Activation and Reaction Volumes in Solution

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I. Introduction

A. Scope

One of the dilemma's facing the review writer in a field which has been reviewed before is that comprehensiveness forces those readers who saw the earlier article to leaf and scan to find the new things, whereas a mere updating compels those who did not see the initial writing to look it up in order to understand the additions. The problem is especially acute if the same author is involved in both stages, since he is apt to feel that his first effort was so well done and is so widely known and remembered that the mere referral to it will suffice.

The earlier comprehensive review was concerned, to all intents and purposes, with activation volumes only; it appeared in 1967[1] and was presumed to be complete through 1966. A thorough review on ionization volumes was published by Hamann in 1974.[2] Our objective here has been to present as complete as possible a listing of both types of volume difference, between those dates and the end of 1976; some 1977 data have become available as well, and these were incorporated also. We realize that the readability of our paper is somewhat limited by the choice of these time slots, but the information available is now so great that total comprehensiveness is not really possible any longer. To cope with this problem to some degree, we have added a somewhat starkly written introduction.

The organization of the data differs a little from that in ref 1. In that paper, the data were organized along strictly mechanistic lines: homolyses, ionizations, bond deformation reactions, bond formation—with and without concomitant formation of ions- and so on. The thrust of the paper was to convince readers that an excellent correlation exists between the activation volume and the main mechanistic features. However, since this relation now seems to be widely accepted and used, there is no longer any need for such an approach; accordingly the present paper is organized more along product lines. In other words, to mention one example, cycloadditions appear together whether they are concerted or not, and if the latter is the case, whether they involve diradicals or zwitterions. In the text, these nuances are pointed out, of course.

Beside the comprehensive data tables quoted above, several reviews have appeared since 1966 which are more limited in scope (though perhaps also more critical); among these there are accounts dealing with physical organic chemistry,[3-8] physical properties,[9] polymerization,[10] cycloadditions,[11] radical reactions,[12] inorganic processes,[13,14] and photoprocesses in the solid phase.[15] Those who consider becoming actively involved in the high-pressure business should also consult the forthcoming Conference Proceedings of the NATO Advanced Study Institute organized by Professor H. Kelm of the University of Frankfurt a.M. in Corfu in the fall of 1977; they include lectures on the basics of all types of spectroscopy of compressed substances, as well as the behavior of chemical systems at or away from equilibrium.

B. The Basic Concepts

In any reaction in solution:

$$\text{reactants (R)} \rightarrow \text{transition state } (\ddagger) \rightarrow \text{products (P)}$$

for which the rate law is known, one can in principle measure the activation volume $\Delta V^{\ddagger}$, defined by

$$\Delta V^{\ddagger} = V^{\ddagger} - V_R \quad (1)$$

The reaction volume, ΔV, given by

$$\Delta V = V_P - V_R \quad (2)$$

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can be determined regardless of the rate law.

We shall deal here exclusively with solutions and not with pure liquids; it should be understood that all volumes referred to in this review are partial volumes in the solvents and under the conditions of interest. For convenience, we have therefore omitted the bar over the V symbol which is customarily used to indicate partiality.[16]

The volume changes defined above can be determined by making use of the fundamental thermodynamic relation

$$\partial G / \partial p = V \qquad (3)$$

Activation volumes are derived from the equation of absolute rates:

$$\Delta G^{\ddagger} = -RT \ln kNh/RT \qquad (4)$$

which gives

$$\Delta V^{\ddagger} = -RT\, \partial \ln k / \partial p \qquad (5)$$

and reaction volumes from eq 6:

$$\Delta G = -RT \ln K \qquad (6)$$

which yields

$$\Delta G = -RT \partial \ln K / \partial p \qquad (7)$$

The activation volume can be *measured* in only one way, i.e., by means of the effect of hydrostatic pressure on the rate constant and subsequent application of eq 5; the reaction volume can be determined by either measuring the effect of pressure on the equilibrium constant and applying eq 7, by dilatometry, or by measuring the partial volumes of products and reactants individually, and then properly combining them. It may be noted from eq 1 that knowledge of both the activation volume and the partial volumes of the reactants yields the partial volume of the transition state alone. The volume is therefore one of the very few properties of the transition state that can be accurately and easily determined (the enthalpy of transfer[17] might be considered another). The partial volume of stable substances can be calculated by extrapolating the apparent molar volume from the densities of dilute solutions to infinite dilution:[16]

$$\phi_{\mathrm{v}} = \frac{M}{d} - \frac{d - d_0}{d_0}\frac{1000}{C}$$

It may be noted here in passing that eq 5 was already known to van't Hoff,[18] and eq 7 to Planck;[19] however, the modern interpretation of $\Delta V^{\ddagger}$ did not begin until the advent of Eyring's theory of absolute rates. Pressure effects on rate constants before 1935 were always listed in tables and never combined in terms of a single result until then.

The question arises: why the stress on dilute solutions in determining volume changes? Experience shows that such changes are rarely much larger than 30 cm^3/mol either way, and inspection of eq 5 shows that, accordingly, k will change by only a fewfold per kilobar of pressure. If we were to attempt to measure the effect of such pressures on gas-phase reactions, we would find that the resulting changes in *rate* would be so much greater than those of the *rate constant* that it would probably be impossible in most cases to extract the latter from the overall effect. We also avoid (initially) pure liquids and even concentrated solutions because unless $\Delta V = 0$, changes in total volume and hence in pressure would occur during the reaction. Even if one constructed a piezostat that automatically and continuously adjusted the pressure, there would still be the problem of a gradual change of medium and, accordingly, of the activity of the reactant(s); the dissipation of heat evolved would present a much greater difficulty, and so on. For these and other reasons piezochemists work with dilute solutions, the more dilute the better. It should be stressed that high dilution need not be an important requirement in synthetic applications, however.

Guggenheim[20] and especially Hamann[2] have pointed out clearly and repeatedly that the application of eq 3 and 4 requires the use of pressure-independent concentration units, such as molal units, mole fractions, or moles per liter *at one atmosphere*, and so on. These warnings are repeated here because the literature continues to produce examples of "corrections" made to allow for the apparent fact that compressed solutions have higher concentrations than those at atmospheric pressure. Such corrections would be in order only if the solutions were prepared (and hence if the concentrations were initially known only) at the high pressures at which they are used; one should then have to correct these numbers so as to produce the corresponding values at atmospheric pressure. In fact, this of course never occurs. The only situation calling for a correction and likely to arise now and then is a reaction other than first order in which spectroscopic analysis is carried out with a cell of constant length and hence pressure-dependent average cross section, since the number of molecules in the light beam is increased then.

A continuously recurring problem with eq 5 and 7 is that the theoretical relations between k and p, and K and p, are not known, and hence that the slopes must be obtained in an empirical manner before $\Delta V^{\ddagger}$ and ΔV can be calculated. These theoretical relations are certainly not linear ones, and although linear behavior is sometimes indicated over modest pressure ranges, the fact is that $\Delta V^{\ddagger}$ and ΔV are always pressure dependent. We will briefly discuss these related problems; first, how to get the slopes.

Various methods have been proposed and used. Perhaps the most realistic method, in view of the empirical nature of the objective, is the graphical method.[16] The alternative is fitting by least squares[16] to some equation having roughly the correct characteristics for the data at hand. These data may portray either positive or negative slope ($\Delta V^{\ddagger}$ and ΔV may be either negative or positive, respectively), but they always tend to level off at high pressure; i.e., $\Delta V^{\ddagger}$ and ΔV tend to zero at high pressures. There are, of course, many equations that mimic this behavior, but in order to be suitable for use, the number of adjustable parameters should be minimal. Among all the equations proposed and used, perhaps the most popular is the parabolic one

$$\ln k = a + bp + cp^2 \qquad (8)$$

so that then, at $p = 0$

$$\Delta V^{\ddagger} = -bRT \qquad (9)$$

The advantage of eq 8 is the simplicity of the arithmetic; the weak point is that its shape (with a maximum or minimum) is not realistic, and especially if data over a wide pressure range are available, the fit may be poor and the absolute magnitude of $\Delta V^{\ddagger}$ or ΔV is likely to be underestimated.

There are also a number of semiempirical equations that have been proposed; these have in the main been based on the Tait equation

$$\frac{V_0 - V_p}{V_0} = C \log\left(1 + \frac{p}{B}\right) \qquad (10)$$

which almost perfectly describes the behavior of water over modest pressure ranges and for which there is some theoretical justification.[21] The assumption is that the Tait equation is also valid for the components of the solution at hand, and for the transition state as well. Earlier debates about this question have been quoted elsewhere,[1] and it has remained of interest;[22,23] however, the authors agree with Whalley[24] and Hyne[25] that with our lack of theoretical understanding and with the precision available, graphical methods and/or eq 9 are the best methods available. One alternative that has not been considered is eq 11, which has the same number of parameters as (8) but is sufficiently more flexible that it may avoid the underestimation of

$\Delta V^{\ddagger}$ at low pressures that so uniformly results from the use of eq 8. Equation 9 would not be changed, except for the value of *b*.

$$\ln k = a + bp + cp^3 \tag{11}$$

The second and related point is that since $\Delta V^{\ddagger}$ and ΔV are pressure dependent, we need to agree on the pressure to which "the" activation and reaction volumes shall refer. The choice has universally been that of zero pressure, and it is understood that throughout this paper $\Delta V^{\ddagger}$ and ΔV are intended to mean $\Delta V_0^{\ddagger}$ and ΔV_0, which differ by immeasurably small amounts from the values at atmospheric pressure. The reasons for this are that these volumes can then be correlated with all other known facts about the reaction or equilibrium, which also virtually always are available for atmospheric pressure only, and furthermore, that reaction volumes derived from partial volume measurements are likewise known only at atmospheric pressure. There is unfortunately one small problem with this convention, which is that the pressure range ends at zero, and hence that the error in estimating $\Delta V^{\ddagger}$ or ΔV from high-pressure data is maximized. From this point of view, data at ½ or 1 kbar ($\Delta V_{1/2}^{\ddagger}$, ΔV_1, etc.) might have been preferable, but it is too late for that.

The curvature in the log *V* vs. *p* plots, of course, provides additional information, and this may be relatable to the compressibility of the transition state; perhaps Gay has made the most progress in this direction.[26] Small temperature effects on the activation volume have been found by numerous workers, most notably by Hyne.[27] That these small effects are measurable to reasonable accuracy was demonstrated by Kelm,[28] who found that the Menshutkin reaction of triethylamine with ethyl iodide in acetone in the range of 0–3 kbars and 20–50 °C closely obeyed the Maxwell relation

$$\left(\frac{\partial \Delta V^{\ddagger}}{\partial T}\right)_p = -\left(\frac{\partial \Delta S^{\ddagger}}{\partial p}\right)_T \tag{12}$$

El'yanov[29-33] has treated the problem of calculating $\Delta V^{\ddagger}$ and ΔV if only high-pressure data are available. His analysis is based on the reasonable assumption that similar reactions will have the same curvature.

As noted before,[1] a minimum or inflection point in the ln *k* vs. *p* curve is indicative of competing pathways with different activation volumes. An example was recently described by Tiltscher,[34] who found that the Friedel–Crafts propylation of benzene with propene, catalyzed with ferric chloride, in nitrobenzene solution exhibited a minimum. The competing mechanisms have not yet been sorted out.

Still another theoretical point of interest, first proposed by Walling,[35] is the pressure-induced transition state progression along the reaction coordinate. A possible example has been claimed by Fujii,[36] who deduced from the pressure coefficient of the rate constant of the HCl catalyzed Orton rearrangement of *N*-chloroacetanilide that the Cl–Cl distance in the transition state increases from 2.5 to 3.5 Å between 0 and 2 kbars, but this conclusion has been disputed.[37] Another possible case has been described by Libby,[38] who found that solid phase dimerization reactions of anthracene at 58 kbars proceed more rapidly at low temperature than at high, and who refers to the "negative activation enthalpy" of the reactions. These conversions, however, require initiation by means of high-energy irradiation; the mechanisms—indeed, the products—have not been established with certainty, and it is not clear that Libby's conclusion is indisputable.

In the earlier review,[1] mention was made of the possibility of making use of the internal pressure[39] of liquids to estimate $\Delta V^{\ddagger}$ of reactions occurring in them (p 230 ff). This suggestion, in one form or another, has been revived by several authors;[40-44] however, the data so generated have not been included here.

TABLE I. Factors in the Estimation of ΔV_0^{*}

Mechanistic feature	Contribution, cm^3/mol
Bond cleavage	+10
Bond deformation	~0
Bond formation	−10
Displacement	−5
Diffusion control	>+20
Cyclization	~0
Ionization	−20
Steric hindrance	(−)
Neutralization	+20
Charge dispersal	+5
Charge concentration	−5

As yet, there are so few demonstrated examples of activation volumes determined in both ways that one can be confident of the solvent-variation method; furthermore, it is rather questionable on many grounds whether reactant molecules are indeed not subject to influences from the solvent host other than a pressure equal to its internal pressure. Neuman[45] has justly criticized such methods for media other than hydrocarbons. Our own attitude[1] is that the assumption is justified only if the reaction can be made to take place in the gas phase, and then at a rate predictable from the known activation volume and the internal pressure of the solvent in which $\Delta V^{\ddagger}$ was measured.

It is desirable to mention here two important strides forward in the determination of partial volumes. One of these is the tuning fork pycnometer (densimeter),[46] in which the density of the solution of interest is deduced from the natural frequency of a tuning fork filled with the solution. This allows much more rapid and more sensitive determination of densities than conventional pycnometers. The second innovation is the determination of the partial volume of individual ions from ionic vibration potential measurements;[47] up till then, these volumes could only be measured for pairs of ions of opposite charge, or as differences of ions of like charge. Useful reviews of partial volumes are available for organic compounds in water[48] and for electrolytes;[49] references to and a discussion of the volume of mixing have been provided by Brower.[50]

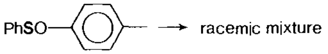
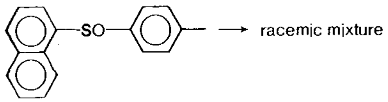
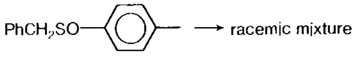
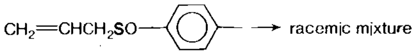
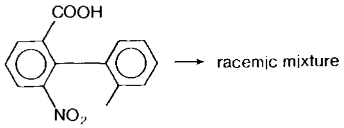
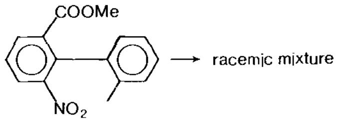
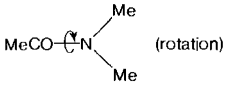
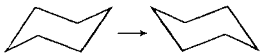
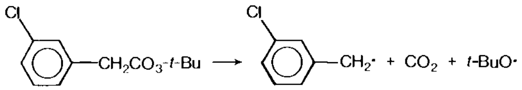
Table I appeared also in ref 1; it is a useful summary of all known data. In applying it, one should be aware that these numbers are no more than averages, and that especially the entries involving ions are strongly solvent dependent.

C. Notes Concerning Apparatus

Important progress has been made in recent years in the marriage of high-pressure equipment with conventional kinetic techniques so that reactions of much greater speed can now be studied under pressure. Among these innovations may be mentioned Eckert's high-pressure mixing apparatus,[51] which allows the mixing of reagents at will after the heat of compression has dissipated, and hence the study of reactions which are over in a matter of minutes; it should be easily extendable to high-pressure quenching as well. Other steps in this direction are provided by Brower's high-pressure p-jump design,[52] the high-pressure T-jump apparatus described by Grieger,[53] Hasinoff,[54] and Jost,[54] the NMR high-pressure probe by Yamada,[55] Jonas,[56] and by Merbach,[56] the ESR probe of Schaafsma,[57] Heremans' high-pressure stopped-flow apparatus,[58] and Caldin's flash photolysis equipment.[59] Moriyoshi has described a new continuous technique of following high-pressure reactions based on the pressure drop;[60] the topic of spectroscopy at high pressure has been reviewed by Ferraro and Basile.[61]

The most recent stage in the never-ending cycle of revisions and renamings of units is recorded in the opening pages of the *Australian Journal of Chemistry* of 1977;[62] the pressure unit is now the pascal, defined as 1 N/m^2 (N = newton). In the past

TABLE II. Activation Volumes for Reactions of Organic Compounds[a]

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^{*}, cm^3/mol	Ref	Remarks
1	t-BuS^{+}(Me)Et ⟶ racemic mixture	H_2O	40			+6.4	63	
2	PhCOCH$_2$S^{+}(Me)Et ⟶ racemic mixture	H_2O	60.5			0	63	
3		MeOH	60.5			0	63	
4		EtOH	60.5			0	63	
5		PhMe	192			−2	63	
6		PhMe	187			0	63	
7		PhMe	141.3			+26	63	
8		PhMe	43			+1.0	63	
9		EtOH	60			+1.4	63	
10		PhMe	90	9.9	13	−283	64	At >3 kbars, $\Delta V^{*} \simeq -1^{s}$
11		PhMe	90	9.1	5	−32	64	At >3 kbars, $\Delta V^{*} \simeq -6$
12		*t*	80	2.0	3	+10.3	65	
13		*b*	−60	2.0	3	−1.9	65	
14	PhCH$_2$CO$_3$-t-Bu ⟶ PhCH$_2$· + CO$_2$ + t-BuO·	*i*-PrPh	79.6	4.1	3	+1.0	66	
15		PhCl	79.6	4.1	3	+1.5	66	
16		*i*-PrPh	79.6	6.1	4	+0.5, +0.4^{c}	67, 68	ΔV^{*} increases with pressure
17		PhCl	79.6	4.1	3	+1.0	67	
18	PhCO$_3$-t-Bu ⟶ PhCOO· + t-BuO·	*i*-PrPh	79.6	4.1	2	+10.0, +10.4	67	
19		PhCl	79.6	4.1	2	+12.5, +12.9	67	
20	c-C$_6$H$_{11}$CO$_3$-t-Bu ⟶ c-C$_6$H$_{11}$· + CO$_2$ + t-BuO·	*i*-PrPh	79.6	4.1	3	+3.9	67, 69	
21	[t-BuO·N$_2$O-t-Bu]$_{cage}$ ⟶ 2t-BuOH	C_8H_{18}	45	4.1	6	+13.8^{d}	70	
22	t-BuON═NO-t-Bu ⟶ 2t-BuO· + N$_2$	C_8H_{18}	55.1	6.3	4	+4.3	71	
23		*i*-PrPh	79.6	6.1	4	+1.6^{c}	68	ΔV^{*} increases with pressure

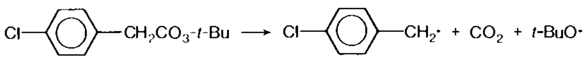
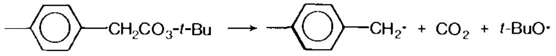
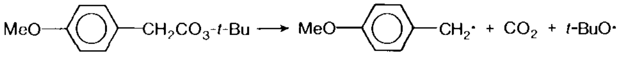
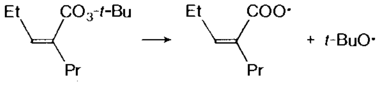
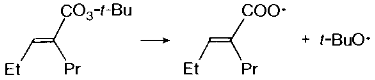
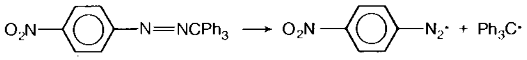
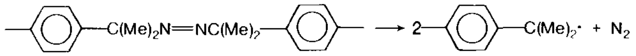
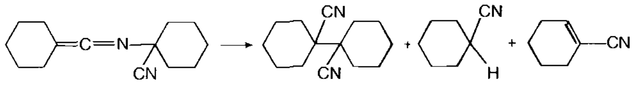
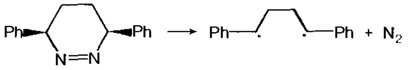
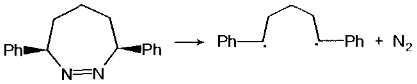
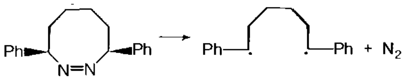
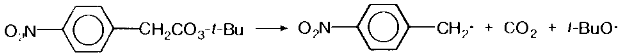
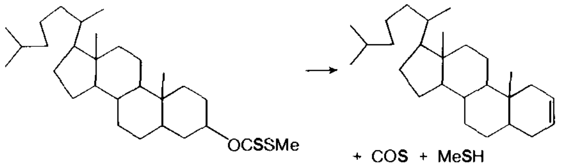
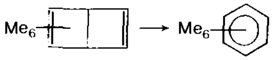
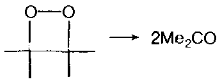
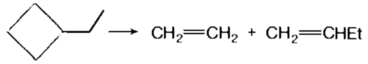
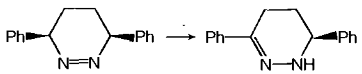
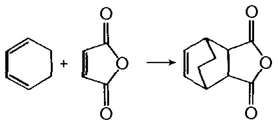
24		*i*-PrPh	79.6	6.1	4	+1.2^c	68	ΔV^* increases with pressure
25		*i*-PrPh	79.6	6.1	4	+0.2^c	68	ΔV^* increases with pressure
26		*i*-PrPh	79.6	4.1	3	+0.2^c	68	ΔV^* increases with pressure
27		*i*-PrPh	100.1	4	5	+6.8	72	
28		*i*-PrPh	100.1	4	5	+9.0	72	
29		C_8H_{18}	60	3.9	5	+18	73	
30		*i*-PrPh	60	3.9	5	+20	73	
31		*t*-BuPh	60	3.9	5	+21	73	
32	$PhC(Me)_2N{=}NC(Me)_2Ph \rightarrow 2PhC(Me)_2\cdot + N_2$	*i*-PrPh	55	6.2	8	+5	73	
33		PhCl	55	4.2	5	+4.3	73	
34		*i*-PrPh	55	4.2	4	+4	73	
35		PhCl	100	4	4	+4.9	74	
36		PhCl	100	3	3	+11^c	74	In the presence of DPPH
37		PhCl	100	4	4	+10^c	74	In the presence of DBNO
38		*i*-PrPh	100	4	4	+9.5^c	74	
39		PhMe	100	4	3	+3.9	74	
40		*t*-BuPh	100	4	4	+5.5	74	
41	$t\text{-BuCO}_3\text{-}t\text{-Bu} \rightarrow t\text{-Bu}\cdot + CO_2 + t\text{-BuO}\cdot$	*i*-PrPh	65	5	6	+0.3^e	75	ΔV^* increases with pressure
42	$i\text{-PrCO}_3\text{-}t\text{-Bu} \rightarrow i\text{-Pr}\cdot + CO_2 + t\text{-BuO}\cdot$	*i*-PrPh	90	5.1	6	+1.6^e	75	ΔV^* increases with pressure
43		PhMe	60	5.3	6	+5.5	76, 77	
44		PhMe	65	5.3	6	+5.5	77	
45		PhMe	60	5.5	6	+7.1	77	
46		*i*-PrPh	85	6.1	6	+2^c	78	
47	$PhCH_2CO_3\text{-}t\text{-Bu} \rightarrow PhCH_2\cdot + CO_2 + t\text{-BuO}\cdot$	*i*-PrPh	85	4.1	3	+1^c	78	

TABLE II (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	$\Delta V^{\ast}$, cm³/mol	Ref	Remarks
48	$\text{DPPH} \xrightarrow[\text{AIBN}]{} \text{disappearance of DPPH}$	PhMe	40	1	9	+10.7	79	
49		$c\text{-}C_6H_{11}Me$	40	1	10	+17.2	79	
50		$c\text{-}C_6H_{12}$	40	0.7	8	+34.9	79	
51	 + COS + MeSH (both Δ^2- and Δ^3-cholestene)	Neat	176	12	5	+12.3	80	
52		$CDCl_3$	90	10.1	12	−34.6	81	At 3 kbars, $\Delta V^{\ast} \simeq -3.7$ cm³/mol
53		PhMe	60	1	5	+9	82	
54		PhCl	60	1	5	+11	82	
55		Gas phase	410	0.2	22	+28.2	83	In the presence of N_2
56		PhMe	60	5.3	6	-7.5^{e}	77	
57	$[t\text{-BuO·N}_2\text{·O-}t\text{-Bu}]_{\text{cage}} \xrightarrow{k_c} t\text{-BuOO-}t\text{-Bu}$	C_8H_{18}	45	4.1	6	-4.2^{f}	70	
58	$\sim CH_2\dot{C}HPh + CH_2{=}CHPh \rightarrow \sim CH_2\dot{C}HPh$	H_2O	40	1.0	6	−23.5	84	Emulsion
59		Neat	30	1.0	5	−17.9	85	
60	$\sim CH_2\dot{C}MeCOOMe + CH_2{=}CMeCOOMe \rightarrow \sim CH_2\dot{C}MeCOOMe$	Neat	30	1.0	5	−19.0	86	
61	$\sim CH_2\dot{C}MeCOOBu + CH_2{=}CMeCOOBu \rightarrow \sim CH_2\dot{C}MeCOOBu$	Neat	30	1.0	5	−23.2	87	
62	$\sim CH_2\dot{C}HCOOBu + CH_2{=}CHCOOBu \rightarrow \sim CH_2\dot{C}HCOOBu$	Neat	30	1.0	5	−22.5	88	
63	$\sim CH_2\dot{C}HOAc + CH_2{=}CHOAc \rightarrow \sim CH_2\dot{C}HOAc$	Neat	30	1.0	5	−24.0	89	
64	$\sim CH_2\dot{C}MeCOOOc + CH_2{=}CMeCOOOc \rightarrow \sim CH_2\dot{C}MeCOOOc$	Neat	30	1.0	5	−24.7	90	
65	$2 \sim CH_2\dot{C}HPh \rightarrow$ term'n	Neat	30	1.0	5	+13.3	89	
66	$2 \sim CH_2\dot{C}MeCOOMe \rightarrow$ term'n	Neat	30	1.0	5	+25.0	89	
67	$2 \sim CH_2\dot{C}MeCOOBu \rightarrow$ term'n	Neat	30	1.0	5	+17.8	89	
68	$2 \sim CH_2\dot{C}HCOOBu \rightarrow$ term'n	Neat	30	1.0	5	+20.8	89	See ref 87 for octyl ester
69	$2 \sim CH_2\dot{C}HOAc \rightarrow$ term'n	Neat	30	1.0	5	+16.3	89	
70		CH_2Cl_2	35	2.1	8	−37.2	91, 92	$\Delta V = -30.3$

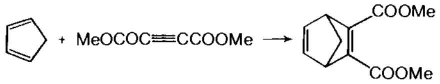
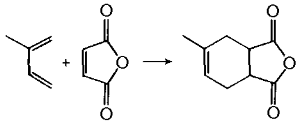
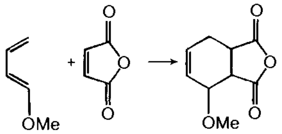
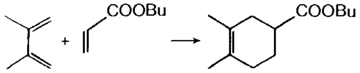
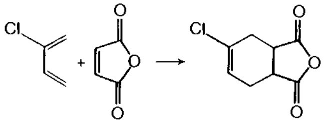
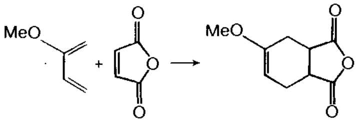
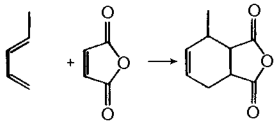
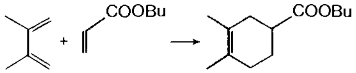
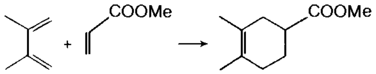
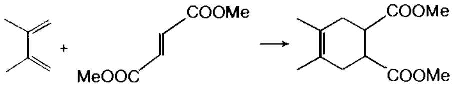
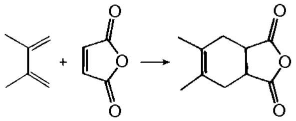
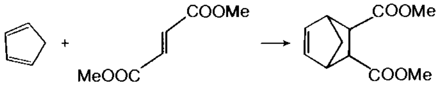
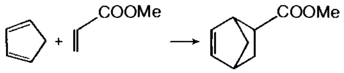
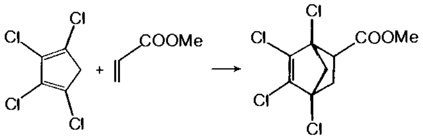
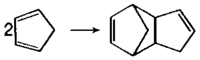
71		AcOEt	10	6.2	12	−30.2	91, 92	$\Delta V = -33.9$
72		Me_2CO	35	1.4	7	−39.0	91, 93	$\Delta V = -35.9$
73		AcOEt	35	1.4^f	7	−37.4	93	$\Delta V = -36.8$
74		CH_2Cl_2	35	1.4	7	−39.8	93	$\Delta V = -33.4$
75		$MeNO_2$	35	1.4	7	−32.5	93	$\Delta V = -30.7$
76		Me_2CO_3	35	1	6	−39.3	93	
77		MeCN	35	1.4	7	−37.5	93	$\Delta V = -34.5$
78		i-Pr_2O	35	1.4	7	−38.5	93	$\Delta V = -38.3$
79		BuCl	35	1.4	7	−38.0	93	
80		CH_2ClCH_2Cl	35	1.4	7	−37.0	93	$\Delta V = -35.5$
81		$MeNO_2$	35	1.4	6	−43.0	94	$\Delta V = -28.2$
82		MeCN	35	1	6	−32.0	94	$\Delta V = -32.4$
83		CH_2ClCH_2Cl	35	1.4	6	−43.7	94	$\Delta V = -30.4$
84		BuCl	35	1.4	7	−45.4	94	$\Delta V = -35.5$
85		Me_2CO_3	35	1.4	7	−53.6	94	$\Delta V = -32.2$
86		Neat	50	1.4	5	−28.7	95	
87		Neat	70	2	6	−28.5	95	
88		$CH_2{=}CHCOOBu$	10	0.7	7	−25.7	95	$AlCl_3$ catalyzed: $\Delta V = -31$
89		Me_2CO	65	1.4	7	−48.6	96	
90		MeCN	65	1.4	7	−41.6	96	$\Delta V = -36.9$
91		BuCl	65	1.4	7	−51.1	96	
92		CH_2ClCH_2Cl	65	1.4	7	−48.2	98	
93		Me_2CO_3	65	1.4	7	−42.9	96	
94		i-Pr_2O	65	1.4	7	−43.7	96	
95		Me_2CO	50	1.7	8	−36.2	96	$\Delta V = -34.1$

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
96		MeCN	50	1.7	8	−33.5	96	$\Delta V = -31.9$
97		BuCl	50	1.7	8	−36.7	96	
98		CCl_4	50	1.7	8	−37.6	96	
99		CH_2ClCH_2Cl	50	1.7	8	−35.5	96	
100		i-Pr_2O	50	1.7	8	−40.7	96	
101		Me_2CO	35	1.4	7	−47.3	96	
102		MeCN	35	1.4	7	−43.1	96	$\Delta V = -31.3$
103		BuCl	35	1.4	7	−48.9	96	
104		CH_2ClCH_2Cl	35	1.4	7	−44.7	96	$\Delta V = -33.3$
105		Me_2CO_3	35	1.4	7	−45.6	96	
106		i-Pr_2O	35	1.4	7	−51.4	96	
107		BuCl	40	0.9	5	−29.6	97	$\Delta V = -36.4$
108		BuCl	40	0.9	5	−30.2	97	$\Delta V = -37.0$
109		BuCl	40	0.9	5	−32.9	97	$\Delta V = -37.2$
110		BuCl	30	0.9	5	−41.3	97	$\Delta V = -36.3$
111		BuCl	30	0.9	5	−32.7	97	$\Delta V = -36.7$
112		BuCl	40	0.9	5	−30.1	97	$\Delta V = -35.7$
113		BuCl	40	0.9	5	−24.6	97	$\Delta V = -33.2$
114		BuCl	40	0.9	5	−23.7	97	$\Delta V = -33.0$

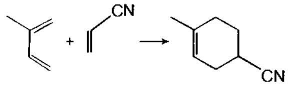
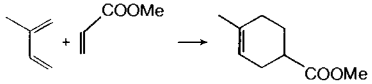
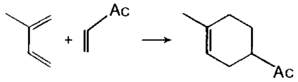
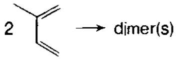
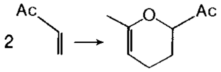
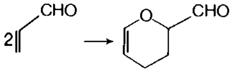
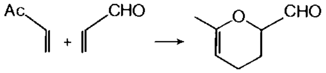
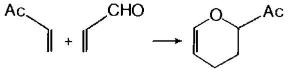
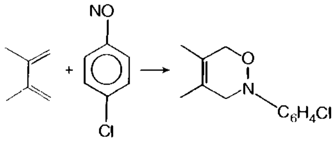
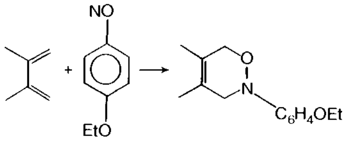
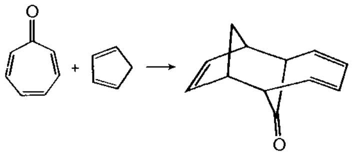
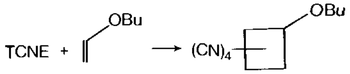
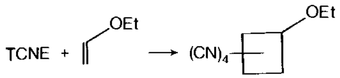
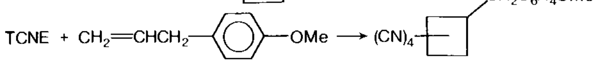
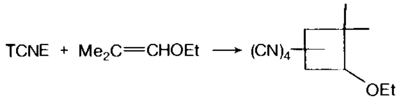
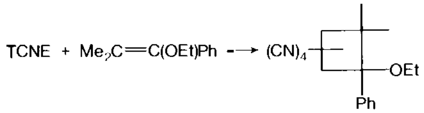
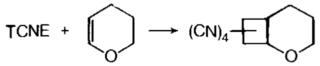
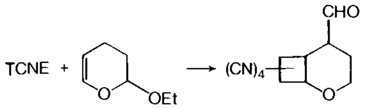
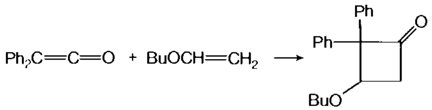
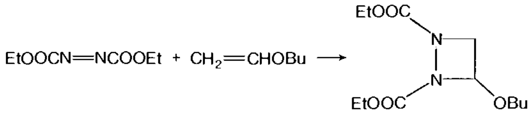
115		BuBr	21	9.9	12	−33.1	98	Δ*V* = −37.0
116		BuBr	21	9.8	11	−30.8	98	Δ*V* = −36.9
117		BuBr	21	2.9	9	−36.9	98	Δ*V* = −37.1
118		BuBr	40	8.1	12	−35.3	99	
119		BuBr	50	8.1	11	−40.4	99	
120		BuBr	60	5	9	−40.0	99	
121		BuBr	70	8.1	10	−41.3	99	
122		C_7H_{16}	70	1.3	9	−41.0	100	
123		C_7H_{16}	70	1.3		−37.0	100	
124		C_7H_{16}	70	1.3		−35.0	100	
125		C_7H_{16}	70	1.3		−36.5	100	
126		$PhNO_2$	25			−21.3	101	
127		EtOH	25			−28.3	101	
128		PhCl	25			−31.4	101	
129		CH_2ClCH_2Cl	25			−32.9	101	
130		CH_2Cl_2	25			−26.4	101	Δ*V* = −36.7
131		PhMe	25			−33.3	101	
132		CCl_4	25			−22.5	101	
133		$PhNO_2$	25			−26.1	101	
134		EtOH	25			−22.1	101	
135		PhCl	25			−30.2	101	
136		CH_2ClCH_2Cl	25			−23.1	101	
137		CH_2Cl_2	25			−28.9	101	Δ*V* = −30.8
138		PhMe	25			−38.3	101	
139		CCl_4	25			−25.6	101	

TABLE II (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm^3/mol	Ref	Remarks
140		*p*-Dioxane	60	4	6	−7.5	102	$\Delta V = -4.3$
141		CCl_4	30	1	5	−44.0	101, 103	
142		PhH	30	0.8	4	−37.0	101, 103	
143		CH_2Cl_2	30	2	7	−33.0	101, 103	
144		Me_2CO	30	2	7	−27.0	101, 103	
145		MeCN	30	2	7	−23.0	101, 103	
146		CH_2Cl_2	25			−34.5	101	$\Delta V = -29.4$
147		CH_2Cl_2	25			−38.0	101	$\Delta V = -31.9$
148		CH_2Cl_2	25			−34.0	101	$\Delta V = -26.7$
149		CH_2Cl_2	25			−46.5	101	$\Delta V = -29.5$
150		CH_2Cl_2	25			−45.5	101	$\Delta V = -27.7$
151		CH_2Cl_2	27.5	1.1	5	−43.0	104	
152		CH_2Cl_2	25	1.5	6	−45.3	104	
153		PhMe	25.5	1.7	9	−50.7	104	
154		PhMe	24.5	2.6	6	−45.9	104	

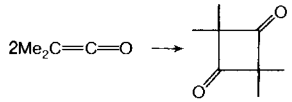
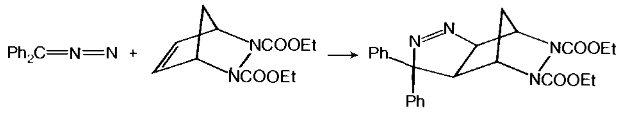
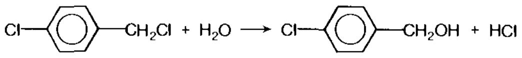
155		PhMe	25	0.9	4	−30.0	104	
156		PhMe	24.5	3.1	7	−32	104	
157	$PhCH_2Cl + H_2O \rightarrow PhCH_2OH + HCl$	Aq MeOH	50.3	2.8	4	−12.13	112	H_2O 90 mol%
158		Aq MeOH	50.3	2.8	4	−15.6	112	H_2O 80 mol%
159		Aq MeOH	50.3	2.8	4	−17.9	112	H_2O 70 mol%
160		Aq MeOH	50.3	4.1	5	−19.8	112	H_2O 60 mol%
161		Aq MeOH	50.3	4.1	5	−18.8	112	H_2O 50 mol%
162		Aq *i*-PrOH	50.3	4.1	5	−23.1	112	H_2O 90 mol%
163		Aq *i*-PrOH	50.3	4.1	5	−19.0	112	H_2O 80 mol%
164		Aq *i*-PrOH	50.3	4.1	5	−18.1	112	H_2O 70 mol%
165		Aq *i*-PrOH	50.3	4.1	5	−13.62	112	H_2O 60 mol%
166		Aq *t*-BuOH	50.3	4.1	5	−25.5	112	H_2O 90 mol%
167		Aq *t*-BuOH	50.3	4.1	5	−22.7	112	H_2O 80 mol%
168		Aq *t*-BuOH	50.3	4.1	5	−17	112	H_2O 70 mol%
169		Aq Me_2CO	50.1	2.8	7	−13.91	113	H_2O 95 mol%
170		Aq Me_2CO	50.1	4.1	8	−17.75	113	H_2O 90 mol%
171		Aq Me_2CO	50.1	4.1	6	−20.22	113	H_2O 85 mol%
172		Aq Me_2CO	50.1	4.1	8	−19.33	113	H_2O 80 mol%
173		Aq Me_2CO	50.1	4.1	6	−20.37	113	H_2O 70 mol%
174		Aq Me_2CO	50.1	4.1	6	−17.32	113	H_2O 59 mol%
175		Aq DMSO	50.1	2.8	7	−11.92	113	H_2O 92.5 mol%
176		Aq DMSO	50.1	4.1	8	−13.10	113	H_2O 85 mol%
177		Aq DMSO	50.1	4.1	8	−14.15	113	H_2O 77.5 mol%
178		Aq DMSO	50.1	4.1	8	−15.87	113	H_2O 70 mol%
179		Aq DMSO	50.1	4.1	6	−16.31	113	H_2O 60 mol%
180		Aq DMSO	50.1	4.1	6	−16.30	113	H_2O 50 mol%
181		Aq DMSO	50.1	4.1	5	−18.85	113	H_2O 40 mol%
182		H_2O	40	3.4	8	−9.09	114	
183		H_2O	50.3	2.7	7	−9.9	114	
184		H_2O	60.5	1.9	12	−10.3	114	
185		Aq *t*-BuOH	40	2.7	6	−10.07	114	H_2O 97.5 mol%
186		Aq *t*-BuOH	50.3	2.7	6	−13.0	114	H_2O 97.5 mol%
187		Aq *t*-BuOH	60.5	2.1	6	−15.2	114	H_2O 97.5 mol%
188		Aq *t*-BuOH	40	4.1	7	−21.54	114	H_2O 95 mol%
189		Aq *t*-BuOH	50.3	2.7	6	−24.7	114	H_2O 95 mol%
190		Aq *t*-BuOH	60.5	2.7	6	−24.5	114	H_2O 95 mol%
191		Aq *t*-BuOH	40	4.1	6	−24.7	114	H_2O 90 mol%
192		Aq *t*-BuOH	50.3	4.1	6	−23.97	114	H_2O 90 mol%
193		Aq *t*-BuOH	60.5	4.1	13	−23.1	114	H_2O 90 mol%
194		Aq *t*-BuOH	40	4.1	6	−18.66	114	H_2O 80 mol%
195		Aq *t*-BuOH	50.3	4.1	6	−20.22	114	H_2O 80 mol%
196		Aq *t*-BuOH	60.5	4.1	6	−22.03	114	H_2O 80 mol%
197		Aq *t*-BuOH	40	3.4	6	−19.8	114	H_2O 70 mol%
198		Aq *t*-BuOH	50.3	4.1	6	−19.5	114	H_2O 70 mol%
199		Aq *t*-BuOH	60.5	4.1	7	−20.71	114	H_2O 70 mol%

