightarrow {}^-HO_3POPO_3^{2-} + H^+$	H_2O	25				−20.7	659	by dilatometry
179	$^{2-}O_3POPO_3H^- \rightarrow {}^{2-}O_3POPO_3^{2-} + H^+$	H_2O	25				−28.9	659	by dilatometry
180	$Me_2AsO_2H \rightarrow Me_2AsO_2^- + H^+$	H_2O	25				−13.3	659	by dilatometry
181	$SO_2 + H_2O \rightarrow H^+ + HSO_3^-$	H_2O	25				−23.1	665	
182	$HSO_4^- \rightarrow H^+ + SO_4^{2-}$	H_2O	25				−21.2	663	
183	$CO_2 + H_2O \rightarrow H^+ + HCO_3^-$	H_2O	25				−26.0	665	
184	$HCO_3^- \rightarrow H^+ + CO_3^{2-}$	H_2O	25				−29.2	663	
185	$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$	H_2O	25	9.1	6	−23.7		666	ΔV at 1 kbar
186	$HCOOH \rightarrow H^+ + HCOO^-$	H_2O	25				−6.0	658	ionic strength 0.02 mol/L
187	$AcOH \rightarrow H^+ + AcO^-$	H_2O	25				−10.6	658	ionic strength 0.02 mol/L
188		H_2O	25				−11.5	667	
189		H_2O	25				−7.8	667	[urea] = 8 mol/L
190	$EtCOOH \rightarrow H^+ + EtCOO^-$	H_2O	25				−12.0	658	ionic strength 0.02 mol/L
191	$n\text{-}PrCOOH \rightarrow H^+ + n\text{-}PrCOO^-$	MeOH	25				−39.4	668	
192	$i\text{-}PrCOOH \rightarrow H^+ + i\text{-}PrCOO^-$	H_2O	25				−13.2	658	ionic strength 0.02 mol/L
193	$t\text{-}BuCOOH \rightarrow H^+ + t\text{-}BuCOO^-$	H_2O	25				−17.1	658	ionic strength 0.02 mol/L
194	$PhCH_2COOH \rightarrow H^+ + PhCH_2COO^-$	H_2O	25				−12.3	669	
195	$PhCOOH \rightarrow H^+ + PhCOO^-$	H_2O	25				−10.7	669	
196		MeOH	25				−38.6	668	
197		MeOH	25				−32.2	668	
198		H_2O	25	1.2	7	−13.5	−13.3	670	
199		H_2O	25	1.2	7	−13.3	−13.3	670	
200	ionization of monensin 	MeOH	25				−41	668	

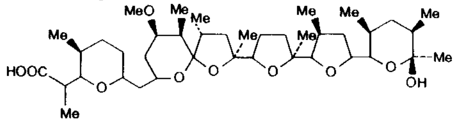
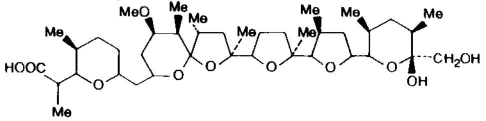
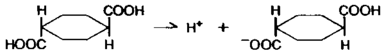
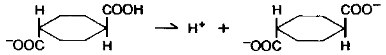
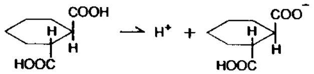
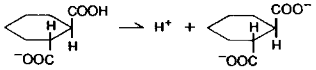
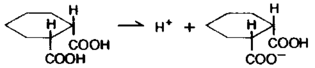
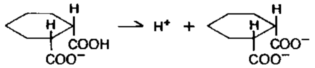
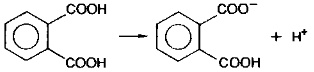
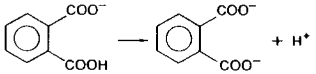
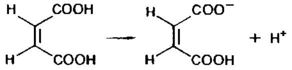
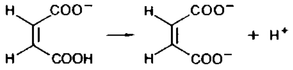
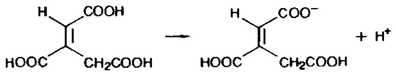
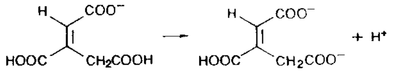
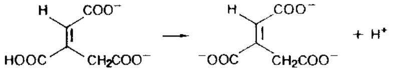
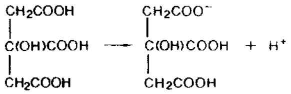
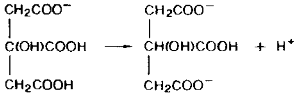
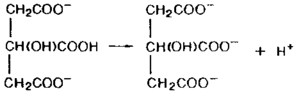
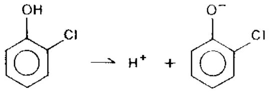
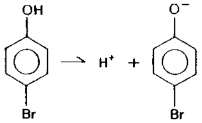
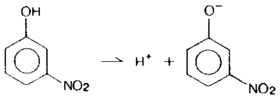
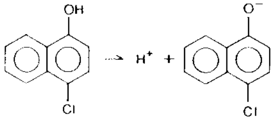
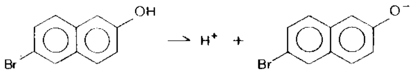
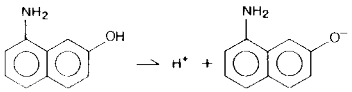
201	ionization of grisorixin 	MeOH	25		−43	668	
202	ionization of nigericin 	MeOH	25		−54	668	
203	$HOOC(CH_2)_3COOH \rightarrow H^+ + {}^-OOC(CH_2)_3COOH$	H_2O	25		−12.1	671	by dilatometry
204	${}^-OOC(CH_2)_3COOH \rightarrow H^+ + {}^-OOC(CH_2)_3COO^-$	H_2O	25		−12.5	671	by dilatometry
205	*meso*-HOOCCH(Me)CH(Me)COOH → $H^+ + {}^-$OOCCH(Me)CH(Me)COOH	H_2O	25		−10.0	671	by dilatometry
206	*meso*-$^-$OOCCH(Me)CH(Me)COOH → $H^+ + {}^-$OOCCH(Me)CH(Me)COO$^-$	H_2O	25		−18.3	671	by dilatometry
207	*d,l*-HOOCCH(Me)CH(Me)COOH → $H^+ + {}^-$OOCCH(Me)CH(Me)COOH	H_2O	25		−9.6	671	by dilatometry
208	*d,l*-$^-$OOCCH(Me)CH(Me)COOH → H^+ + *d,l*-$(CH(Me)COO^-)_2$	H_2O	25		−23.4	671	by dilatometry
209	$HOOCCH_2CMe_2CH_2COOH \rightarrow HOOCCH_2CMe_2CH_2COO^- + H^+$	H_2O	25		−9.1	659	by dilatometry
210	${}^-OOCCH_2CMe_2CH_2COOH \rightarrow {}^-OOCCH_2CMe_2CH_2COO^- + H^+$	H_2O	25		−25.0	659	by dilatometry
211		H_2O	25		−14.0	671	by dilatometry
212		H_2O	25		−14.0	671	by dilatometry
213		H_2O	25		−17.2	671	by dilatometry
214		H_2O	25		−17.2	671	by dilatometry
215		H_2O	25		−12.1	671	by dilatometry
216		H_2O	25		−22.9	671	by dilatometry
217		H_2O	25		−12.5	659	by dilatometry
218		H_2O	25		−19.9	659	by dilatometry
219		H_2O	25		−5.1	659	by dilatometry
220		H_2O	25		−24.4	659	by dilatometry
221		H_2O	25		−7.7	659	by dilatometry

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
222		H_2O	25				−16.4	659	by dilatometry
223		H_2O	25				−19.9	659	by dilatometry
224	 $CH_2COOH-C(OH)COOH-CH_2COOH \rightarrow CH_2COO^- -C(OH)COOH-CH_2COOH + H^+$	H_2O	25				−10.7	659	by dilatometry
225	 $CH_2COO^- -C(OH)COOH-CH_2COOH \rightarrow CH_2COO^- -CH(OH)COOH-CH_2COO^- + H^+$	H_2O	25				−12.3	659	by dilatometry
226	 $CH_2COO^- -CH(OH)COOH-CH_2COO^- \rightarrow CH_2COO^- -CH(OH)COO^- -CH_2COO^- + H^+$	H_2O	25				−22.3	659	by dilatometry
227	$PhOH \rightarrow H^+ + PhO^-$	H_2O	10	1.5	4	−22.2		672	
228		H_2O	20	1.5	4	−28.1		672	
229		H_2O	30	1.5	4	−26.5		672	
230		H_2O	40	1.5	4	−29.8		672	
231		H_2O	10	1.5	4	−13.4		672	
232		H_2O	20	1.5	4	−11.3		672	
233		H_2O	30	1.5	4	−10.9		672	
234		H_2O	40	1.5	4	−12.6		672	
235		H_2O	25	2	5	−7.0		673	
236		H_2O	30	2	5	−5.3		673	
237		H_2O	35	2	5	−4.1		673	
238		H_2O	40	2	5	−4.6		673	
239		H_2O	25	2	5	−8.7		673	
240		H_2O	30	2	5	−5.0		673	
241		H_2O	35	2	5	−4.5		673	
242		H_2O	40	2	5	−4.3		673	
243		H_2O	25	2	5	−24.8		674	ΔV at 1 kbar
244		H_2O	30	2	5	−24.9		674	ΔV at 1 kbar
245		H_2O	35	2	5	−25.8		674	ΔV at 1 kbar
246		H_2O	40	2	5	−26.6		674	ΔV at 1 kbar
247		H_2O	25	2	5	−19.1		674	ΔV at 1 kbar
248		H_2O	30	2	5	−19.5		674	ΔV at 1 kbar
249		H_2O	35	2	5	−19.9		674	ΔV at 1 kbar
250		H_2O	40	2	5	−20.3		674	ΔV at 1 kbar
251		H_2O	25	2	5	−16.9		674	ΔV at 1 kbar
252		H_2O	30	2	5	−17.4		674	ΔV at 1 kbar
253		H_2O	35	2	5	−17.9		674	ΔV at 1 kbar
254		H_2O	40	2	5	−18.1		674	ΔV at 1 kbar