TABLE II (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm^3/mol	Ref	Remarks
200		H_2O	50	1.6	5	−10.7	115	
201		Aq glycerol	50	1.6	5	−10.7	115	H_2O 95 v%
202		Aq glycerol	50	1.6	5	−10.8	115	H_2O 87.5 v%
203		Aq glycerol	50	1.6	5	−10.4	115	H_2O 75 v%
204		Aq glycerol	50	1.6	5	−11.0	115	H_2O 50 v%
205		Aq glycerol	50	1.6	4	−10.7	115	H_2O 25 v%
206		H_2O	0	2	5	$+5^g$	116	
207		H_2O	5	2	5	-6^g	116	
208		H_2O	10	2	5	-10^g	116	
209		H_2O	15	2	5	-13^g	116	
210	$PhCH_2Cl + D_2O \rightarrow PhCH_2OD + DCl$	D_2O	40	2.1	6	−8.89	117	
211		D_2O	60.5	1.7	6	−13.0	117	
212		H_2O	50.3	2.7	5	−11.5	118	
213		Aq EtOH	50.3	2.7	5	−13.8	118	H_2O 95 mol%
214		Aq EtOH	50.3	4.1	6	−17.9	118	H_2O 90 mol%
215		Aq EtOH	50.3	4.1	6	−18.8	118	H_2O 85 mol%
216		Aq EtOH	50.3	4.1	6	−21.8	118	H_2O 80 mol%
217		Aq EtOH	50.3	4.1	6	−19.9	118	H_2O 75 mol%
218		Aq EtOH	50.3	4.1	6	−18.9	118	H_2O 70 mol%
219		Aq EtOH	50.3	4.1	6	−20.8	118	H_2O 60 mol%
220	$Ph_2CHCl + H_2O \rightarrow Ph_2CHOH + HCl$	Aq *p*-dioxane	50	1	5	−14.3	119	H_2O 9.8 w%
221		Aq *p*-dioxane	50	1	5	−14.0	119	H_2O 14.5 w%
222		Aq *p*-dioxane	50	1	5	−14.0	119	H_2O 18.8 w%
223		Aq *p*-dioxane	25	1	5	−13.7	119	H_2O 24.4 w%
224		Aq *p*-dioxane	25	1	5	−13.2	119	H_2O 29.3 w%
225		Aq *p*-dioxane	25	1	5	−13.3	119	H_2O 36.0 w%
226	*t*-BuCl + H_2O → *t*-BuOH + HCl	H_2O	0	1.5	4	−2.0	24	
227		Aq EtOH	0	1.5	6	−7.0	24	H_2O 90 v%
228		Aq EtOH	0	1.5	6	−13.2	24	H_2O 75 v%
229		Aq EtOH	0	3	12	−21.5	24	H_2O 60 v%
230		Aq EtOH	0.2	0.7	3	−9.3	118	H_2O 98 mol%
231		Aq EtOH	0.2	2.1	5	−24.3	118	H_2O 80 mol%
232		Aq EtOH	0.2	2.1	4	−19.9	118	H_2O 70 mol%
233		Aq EtOH	0.2	2.1	4	−17.6	118	H_2O 60 mol%
234	$O_2NCH_2CH_2Cl + H_2O \rightarrow O_2NCH_2CH_2OH + HCl$	Aq *p*-dioxane	70	1	5	−13.1	119	H_2O 9.8 w%
235		Aq *p*-dioxane	70	1	5	−13.9	119	H_2O 18.8 w%
236		Aq *p*-dioxane	70	1	5	−14.4	119	H_2O 24.4 w%
237		Aq *p*-dioxane	70	1	5	−14.8	119	H_2O 36.0 w%
238		Aq *p*-dioxane	70	1	5	−14.6	119	H_2O 49.3 w%
239	$MeBr + H_2O \rightarrow MeOH + HBr$	H_2O	60	3	11	−17.0	120	
240		H_2O	70	3	13	−14.9	120	
241		H_2O	80	1	5	−11.7	120	
242	*i*-PrBr + H_2O → *i*-PrOH + HBr	H_2O	40	3	11	−15.2	120	
243		H_2O	50	3	11	−13.1	120	
244		H_2O	60	1	5	−10.0	120	
245		H_2O	40	2.1	6	−9.65	117	

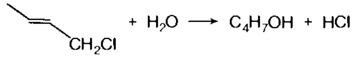
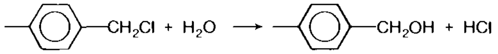
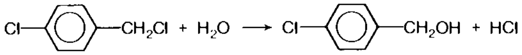
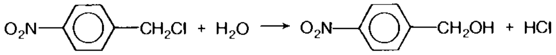
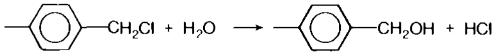
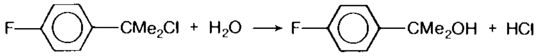
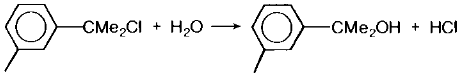
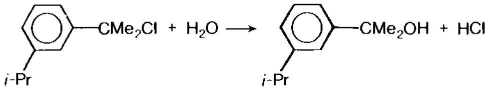
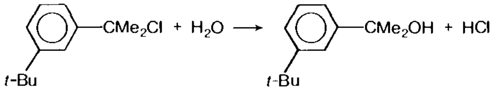
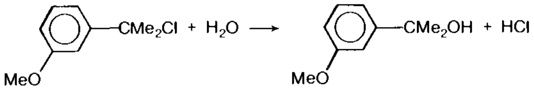
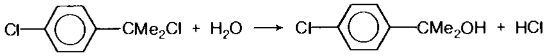
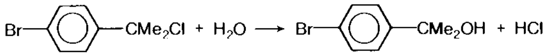
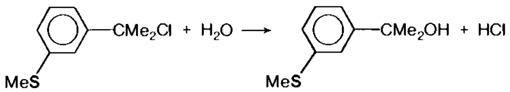
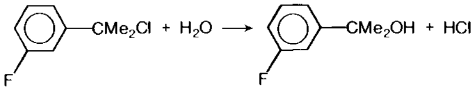
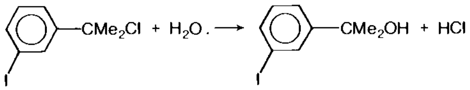
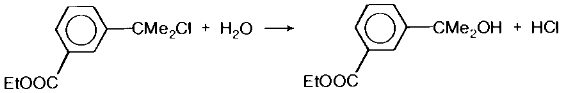
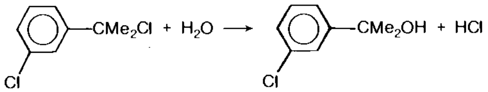
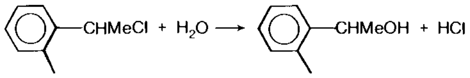
246		H_2O	60	1.4	5	−11.02	117	
247	i-PrBr + D_2O → i-PrOD + DBr	D_2O	40	2.1	6	−9.07	117	
248		D_2O	60	1.7	6	−11.42	117	
249	$CH_2{=}CHCH_2Cl + H_2O \rightarrow CH_2{=}CHCH_2OH + HCl$	H_2O	29.3	2.8	3	−10.2	121	
250		H_2O	40	2.8	4	−10.69	121	
251		H_2O	50.3	2.8	5	−11.40	121	
252		H_2O	60.5	2.8	4	−12.58	121	
253	$CH_2{=}CMeCH_2Cl + H_2O \rightarrow CH_2{=}CMeCH_2OH + HCl$	H_2O	50.3	2.8	6	−10.16	121	
254		H_2O	12	1	6	−14.83	121	
255	$PhCMe_2Cl + H_2O \rightarrow PhCMe_2OH + HCl$	Aq EtOH	45	1	5	-18^h	122	H_2O 30 v%
256		Aq EtOH	45	1	5	-21^h	122	H_2O 25 v%
257		Aq EtOH	45	1	5	-26^h	122	H_2O 20 v%
258		Aq EtOH	45	1	5	-16^h	122	H_2O 15 v%
259		Aq EtOH	45	1	5	-13^h	122	H_2O 10 v%
260		Aq Me_2CO	50	1	4	−20.0	123	H_2O 50.45 mol%
261		Aq Me_2CO	50	1	4	−22.8	123	H_2O 73.08 mol%
262		Aq Me_2CO	50	1	4	−24.0	123	H_2O 80.28 mol%
263		Aq Me_2CO	50	1	4	−18.5	123	H_2O 85.93 mol%
264	$PhCH_2Cl + H_2O \rightarrow PhCH_2OH + HCl$	Aq Me_2CO	50	1	4	−21.4	123	H_2O 85.93 mol%
265		Aq Me_2CO	50	1	4	−21.8	123	H_2O 85.93 mol%
266		Aq Me_2CO	50	1	4	−23.3	123	H_2O 85.93 mol%
267		H_2O	1	2.1	6	−4.3	27	
268		H_2O	20	2.1	5	−6.3	27	
269	$BuBr + H_2O \rightarrow BuOH + HBr$	H_2O	55	3.4	6	−10.5	27	
270		H_2O	69.9	3.4	6	−10.5	27	
271	i-PrBr + H_2O → i-PrOH + HBr	H_2O	25	1	5	−8.8	124	$\Delta V = -7.0$
272	$PhCH_2Br + H_2O \rightarrow PhCH_2OH + HBr$	H_2O	25	1	5	−7.3	124	$\Delta V = -8.8$
273	$CH_2{=}CHCH_2Cl + H_2O \rightarrow CH_2{=}CHCH_2OH + HCl$	H_2O	25	1	4	−9.8	124	$\Delta V = -9.6$
274	$MeOCH_2CMe_2Cl + H_2O \rightarrow MeOCH_2CMe_2OH + HCl$	H_2O	25	1	5	−7.3	124	$\Delta V = -10.6$
275	$MeBr + H_2O \rightarrow MeOH + HBr$	H_2O	30	3	4	−14.5	125	
276	$EtBr + H_2O \rightarrow EtOH + HBr$	H_2O	30	3	5	−11.5	125	
277	$BuCl + H_2O \rightarrow BuOH + HCl$	H_2O	65	3	4	−12	125	
278	t-BuCl + H_2O → t-BuOH + HCl	Aq Me_2CO	25	1.3	4	−16.5	125	H_2O 50 v%
279		Aq Me_2CO	50	2	4	−24	125	H_2O 10 w%
280	$PhCH_2Cl + H_2O \rightarrow PhCH_2OH + HCl$	Aq Me_2CO	25.1	2.5	4	−20	125	H_2O 50 v%
281	$Ph_2CHCl + H_2O \rightarrow Ph_2CHOH + HCl$	Aq Me_2CO	48			−16	126	H_2O 5 w%
282	$PhCH_2Cl + H_2O \rightarrow PhCH_2OH + HCl$	H_2O	50.4	0.6	8	−7.8	127	
283	c-$C_3H_5CH_2Cl + H_2O \rightarrow C_4H_7OH + HCl$	H_2O	16.6	0.5	5	−9.0	127	
284		H_2O	20.5	0.5	4	−9.2	127	
285	c-$C_4H_7Cl + H_2O \rightarrow C_4H_7OH + HCl$	H_2O	30.5	0.7	5	−8.2	127	
286		H_2O	40	0.7	6	−9.2	127	
287	c-$C_5H_9Cl + H_2O \rightarrow C_5H_9OH + HCl$	H_2O	50	0.7	5	−14.7	127	
288		H_2O	60.2	0.7	4	−15.6	127	
289		Aq Me_2CO	25	1	5	−10.9	130	H_2O 11.5 w%

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^{*}, cm^3/mol	Ref	Remarks
290		Aq Me_2CO	25	1	5	−11.2	130	H_2O 11.5 w%
291		Aq Me_2CO	25	1	5	−11.2	130	H_2O 11.5 w%
292		Aq Me_2CO	25	1	5	−11.4	130	H_2O 11.5 w%
293	$PhCMe_2Cl + H_2O \rightarrow PhCMe_2OH + HCl$	Aq Me_2CO	25	1	5	−12.0	130	H_2O 11.5 w%
294		Aq Me_2CO	35	0.8	5	−12.8	130	H_2O 11.5 w%
295		Aq Me_2CO	40	0.8	5	−13.7	130	H_2O 11.5 w%
296		Aq Me_2CO	25	1	5	−10.9	130	H_2O 11.5 w%
297		Aq Me_2CO	25	0.6	4	−17.1	130	H_2O 11.5 w%
298		Aq Me_2CO	25	0.8	5	−18.5	130	H_2O 11.5 w%
299		Aq Me_2CO	25	0.8	5	−18.2	130	H_2O 11.5 w%
300		Aq Me_2CO	25	0.8	5	−19.7	130	H_2O 11.5 w%
301		Aq Me_2CO	25	0.8	5	−20.4	130	H_2O 11.5 w%
302		Aq Me_2CO	25	0.8	5	−17.9	130	H_2O 11.5 w%
303		Aq Me_2CO	25	1	6	−22.5	130	H_2O 11.5 w%
304	$PhCHMeCl + H_2O \rightarrow PhCHMeOH + HCl$	Aq EtOH	25	1	5	−12.6	131	H_2O 20 v%
305		Aq EtOH	25	1	5	−14.1	131	H_2O 20 v%

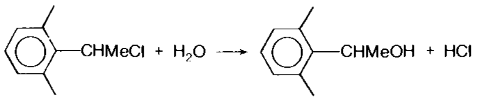
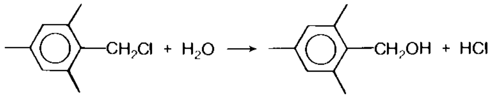
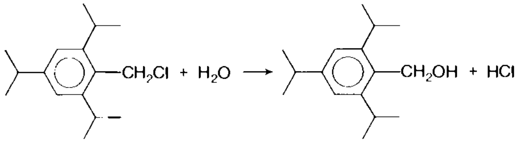
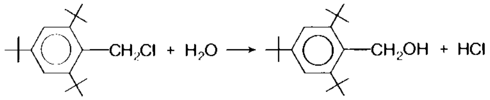
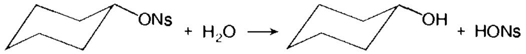
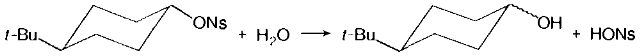
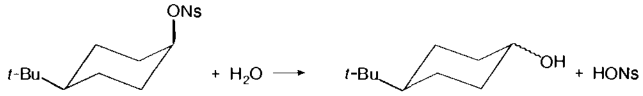
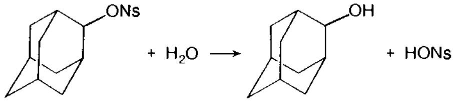
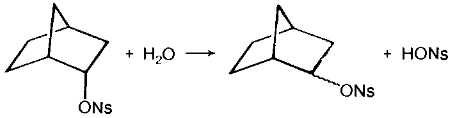
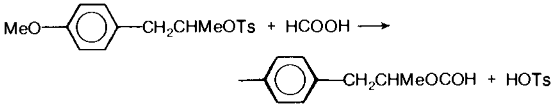
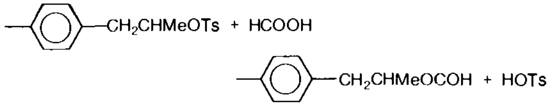
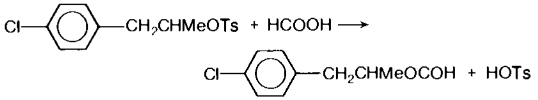
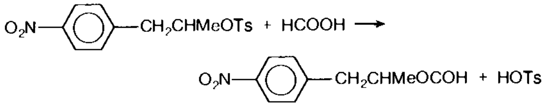
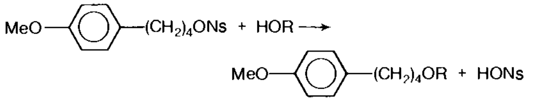
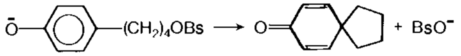
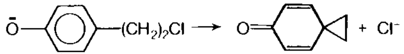
306		Aq EtOH	25	1	5	−11.8	131	H_2O 20 v%
307		Aq EtOH	25	1.5	7	−17.3	131	H_2O 20 v%
308		Aq EtOH	25	1.5	7	−18.4	131	H_2O 20 v%
309		Aq EtOH	25	1.5	7	−15.7	131	H_2O 20 v%
310	*i*-PrOTs + HCOOH → *i*-PrOCOH + HOTs	HCOOH	25	1	5	−14.7	132	
311	EtCHMeOTs + HCOOH → EtCHMeOCOH + HOTs	HCOOH	25	0.7	4	−12.9	132	
312	Et$_2$CHOTs + HCOOH → Et$_2$CHOCOH + HOTs	HCOOH	25	0.7	4	−11.2	132	
313	*i*-PrCHMeOTs + HCOOH → *i*-PrCHMeOCOH + HOTs	HCOOH	25	0.7	5	−11.7	132	
314	*t*-BuCHMeOTs + HCOOH → *t*-BuCHMeOCOH + HOTs	HCOOH	25	0.7	4	−10.5	132	
315	*i*-PrOTs + MeOH → *i*-PrOMe + HOTs	MeOH	25	1	5	−18.9	132	
316	EtCHMeOTs + MeOH → EtCHMeOMe + HOTs	MeOH	25	1	5	−19.4	132	
317	Et$_2$CHOTs + MeOH → Et$_2$CHOMe + HOTs	MeOH	25	1	5	−18.4	132	
318	*i*-PrCHMeOTs + MeOH → *i*-PrCHMeOMe + HOTs	MeOH	25	1	5	−18.3	132	
319	*i*-Pr$_2$CHOTs + MeOH → *i*-Pr$_2$CHOMe + HOTs	MeOH	25	0.7	5	−15.2	132	
320	*t*-Bu(*i*-Pr)CHOTs + MeOH → *t*-Bu(*i*-Pr)CHOMe + HOTs	MeOH	25	0.7	5	−15.4	132	
321	(*t*-Bu)$_2$CHOTs + MeOH → (*t*-Bu)$_2$CHOMe + HOTs	MeOH	25	1	6	−15.6	132	
322	(Et)$_3$C(*t*-Bu)CHOTs + MeOH → (Et)$_3$C(*t*-Bu)CHOMe + HOTs	MeOH	25	0.7	5	−13.9	132	
323		Aq Me$_2$CO	25	0.9	10	−20.0	133	H_2O 45 w%
324		Aq Me$_2$CO	25	0.9	8	−20.5	133	H_2O 45 w%
325		Aq Me$_2$CO	25	0.8	8	−21.6	133	H_2O 45 w%
326		Aq Me$_2$CO	25	0.8	7	−20.6	133	H_2O 45 w%
327		Aq Me$_2$CO	25	0.8	9	−21.0	133	H_2O 45 w%
328		HCOOH	25	0.7		−7.3	134	*i*

TABLE II (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm³/mol	Ref	Remarks
329		HCOOH	25	0.7		−7.1	134	*i*
330	$\mathrm{PhCH_2CHMeOTs + HCOOH \rightarrow PhCH_2CHMeOCOH + HOTs}$	HCOOH	25	0.7	4	−7.8	134	*i*
331		HCOOH	25	0.7		−9.1	134	
332		HCOOH	25	0.7		−13.1	134	
333	$\mathrm{PhCH_2CH_2CHMeOTs + HCOOH \rightarrow PhCH_2CH_2CHMeOCOH + HOTs}$	HCOOH	25	1	4	−9.8	134	
334	$\mathrm{PhCH_2CH_2CHEtOTs + HCOOH \rightarrow PhCH_2CH_2CHEtOCOH + HOTs}$	HCOOH	25	0.7	4	−8.5	134	
335		Aq *i*-PrOH	40	2	5	−21.0[j]	135	H_2O 2 v%
336		Aq *i*-PrOH	25	4	5	−5.4	135	
337		Aq *i*-PrOH	16	3	4	−1.1	135	
338	$\mathrm{EtCl + MeOH \rightarrow EtOMe + HCl}$	MeOH	60	0.9	2	−32	135	
339	*t*-BuCl + MeOH → *t*-BuOMe + HCl	MeOH	25	3	4	−31	135	
340		MeOH	50	1.5	3	−33	135	
341		MeOH	25	2	5	−25.4	136	
342		MeOH	30	2	5	−25.84	137	
343		MeOH	40			−26.7	136	
344	*t*-BuBr + MeOH → *t*-BuOMe + HBr	MeOH	30	1	5	−25.2	138	$\Delta V = -17.6$ at 20 °C
345	*t*-BuBr + EtOH → *t*-BuOEt + HBr	EtOH	50	1	5	−20.2	138	$\Delta V = -15.3$ at 20 °C
346	*t*-BuBr + H_2O → *t*-BuOH + HBr	Aq *N*-Me-2-pyrrolidone	40	1	5	−20.6	138	$\Delta H = -13.8$ at 20 °C; H_2O 10 w%
347		Aq Me_2CO	50	1	5	−41.7	138	H_2O 5 w%
348		Aq Me_2CO	50	1	5	−23.9	138	H_2O 10 w%
349	*t*-BuBr → $\mathrm{Me_2C{=}CH_2}$ + HBr	*N*-Me-2-pyrrolidone	60	2	6	−20.7	138	$\Delta V = -9.2$ at 20 °C
350		DMF	60	1	5	−25.0	138	$\Delta V = -12.2$ at 20 °C
351	$\mathrm{MeOTs + HCOOH \rightarrow MeOCOH + HOTs}$	HCOOH	45	0.7	4	−13.4	139	
352	*i*-PrOTs + HCOOH → *i*-PrOCOH + HOTs	HCOOH	45	0.7	5	−15.6	139	

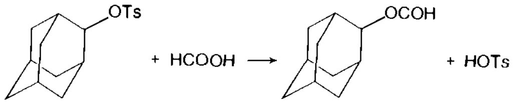
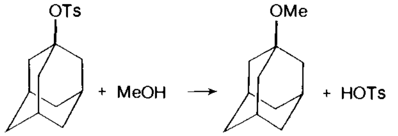
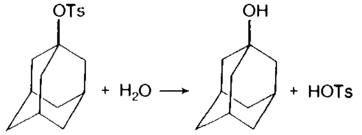
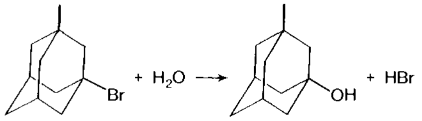
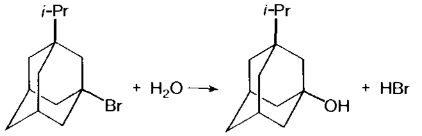
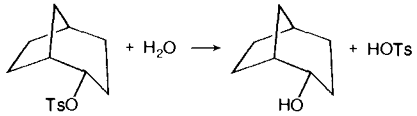
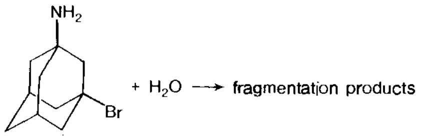
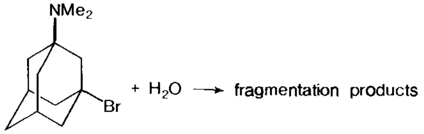
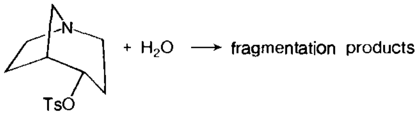
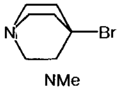
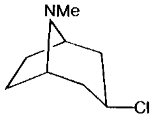
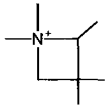
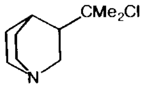
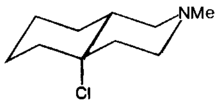
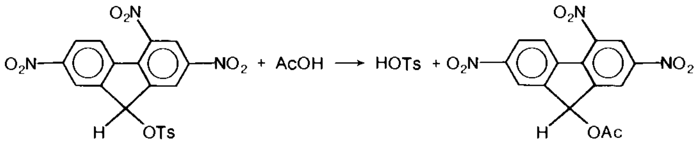
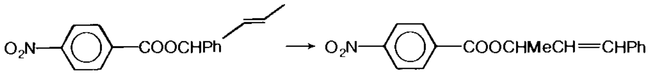
353		HCOOH	25	1	5	−6.9	139	
354	MeOTs + MeOH → Me_2O + HOTs	MeOH	40	0.7	5	−18.2	139	
355	*i*-PrOTs + MeOH → *i*-PrOMe + HOTs	MeOH	40	0.7	5	−20.9	139	
356		MeOH	25	0.5	5	−11.8	139	
357	MeOTs + H_2O → MeOH + HOTs	Aq Me_2CO	40	0.7	5	−14.2	139	H_2O 15 v%
358	*i*-PrOTs + H_2O → *i*-PrOH + HOTs	Aq Me_2CO	40	0.7	5	−16.7	139	H_2O 15 v%
359		Aq Me_2CO	25	0.7	5	−9.0	139	H_2O 15 v%
360		Aq EtOH	50	0.8	9	−21.11	140	H_2O 20 v%
361		Aq EtOH	50	0.8	8	−20.32	140	H_2O 20 v%
362	$Me_2CHCH_2CH_2CMe_2Cl$ + H_2O → S_N1 and E1 products	Aq EtOH	39.3	0.9	8	−23.77	140	H_2O 20 v%
363	$Me_2CHCMe_2CH_2CMe_2Cl$ + H_2O → S_N1 and E1 products	Aq EtOH	10			−23.63	140	H_2O 20 v%
364		Aq EtOH	60			−21.83	140	H_2O 20 v%
365		Aq EtOH	49.6	0.7	8	−16.84	140	H_2O 20 v%
366		Aq EtOH	21.3	0.7	8	−10.45	140	H_2O 20 v%
367		Aq EtOH	12.4			−7.43	140	H_2O 20 v%

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^{*}, cm^3/mol	Ref	Remarks
368	 + H_2O → fragmentation products	Aq EtOH	49.6	0.9	8	−14.39	140	H_2O 20 v%
369	 + H_2O → fragmentation products	Aq EtOH	49.6	0.9	8	−17.36	140	H_2O 20 v%
370	$Me_2NCH_2CH_2CMe_2Cl$ + H_2O → fragmentation, S_N1, and E1 products	Aq EtOH	39.3	0.9	9	−18.19	140	H_2O 20 v%
371	$Me_2NCH_2CMe_2CH(Me)Cl$ + H_2O →  and fragmentation products	Aq EtOH	49.6	0.9	8	−18.02	140	H_2O 20 v%
372	$Me_2NCH_2CMe_2CMe_2Cl + H_2O$ → fragmentation and elimination products	Aq EtOH	2.2			−8.05	140	H_2O 20 v%
373	 + H_2O → fragmentation, S_N1, and E1 products	Aq EtOH	15			−16.34	140	H_2O 20 v%
374		Aq EtOH	25			−17.11	140	H_2O 20 v%
375		Aq EtOH	35			−17.92	140	H_2O 20 v%
376	 + H_2O → fragmentation and E1 products	Aq EtOH	65.5			−27.10	140	H_2O 20 v%
377		AcOH	55.2	1.4	3	−27.2	142	
378		AcOH	55.2	1.4	3	−32.6	142	Via 1:1 complex with 9-methyl-anthracene
379		Aq Me_2CO	26.4			−14	143	H_2O 25 w%
380	$Ph_2CHSCN + H_2O$ → $Ph_2CHOH + HSCN$	Aq Me_2CO	24			−16	143	H_2O 5 w%
381	Ph_2CHSCN → Ph_2CHNCS	Aq Me_2CO	24			−12	143	H_2O 5 w%
382		THF	113.5			−22	143	
383		PhH	116			−21	143	
384		MeCOEt	73			−18	143	
385	t-$BuS^+Me_2 + H_2O$ → t-$BuOH + Me_2S + H^+$	H_2O	60	2.8	6	+9.9	144	
386		Aq EtOH	60	2.7	7	+13.1	144	H_2O 90 mol%
387		Aq EtOH	60	2.7	6	+15.6	144	H_2O 80 mol%
388		Aq EtOH	60	2.7	6	+15.2	144	H_2O 70 mol%
389		Aq EtOH	60	2.7	6	+13.4	144	H_2O 60 mol%
390								

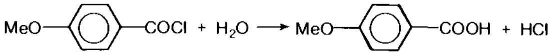
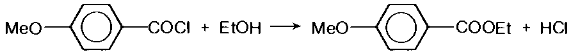
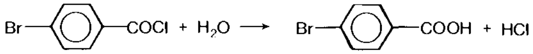
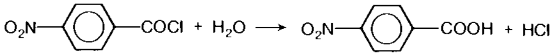
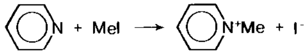
		Aq EtOH	60	2.1	6	+15.0	144	H_2O 50 mol%
391	$PhCOCl + H_2O \rightarrow PhCOOH + HCl$	Aq THF	20	1	5	−33.1	145	H_2O 2.2 w%
392		Aq THF	20	1	5	−31.0	145	H_2O 6.1 w%
393		Aq THF	20	1	5	−37.4	145	H_2O 15.8 w%
394		Aq THF	20	1	5	−38.4	145	H_2O 19.4 w%
395		Aq THF	20	1	5	−41.0	145	H_2O 29.7 w%
396		Aq *p*-dioxane	25	1	5	−20.8	119	H_2O 4.3 w%
397		Aq *p*-dioxane	25	1	5	−23.0	119	H_2O 7.0 w%
398		Aq *p*-dioxane	25	1	5	−27.0	119	H_2O 9.8 w%
399		Aq *p*-dioxane	25	1	5	−27.4	119	H_2O 14.5 w%
400		Aq *p*-dioxane	25	1	5	−24.7	119	H_2O 18.8 w%
401		Aq *p*-dioxane	25	1	5	−24.8	119	H_2O 22.8 w%
402		Aq *p*-dioxane	25	0.5	5	−28.0	119	H_2O 27.7 w%
403		Aq *p*-dioxane	25	0.5	5	−31.4	119	H_2O 29.3 w%
404	$PhCOCl + EtOH \rightarrow PhCOOEt + HCl$	EtOH	0	1	7	−29.1	146	
405		Aq THF	20	1	5	−27.5	145	H_2O 2.2 w%
406		Aq THF	20	1	5	−25.3	145	H_2O 5.7 w%
407		Aq THF	20	1	5	−23.6	145	H_2O 15.8 w%
408		Aq THF	20	1	5	−28.1	145	H_2O 19.4 w%
409		Aq THF	20	0.5	4	−31.2	145	H_2O 29.7 w%
410		EtOH	0	1.5	7	−20.1	146	
411		Aq THF	20	1	5	−33.8	145	H_2O 2.2 w%
412		Aq THF	20	1	5	−28.3	145	H_2O 6.1 w%
413		Aq THF	20	0.5	4	−43.0	145	H_2O 2.2 w%
414	$MeSO_2Cl + H_2O \rightarrow MeSO_3H + HCl$	H_2O	0.5	1.7	6	−9.58	117	
415		H_2O	5	2.1	6	−9.6	27	
416		H_2O	5.1	2	6	−10.7	147	
417		H_2O	11.7	1.7		−9.7	147	
418		H_2O	13	1.7	6	−9.43	117	
419		H_2O	18.7	2		−14.9	147	
420		H_2O	21	2.1	7	−10.2	27	
421		H_2O	24.9	2	5	−13.4	147	
422	$MeSO_2Cl + D_2O \rightarrow MeSO_3D + DCl$	D_2O	5	2.1	7	−9.67	117	
423		D_2O	5.1	1.6	5	−10.5	147	
424		D_2O	8.2	2.1	6	−9.39	117	
425		D_2O	11.5	2.1	7	−9.25	117	
426		D_2O	11.7	1.9		−10.6	147	
427		D_2O	16.2	2.1	6	−9.12	117	
428		D_2O	18.3	1.8		−11.2	147	
429		D_2O	21	2.1	7	−9.43	117	
430		D_2O	24.9	1.9	5	−14.3	147	
431		D_2O	26	1.4	5	−9.60	117	
432	$MeSO_2Cl + H_2O \rightarrow MeSO_3H + HCl$	Aq *p*-dioxane	24.9	1		−30.0	147	H_2O 57.4 mol%
433		Aq *p*-dioxane	24.9	2		−19.2	147	H_2O 84.6 mol%
434								

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
		Aq *p*-dioxane	24.9	2		−12.2	147	H_2O 91.6 mol%
435		Aq *p*-dioxane	24.9	1		−13.6	147	H_2O 95.1 mol%
436	$Et_3N + EtI \rightarrow Et_4N^+ + I^-$	C_6H_{14}	50	2	7	−58.2	149	
437		PhH	50	1.5	5	−50.2	149	
438		MeOH	50	2	7	−38.0	149	
439		PhCl	50	2	7	−45.1	149	
440		Me_2CO	50	2	7	−53.8	149	
441		$PhNO_2$	50	2	7	−30.3	149	
442		MeCN	25	1.5	6	−32.1	150	
443		MeOH	25			−32.0	150	
444		$MeNO_2$	25			−33.8	150	
445		PhH	25	0.9	4	−43.5	150	
446		$PhNO_2$	25	0.9		−30.0	150	
447		*p*-Xylene	45	1.5	6	−49.3	151	
448		*p*-dioxane	45			−40.5	151	
449		PhBr	25			−35.8	151	
450		PhCl	25			−37.8	151	
451		Me_2CO	20.2	2.9	9	−48.7	28	
452		Me_2CO	30	2.9	9	−50.4	28	
453		Me_2CO	40	2.9	9	−52.4	28	
454		Me_2CO	50	2.9	9	−53.8	28	
455		MeOH	30			-22^h	152	
456		MeOH	40			-23^h	152	
457		MeOH	50			-24^h	152	
458		MeOH	60			-25^h	152	
459		MeOH	70			-27^h	152	
460	$Et_3N + MeI \rightarrow Et_3N^+Me + I^-$	C_6H_{14}	50	2	7	−54.3	153	
461		PhH	50	1.5	6	−44.1	153	
462		Me_2CO	20	1.5	6	−43.3	153	
463	$Et_3N + BuI \rightarrow Et_3N^+Bu + I^-$	PhH	50	1.5	6	−56.5	153	
464		Me_2CO	50	2	7	−55.6	153	
465		$PhNO_2$	50	2	7	−33.8	153	
466		PhH	30	0.8	5	−32.0	154	
467		PhH	40	1	5	−34.2	154	
468		PhH	50	1	5	−35.6	154	
469		PhH	60	1	5	−38.0	154	
470		EtOH	30	1	5	−27.3	154	
470		EtOH	40	1	5	−29.7	154	
472		EtOH	50	1	5	−31.5	154	
473		EtOH	60	1	5	−34.5	154	
474		EtOH–PhH	50	1	5	−32.9	154	EtOH 10 v%
475		EtOH–PhH	50	1	5	−32.0	154	EtOH 25 v%
476		EtOH–PhH	30	1	5	−27.7	154	EtOH 50 v%
477		EtOH–PhH	50	1	5	−29.3	154	EtOH 50 v%
478		EtOH–PhH	50	1	5	−28.6	154	EtOH 60 v%
479		EtOH–PhH	50	1	5	−29.7	154	EtOH 75 v%

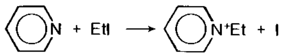
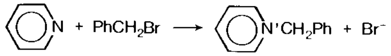
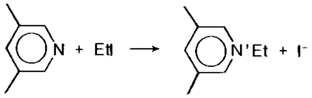
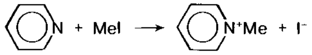
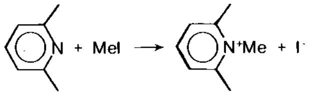
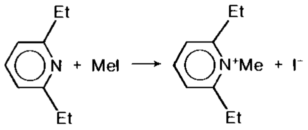
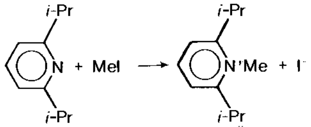
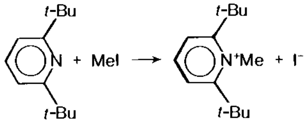
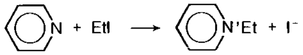
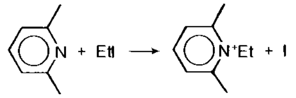
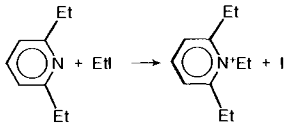
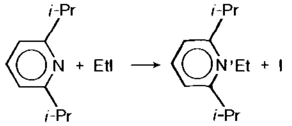
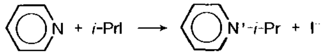
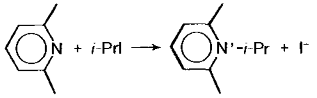
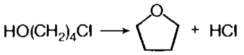
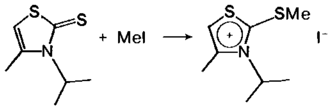
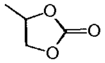
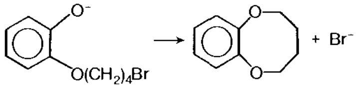
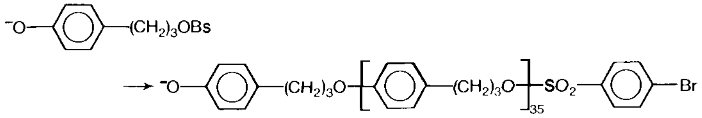
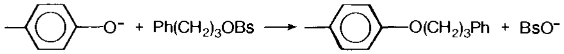
480		PhH	50	1.5	6	−39.8	153	
481		$PhNO_2$	50	2	7	−25.0	153	
482		PhMe	30	1.5	6	−39.1	155	
483		PhH	30	1.5	6	−35.3	155	
484		PhCl	30	1.5	6	−29.1	155	
485		PhBr	30	1.5	6	−24.9	155	
486		$PhNO_2$	30	1.5	6	−23.7	155	
487		Me_2CO	30	1.5	6	−34.9	155	
488		THF	30	1.5	6	−32.3	155	
489		CH_2ClCH_2Cl	30	1.5	6	−25.4	155	
490		*i*-PrOH	30	1.5	6	−20.4	155	
491		MeOH	30	1.5	6	−27.2	155	
492		MeCN	30	1.5	6	−29.2	155	
493		PhH	50	1.4	4	−40.1	156	
494		PhH–$PhNO_2$	50	1.9	5	−38.8	156	PhH 80 mol%
495		PhH–$PhNO_2$	50	1.9	5	−35.6	156	PhH 60 mol%
496		PhH–$PhNO_2$	50	1.9	5	−32.0	156	PhH 40 mol%
497		PhH–$PhNO_2$	50	1.9	5	−25.9	156	PhH 20 mol%
498		$PhNO_2$	50	1.9	5	−22.1	156	
499		Me_2CO	25	5.5	6	−21.9	157	
500		Me_2CO	25	5.5	6	−24.4	157	
501		Me_2CO	25	5.5	6	−27.3	157	
502		Me_2CO	25	5.5	6	−30.2	157	
503		Me_2CO	56	5.5	2	<−50	$157^{k,l}$	
504		Me_2CO	25	5.5	6	−23.3	157	
505		Me_2CO	25	5.5	6	−23.9	157	

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
506		Me_2CO	25	5.5	6	−28.3	157	
507		Me_2CO	25	5.5	2	−35	157^l	
508		Me_2CO	25	5.5	6	−26.5	157	
509		Me_2CO	25	5.5	6	−28.2	157	
510		H_2O	39.8	3	4	−5.8	125	
511		H_2O	49.7	3	4	−7.2	125	
512		H_2O	54.7	3	4	−7.8	125	
513		H_2O	59.6	3	4	−4.8^m	125	
514		Aq Me_2CO	25.1	3	6	−10.5	125	H_2O 50 v%
515		MeOH	25	3	3	−20	125	
516		MeOH	40	3	3	−20	125	
517		MeCN	30	1.5	6	−24.9	155	$\Delta V = -45.4$
518			30	1.5	6	−16.1	155	$\Delta V = -25.6$
519		MeOH	32.1	1.5	4	0	125	
520	$BuBr + EtO^- \rightarrow BuOEt + Br^-$	EtOH	45	1	3	−2.2^n	163	
521	$i\text{-}BuBr + EtO^- \rightarrow i\text{-}BuOEt + Br^-$	EtOH	45	1	3	−1.7^n	163	
522	$EtBr + EtO^- \rightarrow Et_2O + Br^-$	EtOH	45	1	3	−2.7^n	164	
523		i-PrOH	35	4	6	−6.7	165	
524		i-PrOH	35	4	6	−7.5	165	

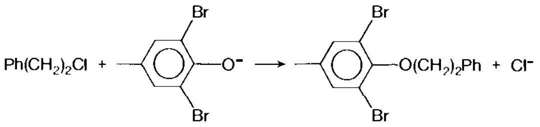
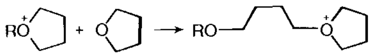
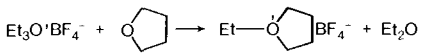
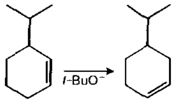
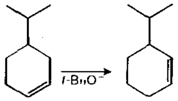
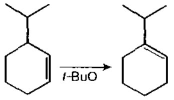
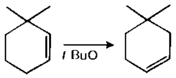
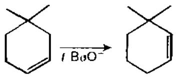
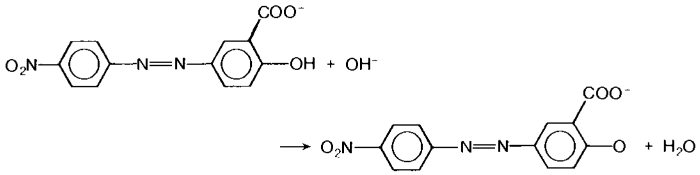
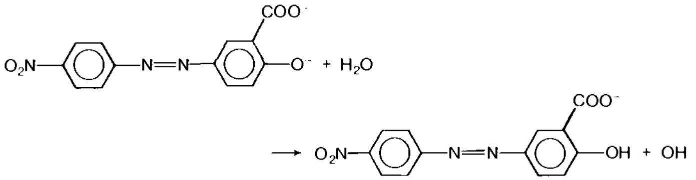
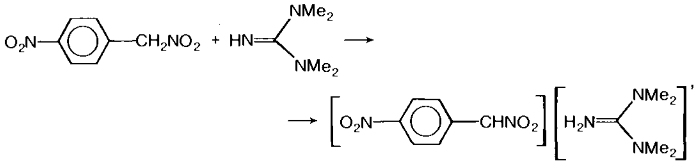
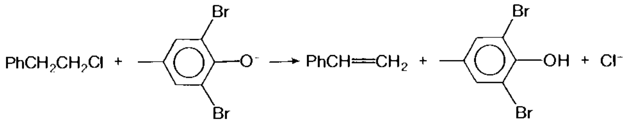
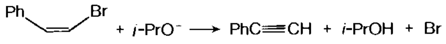
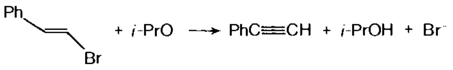
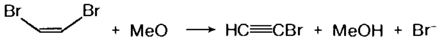
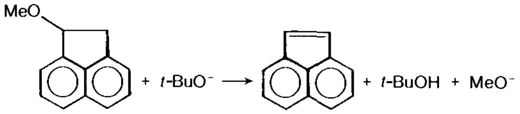
525		EtOH	65	1.4	5	−15	166	[ArO⁻] = 0.15 M
526	$PrCl + I^- \rightarrow PrI + Cl^-$	Me_2CO	30	2	3	−6	167	[KI] = 0.02 M
527	$PrBr + I^- \rightarrow PrI + Br^-$	Me_2CO	20	2	3	−7	167	[KI] = 0.02 M
528	*i*-PrBr + I^- → *i*-PrI + Br^-	Me_2CO	30	2	4	−11	167	[KI] = 0.02 M
529	$CH_2{=\!=}CHCH_2Cl + I^- \rightarrow CH_2{=\!=}CHCH_2I + Cl^-$	Me_2CO	25	2	3	−9	167	[KI] = 0.02 M
530	$PhCH_2Cl + I^- \rightarrow PhCH_2I + Cl^-$	Me_2CO	25	1	2	−9	167	[KI] = 0.02 M
531	$PrI + Cl^- \rightarrow PrCl + I^-$	Me_2CO	25	2	4	−22	167	[LiCl] = 0.03 M
532	*i*-PrI + Cl^- → *i*-PrCl + I^-	Me_2CO	25	2	4	−27	167	[LiCl] = 0.03 M
533	$PrBr + Cl^- \rightarrow PrCl + Br^-$	Me_2CO	25	2	4	−25	167	[LiCl] = 0.03 M
534		CH_2Cl_2	0	2	3	−10.5	168	*m*; BF_4^- anion
535		CH_2Cl_2	0	2	3	−5.0	168	*m*
536		*t*-BuOH–DMSO	78.6	2.5	6	−22.5	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
537		*t*-BuOH–DMSO	93.2	1.5	4	−20.5	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
538		*t*-BuOH–DMSO	78.6	2.5	5	−22.5	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
539		*t*-BuOH–DMSO	93.2	2	5	−18	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
540		*t*-BuOH–DMSO	78.6	2.5	6	−24	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
541		*t*-BuOH–DMSO	93.2	2	5	−25	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
542		*t*-BuOH–DMSO	78.4	3	6	−20.2	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
543		*t*-BuOH–DMSO	78.4	3	6	−19.2	169	BuOH 0.965 w% [BuO⁻] = 0.9 M
544	$HCO_2^- + D_2O \rightarrow DCO_2^- + HDO$	D_2O	180	8	4	−2.8	170	
545		D_2O	190	8	4	−2.6	170	
546		D_2O	200	8	3	−2.0	170	

TABLE II (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm^3/mol	Ref	Remarks
547	$CH_3CO_2^- + D_2O \rightarrow CH_2DCOO^- + HDO$	D_2O	160	8	4	−10.5	170	
548		H_2O	10.1	1.5	4	+10.3	171	$\Delta V = +13.3$; T-jump
549		H_2O	10.1	1.5	4	−5.1	171	T-jump
550		Mesitylene	30	1.7	6	−13.2	172	$\Delta V = -15.9$
551		PhMe	30	1.7	6	−17.8	172	$\Delta V = -25.5$
552		*o*-Xylene	30	1.7	6	−14.6	172	$\Delta V = -21.3$
553		PhOMe	30	1.3	5	−16.3	172	$\Delta V = -29.3$
554		PhCl	30	1.7	6	−13.0	172	$\Delta V = -21.9$
555		EtOH	65	1.4	5	−12	166	$[ArO^-] = 0.15$ M
556		*i*-PrOH	26	1.4	6	−6	166	$[PrO^-] = 0.182$ M
557		*i*-PrOH	118	1.4	6	−5	166	$[PrO^-] = 0.147$ M
558		MeOH	37	1.1	5	−5	166	$[MeO^-] = 0.106$ M
559	$PhSO_2CH_2CH_2Cl + AcO^-$ $\rightarrow PhSO_2CH{=}CH_2 + AcOH + Cl^-$	EtOH	50	1.4	4	−1	166	$[AcO^-] = 0.05$ M
560		*t*-BuOH	82	1.4	4	+3	166	$[BuO^-] = 0.314$ M

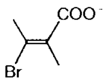
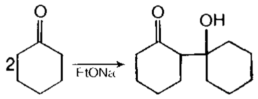
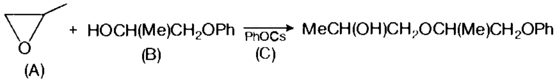
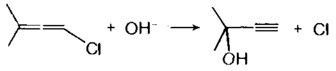
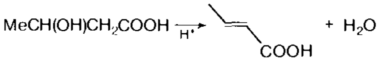
561		t-BuOH	57	1.4	2	+15	166	$[BuO^-] = 0.405$ M In the presence of crown ether
562	$BuBr + EtO^- \rightarrow C_4H_8 + EtOH + Br^-$	EtOH	45	1	3	$+0.9^{n}$	163	
563	$i\text{-}BuBr + EtO^- \rightarrow C_4H_8 + EtOH + Br^-$	EtOH	45	1	3	$+3.5^{n}$	163	
564	$MeCOCH_2C(OH)Me_2 \xrightarrow[OH^-]{} 2Me_2CO$	H_2O	15	1.4	3	+6	166	
565		H_2O	25	1.4	4	+6	166	
566		H_2O	30	1.5	5	−6.6	173	
567		H_2O	35	1.5	4	−1.6	173	
568		H_2O	40	1.5	4	+3.8	173	
569		Aq EtOH	30	1.5	4	−9.0	173	H_2O 90 mol%
570		Aq EtOH	30	1.5	4	−6.8	173	H_2O 80 mol%
571		Aq EtOH	30	1.5	4	−6.9	173	H_3O 76 mol%
572		Aq EtOH	30	1.5	4	−2.3	173	H_2O 58 mol%
573		Aq EtOH	30	1.5	4	−0.8	173	H_2O 49 mol%
574		Aq EtOH	30	1.5	4	+1.9	173	H_2O 37 mol%
575		Aq EtOH	30	1.5	4	+3.4	173	H_2O 24 mol%
576		Aq EtOH	30	1.5	4	+5.7	173	H_2O 2 mol%
577		Aq EtOH	35	1.5	4	−3.6	173	H_2O 90 mol%
578		Aq EtOH	35	1	3	−3.5	173	H_2O 80 mol%
579		Aq EtOH	40	1.5	4	+3.0	173	H_2O 90 mol%
580		Aq EtOH	40	1.5	4	+3.5	173	H_2O 80 mol%
581		Aq EtOH	40	1.5	4	+7.7	173	H_2O 37 mol%
582		Aq MeOH	30	1.5	4	−0.8	173	H_2O 90 mol%
583		Aq MeOH	30	1.5	4	+3.1	173	H_2O 80 mol%
584		Aq MeOH	30	1.5	4	+8.0	173	H_2O 60 mol%
585	$PhCH(OH)CN \xrightarrow[AcO^-]{} PhCHO + HCN$	H_2O	36.5	1.3	5	$+12^{o}$	166	$[AcOH] = 0.1$ M $[AcO^-] = 0.1$ M $\Delta V = +14$
586	 $\xrightarrow[OH^-]{} MeC{\equiv}CMe + CO_2 + Br^-$	H_2O	65	4.1	5	+17.7	174	
587	$ClCH_2CONHNH_2 \xrightarrow[OH^-]{} N_2 + N_2H_4 + Cl^- + AcO^- + AcNHNH_2$	H_2O	25	4	6	-5^{o}	175	
588	$2i\text{-}PrCHO \xrightarrow[OH^-]{} i\text{-}PrCH(OH)CMe_2CHO$	Aq MeOH	40	4.9	4	−6.2	176	$[KOH] = 0.25$ M H_2O 17%
589		Aq MeOH	40	4.9	4	−3.0	176	$[KOH] = 0.25$ M $[H_2O] = 5.56$ M
590		Aq MeOH	40	4.9	4	−6.1	176	$[KOH] = 0.25$ M $[H_2O] = 8.34$ M
591		Aq MeOH	40	4.9	4	−8.5	176	$[KOH] = 0.25$ M $[H_2O] = 13.9$ M
592	$2PrCHO \xrightarrow[OH^-]{} PrCH(OH)CH(Et)CHO$	MeOH	50	4.9	4	+4.9	176	$[KOH] = 0.01$ M
593		MeOH	40	1	2	+7.1	176	$[KOH] = 0.01$ M
594		Aq MeOH	40	1	2	+6.9	176	$[KOH] = 0.01$ M

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV*, cm³/mol	Ref	Remarks
595		Aq MeOH	40	1	2	+4.8	176	H_2O 21 mol% [KOH] = 0.01 M H_2O 51 mol%
596		EtOH	0.7	2	5	−7.4	177	[EtONa] = 0.04 M ΔV = −15.2
597		EtOH	9.8	2	5	−7.8	177	[EtONa] = 0.04 M ΔV = −13.7
598	$i\text{-}Bu_2CO \xrightarrow[BuONa]{} i\text{-}Bu_2CHOH$	BuOH	99	1.2	4	−12.9	178	[BuONa] = 1.8 m
599		BuOH	100.3	1.5	4	−12.6	178	[BuONa] = 2.0 m
600		BuOH	105.4	1	2	−10.0	178	[BuONa] = 2.1 m
601	$AcOEt + OH^- \rightarrow AcO^- + EtOH$	H_2O	10	2.8	6	−7.6	179	
602		H_2O	20	8.1	3	−5.6	180	
603		H_2O	30	8.1	3	−6.4	180	
604		Aq Me_2CO	10	3	6	−16.8	179	H_2O 57.2 w%
605		Aq Me_2CO	10	3	7	−13.1	179	H_2O 69 w%
606		Aq Me_2CO	10	3	7	−8.9	179	H_2O 79.6 w%
607	$AcO\text{-}i\text{-}Pr + OH^- \rightarrow AcO^- + i\text{-}PrOH$	H_2O	20	8.1	4	−6.6	180	
608	$AcOBu + OH^- \rightarrow AcO^- + BuOH$	H_2O	20	8.1	4	−5.6	180	
609	$AcO\text{-}i\text{-}Bu + OH^- \rightarrow AcO^- + i\text{-}BuOH$	H_2O	20	8.1	4	−6.3	180	
610	$AcOC_5H_{11} + OH^- \rightarrow AcO^- + C_5H_{11}OH$	H_2O	20	8.1	5	−5.8	180	
611	$Me_2C{=}CHAc + PhSH \xrightarrow[MeO^-]{} Me_2C(SPh)CH_2Ac$	MeOH	30	1.4	5	−20	181	ΔV = −22 [MeO⁻] = 0.025 M
612	$Me_2C{=}CHAc + PhSH \xrightarrow[OH^-]{} Me_2C(SPh)CH_2Ac$	Aq EtOH	30	1.1	2	−19	181	ΔV = −22 H_2O 45 v% [OH⁻] = 0.025 M
613		Neat	70	1	4	−53.0	182	A:B = 1.13:1 B:C = 1000:5
614		Neat	70	1	3	−55.1	182	A:B = 5:1 B:C = 1000:40
615		Neat	70	1	3	−58.5	182	A:B = 5:1 B:C = 1000:20
616		Aq EtOH	25	6	7	+5	183	H_2O 20 v%
617	$MeOCMe_2CH_2Ac \xrightarrow[H^+]{} Me_2C{=}CHAc + MeOH$	MeOH	30	1.1	2	−13	181	[H_2SO_4] = 0.05 M
618		H_2O	83	1.4	3	−15.0	185	
619		H_2O	88.4	2.1	5	−14.6	185	
620	$CH_2(OH)CH_2COOH \xrightarrow[H^+]{} CH_2{=}CHCOOH + H_2O$	H_2O	80	1.4	4	−9.6	186	

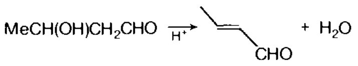
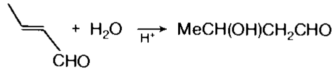
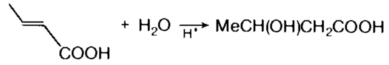
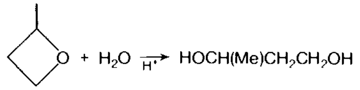
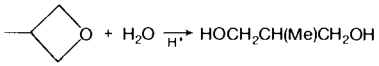
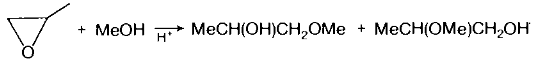
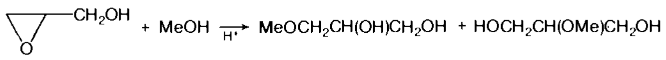
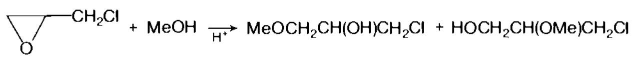
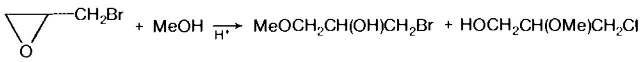
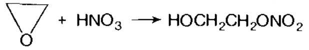
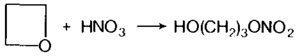
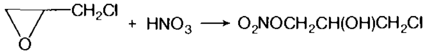
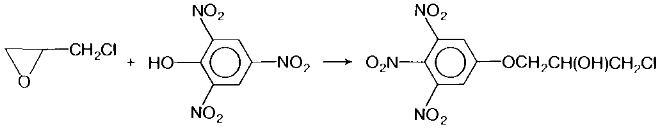
621		H_2O	85	1.7	5	−10.4	186	
622		H_2O	90	1.4	5	−11.1	186	
623		H_2O	30	2.1	4	−5.8	187	
624		H_2O	35	2.1	5	−5.7	187	
625	$MeCH{=}CH_2 + H_2O \xrightarrow[H^+]{} i\text{-}PrOH$	H_2O	180	4.9	6	−21.9	188	$p \geq 0.3$ kbars
626	$MeCH{=}CH_2 + H_2O \rightarrow i\text{-}PrOH$	H_2O	180	4.9	6	−30.7	188	$p \geq 0.3$ kbars
627	$CH_2{=}CHCOOH + H_2O \xrightarrow[H^+]{} HOCH_2CH_2COOH$	H_2O	80	1.4	4	−14.0	186	
628		H_2O	85	1.7	5	−14.4	186	
629		H_2O	90	1.4	5	−15.8	186	
630		H_2O	30	2.1	4	−19.8	187	
631		H_2O	35	2.1	5	−19.6	187	
632		H_2O	83	1.4	3	−17.9	185	
633		H_2O	88.4	2.1	5	−18.1	185	
634	$Me_2C{=}CHAc + H_2O \xrightarrow[H^+]{} Me_2C(OH)CH_2Ac$	H_2O	30	1.4	5	−14.5	181	$\Delta V = -9$ [HCl] = 0.49 M
635	$Me_2C{=}CHAc + MeOH \xrightarrow[H^+]{} Me_2C(OMe)CH_2Ac$	MeOH	30	1.4	5	−23	181	$\Delta V = -11$ $[H_2SO_4] = 0.05$ M
636	$Me_2C{=}CHAc + NH_3 \rightarrow Me_2C(NH_2)CH_2Ac$	H_2O	30	1.4	5	−14	181	$\Delta V = -9$
637		MeOH	30	1.4	5	−22	181	$\Delta V = -9$
638		H_2O	25	2.5	7	−11.5	189	
639		H_2O	40	2.5	7	−9.9	189	
640		H_2O	25	2.5	7	−11.3	189	
641		H_2O	40	2.5	7	−9.7	189	
642		MeOH	25	1.5	4	−9.4	190	$[H^+] \simeq 5 \times 10^{-4}$ M
643		MeOH	25	2.5	6	−14.7	190	$[H^+] \simeq 5 \times 10^{-4}$ M
644		MeOH	25	2.5	6	−9.1	190	$[H^+] \simeq 5 \times 10^{-4}$ M
645		MeOH	25	2.5	6	−10.7	190	$[H^+] \simeq 5 \times 10^{-4}$ M

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
646		*N*-Me-2-pyrrolidone	25	2	5	−17.3	191	$[HNO_3] = 0.05$ M
647		*N*-Me-2-pyrrolidone	25	2	5	−14.2	191	$[HNO_3] = 0.10$ M
648		*N*-Me-2-pyrrolidone	25	2	5	−15.0	191	$[HNO_3] = 0.10$ M
649		*N*-Me-2-pyrrolidone	25	2	5	−15.0	191	[Pic] = 0.20 M
650	$MeCHO + 2EtOH \rightarrow MeCH(OEt)_2 + H_2O$	Neat	60	3	3	−6.9	192	EtOH 67 mol% $P \geq 1$ kbar
651		Neat	50	5	3	−6.3	192	EtOH 67 mol% $P \geq 1$ kbar
652		Neat	40	5	3	−5.6	192	EtOH 67 mol% $P \geq 1$ kbar
653		Neat	40			−7.0	192	EtOH 80 mol% $P \geq 1$ kbar
654		Neat	40			−6.0	192	[EtOH] = 13 M [MeCHO] = 4.34 M $P \geq 1$ kbar
655		$MeCHO–EtOH–H_2O$	40			−5.4	192	[EtOH] = 12.7 M [MeCHO] = 4.24 M $[H_2O] = 1.12$ M $P \geq 1$ kbar
656		$MeCHO–EtOH–H_2O$	40			−6.0	192	[EtOH] = 12.7 M [MeCHO] = 4.22 M $[H_2O] = 1.44$ M $P \geq 1$ kbar
657		$MeCHO–EtOH–H_2O$	40			−5.9	192	[EtOH] = 12.2 M [MeCHO] = 4.08 M $[H_2O] = 3.36$ M $P \geq 1$ kbar
658		$MeCHO–EtOH–H_2O$	40			−6.9	192	[EtOH] = 9.96 M [MeCHO] = 3.32 M $[H_2O] = 13$ M $P \geq 1$ kbar
659		$MeCHO–EtOH–H_2O$	40			−7.1	192	[EtOH] = 9.69 M [MeCHO] = 3.23 M $[H_2O] = 14.3$ M $P \geq 1$ kbar

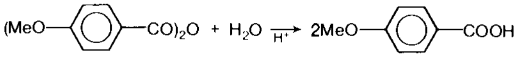
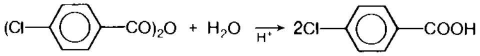
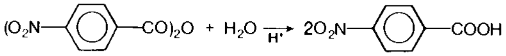
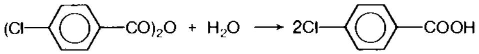
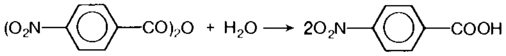
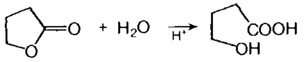
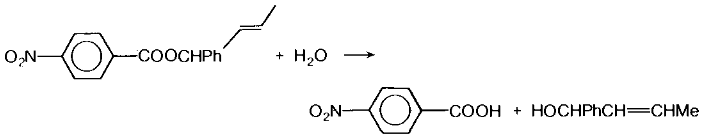
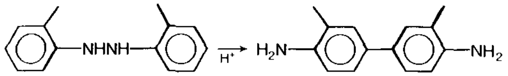
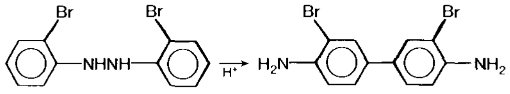
660	$EtCHO + 2EtOH \rightarrow EtCH(OEt)_2 + H_2O$	Neat	40			−9.9	192	EtOH 80 mol% $P \geq 1$ kbar
661	$PrCHO + 2EtOH \rightarrow PrCH(OEt)_2 + H_2O$	Neat	40			−10.5	192	EtOH 80 mol% $P \geq 1$ kbar
662		Aq *p*-dioxane	60	2	5	+7.5	193	H_2O 0.023 M
663		Aq *p*-dioxane	60	2	5	+7.5	193	H_2O 0.10 M
664		Aq *p*-dioxane	60	2	5	+4.8	193	H_2O 1.0 M
665		Aq *p*-dioxane	60	2	5	+0.6	193	H_2O 10.0 M
666	$(PhCO)_2O + H_2O \xrightarrow[H^+]{} 2PhCOOH$	Aq *p*-dioxane	60	2	5	+6.7	193	H_2O 0.017 M
667		Aq *p*-dioxane	60	2	5	+5.0	193	H_2O 0.107 M
668		Aq *p*-dioxane	60	2	5	−5.6	193	H_2O 1.07 M
669		Aq *p*-dioxane	60	2	5	−17.8	193	H_2O 10.0 M
670		Aq *p*-dioxane	60	2	5	−25.4	193	H_2O 27.6 M
671		Aq *p*-dioxane	60	2	5	+6.0	193	H_2O 0.020 M
672		Aq *p*-dioxane	60	2	5	+5.3	193	H_2O 0.100 M
673		Aq *p*-dioxane	60	2	5	−9.5	193	H_2O 1.00 M
674		Aq *p*-dioxane	60	2	5	−22.6	193	H_2O 5.00 M
675		Aq *p*-dioxane	60	2	5	+6.8	193	H_2O 0.024 M
676		Aq *p*-dioxane	60	2	5	−5.6	193	H_2O 0.10 M
677		Aq *p*-dioxane	60	2	5	−9.0	193	H_2O 1.00 M
678	$(PhCO)_2O + H_2O \rightarrow 2PhCOOH$	Aq *p*-dioxane	60	2	2	−13.3	193	H_2O 1.07 M
679		Aq *p*-dioxane	60	2	5	−21.1	193	H_2O 10.1 M
680		Aq *p*-dioxane	60	2	5	−26.6	193	H_2O 27.8 M
681		Aq *p*-dioxane	60	2	2	−11.1	193	H_2O 1.0 M
682		Aq *p*-dioxane	60	2	5	−17.6	193	H_2O 5.0 M
683		Aq *p*-dioxane	60	2	5	−9.3	193	H_2O 1.0 M
684	$(EtOCO)_2O + H_2O \rightarrow 2EtOCOOH$	H_2O	0	1.5	7	−14.7	194	
685		Aq Me_2CO	0	1	4	−18.9	194	H_2O 80 v%
686	$AcO\text{-}t\text{-}Bu + H_2O \xrightarrow[H^+]{} AcOH + t\text{-}BuOH$	H_2O	40	2	5	+0.4	195	
687		Aq *p*-dioxane	40	2	4	−5.7	195	H_2O 80 v%
688		Aq *p*-dioxane	40	2	5	−10.0	195	H_2O 70 v%
689		Aq *p*-dioxane	40	2	5	−9.9	195	H_2O 60 v%
690		Aq *p*-dioxane	40	2	5	−22.5	195	H_2O 40 v%
691		Aq *p*-dioxane	40	2	5	−16.0	195	H_2O 30 v%
692		Aq *p*-dioxane	40	2	5	−23.7	195	H_2O 20 v%
693	$AcOEt + H_2O \xrightarrow[H^+]{} AcOH + EtOH$	H_2O	39.9	1	5	−7.4	196	
694		Aq *p*-dioxane	39.9	1	5	-8^h	196	H_2O 90 v%
695		Aq *p*-dioxane	39.9	0.7	4	-9^h	196	H_2O 80 v%
696		Aq *p*-dioxane	39.9	0.7	4	-10^h	196	H_2O 70 v%
697		Aq *p*-dioxane	39.9	0.7	4	-11^h	196	H_2O 60 v%

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	$\Delta V^{\ddagger}$, cm^3/mol	Ref	Remarks
698		Aq p-dioxane	39.9	1	5	-14^h	196	H_2O 40 v%
699		Aq p-dioxane	39.9	1	5	-15^h	196	H_2O 30 v%
700		Aq p-dioxane	39.9	1	5	-15.9	196	H_2O 20 v%
701		H_2O	30	2	6	-9.6	197	
702		Aq Me_2CO	26.4			-14	143	H_2O 25 w%
703	$AcOCHPh_2 + H_2O \rightarrow AcOH + Ph_2CHOH$	Aq Me_2CO	96.2			-18	143	H_2O 25 w%
704	$AcOEt + H_2O \rightarrow AcOH + EtOH$	EtOH	80	8		-34.3	198	
705	$t\text{-}BuCOOEt + H_2O \rightarrow t\text{-}BuCOOH + EtOH$	EtOH	80	20	7	-22.3	198	
706	$AcNH\text{-}t\text{-}Bu + H_2O \xrightarrow[H^+]{} AcNH_2 + t\text{-}BuOH$	H_2O	80.2	1	5	-1.9	199	[HCl] = 0.2 M
707		H_2O	80.2	1	5	-5.5	199	[HCl] = 0.4 M
708		H_2O	80.2	1	5	-6.9	199	[HCl] = 0.6 M
709		H_2O	80.2	1	5	-9.2	199	[HCl] = 1 M
710	$(EtO)_2CH_2 + H_2O \xrightarrow[H^+]{} 2EtOH + HCHO$	H_2O	39.9	1	5	0.0	196	
711		Aq p-dioxane	39.9	1	5	-1^h	196	H_2O 90 v%
712		Aq p-dioxane	39.9	1	5	-2^h	196	H_2O 80 v%
713		Aq p-dioxane	39.9	1	5	-3^h	196	H_2O 70 v%
714		Aq p-dioxane	39.9	1	5	-4^h	196	H_2O 60 v%
715		Aq p-dioxane	39.9	1	5	-6^h	196	H_2O 50 v%
716		Aq p-dioxane	39.9	1	3	-6^h	196	H_2O 40 v%
717		Aq p-dioxane	39.9	1	5	-8.1	196	H_2O 20 v%
718	$Et_2O + H_2O \xrightarrow[H^+]{} 2EtOH$	H_2O	200	3	5	-10.0	200	
719	$Et_2O + H_2O \xrightarrow[H^+, I^-]{} 2EtOH$	H_2O	200	3	5	$+1.0$	200	[NaI] = 0.2 M
720	sucrose $+ H_2O \xrightarrow[H^+]{}$ glucose + fructose	H_2O	25	1.5	5	$+6.0$	60	
721		Aq EtOH	24.7	2.9	4	-2.5^p	201	H_2O 4 v%
722		Aq EtOH	24.7	2.9	4	-7.2^q	201	H_2O 4 v%
723		Aq EtOH	25	2.9	4	-10.7^p	202	H_2O 15 v%
724		Aq EtOH	25	2.9	4	-0.4^q	202	H_2O 15 v%
725		Aq EtOH	30	2.9	4	-10.0^p	202	H_2O 15 v%
726		Aq EtOH	30	2.9	4	-0.5^q	202	H_2O 15 v%
727		Aq EtOH	40	2.9	4	-9.1^p	202	H_2O 15 v%

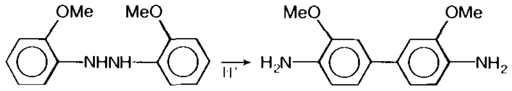
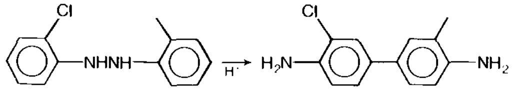
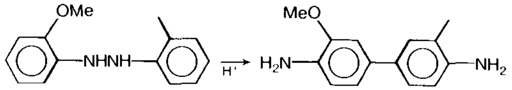
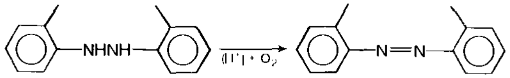
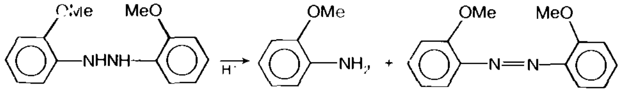
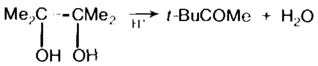
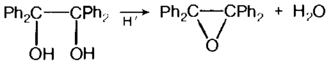
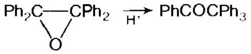
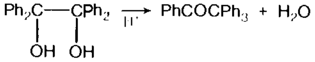
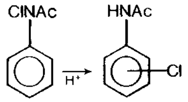
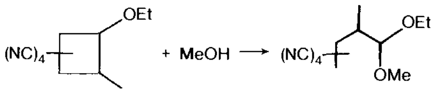
728		Aq EtOH	40	2.9	4	+0.2[q]	202	H_2O 15 v%
729		Aq EtOH	5	2	4	−12[p]	203	H_2O 15 v%
730		Aq EtOH	10	2	4	−12[p]	203	H_2O 15 v%
731		Aq EtOH	25	1.5	4	−6.8[p]	204	H_2O 15 v%
732		Aq EtOH	25	1.5	4	−3.2[q]	204	H_2O 15 v%
733		Aq EtOH	25	1.5	4	−8.5[p]	205	H_2O 15 v%
734		Aq EtOH	24.7	3	4	−40	201	H_2O 4 v%
735		Aq EtOH	24.7	3	4	−50	201	H_2O 4 v%, *p*
736		Aq EtOH	5	2	4	+5	203	H_2O 15 v%, *p*
737		Aq EtOH	10	2	4	+5	203	H_2O 15 v%, *p*
738	 $Me_2C(OH)-C(OH)Me_2 \xrightarrow[H^+]{} t\text{-}BuCOMe + H_2O$	H_2O	60	1.4	4	+8.4	206	HCl catalyzed
739		H_2O	65	1.4	4	+7.6	206	HCl catalyzed
740		H_2O	70	1.4	4	+6.8	206	HCl catalyzed
741		H_2O–H_2SO_4	25	1.4	5	+6.1	206	H_2O 52.5 w%
742		H_2O–H_2SO_4	25	1.4	5	+5.6	206	H_2O 44.2 w%
743		AcOH	35	0.5	3	+2.3	206	
744		AcOH	40	1	4	+2.1	206	Δ*V* = +19
745		AcOH	45	1	4	+1.9	206	
746		AcOH	35	0.5	3	−15.5	206	
747		AcOH	40	1	5	−17.6	206	Δ*V* = +1
748		AcOH	45	1	5	−18.6	206	
749		AcOH	35	0.5	3	−44	206	Direct rearrangement
750		AcOH	40	1	4	−34	206	Direct rearrangement Δ*V* = +20
751		AcOH	45	1	4	−28	206	Direct rearrangement

TABLE II (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
752		H_2O	15	2.1	3	+4.0	36	
753		H_2O	25	2.1	3	+5.3	36	
754		H_2O	35	2.1	3	+6.5	36	
755	$AcOH + EtOH \rightarrow AcOEt + H_2O$	EtOH	80	8		−32.6	198	Self-catalyzed
756	t-BuCOOH + EtOH → t-BuCOOEt + H_2O	EtOH	80	20	7	−26.2	198	Self-catalyzed
757	$Ph_3SnCH_2C{\equiv}CH \rightarrow Ph_3SnCH{=}C{=}CH_2$	$CHCl_3$–MeOH	37	1.2	8	−44	207	$CHCl_3$/MeOH = 8/2
758		C_5H_5N–PhMe	37	0.8	7	−32	207	C_5H_5N/PhMe = 16.7/83.3
759	i-PrBr + $Ag^+ + H_2O \rightarrow$ i-PrOH + AgBr + H^+	Aq EtOH	25	2	4	−16	167	H_2O 40 v%; [$AgNO_3$] = 0.013 M
760	$PhCH_2Cl + Hg^{2+} + H_2O \rightarrow PhCH_2OH + HgCl_2 + H^+$	Aq p-dioxane	25	1	3	−6	167	H_2O 25 v%; [$Hg(NO_3)_2$] = 0.01 M
761	$PrBr + Hg^{2+} + H_2O \rightarrow PrOH + HgBr_2 + H^+$	Aq p-dioxane	25	1	3	−8	167	H_2O 25 v%; [$Hg(NO_3)_2$] = 0.012 M
762		MeOH	25	2.1	6	−16.7	208	
763	$PhH + CH_2{=}CHCH_3 \xrightarrow[FeCl_3]{}$ i-PrPh	$PhNO_2$	50	2	7	0<[r]	34	[$FeCl_3$] = 6.2 × 10^{-3} M
764		$PhNO_2$	50	1	3	0<[r]	34	[$FeCl_3$] = 1.63 × 10^{-2} M
765	$PhCOOH + Ph_2CN_2 \rightarrow PhCOOCHPh_2 + N_2$	Bu_2O	17.1	1.1	6	−13.1	210	

[a] Abbreviations used in the table: AIBN, azobisisobutyronitrile; DBNO, di-*tert*-butyl nitroxide; DMSO, dimethyl sulfoxide; DPPH, diphenylpicrylhydrazyl; TCNE, tetracyanoethylene. [b] Cyclohexane 40 v%, tetramethylsilane 30 v%, dichloromethane-d_2 15 v%, and methylcyclohexane-d_{14}, 15 v%. [c] Calculated from the rates at 1 and 2000 atm. [d] At 500 atm, calculated from pressure and viscosity effects on k_c/k_d. [e] Calculated from the rates at 1 and 1000 or 1350 atm. [f] Rate constants up to 6.2 kbars are given in *AIChE J.*, **16**, 766 (1970). [g] Calculated from the rates at 1 and 500 atm. [h] Estimated from the figure. [i] The reaction goes through anchimerically assisted and unassisted processes. The estimated activation volumes (cm^3/mol) for each process follow with assisted, then unassisted value given: MeO, −7.3, −13.3; Me, −6.8, −13.4; H, −6.5, −13.2. [j] From the sum of anchimerically assisted and unassisted reaction rates. [k] Not a pure Menshutkin reaction.[158] [l] The reaction does not proceed at lower pressures. [m] Estimated by present authors. [n] Pressure effect on the dissociation of EtOK is taken into account in the calculation. [o] Corrected for pH changes under pressure. [p] First order in H^+. [q] Second order in H^+. [r] $\Delta V^* > 0$ above 0.5 kbar. [s] ΔV values in cm^3/mol throughout. [t] Dimethylacetamide 60 v%, tetramethylsilane 20 v%, and acetone-d_6, 20 v%.

decade most chemists active in the field had become used to bars and kbars; since virtually all data reviewed here were published in those units, we continue to use them here. The conversion is trivial: 1 kbar = 0.1 GPa (gigapascal).

II. Activation Volumes of Organic Reactions

A. The Data in Tabular Form

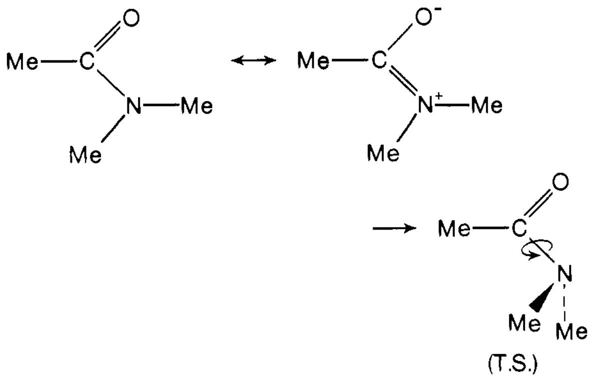
Comments on the information in Table II are in the following sections on the more important and interesting cases; some individual entries are skipped in the narrative if the mechanism is unknown, or if the information is of a routine nature.

B. Racemization and Related Reactions (Entries 1–13)

Brower[63] has found that the racemization of *tert*-butylsulfonium cation has a positive activation volume of 6.4 cm^3/mol, consistent with dissociation into and recombination of *tert*-butyl cation and the sulfide. Sulfoxides appear to racemize by simple inversion, with zero volume requirements. The exception is a benzyl sulfoxide; dissociation (homolysis) is indicated in that instance, though it seems likely that the high temperature (hence expanded solvent) contributes to the large value of $\Delta V_0^{\ddagger}$. Somewhat surprisingly, the allylic sulfoxide is almost indifferent to pressure; this was attributed to a concerted [2,3] sigmatropic shift, but with a transition state looser than is common in such reactions.

The biphenyl racemizations reported by Plieninger[64] are apparently subject to incredible accelerations by pressure; the volume decrease is virtually that of the entire molecule. Such a decrease is conceivable if the reaction involves ionization of the acid (in toluene, at 90 °C) as a necessary first step. On the other hand, that seems hardly likely since a solvated carboxylate group is surely not smaller than carboxyl. Close, known analogs of these reactions reviewed elsewhere[1] are known to be virtually pressure independent, and it seems desirable that these studies be repeated and the results confirmed.

The data obtained by Lüdemann[65] are a consequence of the advances in technology mentioned above. The rotation of the C–N bond in dimethylacetamide must surely involve loss of the resonance-induced dipole, and the pressure inhibition is reasonable on that basis (see eq 13). The inversion of cyclohexane involves no such change of dipole, and the activation volume is close to zero.



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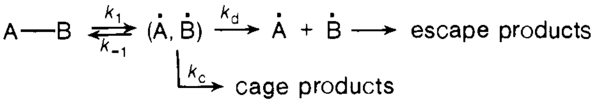
C. Homolysis and Related Reactions (Entries 14–56)

A great deal has been learned about homolytic bond scission under pressure in the past decade or so, principally through the work of Neuman. As he has pointed out in many papers and in his review,[12] the products through which we become aware that bond scission has occurred arise through several competing and successive steps, which may be symbolized as in eq 14. This scheme brought order to what is otherwise a bewildering variety of activation volumes in free radical decomposition reactions. The following assumptions are made: (a) that the transition state in the bond fission process is early, at least so far as the geometry of the breaking bond is concerned, and hence that the activation volume is small (of the order of 4–5 cm^3/mol); (b) that the activation volume for diffusion is relatively large (of the order of 10 cm^3/mol); (c) that diffusion from the cage is irreversible; (d) that the first step may have a polar component, i.e., that the approach to the transition state may be characterized by a change in dipole moment; (e) that in molecules capable of two or more bond scissions, the resulting fragmentation may or may not occur concertedly, and that if it does, $\Delta V^{\ddagger}$ will be less positive than if it does not. The concerted reaction is assumed to be irreversible. These generalizations work out in the following ways.



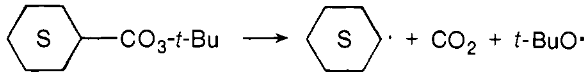
$$\begin{tikzcd} \text{A—B} \arrow[r, shift left, "k_1"] & (\dot{\text{A}}, \dot{\text{B}}) \arrow[l, shift left, "k_{-1}"] \arrow[r, "k_d"] \arrow[d, "k_c"'] & \dot{\text{A}} + \dot{\text{B}} \arrow[r] & \text{escape products} \\ & \text{cage products} & & \end{tikzcd} \quad (14)$$

When *tert*-butyl phenylperacetate and perbenzoate are compared, the large difference in $\Delta V^{\ddagger}$ (about 1 cm^3/mol for the former and 10 for the latter) is thought to be due to concerted two-bond scission in the peracetate, and stepwise reaction in the perbenzoate:[66]

$$PhCH_2CO_3\text{-}t\text{-}Bu \rightarrow Ph\dot{C}H_2 + CO_2 + t\text{-}BuO\cdot$$

$$PhCO_3\text{-}t\text{-}Bu \rightarrow PhCO_2\cdot + t\text{-}BuO\cdot$$

Dipolar character of the first of these two transition states, $Ph\text{-}CH_2{}^{+\delta}\text{- -}CO_2\text{- - -}O^{-\delta}\text{-}t\text{-}Bu$, is partly responsible for the very small value; thus, in reaction 15 $\Delta V^{\ddagger}$ is found to be +4 cm^3/mol.[69] Similar values obtain in the case of azo compounds, and Neuman was able to correlate his rate studies with product distributions; thus, the formation of products arising from substrate and radical scavengers generally has a $\Delta V^{\ddagger}$ value of about +10 cm^3/mol or more, whereas cage products have $\Delta V^{\ddagger}$ values of about +5 cm^3/mol. The decomposition of *N*-(1-cyanocyclohexyl)pentamethyleneketenimine has an activation volume of 5 cm^3/mol in chlorobenzene and gives rearrangement products only; in cumene, escape products become important and $\Delta V^{\ddagger}$ = +13 cm^3/mol.[73] Among cyclic azo compounds, the six- and seven-membered rings open concertedly with $\Delta V^{\ddagger}$ = 5.5 cm^3/mol; the eight-membered analog opens stepwise, as suggested by the appearance of relatively large amounts of trans hydrocarbon product, and $\Delta V^{\ddagger}$ is now +7 cm^3/mol.[77] It is obvious in any case that with the complex scheme operating in these reactions, both rates and product distributions under pressure provide valuable information, but this cannot be reproduced here in all detail for all cases, and the interested reader must be referred to Neuman's review[12] and other publications.[66-78]



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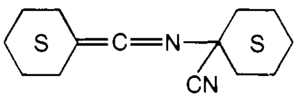
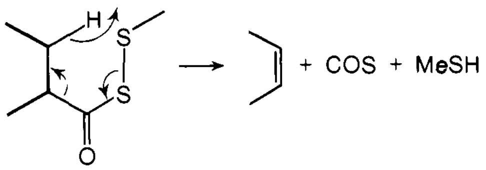
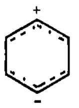


The decomposition of α,α′-azobisisobutyronitrile under pressure has been discussed in similar terms by Ogo.[79] The rather large value of $\Delta V^{\ddagger}$ in cyclohexane was ascribed to the unusually large value of the same parameter for viscous flow in that solvent; evidently a relatively large cavity must be created in this medium to permit diffusion.

The xanthate elimination studied by Eyring[80] has an activation volume of +12.3 cm^3/mol, a value consistent with much bond breaking in the transition state as might be expected from such a fragmentation:



The very large pressure-induced acceleration of the aromatization of hexamethyl(Dewar benzene)[81] is at present a major mystery. The volume decrease (−35 cm^3/mol) is well over one-third of the volume of the aromatic nucleus; clearly no mere rearrangement could produce this. It is conceivable that the transition state has dipolar character, but it is certainly not expected. Repetition of the measurement and other mechanistic studies are in order. The dioxetane decomposition of tetramethyldioxetane was studied by Kelm,[82] with measurements based on the chemiluminescence of that reaction. It proved difficult to extract $\Delta V^{\ddagger}$ from the data, and the result of about +10 cm^3/mol could not be interpreted with certainty in terms of the hotly debated question concerning the stepwise or concerted nature of the reaction (the authors favored the concerted mechanism); thus, this case illustrates the experience so often gained with other techniques that no approach is fully reliable if analogs with known mechanism are unavailable.



The decomposition of ethylcyclobutane[83] at 410 °C at nitrogen pressures to 2 kbars is one of the few carried out in the gas phase. There are no stereochemical features in the molecule that hint at the mechanism; the result chiefly confirms that the absolute values of activation volumes tend to be larger at higher temperatures.

D. Bond Forming Reactions and Cycloadditions of Neutral Species (Entries 57–156)

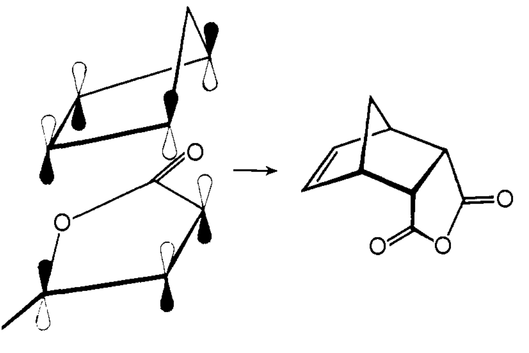
One-bond-formation processes not involving ions are relatively rare, at least in tables of pressure effects, but what little there is proves interesting. The simple combination of radicals has been studied in the termination step of polymerizations, and it was reported—and now confirmed by Ogo[89]—that $\Delta V^{\ddagger}$ is quite large and positive.[1] To account for this result, at first seemingly so surprising, it was noted that this step is almost certainly diffusion controlled, and that the diffusion steps through the increasingly viscous medium must surely be pressure inhibited. An example is now known in which two radicals, created together in a cage, combine; the $\Delta V^{\ddagger}$ for this process is −4.2 cm^3/mol.[70] This is of the right order of magnitude; however, it should be remembered that for a process such as this, in which the activation barrier must be small or even zero, the transition state theory may not be valid (since there is then no equilibrium between initial and transition states, a condition essential in the derivation of eq 4). That is not to say, of course, that there is no pressure effect, only that the transition state formalism may not be suitable to represent the results.