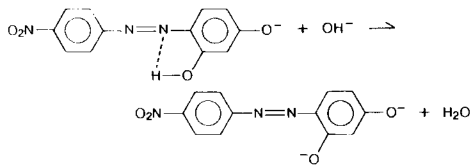
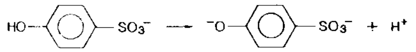
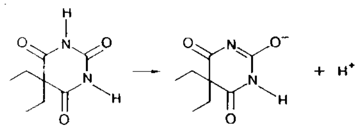
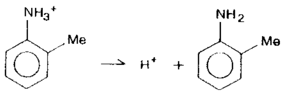
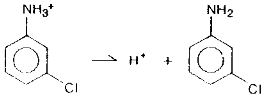
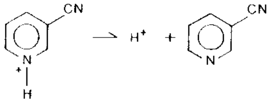
255		H_2O	10	2	5	+0.3		565	
256		H_2O	25				−18.4	659	by dilatometry
257		H_2O	25				−12.5	659	by dilatometry
258	$NH_4^+ \rightarrow H^+ + NH_3$	H_2O	25				+6.6	658	ionic strength 0.02 mol/L
259	$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$	H_2O	25	2	11	−28.8		675	
260		H_2O	100	2	11	−31.7		675	
261		H_2O	150	2	11	−39.5		675	
262		H_2O	200	2	11	−47.7		675	
263		H_2O	250	2	11	−67		675	
264	$MeNH_3^+ \rightarrow H^+ + MeNH_2$	H_2O	25				+2.4	658	ionic strength 0.02 mol/L
265	$EtNH_3^+ \rightarrow H^+ + EtNH_2$	H_2O	25				+1.9	658	ionic strength 0.02 mol/L
266	$n\text{-}PrNH_3^+ \rightarrow H^+ + n\text{-}PrNH_2$	H_2O	25				+3.4	667	
267		H_2O	25				+4.7	667	[urea] = 8 mol/L
268	$i\text{-}PrNH_3^+ \rightarrow H^+ + i\text{-}PrNH_2$	H_2O	25				+2.0	658	ionic strength 0.02 mol/L
269	$t\text{-}BuNH_3^+ \rightarrow H^+ + t\text{-}BuNH_2$	H_2O	25				+0.6	658	ionic strength 0.02 mol/L
270	$Et_3N + MeOH \rightarrow Et_3NH^+ + MeO^-$	MeOH	25	2	11	−47.7		676	
271		MeOH	30	1.6	9	−52.0		676	
272		MeOH	40	1.6	9	−59.0		676	
273		MeOH	25	2	11	−46.4		677	
274	$NH_2NH_3^+ \rightarrow H^+ + NH_2NH_2$	H_2O	25				+7.6	678	
275	$NH_2(CH_2)_2NH_3^+ \rightarrow H^+ + NH_2(CH_2)_2NH_2$	H_2O	25				+6.7	678	
276	$NH_2(CH_2)_3NH_3^+ \rightarrow H^+ + NH_2(CH_2)_3NH_2$	H_2O	25				+5.5	678	
277	$NH_2(CH_2)_4NH_3^+ \rightarrow H^+ + NH_2(CH_2)_4NH_2$	H_2O	25				+3.9	678	
278	$NH_2(CH_2)_5NH_3^+ \rightarrow H^+ + NH_2(CH_2)_5NH_2$	H_2O	25				+3.3	678	
279	$NH_2(CH_2)_6NH_3^+ \rightarrow H^+ + NH_2(CH_2)_6NH_2$	H_2O	25				+2.8	678	
280	$NH_2(CH_2)_7NH_3^+ \rightarrow H^+ + NH_2(CH_2)_7NH_2$	H_2O	25				+3.8	678	
281	$NH_2(CH_2)_8NH_3^+ \rightarrow H^+ + NH_2(CH_2)_8NH_2$	H_2O	25				+3.5	678	
282	$NH_2(CH_2)_9NH_3^+ \rightarrow H^+ + NH_2(CH_2)_9NH_2$	H_2O	25				+3.1	678	
283	$NH_2(CH_2)_{10}NH_3^+ \rightarrow H^+ + NH_2(CH_2)_{10}NH_2$	H_2O	25				+2.8	678	
284	$NH_3^+(CH_2)_2NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_3NH_2$	H_2O	25				+11.5	678	
285	$NH_3^+(CH_2)_3NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_3NH_2$	H_2O	25				+10.1	678	
286	$NH_3^+(CH_2)_4NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_4NH_2$	H_2O	25				+9.0	678	
287	$NH_3^+(CH_2)_5NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_5NH_2$	H_2O	25				+8.1	678	
288	$NH_3^+(CH_2)_6NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_6NH_2$	H_2O	25				+6.4	678	
289	$NH_3^+(CH_2)_7NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_7NH_2$	H_2O	25				+5.2	678	
290	$NH_3^+(CH_2)_8NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_8NH_2$	H_2O	25				+5.7	678	
291	$NH_3^+(CH_2)_9NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_9NH_2$	H_2O	25				+5.7	678	
292	$NH_3^+(CH_2)_{10}NH_3^+ \rightarrow H^+ + NH_3^+(CH_2)_{10}NH_2$	H_2O	25				+5.6	678	
293	cryptand[2.2.2]$H^+ \rightarrow H^+ +$ cryptand[2.2.2]	H_2O	25				+2	679	
294	cryptand[2.2.2]$2H^+ \rightarrow H^+ +$ cryptand[2.2.2]H^+	H_2O	25				−4	679	

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
295	$PhNH_3^+ \rightarrow H^+ + PhNH_2$	H_2O	10	1.5	4	+4.3		672	
296		H_2O	20	1.5	4	+2.7		672	
297		H_2O	25				+5.4	669	
298		H_2O	30	1.5	4	+2.5		672	
299		H_2O	40	1.5	4	+3.6		672	
300	$PhNH_2Me^+ \rightarrow H^+ + PhNHMe$	H_2O	25				+4.3	669	
301	$PhNHMe_2^+ \rightarrow H^+ + PhNMe_2$	H_2O	25				+2.5	669	
302		H_2O	10	1.5	4	+9.0		672	
303		H_2O	20	1.5	4	+8.0		672	
304		H_2O	30	1.5	4	+6.4		672	
305		H_2O	40	1.5	4	+7.8		672	
306		aq EtOH	20	1.5	4	+12.4		680	EtOH 10.5 vol %, ionic strength 0.04 mol/kg
307		aq EtOH	20	1.5	4	+9.4		680	EtOH 10.5 vol %, ionic strength 0.06 mol/kg
308		aq EtOH	20	1.5	4	+8.6		680	EtOH 10.5 vol %, ionic strength 0.08 mol/kg
309		aq EtOH	20	1.5	4	+7.8		680	EtOH 10.5 vol %, ionic strength 0.10 mol/kg
310		aq EtOH	30	1.5	4	+12.2		680	EtOH 10.5 vol %, ionic strength 0.04 mol/kg
311		aq EtOH	30	1.5	4	+9.6		680	EtOH 10.5 vol %, ionic strength 0.06 mol/kg
312		aq EtOH	30	1.5	4	+8.8		680	EtOH 10.5 vol %, ionic strength 0.08 mol/kg
313		aq EtOH	30	1.5	4	+9.8		680	EtOH 10.5 vol %, ionic strength 0.10 mol/kg
314		aq EtOH	40	1.5	4	+12.2		680	EtOH 10.5 vol %, ionic strength 0.04 mol/kg
315		aq EtOH	40	1.5	4	+9.9		680	EtOH 10.5 vol %, ionic strength 0.06 mol/kg
316		aq EtOH	40	1.5	4	+11.1		680	EtOH 10.5 vol %, ionic strength 0.08 mol/kg
317		aq EtOH	40	1.5	4	+11.4		680	EtOH 10.5 vol %, ionic strength 0.10 mol/kg
318		aq EtOH	50	1.5	4	+11.7		680	EtOH 10.5 vol %, ionic strength 0.04 mol/kg
319		aq EtOH	50	1.5	4	+12.6		680	EtOH 10.5 vol %, ionic strength 0.06 mol/kg
320		aq EtOH	50	1.5	4	+13.2		680	EtOH 10.5 vol %, ionic strength 0.08 mol/kg
321		aq EtOH	50	1.5	4	+14.4		680	EtOH 10.5 vol %, ionic strength 0.10 mol/kg
322		H_2O	15	2.5	6	+1.1		681	
323		H_2O	20	2.5	6	+1.1		681	
324		H_2O	25	2.5	6	+1.1		681	
325		H_2O	30	2.5	6	+1.1		681	
326		H_2O	35	2.5	6	+1.2		681	
327		H_2O	40	2.5	6	+1.2		681	

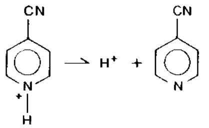
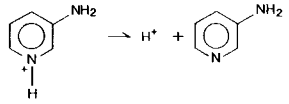
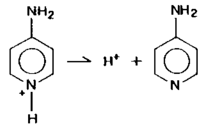
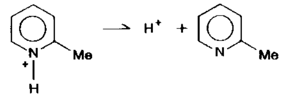
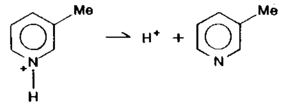
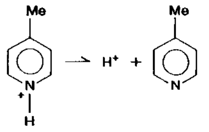
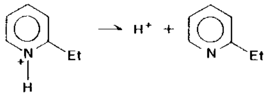
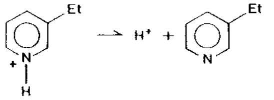
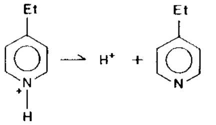
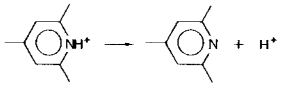
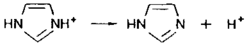
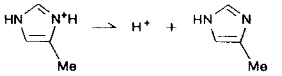
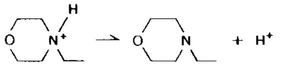
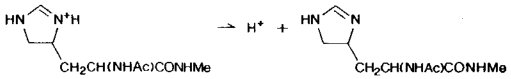
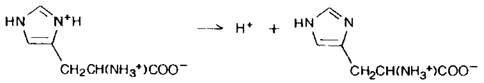
328		H_2O	15	2.5	6	+1.4	681
329		H_2O	20	2.5	6	+1.4	681
330		H_2O	25	2.5	6	+1.4	681
331		H_2O	30	2.5	6	+1.5	681
332		H_2O	35	2.5	6	+1.6	681
333		H_2O	40	2.5	6	+1.4	681
334		H_2O	15	2.5	6	+4.4	681
335		H_2O	20	2.5	6	+4.4	681
336		H_2O	25	2.5	6	+4.9	681
337		H_2O	30	2.5	6	+4.9	681
338		H_2O	35	2.5	6	+4.9	681
339		H_2O	40	2.5	6	+4.7	681
340		H_2O	15	2.5	6	+6.5	681
341		H_2O	20	2.5	6	+6.4	681
342		H_2O	25	2.5	6	+6.3	681
343		H_2O	30	2.5	6	+5.7	681
344		H_2O	35	2.5	6	+7.0	681
345		H_2O	40	2.5	6	+6.7	681
346		H_2O	5	3	7	+3.1[i]	682
347		H_2O	10	3	7	+3.1[i]	682
348		H_2O	15	3	7	+4.0[i]	682
349		H_2O	20	3	7	+3.3[i]	682
350		H_2O	25	3	7	+4.0[i]	682
351		H_2O	30	3	7	+3.4[i]	682
352		H_2O	35	3	7	+3.9[i]	682
353		H_2O	40	3	7	+3.5[i]	682
354		H_2O	45	3	7	+3.5[i]	682
355		H_2O	50	3	7	+3.5[i]	682
356		H_2O	55	3	7	+3.9[i]	682
357		H_2O	60	3	7	+3.7[i]	682
358		H_2O	65	3	7	+3.7[i]	682
359		H_2O	70	3	7	+3.8[i]	682
360		H_2O	5	3	7	+3.2[i]	682
361		H_2O	10	3	7	+2.7[i]	682
362		H_2O	15	3	7	+3.6[i]	682
363		H_2O	20	3	7	+3.3[i]	682
364		H_2O	25	3	7	+3.8[i]	682
365		H_2O	30	3	7	+3.4[i]	682
366		H_2O	35	3	7	+3.4[i]	682
367		H_2O	40	3	7	+3.6[i]	682
368		H_2O	45	3	7	+3.9[i]	682
369		H_2O	50	3	7	+3.6[i]	682
370		H_2O	55	3	7	+3.7[i]	682
371		H_2O	60	3	7	+4.6[i]	682
372		H_2O	65	3	7	+3.7[i]	682
373		H_2O	70	3	7	+3.8[i]	682
374		H_2O	5	3	7	+3.9[i]	682
375		H_2O	10	3	7	+3.3[i]	682
376		H_2O	15	3	7	+3.4[i]	682
377		H_2O	20	3	7	+3.1[i]	682
378		H_2O	25	3	7	+3.4[i]	682
379		H_2O	30	3	7	+3.5[i]	682
380		H_2O	35	3	7	+3.3[i]	682

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^{a}/ (cm^3 mol^{-1})	ΔV^{b}/ (cm^3 mol^{-1})	ref	remarks
381		H_2O	40	3	7	$+3.5^{i}$		682	
382		H_2O	45	3	7	$+3.5^{i}$		682	
383		H_2O	50	3	7	$+6.4^{i}$		682	
384		H_2O	55	3	7	$+3.6^{i}$		682	
385		H_2O	60	3	7	$+3.7^{i}$		682	
386		H_2O	65	3	7	$+3.7^{i}$		682	
387		H_2O	70	3	7	$+7.2^{i}$		682	
388		H_2O	25	2.5	6	$+2.9^{i}$		682	
389		H_2O	25	2.5	6	$+3.0^{i}$		682	
390		H_2O	25	2.5	6	$+1.8^{i}$		682	
391		H_2O	25				+0.2	659	by dilatometry
392		H_2O	25				+1.8	659	by dilatometry
393		H_2O	25				+0.8	667	
394		H_2O	25				+2.3	667	[urea] = 8 mol/L
395		H_2O	25				+4.6	659	by dilatometry
396	$(HOCH_2CH_2)_3NH^+ \rightarrow (HOCH_2CH_2)_3N + H^+$	H_2O	25				+4.5	659	by dilatometry
397	$(HOCH_2)_3CNH_3^+ \rightarrow (HOCH_2)_3CNH_2 + H^+$	H_2O	25				+4.3	659	by dilatometry
398	$(HOCH_2)_2CMeNH_3^+ \rightarrow (HOCH_2)_2CMeNH_2 + H^+$	H_2O	25				+3.5	659	by dilatometry
399	$(HOCH_2CH_2)_2NH_2^+ \rightarrow (HOCH_2CH_2)_2NH + H^+$	H_2O	25				+6.2	659	by dilatometry
400	$(HOCH_2)_3CNH_2^+CH_2CH_2CH_2NHC(CH_2OH)_3 \rightarrow (HOCH_2)_3CNHCH_2CH_2CH_2NHC(CH_2OH)_3 + H^+$						−3.1	659	by dilatometry
401	$(HOCH_2CH_2)_2NH^+C(CH_2OH)_3 \rightarrow (HOCH_2CH_2)_2NC(CH_2OH)_3 + H^+$	H_2O	25				+3.1	659	by dilatometry
402	$[(HOCH_2)_3CNH_2^+CH_2]_2CH_2 \rightarrow (HOCH_2)_3CNHCH_2CH_2CH_2NH_2^+C(CH_2OH)_3 + H^+$	H_2O	25				+10.5	659	by dilatometry
403		H_2O	10–30	1.5	4	+1		683	
404		H_2O	20	1.5	4	+1		683	
405	$H_3N^+CH_2COOH \rightarrow H^+ + H_3N^+CH_2COO^-$	H_2O	25				−7.5	684	
406		H_2O	25				−5.9	685	
407	$H_3N^+CH_2COO^- \rightarrow H^+ + H_2NCH_2COO^-$	H_2O	25				+1.7	684	

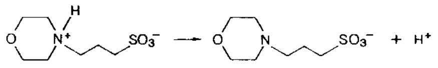
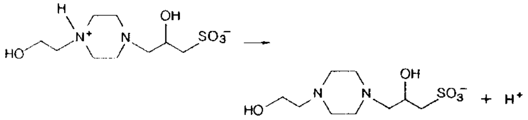
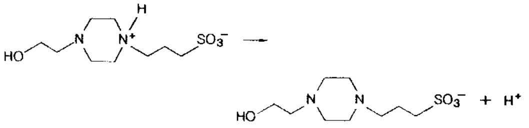
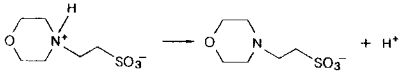
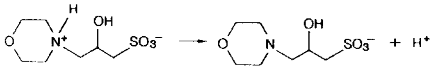
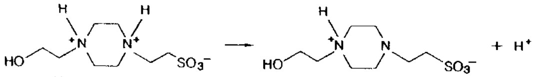
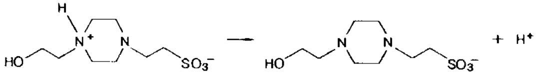
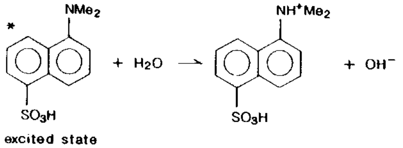
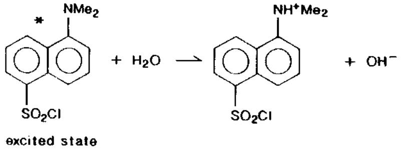
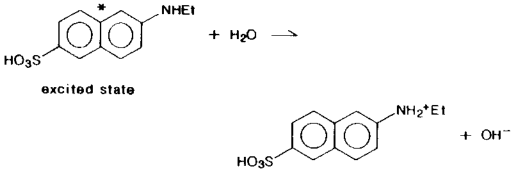
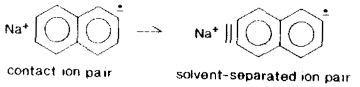
408		H_2O	25	+0.5	685	
409	$Me(NH_3^+)CHCOOH \rightarrow H^+ + Me(NH_3^+)CHCOO^-$	H_2O	25	−8.5	684	
410	$Me(NH_3^+)CHCOO^- \rightarrow H^+ + Me(NH_2)CHCOO^-$	H_2O	25	+0.5	684	
411	$H_3N^+CH_2CH_2COOH \rightarrow H^+ + H_3N^+CH_2CH_2COO^-$	H_2O	25	−7.7	684	
412		H_2O	25	−6.7	685	
413	$H_3N^+CH_2CH_2COO^- \rightarrow H^+ + H_2NCH_2CH_2COO^-$	H_2O	25	+2.5	684	
414		H_2O	25	+1.5	685	
415	$H_3N^+(CH_2)_3COOH \rightarrow H^+ + H_3N^+(CH_2)_3COO^-$	H_2O	25	−9.6	684	
416		H_2O	25	−8.5	685	
417	$H_3N^+(CH_2)_3COO^- \rightarrow H^+ + H_2N(CH_2)_3COO^-$	H_2O	25	+3.5	684	
418		H_2O	25	+2.0	685	
419	$H_3N^+(CH_2)_4COOH \rightarrow H^+ + H_3N^+(CH_2)_4COO^-$	H_2O	25	−11.4	684	
420		H_2O	25	−10.9	685	
421	$H_3N^+(CH_2)_4COO^- \rightarrow H^+ + H_2N(CH_2)_4COO^-$	H_2O	25	+4.0	684	
422		H_2O	25	+3.2	685	
423	$H_3N^+(CH_2)_5COOH \rightarrow H^+ + H_3N^+(CH_2)_5COO^-$	H_2O	25	−12.4	684	
424		H_2O	25	−10.8	685	
425	$H_3N^+(CH_2)_5COO^- \rightarrow H^+ + H_2N(CH_2)_5COO^-$	H_2O	25	+3.9	684	
426		H_2O	25	+3.0	685	
427	$H_3N^+(CH_2)_6COOH \rightarrow H^+ + H_3N^+(CH_2)_6COO^-$	H_2O	25	−11.6	685	
428	$H_3N^+(CH_2)_6COO^- \rightarrow H^+ + H_2N(CH_2)_6COO^-$	H_2O	25	+3.1	685	
429	$H_3N^+(CH_2)_7COOH \rightarrow H^+ + H_3N^+(CH_2)_7COO^-$	H_2O	25	−13.3	684	
430		H_2O	25	−11.6	685	
431	$H_3N^+(CH_2)_7COO^- \rightarrow H^+ + H_2N(CH_2)_7COO^-$	H_2O	25	+4.1	684	
432		H_2O	25	+3.1	685	
433	$H_3N^+(CH_2)_8COOH \rightarrow H^+ + H_3N^+(CH_2)_8COO^-$	H_2O	25	−12.3	685	
434	$H_3N^+(CH_2)_8COO^- \rightarrow H^+ + H_2N(CH_2)_8COO^-$	H_2O	25	+4.0	685	
435	$H_3N^+(CH_2)_9COOH \rightarrow H^+ + H_3N^+(CH_2)_9COO^-$	H_2O	25	−13.0	685	
436	$H_3N^+(CH_2)_9COO^- \rightarrow H^+ + H_2N(CH_2)_9COO^-$	H_2O	25	+3.9	685	
437	$H_3N^+(CH_2)_{10}COOH \rightarrow H^+ + H_3N^+(CH_2)_{10}COO^-$	H_2O	25	−13.9	684	
438		H_2O	25	−13.3	685	
439	$H_3N^+(CH_2)_{10}COO^- \rightarrow H^+ + H_2N(CH_2)_{10}COO^-$	H_2O	25	+4.6	684	
440		H_2O	25	+4.6	685	
441	$(HOCH_2)_3CNH_2^+CH_2COO^- \rightarrow (HOCH_2)_3CNHCH_2COO^- + H^+$	H_2O	25	−2.8	659	by dilatometry
442	$(HOCH_2CH_2)_2NH^+CH_2COO^- \rightarrow (HOCH_2CH_2)_2NCH_2COO^- + H^+$	H_2O	25	−2.0	659	by dilatometry
443	$(HOCH_2)_3CNH_2^+(CH_2CH_2SO_3^-) \rightarrow (HOCH_2)_3CNH(CH_2CH_2SO_3^-) + H^+$	H_2O	25	−1.5	659	by dilatometry
444	$(HOCH_2)_3CNH_2^+(CH_2CH_2CH_2SO_3^-) \rightarrow (HOCH_2)_3CNH(CH_2CH_2CH_2SO_3^-) + H^+$	H_2O	25	+0.5	659	by dilatometry
445	$H_2NCOCH_2NH_2^+(CH_2CH_2SO_3^-) \rightarrow H_2NCOCH_2NH(CH_2CH_2SO_3^-) + H^+$	H_2O	25	+4.0	659	by dilatometry
446	$(HOCH_2CH_2)_2NH^+CH_2CH(OH)CH_2SO_3^- \rightarrow (HOCH_2CH_2)_2NCH_2CH(OH)CH_2SO_3^- + H^+$	H_2O	25	+2.7	659	by dilatometry
447	$(HOCH_2)_3CNH_2^+CH_2CH(OH)CH_2SO_3^- \rightarrow (HOCH_2)_3CNHCH_2CH(OH)CH_2SO_3^- + H^+$	H_2O	25	+1.5	659	by dilatometry
448	$cy\text{-}C_6H_{11}NH_2^+(CH_2CH_2SO_3^-) \rightarrow cy\text{-}C_6H_{11}NH(CH_2CH_2SO_3^-) + H^+$	H_2O	25	+1.2	659	by dilatometry
449	$cy\text{-}C_6H_{11}NH_2^+(CH_2CH_2CH_2SO_3^-) \rightarrow cy\text{-}C_6H_{11}NH(CH_2CH_2CH_2SO_3^-) + H^+$	H_2O	25	+0.4	659	by dilatometry
450	$(HOCH_2CH_2)_2NH^+(CH_2CH_2SO_3^-) \rightarrow (HOCH_2CH_2)_2NCH_2CH_2SO_3^- + H^+$	H_2O	25	+2.6	659	by dilatometry
451		H_2O	25	+4.7	659	by dilatometry