The propagation step in several free-radical polymerization reactions has an activation volume averaging around −22 cm^3/mol. This rather large contraction is likely the result of the large volume requirement of the π bond; the presence of a double bond is known to necessitate a large correction in parachor calculations.[1]

Cycloadditions under pressure have become a fruitful area of research, largely as a result of work by Eckert and his coworkers. Walling had previously claimed that $\Delta V^{\ddagger}$ was too small in comparison to ΔV for a concerted nature of the Diels–Alder reaction and that singlet diradicals must be involved;[1] however, Eckert[91,92] showed that $\Delta V^{\ddagger}/\Delta V$ was far in excess of 0.5 in several cases examined with great care, and hence that the reaction must be concerted. Certain caveats are possible, of course. Thus, a two-step reaction with the second step rate controlling would also produce this result; however, this assumption would be at variance with the clean stereochemistry of the reaction. Intermediate diradicals would not be expected to return to the initial state molecules in the same configuration if a rapid preequilibrium occurred.

Several results stand out when the list of Diels–Alder reactions is scanned. One of these is that there are at best only small solvent effects such as would be expected if these reactions were two-step sequences with a zwitterionic intermediate; this is an important consideration because an ionic contribution would obviously also be able to account for large negative activation volumes. In one instance, the cycloaddition of maleic anhydride to 1-methoxy-1,3-butadiene, a somewhat larger solvent dependence can be discerned; in this case a contribution from charge transfer between the two partners, so different in electron wealth, may have contributed.

A second observation of great interest is that $\Delta V^{\ddagger}/\Delta V$ in several cases exceeds unity. Eckert[92] has attributed this to secondary orbital interactions, a feature which provides an attractive force between atoms in the transition state which must recede at least to van der Waals distances again in the product. In support of this notion, he points out that this remarkable $\Delta V^{\ddagger}/\Delta V$ ratio is common in those cases in which such interactions are geometrically possible, but they are not observed with such dienophiles as acetylenedicarboxylates (see eq 16).

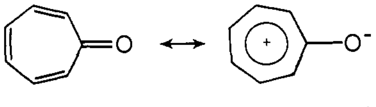


(16)

A third feature is concerned with the remarkable contrast between volume and energy descriptions of the Diels–Alder reactions. According to the volume criterion, one should have to describe this reaction as having a very late transition state: the nuclei are already at or very near their final positions. On the other hand, the Diels–Alder reaction is considered by physical organic chemists as a textbook case of an early transition state; this is deduced from the facts that activation energies are very small and that the reactions are highly exothermic. Actually these descriptions are not really at variance; the volume is a criterion for the nuclear positions, and the energy is principally a measure of the electronic progress of the reaction. One may picture the Diels–Alder reaction as one in which it is necessary for the nuclei to approach their final places closely before the electrons will flow to theirs. In this connection it should perhaps be pointed out that the $\Delta V^{\ddagger}/\Delta V > 1$ criterion does not *prove* the operation of secondary orbital interactions; it is conceivable that the electrons will simply not flow unless the atoms to be bound have first bounced to *within* single bond length of their partners to be.

One important piece in this puzzle is still missing: there is as yet no example of a retro Diels–Alder reaction in which secondary orbital interactions force endo stereochemistry. In such a reaction the activation volume should be negative. This would be a remarkable result: a reaction in which two bonds are breaking, and with yet an initial volume decrease. Such an observation would provide important support because the very large, negative activation volumes in the forward direction are notoriously difficult to measure precisely.

The [4 + 6] cycloaddition of tropone to cyclopentadiene is an instructive example in piezochemistry.[102] The reaction is a close analog of the Diels–Alder reaction in that it is symmetry allowed, though with exo stereochemistry. The activation volume is only -7.5 cm^3/mol, and on that basis alone it would surely be deduced that the reaction proceeds in stepwise fashion; however, the equally small reaction volume (-4 cm^3/mol) shows that the reaction is concerted. Measurements of the individual partial volumes of all three species participating in the reaction show that the reason for the unexpectedly small volume changes is the remarkably small volume of tropone, which can be attributed to its dipolar nature.



Very different behavior is indicated by the high-pressure results for the [2 + 2] cycloadditions. Here again, $\Delta V^{\ddagger}$ is very large and negative, but now for a different reason. The reaction occurs in two steps, via a zwitterionic intermediate as is indicated by lack of stereospecificity, solvent effects, and trapping experiments.[105] Electrostriction thus is responsible for the small volume. This explains the solvent sensitivity of $\Delta V^{\ddagger}$ (as well as a large, negative $\Delta V^{\ddagger}$ for the reverse reaction listed in section III).

As yet there have been no reports of pressure effects in allowed, antarafacial [2 + 2] cycloadditions, in stepwise [2 + 2] cycloadditions proceeding via diradicals (the competition of one such reaction with a Diels–Alder reaction under pressure has been described; see section III).

The very substantial pressure-induced rate increases in all manner of cycloadditions have attracted the attention of synthetic chemists as well. There are instances in which the avoidance of high temperature was achieved,[106] others in which pyrone[107] and even benzene[108] become involved in Diels–Alder reactions, and one[109] in which a pressure-stabilized intermediate (a styrene–TCNE adduct) is obtainable in such high concentrations at 8 kbars that it is directly observable. Dipolar [2 + 3] cycloadditions can also be carried out at high pressure with great advantage in yield; sometimes changes from 0 to 100% are effected! Examples include diazomethane[110] and nitronic esters.[111]

E. Solvolysis (Entries 157–435)

The large number of available data makes it somewhat difficult to organize them in a satisfactory way. The activation volumes are subject to relatively small structural effects (including leaving group effects) superimposed on sometimes much larger solvent effects. The temperature also causes fluctuations, and since there are, of course, variations in precision and accuracy, the impression one gets from a first inspection does not inspire much confidence. Our organizing principle has been as much as possible to group together those data which allow a single question to be considered, even though in several instances this leads to the same reaction being entered in several places.

Perhaps the largest single effect is the solvent composition when one of the components is water. At first glance, there seems to be a bewildering series of variations in the $\Delta V^{\ddagger}$ of solvolysis of benzyl chloride in aqueous solvents. Closer inspection, however, uncovers several interesting features. First of all, there is in most instances a maximum in the value of ($-\Delta V^{\ddagger}$). This maximum is in most cases close to pure water, and the approach to the maximum from the pure water end of the solvent spectrum is very steep; thus, at 50 °C in pure water, $\Delta V^{\ddagger}$ is about -10 cm^3/mol, but with 5 mol % *t*-BuOH present, $\Delta V^{\ddagger}$ is already -25 cm^3/mol. Similar though less drastic effects occur with other organic cosolvents, at other temperatures, and with other substances. The variations on the organic side of the maximum are much smaller; thus, with dioxane, water content variation from 10 to 36 mol % has no discernible effect at all. Partial molal volume measurements have shown that a major part of these variations is due to the initial states; i.e., to the substrates.[112] These data therefore reveal more about the solvent mixtures than about solvolysis or its pressure dependence. As is well known now, water is a highly structured solvent; the introduction of small amounts of solvent often brings about drastic alterations in this structure, and large effects on the partial volume of the solute are the result. The solvent effect on $\bar{V}$ of the transition state alone in the aqueous medium resembles that of inorganic salts.[112]

This information led Whalley to consider the difference in activation energy for solvolysis at constant pressure and at constant volume;[128] he concludes that the variations so often seen in aqueous mixtures as a function of composition are much smaller if the constant-volume parameter is used. Along the same lines, if the cosolvent considered is glycerol, which has thermal expansivity nearly independent of added water, the extremum behavior virtually disappears.[129] Whatever use can be made of these arguments, one conclusion is clear: if one is going to study structural effects, water or highly aqueous solvents should not be used.

There are several sets of data which show that $\Delta V^{\ddagger}$ is also temperature dependent. In most instances, $\Delta V^{\ddagger}$ becomes more negative in solvolysis at higher temperatures, which is not surprising since both the density and the dielectric constant decrease as the temperature is raised. The temperature coefficient of $\Delta V^{\ddagger}$ of benzyl chloride hydrolysis in pure water is surprisingly large near 0 °C; perhaps this is related to the abnormal behavior of the coefficient of thermal expansion in that range. The two sets of data for isopropyl bromide in water have contradicting trends, and one of these must be wrong. In any event, these variations further diminish the value of structural comparisons that one might otherwise have been able to make.

The first set of data in this group that seems to have true structural information is that gathered by Sera et al.[130] at 25 °C in acetone containing only 11.5 wt % water; it concerns the hydrolysis of cumyl chlorides. The data correlate crudely with σ^+; the slowest of these chlorides seem to solvolyze with the most negative activation volumes. This is what would be expected if the Hammond postulate were applied to the series; unfortunately there appears to be no independent evidence that this is valid.

One of the reasonable suppositions one can make about $\Delta V^{\ddagger}$ for solvolysis is that it should be sensitive to steric factors; thus, if approach to the ionic sites is hindered, solvation might suffer interference and $\Delta V^{\ddagger}$ would be less negative.

Inspection of the available data does not support this line of reasoning; the solvolysis in aqueous alcohol (20 vol % water) of benzyl chlorides does not show pressure effects that can be said to fluctuate abnormally because of *o*-methyl, isopropyl, or even *tert*-butyl substitution.[131] The formolysis and methanolysis of secondary tosylates under pressure are at best barely affected by even the most extreme alkyl crowding.[132] In cyclohexyl derivatives, $\Delta V^{\ddagger}$ is if anything slightly more negative if the leaving group has to depart in the axial direction, nor are any effects visible in the solvolyes of 2-adamantyl or *endo*-2-norbornyl tosylates.[133] How does one explain it?

We should probably not consider the alkyl groups as hindering solvating molecules any more than we view the first solvent shell as hindering the second. The alkyl groups simply become part of the solvent shell, which because of its low dielectric constant furthermore efficiently transmits the electric field to be felt by solvent molecules outside. We should perhaps be reminded that ΔV_e is very large in nonpolar media.

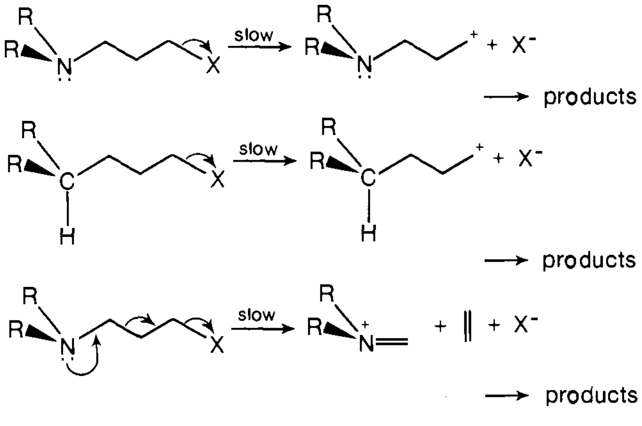
The lack of sensitivity of $\Delta V^{\ddagger}$ to steric influences is actually a fortunate circumstance, because it allows us to use the activation volume as a criterion to judge the likelihood of participation; it is well known that steric hindrance to ionization is often brought up as an alternative to participation to explain rate ratios and stereochemical discrepancies between epimers. Following our initial demonstration of the effect of charge delocalization on $\Delta V^{\ddagger}$, several additional instances have come to light. Sera's study of phenyl participation is an impressive case in point.[134] He was able to measure $\Delta V^{\ddagger}$ in formolysis of a number of para-substituted phenylethyl tosylates and, on the basis of deviations from the Hammett plot, calculate $\Delta V^{\ddagger}$ for both the solvent- and phenyl-assisted rates. The data show that $\Delta V^{\ddagger}_{\mathrm{obsd}}$ decreases from -7 to -13 cm^3/mol as the electron-donating methoxy substituent is changed to nitro; careful data dissection furthermore shows that, even with methoxy, a very minor unassisted pathway with a $\Delta V^{\ddagger}$ of -13 cm^3/mol is contributing. Since the reality of phenyl participation is now conceded by all, this demonstration thus provides a powerful shot in the arm for the original claim that pressure effects could provide such a criterion.

Possibly an even more dramatic case had been recorded earlier with a para oxide substituent; in that case participation leads not to ionization but to electron transfer through the ring to the carbonium ion site, and $\Delta V^{\ddagger}$ is reduced from -20 to -1 cm^3/mol! Even a much more distant phenyl ring can be effective under such circumstances: 4-*p*-oxidophenylbutyl tosylate produces tosylate ion with $\Delta V^{\ddagger} = -5.4$ cm^3/mol.[135]

Less success has been achieved so far in discerning from the activation volume to what degree the solvent is active as a nucleophile, or displacing agent, apart from its solvating role. Especially with unstabilized and/or unhindered cations it might be supposed that the solvent would engage in bonding to the cationic site, and that this should lead to contraction relative to cases in which such bonding is either geometrically impossible or energetically not necessary.

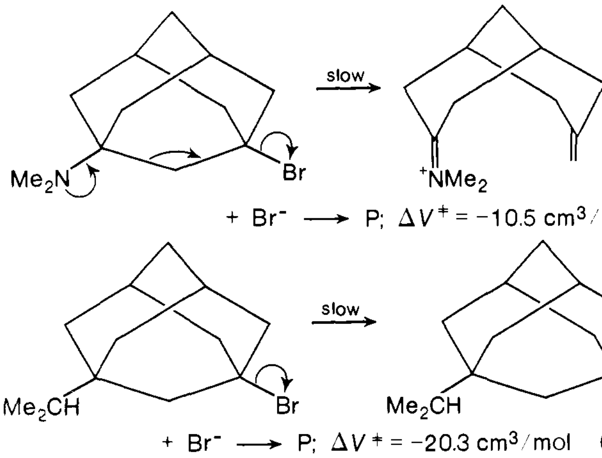
The evidence is somewhat conflicting. There is virtually no difference in $\Delta V^{\ddagger}$ of the methanolyses of ethyl chloride and *tert*-butyl chloride. Sera reports[139] that methyl and isopropyl tosylates have increasingly negative activation volumes as the solvent is varied to a more nucleophilic one (formic acid to aqueous acetone to methanol), but 1- and 2-adamantyl tosylate, in which such bonding is geometrically not possible, also show this behavior. Additional information is needed here.

High-pressure measurements have provided a satisfying answer to the problem of how to distinguish concerted ionogenic fragmentation from stepwise analogs.[140] This is not to say that there is no alternative answer to the question: thus, Grob had noted[141] that rate accelerations up to 5 × 10^4 occurred in the fragmentations of many γ-haloamines compared to the carbon homomorphs, where inductive retardation should have been expected if the mechanism in the former had been analogous to that of the latter:



On the other hand, the haloamines produce fragmentation products even when the inductive effect outweighs the driving force of concerted reaction, and hence there is no way to tell where the limit lies.

The high-pressure criterion is simple: in a concerted fragmentation one may expect that the effect of the extra breaking bond will reduce the pressure acceleration. In the event, in view of the enormous spread in rates, it was necessary to resort to differences in leaving group and temperature; however, comparisons with known compounds allowed small corrections for these changes to be applied. Table II only shows the observed $\Delta V^{\ddagger}$ values; for the calculated ones corrected to a common temperature and leaving group, one should consult the original papers. A single example may suffice here (eq 17). The entire group of data in that paper may be summarized by $\Delta V_c^{\ddagger} = -21.5 \pm 1.8$ cm^3/mol; $\Delta V_N^{\ddagger} = -13.3 \pm 2.0$ cm^3/mol. There is one amine which falls outside that limit; for



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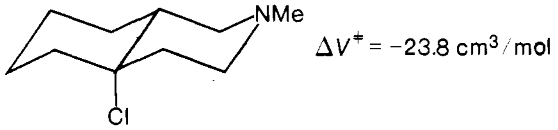


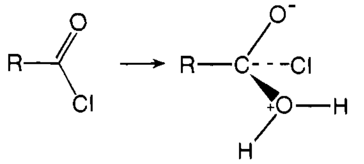
This amine also happens to be the slowest, slower by a factor of 8 than the carbon homomorph. Clearly, the inductive effect operates to its full extent here, there is no concertedness, and the reaction proceeds stepwise to the fragmentation products.

Solvolysis and the pressure effect on it have been used to advantage by Colter[142] to demonstrate charge-transfer catalysis. The transition state of acetolysis of 9-(2,4,7-trinitrofluorenyl) tosylate is reduced by about 5.5 cm^3/mol in size if 9-methylanthracene is present; this figure is in good agreement with equilibrium data for charge-transfer complexation. It is considered to be a 10-cm^3 volume decrease, tempered by a 5-mL increase due to delocalization.

The linkage isomerization in benzhydryl isothiocyanate and its competition with solvolysis give important information about charge separation.[143] The former reaction surely occurs within the tight-ion-pair stage, and the latter within the loose stage. The difference is 4 cm^3/mol. We may compare this value with equilibrium data obtained in ion-pair studies in nonpolar solvents (see section V).

The decomposition of *tert*-butyldimethylsulfonium salts[144] stands in interesting contrast to the other solvolysis data in that the charges are already there, and delocalization in the transition state will if anything reduce electrostriction. The activation volume is large and positive.

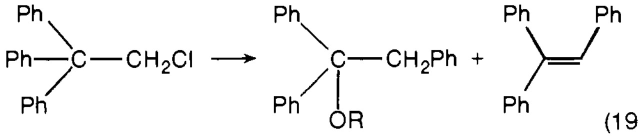
This series of data ends with information on the hydrolysis of acyl chlorides, in which the rate-controlling step combines the features of ionization and conversion of a carbonyl carbon into a tetrahedral atom (eq 18). The large contraction that occurs may



(18)

be explained in that way. The data parallel those of solvolysis of simple halides in that $\Delta V^{\ddagger}$ is again strongly dependent on the composition of the aqueous solvent: it varies from -30 cm^3/mol in THF containing little water to about -10 in pure water. With $MeSO_2Cl$, virtually no differences are observed between H_2O and D_2O; this is an example of the fact that transition states as well as normal molecules only rarely have measurably different steric requirements upon isotopic substitution.

Mention should be made here of several qualitative results obtained by Okamoto.[148] He finds that the application of 5 kbars on the solvolysis reaction has quite drastic effects on the product



(19)

ratio, the substitution product being favored over the olefin, as might be expected. The same result obtains if base is present; under those conditions the unrearranged alkoxy compound is also formed, but in decreasing yield as the pressure is raised, in agreement with expectation since S_N1 solvolysis invariably has a more negative activation volume than ionic S_N2 substitution (cf. also the following section).

F. Bimolecular Nucleophilic Substitutions (Entries 436–535)

The Menshutkin reaction has continued its role in the limelight of piezo chemistry. This is for obvious reasons: because of the combination of displacement and ionization features, it is subject to large pressure effects, and in spite of its ionic nature, it can be carried out in even highly nonpolar solvents; it obeys clean second-order kinetics and is believed to have simple least motion characteristics with an early transition state.

The data pertaining to the influence of solvent are unfortunately for the most part not usable, since they were "corrected" for compressibility; in most of these cases the magnitude of the alterations are of the order of 10% or so. This introduces a systematic error which may in some cases overshadow the solvent effects. Nevertheless, it is clear that there are real solvent effects, and that they are roughly predictable on Drude–Nernst grounds: $-\Delta V^{\ddagger}$ is largest in hexane, and smallest in methanol, nitrobenzene, and so on. The pressure accelerations increase with increasing temperature, and vary in capricious ways with composition in mixed solvents.

The Menshutkin reaction and its sensitivity to pressure have provided the means for experimental support of the Hammond postulate, a principle often used by kineticists to rationalize comparative rate data. The principle as used by most chemists states that when two reactions of the same sort differ significantly in exothermicity, the one liberating the most energy will have the earlier transition state. It is often used in conjunction with the principle of Polanyi according to which that reaction will also be faster (have a lower barrier).[159]

When we compare the reactions of 2,6-dialkylpyridines with alkyl iodides,[157] we find that the rates are greatly depressed by increases in size and branching of either alkyl group. This then should mean that increases in hindrance are raising the barrier and shifting it in the direction of product. Gonikberg[1] has explained the increasingly negative $\Delta V^{\ddagger}$ values in terms of overlapping, or interpenetrating groups; however, relatively facile bond bending and hard-sphere characteristics are now such a well-established part of the scene that this explanation does not satisfy, and the Hammond postulate provides a much better rationale.[160] It has been found that neither the pyridines nor the pyridinium salts have large volume abnormalities; when the $\Delta V^{\ddagger}$ values for these reactions are compared with ΔV, one observes that the ratio $\Delta V^{\ddagger}/\Delta V$ steadily increases as the hindrance is raised. Thus, we regard the special pressure acceleration of highly hindered Menshutkin reactions as simply a manifestation of the Hammond postulate.

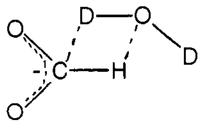
Several additional comments are of interest here. For one, this explanation has received further support in that if methyl chloride is used, one observes[161] a measurable increase in the chlorine 35/37 isotope effect between pyridine and 2,6-lutidine; for another, an independent estimate by Kondo[155] has led to a value of 20–40% charge development in the benzylation of pyridine, in rough agreement with our estimate for the methylation. These estimates explain why the activation volume of the Menshutkin reaction is so much more sensitive to steric hindrance than that of the superficially similar solvolysis reaction; the latter has a very late transition state, and the application of pressure cannot make it much later. Finally, it is perhaps worthwhile to emphasize just how great the effect is; for instance, 2,6-di-*tert*-butylpyridine is ordinarily not methylated at all, but even at 5 kbars the reaction is rapid.[162]

The other data are all for ionic displacement reactions. Previously known listings generally reported $\Delta V^{\ddagger}$ for such reactions in the range of 0 to -10 cm^3/mol, and hence there are few surprises here. One item of interest is the large value of -24 cm^3/mol when lithium chloride is used in acetone. This is due to the fact that the ion pairs or clusters must first dissociate (see Appendix); it warns us that uncritical conclusions from S_N2 reactions of this sort are fraught with danger. Another point of interest is Ewald's[125] conclusion that displacements leading to cyclic products have less negative activation volumes than open-chain analogs.

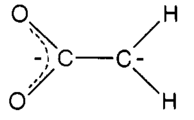
G. Carbanion Reactions (Entries 536–616)

A conceptually simple reaction is rate-controlling proton transfer, and this is essentially the mechanism in the base-promoted isomerizations of several substituted cyclohexenes studied by Steinberg.[169] A priori, one expects that $\Delta V^{\ddagger}$ will be negative since this is essentially an S_N2 reaction at hydrogen; however, the value might be less negative than usual since the incipient product is a charge-delocalized allylic anion. The surprising result is that $\Delta V^{\ddagger}$ is about -20 cm^3/mol in most instances. It is known that anions are not very well solvated in dimethyl sulfoxide ("naked anions"). These large pressure induced accelerations may be due to that, and to the dissociation of *t*-BuOK under pressure; at present we will have to wait for further results in that medium.

Hamann and Linton[170] have found that different mechanisms apply to the base-catalyzed D-exchanges of formate and acetate ions. Formate ion exchanges with first-order kinetics and an activation volume of -2 cm^3/mol, via a transition state best pictured as



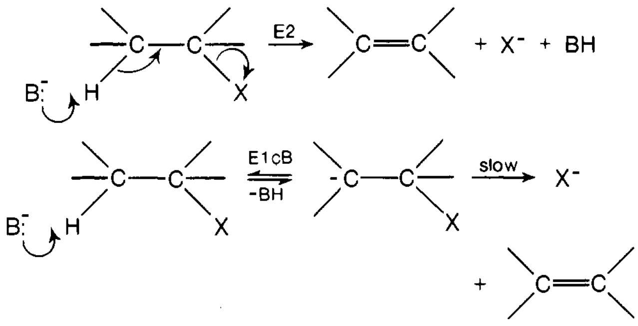
whereas the acetate, with second-order kinetics and an activation volume of -10 cm^3/mol, has at least a substantial pathway via the carbanion



Jost[171] has examined the kinetics of proton exchange in very fast processes by means of T-jumps. His *p*-nitrophenol analog has a very large positive activation volume for proton donation to hydroxide, fully in accord with the highly delocalized nature of the incipient anion.

The proton transfers examined by Caldin[172] are of interest especially in that extremely large k_H/k_D ratios (up to 50) strongly suggest that tunnelling characterizes the process. The indifference of $\Delta V^{\ddagger}$ to solvent effects contrasts with quite a bit of variation of ΔV, and Caldin has argued that this is consistent with his mechanism; however, the activation volumes for the reverse reactions are sensitive to pressure, yet tunnelling must characterize them too if microscopic reversibility holds.

In base-catalyzed eliminations Brower[166] has found an answer for a long-standing puzzle: how to assign the so-called E2 and E1cB mechanisms (concerted reaction and carbanion intermediacy):



He reasoned that E2 reactions should have negative activation volumes because of their resemblance to displacements, and that E1cB reactions should have positive $\Delta V^{\ddagger}$ values because there should be essentially no volume change in the proton-transfer preequilibrium step, and a volume increase in the C–X bond cleavage. His study of several textbook examples bears him out. Again, we should be mindful of the ever present complication of ion pairing in these organic media; a large change in $\Delta V^{\ddagger}$ resulted in one instance from the addition of a crown ether.

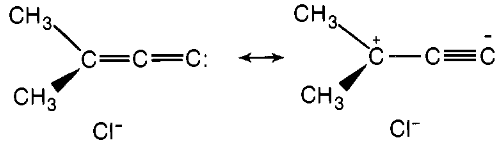
A perplexing case is that of the base-promoted diacetone alcohol decomposition. There is no doubt in this case about the fact that proton removal is extremely fast and that the reaction is E1cB. Brower does indeed find $\Delta V^{\ddagger}$ to be +6 cm^3/mol; however, Moriyoshi[173] finds an activation volume varying from −9 to +8 cm^3/mol, depending on temperature and solvent composition, with lower temperatures and the more aqueous alcohols favoring the negative end of the spectrum. Further data would be welcome here.

The fragmentations of β-bromoangelate[174] ion and of chloroacetylhydrazide[175] provide us with as convincing a pair of examples of the power of high-pressure kinetics as can be imagined. In the former case, concerted bond cleavages can be assumed since the activation volume is roughly double that normally observed in simple decarboxylation;[1] in the latter case $\Delta V^{\ddagger} = -5$ cm^3/mol, which was a divergence from the expected value so great that the "known" mechanism could be scrapped on that basis alone. Reinvestigation revealed that the slow step—following ionization of the α-NH group—is internal displacement, and the final products are preceded by a long series of intermediates. Regarding the difference in $\Delta V^{\ddagger}$ for the base-catalyzed condensations of *n*- and isobutyraldehyde, this has been attributed to prior hydration of the carbonyl function in the case of the latter.[178]

The Meerwein–Ponndorf type reduction of diisobutyl ketone with *n*-butoxide is second order in both base and substrate.[178] With that many species congregating in the transition state, the negative activation volume is reasonable, though its magnitude could certainly not have been predicted with confidence.

The activation volume of the hydrolysis of esters via base catalysis is consistent with the formation of a tetrahedral intermediate, which then partitions into acid and ester. The bond formation is responsible for the negative value. A much more negative value obtains in the addition of thiophenoxide to mesityl oxide; this is in accord with the less extensive electrostriction by the more delocalized thiophenoxide ion. The activation volumes observed by Tiltscher[182] for the cesium phenoxide catalyzed additions are such that no bond formation alone can account for them, and ion pair separation is part of the activation process.

The base-promoted hydrolysis of chloroallenes has a positive, but small activation volume. Since this is a clear-cut case of a carbene reaction, and since the volumes of the transition states of formation of the carbene are virtually the same whether one begins with the chloroallene or the isomeric acetylene, the authors deduced that the carbene must initially be paired with the leaving anion (eq 20).[183] During the reaction the chloroacetylene

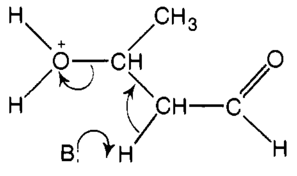


(20)

rearranges to a small extent to the allene, and this isomerization was shown to be base promoted (hence via the anion), and to take place via internal return. Further support for these conclusions must await stereochemical proof.[184]

H. Acid-Catalyzed Reactions (Entries 617–756)

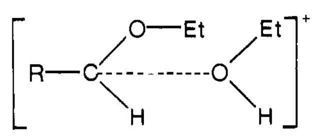
It seems a bit surprising that the acid-catalyzed dehydration leading to α,β-unsaturated carbonyl compounds is accelerated by pressure, since the main process is the splitting into two molecules. It must be assumed that in the transition state the base removing the proton is quite tightly bound and the leaving water molecule not yet very loose.



In any case, the reverse reaction (the hydration of the olefin) is also accelerated, and the difference between the two $\Delta V^{\ddagger}$ values is indeed consistent with the bond cleavage (−5.8 − (−19.8) = +14 cm^3/mol). The activation volumes for addition of methanol or ammonia to a double bond are comparable to that for hydration.

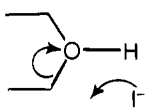
The opening of small cyclic ethers can be seen in light of Whalley's criterion,[6] negative activation volumes denoting an A2 mechanism, and positive values an A1 path and free carbonium ion. In every instance reported in Table III, $\Delta V^{\ddagger}$ is negative.

The acetal formation reactions reported by Imoto[192] are surely acid catalyzed, and hence autoionization should be part of the activation process. Since ΔV_i is quite large and negative in such media (<−20 cm^3/mol), the observed negative values seem quite small. The reverse reactions (some of which are shown further below) have in any case been identified as A1 reactions traversing an alkoxy-stabilized carbonium ion; the main transition state is probably close to



An interesting example of the use of $\Delta V^{\neq}$ as a criterion in A1–A2 reactions is the hydrolysis of benzoic acid anhydrides. Koskikallio[193] has found a very sharp change of sign from plus to minus as a function of solvent composition in aqueous dioxane. If little water is present, the mechanism is A1 ($\Delta V^{\neq} = +$), and in more aqueous solutions this changes to A2 ($\Delta V^{\neq} = -$). This conclusion is supported by that of a substituent effect: *p*-methoxy leads to A1 over the entire range of solvents, and *p*-nitro to A2 in all solutions save those containing virtually no water at all! In some instances in which the A1 mechanism is slighly favored, modest pressure may conceivably suffice to bring about a change, leading to minima in the ln *k* vs. *p* curves. When no acid is present, the autoionization again becomes part of the activation process, and much more negative $\Delta V^{\neq}$ values result. The same thing is true of ethyl esters.

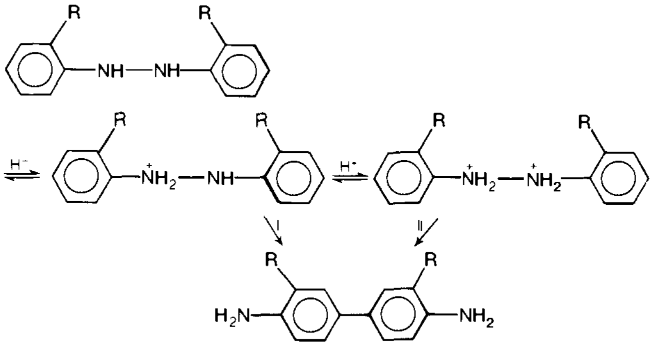
A change of sign occurs[200] in $\Delta V^{\neq}$ in the acid-catalyzed hydrolysis if iodide ion is present. Evidently this anion, rather than a water molecule, then serves to displace alcohol. The product is still ethanol, so that ethyl iodide is only an intermediate in the reaction.

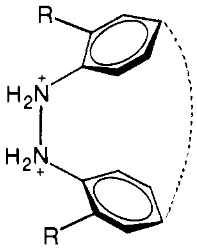


The sucrose inversion is, of course, the classic example of an A1 hydrolysis.[1]

Osugi and co-workers[201-205] have made a thorough study of the acid-catalyzed benzidine rearrangement. They found that in most cases two pathways (I and II in Scheme I) contribute to the reaction, and they were able to measure the pressure effects on both. It was found that $\Delta V^{\neq}_{\text{I}}$ is about -10 cm^3/mol, and $\Delta V^{\neq}_{\text{II}}$ is much less negative. The results are consistent with considerable bond formation in advance of bond breaking in process I. The less negative value of $\Delta V^{\neq}_{\text{II}}$ is harder to understand in view of the increased electrostriction that characterizes divalent ions. Simple bond cleavage of the monocation would account for $\Delta V^{\neq}$ of the disproportionation. The mechanism of the oxidation to the azobenzene is not known, but the very large negative activation volume of -50 cm^3/mol will be difficult to explain without the creation of ionic charges in or prior to the transition state.

SCHEME I





The pinacol rearrangement has been dissected in remarkable detail. It is known that the protonated diol eliminates water via both hydroxy- and phenyl-assisted paths; in the former case, the epoxide then formed may undergo C–O fission a second time to form the same ketone by phenyl participation. Moriyoshi and Tamura have measured the appropriate volume terms;[206] their results may be symbolized as shown in Scheme II. The values for process I seem reasonable, but it is not clear why transition states I and II should be similar in volume—the latter differing from the former by a bound water molecule. The volume changes in process III seem extremely large, and the authors conceded that large experimental errors may be responsible.

Fujii's results are reasonably explained in terms of the known formation of molecular chlorine in that reaction: a displacement of acetanilide from chlorine by chloride ion. The charge neutralization is responsible for the positive volume change.[36]

The self-catalysis in Hamann's esterification and hydrolysis should be seen as proceding via autoionization.[198] He noted that pivalic acid gives no abnormally large effect and warned that it is not wise to expect all sterically hindered reactions to show special pressure effects.

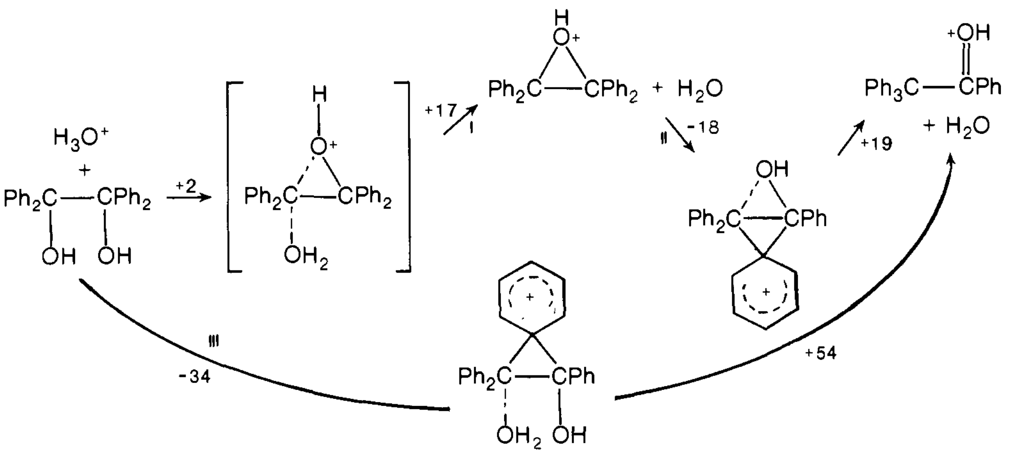
I. *Miscellaneous Organic Reactions* (Entries 757–765)

The very large acceleration in the isomerization of $PhSnCH_2CCH$ has been explained by Brower in terms of ion-pair formation, a sound suggestion since the reaction is known to be catalyzed by Lewis acids.[207]

Hamann[167] has studied the transition metal catalyzed displacements of some alkyl bromides. With silver ion, $\Delta V^{\neq}$ becomes more negative than usual in S_N2 reactions; silver ion assisted ionization is consistent with this.

$$R - X + Ag^+ \rightarrow R^{+\delta}\text{- - -}X^{-\delta}\text{- - -}Ag^+$$

SCHEME II



With mercuric chloride, this effect is much smaller. It is known that mercury–halogen bonds are more covalent in nature, but perhaps the reason is not that simple; the mechanisms of these reactions have not been elucidated, and, in fact, the exact rate laws are not known.

The reopening of the enol ether–tetracyanoethylene adduct is of interest in that it is perhaps the only C–C bond cleavage known so far which is accelerated by pressure.[208] The activation volume, in fact, is similar to that in solvolysis, proving the fully zwitterionic nature of the cycloaddition and the reverse reaction. In this way it provides an interesting contrast with that of cyclopropanes to tetracyanoethylene: that reaction is retarded by pressure, and CIDNP is further testimony to the radical nature of that reaction.[209]

Mention should be made here of several qualitative observations that have synthetic value or potentially so. It was already noted that hindered Menshutkin reactions seem subject to special acceleration by pressure. Beside the examples noted above, Okamoto has reported the reactions of 2,6,*N*,*N*-tetramethylaniline[211] and 2,4,6-tri-*tert*-butyl-*N*-methylaniline[212] with simple alkyl iodides under pressure, as well as the reaction of trityl salts with pyridine.[213] Once again, one should not assume that all hindered reactions are going to be greatly accelerated by pressure; thus, Okamoto has also found that the solvolyses of neopentyl and 1-adamantylcarbinyl tosylates are virtually unaffected by pressure, with $\Delta V^{\ddagger}$ close to zero in both cases![214]

Several qualitative studies by Plieninger are also of interest; thus, he has reported high-pressure studies of the cycloaddition of carbon disulfide to norbornene[215] and a case of pressure-improved enantioselectivity in a chiral medium.[216] The dimerization of cyclooctatetraene under pressure has been described by Korte.[217]

III. Activation Volume Differences

A. The Data in Tabular Form (Table III)

It should be noted that $\Delta\Delta V^{\ddagger}$ in all instances equals the difference in activation volume between the *n*th and 1st reactions given:

$$\Delta\Delta V^{\ddagger} = \Delta V^{\ddagger}_n - \Delta V^{\ddagger}_1$$

In many instances the two reactions have the initial states in common: $\Delta\Delta V^{\ddagger}$ is then simply $V^{\ddagger}_n - V^{\ddagger}_1$. This is of course not so when a mixture of substrates is made to compete for the same reagent or intermediate. In a few entries, both types of data were produced in a single experiment.

B. Competing Radical Reactions (Entries 1–24)

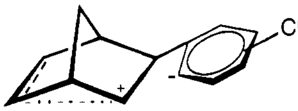
The inhibition of the formation of radical pairs by pressure is relatively small compared to their further separation, a fact already alluded to in the preceding section. This becomes especially clear when the effect of pressure on product distribution is studied: product formation within the cage is suppressed little compared to escape product yields. The difference in activation volume amounts to at least 10 cm^3/mol in all known cases. It is interesting to see that this difference is apparently steeply solvent dependent: in five instances, $\Delta\Delta V^{\ddagger}$ equals 13 ± 1 cm^3/mol in cumene, but much larger values obtain in other solvents. Diffusion is, of course, very dependent on the shapes of the molecules in the system; nearly spherical molecules have large activation volumes for self-diffusion, for example. A study of $\Delta\Delta V^{\ddagger}$ for a single substrate in a series of solvents would be valuable to see if a correlation with shape can be found. Small differences are found if two cage reactions are compared; thus, pressure has much smaller effects on ratios of recombination and disproportionation.

Zhulin[222] has observed a systematic effect of pressure on the competition of substituted toluenes for the *N*-bromosuccinimide derived radical. The linear variation with the σ constants of the substituents has a very high correlation constant; the Hammond postulate correctly predicts the direction of the effect. In many other instances of competition of aromatic substrates for radicals one can correctly guess which products will be favored under pressure by assuming it will be the most crowded or branched product.

C. Competing Cycloadditions (Entries 25–39)

It was noted in section II that in many Diels–Alder reactions capable of secondary orbital interactions, $|\Delta V^{\ddagger}|$ exceeds $|\Delta V|$, and hence that these interactions are supported by that observation. A caveat was also expressed: very large $\Delta V^{\ddagger}$ values are notoriously difficult to measure precisely, and no case has yet been reported in which a retro-Diels–Alder reaction was accelerated by pressure. The data in Table III raise a further question. In those instances in which competing reactions take place, one presumably with, and the other without secondary orbital interactions, pressure should favor the former. Sera[225] has reported examples in which cyclopentadiene and acrylic acid derivatives give both *exo*- and *endo*-norbornenes, and in no case does $\Delta\Delta V^{\ddagger}$ exceed 1 cm^3/mol; furthermore, in two instances $\Delta\Delta V^{\ddagger}$ has the wrong sign, with the exo product favored by pressure over the endo stereoisomer.

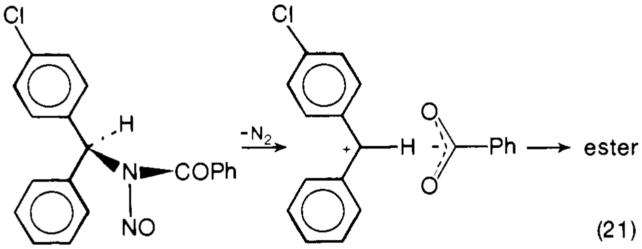
Stewart's data[229] provide an interesting piece of evidence for the concertedness of Diels–Alder reactions as compared to radical [2 + 2] cycloadditions; chloroprene dimerization provides both types of products, and the latter are suppressed in yield by the application of pressure. It should be pointed out in passing that the diradical intermediates *can* close to six-membered rings, and these compounds are therefore not necessarily Diels–Alder products; for the arguments which lead to the assignment of mechanism to the cyclohexenes, one should read Stewart's papers. The cycloaddition of tetrachlorobenzyne to norbornadiene is one in which the [2 + 2 + 2] reaction competes with a zwitterionic intermediate; electrostriction then provides an added incentive for the latter, and competition is about even.



D. Miscellaneous Organic Reactions (Entries 40–59)

In a symmetrical pinacol, it has been found that pressure favors the migration of phenyl over that of *o*-anisyl.[234] This has been ascribed to the need for the migrating group to be desolvated.