TABLE IX (Continued)

no.	reaction	solvent	$T/°C$	$P/$ kbar	no. of K	$\Delta V^a/$ (cm^3 mol^{-1})	$\Delta V^b/$ (cm^3 mol^{-1})	ref	remarks
452		H_2O	25				+2.6	659	by dilatometry
453		H_2O	25				+3.4	659	by dilatometry
454		H_2O	25				+3.9	659	by dilatometry
455		H_2O	25				+3.9	659	by dilatometry
456		H_2O	25				+9.4	659	by dilatometry
457		H_2O	25				+4.8	659	by dilatometry
458		H_2O	ambient	5	6	−17		686	
459		D_2O	ambient	5	6	−11		686	
460		H_2O	ambient	5	6	−18		686	
461		H_2O	ambient	5	6	+4		686	
462	$Co(edda)(H_2NCH_2CH_2OH)^+ + OH^- \rightarrow Co(edda)(H_2NCH_2CH_2O) + H_2O$	H_2O	25				+17.5	34, 687	
463		H_2O	25				+16.9	687	ionic strength 0.005 mol/L, by dilatometry
464	$NaH_2PO_4 \rightarrow Na^+ + H_2PO_4^-$	H_2O	25	2	7	+0.6		662	
465	$KH_2PO_4 \rightarrow K^+ + H_2PO_4^-$	H_2O	25	2	7	0.0		662	
466	$(NH_4)SO_4^- \rightarrow NH_4^+ + SO_4^{2-}$	H_2O	25	2	9	−3.4		688	
467	$LiSO_4^- \rightarrow Li^+ + SO_4^{2-}$	H_2O	25	2	9	−5.8		688	
468	$NaSO_4^- \rightarrow Na^+ + SO_4^{2-}$	H_2O	25	2	9	−7.3		688	

469	$KSO_4^- \rightarrow K^+ + SO_4^{2-}$	H_2O	25	2	9	−5.9		688	
470	$RbSO_4^- \rightarrow Rb^+ + SO_4^{2-}$	H_2O	25	2	9	−3.3		688	
471	$CsSO_4^- \rightarrow Cs^+ + SO_4^{2-}$	H_2O	25	2	9	−6.2		688	
472	$Na_2SO_4 \rightarrow Na^+ + NaSO_4^-$	H_2O	25	2	9	−8.3		689	
473	$MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-}$	H_2O	15	2	9	−10.8		690	
		H_2O	15	1.5	7	−9.9		691	
474	$NaSO_4^- \rightarrow Na^+ + SO_4^{2-}$	H_2O	25	2	9	−5.4		692	
475	$KSO_4^- \rightarrow K^+ + SO_4^{2-}$	H_2O	25	2	9	−8.8		692	
476	$MgCl^+ \rightarrow Mg^{2+} + Cl^-$	H_2O	25	2	9	−5.9		692	
477	$MnSO_4 \rightarrow Mn^{2+} + SO_4^{2-}$	H_2O	15	1.6	5	−9.9		693	
478		H_2O	25	1.6	5	−7.4		693	
479		H_2O	40	1.6	5	−6.1		693	
480	$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$	H_2O	15	1.6	5	−9.2		693	
481		H_2O	25	1.6	5	−8.1		693	
482		H_2O	40	1.6	5	−6.9		693	
483	$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$	H_2O	15	1.6	5	−6.6		693	
484		H_2O	25	1.6	5	−6.0		693	
485		H_2O	40	1.6	5	−5.1		693	
486	$MgSO_4 \rightarrow Mg^{2+} + SO_4^{2-}$	H_2O	20	2	9	−9.3		690	
487		H_2O	25	1.5	7	−7.8		691	
488		H_2O	25	2	9	−9.0		690	
489		H_2O	35	1.5	7	−6.9		691	
490	$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$	H_2O	10	2	9	−11.6		690	
491		H_2O	15	2	9	−11.6		690	
492		H_2O	15	1.5	7	−11.9		691	
493		H_2O	20	2	9	−11.7		690	
494		H_2O	25	2	9	−11.7		690	
495		H_2O	25	1.5	7	−10.1		691	
496		H_2O	25				−25	694	
497		H_2O	30	2	9	−12.0		690	
498		H_2O	35	1.5	7	−9.1		691	
499	$MnSO_4 \rightarrow Mn^{2+} + SO_4^{2-}$	H_2O	25				−7.4	695	
500	$CoSO_4 \rightarrow Co^{2+} + SO_4^{2-}$	H_2O	15	2	9	−10.5		690	
501		H_2O	25	2	9	−11.5		690	
502		H_2O	25				−10.9	695	
503	$NiSO_4 \rightarrow Ni^{2+} + SO_4^{2-}$	H_2O	15	2	9	−11.1		690	
504		H_2O	25	2	9	−11.6		690	
505		H_2O	25				−11.4	695	
506	$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$	H_2O	10	1.4	8	−10.7		696	
507		H_2O	25	1.4	8	−10.0		696	
508		H_2O	25				−11.3	695	
509		H_2O	40	1.4	8	−11.3		696	
510	$ZnSO_4 \rightarrow Zn^{2+} + SO_4^{2-}$	H_2O	25				−10.0	695	
511	$CdSO_4 \rightarrow Cd^{2+} + SO_4^{2-}$	H_2O	25				−3.4	695	
512		H_2O	25				−9.3	697	
513		aq MeCN	25				−7.2	697	MeCN 3 mol %
514		aq MeCN	25				−61	697	MeCN 20.9 mol %
515		aq MeCN	25				−96	697	MeCN 21.3 mol %
516	$LaSO_4^+ \rightarrow La^{3+} + SO_4^{2-}$	H_2O	25				−22.8	698	
517	$NaCl \rightarrow Na^+ + Cl^-$	aq 1,4-dioxane	25				−7	699	1,4-dioxane 60 wt %
518	$HgCl^+ \rightarrow Hg^{2+} + Cl^-$	H_2O	25				−13	700	ionic strength 0.7 mol/kg
519	$HgCl_2 \rightarrow HgCl^+ + Cl^-$	H_2O	25				−14	700	ionic strength 0.7 mol/kg

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
520	$HgCl_3^- \rightarrow HgCl_2 + Cl^-$	H_2O	25				−3	700	ionic strength 0.7 mol/kg
521	$HgCl_4^{2-} \rightarrow HgCl_3^- + Cl^-$	H_2O	25				−2	700	ionic strength 0.7 mol/kg
522	$Co(en)_3Cl_3 \rightarrow Co(en)_3Cl_2^+ + Cl^-$	H_2O	25	2	5	−1.9		701	
523	$Co(NH_3)_6Cl_3 \rightarrow Co(NH_3)_6Cl_2^+ + Cl^-$	H_2O	25	2	5	−1.2		701	
524	$(n\text{-Bu})_4NBr \rightarrow (n\text{-Bu})_4N^+ + Br^-$	acetone	25	2.8	8	−17.3		702	
525		*i*-BuCOMe	25	1.7	8	−21.5		702	
526	$LiBr \rightarrow Li^+ + Br^-$	MeCN	25	2.1	7	−14.8		702	
527	$CoBr_2 \rightarrow Co^{2+} + 2Br^-$	acetone	25	5.5	7	−109		703	
528	$CoBr_3^- \rightarrow CoBr_2 + Br^-$	acetone	25	5.5	7	+5.2		703	
529	$CoBr_4^{2-} \rightarrow CoBr_3^- + Br^-$	acetone	25	4.9	5	+0.8		703	
530	$NiBr_4^{2-} \rightarrow NiBr_3^- + Br^-$	acetone	25	3.9	5	+4.3		703	
531	$(n\text{-Bu})_4NI \rightarrow (n\text{-Bu})_4N^+ + I^-$	acetone	25	2.8	8	−14.0		702	
532		*i*-BuCOMe	25	1.7	8	−23.8		702	
533	$LiI \rightarrow Li^+ + I^-$	MeCN	25	2.1	7	−24.0		702	
534		acetone	30	2	7	−21		704	
535	$NaI \rightarrow Na^+ + I^-$	MeCN	25	2.1	7	−33.4		702	
536		acetone	30	2	7	−25		704	
537	$KI \rightarrow K^+ + I^-$	acetone	30	2	7	−23		704	
538	$CsI \rightarrow Cs^+ + I^-$	acetone	30	2	7	−24		704	
539		THF	−7.0	0.6	7	−15.4		71	
540		THF	−4.0	0.6	7	−15.0		71	
541		THF	−2.5	0.6	7	−13.1		71	
542		THF	−1.9	0.6	7	−16.4		71	
543		THF	1	0.6	7	−13.1		71	
544		THF	3	0.6	7	−15.1		71	
545	$(n\text{-Bu})_4N^+Pic^- \rightarrow (n\text{-Bu})_4N^+ + Pic^-$	PhH	25	0.7	6	−61.6		508	
546		PhCl–PhH	25	0.7	6	−54.5		508	PhCl 11 vol %
547		PhCl–PhH	25	0.7	6	−57.3		508	PhCl 16 vol %
548		PhCl–PhH	25	0.7	6	−51.8		508	PhCl 30 vol %
549		PhCl–PhH	25	0.7	6	−48.5		508	PhCl 40 vol %
550		PhCl–PhH	25	0.7	6	−50.8		508	PhCl 50 vol %
551	$AlI_{3(l)} \rightarrow$ ions (not identified)	neat	223	1	9	−84		705	
552		neat	245	1	7	−105		705	
553	$GaI_{3(l)} \rightarrow$ ions (not identified)	neat	270	1	10	−121		705	
554		neat	293	1	10	−132		705	
555		neat	310	1	7	−136		705	
556	$InI_{3(l)} \rightarrow$ ions (not identified)	neat	252	1	9	−11		705	
557		neat	301	1	6	−22		705	
558		neat	380	1	9	−28		705	
559		neat	428	1	8	−35		705	
560	$BiI_{3(l)} \rightarrow$ ions (not identified)	neat	447	1	7	−6.0		705	
561		neat	481	1	8	−10.4		705	
562	$CdI_{2(l)} \rightarrow$ ions (not identified)	neat	388	1		−0.4		705	
563		neat	430	1	10	−1.7		705	
564		neat	459	1	8	−3.4		705	
565		neat	492	1	9	−3.8		705	
566	$I_{2(l)} \rightarrow$ ions (not identified)	neat	139	1	7	−26		705	
567		neat	159	1	11	−29		705	
568		neat	176	1	11	−35		705	
569	$Al(SCN)^{2+} \rightarrow Al^{3+} + SCN^-$	H_2O	20	3	2	−5		706, 707	by Raman spectroscopy, ionic strength 4 mol/L

570	$Mn(SCN)^+ \rightarrow Mn^{2+} + SCN^-$	H_2O	20	3	2	0		706, 707	by Raman spectroscopy, ionic strength 2.8 mol/L
571	$Mn(SCN)_2 \rightarrow Mn^{2+} + 2SCN^-$	H_2O	20	3	2	−7.3		706, 707	by Raman spectroscopy, ionic strength 2.8 mol/L
572	$Fe(SCN)^{2+} \rightarrow Fe^{3+} + SCN^-$	H_2O	20	2	9	−8.3		147	
573	$Zn(SCN)^+ \rightarrow Zn^{2+} + SCN^-$	H_2O	20	3	2	+11		706, 707	by Raman spectroscopy, ionic strength 2.8 mol/L
574	$Zn(SCN)_2 \rightarrow Zn^{2+} + 2SCN^-$	H_2O	20	3	2	−9		706, 707	by Raman spectroscopy, ionic strength 2.8 mol/L
575	$Zn(SCN)_4^{2-} \rightarrow Zn^{2+} + 4SCN^-$	H_2O	20	3	2	−19		706, 707	by Raman spectroscopy, ionic strength 2.8 mol/L
576	$In(SCN)_3 \rightarrow In^{3+} + 3SCN^-$	H_2O	20	3	2	+3		706, 707	by Raman spectroscopy, ionic strength 1.9 mol/L
577	$In(SCN)_4^- \rightarrow In^{3+} + 4SCN^-$	H_2O	20	3	2	−21		706, 707	by Raman spectroscopy, ionic strength 1.9 mol/L
578	$Hg(SCN)_4^{2-} \rightarrow Hg^{2+} + 4SCN^-$	H_2O	20	3	2	−6		706, 707	by Raman spectroscopy, ionic strength 2.1 mol/L
579	$Th(SCN)^{3+} \rightarrow Th^{4+} + SCN^-$	H_2O	20	3	2	−15		706, 707	by Raman spectroscopy, ionic strength 2.4 mol/L
580	$Th(SCN)_3^+ \rightarrow Th^{4+} + 3SCN^-$	H_2O	20	3	2	−19		706, 707	by Raman spectroscopy, ionic strength 2.4 mol/L
581	$Mg^{2+} + H_2edta^{2-} \rightarrow Mg(edta)^{2-} + 2H^+$	H_2O	25				+31.3	708	ionic strength 0.1 mol/kg
582	$Ca^{2+} + H_2edta^{2-} \rightarrow Ca(edta)^{2-} + 2H^+$	H_2O	25				+20.6	708	ionic strength 0.1 mol/kg
583	$Mn^{2+} + H_2edta^{2-} \rightarrow Mn(edta)^{2-} + 2H^+$	H_2O	25				+22.4	708	ionic strength 0.1 mol/kg
583b	$Co^{2+} + H_2edta^{2-} \rightarrow Co(edta)^{2-} + 2H^+$	H_2O	25				+36.4	708	ionic strength 0.1 mol/kg
584	$Ni^{2+} + H_2edta^{2-} \rightarrow Ni(edta)^{2-} + 2H^+$	H_2O	25				+36.7	708	ionic strength 0.1 mol/kg
585	$Cu^{2+} + H_2edta^{2-} \rightarrow Cu(edta)^{2-} + 2H^+$	H_2O	25				+34.0	708	ionic strength 0.1 mol/kg
586	$Zn^{2+} + H_2edta^{2-} \rightarrow Zn(edta)^{2-} + 2H^+$	H_2O	25				+36.3	708	ionic strength 0.1 mol/kg
587	$Al^{3+} + H_2edta^{2-} \rightarrow Al(edta)^- + 2H^+$	H_2O	25				+53.2	708	ionic strength 0.1 mol/kg
588	$Fe^{3+} + H_2edta^{2-} \rightarrow Fe(edta)^- + 2H^+$	H_2O	25				+46.9	708	ionic strength 0.1 mol/kg
589	$Mn^{2+} + edta^{4-} \rightarrow Mn(edta)^{2-}$	H_2O	25				+32.8	144	
590	$Co^{2+} + edta^{4-} \rightarrow Co(edta)^{2-}$	H_2O	25				+44.1	144	
591	$Ni^{2+} + edta^{4-} \rightarrow Ni(edta)^{2-}$	H_2O	25				+44.4	144	
592		H_2O	25				+25.5	709	
593	$Cu^{2+} + edta^{4-} \rightarrow Cu(edta)^{2-}$	H_2O	25				+45.8	144	
594	$Zn^{2+} + edta^{4-} \rightarrow Zn(edta)^{2-}$	H_2O	25				+44.4	144	
595	$Mn^{2+} + Hedta^{3-} \rightarrow Mn(Hedta)^-$	H_2O	25				+43.3[j]	144	
596	$Co^{2+} + Hedta^{3-} \rightarrow Co(Hedta)^-$	H_2O	25				+52.5[j]	144	
597	$Ni^{2+} + Hedta^{3-} \rightarrow Ni(Hedta)^-$	H_2O	25				+51.8[j]	144	
598	$Cu^{2+} + Hedta^{3-} \rightarrow Cu(Hedta)^-$	H_2O	25				+54.6[j]	144	
599	$Zn^{2+} + Hedta^{3-} \rightarrow Zn(Hedta)^-$	H_2O	25				+51.7[j]	144	
600	$Ni^{2+} + 2MeN(CH_2COO^-)_2 \rightarrow Ni[MeN(CH_2COO)_2]_2^{2-}$	H_2O	25				+26.8	709	
601	NH_4^+ + 18-crown-6 → complex	H_2O	25				+6.9	710	
602	$MeNH_3^+$ + 18-crown-6 → complex	H_2O	25				+2.4	710	
603	$EtNH_3^+$ + 18-crown-6 → complex	H_2O	25				+2.5	710	
604	*n*-$BuNH_3^+$ + 18-crown-6 → complex	H_2O	25				+2.9	710	
605	*n*-$HexNH_3^+$ + 18-crown-6 → complex	H_2O	25				+3.1	710	
606	Na^+ + 18-crown-6 → complex	H_2O	25				+11.7	711	[crown] = 0.099 mol/L
607		H_2O	25				+12.1	711	[crown] = 0.144 mol/L
608		H_2O	25				+11.9	711	[crown] = 0.185 mol/L
609	K^+ + 18-crown-6 → complex	H_2O	25				+13.0	711	[crown] = 0.060 mol/L
610		H_2O	25				+12.9	711	[crown] = 0.144 mol/L
611		H_2O	25				+13.0	711	[crown] = 0.211 mol/L
612	Rb^+ + 18-crown-6 → complex	H_2O	25				+9.0	712	[crown] = 0.092 mol/L
613		H_2O	25				+9.3	712	[crown] = 0.144 mol/L
614		H_2O	25				+9.3	712	[crown] = 0.202 mol/L

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
615	Cs$^+$ + 18-crown-6 → complex	H_2O	25				+9.1	711	[crown] = 0.103 mol/L
616		H_2O	25				+8.5	711	[crown] = 0.151 mol/L
617		H_2O	25				+8.7	711	[crown] = 0.180 mol/L
618	Ca^{2+} + 18-crown-6 → complex	H_2O	25				+24.0	712	[crown] = 0.104 mol/L
619		H_2O	25				+22.7	712	[crown] = 0.158 mol/L
620		H_2O	25				+22.8	712	[crown] = 0.184 mol/L
621	Ba^{2+} + 18-crown-6 → complex	H_2O	25				+18.9	712	[crown] = 0.103 mol/L
622		H_2O	25				+18.8	712	[crown] = 0.133 mol/L
623		H_2O	25				+18.8	712	[crown] = 0.200 mol/L
624	Na$^+$ + 15-crown-5 → complex	H_2O	25				+8.3	712	[crown] = 0.098 mol/L
625		H_2O	25				+8.4	712	[crown] = 0.153 mol/L
626		H_2O	25				+8.8	712	[crown] = 0.209 mol/L
627	K$^+$ + 15-crown-5 → complex	H_2O	25				+8.2	712	[crown] = 0.112 mol/L
628		H_2O	25				+8.0	712	[crown] = 0.196 mol/L
629		H_2O	25				+8.3	712	[crown] = 0.218 mol/L
630	Rb$^+$ + 15-crown-5 → complex	H_2O	25				+4.4	712	[crown] = 0.116 mol/L
631		H_2O	25				+4.6	712	[crown] = 0.142 mol/L
632		H_2O	25				+4.4	712	[crown] = 0.196 mol/L
633	Cs$^+$ + 15-crown-5 → complex	H_2O	25				+1.7	712	[crown] = 0.099 mol/L
634		H_2O	25				+1.6	712	[crown] = 0.151 mol/L
635		H_2O	25				+1.9	712	[crown] = 0.226 mol/L
636	Ca^{2+} + 15-crown-5 → complex	H_2O	25				+0.1	712	[crown] = 0.100 mol/L
637		H_2O	25				+0.2, +0.3	712	[crown] = 0.201 mol/L
638	Li$^+$ + 12-crown-4 → complex	H_2O	25				0	712	[crown] = 0.101 mol/L
639		H_2O	25				+0.1	712	[crown] = 0.147 mol/L
640	Na$^+$ + 12-crown-4 → complex	H_2O	25				+0.1	712	[crown] = 0.102 mol/L
641		H_2O	25				+0.2	712	[crown] = 0.155 mol/L
642		H_2O	25				0	712	[crown] = 0.206 mol/L
643	K$^+$ + 12-crown-4 → complex	H_2O	25				0	712	[crown] = 0.118 mol/L
644		H_2O	25				+0.2	712	[crown] = 0.162 mol/L
645		H_2O	25				0	712	[crown] = 0.215 mol/L
646	Li$^+$ + cryptand[2.2.2] → complex	MeOH	25				−1.8	713	
647	Na$^+$ + cryptand[2.2.2] → complex	MeOH	25				+10.6	713	
648	Na$^+$ + cryptand[2.2.2] → complex	H_2O	25				+14.2	713	
649	K$^+$ + cryptand[2.2.2] → complex	MeOH	25				+15.9	713	
650	K$^+$ + cryptand[2.2.2] → complex	H_2O	25				+17.4	713	
651	Rb$^+$ + cryptand[2.2.2] → complex	MeOH	25				+13.1	713	
652	Rb$^+$ + cryptand[2.2.2] → complex	H_2O	25				+14.2	713	
653	Cs$^+$ + cryptand[2.2.2] → complex	MeOH	25				+7.4	713	
654	Ca^{2+} + cryptand[2.2.2] → complex	MeOH	25				+10.0	713	
655	Ca^{2+} + cryptand[2.2.2] → complex	H_2O	25				+26.1	713	
656	Sr^{2+} + cryptand[2.2.2] → complex	MeOH	25				+14.6	713	
657	Sr^{2+} + cryptand[2.2.2] → complex	H_2O	25				+26.6	713	
658	Ba^{2+} + cryptand[2.2.2] → complex	MeOH	25				+9.7	713	
659	Ba^{2+} + cryptand[2.2.2] → complex	H_2O	25				+28.6	713	
660	Li$^+$ + cryptand[2.2.2] → complex	H_2O	25				+2	714	withdrawn in 713
661		MeOH	25				+3	715	
662	Na$^+$ + cryptand[2.2.2] → complex	H_2O	25				+15	714	
663		MeOH	25				+11	715	
664	K$^+$ + cryptand[2.2.2] → complex	H_2O	25				+18	714	
665		MeOH	25				+16	715	