In the ion-pair reaction (eq 21), a substantial amount of racemic ester is formed. The racemization occurs in the loose pair stage, and it depends clearly on the rotation of the cation, or its circumnavigation by the anion. Evidently these reactions, though dependent on diffusion, can compete with immediate collapse under pressure, since that reaction is characterized by loss of solvation.[235]



(21)

TABLE III. Activation Volume Differences

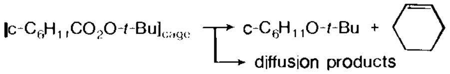
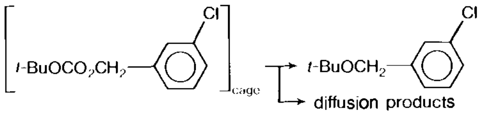
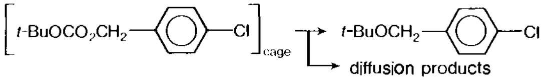
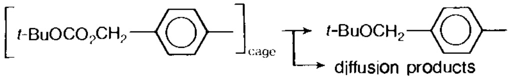
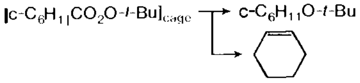
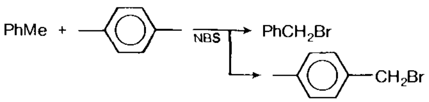
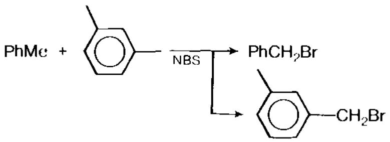
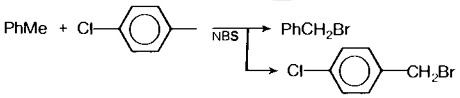
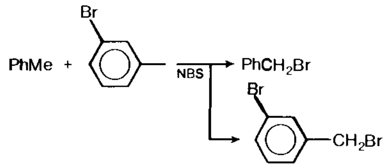
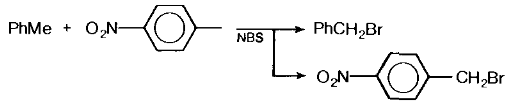
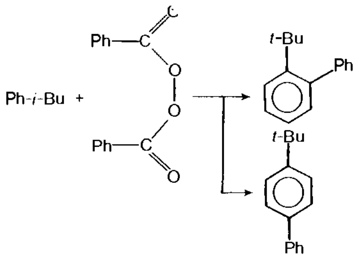
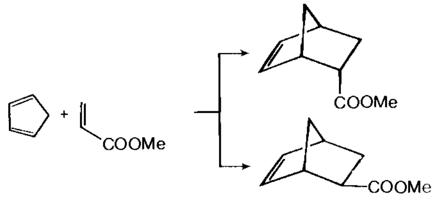
No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	$\Delta\Delta V^*$, cm^3/mol	Ref	Remarks
1	$[PhN_2CPh_3]_{cage} \rightarrow Ph_4C$ $\rightarrow$ diffusion product (PhI)	c-$C_6H_{11}Me$	60	2.5	5	0 +51	218	In the presence of I_2
2		i-PrPh	79.6	4.1	3	0 +11	67, 69	
3	$[t\text{-}BuON_2O\text{-}t\text{-}Bu]_{cage} \rightarrow t\text{-}BuOO\text{-}t\text{-}Bu$ $\rightarrow$ diffusion produc	C_8H_{18}	45	4	9	0 +30.0	71	
4	$[t\text{-}BuOCO_2CH_2Ph]_{cage} \rightarrow t\text{-}BuOCH_2Ph$ $\rightarrow$ diffusion products	i-PrPh	79.6	6.1	4	0 +14	219	
		i-PrPh	79.6	6.1	4	0 +14	219	
6		i-PrPh	79.6	6.1	4	0 +14	219	
7		i-PrPh	79.6	6.1	4	0 +12	219	
8		i-PrPh	79.6	4.1	3	0 −1	67,[a] 69	
9	$[EtN_2Et]_{cage} \rightarrow C_2H_4 + C_2H_6$ $\rightarrow C_4H_{10}$	PhMe	35	4	3	0 +2.8	220	In the presence of $Ph_2C{=}CH_2$
		i-$PrCH_2$-t-Bu	35	6	4	+2.6	220	In the presence of $Ph_2C{=}CH_2$
10	PhMe + i-PrPh $\xrightarrow{NBS}$ $PhCH_2Br$ $\rightarrow PhCMe_2Br$	CH_2Cl_2	50	4.9	4	0 −5.5	221	
11	PhMe + PhEt $\xrightarrow{NBS}$ $PhCH_2Br$ $\rightarrow PhCHMeBr$	CH_2Cl_2	50	7.8	5	0 −4.8	221	
12	PhMe + Ph_2CH_2 $\xrightarrow{NBS}$ $PhCH_2Br$ $\rightarrow Ph_2CHBr$	CH_2Cl_2	50	4.9	4	0 −2.4	221	
13		CH_2Cl_2	70	5.9	4	0 +2.50	222	
14		CH_2Cl_2	70	5.9	4	0 +1.65	222	
15		CH_2Cl_2	70	5.9	4	0 −1.10	222	

TABLE III (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔΔ*V**, cm³/mol	Ref	Remarks
16		CH_2Cl_2	70	5.9	4	0 −2.80	222	
17		CH_2Cl_2	70	5.9	4	0 −6.35	222	
18	PhMe + C_7H_{16} $\xrightarrow{\text{NBS}}$ $PhCH_2Br$ $C_7H_{15}Br$	CH_2Cl_2	70	5.9	4	0 +6.1	221	
19	PhEt $\xrightarrow{t\text{-BuOCl}}$ $PhCH_2CH_2Cl$ PhCHClMe	Neat	40	5.9	6	0 −7.7	223	
20	*i*-PrPh $\xrightarrow{t\text{-BuOCl}}$ $PhCHMeCH_2Cl$ $PhCClMe_2$	Neat	40	5.9	5	0 −8.9	223	
21	PhMe + PhEt $\xrightarrow{t\text{-BuOCl}}$ $PhCH_2Cl$ PhCHClMe $PhCH_2CH_2Cl$	Neat	40	5.9	5	0 −1.0 +6.7	223	
22	PhMe + *i*-PrPh $\xrightarrow{t\text{-BuOCl}}$ $PhCH_2Cl$ $PhCClMe_2$ $PhCHMeCH_2Cl$	Neat	50	5.9	4	0 −3.0 +5.9	223	
23	PhMe + *t*-BuPh $\xrightarrow{t\text{-BuOCl}}$ $PhCH_2Cl$ $PhCMe_2CH_2Cl$	Neat	50	5.9	5	0 +5.7	223	
24				6	4	0 +8.1	224	
25		CH_2Cl_2	35	2.9	4	0 +0.52	225	

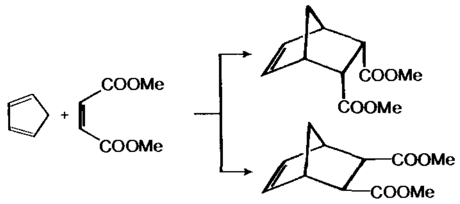
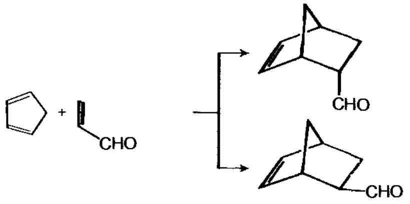
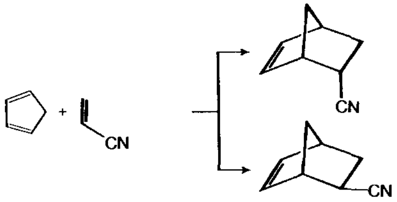
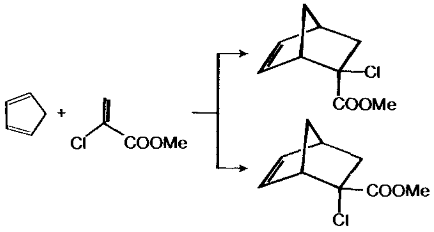
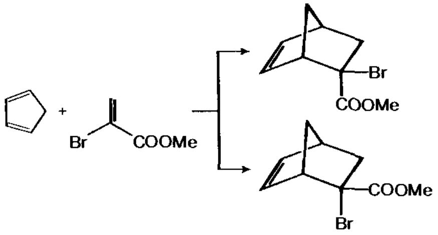
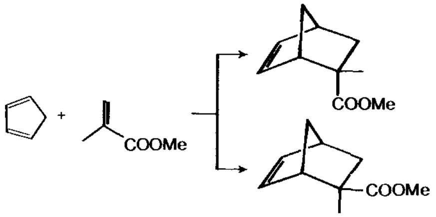
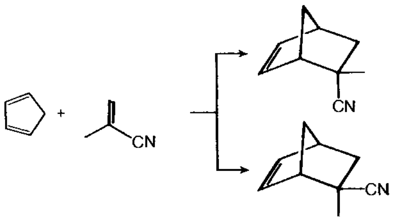
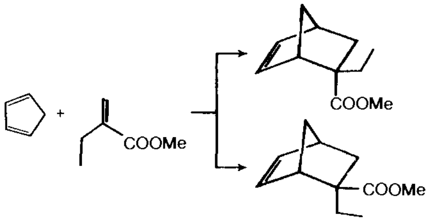
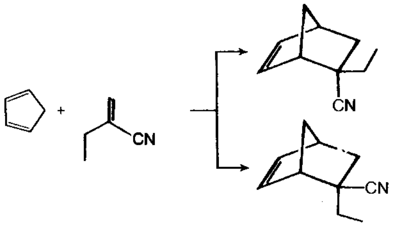
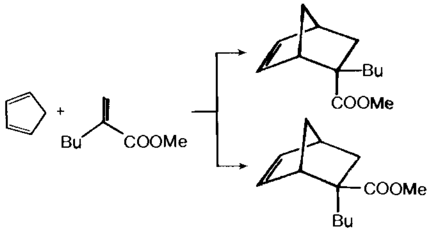
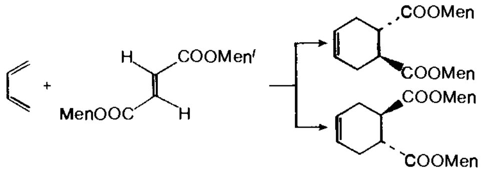
26		CH$_2$Cl$_2$	35	2.9	4	0	225
						+0.82	
27		CH$_2$Cl$_2$	35	2.9	4	0	225
						+0.50	
28		CH$_2$Cl$_2$	35	2.9	4	0	225
						+0.22	
29		CH$_2$Cl$_2$	35	2.9	4	0	225
						−0.21	
30		CH$_2$Cl$_2$	35	2.9	4	0	225
						−0.52	
31		CH$_2$Cl$_2$	35	2.9	4	0	225
						+0.78	

TABLE III (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔΔ*V**, cm³/mol	Ref	Remarks
32		CH_2Cl_2	35	2	3	0 +0.75	225	
33		CH_2Cl_2	35	2.9	4	0 +0.82	225	
34		CH_2Cl_2	35	2	3	0 +0.99	225	
35		CH_2Cl_2	35	2.9	4	0 +0.83	225	
36		*m*-Xylene	70	4.9	3	0 −0.9	226	

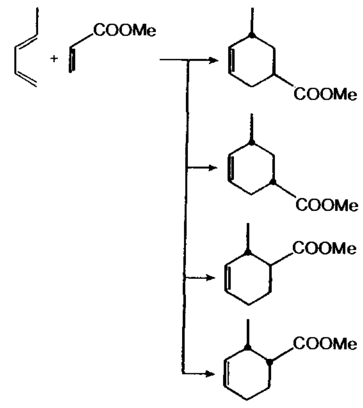
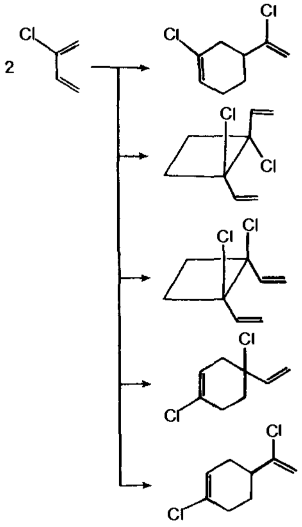
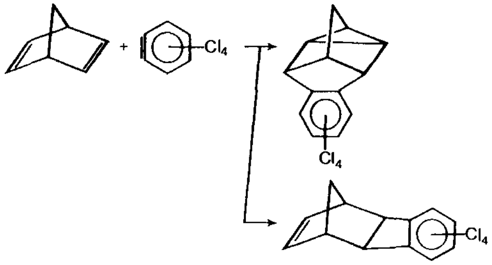
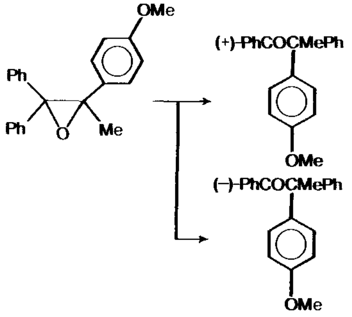
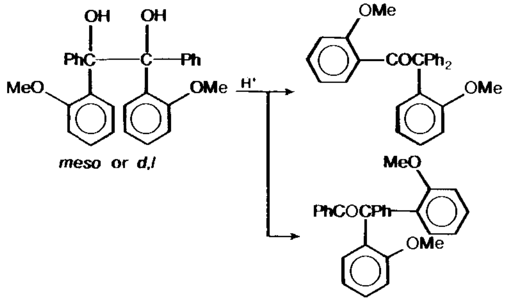
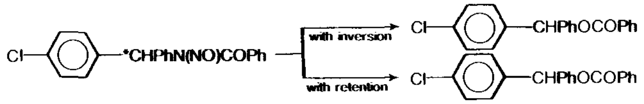
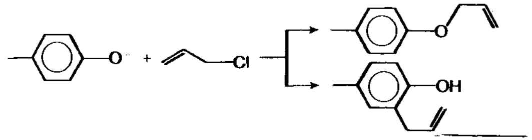
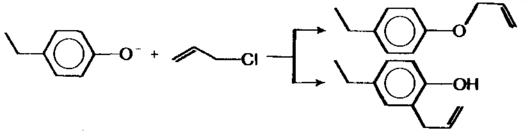
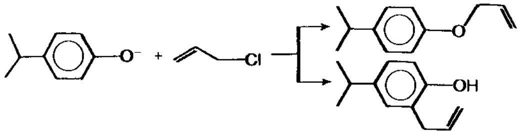
37		*m*-Xylene *i*-PrPh	80 80	5.9 12.6	3 6	0 0	227 228
						<0 −2.3	
						≃0 −1.0	
						<0 −3.3	
38		Neat	23	10.1	4	0	229
						+8.4	
						+9.4	
						+9.4	
						+2.2	
39		EtOEt	Room temp	5	6	0	230
						−0.7	
40	*t*-BuCOMe $\xrightarrow[\text{EtMgI}]{}$ *t*-BuC(OH)MeEt → *t*-BuCH(OH)Me			5	2	0 +1.3	231

TABLE III (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔΔ*V**, cm^3/mol	Ref	Remarks
41	PhCOCOOMen^l $\xrightarrow{\text{MeMgI}}$ (−)-PhC(OH)MeCOOH (+)-PhC(OH)MeCOOH	EtOEt	25	4.9	4	0 −1.2	232	
42		Diethyl *d*-tartarate	80	10	2	0	233	
						−0.4^b		
43		AcOH MeCN	77.4	3	4	0 0	234	
		AcOH MeCN				+3.4 +3.4 +4.0		*meso* or *d,l* *meso* *d,l*
44		CH_2Cl_2	25	5.3	5	0 +0.55	235	
45		H_2O	40			0 −3.5	236	
46		H_2O	40			0 −3.3	236	
47		H_2O	50			0 −2.5	236	

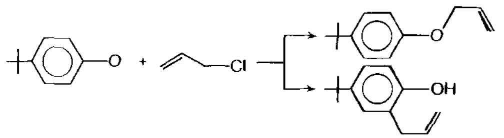
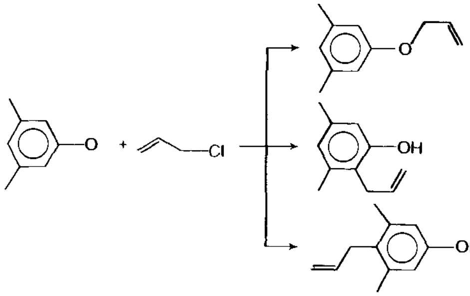
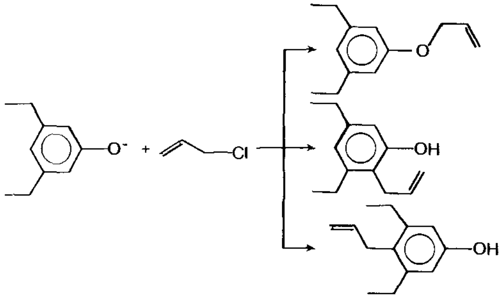
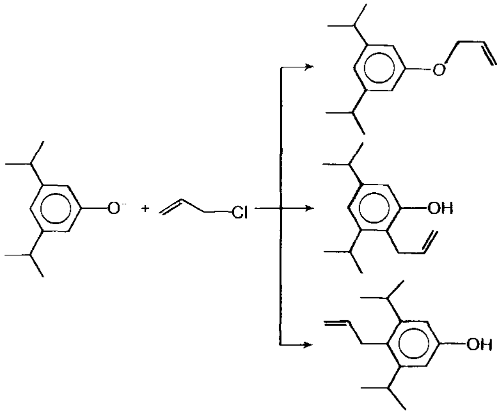
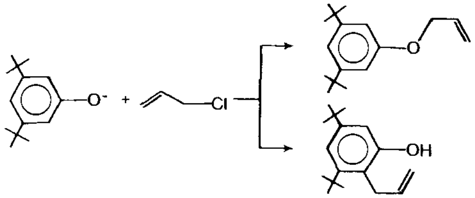
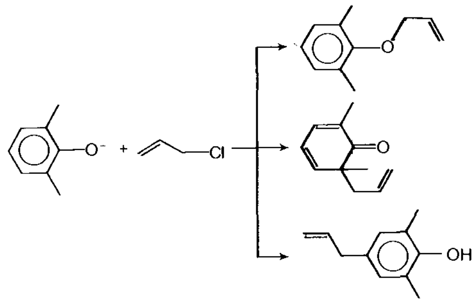
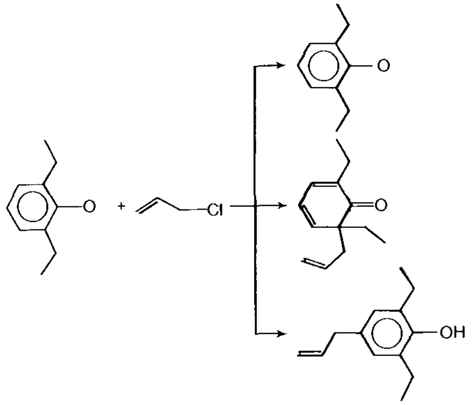
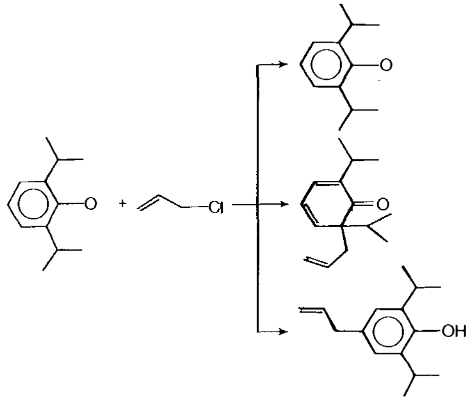
48		H_2O	50			0	
						−2.2	236
49		H_2O	25			0	236
						−2.0	
						−3.6	
50		H_2O	25			0	236
						−5.7	
						−7.6	
51		H_2O	25	6	7	0	236
						−3.5	
						−7.5	
52		H_2O				0	
						−6.2	236

TABLE III (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	$\Delta\Delta V^*$, cm^3/mol	Ref	Remarks
53		H_2O	25			0 −3.0 −2.4	236	
54		H_2O	25			0 −2.0 −3.0	236	
55		H_2O	25			0 −1.9 −4.9	236	

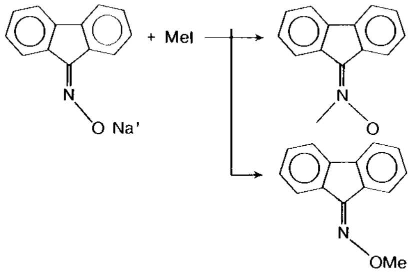
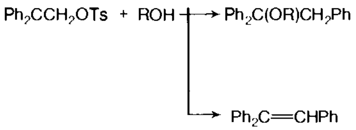
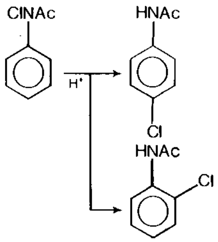
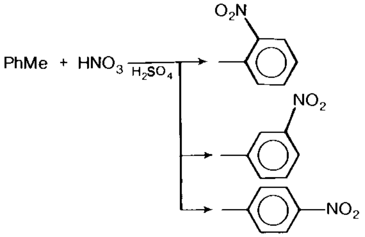
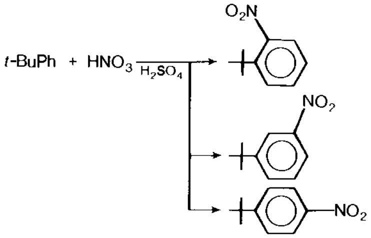
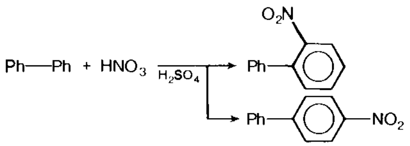
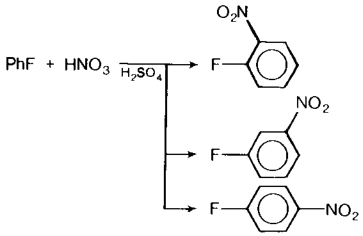
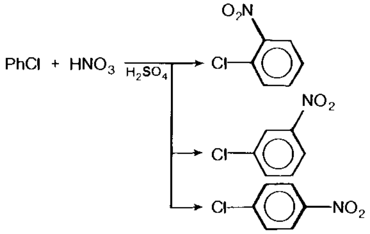
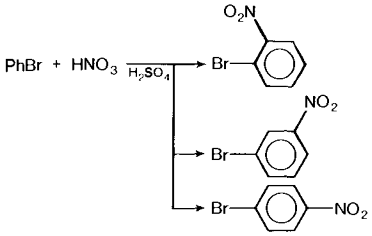
56		*t*-BuOH–MeCN	25	1.4	4	0	237	*c* MeCN 33 v%
						<0		
57		MeOH–dioxane	90	5	2	0	148	*d*
		EtOH–dioxane	90	5	2	0	148	
		i-PrOH–dioxane	90	5	2	0	148	
		MeOH–dioxane				+13^e		[MeOH] = 8 M
		EtOH–dioxane				+7^e		[EtOH] = 8 M
		i-PrOH–dioxane				+12^e		[PrOH] = 8 M
58		H_2O		2.1	3	0	36	
			15			+4.0		
			25			+3.3		
			35			+2.4		
59	$PhH + HNO_3 \xrightarrow[H_2SO_4]{} PhNO_2$	AcOH	45			0	238	
				2	3	+2.1		
				2	3	+1.2		
				2	3	+3.2		
				2	3	+0.6		
				2	3	+1.6		
				2	3	+3.5		

TABLE III (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	$\Delta\Delta V^*$, cm^3/mol	Ref	Remarks
				2	4	+6.2		
				2	4	+6.6		
				2	3	+0.1		
				2	3	−3.1		
				2	3	+0.4		
				2	3	−1.2		
				2	3	−5.0		
				2	3	−0.5		
				2	3	−2.0		
				2	3	−5.2		
				2	3	−1.1		

[a] Product yields in the decomposition of *tert*-butyl phenylperacetate in cumene and chlorobenzene at 1 and 4000 atm are also given in this paper. [b] Estimated from the optical rotation of the product by the present authors. [c] The free oximate ion and the ion pair exist in equilibrium under the reaction conditions. At high dilution O-alkylation decreases with pressure. [d] The reaction of alkoxide ion with the same substrate was studied. See ref 148. [e] Calculated from the product ratios by the present authors. [f] Men = (−)-menthyl.

An extensive investigation of the allylation of phenoxide ions was aimed at the question of the generality of the proposition that sterically hindered reactions are enhanced more than unhindered ones. The reaction of the parent phenol under pressure had revealed that the transition state for O-alkylation is more voluminous than that for ortho alkylation, which in turn is larger than that for the formation of the para isomer; this had been interpreted in terms of a need for desolvation of the nucleophile prior to displacement. The same trend is visible in the series of 4-mono-, and 3,5- and 2,6-disubstituted phenols; however, the special effects one might have expected on steric grounds do not show up. Thus, while $V_O{}^* - V_p{}^{\ddagger}$ equals 7.6 cm^3/mol in the parent case, it is 7.5 cm^3/mol in the presence of 3,5-diisopropyl substitution! The other results lead to similar conclusions, and one can only summarize by saying that the large, special pressure effect in hindered Menshutkin reactions has to date found no parallel in other chemistry.

The methylation of fluorenone oxime takes place in ion-pair stages, free ions producing the *O*-methyl derivative and ion pairs the N isomer. As a result one might expect that O-methylation would be favored under pressure, opposite to the result with the phenoxides. This was indeed observed.[237]

A comparison of the pressure effects of nitration of benzene and of substituted benzenes has been carried out.[238] Again, no systematic favoring of the more hindered products was observed. Certain regularities do appear in $\Delta\Delta V^{\ddagger}$ as a function of substituent; these may have the same origin as did Zhulin's results referred to above.

IV. Activation Volumes of Inorganic Reactions

A. The Data in Tabular Form (Table IV)

TABLE IV. Activation Volumes for Reactions of Inorganic Compounds[a]

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm^3/mol	Ref	Remarks
1	$K_3[Co(ox)_3]\cdot xH_2O \rightarrow$ racemic mixture	solid	23–28	44.4	8	−1.54	239	$P \geq 8$ kbars
2		solid	23–28	46.6	7	−1.79	239	$P \geq 16.1$ kbars
3	$[Ni(phen)_3](ClO_4)_2\cdot 2H_2O \rightarrow$ racemic mixture	solid	21	42	10	−1.00	240	$P \geq 10.3$ kbars
4	$(-)$-$K_3[Cr(ox)_3] \rightarrow (\pm)$-$K_3[Cr(ox)_3]$	H_2O	15.0	1.4	5	−16.3	241	$[HCl] = 0.05$ M
5	$(+)$-$K[Cr(ox)_2(phen)] \rightarrow (\pm)$-$K[Cr(ox)_2(phen)]$	H_2O	25.0	1.4	5	−12.3	241	$[HCl] = 0.05$ M
6	$(+)$-$K[Cr(ox)_2(bpy)] \rightarrow (\pm)$-$K[Cr(ox)_2(bpy)]$	H_2O	25.0	1.4	5	−12.0	241	$[HCl[= 0.05$ M
7	$(+)$-$[Cr(ox)(phen)_2]ClO_4 \rightarrow (\pm)$-$[Cr(ox)(phen)_2]ClO_4$	H_2O	45.0	2.1	4	−1.5	241	$[HCl] = 0.05$ M
8	$(+)$-$[Cr(ox)(bpy)_2]PF_6 \rightarrow (\pm)$-$[Cr(ox)(bpy)_2]PF_6$	H_2O	45.0	2.1	4	−1.0	241	$[HCl] = 0.05$ M
9	$(-)$-$[Cr(phen)_3](ClO_4)_3 \rightarrow (\pm)$-$[Cr(phen)_3](ClO_4)_3$	H_2O	75.0	2.1	4	+3.3	241	$[HCl] = 0.05$ M
10	$(-)$-$[Cr(bpy)_3](ClO_4)_3 \rightarrow (\pm)$-$[Cr(bpy)_3](ClO_4)_3$	H_2O	75.0	2.1	4	+3.4	241	$[HCl] = 0.05$ M
11	*trans*-$Co(en)_2(OH_2)_2{}^{3+} \rightarrow$ *cis*-$Co(en)_2(OH_2)_2{}^{3+}$	H_2O	34.5	1.0	5	+14.3	242	$[HClO_4] = 0.05$ M
12		H_2O	46.0	0.9	5	+14.2	242	$[HClO_4] = 0.05$ M
13		H_2O	48.0	1.0	5	+14.2	242	$[HClO_4] = 0.5$ M
14		H_2O	45.0	1.4	7	+12.6	242	$[HClO_4] = 1$ M
15		H_2O	45.0	1.0	5	+13.7	242	$[NaClO_4] = 1$ M
16		H_2O	50.5	1.0	5	+13.7	242	$[HClO_4] = 1$ M
17	*trans*-$Cr(ox)_2(OH_2)_2{}^- \rightarrow$ *cis*-$Cr(ox)_2(OH_2)_2{}^-$	H_2O–THF	25	2.5	9	−16	243	50–100 wt % H_2O
18		H_2O–MeOH	25	2.5	9	−16	243	50–100 wt % H_2O
19		H_2O	25	2.5	9	−10	243	0.2 M $Ca(NO_3)_2$
20		H_2O	25	2.5	9	−5.5	243	0.2 M $HClO_4$
21	β-$Co(edda)tn^+ \rightarrow \alpha$-$Co(edda)tn^+$	H_2O	58.6	3	4	+14[b]	244	0.2 M carbonate buffer
22	β-$Co(edda)en^+ \rightarrow \alpha$-$Co(edda)en^+$	H_2O	63.6	3	4	+20.0[b]	244	0.2 M carbonate buffer
23	*trans*-$Co(en)_2(SeO_3)OH_2{}^+ \rightarrow$ *cis*-$Co(en)_2(SeO_3)OH_2{}^+$	H_2O	15			+7.6	246	
24	$Co(en)_3{}^{2+} + {}^*Co(en)_3{}^{3+} \rightarrow Co(en)_3{}^{3+} + {}^*Co(en)_3{}^{2+}$	H_2O	65			−19.8	246	$\mu = 0.5$ M $(ClO_4{}^-)$
25	$Fe(OH_2)_6{}^{2+} + {}^*Fe(OH_2)_6{}^{3+} \rightarrow Fe(OH_2)_6{}^{3+} + {}^*Fe(OH_2)_6{}^{2+}$	H_2O	2	2		−12.2[c]	246	
26		H_2O	2	2		−0.4[d]	246	
27	$Cr(OH_2)^{2+} + Cr(OH_2)_3OH^{2+} \rightarrow Cr(OH_2)^{3+} + Cr(OH_2)_5OH^+$	H_2O	25			+4.2	246	$\mu = 0.5$ M $(ClO_4{}^-)$
28	$Tl(OH_2)_6{}^+ + {}^*Tl(OH_2)_6{}^{3+} \rightarrow Tl(OH_2)_6{}^{3+} + {}^*Tl(OH_2)_6{}^+$	H_2O	30	2	4	−13.2	247	4.5 M $HClO_4$
29		H_2O	30	2.7	7	−13.2	247	1.1 M $HClO_4$
30	$TaBr_5OMe_2 + Me_2O^* \rightarrow TaBr_5OMe_2{}^* + Me_2O$	CH_2Cl_2	13.0	1.8	6	+30.5	248	By ^1H NMR
31	$TaBr_5SMe_2 + {}^*Me_2S \rightarrow TaBr_5SMe_2{}^* + Me_2S$	CH_2Cl_2	12.5	2.1	6	−12.6	248	By ^1H NMR
32	$Co(NH_3)_5(DMSO^{3+}$-$d_6) + DMSO \rightarrow Co(NH_3)_5DMSO + DMSO$-$d_6$	DMSO	45	2	4	+10.0	249	
33	$Cr(DMSO)_6{}^{3+} + 6DMSO$-$d_6 \rightarrow Cr(DMSO$-$d_6)_6{}^{3+} + 6DMSO$	DMSO-d_6	75	3	6	−11.3	250	

TABLE IV (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
34	$Cr(DMF\text{-}d_7)_6^{3+} + 6DMF \rightarrow Cr(DMF)_6^{3+} + 6DMF\text{-}d_7$	DMF	65.1	4	8	−6.3	251	
35	*trans*-$Co(en)_2(^{18}OH_2)_2^{3+} \rightarrow$ *trans*-$Co(en)_2(OH_2)_2^{3+}$	H_2O	34.8	3	7	+5.9	252	$[HClO_4] = 0.8$ M, $\mu = 2.0$ m
36	*trans*-$Co(en)_2(SeO_3H)^*OH_2^{2+} + H_2O \rightarrow$ *trans*-$Co(en)_2(SeO_3H)\text{-}OH_2^{2+} + H_2O^*$	H_2O	25			+8.0	246	
37	$Cr(OH_2)_6^{3+} + H_2O^* \rightarrow Cr(OH_2)_5\text{-}^*OH_2^{+} + H_2O$	H_2O^*	45	2.5	7	−9.3	253	$[HClO_4] = 0.1$ M
38	$Cr(NH_3)_5{}^*OH_2^{3+} + H_2O \rightarrow Cr(NH_3)_5OH_2^{3+} + H_2O^*$	H_2O	25	2.1	5	−5.8	254	$[HClO_4] = 0.1$ M
39	$Ir(NH_3)_5{}^*OH_2^{3+} + H_2O \rightarrow Ir(NH_3)_5OH_2^{3+} + H_2O^*$	H_2O	70.5	4	6	−3.2	255	$[HClO_4] = 0.01$ M
40	$Rh(NH_3)_4{}^*OH_2^{3+} + H_2O \rightarrow Rh(NH_3)_5OH_2^{3+} + H_2O^*$	H_2O	35	2.1	5	−4.1	254	$[HClO_4] = 0.01$ M
41	$Co(NH_3)_5NCS^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + NCS^-$	H_2O	88	2.6	3	−4.0	256	$\mu = 0.1$ M (ClO_4^-)
42	$Co(NH_3)_5NO_3^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + NO_3^-$	H_2O	25	4.1	18	−6.3	257	$\Delta V = -7.2$ cm^3/mol^e
							256	$[LiClO_4] = 0.1$ M
43	$Co(NH_3)_5Br^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + Br^-$	H_2O	25	4.1	7	−9.2	257	$\Delta V = -10.8$ cm^3/mol^e
							256	$[LiClO_4] = 0.1$ M
44		H_2O	30	2.9	4	+2.5	258	*f*
45	$Co(NH_3)_5Cl^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + Cl^-$	H_2O	25	4.1	8	−10.6	257	$\Delta V = -11.6$ cm^3/mol^e
							256	$[LiClO_4] = 0.1$ M
46		H_2O	59.8	1.4	4	−7.5	259	$[HClO_4] = 0.1$ M
47	$Co(NH_3)_5SO_4^{+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + SO_4^{2-}$	H_2O	25	4.1	6	−18.5	257	$\Delta V = -19.2$ cm^3/mol^e
							256	$[LiClO_4] = 0.1$ M
48	$Co(NH_3)_5N_3^{2+} + H_2O \rightarrow Co(NH_3)_5OH_2^{3+} + N_3^-$	H_2O	75	4.1	10	+16.8	256	$[LiClO_4] = 0.1$ M
49	*trans*-$Co(en)_2Cl_2^{+} + H_2O \rightarrow Co(en)_2(OH_2)Cl^{2+} + Cl^-$	H_2O	19	2.5	4	+11.6	260	At pH 3.3
50		H_2O	25	2.5	4	+11.0	260	At pH 3.3
51		H_2O	40	2.5	4	+9.45	260	At pH 3.3
52		H_2O	55	2.5	4	+7.87	260	At pH 3.3
53	$Cr(OH_2)_5NO_3^{2+} + H_2O \rightarrow Cr)OH_2)_6^{3+} + NO_3^-$	H_2O	25	2	5	−12.7	261	$[HClO_4] = 1.1$ M
54	$Cr(OH_2)_5I^{2+} + H_2O \rightarrow Cr(OH_2)_6^{3+} + I^-$	H_2O	25	2.5	7	−5.4^c	262	$\Delta V = -3.3$ cm^3/mol 1 m $HClO_4$–ClO_4^-
55		H_2O	25	2.5	7	−1.6^d	262	$\Delta V = -3.3$ cm^3/mol 1 m $HClO_4$–ClO_4^-
56	$Cr(NH_3)_5NCS^{2+} + H_2O \rightarrow Cr(NH_3)_5OH_2^{3+} + NCS^-$	H_2O	79.8	1.4	4	−8.6	259	$[HClO_4] = 0.1$ M
57	$Cr(NH_3)_2(NCS)_4^- + H_2O \rightarrow Cr(NH_3)_2(NCS)_3OH_2 + NCS^-$	H_2O	50	2.1	4	−2.4	263	$[HClO_4] = 0.006$ M
58	$Cr(NCS)_6^{3-} + H_2O \rightarrow Cr(NCS)_5OH_2^{2-} + NCS^-$	H_2O	50	2.1	5	+16	263	$[HClO_4] = 0.006$ M
59	$Cr(NH_3)_5I^{2+} + H_2O \rightarrow Ce(NH_3)_5OH_2^{3+} + I^-$	H_2O	25	3.5	7	−9.4	264	$\Delta V = -6.0$ cm^3/mol $[NH_4ClO_4] = 0.1$ m
60	$Cr(NH_3)_5Br^{2+} + H_2O \rightarrow Cr(NH_3)_5OH_2^{3+} + Br^-$	H_2O	25	4	9	−10.2	264	$\Delta V = -7.2$ cm^3/mol $[NH_4ClO_4] = 0.1$ m
61	$Cr(NH_3)_5Cl^{2+} + H_2O \rightarrow Cr(NH_3)_5OH_2^{3+} + Cl^-$	H_2O	25	3.1	6	−10.8	264	$\Delta V = -8.4$ cm^3/mol $[NH_4ClO_4] = 0.1$ m
62	$Fe(phen)_3^{2+} + 6H_2O \rightarrow Fe(OH_2)_6^{2+} + 3phen$	H_2O	35	1.4	3	+15.4	265	$[H_2SO_4] = 1$ M
63	$Fe(5\text{-}NO_2\text{-}phen)_3^{2+} + 6H_2O \rightarrow Fe(OH_2)_6^{2+} + 3(5\text{-}NO_2\text{-}phen)$	H_2O	35	1.7	6	+17.9	265	$[H_2SO_4] = 1$ M
64	$Fe(4,7\text{-}Me_2\text{-}phen)_3^{2+} + 6H_2O \rightarrow Fe(OH_2)_6^{2+} + 3(4,7\text{-}Me_2\text{-}phen)$	H_2O	35	1.4	5	+11.6	265	$[H_2SO_4] = 1$ M
65	$PtCl_4^{2-} + H_2O \rightarrow PtCl_3(OH_2)^- + Cl^-$	H_2O	25	1.2	8	−17	266	
66	$Pt(NH_3)Cl_3^- + H_2O \rightarrow Pt(NH_3)Cl_2(OH_2) + Cl^-$	H_2O	26	1.1	9	−14	266	
67	$Cr(OH_2)_6^{3+} + OH^- \rightarrow H_2O + Cr(OH_2)_5OH^{2+}$	H_2O				−3.8	267	
68	$Co(NH_3)_5Cl^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + Cl^-$	H_2O	35	1.5	4	+33.4	268	Carbonate buffer; k corrected for p effect on D
69	$Co(NH_3)_5SO_4^{+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + SO_4^{2-}$	H_2O	15			+19.5	246	

TABLE IV (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm^3/mol	Ref	Remarks
70	$Co(NH_3)_5SeO_3^+ + OH^- \rightarrow Co(NH_3)_5OH^{2+} + SeO_3^{2-}$	H_2O	25			−17.1	246	
71	$Co(NH_3)_5PO_4 + OH^- \rightarrow CO(NH_3)_5OH^{2+} + PO_4^{3-}$	H_2O	55			+28.9	246	
72	$Pt(dien)Br^+ + OH^- \rightarrow Pt(dien)OH^+ + Br^-$	H_2O	25	1.5	8	−18.0[l]	269	$[OH^-] = 0.01$ M $\mu = 0.2$ M ($NaClO_4$)
73	$Co(en)_2(OH_2)_2^{3+} \cdot HC_2O_4^- \rightarrow Co(en)_2ox^+ + H^+$	H_2O				+4.7	246	
74	*cis*-$Co(en)_2(OH_2)_2^{3+} + H_2C_2O_4 \rightarrow Co(en)_2C_2O_4^+ + 2H_2O^+$	H_2O	60.0	1.5	4	+4.8	270	*g*, $[HNO_3] = 0.5$ M, $\mu = 2.0$ M ($NaNO_3$)
75	*cis*-$Co(en)_2(OH)OH_2^{2+} + C_2O_4^{2-} \rightarrow Co(en)_2(OH)C_2O_4 + H_2O$		30	1.6	4	+4.6	270	*h*, pH 7.2, Trizma buffer, $\mu = 0.32$ M ($NaNO_3$)
76	$Co(en)_2(OH)C_2O_4 + H^+ \rightarrow Co(en)_2C_2O_4^+ + H_2O$	H_2O	50.0	1.4	5	0	270	*i*, pH 7.8, Trizma buffer $\mu = 0.37$ M ($NaNO_3$)
77	$Co(en)_2(ox)OH_2^+ \rightarrow Co(en)_2ox^+ + H_2O$	H_2O				+3.5	246	Ring closure
78	$Cr(OH_2)_6^{3+} + ox \rightarrow Cr(OH_2)_4ox^+ + 2H_2O$	H_2O	25	1.5	7	−2.2	271	At pH 2.7, $\mu = 1$ M
79	$Cr(OH_2)_4ox^+ + ox \rightarrow Cr(OH_2)_2(ox)_2^- + 2H_2O$	H_2O	25	2	8	−8.2	271	At pH 2.7, $\mu = 1$ M
80	$Cr(OH_2)_2(ox)_2^- + ox \rightarrow Cr(ox)_3^{3-} + 2H_2O$	H_2O	25	2	8	−10.0	271	At pH 2.7, $\mu = 1$ M
81	$Fe^{3+} + NCS^- \rightarrow FeNCS^{2+}$	H_2O	25	1.4	3	+5 ~+6	272	P-jump, *j*
82		H_2O	25	2	5	−4.9 ~+4.4	273	T-jump, $\mu = 0.2$ m ($NaClO_4$), $\Delta V = +8.9$ cm^3/mol
83	$FeOH^{2+} + NCS^- \rightarrow Fe(OH)NCS^+$	H_2O	25	2	5	+7.1	273	T-jump, $\mu = 0.2$ m ($NaClO_4$)
84	$Fe^{3+} + Cl^- \rightarrow FeCl^{2+}$	H_2O	25	2.8	5	−4.5	274	T-jump, *c* $\mu = 1.5$ M ($NaClO_4$)
85	$FeCl^{2+} \rightarrow Fe^{3+} + Cl^-$	H_2O	25	2.8	5	−9.2	274	T-jump, *c* $\mu = 1.5$ M ($NaClO_4$), $\Delta V = -4.6$ cm^3/mol
86	$Fe^{3+} + Cl^- \rightarrow FeCl^{2+}$	H_2O	25	2.8	5	+6.8	274	T-jump, $\mu = 1.5$ M ($NaClO_4$), d, *k*
87	$FeCl^{2+} \rightarrow Fe^{3+} + Cl^-$	H_2O	25	2.8	5	+2.2	274	T-jump, $\mu = 1.5$ M ($NaClO_4$), *d*, *l*
88	$[Fe(CN)_5(3,5\text{-}Me_2\text{-}py)]^{3-} + CN^- \rightarrow [Fe(CN)_6]^{4-} + 3,5\text{-}Me_2\text{-}py$	H_2O	25	1.4	5	+20.5	275	$\mu = 0.5$ M ($NaClO_4$)
89	$[Fe(CN)_5(3,5\text{-}Me_2\text{-}py)]^{3-} + pz \rightarrow [Fe(CN)_5(pz)]^{3-} + 3,5\text{-}Me_2\text{-}py$	H_2O	25	1.4	5	+21.2	275	$\mu = 0.5$ M ($NaClO_4$)
90	$[Fe(CN)_5(3,5\text{-}Me_2\text{-}py)]^{3-} + imH \rightarrow [Fe(CN)_5(imH)]^{3-} + 3,5\text{-}Me_2\text{-}py$	H_2O	25	1.4	5	+20.3	275	$\mu = 0.5$ M ($NaClO_4$)
91	$[Fe(CN)_5(3\text{-}CN\text{-}py)]^{3-} + CN^- \rightarrow [Fe(CN)_6]^{4-} + 3\text{-}CN\text{-}py$	H_2O	25	1.4	5	+20.6	275	$\mu = 0.5$ M ($NaClO_4$)
92	$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$	H_2O	35	1.5	4	+33.4	268	Carbonate buffer
93	$Co^{2+} + pada \rightarrow Co(pada)^{2+}$	H_2O	25	2.1	6	+7.2	276 277	T-jump, $\mu = 0.1$ M ($NaNO_3$), $\Delta V = +5.8$ cm^3/mol
94		Glycerol	20	2.8	6	+9.6	278	T-jump
95		Glycerol	43	2.8	6	+7.6	278	T-jump
96	$Co(pada)^{2+} \rightarrow Co^{2+} + pada$	Glycerol	43	2.8	6	+7.9[m]	278	T-jump
97	$Co^{2+} + NH_3 \rightarrow CoNH_3^{2+}$	H_2O	10	1.4	5	+4.8	276	T-jump, $\mu = 0.1$ M (NH_4NO_3), $\Delta V = -8.6$ cm^3/mol
98	$Co(gly)^+ \rightarrow Co^{2+} + gly$	H_2O	25	2.8	6	+0.3	279	T-jump, $\mu = 0.2$ M ($NaNO_3$)
99	$Co^{2+} + gly \rightarrow Co(gly)^+$	H_2O	25	2.8	6[n]	+8	279	$\Delta V = +7.3$ cm^3/mol
100	CBM[o] + $I^- \rightarrow$ CBM-I	H_2O	25	1.4	5	+5.5	280	T-jump, $\mu = 0.2$ M (KNO_3), $\Delta V = -5.8$ cm^3/mol
101	CBM-I $\rightarrow$ CBM + I^-	H_2O	25	1.4	5	+11.5	280	T-jump, $\mu = 0.2$ M (KNO_3)
102	$Ni(tren)^{2+} + pada \rightarrow Ni(tren)(pada)^{2+}$	H_2O	20	2.7	6	+2.9	281	T-jump, $\mu = 0.3$ M ($NaNO_3$)
103	$Ni(tren)(pada)^{2+} \rightarrow Ni(tren)^{2+} + pada$	H_2O	20	2.7	6	+5.2	281	T-jump, $\mu = 0.3$ M ($NaNO_3$)
104	$Ni(gly)^+ \rightarrow Ni^{2+} + gly$	H_2O	25	2.8	6	+8.0	279	P-jump, $\mu = 0.2$ M ($NaNO_3$)
105	$Ni^{2+} + gly \rightarrow Ni(gly)^+$	H_2O	25	2.8	6[n]	+10	279	$\Delta V = +2.1$ cm^3/mol
106	$Ni(CO)_4 + (EtO)_3P \rightarrow Ni(CO)_3P(OEt)_3 + CO$	C_7H_{16}	0	1.4	5	+8	282	

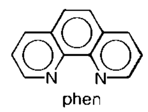
TABLE IV (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	ΔV^*, cm³/mol	Ref	Remarks
107	Ni^{2+} + pada → $Ni(pada)^{2+}$	H_2O	49	2.1	6	+7.7	276 277	T-jump μ = 0.1 M ($NaNO_3$), ΔV = +0.9 cm³/mol
108	$Ni^{2+} + NH_3 \rightarrow NiNH_3^{2+}$	H_2O	30	1.4	7	+6.0	276 277	T-jump μ = 0.1 M (NH_4NO_3), ΔV = −2.3 cm³/mol
109	Ni^{2+} + mu → $Ni(mu)^+$	H_2O	25	1.5	4	+12.2	283	T-jump, μ = 0.1 M ($NaClO_4$), ΔV = +22.6 cm³/mol
110	$Ni(mu)^+ \rightarrow Ni^{2+}$ + mu	H_2O	25	1.5	4	−10.4	283	T-jump, μ = 0.1 M ($NaClO_4$)
111	Ni(edda) + pada → Ni(edda)(pada)	H_2O	25	2.7	6	+5.2	281	T-jump, μ = 0.3 M ($NaNO_3$)
112	$Ni(nta)^-$ + pada → $Ni(nta)(pada)^-$	H_2O	25	2.7	6	+6.9	281	T-jump, μ = 0.3 M ($NaNO_3$)
113	$Ni(nta)(pada)^- \rightarrow Ni(nta)^-$ + pada	H_2O	25	2.7	6	+7.0	281	T-jump, μ = 0.3 M ($NaNO_3$)
114	$Ni(dien)^{2+}$ + pada → Ni(dien)-$(pada)^{2+}$	H_2O	25	2.7	6	+4.2	281	T-jump, μ = 0.3 M ($NaNO_3$)
115	$Ni(dien)(pada)^{2+} \rightarrow Ni(dien)^{2+}$ + pada	H_2O	25	2.7	6	+3.6	281	T-jump, μ = 0.3 M ($NaNO_3$)
116	$Ni(trien)^{2+}$ + pada → Ni(trien)-$(pada)^{2+}$	H_2O	25	2.7	6	+2.6	281	T-jump, μ = 0.3 M ($NaNO_3$)
117	$Ni(trien)(pada)^{2+} \rightarrow Ni(trien)^{2+}$ + pada	H_2O	25	2.7	6	+5.9	281	T-jump, μ = 0.3 M ($NaNO_3$)
118	$Zn(gly)^+ \rightarrow Zn^{2+}$ + gly	H_2O	10	2.8	6	+2.0	279	T-jump, μ = 0.2 M ($NaNO_3$)
119	Zn^{2+} + gly → $Zn(gly)^+$	H_2O	10	2.8	6^n	+7	279	ΔV = +5.2 cm³/mol
120	Zn^{2+} + pada → $Zn(pada)^{2+}$	Glycerol	20	2.8	6	+12.2	278	T-jump
121	$Zn(pada)^{2+} \rightarrow 2n^{2+}$ + pada	Glycerol	20	2.8	6	$+13.1^m$	278	T-jump
122	$Cu(gly)^+ \rightarrow Cu^{2+}$ + gly	H_2O	25	2.8	6	−1.7	279	T-jump, μ = 0.2 M ($NaNO_3$)
123	Cu^{2+} + gly → $Cu(gly)^+$	H_2O	25	2.8	6^n	+12	279	ΔV = +13.4 cm³/mol
124	$Mo(CO)_6 + Ph_3P \rightarrow Mo(CO)_5PPh_3 + CO$	Me_2CHCH_2-CMe_3	103	1.4	5	+10	282	
125	$Cr(CO)_6 + Ph_3P \rightarrow Cr(CO)_5PPh_3 + CO$	c-C_6H_{12}	124	1.4	5	+15	282	
126	$W(CO)_6 + Bu_3P \rightarrow W(CO)_5PBu_3 + CO$	c-C_6H_{12}	120	1.4	5	−10	282	
127	$Cr(CO)_6 + N_3^- \rightarrow Cr(CO)_5NCO^- + N_2$	Me_2CO	24	1.4	5	0	282	
128	$Pd(Et_4dien)Cl^+ + N_3^- \rightarrow Pd(Et_4dien)N_3^+ + Cl^-$	H_2O	25			−14.3	284	*p*
129	$Pd(Et_4dien)Cl^+ + I^- \rightarrow Pd(Et_4dien)I^+ + Cl^-$	H_2O	25			−13.8	284	*p*
130	$Pd(Et_4dien)Br^+ + N_3^- \rightarrow Pd(Et_4dien)N_3^+ + Br^-$	H_2O	25			−11.4	284	*p*
131	$Pd(Et_4dien)Br^+ + I^- \rightarrow Pd(Et_4dien)I^+ + Br^-$	H_2O	25			−12.5	284	*p*
132	$Pd(Et_4dien)I^+ + N_3^- \rightarrow Pd(Et_4dien)N_3^+ + I^-$	H_2O	25			−10.8	284	*p*
133	$Pd(Et_4dien)I^+ + Br^- \rightarrow$	H_2O	25			−10.6	284	*p*
134	$Pd(Et_4dien)Br^+ + I^-$	H_2O	40			−10.2	284	*p*
135		DMSO	40			−9.2	284	*p*
136		DMF	40			−7.9	284	*p*
137		MeOH	40			−11.7	284	*p*
138	$PtCl_4^{2-} + H_2O \rightarrow PtCl_3(OH_2)^- + Cl^-$	H_2O	25	1.2	8	−17	266	
139	$Pt(NH_3)Cl_3^- + H_2O \rightarrow Pt(NH_3)Cl_2(OH_2) + Cl^-$	H_2O	26	1.1	9	−14	266	
140	$Pt(dien)Br^+ + N_3^- \rightarrow Pt(dien)N_3^+ + Br^-$	H_2O	25	1.5	6	-15^l	269	ΔV = −1.2 cm³/mol, μ = 0.2 M ($NaClO_4$)
141		H_2O	25	1.5	6	-8.5^q	269	μ = 0.2 M ($NaClO_4$)
142	$Pt(dien)Br^+ + py \rightarrow Pt(dien)py^{2+} + Br^-$	H_2O	25	1.5	6	$<0^t$	269	ΔV = +23.5 cm³/mol, μ = 0.2 M ($NaClO_4$)
143		H_2O	25	1.5	6	-7.7^q	269	μ = 0.2 M ($NaClO_4$)
144	$Pt(dien)Br^+ + OH^- \rightarrow Pt(dien)OH^+ + Br^-$	H_2O	25	1.5	8	-18.0^t	269	$[OH^-]$ = 0.01 M, μ = 0.2 M ($NaClO_4$)
145	$Pt(dien)Br^+ + NO_2^- \rightarrow Pt(dien)NO_2^+ + Br^-$	H_2O	25	1.5	6	-18^t	269	ΔV = +0.9 cm³/mol, μ = 0.2 M ($NaClO_4$)
146		H_2O	25	1.5	6	-6.4^q	269	μ = 0.2 M ($NaClO_4$)
147	$Pt(dien)Cl^+ + N_3^- \rightarrow Pt(dien)N_3^+ + Cl^-$	H_2O	25	1.5	6	-17^t	269	ΔV = −2.7 cm³/mol, μ = 0.2 M ($NaClO_4$)

TABLE IV (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm³/mol	Ref	Remarks
148		H_2O	25	1.5	6	-8.2^q	269	μ = 0.2 M ($NaClO_4$)
149	$Pt(dien)I^+ + N_3^- \rightarrow Pt(dien)N_3^+ + I^-$	H_2O	25	1.5	6	-18^l	269	ΔV = +0.8 cm³/mol, μ = 0.2 M ($NaClO_4$)
150		H_2O	25	1.5	6	-8.2^q	269	μ = 0.2 M ($NaClO_4$)
151	$Pt(dien)N_3^+ + I^- \rightarrow Pt(dien)I^+ + N_3^-$	H_2O	25	1.5	6	$<0^l$	269	ΔV = −0.8 cm³/mol, μ = 0.2 M ($NaClO_4$)
152		H_2O	25	1.5	6	-12.2^q	269	μ = 0.2 M ($NaClO_4$)
153	$Pt(dien)N_3^+ + NCS^- \rightarrow Pt(dien)NCS^+ + N_3^-$	H_2O	25	1.5	6	$<0^l$	269	ΔV = +11.8 cm³/mol, μ = 0.2 M ($NaClO_4$)
154		H_2O	25	1.5	6	-7.3^q	269	μ = 0.2 M ($NaClO_4$)
155	*trans*-$Pt(PEt_3)_2Cl_2 + Br^- \rightarrow$ *trans*-$Pt(PEt_3)_2ClBr + Cl^-$	MeOH	25	1	4	-27^r	285	[Bu_4NBr] = 0.1 M
156		Aq MeOH	25	0.5	4	-28^t	285	H_2O mol %, μ = 0.1 M ($LiClO_4$)
157		Aq MeOH	25	0.5	4	-28^q	285	H_2O 60 mol %, μ = 0.1 M ($LiClO_4$)
158	*trans*-$IrCl(CO)(PPh_3)_2 + MeI \rightarrow IrClI(CO)(PPh_3)_2Me$	PhMe	25	1	5	−28.2	286	
159		PhH	25	0.8	4	−29.8	286	
160		$CHCl_3$	25	1	5	−19.2	286	
161		PhCl	25	1	6	−23.6	286	
162		Me_2CO	25	1	5	−20.5	286	
163		DMF	25	1	4	−15.2	286	
164	*trans*-$IrCl(CO)(PPh_3)_2 + H_2 \rightarrow IrClH_2(CO)(PPh_3)_2$	DMF	10	1.5	6	−18.0	287	
165		PhCl	10	1.5	6	−19.0	287	
166		PhMe	10	1.5	6	−20.4	287	
167	$Me_2Hg + HCl \rightarrow MeHgCl + CH_4$	H_2O	25.0	1.0	4	−22.0	288	[HCl] = 0.01 ~ 0.10 M
168	$Me_2Hg + HBr \rightarrow MeHgBr + CH_4$	H_2O	25.0	1.0	4	−37	288	[HBr] = 0.01 ~ 0.17 M
169	$Ce(DCTA)^- + Er^{3+} \rightarrow Ce^{3+} + Er(DCTA)^-$	H_2O	25.0	1.5	6	−3.2	289	pH ≃ 5.3, μ = 0.1 M (KCl)
170	$Eu(DCTA)^- + Er^{3+} \rightarrow Eu^{3+} + Er(DCTA)^-$	H_2O	25.0	1.5	6	−2.2	289	pH ≃ 3.9, μ = 0.1 M (KCl)
171	$Tb(EDTA)^- + Er^{3+} \rightarrow Tb^{3+} + Er(DCTA)^-$	H_2O	25.0	1.5	6	−4.7	289	pH ≃ 3.6, μ = 0.1 M (KCl)
172	$HNF_2 \xrightarrow{OH^-} N_2F_2 + F^- + H_2O$	Aq MeOH	15	4.1	5	$+7^s$	290	H_2O 93%, phosphate buffer, pH 7.42
173	$HNF_2 + OAc^- \rightarrow F^- +$ other products	H_2O	20	3.2	4	−17.6	290	Acetate buffer, pH 5.5

[a] Abbreviations: ox, $C_2O_4^{2-}$; en, $H_2NCH_2CH_2NH_2$; tn, $H_2NCH_2CH_2CH_2NH_2$; dien, $H_2NCH_2CH_2NHCH_2CH_2NH_2$; trien, $H_2NCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$; tren, $N(CH_2CH_2NH_2)_3$; gly, $H_2NCH_2COO^-$; edda, $^-OCONHCH_2CH_2NHCOO^-$; nta, $N(CH_2COO^-)_3$;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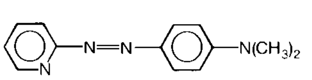

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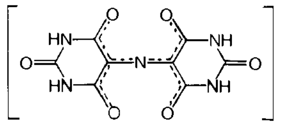

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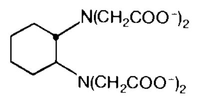

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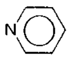
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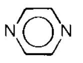
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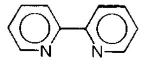
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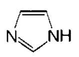
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[b] Corrected for pH change by pressure. [c] Acid-independent path. [d] Inversely acid-dependent path. [e] From data published by T. G. Spiro, A. Revesz, and J. Lee, *J. Am. Chem. Soc.*, **90**, 4000 (1968). [f] Catalyzed by Pb^{2+} (4×10^{-4} M) and sodium polyethylenesulfonate (10^{-3} M). [g] For k in the following scheme, obtained from the overall rates at various oxalic acid concentrations:

$$cis\text{-}Co(en)_2(OH_2)_2^{3+} + \left\{\begin{matrix} H_2C_2O_4 \rightleftarrows Co(en)_2(OH_2)_2^{3+} \cdot H_2C_2O_4 \\ \upharpoonleft\downharpoonright \qquad\qquad\qquad \upharpoonleft\downharpoonright \\ HC_2O_4^- \rightleftarrows Co(en)_2(OH_2)_2^{3+} \cdot HC_2O_4^- \end{matrix}\right\} \xrightarrow{k} Co(en)_2(OH_2)C_2O_4^+ \xrightarrow{fast} Co(en)_2C_2O_4^+$$

[h] For k' in the following scheme, obtained from the overall rates at various oxalate concentrations:

$$Co(en)_2(OH)OH_2^{2+} + C_2O_4^{2-} \rightleftarrows Co(en)_2(OH)OH_2^{2+} \cdot C_2O_4^{2-} \qquad Co(en)_2(OH)OH_2^{2+} \cdot C_2O_4^{2-} \xrightarrow{k'} Co(en)_2(OH)C_2O_4 + H_2O$$

[i] For k'' in the following scheme. The volume change for the preequilibrium is assumed to be +2.3 cm³/mol.

$$Co(en)_2(OH)C_2O_4 + H^+ \rightleftarrows Co(en)_2(OH_2)C_2O_4^+ \qquad Co(en)_2(OH_2)C_2O_4^+ \xrightarrow{k''} Co(en)_2C_2O_4^+ + H_2O$$

[j] ΔV is estimated to be +17.5 cm³/mol from the pressure effect on the equilibrium ([$HClO_4$] = 0.2 M], and +8 cm³/mol from dilatometric measurements [HNO_3] = 0.7 M). [k] The observed activation volume consists of two terms, $\Delta V_{OH} + \Delta V^*_{-2}$: $Fe^{3+} \rightarrow FeOH^{2+} + H^+$ (K_{OH}), $FeOH^{2+} + Cl^- \rightarrow Fe(OH)Cl^+$ (k_2). [l] The observed activation volume consists of two terms, $\Delta V_{OHCl} + \Delta V^*_{-2}$: $FeCl^{2+} \rightarrow FeOHCl^+ + H^+$ (K_{OHCl}), $Fe(OH)Cl^+ \rightarrow FeOH^{2+} + Cl^-$ (k_{-2}). [m] Calculated by the present authors assuming $\ln k = a + bP$. [n] Calculated from the equilibrium constant and the reverse reaction rate. [o] Cobalamin. [p] No k_2 path is observed. [q] Nucleophile dependent path: rate = k_1[complex] + k_2[nucleophile][complex]. [r] No k_1 path is observed. [s] After correction for pH change by pressure. [l] Nucleophile independent path.

B. Isomerizations (Entries 1–23)

Schmulbach[239] was the first chemist to study inorganic racemizations under pressure. He found only very small effects in the case of tris(oxalato)cobalt(III), and concluded that no bond making or breaking was involved. A concerted distortion from octahedral coordination to a trigonal prism was postulated, and this conclusion is surely correct. This mechanism (twist about a single atom) is not known in organic chemistry. Conversion of a tetrahedral nickel complex into the planar isomer has been achieved by Ferraro by means of high pressure;[245] a twist mechanism was postulated.

The racemization of compounds in which an asymmetric carbon atom is the source of the chirality always requires prior dissociation to a trivalent species. This mechanism also operates in many inorganic compounds, and it makes itself known by way of much larger activation volumes. Both negative and positive activation volumes are possible. Thus, Stranks argues that racemization of tris- and bis(oxalato)chromium(III) complexes takes place by a dissociative mechanism in which the volume decrease is produced by an increase in electrostriction,[241] and so does cis–trans isomerization according to Kelm,[243] but when the ligands are all neutral, as in the bisaquobis(ethylenediamine)cobalt(III) ion, $\Delta V^{\ddagger}$ is large and positive. These large values suggest that the radius of the complex ion does not change much as one of the ligands is ejected. Conversely, the large negative numbers *could* be indicative of prior expansion of the first coordination sphere to seven with the entry of a water molecule, but it is not easy to see why such a species would racemize much more easily than the initial state. On the other hand, the reduction in $\Delta V^{\ddagger}$ in the calcium nitrate or perchloric acid catalyzed isomerizations is readily understandable in terms of prior association of the oxalate ligand with another cation.

C. Redox Reactions (Entries 24–29)

In the oxidation of one complex ion by another, the question arises whether one of the ligands must first be removed (inner-sphere mechanism) or not (outer sphere). Halpern was the first chemist to approach this question by means of high-pressure arguments: $\Delta V^{\ddagger}$ should be positive if the former mechanism applies, and he found that this is indeed so in a number of known inner-sphere reductions of halo- and azidocobalt(III) complexes by aquoiron(II).[1] One somewhat surprising feature of both the detailed and preliminary results recorded by Halpern is that they showed only little or no correlation with total charge: some formal (+4) transition states are formed with volume decreases smaller than some (+1) analogs. Nevertheless, the argument has now been strengthened significantly by the finding that known outer-sphere redox reactions—in which the expected increase in electrostriction is not complicated by prior dissociation of a ligand—have fairly large negative activation volumes: among them are the electron exchange between thallous and thallic ions, between tris(ethylenediamine)cobalt(II) and -(III) complexes, and hexaaquoiron(II) and -(III); in the latter case both mechanisms compete, and there is a clear difference in $\Delta V^{\ddagger}$ between both.

D. Solvent Exchange (Entries 30–40)

These are surely the simplest substitution reactions of complex ions since the reaction volume is zero and the two solvent molecules involved in the exchange are equally bound (or free). As in the earlier groups of reactions, the important question is between prior association (expansion of the coordination sphere) and dissociation, with the corresponding activation volumes negative and positive, respectively.

The tantalum pentabromide adducts studied by Merbach[248] provide a striking example: dimethyl ether exchange, which is a known example of dissociative exchange, has an activation volume of +30 cm^3/mol, whereas dimethyl sulfide exchange, known to be of the associative type, has a $\Delta V^{\ddagger}$ of −12.6 cm^3/mol. The dimethyl sulfoxide adducts of cobalt(III) (+10 cm^3/mol) and chromium(III) (−11 cm^3/mol) are other such pairs. This difference carries over into other solvents as well; as in the isomerization reactions, one observes positive activation volumes with cobalt, negative ones with chromium. Iridium and rhodium resemble chromium in this respect.

E. Other Substitution Reactions (Entries 41–173)

When the leaving groups and nucleophiles are not the same but both are neutral molecules, the simple distinction between associative and dissociative mechanisms on the basis of the sign of the activation volume still holds, but when either or both are ions, the results are made more complex by changes in electrostriction.

The pentaamminecobalt(III) complexes are subject to hydrolysis which is accelerated by pressure, yet, in these reactions a dissociative mechanism has been assigned by Swaddle et al.[256] The reason for the volume decrease is the same as that advanced to explain the pressure-induced acceleration in organic reactions: there is an increase in total charges, and the corresponding electrostriction is what is observed. The sequence of accelerations $NCS^- < NO_3^- < Br^- < Cl^- \ll SO_4^{2-}$ is in good agreement with this assignment, as is the fact that $\Delta V^{\ddagger} \approx \Delta V$. Association, and entrance of water in the coordination sphere of cobalt, would also have produced an increase in rate, but these increases should not have been a sensitive function of the leaving group. The slight pressure retardation if lead ion and polyethylenesulfonate polymer are present is a somewhat special case that is not closely related to the reactions in water;[258] the azide reaction with its positive activation volume suggests that the azido ligand leaves as HN_3 rather than as N_3^-. The *trans*-dichlorocobalt(III) complex hydrolyzes with a positive activation volume. Before it can be concluded that this is a unique case of a pressure-retarded ionization process, further information is needed, however. Thus, the activation volume was derived from first-order rate constants, but it was also reported that these are pH dependent; yet, apparently no corrections were made for the change in pH with pressure. The pentaaquochromium(III) complexes are described by prior association with water, in analogy to the mechanism of water exchange.[262]

The very large, positive value of the hexathiocyanatochromium(III) complex is due to dissociation, and the delocalization and loss of electrostriction that is expected of a reaction of the type $3\theta \rightarrow 2\theta + \theta$. The bisammine analog has a small, negative value; the authors[263] ascribe this to a frontside displacement. The interpretation of the pressure effect on the hydrolysis rate of iron(III) complexes is straightforward.[264] The platinum complexes show unexpectedly great acceleration in the liberation of chloride, which Brower[266] attributes to association of two water molecules.

Tantalizingly large fluctuations occur in the brief list of reactions involving hydroxide ion. These variations bear little relation to the formal charge type of the reactions. Thus, the reaction with hexaaquochromium(III) has a negative activation volume even though neutralization formally occurs, whereas the phosphatocobalt(III) complex is greatly retarded, even though formally there is a great increase in total charges. As noted by Swaddle,[267] the complex ions should probably not be thought of as point charges. The phosphate complex, for example, is surely not a neutral species but rather a zwitterion with three negatively charged oxygen atoms at one end and pentaamminecobalt(III) at the other. The very large value for chloropentaamminecobalt(III) has been attributed to proton abstraction from the coordinated ammonia by Kitamura.[268]

The reactions involving oxalate ions are difficult to interpret because of the uncertain state of protonation of both reagents.

Dissociation is clearly the rule with the nickel through copper complexes. One trend that seems fairly obvious is that the heavier metals have evidently a greater ability to accommodate expansion of the coordination spehre as might be expected; examples are the more negative $\Delta V^{\ddagger}$ values in the series Cr–Mo–W, the platinum displacements compared to palladium, and the large, negative values characteristic in the iridium complexes.

There are very few examples of inorganic reactions under pressure that do not involve complex ions. One of these is the hydrolysis of difluoramine, which offers an interesting contrast with the reaction of the same compound with acetate ion. The former reaction is retarded by pressure, and this was claimed[290] to be so because of HN–F anion dissociation into fluoride and fluoronitrene, NF; the latter reaction was thought to be a simple displacement. These assignments are in agreement with the fact that the reaction with hydroxide is enormously faster than that with acetate. It proved possible to capture the supposed intermediate,[291] and subsequent work with $HNCl_2$ led to the formation of an N–Cl adduct as well.[292] It should also be mentioned here that Hagen has reported[293] much valuable information regarding the use of high pressure in inorganic synthesis; the simplicity of his apparatus renders his approach as the most attractive route to many of the compounds he describes. Finally, attention should also be called to work by Adams and Laidler,[294] who have deduced activation volumes of diffusion of tertiary ammonium salts in acetone (approximately +10 cm^3/mol) from conductance data under pressure; the data are shown to be in reasonable agreement with hole-free volume theory of liquids.

V. Reaction Volumes

A. The Data in Tabular Form (Table V)

It should be noted here that a number of reaction volumes are given under Remarks in the preceding tables; some but not all of these data are repeated in Table V.

B. Inorganic Acids: Ionization Volumes (Entries 1–46)

The ionization volume of water shows the temperature and ionic strength dependence that would be anticipated on the basis of an assumption that water has a relatively open (ice-like) structure near 0 °C which is in equilibrium with a denser structure at higher temperatures. The less dense structure should be subject to greater electrostriction. A minimum in the ionization volume is observable at about 32 °C, reminiscent of and perhaps related to the temperature of maximum density of water. ΔV_i is reduced by a few cm^3/mol if the ionic strength is 0.1; the ions to be solvated then have to compete with the electrolyte.

The large, negative ionization volume of boric acid is due in part to the fact that it is not merely a dissociation, but a water molecule becomes bound in the process. The temperature and ionic strength dependence are similar to those observed in the ionic dissociation of water itself. The same remarks apply to carbonic acid except that the temperature range is wider: ΔV_i equals −88 cm^3/mol at 250 °C. No water becomes bound in the ionization of cacodylic acid, and its ionization volume is more modest.

Diphosphate ion has a larger ΔV_i again (−25 cm^3/mol at 25 °C), but now for a different reason: a dianion is formed, and according to the Drude–Nernst picture, electrostriction is proportional to the square of the charge. The very modest volume decreases characteristic of the acid ionizations of hexaaquochromium and -iron(III) may have the same origin. They are essentially proton transfers from one hydronium ion to another, and there is net charge dispersal in the process.

C. Carboxylic Acids: Ionization Volumes (Entries 47–124)

The ionization volume of carboxylic acids is in general about −14 cm^3/mol, but for the first few two members of the series these volume decreases are significantly smaller, −8 and −11 cm^3/mol, respectively. The same anomaly is visible with oxalic and malonic acid, and with glycolic acid. The nature of these deviations is not known at present; any theory to account for it should explain why the effect of small alkyl groups on the ionization volume does not apply to amines. The explanation need not concern the anion alone, of course; it should always be remembered that when abnormal volume differences are encountered, the abnormality is not necessarily due to the species to the right of the arrow sign.[309] If the small, free acid molecules have abnormally small partial volume, due, for example, to hydration to ortho acids, to dimerization, or to hydrogen bonding, the effects would be explained. That these attributes would indeed reduce the volume of the intial species may be gleaned from Table VI; pure oxalic, in fact, is known in the form of a dihydrate.

The Drude–Nernst formulation predicts that with dicarboxylic acids ΔV_2 should be larger than ΔV_1, and that this difference should diminish as the distance between the two centers is raised. The data nicely bear this out, with $\Delta\Delta V_i$ = 6–8 cm^3/mol at the lower members in the series, and then dropping off until it has vanished at adipic acid.

No outstandingly unusual features are encountered with the hydroxy acids. Glycinium ion is still subject to contraction when it transfers a proton to water, because even though it becomes formally neutral, it is in fact a zwitterion with two charges interacting with at least the nearest-neighbor water molecules. The *o*-hydroxybenzoic acid[307] is a bit surprising with a ΔV_i of −4.6 cm^3/mol (for benzoic acid, −10.9 cm^3/mol); the internal H bond might be considered responsible, but an analogous effect is not discernible with the aliphatic hydroxyacids. Perhaps the rigidly enforced nature of the H bond in the phenolic benzoate ion is the origin of this effect.

D. Phenols (Entries 125–159)

Once again the Drude–Nernst equation is helpful in categorizing the data. First of all, ΔV_i of phenol itself is more negative than that of carboxylic acids because, although charge delocalization occurs, it is less complete; for the same reason, it is less negative than water itself. Secondly, the volume diminution is less pronounced for thiophenol, for which the negative charge is located on a larger atom. Thirdly, the possibilities of an electron-withdrawing group either attracting negative charge to itself by virtue of resonance, or to neighboring carbon atoms in an inductive way, both serve to reduce ΔV_i. With some minor exceptions, one finds that the more such groups are present, the more pronounced the effect is. An increase is, on the other hand, observed when a neighboring carboxylate center serves to increase charge concentration. We note parenthetically that this review includes some data also listed in Hamann's survey[2] which were then referred to as unpublished work; the full publication has meanwhile appeared.[311]

E. Amines (Entries 160–222)

The data given are those of the conjugate acids; to get the data for the ionization process

$$NR_3 + H_2O \rightarrow HNR_3^+ + OH^-$$

the ΔV data given should be subtracted from ΔV_i for water (i.e., from −22 cm^3/mol at 25 °C).

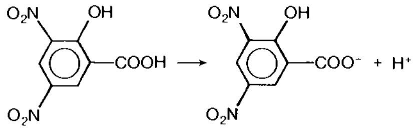
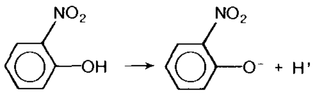
The data show a small but discernible trend: more highly substituted ammonium ions deprotonate with smaller volume

TABLE V. Reaction Volumes[a]

No.	Reaction	Solvent	T, °C	P, kbars	No. of K data	ΔV, cm³/mol[b] (a)	(b)	Ref	Remarks
1	$H_2O \rightarrow H^+ + OH^-$	H_2O	0				−25.75	295	
2		H_2O	0				−23.53	295	$\mu = 0.1$ m
3		H_2O	5				−24.64	295	
4		H_2O	5				−22.84	295	$\mu = 0.1$ m
5		H_2O	10				−23.71	295	
6		H_2O	10				−22.27	295	$\mu = 0.1$ m
7		H_2O	15				−22.97	295	
8		H_2O	15				−21.79	295	$\mu = 0.1$ m
9		H_2O	20				−22.43	295	
10		H_2O	20				−21.43	295	$\mu = 0.1$ m
11		H_2O	25				−22.07	295	
12		H_2O	25				−21.17	295	$\mu = 0.1$ m
13		H_2O	30				−21.89	295	
14		H_2O	30				−21.02	295	$\mu = 0.1$ m
15		H_2O	35				−21.91	295	
16		H_2O	35				−20.98	295	$\mu = 0.1$ m
17		H_2O	40				−22.12	295	
18		H_2O	40				−21.04	295	$\mu = 0.1$ m
19		H_2O	45				−22.51	295	
20		H_2O	45				−21.21	295	$\mu = 0.1$ m
21		H_2O	50				−23.09	295	
22		H_2O	50				−21.49	295	$\mu = 0.1$ m
23	$B(OH)_3 + H_2O \rightarrow B(OH)_4^- + H^+$	H_2O	0				−38.68	296	
24		H_2O	0				−38.72	297	
25		H_2O	0				−29.05	297	At 0.725 m
26		H_2O–NaCl	0				−29.64	297	[NaCl] = 0.725 m
27		H_2O	15				−36.59	296	
28		H_2O	25				−35.45	296	
29		H_2O	25				−35.46	297	
30		H_2O	25				−28.52	297	At 0.725 m
31		H_2O–NaCl	25				−26.37	297	[NaCl] = 0.725 m
32		H_2O	25	6	15	−30.2		298	0.05 M borate buffer, cresol red indicator
33		H_2O	25	6	15	−30.9		298	0.05 M borate buffer, *p*-nitrophenol indicator
34		H_2O	50				−35.90	296	
35	$H_2CO_3 \rightarrow HCO_3^- + H^+$	H_2O	25	2	11	−27.6		299	H_2CO_3: total carbon dioxide
36		H_2O	99.4	2	11	−33.0		299	
37		H_2O	100	2	11	−33.0		299	
38		H_2O	150	2	11	−43.5		299	
39		H_2O	200	2	11	−59.0		299	
40		H_2O	250	2	11	−88		299	
41	$Me_2AsO_2H \rightarrow Me_2AsO_2^- + H^+$	H_2O	25	6.5	11	−13.2		300	0.05 M cacodylate buffer, 2,5-dinitrophenol indicator

42	$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$	H_2O	25	6.5	11	−25.3		300	pH 6.31 phosphate buffer, 2,5-dinitrophenol indicator
43		H_2O	25	6.5	11	−24.5		300	pH 6.11 phosphate buffer, 2,5-dinitrophenol indicator
44		H_2O	25	6.5	11	−23.8		300	pH 7.97 phosphate buffer, *p*-nitrophenol indicator
45	$Cr(H_2O)_6^{3+} \rightarrow Cr(H_2O)_5(OH)^{2+} + H^+$	H_2O	25	3	7	−3.8		301	μ = 0.5 m
46	$Fe(H_2O)_6^{3+} \rightarrow Fe(H_2O)_5(OH)^{2+} + H^+$	H_2O				−1.2		246	
47	$HCOOH \rightarrow HCOO^- + H^+$	H_2O	25	1.2	7	−8.5		302	
48		H_2O	30	5.9	8	−8.3		303	
49		H_2O	35	1.2	7	−9.4		302	
50		H_2O	45	1.2	7	−10.7		302	
51	$MeCOOH \rightarrow MeCOO^- + H^+$	H_2O	25	1.2	7	−11.3		302	
52		H_2O	30	5.9	8	−11.5		303	
53		H_2O	35	1.2	7	−12.2		302	
54		H_2O	45	1.2	7	−13.5		302	
55	$EtCOOH \rightarrow EtCOO^- + H^+$	H_2O	25	2	9	−14.1		304	
56		H_2O	25	1.2	7	−13.0		302	
57		H_2O	30	5.9	8	−13.5		303	
58		H_2O	35	1.2	7	−13.8		302	
59		H_2O	45	1.2	7	−14.9		302	
60	$PrCOOH \rightarrow PrCOO^- + H^+$	H_2O	25	2	9	−14.6		304	
61		H_2O	25	1.2	7	−13.9		302	
62		H_2O	30	5.9	8	−15.0		303	
63		H_2O	35	1.2	7	−14.9		302	
64		H_2O	45	1.2	7	−16.2		302	
65	$BuCOOH \rightarrow BuCOO^- + H^+$	H_2O	25	1.2	7	−14.2		302	
66		H_2O	35	1.2	7	−14.9		302	
67		H_2O	45	1.2	7	−16.1		302	
68	$Me(CH_2)_4COOH \rightarrow Me(CH_2)_4COO^- + H^+$	H_2O	25	1.2	7	−14.2		302	
69		H_2O	35	1.2	7	−15.0		302	
70		H_2O	45	1.2	7	−16.3		302	
71	*i*-$PrCOOH \rightarrow$ *i*-$PrCOO^- + H^+$	H_2O	25	2	9	−14.8		304	
72		H_2O	25	1.2	7	−14.9		302	
73		H_2O	35	1.2	7	−15.7		302	
74		H_2O	45	1.2	7	−17.1		302	
75	*i*-$BuCOOH \rightarrow$ *i*-$BuCOO^- + H^+$	H_2O	25	1.2	7	−14.9		302	
76		H_2O	35	1.2	7	−15.7		302	
77		H_2O	45	1.2	7	−17.0		302	
78	$HOOCCOOH \rightarrow HOOCCOO^- + H^+$	H_2O	25				−6.72	305	
79	$HOOCCOO^- \rightarrow {}^-OOCCOO^- + H^+$	H_2O	25				−11.91	305	
80	$HOOCCH_2COOH \rightarrow HOOCCH_2COO^- + H^+$	H_2O	25				−10.06	305	
81	$HOOCCH_2COO^- \rightarrow {}^-OOCCH_2COO^- + H^+$	H_2O	25				−18.55	305	
82	$HOOCCH_2CH_2COOH \rightarrow HOOCCH_2CH_2COO^- + H^+$	H_2O	25				−12.86	305	
83	$HOOCCH_2CH_2COO^- \rightarrow {}^-OOCCH_2CH_2COO^- + H^+$	H_2O	25				−13.58	305	
84	$HOOC(CH_2)_3COOH \rightarrow HOOC(CH_2)_3COO^- + H^+$	H_2O	25				−13.17	305	
85	$HOOC(CH_2)_3COO^- \rightarrow {}^-OOC(CH_2)_3COO^- + H^+$	H_2O	25				−13.59	305	
86	$HOOC(CH_2)_4COOH \rightarrow HOOC(CH_2)_4COO^- + H^+$	H_2O	25				−13.48	305	
87	$HOOC(CH_2)_4COO^- \rightarrow {}^-OOC(CH_2)_4COO^- + H^+$	H_2O	25				−13.54	305	
88	$HOOC(CH_2)_5COOH \rightarrow HOOC(CH_2)_5COO^- + H^+$	H_2O	25				−14.14	305	
89	$HOOC(CH_2)_5COO^- \rightarrow {}^-OOC(CH_2)_5COO^- + H^+$	H_2O	25				−13.55	305	
90	$HOCH_2COOH \rightarrow HOCH_2COO^- + H^+$	H_2O	25	1.2	7	−11.9	−11.8	306	

TABLE V (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of K data	ΔV, cm^3/mol^b (a)	(b)	Ref	Remarks
91		H_2O	30	1.2	7	−12.0	−11.9	306	
92		H_2O	35	1.2	7	−12.1	−11.9	306	
93	$MeCH(OH)COOH \rightarrow MeCH(OH)COO^- + H^+$	H_2O	25	1.2	7	−13.5	−13.4	306	
94		H_2O	30	1.2	7	−13.4	−13.4	306	
95		H_2O	35	1.2	7	−13.6	−13.4	306	
96	$EtCH(OH)COOH \rightarrow EtCH(OH)COO^- + H^+$	H_2O	25	1.2	7	−13.8	−13.8	306	
97		H_2O	30	1.2	7	−13.9	−13.8	306	
98		H_2O	35	1.2	7	−13.9	−13.8	306	
99	$PrCH(OH)COOH \rightarrow PrCH(OH)COO^- + H^+$	H_2O	25	1.2	7	−13.8	−13.7	306	
100		H_2O	30	1.2	7	−13.9	−13.8	306	
101		H_2O	35	1.2	7	−13.9	−13.8	306	
102	$BuCH(OH)COOH \rightarrow BuCH(OH)COO^- + H^+$	H_2O	25	1.2	7	−14.0	−13.8	306	
103		H_2O	30	1.2	7	−14.1	−13.9	306	
104		H_2O	35	1.2	7	−14.0	−13.9	306	
105	$Me_2C(OH)COOH \rightarrow Me_2C(OH)COO^- + H^+$	H_2O	25	1.2	7	−14.1	−14.0	306	
106		H_2O	30	1.2	7	−14.2	−14.0	306	
107		H_2O	35	1.2	7	−14.1	−14.0	306	
108	$i\text{-}PrCH(OH)COOH \rightarrow i\text{-}PrCH(OH)COO^- + H^+$	H_2O	25	1.2	7	−13.9	−13.9	306	
109		H_2O	30	1.2	7	−14.1	−13.8	306	
110		H_2O	35	1.2	7	−14.1	−13.8	306	
111	$MeCH(OH)CH_2COOH \rightarrow MeCH(OH)CH_2COO^- + H^+$	H_2O	25	1.2	7	−12.4		306	
112		H_2O	30	1.2	7	−12.5		306	
113		H_2O	35	1.2	7	−12.7		306	
114	$HOCH_2CH_2COOH \rightarrow HOCH_2CH_2CH_2COO^- + H^+$	H_2O	25	1.2	7	−13.0		306	
115		H_2O	30	1.2	7	−13.1		306	
116		H_2O	35	1.2	7	−13.3		306	
117	$d\text{-}HOOCCH(OH)CH(OH)COOH \rightarrow d\text{-}HOOCCH(OH)CH(OH)COO^- + H^+$	H_2O	25				−11.96	306	
118		H_2O	30				−11.78	306	
119		H_2O	35				−11.75	306	
120	$d\text{-}HOOCCH(OH)CH(OH)COO^- \rightarrow d\text{-}^-OOCCH(OH)CH(OH)COO^- + H^+$	H_2O	25				−13.37	306	
121		H_2O	30				−13.38	306	
122		H_2O	35				−13.49	306	
123	$HOOCCH_2NH_3^+ \rightarrow {}^-OOCCH_2NH_3^+ + H^+$	H_2O	25	2.8	6	−8.1		279	μ = 0.2 M ($NaNO_3$)
124		H_2O	25	2	5	−4.6		307	μ = 0.5 M (HCl)
125	$PhOH \rightarrow PhO^- + H^+$	H_2O	25				−18.7	308	
126		H_2O	25				−18.4	307	
127		H_2O	25	2	5	−13.5		307	Phosphate buffer, μ = 0.124 M