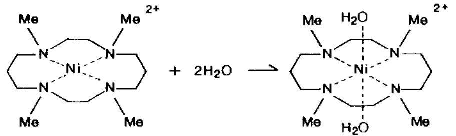
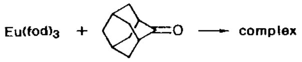
666	Rb^+ + cryptand[2.2.2] → complex	H_2O	25				+15	714	
667		MeOH	25				+15	715	
668	Cs^+ + cryptand[2.2.2] → complex	H_2O	25				+2	714	withdrawn in 713
669		MeOH	25				+7	715	
670	Tl^+ + cryptand[2.2.2] → complex	H_2O	25				+17	715	
671	Ca^{2+} + cryptand[2.2.2] → complex	H_2O	25				+26	715	
672	Sr^{2+} + cryptand[2.2.2] → complex	H_2O	25				+24	715	
673	Ba^{2+} + cryptand[2.2.2] → complex	H_2O	25				+19	715	withdrawn in 713
674	Cd^{2+} + cryptand[2.2.2] → complex	H_2O	25				+20	715	
675	Hg^{2+} + cryptand[2.2.2] → complex	H_2O	25				+23	715	
676	Pb^{2+} + cryptand[2.2.2] → complex	H_2O	25				+28	715	
677	Li^+ + cryptand[2.2.1] → complex	MeOH	25				+4	715	
678	Na^+ + cryptand[2.2.1] → complex	MeOH	25				+13	715	
679	K^+ + cryptand[2.2.1] → complex	MeOH	25				+9	715	
680	Rb^+ + cryptand[2.2.1] → complex	MeOH	25				+5	715	
681	Cs^+ + cryptand[2.2.1] → complex	MeOH	25				+1	715	
682	Li^+ + cryptand[2.1.1] → complex	MeOH	25				+7	715	
683	Na^+ + cryptand[2.1.1] → complex	MeOH	25				+9	715	
684	K^+ + cryptand[2.1.1] → complex	MeOH	25				+6	715	
685	Rb^+ + cryptand[2.1.1] → complex	MeOH	25				+3	715	
686	Fe^{2+} + 3phen → $Fe(phen)_3{}^{2+}$	H_2O	25				+4.7	716	
687	Co^{2+} + 3phen → $Co(phen)_3{}^{2+}$	H_2O	25				+19.5	716	
688	Ni^{2+} + 3phen → $Ni(phen)_3{}^{2+}$	H_2O	25				+20.4	716	
689	Cu^{2+} + 3phen → $Cu(phen)_3{}^{2+}$	H_2O	25				+19.4	716	
690	Zn^{2+} + 3phen → $Zn(phen)_3{}^{2+}$	H_2O	25				+20.6	716	
691	$CoCl_2(py)_2 \rightarrow CoCl_2(py)_4$	pyridine	25	3	7	−41		205	
692	$CoBr_2(py)_2 \rightarrow CoBr_2(py)_4$	pyridine	20	3	7	−29		205	
693	$CoI_2(py)_2 \rightarrow CoI_2(py)_4$	pyridine		3		−6		206	
694	$CoCl_2(3\text{-Me-py})_2 \rightarrow CoCl_2(3\text{-Me-py})_4$	3-methylpyridine	17	3	7	−18		207	
695	$CoBr_2(3\text{-Me-py})_2 \rightarrow CoBr_2(3\text{-Me-py})_4$	3-methylpyridine	18.5	1.5	4	−19		207	
696		H_2O	−3 to ~87	1.4	9	−10.0		217	
697	$Nd(DMF)_8{}^{3+} \rightarrow Nd(DMF)_9{}^{3+}$	DMF	−42, −17			−9.8		249	
698	$Nd(TMP)_6{}^{3+} \rightarrow Nd(TMP)_7{}^{3+}$	trimethyl phosphate	25			−23.8		249	
699		$CHCl_3$	22	1.5	6	+8		717	
700	$Ni(MeNHCH_2CH_2NHMe)_2(ONO)_2 \rightarrow Ni(MeNHCH_2CH_2NHMe)_2(NO_2)_2$	$CHCl_3$	25	1.7	6	−4.5		269	
701	$Ni(EtNHCH_2CH_2NHEt)_2(ONO)_2 \rightarrow Ni(EtNHCH_2CH_2NHEt)_2(NO_2)_2$	$CHCl_3$	25	1.4	5	−7.2		269	
702	SCN^- + α-cyclodextrin → complex	H_2O	15				−3.5	718	
703		H_2O	25				−4.2	718	
704		H_2O	25	1.2	5	−3.1		718	
705		H_2O	35				−5.1	718	
706	ClO_4^- + α-cyclodextrin → complex	H_2O	15				−1.6	718	
707		H_2O	25				−1.9	718	
708		H_2O	25	1.5	5	−1.4		718	
709		H_2O	35				−2.0	718	
710	I^- + α-cyclodextrin → complex	H_2O	15				−7.4	718	
711		H_2O	25				−5.8	718	
712		H_2O	25	1.5	6	−7.0		718	

TABLE IX (Continued)

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a/ (cm^3 mol^{-1})	ΔV^b/ (cm^3 mol^{-1})	ref	remarks
713		H_2O	35				−5.2	718	
714	SCN^- + β-cyclodextrin → complex	H_2O	25				0	718	
715		H_2O	25	1.2	5	+1.5		718	
716	ClO_4^- + β-cyclodextrin → complex	H_2O	25				+6.5	718	
717		H_2O	25	1.2	5	+8.0		718	
718	I^- + β-cyclodextrin → complex	H_2O	25				0	718	
719		H_2O	25	1.2	5	+1.1		718	

[a] From equilibrium constants. [b] From partial molar volumes or by dilatometry. [c] Polycarbonate (Aldrich) film. [d] Adsorption on ZnO single crystal is also studied under pressure (ref 627). [e] Poly(methyl methacrylate) (Aldrich) film. [f] EDA complex. [g] Calculated by T.A. by means of ln $K_p/K_1 = aP + b \ln(1 + cP)$. [h] For water ionization, the following equation is proposed:[719] $\Delta V° = -25.044 + 3.3858 \times 10^{-1}T - 1.1763 \times 10^{-2}T^2 + 1.6880 \times 10^{-4}T^3$ (T/°C). [i] Calculated by T.A. by means of ln $K = a + bP + cP^2$. [j] Calculated by $\Delta V° = V°[M(Hedta)^-] - V°[M^{2+}] - V°[Hedta^{3-}]$. The original authors recommend $\Delta V° = V°[M(Hedta)^-] - V[H_2O] - V°[M^{2-}] - V°[Hedta^{3-}]$.

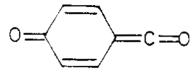
zation in the former. In the bridge-flipping process of the 7-norbornadienyl cation, just the opposite feature is present: the charge must then become localized in the transition state, and indeed, expansion then fails to occur.[532]

I. Acyl-Transfer Processes (Entries 804–944)

The first two cases are important as they exemplify the formation of the tetrahedral intermediate so characteristic of this class. In both, ΔV^* is negative[533] as expected for an addition, the second rather more so than the first because of the intramolecular nature of the first reaction. In all other examples, the activation volume is for the more complex process that includes the breakdown of this intermediate.

Unfortunately, the papers reporting catalyzed hydrolysis reactions together present a complex pattern that does not allow general conclusions to be drawn, but rather gives the impression that each result is specific to the case at hand. The use of polymer catalysts, micelles, and highly aqueous mixed solvents are complicating factors leading us to advise the study of each paper as a separate entity and to regard the field as a whole as one in a state of development. Only a few results can be singled out here.

The hydrolysis of phosphate ester in entry 854 is of interest in that it addresses the question of water assistance in that case or, in other words, whether metaphosphate ion is capable of existence as a free species in water. The negative activation volume strongly argues[545] that it cannot, although this species can be detected in nonaqueous medium[739] and in the gas phase.[740] Doubt was expressed by Jencks[802] about the validity of using the activation volume as a criterion in this case; however, Cullis[803] has more recently reported the activation volume of a thia analogue of metaphosphate in which all the alternative evidence indicates that that species, in contrast to metaphosphate itself, is capable of independent existence as a free species in water. The large and positive volume change found (+11 cm^3 mol^{-1}) conclusively shows that Jencks' doubt is unjustified. The remarkable difference between the apparently similar p-nitrophenyl esters of entries 884–886 can be ascribed[549] to the fit of the acyl entities in the cyclodextrin additives employed as enzyme-like catalysts. The ferrocene moiety is a nearly ideal guest for the β-cyclodextrin host, while the fit of the p-*tert*-butylanisole group is so poor that the complex is essentially incapable of existence at high pressure. Taniguchi[551] has in related studies suggested the formal existence of two types of complexes with cyclodextrins, named tight and loose. A special mechanism for the hydrolysis of p-hydroxyphenyl esters has been proposed by Isaacs[543,553] to account for the unusual pressure-induced retardation: elimination occurs in the anion to produce a ketene intermediate, which is then rapidly hydrated.

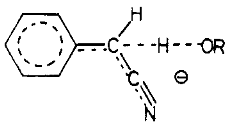


It is interesting that malonate and methyl malonate esters show the same effect while dimethyl malonate esters do not: the latter cannot form the required precursor anion. Finally, the elimination reactions of Asano[555] and of Sen and Palit[556] are of interest in that they apply in cases where the concentration of negative charge might be expected to lead to activation volumes more negative than normal. But it is not obvious from the results that this is the case; if the effect exists, it cannot be very large.

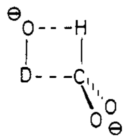
J. Miscellaneous Reactions (Entries 945–1137)

The monosaccharide epimerizations (mutarotations) reported at high pressures were of the catalytic type (by enzyme and by Cu(II)); for the interpretations, the original papers by Andersen[559] and O'Connor[560] should be consulted. The glycoside hydrolyses listed appear to fall in two categories, with those of the pyranosides retarded by pressure and those of the furanosides showing mostly small negative activation volumes; thus, these results suggest A_1 and A_2 mechanism, respectively (see our earlier review for a fuller discussion of this distinction).

Nucleophilic aromatic substitution falls clearly in two categories depending on whether the nucleophile is neutral or anionic. The charge separation that develops in the former case clearly leads to much larger negative volumes of activation. The deviation of values from a possible limiting value of -10 cm^3 mol^{-1} seen in Brower's extensive investigation[554] of dedeuteriation was explained in terms of relatively late transition states for these reactions. The very large value observed by Inoue[564] in methanol points to a highly delocalized transition state in that case.



Hamann's proton exchange in formate anion at 200 °C is mildly accelerated by pressure, in accord with a four-membered transition state:[566]



Indeed, it is hard to visualize any other pathway. The acetate case may involve the dianion; the value of ΔV^{*}_{0} is close to Brower's limiting value. Tamura has used the pressure effect on the ketonization rate of pentanedione enol in the presence of reversed micelles to make an estimate of the polarity of the microenvironment.[567] The pressure effect on the Wittig reaction primarily reflects the bond being formed between the reagents;[568] the reaction of hydroxide ion to give initially the phosphorus ylide is strongly retarded, and charge neutralization is expected to be largely responsible.[544] Both charge formation *and* bonding must surely be involved in the reduction of quinones by secondary amines and triphenylmethanes; the accelerations by pressure are very large. The same can be said about the halogenation reactions listed.

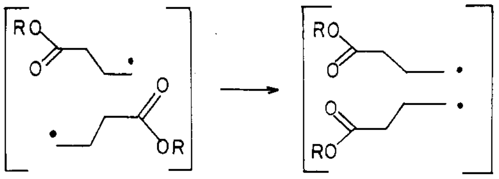
The proton exchanges of entries 1053–1079 are of interest when the question of tunneling arises. Ordinarily, the molar volumes of species differing only isotopically are virtually identical, and this is true of transition states as well. The substantial difference seen in the activation volumes of proton and deuteron transfer from α,p-dinitrotoluene to tetramethylguanidine in toluene at 25 °C is clear evidence for a tunneling contribution; so is the pressure dependence of this difference.[577]

The organic photochemical processes noted in Table VII include several small negative activation volumes attributable to complex formation, and positive values that can be ascribed to viscosity effects. The last value in Table VII is the activation volume[595] for the ionophore-assisted transport of gadolinium ion through vesicle walls, as indicated by simultaneously observable ESR signals of inside and outside TEMPONE; the enormous positive value is explained as an indication that dehydration of the cation is a vital part of the activation process. The observation strongly favors Eigen's point of view[741] over Chock's[742] in their controversy on this issue.