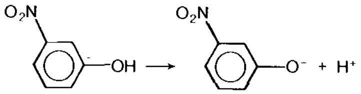
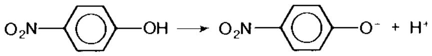
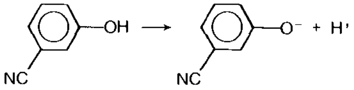
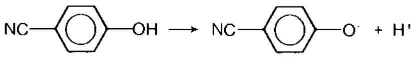
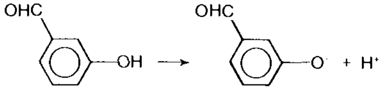
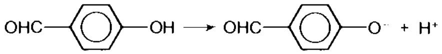
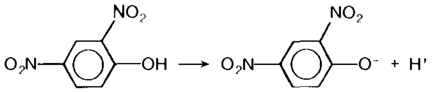
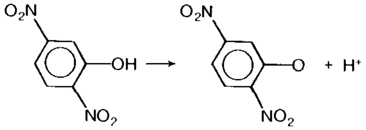
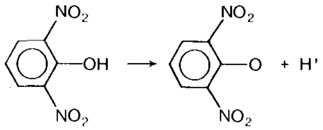
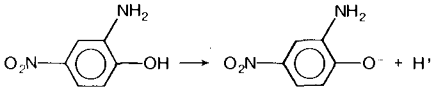
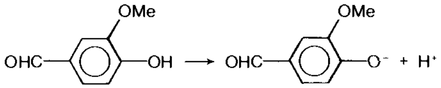
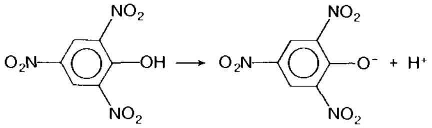
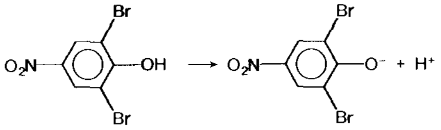
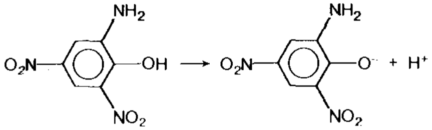
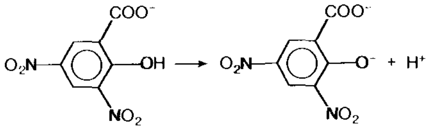
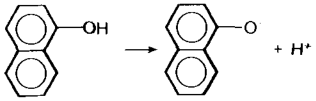
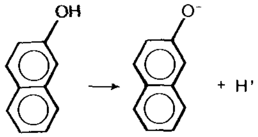
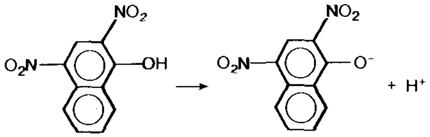
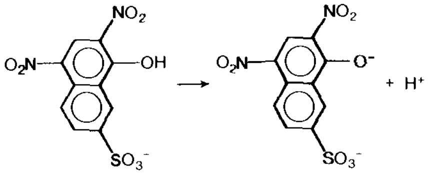
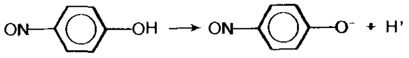
128		H_2O	25	2	5	−14.1		307	Phosphate buffer, $\mu = 0.124$ M
129		H_2O	25				−12.84	309	
130		H_2O	25				−13.6	308	
131		H_2O	25	2	5	−10.9		307	Phosphate buffer, $\mu = 0.05$ M
132		H_2O	25	6.5	11	−11.3		300	Cacodylate buffer
133		H_2O	25				−11.32	309	
134		H_2O	25				−11.9	308	
135		H_2O	25				−12.9	308	
136		H_2O	25				−13.0	308	
137		H_2O	25				−13.35	309	
138		H_2O	25				−12.21	309	
139		H_2O	25	2	5	−11.0		307	Acetate buffer, $\mu = 0.06$ M
140		H_2O	25	2	5	−11.9		307	Acetate buffer, $\mu = 0.05$ M
141			25	6.5	11	−11.3		300	Acetate buffer
142		H_2O	25	2	5	−14.7		307	Acetate buffer, $\mu = 0.022$ M
143		H_2O	25	2	5	−11.3		307	Phosphate buffer, $\mu = 0.05$ M
144		H_2O	25	2	5	−14.2		307	Phosphate buffer, $\mu = 0.078$ M
145		H_2O	25	2	5	−9.9		307	$\mu = 1.0$ M (HCl)

TABLE V (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of K data	ΔV, cm^3/mol^b (a)	(b)	Ref	Remarks
146		H_2O	25	2	5	−12.7		307	Acetate buffer, μ = 0.11 M
147		H_2O	25	2	5	−8.2		307	Acetate buffer, μ = 0.015 M
148		H_2O	25	2	5	−21.1		307	Phosphate buffer, μ = 0.072 M
149		H_2O	25	2	5	−17.2		307	Carbonate buffer, μ = 0.063 M
150		H_2O	25	2	5	−17.1		307	Carbonate buffer, μ = 0.063 M
151		H_2O	25	2	5	−9.9		307	μ = 0.024 M (HCl-NaCl)
152		H_2O	25	2	5	−11.8		307	μ= 0.005 M (HCl)
153		H_2O	25	2	5	−11.6		307	Phosphate buffer, μ = 0.035 M, *c*
154	$PhSH \rightarrow PhS^- + H^+$	H_2O	25				−12.76	310	
155	phenol red → phenol red$^-$ + H^+	H_2O	25	2.8	6	−11.6		279	Ammonium buffer, μ = 0.2 M ($NaNO_3$)
156	bromcresol green → bromcresol green$^-$ + H^+	H_2O	25	2.8	6	−16.8		279	Acetate buffer, μ = 0.2 M ($NaNO_3$)

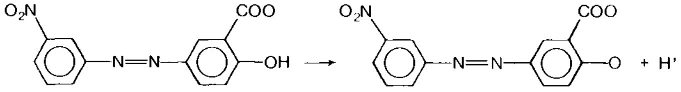
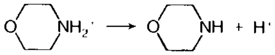
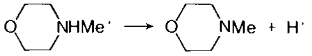
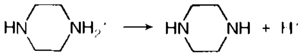
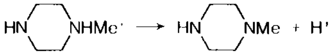
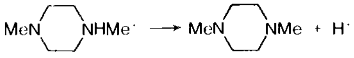
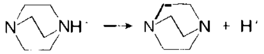
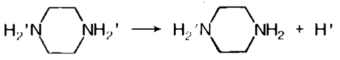
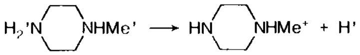
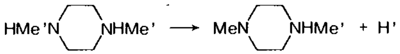
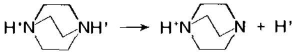
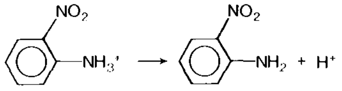
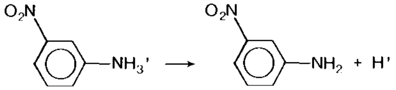
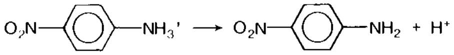
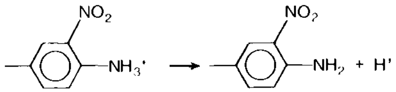
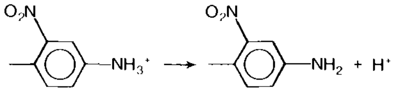
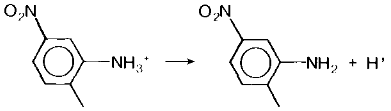
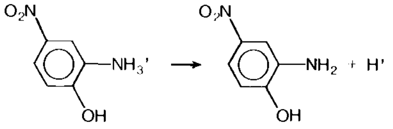
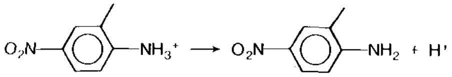
157	bromphenol blue → bromphenol blue$^-$ + H^+	H_2O	25	2.8	6	−12.8		279	Acetate buffer, μ = 0.2 M ($NaNO_3$)
158	cresol red → cresol red$^-$ + H^+	H_2O	25	6	15	−10.1		298	Phosphate buffer
159		H_2O	10.1	1.5	4	−9.0[d]		171	μ = 0.1 m
160	$NH_4^+ \rightarrow NH_3 + H^+$	H_2O	25				+7.00[e]	312	
161	$NH_4^+ \rightarrow NH_3 + H^+$	H_2O	25				+7.0	313	*f*
162	$MeNH_3^+ \rightarrow MeNH_2 + H^+$	H_2O	25				+5.6	313	*f*
163	$EtNH_3^+ \rightarrow EtNH_2 + H^+$	H_2O	25				+5.4	313	*f*
164	$PrNH_3^+ \rightarrow PrNH_2 + H^+$	H_2O	25				+4.7	313	*f*
165	$BuNH_3^+ \rightarrow BuNH_2 + H^+$	H_2O	25				+4.3	313	*f*
166	$PentNH_3^+ \rightarrow PentNH_2 + H^+$	H_2O	25				+4.3	313	*f*
167	$HexNH_3^+ \rightarrow HexNH_2 + H^+$	H_2O	25				+4.3	313	*f*
168	$HeptNH_3^+ \rightarrow HeptNH_2 + H^+$	H_2O	25				+4.4	313	*f*
169	$Me_2NH_2^+ \rightarrow Me_2NH + H^+$	H_2O	25				+5.1	313	*g*
170	$Et_2NH_2^+ \rightarrow Et_2NH + H^+$	H_2O	25				+2.8	313	*g*
171	$Pr_2NH_2^+ \rightarrow Pr_2NH + H^+$	H_2O	25				+2.2	313	*h*
172	$Bu_2NH_2^+ \rightarrow Bu_2NH + H^+$	H_2O	25				+2.5	313	*h*
173	$Me_3NH^+ \rightarrow Me_3N + H^+$	H_2O	25				+6.0	313	*g*
174	$Et_2MeNH^+ \rightarrow Et_2MeN + H^+$	H_2O	25				+1.8	313	
175	$Et_3NH^+ \rightarrow Et_3N + H^+$	H_2O	25				+0.1	313	*g*
176		H_2O	25				+7.4	317	
177		H_2O	25				+7.4	317	
178		H_2O	25				+6.2	317	
179		H_2O	25				+6.2	317	
180		H_2O	25				+6.2	317	
181		H_2O	25				+6.8	317	
182		H_2O	25				+6.5	318	
183	$HOCH_2CH_2NH_3^+ \rightarrow HOCH_2CH_2NH_2 + H^+$	H_2O	25				+6.2	319	
184	$HO(CH_2)_3NH_3^+ \rightarrow HO(CH_2)_3NH_2 + H^+$	H_2O	25				+5.6	319	
185	$MeOCH_2CH_2NH_3^+ \rightarrow MeOCH_2CH_2NH_2 + H^+$	H_2O	25				+5.9	319	
186	$MeO(CH_2)_3NH_3^+ \rightarrow MeO(CH_2)_3NH_2 + H^+$	H_2O	25				+5.5	319	
187	$H_2NCH_2CH_2NH_3^+ \rightarrow H_2NCH_2CH_2NH_2 + H^+$	H_2O	25				+6.7	319	
188	$H_2N(CH_2)_2NH_3^+ \rightarrow H_2N(CH_2)_3NH_2 + H^+$	H_2O	25				+5.6	319	
189	$HOCH_2CH_2NH_2Me^+ \rightarrow HOCH_2CH_2NHMe + H^+$	H_2O	25				+5.4	319	
190	$HOCH_2CH_2NH_2Et^+ \rightarrow HOCH_2CH_2NHEt + H^+$	H_2O	25				+4.7	319	
191	$HOCH_2CH_2NHMe_2^+ \rightarrow HOCH_2CH_2NMe_2 + H^+$	H_2O	2				+5.0	319	
192	$HOCH_2CH_2NHEt_2^+ \rightarrow HOCH_2CH_2NEt_2 + H^+$	H_2O	25				+2.9	319	
193	$(HOCH_2)_2CNH_3^+ \rightarrow (HOCH_2)_3CNH_2 + H^+$	H_2O	25	6.5	11	+1		300	*p*-Nitrophenol indicator
194	$^-OOCCH_2NH_3^+ \rightarrow {}^-OOCCH_2NH_2 + H^+$	H_2O	25	2.8	6	+1.9		279	μ = 0.2 M ($NaNO_3$)
195	$H_3N^+CH_2CH_2NH_3^+ \rightarrow H_2NCH_2CH_2NH_2 + 2H^+$	H_2O	25				+18.4	320	
196	$H_3{}^+NCH_2CH_2NH_3^+ \rightarrow H_3{}^+NCH_2CH_2NH_2 + H^+$	H_2O	25				+21.1	319	
197	$H_3{}^+N(CH_2)_3NH_3^+ \rightarrow H_3{}^+N(CH_2)_3NH_2 + H^+$	H_2O	25				+10.0	319	

TABLE V (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of K data	ΔV, cm^3/mol^b (a)	(b)	Ref	Remarks
198		H_2O	25				+13.7	317	
199		H_2O	25				+14.3	317	
200		H_2O	25				+14.7	317	
201		H_2O	25				+16.3	317	
202	$H_3N^+(CH_2CH_2NH_2{}^+)_2H \rightarrow H_2N(CH_2CH_2NH)_2H + 3H^+$	H_2O	25				+28.8	320	
203	$H_3N^+(CH_2CH_2NH_2{}^+)_3H \rightarrow H_2N(CH_2CH_2NH)_3H + 4H^+$	H_2O	25				+31.2	320	
204	$H_3N^+(CH_2CH_2NH_3{}^+)_4H \rightarrow H_2N(CH_2CH_2NH)_4H + 5H^+$	H_2O	25				+32.6	320	
205	$H_3N^+(CH_2CH_2NH_2{}^+)_nH^i \rightarrow H_2N(CH_2CH_2NH)_nH + (n + 1)H^+$	H_2O	25				-0.5^j	320	
206	$PhNH_3{}^+ \rightarrow PhNH_2 + H^+$	H_2O	25				$+4.42^k$	312	
207		H_2O	25	2	5	+4.2		321	[HCl] = 1 m
208		H_2O	25	2	5	+6.1		321	[HCl] = 0.002 m [NaCl] = 0.01 m
209		H_2O	25	2	5	+6.5		321	[HCl] = 0.1 m
210		H_2O	25	2	5	+3.9		321	[HCl] = 0.5 m
211		H_2O	25	2	5	+3.8		321	[HCl] = 0.001 m [NaCl] = 0.01 m
212		H_2O	25	2	5	+5.0		321	[HCl] = 0.005 m
213		H_2O	25	2	5	+2.8		321	[HCl] = 0.001 m [NaCl] = 0.01 m
214		H_2O	25	2	5	+4.7		321	[HCl] = 0.1 m

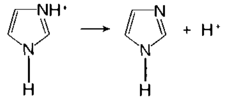
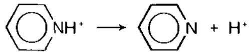
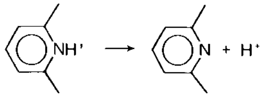
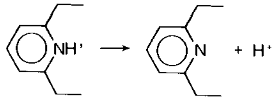
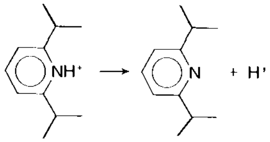
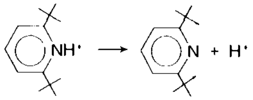
215		H_2O	25	6	15	−2.4		298	Cresol red indicator
216		H_2O	25	6	15	−2.0		298	*p*-Nitrophenol indicator
217		MeOH	25				+9.8	322	
218		MeOH	25				+8.1	322	
219		MeOH	25				+10.0	322	
220		MeOH	25				+10.8	322	
221		MeOH	25				+22.0	322	
222	*t*-$BuNH_2{}^+Ac \rightarrow$ *t*-$BuNHAc + H^+$	H_2O	80.2	1	5	−20.6		199	*l*
223	$RbNO_3 \rightarrow Rb^+ + NO_3{}^-$	H_2O	25				−5.2	323	*m*, at 0.1 m
224		H_2O	25				−4.9	323	*m*, at 0.15 m
225		H_2O	25				−4.6	323	*m*, at 0.2 m
226	$TlNO_3 \rightarrow Tl^+ + NO_3{}^-$	H_2O	25				−12.2	323	*m*, at 0.1 m
227		H_2O	25				−9.9	323	*m*, at 0.15 m
228		H_2O	25				−9.0	323	*m*, at 0.2 m
229	$NaB(OH)_4 \rightarrow Na^+ + B(OH)_4{}^-$	H_2O	25				−29.3	297	*m*, μ = 0.725 m
230		H_2O–NaCl	25				−29.5	297	*m*, μ = 0.725 m
231	$CaSO_4 \rightarrow Ca^{2+} + SO_4{}^{2-}$	H_2O	15	1.2	7	−12.9		324	
232		H_2O	25	1.2	7	−10.2		324	
233		H_2O	40	1.2	7	−5.7		324	
234		H_2O	25				−25	325	
235	$MgSO_4 \rightarrow Mg^{2+} + SO_4{}^{2-}$	H_2O	25	1.2	7	−7.7		324	*m*
236	$ZnSO_4 \rightarrow Zn^{2+} + SO_4{}^{2-}$	H_2O	25	2.9	7	−8.0		327	
237	$NiSO_4 \rightarrow Ni^{2+} + SO_4{}^{2-}$	H_2O	15	1.6	5	−10.1		328	
238		H_2O	25	1.6	5	−8.6		328	
239		H_2O	40	1.6	5	−7.4		328	
240	$CoSO_4 \rightarrow Co^{2+} + SO_4{}^{2-}$	H_2O	15	1.6	5	−9.2		329	
241		H_2O	25	1.6	5	−7.0		329	
242		H_2O	40	1.6	5	−5.5		329	
243	$[Co(NH_3)_5NO_2]SO_4 \rightarrow Co(NH_3)_5NO_2{}^{2+} + SO_4{}^{2-}$	H_2O	15	2.9	7	−12.5		330	
244		H_2O	25	2.9	7	−9.5		330	
245		H_2O	40	2.9	7	−8.2		330	
246	*cis*-$Co(en)_2(OH)OH_2{}^{2+} + C_2O_4{}^{2-} \rightarrow$ *cis*-$Co(en)_2(OH)(OH_2)^{2+} \cdot C_2O_4{}^{2-}$	H_2O	30	1.6	4	−1.0		270	pH 7.2, Trizma buffer, μ = 0.32 M ($NaNO_3$)

TABLE V (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *K* data	ΔV, cm³/mol[b]		Ref	Remarks
						(a)	(b)		
247	Cu(II) malonate $\rightarrow {}^{-}OOCCH_2COO^{-} + Cu^{2+}$	H_2O	30				−27	331	[Cu] = 0.05 M
248		H_2O–urea	30				−20	331	[Cu] = 0.05 M [Urea] = 8 M
249	Cu(II) tartrate $\rightarrow {}^{-}OOCCH(OH)CH(OH)COO^{-} + Cu^{2+}$	H_2O	30				−29	331	[Cu] = 0.05 M
250	Cu(II) maleate $\rightarrow {}^{-}OOCCH{=}CHCOO^{-} + Cu^{2+}$	H_2O	30				−28	331	[Cu] = 0.05 M
251		H_2O–urea	30				−22	331	[Cu] = 0.05 M [Urea] = 8 M
252	$[Co(NH_3)_6]SO_4^{+} \rightarrow Co(NH_3)_6^{3+} + SO_4^{2-}$	H_2O	15	5.1	11	−10.8		332	
253		H_2O	25	5.1	11	−6.8		332	
254		H_2O	40	5.1	11	−4.5		332	
255	$FeNCS^{2+} \rightarrow Fe^{3+} + NCS^{-}$	H_2O	25	1.4	6	−17.5		272	$[HClO_4] = 0.2$ M
256		H_2O	25				−17	272	At high dilution
257		H_2O	25	2	5	−8.9		273	$\mu = 0.2$ m ($NaClO_4$)
258	$FeOH^{2+} \rightarrow Fe^{3+} + OH^{-}$	H_2O	25	2	5	−24[c]		273	$\mu = 0.2$ m ($NaClO_4$)
259	$FeCl^{2+} \rightarrow Fe^{3+} + Cl^{-}$	H_2O	25	2.8	5	−4.6		274	$\mu = 1.5$ M ($NaClO_4$)
260	$CeNO_3^{2+} \rightarrow Ce^{3+} + NO_3^{-}$	H_2O	30				−3.4	333	$[NaClO_4] = 1$ M
261	$CeCl^{2+} \rightarrow Ce^{3+} + Cl^{-}$	H_2O	30				−0.8	333	$[NaClO_4] = 1$ M
262	$CeOOCEt^{2+} \rightarrow Ce^{3+} + EtCOO^{-}$	H_2O	30				−23.6	333	$[NaClO_4] = 1$ M
263	$CeSO_4^{+} \rightarrow Ce^{3+} + SO_4^{2-}$	H_2O	30				−15.1	333	$[NaClO_4] = 1$ M
264	$EuNO_3^{2+} \rightarrow Eu^{3+} + NO_3^{-}$	H_2O	30				−4.2	333	$[NaClO_4] = 1$ M
265	$Co(NH_3)_5OH^{2+} \rightarrow Co(NH_3)_5H_2O^{3+} + OH^{-}$	H_2O	30				−19.4	333	$[NaClO_4] = 1$ M
266		H_2O	30				−20.6	333	
267	$Co(NH_3)_5OOCEt^{2+} \rightarrow Co(NH_3)_5H_2O^{3+} + EtCOO^{-}$	H_2O	30				−17.4	333	$[NaClO_4] = 1$ M
268		H_2O	30				−19.6	333	
269	$Co(NH_3)_5Cl^{2+} \rightarrow Co(NH_3)_5H_2O^{3+} + Cl^{-}$	H_2O	30				−10.4	333	$[NaClO_4] = 1$ M
270	$Co(NH_3)_5Br^{2+} \rightarrow Co(NH_3)_5H_2O^{3+} + Br^{-}$	H_2O	30				−9.6	333	$[NaClO_4] = 1$ M
271	$Co(NH_3)_5NO_3^{2+} \rightarrow Co(NH_3)_5H_2O^{3+} + NO_3^{-}$	H_2O	30				−6.0	333	$[NaClO_4] = 1$ M
272	$Co(NH_3)_5SO_4^{+} \rightarrow Co(NH_3)_5H_2O^{3+} + SO_4^{2-}$	H_2O	30				−15.2	333	$[NaClO_4] = 1$ M
273	$Co(NH_3)_5SO_4^{+} \rightarrow Co(NH_3)_5H_2O^{3+} + SO_4^{2-}$	H_2O	30				−19.2	333	
274	$[Co(en)_2(H_2O)_2]HC_2O_4^{2+} \rightarrow Co(en)(H_2O)_2^{3+} + HC_2O_4^{-}$	H_2O				−2.6		246	
275	$HCOOCu^{+} \rightarrow Cu^{2+} + HCOO^{-}$	H_2O	30				−7	331	[Cu] = 0.05 M
276		H_2O–urea	30				−5	331	[Cu] = 0.05 M, [Urea] = 8 M
277	$MeCOOCu^{+} \rightarrow Cu^{2+} + MeCOO^{-}$	H_2O	30				−13	331	[Cu] = 0.05 M
278		H_2O–urea	30				−10.5	331	[Cu] = 0.05 M, [Urea] = 8 M
279	$EtCOOCu^{+} \rightarrow Cu^{2+} + EtCOO^{-}$	H_2O	30				−13	331	[Cu] = 0.05 M
280		H_2O–urea	30				−11	331	[Cu] = 0.05 M, [Urea] = 8 M
281	$H_2NCH_2COOCu^{+} \rightarrow Cu^{2+} + H_2NCH_2COO^{-}$	H_2O	30				−14	331	[Cu] = 0.05 M
282		H_2O	25	2.8	6	−13.4		279	$\mu = 0.2$ M ($NaNO_3$)
283	$H_2NCHMeCOOCu^{+} \rightarrow Cu^{2+} + H_2NCHMeCOO^{-}$	H_2O	30				−15	331	[Cu] = 0.05 M
284	$H_2NCH_2COOCo^{+} \rightarrow Co^{2+} + H_2NCH_2COO^{-}$	H_2O	25	2.8	6	−7.3		279	$\mu = 0.2$ M ($NaNO_3$)
285	$H_2NCH_2COONi^{+} \rightarrow Ni^{2+} + H_2NCH_2COO^{-}$	H_2O	25	2.8	6	−2.1		279	$\mu = 0.2$ M ($NaNO_3$)
286	$Nimu^{+} \rightarrow Ni^{2+} + mu$	H_2O	25	1.5	4	−22.6		283	$\mu = 0.1$ M ($NaClO_4$)

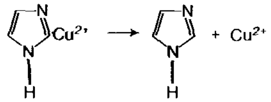
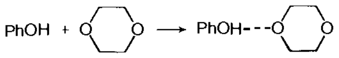
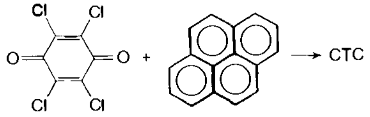
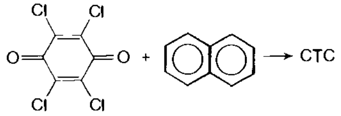
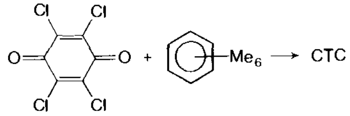
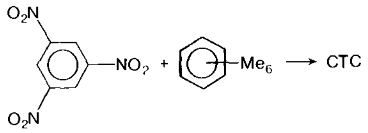
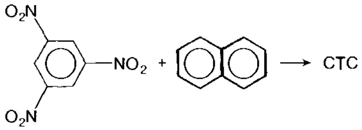
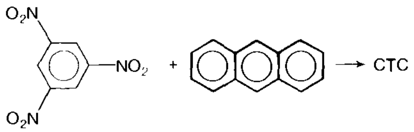
287	$H_2NCH_2COOZn^+ \rightarrow Zn^{2+} + H_2NCH_2COO^-$	H_2O	25	2.8	6	−5.2		279	$\mu = 0.2$ M ($NaNO_3$)
288	$NaSO_4^- \rightarrow Na^+ + SO_4^{2-}$	H_2O	1.5	1	3	−15.8		334	[NaCl] = 0.11 M, [Na_2SO_4] = 0.29 M
289		H_2O	30				−1.7	331	[Cu] = 0.05 M
290	$Co(pada)^{2+} \rightarrow Co^{2+} + pada$	H_2O	25	2.1	6	−5.8		276	$\mu = 0.1$ M ($NaNO_3$)
291	$CoNH_3^{2+} \rightarrow Co^{2+} + NH_3$	H_2O	10	1.4	7	+8.6		276	$\mu = 0.1$ M (NH_4NO_3)
292	$Ni(pada)^{2+} \rightarrow Ni^{2+} + pada$	H_2O	49	2.1	6	−0.9		276	$\mu = 0.1$ M ($NaNO_3$)
293	$NiNH_3^{2+} \rightarrow Ni^{2+} + NH_3$	H_2O	30	1.4	5	+2.3		276	$\mu = 0.1$ M (NH_4NO_3)
294	$EtOK \rightarrow EtO^- + K^+$	EtOH	45	1	5	−39		164	
295	$Me_4NBr \rightarrow Me_4N^+ + Br^-$	PrOH	25	3	7	-16.2^p		335	
296		*i*-PrOH	25	3	7	-20.7^p		335	
297	$NaFl \rightarrow Na^+\|THF\|Fl^-$	THF	≃22	5	6	−16		336, 337	*q*
298	$NaFl \rightarrow Na^+\|DME\|Fl^-$	DME	≃22	3	6	−21		337	*q*
299	$LiFl \rightarrow Li^+\|THF\|Fl^-$	THF	≃22	5	6	−10		336, 337	*q*
300	$LiFl \rightarrow Li^+\|THP\|Fl^-$	THP	≃22	2.5	6	−11		337	*q*
301	$LiFl \rightarrow Li^+\|MeTHF\|Fl^-$	2-MeTHF	≃22	2.5	6	−23		337	*q*
302	$LiFl \rightarrow Li^+\|glyme\|Fl^-$	Et_2O	≃22	5	6	−7		338	*q*
303	$LiFl \rightarrow glyme\|LiFl$	Et_2O	≃22	5	6	+5		338	*r*
304	$glyme\|LiFl \rightarrow Li^+\|glyme\|Fl^-$	Et_2O	≃22	5	6	−11		338	
305	$Li2\text{-}C_6H_{13}Fl \rightarrow Li^+\|MeTHF\|2\text{-}C_6H_{13}Fl^-$	2-MeTHF	≃22	3	7	−38		337	*q*
306	$CoCl_2 \rightarrow Co^{2+} + 2Cl^-$	EtOH	RT	2.5	6	−154		341	
307		PrOH	RT	2.9	6	−396		341	
308		BuOH	RT	4.9	8	−497		341	
309		*i*-BuOH	RT	7.8	11	−425		341	
310		*i*-PrOH	RT	9.8	9	−64.6		341	
311		*s*-BuOH	RT	9.8	7	−33.7		341	
312		Me_2CO	RT	7.8	9	−34		342	
313	$CoBr_2 \rightarrow Co^{2+} + 2Br^-$	EtOH	RT	3.9	5	−230.4		341	
314		PrOH	RT	4.9	6	−247.3		341	
315		BuOH	RT	4.9	6	−463.1		341	
316		*i*-BuOH	RT	7.8	5	−330.5		341	
317		*i*-PrOH	RT	9.8	4	−36.5		341	
318		*s*-BuOH	RT	9.8	5	−29.2		341	
319		Me_2CO	RT	7.8	9	−36		342	
320	$CoCl_3^- \rightarrow CoCl_2 + Cl^-$	Me_2CO	RT	7.8	9	+2		342	
321	$CoBr_3^- \rightarrow CoBr_2 + Br^-$	Me_2CO	RT	7.8	9	+4		342	
322	$NiCl_6^{4-} \rightarrow NiCl_4^{2-} + 2Cl^-$	*s*	−24.5	3.5	2	+25		343	
323		*s*	−21			+26.6		343	
324	$CaCO_{3(s)} \rightarrow Ca^{2+} + CO_3^{2-}$	H_2O	1	0.9	7	−57.1		344	Calcite
325		H_2O	8	0.8	6	−57.5		344	Calcite
326		H_2O	23	0.9	13	−54.9		344	Calcite
327		H_2O	25	1	6	−58.0		344	Calcite
328	$CaF_{2(s)} \rightarrow Ca^{2+} + 2F^-$	H_2O	23	0.8	6	−44.3		344	
329		H_2O	25	1	5	−43.4		344	
330	$SrSO_{4(s)} \rightarrow Sr^{2+} + SO_4^{2-}$	H_2O	2	1	5	−48.1		344	
331		H_2O	22	1	8	−51.8		344	
332		H_2O	35	1	5	−53.2		344	

TABLE V (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of K data	ΔV, cm^3/mol[b] (a)	(b)	Ref	Remarks
333		H_2O	2	1.0	5	−44.7		345	t
334	$2HCOOH \rightarrow (HCOOH)_2$[u]	H_2O	30	5.9	8	−14		303	
325	$2MeCOOH \rightarrow (MeCOOH)_2$[u]	H_2O	30	5.9	8	−13		303	
336	$2EtCOOH \rightarrow (EtCOOH)_2$[u]	H_2O	30	5.9	8	−8.8		303	
337	$2PrCOOH \rightarrow (PrCOOH)_2$[u]	H_2O	30	5.9	8	−6.2		303	
338		C_6H_{14}	30	1.5	4	−3.2		346	
339		CH_2Cl_2	30	6.1	5	−5		347	
340		CH_2Cl_2	25	6.1	5	−5		347	
341		Me-*c*-C_6H_{11}	30	4.1	4	−11		347	
342		Me-*c*-C_6H_{11}	50	4.1	4	−8		347	
343		Me-*c*-C_6H_{11}	30	4.1	4	−10		347	
344		Me-*c*-C_6H_{11}	40	4.1	4	−10		347	
345		CH_2Cl_2	25	6.1	5	−3		347	
346		CH_2Cl_2	30	4.1	4	−5		347	
347		Me-*c*-C_6H_{11}	30	4.1	4	−5		347	

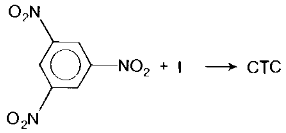
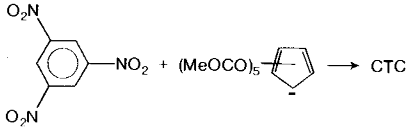
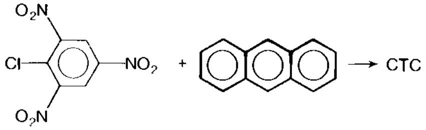
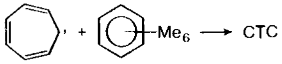
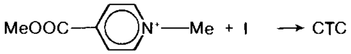
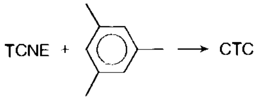
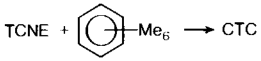
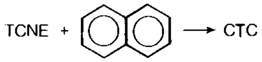
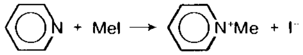
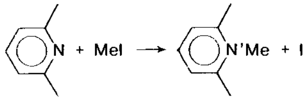
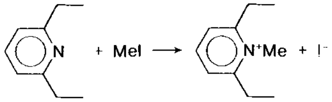
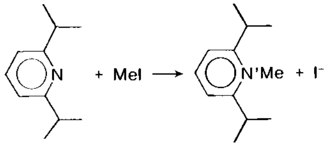
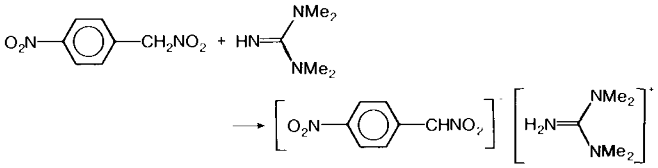
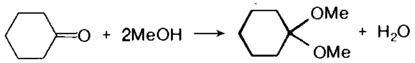
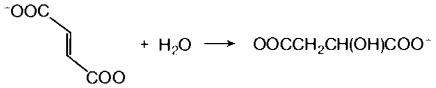
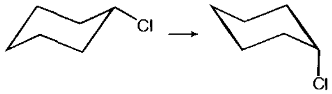
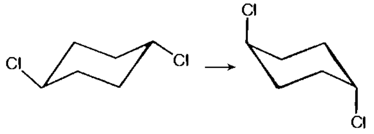
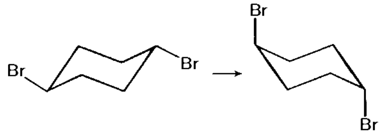
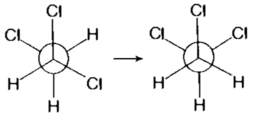
348		MeOH	25	3	5	0		348
349		MeOH	30	3	5	0		348
350		CH_2Cl_2	30	4.1	3	−8		347
351		Me-*c*-C_6H_{11}	30	4.1	4	−12		347
352		MeCN	30	3	5	0		348
353		Me_2CO	30	3	5	+16		348
354		*i*-BuOH	30	3	5	+17		348
355	TCNE + PhH → CTC	CH_2CL_2	30	6.1	5	−3		347
356		CCl_4	25	1.5	5	−3.4		349
357	TCNE + PhMe → CTC	CCl_4	25	1.5	5	−4.9		349
358		CCl_4	25	1.4	5	−7.1		350
359		CH_2Cl_2	30	6.1	5	−12		347
360		CCl_4	25	1.4	5	−14.1		350
361		CH_2Cl_2	30	6.1	5	−4		347
362		MeOH	25				−46.1	351
363		MeOH	25				−48.5	351
364		MeOH	25				−49.0	351

TABLE V (*Continued*)

No.	Reaction	Solvent	T, °C	P, kbars	No. of K data	ΔV, cm^3/mol^b (a)	ΔV, cm^3/mol^b (b)	Ref	Remarks
365		MeOH	25				−51.0	351	
366		Mesitylene	30	1.7	6	−15.9		172	
367		*o*-Xylene	30	1.7	6	−21.3		172	
368		PhCl	30	1.7	6	−21.9		172	
369		PhMe	30	1.7	6	−25.5		172	
370		PhOMe	30	1.7	6	−29.3		172	
371	$HCHO + H_2O \rightarrow HCH(OH)_2$	H_2O	25	2.1	30	−4.00		352	
372	$MeCHO + H_2O \rightarrow MeCH(OH)_2$	H_2O	25	2.1	30	−7.84		352	
373	$EtCHO + H_2O \rightarrow EtCH(OH)_2$	H_2O	25	2.1	30	−12.25		352	
374	$PrCHO + H_2O \rightarrow PrCH(OH)_2$	H_2O	25	2.1	30	−12.45		352	
375	$BuCHO + H_2O \rightarrow BuCH(OH)_2$	H_2O	25	2.1	30	−11.96		352	
376	$i\text{-}PrCHO + H_2O \rightarrow i\text{-}PrCH(OH)_2$	H_2O	25	2.1	30	−13.12		352	
377	$t\text{-}BuCHO + H_2O \rightarrow t\text{-}BuCH(OH)_2$	H_2O	25	2.1	30	−11.77		352	
378	$dl\text{-}HOCH_2CH(OH)CHO + H_2O \rightarrow dl\text{-}HOCH_2CH(OH)CH(OH)_2$	H_2O	25	2.1	30	−1.54		352	
379	$MeCOCOMe + H_2O \rightarrow MeCOC(OH)_2Me$	H_2O	25	2.1	30	−10 ∼ −11		352	
380	$MeCHO + HSCH_2CH_2OH \rightarrow MeCH(OH)SCH_2CH_2OH$	H_2O	25	2.1	30	−14.00		352	
381	$EtCHO + 2MeOH \rightarrow EtCH(OMe)_2 + H_2O$	MeOH	25	2.1	6	−4.6		353	
382	$PhCHO + 2MeOH \rightarrow PhCH(OMe)_2 + H_2O$	MeOH	25	2.1	5	−17.5		353	
383		MeOH	25	2.1	6	−12.5		353	
384	$PhCN + MeOH \rightarrow PhC(NH)OMe$	Neat	110	9.8	9	−17.9		354	
385		H_2O	RT	2	3	≃−10^v		355	0.05 M phosphate buffer, fumarase catalyzed
386	$CBM^w + I^- \rightarrow CBM\text{-}I$	H_2O	25	1.4	5	−5.8		280	μ = 0.2 M (KNO_3)
387		CS_2	≃50	10		−1.87		356	

388		CS_2	≃50	10		−2.8	
389		CS_2	≃50	10		−3.8	356
390		Neat	≃45	4.2	13	−3.8	357
391		CS_2	≃45	7		−1.8	357
392	$CaC^{16}O_{3(s)} + H_2{}^{18}O \rightarrow CaC^{18}O_{3(s)} + H_2{}^{16}O$	H_2O	500	20	6	0	358
393	$MeCOCH_2COOEt \rightarrow MeC(OH){=}CHCOOEt$	MeOH	20	3	4	+3	360
394		EtOH	20	3	4	+3	360
395		Me_2CHOH	20	3	4	+1	360
396		$n\text{-}C_6H_{14}$	20	3	4	0	360
397		$n\text{-}C_7H_{16}$	20	3	4	−0.5	360
398	$MeCOCH_2COMe \rightarrow MeCOCH{=}C(OH)Me$	MeOH	20	3	4	+12	360
399		EtOH	20	3	4	0	360
400		Me_2CHOH	20	3	4	−1	360
401		$n\text{-}C_6H_{14}$	20	3	4	+7	360
402		$n\text{-}C_7H_{16}$	20	3	4	+5	360
403		Neat	17	0.35		+4.7	361
404		Neat	63	0.35	4	+4.7	361
405		Neat	116	0.35	6	+4.7	361

[a] Abbreviations: CTC, charge-transfer complex; RT = room temperature; DME, $H_3COCH_2CH_2OCH_3$; THP, tetrahydropyran; glyme, $H_3CO(CH_2CH_2O)_3CH_3$; Fl^-, 9-fluorenyl; TCNE, tetracyanoethylene; pada and mu, see footnote *a* in Table IV. [b] Values in (a) column derived from pressure effect on equilibrium constant; values in (b) column derived from molar volumes of reactant(s) and product(s) or measured dilatometrically. [c] This phenol exists in water mainly in the form of 4-benzoquinone monoxime. [d] Calculated from ΔV (=+13.3 cm^3/mol) for 2-hydroxy-3-[(4-nitrophenyl)azo]benzoic acid + OH^- and for $H_2O \rightarrow H^+ + OH^-$. [e] Calculated from ΔV (=−29.07 cm^3/mol) for $NH_3 + H_2O \rightarrow NH_4{}^+\ OH^-$ and for $H_2O \rightarrow H^+ + OH^-$. [f] Partial molar volume of the volume of the bromide from ref 314. [g] Partial molar volume of the chloride from ref 315. [h] Partial molar volume of the chloride from ref 316. [i] Molecular weight ca. 4000. [j] For 1 mol of H^+. [k] Calculated from ΔV (=−26.49 cm^3/mol) for $PhNH_2 + H_2O \rightarrow PhNH_3 + OH^-$ and for $H_2O \rightarrow H^+ + OH^-$. [l] Estimated from the acid-catalyzed hydrolysis rate constant of *N-tert*-butylacetamide. [m] Calculated from the apparent molal volume of the salt and semiempirically estimated molal volume of the completely dissociated salt. [n] See ref 326 for semiempirical calculations. [o] Calculated from ΔV (= +3 cm^3/mol) for $FeOH^{2+} + H^+ \rightarrow Fe^{3+} + H_2O$ by assuming ΔV for ionization of water is −21 cm^3/mol. [p] Calculated by the present authors from the association constants at 1500 and 1000 bars assuming in $K = a + bP$. [q] Tight and loose ion-pair equilibrium. [r] Tight ion-pair and externally triglyme-complexed tight ion-pair equilibrium. [s] α-Picolinium chloride (59.9 mol%) + ethanolaminium chloride (40.1 mol%). [t] $SrSO_4$ is probably the trihydrate. [u] Dimer. [v] Estimated by the present authors. [w] Cobalamin.

increases. There is at present not a good rationale for this effect. Once again we see that the volume changes involved in multicharged ions are larger, the more so the closer the charges are together. The imidazolium ion represents once again a case of a charge delocalized and not efficiently solvated, and hence a volume decrease occurs upon proton transfer to water. The 2,6-pyridines show no regular trend until *tert*-butyl substitution is considered: the discontinuity found there was attributed[322] to the impossibility then arising in the formation of N–H hydrogen bonds to the solvent. *N-tert*-Butylacetamide has a large negative volume change associated with deprotonation;[199] in this case the rationale is that amides have pronounced zwitterionic character which is lost upon protonation of the nitrogen atom.