4. *Activation Volume Differences (Table VIII)*

It is perhaps unfortunate that relatively few data of this sort are available, because product ratios can usually be measured to greater precision than individual concentrations, and errors in timing, sampling, and so on are unimportant. While this sort of information only gives comparative values, one usually wants to make comparisons in any case. The data listed have proved to be especially helpful in studies of free radicals, in which complex mixtures are the rule rather than the exception.

The dissociation of caged radicals requires more space than their combination or recombination;[424] this datum is one example of the space needed for diffusion. The result of Zhulin[422] (entry 2) is unexpected, as noted by him; it may mean that the initial fission reaction(s) may not leave the pair in the best orientation for recombination, so that diffusional motion is required not only for separation but also for bond formation ("cage rearrangement"):



Several entries show that radical fission is much more space consuming than hydrogen abstraction or than attack on olefinic double bonds. Entry 6 reveals the often-observed small space advantage of a more crowded transition state, and entry 7 shows that tunneling must characterize the act of hydrogen atom abstraction. In several other entries, the products and reactants are related by more than one simple step, and the results are then not easily interpreted.

Inspection of entries 14 and 15 leads one to recall Eckert's proposal[743] that the minima sometimes observed in the volume profiles of Diels–Alder reactions of one diene to another are evidence of secondary orbital interactions.[744] It has been noted that volume differences between the exo and endo transition states are often negligible, however, which tends to weaken this proposal. In Jurczak's cases,[602] in fact, these pressure effects are in the opposite direction: exo is favored at high pressure. Eckert's proposal may still well be right in those cases in which a volume minimum and endo stereochemistry are established, but a one-to-one relationship between secondary orbital interactions and smaller endo transition states cannot be considered proved at present.

The remaining data in Table VIII show mostly small and somewhat random effects in the ratio of stereo- and regioisomers in several reactions. In this connection, it is worth noting that synthetic chemists often wonder whether high pressure will alter ratios of products in favor of the more symmetrical structures. All experience is that such an expectation is not generally justified. One can certainly defend the use of pressure as one additional variable to try in attempts to optimize yields, but while there are several factors that have known beneficial effects at high pressure as noted repeatedly above, mere symmetry is not among them.

5. Reaction Volumes in Tabular Form

Reaction volumes for chemical processes are listed in Table IX.

A. Conformational Equilibria (Entries 1–66)

In the large majority of cases, the more crowded gauche conformers are favored over the anti conformers by the application of high pressures; the volume differences are usually a few cm^3 mol^{-1}. The interfering groups seem slightly compressed, as it were, unable to distance themselves from one another.

B. Complex Formation (Entries 67–150)

Hydrogen bonds serve to bring nuclei more closely together; on the average, each such bond reduces the volume by about 4 cm^3 mol^{-1}. The strong directionality of the HO···H bond tempers this decrease and may even reverse it; thus, the open structure and low density of ice are brought about by linear hydrogen bonds.

Charge-transfer complexes generally reduce volume, probably in part by the formation of dipolar products, especially in the case of the iodine complexes. It seems at first sight surprising that the association of iodide ion with various cations would be enhanced by pressure, as claimed by Jee[646,648] and Williams.[649,650] Further work will be desirable; one question that needs to be considered is whether the initial ions depicted as free really are that way, or paired (note the high ionic strength in entries 137–139, for example). The huge decrease in volume upon dissociation of ribosomes and of the cytochrome complex of entry 144 underscores the fact that one must not uncritically extrapolate generalizations derived from small-molecule behavior to macromolecules. It seems probable that in the fission of these species, polar interior surfaces become exposed to water and that the hydration of these surfaces is responsible. In other words, these cleavage processes resemble ionization.

C. Ionic Processes (Entries 151–257)

It is well-known that ionization is enhanced by pressure and that the volume changes can be understood in terms of the Drude–Nernst equation,[745] which predicts that electrostriction will be most pronounced when the ion is small, the charge large and localized, and the solvent nonpolar. These effects dominate this part of Table IX. Thus, the ionization volume of H_2S in water is less than that of water itself, the ionization volume changes for phosphoric acids become larger with every step, and the values in methanol are much larger than in water. The values of boric acid and carbonic acid are larger than average, since in addition to charge formation, bonding occurs in the process. For carboxylic acids other than formic, ΔV_i is relatively constant, as was already known.[1] The volume effects of proton transfer from nitrogen to oxygen likewise have been discussed at length before, as have simple ion-pair equilibria.

The positive values describing the volume changes upon complexing aqueous cations with crown ethers indicate the need for dehydration, as noted above; the effect of doubling the charge is to increase the expansion. However, the simple act of increasing the coordination number is normally expected to lead to overall contraction. The possibility that this effect can be offset by simultaneous increases in length in the distances in the bonds from the metal ion to the ligands already there[746] may have been realized with entry 699; it is one example among many observed qualitatively of pressure-induced reversals in the shifts of NMR signals brought about by shift reagents.[717]

6. Related Topics and Concluding Remarks

A few papers that escaped our early notice or did not appear until after the completion of the tables nevertheless need to be mentioned; they report pressure effects of Hammett ρ and Brønsted β values,[747] on cyclohexanol relaxation,[748] on chemically induced ethylene polymerization,[749] on the polymerization of acrylonitrile, both redox[750] and free radical,[751] on hindered Diels–Alder reactions,[752] on Diels–Alder reactions with inverse electron demand,[753] on the protonation of a 1,3,5-trisaminobenzene,[756] and on the association of pyridinium iodides in aqueous ethanol.[757]

In addition, we wish to call attention to related papers on new techniques in studying conductance in the 100-kbar range,[758] on EXAFS measurements at high pressure,[759] on Raman spectroscopy at high pressure,[760] on the relation between ΔV and ΔS,[784,785] on data handling with activation parameters,[761] on a discussion of activation parameters,[762] on isochoric vs isobaric behavior,[763] on additivity of partial volumes,[764–767] on electron mobility,[768] on high-pressure FTIR studies of catalytic surfaces,[769] on micellar microfluidity,[770] on densities of aqueous solutions of nonelectrolytes,[771] on volume profiles of polymerization,[772,773] on synthesis,[774–776] on rotational reorientation,[777] on photochemistry of gas–liquid systems,[778] on the kinetics of phase separation,[779] on enzyme behavior in compressed solutions,[780] on CO exchange of carbonyl complexes,[781] on syngas conversion,[782] on $\Delta V^{\ddagger}$ as a tool for understanding the mechanism of action of additives in electrodeposition,[783] on pressure-induced reduction of ferric salts,[784,785] and on the application of Gibson's concept of an excess pressure to an analysis of the properties of solutions containing both salts and neutral solutes in terms of partial and apparent molar volumes[786] and high-pressure flames.[787]

TABLE X. Supplementary Values of Activation Volumes

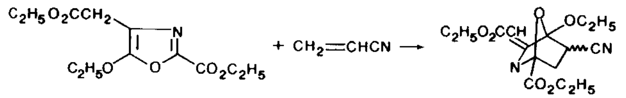
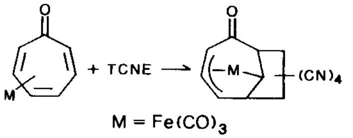
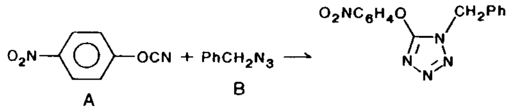
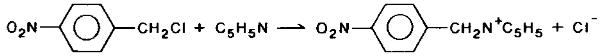
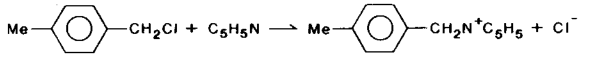
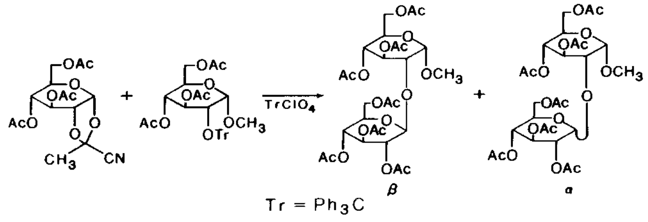
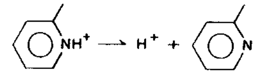
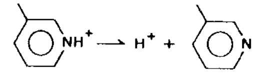
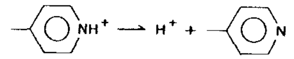
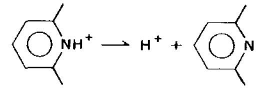
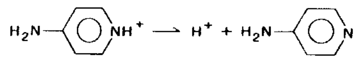
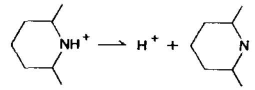
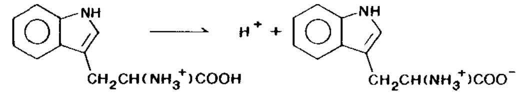
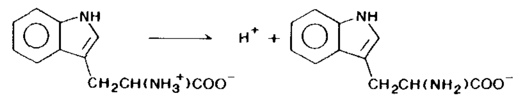
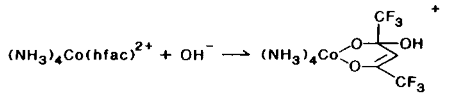
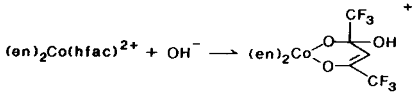
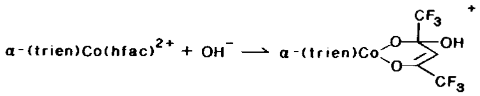
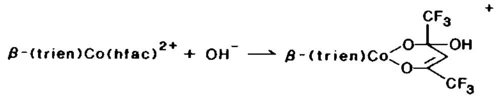
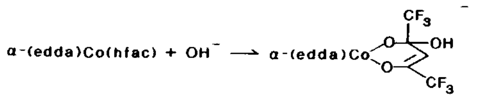
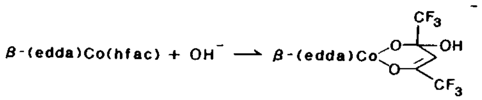
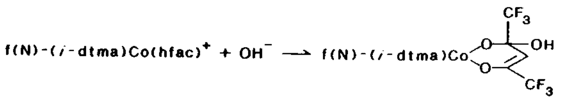
no.	reaction	solvent	T/°C	P/kbar	no. of k	$\Delta V^{\ddagger}$/ (cm^3 mol^{-1})	ref	remarks
1		CH_2Cl_2	20	12	7	−22	788	$\Delta V^{\ddagger}$ increases with pressure ΔV = −30 (30 °C)
2		MeCN	20	12	12	−22	788	$\Delta V^{\ddagger}$ increases with pressure ΔV = −26 (30 °C)
3		CH_2Cl_2	25	0.7	5	−29	789	
4		acetone	25	0.5	4	−33	789	
5		MeCN	25	0.7	3	−31	789	
6		PhH	80	8	14	−19.4	790	$x_A = x_B = 0.171$ $\Delta V^{\ddagger}$ = −33.6 at $P > 3$ kbar
7		CH_2Cl_2	80	14	5	−18.4	790	$x_A = x_B = 0.0278$
8		MeCN	80			−14.5	790	$x_A = 0.0394$, $x_B = 0.1580$
9		MeCN	80			−18.2	790	$x_A = x_B = 0.0724$
10		MeCN	80			−23.4	790	$x_A = 0.094$, $x_B = 0.0392$
11	$Me_3SiOOCMe_2Ph \rightarrow Me_2(MeO)SiOCMe_2Ph$	cy-C_6H_{10}	160	10	6	−21.8	791	
12		cy-C_6H_{10}	170	10	8	−20.3	791	
13		cy-C_6H_{10}	180	7.5	5	−18.0	791	
14		PhMe	170	10	7	−9.9	791	
15	$Me_3SiOOCPh_3 \rightarrow Me_2(MeO)SiOCPh_3$	cy-C_6H_{10}	160	10	6	−14.9	791	
16	$PhCH_2Cl + ROH \rightarrow PhCH_2OR + HCl$	H_2O	30	1.6	6	−8.7	792	
17		H_2O	40	1.6	6	−9.4	792	
18		aq EtOH	30	1.6	6	−14.9	792	EtOH 10 mol %
19		aq EtOH	40	1.6	6	−15.9	792	EtOH 10 mol %
20		aq EtOH	30	1.6	6	−18.7	792	EtOH 20 mol %
21		aq EtOH	40	1.6	6	−19.7	792	EtOH 20 mol %
22		aq EtOH	30	1.6	6	−22.0	792	EtOH 30 mol %
23		aq EtOH	40	1.6	6	−22.8	792	EtOH 30 mol %
24		aq EtOH	30	1.6	6	−16.3	792	EtOH 40 mol %
25		aq EtOH	40	1.6	6	−17.2	792	EtOH 40 mol %
26	$PhCH_2Cl + C_5H_5N \rightarrow PhCH_2N^+C_5H_5 + Cl^-$	MeOH	40	2	6	−9.4	793	
27		MeOH	50	2	6	−12.1	793	
28		MeOH	40	2	6	−7.3	793	
29		MeOH	50	2	6	−12.0	793	
30		MeOH	40	2	6	−10.7	793	
31		MeOH	50	2	6	−13.5	793	
32		DMSO	79	3	5	−10.0	794	[t-BuOK] = 0.9 mol/L $\Delta V^{\ddagger}$ = −10.2 for the reverse reaction
33	$MeCOCH(OH)Me + 2V(V) \rightarrow MeCOCOMe + 2V(IV) + 2H^+$	H_2O	25	2	5	+3.5	795	
34	$MeCOCH_2OH + 2V(V) \rightarrow MeCOCHO + 2V(IV) + 2H^+$	H_2O	35	2	5	+1.3	795	
35		CH_2Cl_2	20	14	8	−5	796	$\Delta V^{\ddagger}(\beta) - \Delta V^{\ddagger}(\alpha)$ = −8.5

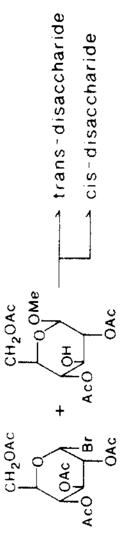
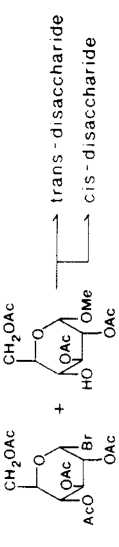
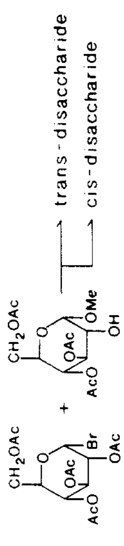
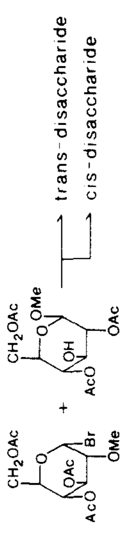
TABLE XI. Supplementary Values of Reaction Volumes

no.	reaction	solvent	T/°C	P/ kbar	no. of K	ΔV^a	ΔV^b	ref	remarks
1	$C_5H_5NH^+ \rightarrow C_5H_5N + H^+$	H_2O	25				+4.4	797	
2		H_2O	25				+3.1	797	
3		H_2O	25				+3.4	797	
4		H_2O	25				+3.6	797	
5		H_2O	25				+1.7	797	
6		H_2O	25				+0.9	797	
7		H_2O	25				+0.4	797	
8	$H_3N^+CH_2COOH \rightarrow H^+ + H_3N^+CH_2COO^-$	H_2O	15	2.5	6	−8.0^c		798	
9		H_2O	20	2.5	6	−8.1^c		798	
10		H_2O	25	2.5	6	−7.6^c		798	
11		H_2O	30	2.5	6	−7.8^c		798	
12		H_2O	35	2.5	6	−7.4^c		798	
13	$H_3N^+CH_2COO^- \rightarrow H^+ + H_2NCH_2COO^-$	H_2O	15	2.5	6	+7.4^c		798	
14		H_2O	20	2.5	6	+4.1^d		798	
15		H_2O	25	2.5	6	+3.3^d		798	
16		H_2O	30	2.5	6	+2.6^d		798	
17		H_2O	35	2.5	6	+2.0^d		798	
18	$MeCH(NH_3^+)COOH \rightarrow H^+ + MeCH(NH_3^+)COO^-$	H_2O	15	2.5	6	−10.4^c		798	
19		H_2O	20	2.5	6	−9.9^c		798	
20		H_2O	25	2.5	6	−10.2^c		798	
21		H_2O	30	2.5	6	−10.1^c		798	
22		H_2O	35	2.5	6	−9.7^c		798	
23	$MeCH(NH_3^+)COO^- \rightarrow H^+ + MeCH(NH_2)COO^-$	H_2O	15	2.5	6	+8.0^e		798	
24		H_2O	20	2.5	6	+4.3^d		798	
25		H_2O	25	2.5	6	+3.8^d		798	
26		H_2O	30	2.5	6	+3.0^d		798	
27		H_2O	35	2.5	6	+2.6^d		798	
28		H_2O	15	2.5	6	−7.6^c		798	
29		H_2O	20	2.5	6	−8.7^c		798	
30		H_2O	25	2.5	6	−8.9^c		798	
31		H_2O	30	2.5	6	−9.0^c		798	
32		H_2O	35	2.5	6	−8.1^c		798	
33		H_2O	15	2.5	6	−5.1^e		798	
34		H_2O	20	2.5	6	−5.1^e		798	
35		H_2O	25	2.5	6	−5.1^e		798	
36		H_2O	30	2.5	6	−5.1^e		798	
37		H_2O	35	2.5	6	−5.3^e		798	

38	$Me_2CHCH_2CH(NH_3^+)COOH \rightarrow$	H_2O	15	2.5	6	-9.8^c		799	
39	$H^+ + Me_2CHCH_2CH(NH_3^+)COO^-$	H_2O	20	2.5	6	-8.3^c		799	
40		H_2O	25	2.5	6	-7.0^c		799	
41		H_2O	30	2.5	6	-6.8^c		799	
42		H_2O	35	2.5	6	-7.0^c		799	
43		H_2O	40	2.5	6	-5.7^c		799	
44	$Me_2CHCH_2CH(NH_3^+)COO^- \rightarrow$	H_2O	15	2.5	6	$+2.3^d$		799	
45	$H^+ + Me_2CHCH_2CH(NH_2)COO^-$	H_2O	20	2.5	6	$+1.2^d$		799	
46		H_2O	25	2.5	6	$+1.0^d$		799	
47		H_2O	30	2.5	6	$+0.7^d$		799	
48		H_2O	35	2.5	6	-0.2^d		799	
49		H_2O	40	2.5	6	-1.1^d		799	
50		H_2O	25				+11.2	800	*f*
51		H_2O	25				+10.7	800	
52		H_2O	25				+8.9	800	
53		H_2O	25				+11.1	800	
54		H_2O	25				−8.3	800	
55		H_2O	25				−3.9	800	
56		H_2O	25				+1.6	800	*g*

[a] From equilibrium constants. [b] From partial molar volumes or by dilatometry. [c] Calculated by T.A. by means of $\ln K_P/K_{0.001} = aP + b \ln (1 + cP)$. [d] Calculated by T.A. by means of $\ln K = a + bP$. [e] Calculated by T.A. by means of $\ln K = a + bP + cP^2$. [f] hfac = hexafluoroacetone. [g] *i*-dtma = *N*,*N*-bis(2-aminoethyl)glycinmate.

TABLE XII. Supplementary Values of Activation Volume Differences

no.	reaction	solvent	T/°C	P/ kbar	no. of k	$\delta\Delta V^{\ddagger}$/ ($cm^3\ mol^{-1}$)	ref	remarks
1	 trans-disaccharide cis-disaccharide	MeCN	20	12	3	0 +2.8[a]	801	[b]
2	 trans-disaccharide cis-disaccharide	MeCN	20	12	2	0 +5.6	801	[b]
3	 trans-disaccharide cis-disaccharide	MeCN	20	12	3	0 +3.7	801	[b]
4	 trans-disaccharide cis-disaccharide	MeCN	20	8	2	0 +4.6	801	[b]

[a] Calculated by T.A. by means of ln $k = a + bP$. [b] Helferich glycosylation. 0.2 mmol of $Hg(CN)_2$ in 3.8 mL of MeCN.

The continuing rapid increase in the number of laboratories equipped to study chemical properties and processes at high pressure and in the number of publications describing effects of high pressure will, in our opinion, soon make it impossible to write or to read complete listings of these results. In a sense, solution high-pressure chemistry is now so common that it can no longer be considered a special area. We are rapidly approaching the time that essentially every chemist, in every experiment, decides the pressure to be used much as he chooses the temperature. The miniaturization of the amounts of chemicals handled and the proliferation of physical techniques amenable to high-pressure extension have contributed to this desirable state of affairs. Of course, there will always be a range of pressures that is not readily accessible to everyone (currently at 100 kbar to 10 Mbar), and that will help preserve the character of High-Pressure Chemistry as a specialty area, just as there will also always be a High-Temperature Chemistry. But beyond 20 kbar or so, there are few media that are still liquid, and at ultrahigh pressure there is as little opportunity for solution chemists as there is as ultralow temperatures. Further research using high pressure is likely to move into more specialized areas, and accordingly, future reviews of high pressure are likely to be much more narrow in scope.

7. Appendix

Tables X, XI, and XII show a limited number of data that came to our attention too late for inclusion in Tables VII–IX.

Acknowledgments. Many investigators in this field responded to our request to check our tables for omissions and help us make them as complete as possible; for this we thank Drs. H.-D. Brauer, K. R. Brower, M. Buback, J. Devaure, B. El'yanow, J. B. F. N. Engberts, D. J. Gardiner, K. Hara, E. U. Franck, K. Heremans, N. S. Isaacs, G. Jenner, Y. Kitamura, F. G. Klärner, H.-D. Lüdemann, G. Luft, A. E. Merbach, J.-P. Morel, T. Nakayama, R. C. Neuman, J. Osugi, S. K. Palit, J. W. Scheeren, G. M. Scheneider, E. Whalley, A. Würflinger, and S.-D. Yoh. R.v.E. gratefully acknowledges financial support from the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, the Max-Buchner Forschungsstiftung, and the Scientific Affairs Division of NATO under Grant No. RG 85/0681. He sincerely appreciates the fine collaboration with the members of his group, and especially thanks Sabine Franken and Dieter Projahn for their assistance with the preparation of the manuscript. T.A. thanks Mombusho (Japan Ministry of Education, Science, and Culture) for supporting his own work in this field. W.leN. thanks the National Science Foundation for its support and Mombusho for a Special Visiting Professorship at Oita University, where a large fraction of this article was written.

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