F. Ion-Pair Equilibria and Inorganic Reaction Volumes (Entries 223–333)

In the successive reaction stages:

$$\text{solid} \rightleftarrows \text{ionic aggregates} \rightleftarrows \text{tight ion-pairs} \rightleftarrows \text{loose ion-pairs} \rightleftarrows \text{free ions}$$

electrostriction should increase to the right and pressure should shift all these equilibria in that direction. However, it is difficult to say by how much. Thus, solids are notoriously hard to classify as covalent or ionic, aggregates are undefined as to the size of the clusters, and ion pairs are structurally not as well defined as the words intimate, solvent-separated, and ion would suggest. Add to this a fair degree of experimental difficulty and variety, and we have the ingredients of much confusion and disagreement.

Millero[323] has determined the volume change involved in the dissociation of ion pairs of rubidium and thallous nitrate. This was done by measuring densities of dilute solutions as a function of concentration, and by comparing the partial volumes with the estimated partial volumes of the free ions. He explains the difference between the two salts as possibly due to a contact ion pair in the thallium case vs. a solvent-separated pair with rubidium.

The very large value for sodium borate was attributed[297] to the binding of water, by what is apparently really the reaction

$$H_2O + Na^+,H_2BO_3^- \rightleftarrows Na^+ + B(OH)_4^-$$

In the next several cases of ion-pair dissociation, studied mostly as a pressure effect on electrical conductance, ΔV tends to be -8 to -10 cm^3/mol, and the one rather different result of -25 cm^3/mol for $CaSO_4$ was ascribed by Millero[325] to tight ion-pair character in this case; however, there are also some results by Osugi[324] showing this salt to be more or less unexceptional.

The copper(II) malonate and tartrate complexes show large negative volume changes upon dissociation that require the assumption of largely covalent character. The effect is somewhat smaller in highly concentrated urea solutions since this solute is known to break down the structure of water by competing with it in H-bond formation. Among the remaining observations of ion-pair behavior in water, there are several which are not easily accounted for. Thus, it is not clear why $CeCl^{2+}$ and $CeOOCEt^{2+}$ have contractions of -0.8 and -23.6 cm^3/mol, respectively.

When we turn to nonaqueous solutions, the effects become larger as the Drude–Nernst equation requires. Particularly interesting in this group is the tight–loose equilibrium of several ion pairs in ethereal solvents. Szwarc and Claesson[336–338] have found that alkali metal fluorenides are subject to contractions of 7 to 23 cm^3/mol in the loosening process. These species have UV spectra which are themselves pressure dependent, and hence their use to evaluate ΔV is not without hazards;[339] however, a similar result has been obtained by means of ESR in the sodium naphthalene ion pair (-15 cm^3/mol in THF at 0 °C).[57] A conductance method for some quaternary salts in acetone has given[340] values of about -15 to -25 cm^3/mol.

It should be expected that complete ionization in nonaqueous media should then be characterized by extremely large contractions, and there is evidence that this is so.[341] Kitamura has deduced volume decreases of several hundred cm^3/mol in alcoholic media when $CoCl_2$ ionizes; this result was obtained from conductance increases under pressure. Relaxation measurements of solutions of tetra-*n*-butylammonium picrate in ether at 25 °C (five measurements, over a 400-bar range) have led to a result of -125 cm^3/mol in that case.

The solubility of several sparingly soluble salts has been examined as a function of pressure,[344] and large volume decreases were found. Corrections were made for the hydrolysis of the anions. The ΔV° values were, in fact, in some cases not as large as listings of ionic partial volumes suggested, and the authors felt that some of the salts may form a hydrated surface under pressure, so that the equilibrium equation is accordingly altered.

Dimerization of acids has a negative reaction volume as might be expected from bond formation processes.[303] The reaction presumably involves the formation of several extra hydrogen bonds; for each such bond, a volume change of -4 cm^3/mol is expected (note, for example, the volume change in the complexation of phenol by *p*-dioxane).

Charge-transfer complexation has been studied extensively by Ewald. He finds an average of -7 cm^3/mol, if the donor and acceptor molecules are themselves neutral. Since this value applies in nonpolar solvents, we must attribute it primarily to a change in separation rather than to dipole development; in other words, there is not much charge transfer! When one of the members is charged, however, the effect of transfer is observable; complexation then, in fact, means delocalization, and the pressure effect is diminished to the vanishing point. When both members are charged (oppositely), neutralization occurs, and the reaction volume becomes large and positive.

The reaction volume in pyridine Menshutkin reactions has been mentioned earlier (in comparison with the activation volumes), or as has the proton transfer from α,*p*-dinitrotoluene to *sym*-tetramethylguanidine.

The hydration of carbonyl functions reduces the volume by amounts in excess of 10 cm^3/mol; clearly, the process does not diminish the ability of the hydroxy groups to participate in H-bonding. Interestingly, the two smallest members have sharply reduced reaction volumes. The same anomaly was observed in the case of the ionization volumes of carboxylic acids.

The conformational equilibria involving halogenated cyclohexanes and ethanes are all in favor of the more crowded conformers by small amounts. There are no instances as yet of pressure effects on isotopic exchange equilibria, nor are there likely to be many; atomic loccations in molecules are virtually independent of the isotopic mass. Even such substances as H_2O and D_2O have almost identical molar volumes. On the other hand, there are some examples of small changes in steric effects due to isotopic substitution;[359] these have been attributed to small differences in the amplitude of the zero-point vibration. Conceivably there may be small differences in volume in these instances as well.

Osugi[360] and Heidberg[361] have reported pressure effects on some keto–enol equilibria, by means of UV and NMR, respectively. Generally the values, in agreement with earlier ones (using more tedious chemical analysis),[362] are small and positive, roughly in agreement with parachor-based predictions.

VI. Photochemistry and Related Processes

Mechanistic investigations in photochemistry have become fashionable in recent years, and some high-pressure work has been reported as well. There are a number of special experimental problems in this, however, and the interpretation of observed effects is not always straightforward. We begin this section therefore with some general remarks.

First of all, while the literature now contains several photochemical "activation volumes", these results do not fit the simple definitions applicable in thermal reactions. The pressure effects may, in fact, be describable by a single number, but it seems best to us not to call this the activation volume; perhaps pseudoactivation volume is suitable.

By definition, the process begins with the molecular absorption of a photon.[363] Since the speed of light exceeds the velocity of molecules, or even the fastest moving parts of vibrating molecules by several orders of magnitude, one may assume that the absorption process does not involve significant nuclear displacements; the volume should not change during this part of the reaction (Franck–Condon principle). This does not mean that absorption is pressure independent; quite to the contrary, examples of (usually fairly small) pressure effects on spectra abound in the literature.[364] However, these effects are due to pressure-induced changes in the solvation of the molecule, and perhaps to minute distortions; in any case, they are certainly not due to any volume changes in the absorption process itself. In any case, any quantitative work which seeks to unravel true activation processes in the individual steps of a photochemical reaction must surely include measurements of the effect of pressure on the quantum yield and energy of absorption, i.e., on the spectrum. After the absorption, the molecule will assume its new shape, relax vibrationally, and reequilibrate with surrounding molecules. It will thereafter have a new partial volume; as yet this quantity is not yet known in even a single case, but since both its shape and dipole will normally have changed, it may be more than trivially different from that of the ground state.

The excited singlet is one of several possible branch points in the overall process. Thus, it may simply undergo radiationless decay, by transferring its excess energy into some ground-state vibrational mode (internal conversion). It is usually not clear what role surrounding molecules have in this process, and hence what effect pressure is likely to have on it. Alternatively, the singlet may fluoresce. Since the simple decay is usually very fast, fluorescence (or any other competing process, for that matter) must be fast also if it is to compete effectively; the time scale is of the order of 10^{-8} s or so. The fluorescence process, if it is spontaneous, is subject to exactly the same considerations as is the absorption process; i.e., there is no change in volume during emission, but both intensity and energy (wave length) may be pressure dependent. After emission, the hot ground state then quickly reestablishes its initial geometry and surroundings. One of the complications arising in fluorescence is that it may be (in part) induced by another molecule, the so-called quencher. Since the quenching process must be fast, we are dealing with a bimolecular reaction which will often be diffusion controlled. Such reactions are obviously retarded by pressure; the pressure dependence of the rate in such cases should parallel the viscosity dependence.

Intersystem crossing to the lowest triplet state is another possible fate of the excited singlet, but the pressure dependence of this process is difficult to predict. Lastly a chemical reaction may occur to give new products, almost always in their (hot) ground states. The pressure effect for these reactions may be interpretable simply in terms of their volume profiles, with the excited state serving as the initial state. Since one ordinarily does not know the absolute rate constant, the best that can be done is to measure the effect of pressure on the quantum yield, but ϕ is usually a complex function of several rate constants and hence not readily interpretable in terms of activation volumes. Absolute rate constants for chemical conversion of excited states can be determined by means of single photon-counting techniques, but these have not yet been applied with sufficient accuracy to consider adaptation to high-pressure apparatus.

If crossing to the triplet state does occur, after cooling has progressed to the vibrationally lowest level, the same possibilities of radiationless decay, emission (phosphorescence), energy transfer to another molecule (sensitization), or chemical reaction present themselves. They differ from those of the singlet in that the element of spin inversion necessary for return to the ground state leaves the triplet a longer lived species; 1 ms or so lifetime is quite common, and hence slower processes can compete. This is an important consideration because one of the problems to consider in studies of pressure effects on photochemical reactions is that if the reactions are exceedingly fast and hence the barriers very low, the formalism of the absolute rate theory may not be applicable. If the reactant excited state can get over the barrier on the first few tries, so to speak, a condition central to the derivation of the Eyring equation is not fulfilled. This is not to say that no pressure effects will occur, or that these effects will not resemble those observed in slower reactions, but they cannot be confidently related to differences in partial volume between reactant and activated complex.

To continue this list of woes, there is a general lack of information about elementary photoprocesses that is usually taken for granted in thermal reactions. For example, it is not known in general how closely the reaction partners must approach in quenching or sensitization processes. They seem only modestly sensitive to steric factors[365] and hence very close approach is not needed, but nothing more quantitative is known. And finally, there are still some experimental problems to be tackled as well. The weakness of window materials means that the vessel apertures are generally small, usually about 5 mm or so. Internal actinometers cannot be used until their pressure sensitivity has been determined. Most optical cells that have been used to date succeed in exposing only a small fraction of the solution to the light traversing the pressure vessel, so that uncertainties arise (due to pressure inhibited diffusion) when yields are considered: diffusion of reactant molecules into the irradiated zone plays a role, and under pressure, an increasingly adverse one. This factor alone casts doubts on much of the work reported so far. Clearly, the high-pressure photochemist has his work cut out for him! Nevertheless, some beginnings have been made, and the rest of this section is devoted to a review of these contributions.

An all-quartz cell is now available[366] so that the errors and uncertainties due to contacts of the solution of interest with plastic and metal parts or mercury bridges can be avoided. It is essentially a quartz syringe, with a quartz window seal at each end. It makes an economic use of the cylindrical space usually available in high-pressure vessels, and since its length is the only dimension that varies with pressure, compressibility corrections are obviated.

Ewald[367] has studied the fluorescence of anthracene under pressure, and learned that the quenching by carbon tetrabromide is inhibited in a way which is just opposite to the pressure-induced increase in solvent viscosity. Variations in the quenching efficiency with solvent viscosity at atmospheric pressure are also observed, and the conclusion is clear: fluorescence quenching is a diffusion-controlled process in this case. The pressure dependence may therefore be used as a more convincing, if less accessible, method to show that a given process is diffusion controlled.

Metcalf[368] reached a similar conclusion on the same grounds regarding the fluorescence of 9,10-diphenylanthracene and its quenching by oxygen; on the other hand, quenching by carbon tetrachloride in this instance was virtually unaffected by pressure, and this process is evidently not diffusion limited.

A still more complicated situation was analyzed by Weller.[369] Pyrene has a fluorescence band which increases in intensity with concentration up to a maximum, but with further concentration increases it gives way to a new band which is clearly due to an excimer. The excimer emission is inhibited by pressure in such a way as to reveal the diffusion control of excimer formation. When excimer fluorescence of benz[1,2]anthracene is examined, one finds that it increases with pressure at low pressures, reaches a maximum at 2–3 kbars, and then declines. The authors interpreted the initial increase as due to equilibrium excimer formation, which has a reaction volume of -6 cm^3/mol associated with it, and they assume that at higher pressures diffusion control begins to limit the rate. It is interesting that the singlet forms a charge-transfer complex with a volume decrease similar to that of ordinary ground-state acceptors. Perhaps equally interesting,[370] the effects of pH and of pressure on the fluorescence spectrum of acridine in water has revealed that ΔV_i for excited acridine is -25 cm^3/mol, similar to that of ground-state amines; however, ΔV_i for β-naphthol is only -6 cm^3/mol,[371] indicating that this phenol must be highly polarized in the excited state.

Osugi[372] studied the photochemistry of anthracene and 9-methylanthracene in *n*-hexane. He finds that the photodimerization is retarded in a way approximately expected for diffusion control. Tanaka[373] found that the pressure effect on the fluorescence quantum yield of anthracene is remarkably dependent on substituents: steep increases occur with 9-alkyl groups, but not with anthracene itself. It was considered that the fluorescence rate is unaffected, and that effects are due to changes in intersystem crossing. The Kyoto group has also reported a comparison of the pressure effects on the thermal and photodissociations of azobisisobutyronitrile, and found only a slight difference in pressure effect.[374]

Other work reported in this area includes work by Neuman,[375] who has compared the behavior of diradicals generated thermally and photolytically, a study by Kelm,[82] who made use of the chemiluminescence generated in the decomposition of oxetanes to follow that reaction, one by Hamann who found that pressure promotes the photodimerization of methyl 3-methoxy-2-naphthoate,[376] and two studies carried out in Stony Brook to compare cycloadditions carried out photochemically with those done thermally. The well-known pressure-bestowed advantage of $[4n + 2]$ cycloadditions becomes that of the $4n$ analogs in the photoreactions. Thus, pressure does not favor photosubstitution over $[2 + 2]$ cycloaddition in the irradiation of mixtures of naphthalene and acrylonitrile even though the former reaction has the volume advantage of an ionic transition state;[377] in a direct comparison of the allowed and forbidden photocycloadditions, the $[4 + 4]$ cycloaddition of 9-cyanoanthracene to cycloheptatriene was found to be promoted by pressure over the $[4 + 2]$ mode.[378] An intriguing observation by Mataga, a pressure-induced and reversible formation of a photoproduct of pyrene in oxygenated alcohol, is as yet unexplained.[379]

The work by Schindewolf on solvated electrons under pressure, and by Hentz et al. on γ radiolysis under pressure has provided us with some additional insights in this area. Schindewolf reports[380] that electrons in ammonia (from dissolved sodium metal) have an optical spectrum quite sensitive to pressure (blue shift of ~1 Å/atm) and temperature (red shift of ~25 Å/°C); from these data he shows that ammoniated electrons have a compressibility and thermal expansion considerably in excess of those of ammonia itself. The equilibrium constant for the process

$$H_2 + KNH_2 \rightleftarrows NH_3 + K^+ + e^-$$

at -33 °C under pressure was evaluated from the intensities; ΔV was found to be about $+63$ cm^3/mol. By combining this information with partial volume data of the other species in the equation, Schindewolf[381] was able to appraise $\overline{V}_{e^-}$ as 84 cm^3/mol; thus the electron is in a cavity of 3-Å radius. Virtually the same information applies to the spin-compensated electron pairs in ammonia, studied at higher concentration by ESR.[382] Interestingly, the effect of pressure on the optical spectra of electrons in water and simple alcohols (obtained by γ-pulse radiolysis techniques) is much less drastic;[383] in that medium, electrons apparently occupy much smaller cavities.

The rates of solvated electron-mediated processes are slow enough to be measurable, and this has been done now in many cases under pressure by the groups of Freeman, and of Hentz and Farhataziz. It has been learned that the reaction

$$e^- + ROH \rightarrow RO^- + \dot{H}$$

has an activation volume of about -20 cm^3/mol, due perhaps to the collapse of the cavity; for the "slow" reaction with aromatic hydrocarbons to give the radical anions, $\Delta V^{\ddagger} \approx -6$ cm^3/mol. For most other species, reaction is rapid and probably diffusion controlled; the activation volumes are positive.[384] The reaction:

$$Fe^{2+} + H \rightarrow FeH^{2+}$$

which is probably the first step in

$$Fe^{2+} + H + H^+ \rightarrow Fe^{3+} + H_2$$

has an activation volume of -9 cm^3/mol;[385] a value of -16.8 cm^3/mol applies to[386]

$$e^- + HCO_3^- \xrightarrow{H_2O} H + CO_3^{2-}$$

The reactions[387]

$$e^- + H_2O \rightarrow H + OH^-$$

$$e^- + H_2O^+ \rightarrow H + H_2O$$

have activation volumes of -14 and about 0 cm^3/mol, respectively. All these results have been deduced from the quantum yields in pulse radiolyses of compressed aqueous solutions. While most of them rest on certain assumptions (such as values for $\overline{V}(H^+)$, $\eta(H_2O)$, or f(p), etc), it is clear from the results that $\overline{V}_e$ is relatively small and the electron cavity in water is tiny compared to that in ammonia. The most recent estimate by Hentz[388] is that the radius is about 0.7–1.3 Å.

To conclude this section, it is clear that the combination of irradiative processes and high pressure offers possibilities for study of both fundamental questions and applications. In the latter area, such simple experiments as pressure-induced changes in product distributions and stationary-state compositions have been reported in only few cases, even though shifts in the direction of more highly branched or crowded products seem both likely and desirable in many cases. More experience in this area is certain eventually to be helpful in more fundamental questions as well.

VII. Biological and Biochemical Processes

The state of the art in this area is similar to that in the photochemical area: so little is known that it is difficult to interpret the pressure effects in even the simplest experiments. There are several reasons for this. The systems of interest are often at once both aqueous and organic, and little is known about processes occurring at the interface. The molecules are large, often with unknown conformation. The volume changes in many instances seem very large on a molar basis, but in terms of volume fractions they are small. As with small molecules, volume changes may have any of several causes, but in biochemistry and biology, the background information available is usually so much poorer that it is hard to argue convincingly for any one of them. We consider here systems of increasing complexity: relatively small and well-defined molecules, polymeric substances with regularly reoccurring units, and proteins and enzymes.

Micelles have been studied under pressure in several laboratories. When an ionic substance in which one of the ions carries one or more large hydrocarbon groups is dissolved in water, the ions may congregate at some concentration to form micelles; these are globules in which the hydrocarbon residues have joined together in such a way as to leave the ionic sites in peripheral positions. A number of counterions are associated with the charged sphere, which may contain from 50 to 100 of the large ions. In hydrocarbon media inverse micelles can sometimes be observed, but these are of course of little interest in biology. If we consider large anions, the process may be represented by:

$$nA^- + (n - z)C^+ \rightleftarrows M^{z-}$$

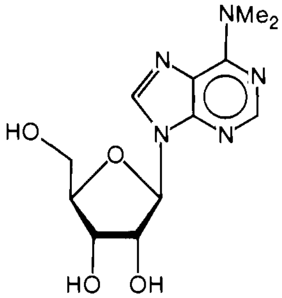
The concentration at which the formation of micelles begins is known as the critical micelle concentration (cmc); this can be determined in several ways, for example, by means of conductivity measurements. The effect of pressure can easily be determined, giving the volume change for the process in terms of cm^3/mol of anions. Dilatometric experiments are of course also possible.

Several electrolytes have now been studied in this way, and the general result is that the volume increases substantially in the process: expansions of 5 to 10 cm^3/mol anion are usually observed. Small variations occur from one case to another; for example, among *n*-alkanesulfonates, ΔV (room temperature) is +5 cm^3/mol at C_8,[389] +8 cm^3/mol at C_{10},[390] 10 cm^3/mol at C_{12},[391] and 11 cm^3/mol at C_{14};[391] with *n*-alkyltrimethylammonium bromides, similar variations hint at larger volume increases with longer chains.[389,392] Various responses of the cmc to pressures have been noticed; a maximum at some pressure is not uncommon.[392]

Most of the discussion of the volume increase has centered about the so-called hydrophobic interaction. When a hydrocarbon moiety is introduced in water, the water structure is locally perturbed, and the effects on thermodynamic properties are measurable. Thus, when the partial molal volumes of alcohols and amines in water are compared with the molar volumes, one finds that the latter are larger: in other words, a contraction occurs upon dissolution. Small increases furthermore occur at higher molecular weights. One may consider this the result of a molecule being transferred from a region of relatively low internal pressure to a much higher one; in any case, a fairly convincing case can be made for the proposition that micelle formation should have a positive volume contribution from this phenomenon. The difficulty is that there must be other contributions that are hard to evaluate, so that the overall result and its interpretation are only deceptively simple. The mere fact that the sign of ΔV is right is not sufficient!

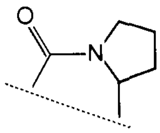
Thus, the electrostriction is subject to two effects which are potentially large. One of these is charge concentration. The survey of activation and reaction volumes repeatedly reveals that bringing together like charges causes a decrease in volume, and creating a spherical surface of more or less uniform charge density should make a large negative contribution to the volume. This is offset by association with cations. It is not clear whether the association is tight or loose, and how the hydration of the ionic sites changes in the process; these are questions that cannot now be answered. Nor is the structure of the interior of the micelles known; thus, the question arises whether it is better considered a liquid or solid, and whether the chains are extended or coiled. The volume of melting is quite large for hydrocarbons, and this contribution alone, in absolute terms, may be comparable to or larger than the observed volume change. The burial of one or more ionic sites inside the micelle would likewise have implications for the volume. Thus, even if the simple interpretation is correct and hydrophobic interactions are characterized by net volume decreases, the case has then been made only for simple saturated hydrocarbon chains, and extrapolation even to aromatic rings is hazardous.

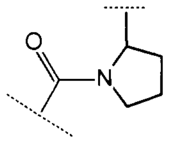
A second major question that arises is the effect of conformational change. Even in small molecules such as dimethylformamide, a single bond rotation may have a substantial activation volume, as noted above. A related instance in a molecule of biological interest is that of N^6,N^6-dimethyladenosine; Lüdemann has studied the effect of pressure on the coalescence temperature of the methyl proton magnetic resonances; the activation volume is about +10 cm^3/mol.[393]



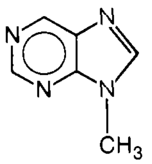
It is tempting, of course, to ascribe this result, so similar to that with simple amides, to loss of the dipole as the conformation reaches the perpendicular stage; however, for the same reason, loss of the dipole, the primary hydroxy group may lose its favorite H-bonding partner, the adenine group may change its ability to stack (see below), and so on. In high molecular weight substances, the rotation of just a few, or even one bond could conceivably bring about a fairly drastic change in shape. If such a change caused the exposure to solvent of parts of the molecule previously hidden inside, the volume change could be large, and have either sign; if polar or ionizable groups are exposed, the volume may decrease, and if hydrocarbon moieties become shielded, it may increase. In large molecules furthermore, another problem may arise, that of cooperativity, as is demonstrated by the following example.

Poly-L-proline is known in two helical forms, one containing cis amide linkages and the other trans. For certain 1-propanol–acetic acid mixtures the two forms are in equilibrium, and ΔV can be measured by the pressure effect on the equilibrium. This has been done by Rifkind and Applequist;[394] the effects observed could only be interpreted by assuming a high degree of cooperativity (each unit preferring another of like conformation as its neighbor). At 7 kbars the conversion of the trans form to the cis is complete. The direction is in agreement with the known fact that the cis helix is much shorter per unit proline, but the reason for the volume difference is not known. The same comment must be made about the helix–coil transitions under pressure; pressure effects have been observed in both directions (for example, poly-γ-benzyl-L-glutamate,[395] and poly-RNA and -DNA[396]). Protein denaturation is affected by pressure in only one way: it is always favored. The effects vary in magnitude; for ribonuclease A, ΔV can be as low −5 cm^3/mol;[397] for chymotrypsinogen, $\Delta V = -40$ cm^3/mol;[398] for metmyoglobin, under certain conditions,[399] the volume decrease is 100 cm^3/mol or more. In all of these cases, the pressure-induced denaturation is reversible.

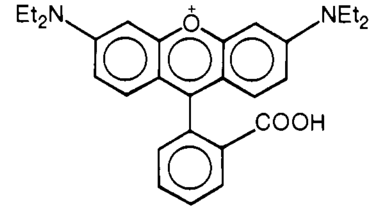


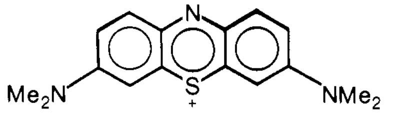


A third special effect with molecules or biological interest is the so-called base stacking; this phenomenon may be caused by charge transfer, by bridging water H-bonded water molecules, or as a result of hydrophobic interactions. Lüdemann has deduced[400] from the pressure effect on the chemical shifts of 9-



methylpurine that self-association has a volume change of −4 cm^3/mol, opposite to that expected from hydrophobic interactions. Sound absorption measurements under pressure have similarly yielded a volume decrease of about 7 cm^3/mol for N^6,N^9-dimethyladenine.[401] The self-association of the dyes rhodamine B and methylene blue is characterized by volume decreases of 10.5 cm^3/mol; hydrophobic interactions were consequently ruled out, and bridging water molecules favored by the authors[402] (however, charge concentration may have contributed).





The pressure-jump technique was used to measure the entire volume profile of the two-step reaction of bromphenol blue with β-lactoglobulin B. The profile is perhaps best described by the phrase that the initial state is the densest state. The expansion was ascribed[403] to hydrophobic interactions, but this is only one possibility. Rather complex behavior is observed in the complexation of riboflavin binding protein with flavin mononucleotide; fluorescence was used as the probe in this case. The association is characterized by a small volume decrease (3 cm^3/mol); perhaps more interesting is the fact that there is a red shift in the spectrum of the protein alone which was attributed to increased exposure of the tryptophan to solvent.[404] At very high pressure the complex dissociates again and the protein is reversibly denatured with a characteristic large and negative reaction volume (−75 cm^3/mol). A somewhat similar case is the association of β-casein, studied by Payens and Heremans[405] by means of light scattering. They find that depolymerization occurs at low pressures (below 1.5 kbars), but above that pressure reassociation takes place: the low- and high-pressure results clearly involve different β-casein molecules. The change was described by the authors as a conformational one.

Related findings have been reported as pressure effects on the visible spectrum of metmyoglobin fluoride (attributed to conformational changes),[406] on the complexation of polyadenylic and polyuridylic acids (inhibition attributed to counterion binding),[407] on the rate and equilibrium constants of complexation of several nucleotides,[408] on the reaction of adenosine and adenosine 5′-phosphate with hydroxide and the formation of double-stranded polyriboadenylic acid,[409] on the unfolding of ribonuclease,[410] on the equilibration of the two forms of metarhodopsin,[411] on the antibody–antigen reaction,[412] and on the association of *E. coli* ribosomes.[413]

The formation of chemical bonds would be expected to be characterized by a volume decrease; as an example, the binding of methionine to iron in cytochrome *c* is strongly promoted by pressure.[414] Yet this is not always the case; both positive and negative volume changes have been encountered in the binding of small molecules to the hemo- and myoglobins. Such variations may be caused by hydration and conformation changes; the magnitude is often pH dependent.[415] Perhaps the most important results are that oxygen binding to hemo- and myoglobin is retarded, and that of carbon monoxide is accelerated.[416] In one case, the cause of a positive value was identified:[417] the binding of carbon monoxide to ferroprotoporphyrin IX is retarded by pressure because of diffusion control, as was evident from solvent effects.

The intriguing question of the mechanism of enzyme catalysis has attracted a fair share of the attention of high-pressure investigations. Thus, Neuman has measured the rates of hydrolysis of *p*-nitrophenyl esters catalyzed by hydroxide ion, by Tris buffer, and by chymotrypsin. All these reactions are accelerated by pressure, but no startling differences between the pressure effects were noted.[418-420] Other enzyme experiments under pressure have included dextransucrase,[421] fumarase,[422] glycolytic enzymes,[423] lactate dehydrogenase,[424] lysozyme,[425] ribonuclease,[426] and liver dehydrogenase;[427] as yet, no real breakthrough has occurred in any case as a result of these experiments.

VIII. Appendix

In this section we list items that reached our attention after the preceding sections had been completed.

In view of the increasing use of the diamond cell in the studies of liquids, it is well to call attention to a paper by Christian,[428] which reports that the actual pressure in the liquid sample may be vastly below the applied pressure, most of the resistance being taken up by the metal gasket.

Table VI lists a number of recently measured activation volumes.

One of the results that stands out in Table VI is that Kelm could find no difference in the activation volumes of the hydrogen and deuterium abstractions of phenols and deuterated phenols by 2,2-diphenylpicrylhydrazyl. This is not unexpected, since among stable molecules there are no known examples of significant differences in molar volume between substances that differ only isotopically; however, a difference of no less than 10 cm^3/mol was reported by Isaacs for the chloranil oxidations of a pair of protio- and deuteriotriphenylmethanes. If this result stands up, it would provide a unique example of a pressure effect on an isotope effect. It is perhaps one of the strongest hints of the intervention of tunnelling in a chemical reaction as yet uncovered.

The table concludes with remarkably clear-cut results on the mechanism of solvent exchange of a number of niobium and

TABLE VI. Activation Volumes

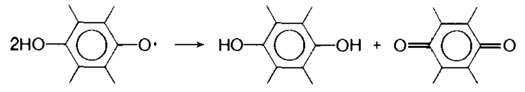
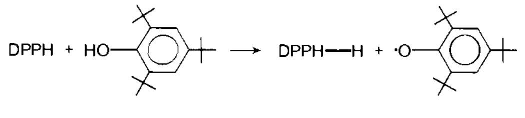
No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	Δ*V**, cm^3/mol	Ref	Remarks
1	$Me_2C(CN)N{=}NC(CN)Me_2 \rightarrow [Me_2C(CN){\cdot}N_2{\cdot}C(CN)Me_2]_{cage}$	PhMe	62.3	4.9	5	+2.5	429	
2	$Me_2C(CN)N{=}NC(CN)Me_2 + I_2 \rightarrow 2Me_2C(CN)I + N_2$	PhMe	62.3	4.9	5	+6.0	429	
3		PrOH	25	2.5	5	+5	430	
4		PhMe	25	1.5	7	−13.7	431	

TABLE VI *(Continued)*

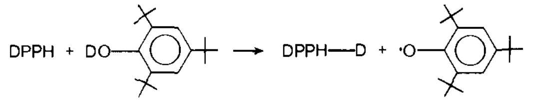
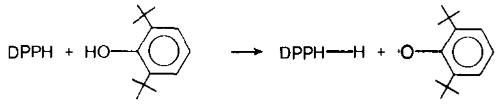
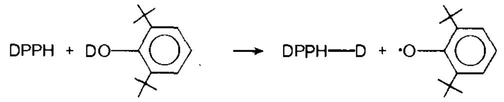
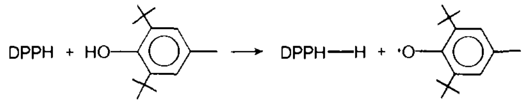
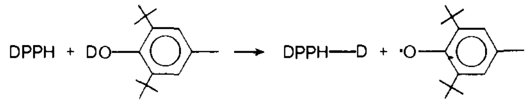
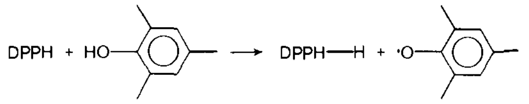
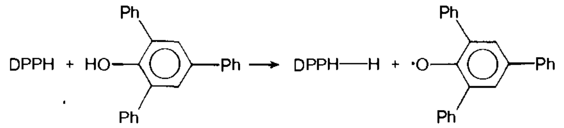
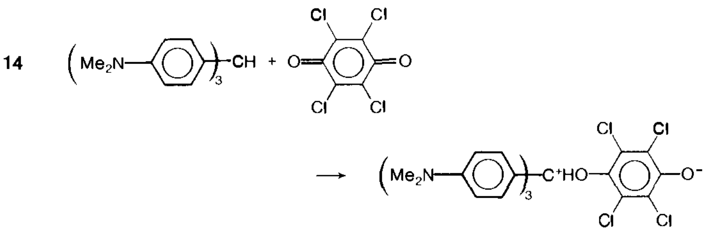
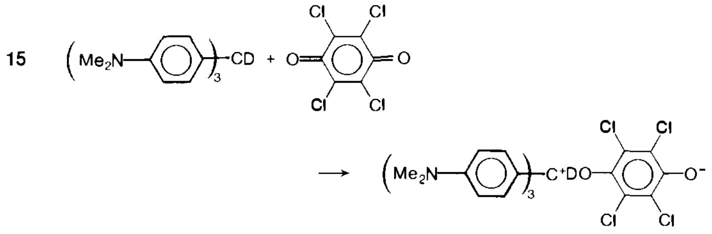
No.	Reaction	Solvent	T, °C	P, kbars	No. of k data	ΔV^*, cm^3/mol	Ref	Remarks
5		PhMe	25	1.5	7	−12.7	431	
6		PhMe	25	2.0	9	−13.3	431	
7		PhMe	25	1.5	7	−13.1	431	
8		PhMe	25	2.0	8	−13.1	431	
9		PhMe	25	1.5	7	−13.2	431	
10		PhMe	25	0.3	4	−13.5	431	
11		PhMe	25	1.5	7	−11.4	431	
12	$Ph_2CN_2 + PhCOOH \rightarrow Ph_2CHOCOPh + N_2$	Bu_2O	26.5	1.1	6	−13.1	432, 433	
13	$Ph_2CN_2 + PhCOOD \rightarrow Ph_2CDOCOPh + N_2$	Bu_2O	26.5	1	5	−12.8	432	
14		MeCN	29.5	2	11	−25.5	432	
15		MeCN	29.5	2	11	−35.8	432	
16	$SnMe_4 + I_2 \rightarrow SnMe_3I + MeI$	Bu_2O	29.1	1.1	12	−50	434	
17	$Ni(MeOH)_6^{2+} + {}^*MeOH \rightarrow Ni(MeOH)_5{}^*MeOH + MeOH$	MeOH	34	2		+10.9	435	From p effect on NMR
18	$NbCl_5{\cdot}Me_2O + {}^*Me_2O \rightarrow NbCl_5{\cdot}{}^*Me_2O + Me_2O$	CH_2Cl_2		2		+28.7	436	"
19	$NbCl_5{\cdot}MeCN + {}^*MeCN \rightarrow NbCl_5{\cdot}{}^*MeCN + MeCN$	$CHCl_3$		2		+19.3	436	"
20	$NbCl_5{\cdot}t\text{-}BuCN + {}^*t\text{-}BuCN \rightarrow NbCl_5{\cdot}{}^*t\text{-}BuCN + t\text{-}BuCN$	$CHCl_3$		2		+15.2	436	"
21	$NbCl_5{\cdot}(MeO)Cl_2PO + {}^*(MeO)Cl_2PO \rightarrow NbCl_5{\cdot}{}^*(MeO)Cl_2PO + (MeO)Cl_2PO$	$CHCl_3$		2		+20.5	436	"
22	$NbCl_5{\cdot}(Me_2N)_3PS + {}^*(Me_2N)_3PS \rightarrow NbCl_5{\cdot}{}^*(Me_2N)_3PS + (Me_2N)_3PS$	CH_2Cl_2		2		+19.3	436	"
23	$NbBr_5{\cdot}Me_2S + {}^*Me_2S \rightarrow NbBr_5{\cdot}{}^*Me_2S + Me_2S$	CH_2Cl_2		2		−12.6	436	"
24	$TaCl_5{\cdot}Me_2O + {}^*Me_2O \rightarrow TaCl_5{\cdot}{}^*Me_2O + Me_2O$	CH_2Cl_2		2		+27.8	436	"
25	$TaCl_5{\cdot}Me_2S + {}^*Me_2S \rightarrow TaCl_5{\cdot}{}^*Me_2S + Me_2S$	CH_2Cl_2		2		−19.8	436	"
26	$TaCl_5{\cdot}Me_2Se + {}^*Me_2Se \rightarrow TaCl_5{\cdot}{}^*Me_2Se + Me_2Se$	CH_2Cl_2		2		−18.7	436	"
27	$TaCl_5{\cdot}Me_2Te + {}^*Me_2Te \rightarrow TaCl_5{\cdot}{}^*Me_2Te + Me_2Te$	CH_2Cl_2		2		−10.7	436	"
28	$TaBr_5{\cdot}Me_2Se + {}^*Me_2Se \rightarrow TaBr_5{\cdot}{}^*Me_2Se + Me_2Se$	CH_2Cl_2		2		−13.6	436	"
29	$TaBr_5{\cdot}Me_2Te + {}^*Me_2Te \rightarrow TaBr_5{\cdot}{}^*Me_2Te + Me_2Te$	CH_2Cl_2		2		−16.4	436	"

TABLE VII. Activation Volume Differences

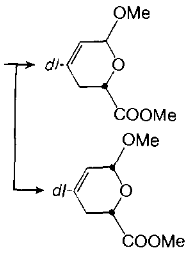
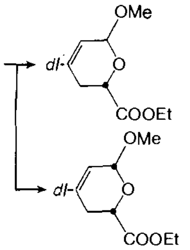
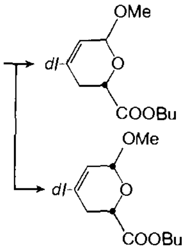
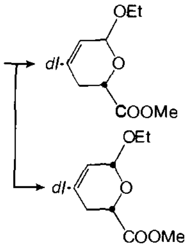
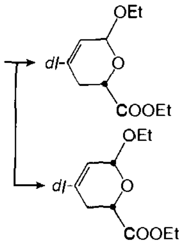
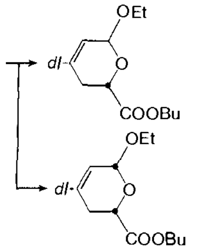
No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	$\delta\Delta V^{\ddagger}$ cm³/mol	Ref	Remarks
1	$Me_2C(CN){\cdot}N_2{\cdot}Me_2C(CN) \rightarrow Me_2C(CN)C(CN)Me_2 + N_2$ $\xrightarrow{I_2} 2Me_2C(CN)I$	PhMe	62.3	4.9	5	0 +9.97	429	
2	pentane or hexane + $Cl_2 \xrightarrow{AIBN}$ primary carbon chlorination $\rightarrow$ secondary carbon chlorination	Neat	40	5.9	4	0 −0.7	437	
3	$Me_2CHCHMe_2 + Cl_2 \xrightarrow{AIBN} Me_2CHCHMeCH_2Cl$ $\rightarrow Me_2CHCMe_2Cl$	Neat	40	5.9	4	0 −0.9	438	
4	$t\text{-}BuO{\cdot} \xrightarrow{AIBN - t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{t\text{-}BuPh} t\text{-}BuOH + PhCMe_2CH_2{\cdot}$	PhCl	50	3.9	4	0 −10.0	439	*b*
5	$t\text{-}BuO{\cdot} \xrightarrow{AIBN + t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{MePh} t\text{-}BuOH + PhCH_2{\cdot}$	PhCl	50	3.9	4	0 −14.0	439	*b*
6	$t\text{-}BuO{\cdot} \xrightarrow{AIBN - t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{c\text{-}HexH} t\text{-}BuOH + c\text{-}Hex{\cdot}$	PhCl	50	2.0	3	0 −14.4	439	*b*
7	$t\text{-}BuO{\cdot} \xrightarrow{AIBN + t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{HeptH} t\text{-}BuOH + s\text{-}C_7H_{15}{\cdot}$	PhCl	50	2.0	3	0 −15.5	439	*b*
8	$t\text{-}BuO{\cdot} \xrightarrow{AIBN + t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{EtPh} t\text{-}BuOH + PhCHMe{\cdot}$	PhCl	50	2.0	3	0 −12.6	439	*b*
9	$t\text{-}BuO{\cdot} \xrightarrow{AIBN - t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{Ph_2CH_2} t\text{-}BuOH + Ph_2CH{\cdot}$	PhCl	50	2.0	3	0 −16.5	439	*b*
10	$t\text{-}BuO{\cdot} \xrightarrow{AIBN - t\text{-}BuOCl} MeCOMe + Me{\cdot}$ $\xrightarrow{i\text{-}PrPh} t\text{-}BuOH + PhCMe_2{\cdot}$	PhCl	50	2.0	3	0 −17.1	439	*b*
11	$CH_2{=}CH{-}CH{=}CHOMe$ + MeOCOCHO 	MeOPh	50	5.9	2	0 −0.9[a]	440	
12	$CH_2{=}CH{-}CH{=}CHOMe$ + EtOCOCHO 	MeOPh	50	5.9	2	0 −1.1[a]	440	
13	$CH_2{=}CH{-}CH{=}CHOMe$ + BuOOCCHO 	MeOPh	50	5.9	2	0 −0.9[a]	440	
14	$CH_2{=}CH{-}CH{=}CHOEt$ + MeOOCCHO 	MeOPh	50	5.9	2	0 −1.1[a]	440	
15	$CH_2{=}CH{-}CH{=}CHOEt$ + EtOOCCHO 	MeOPh	50	5.9	2	0 −0.7[a]	440	

TABLE VII (*Continued*)

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *k* data	$\delta\Delta V^*$ cm³/mol	Ref	Remarks
16	CH_2=CH—CH=CHOEt + BuOOCCHO → 	MeOPh	50	5.9	2	0	440	
						-0.7^a		

^{a} Calculated by the authors. ^{b} In the presence of trichloroethylene.

TABLE VIII. Reaction Volumes

No.	Reaction	Solvent	*T*, °C	*P*, kbars	No. of *K* data	ΔV, cm³/mol^a	Ref	Remarks
1	PhMe + I_2 → CTC	Hexane	25	2.0	6	−7.10	442	
2		Hexane	40	2.0	6	−6.20	442	
3		Hexane	60	2.0	6	−5.10	442	
4	$2Ag + Hg_2Cl_2 \rightarrow 2Hg + 2AgCl$	H_2O	25	10.0	11	−5.4	443	From electromotive force of $Ag \mid AgCl \Vert Hg_2Cl_2 \mid Hg$
5	$2Ag + Hg_2Br_2 \rightarrow 2Hg + 2AgBr$	H_2O	25	10.0	11	−6.0	443	From electromotive force of $Ag \mid AgBr \mid Hg_2Br_2 \mid Hg$
6	$Zn + Hg_2I_2 \rightarrow ZnI_2 + 2Hg$	H_2O	25	10.0	11	$+1.62^b$	444	From electromotive force of $Zn \mid ZnI_2 \Vert Hg_2I_2 \mid Hg$
7	$Li^+, Br^- \rightarrow Li^+ + Br^-$	Me_2CO	25	5	6	−25	445	
8	$Et_2O + I_2$ → CTC	C_7H_{16}	25	3.3	4	−6.7	446	

^{a} Derived from pressure effect on equilibrium constant. ^{b} The reaction volume is negative above 6 kbars.

tantalum complexes. Both dissociative and associative reactions are observed.

Table VII lists the most recent activation volume differences. Perhaps the most worthwhile data there are Zhulin's observations on the effect of pressure on the competition between the decomposition of the *tert*-butoxy radical (to acetone and methyl radical) and its abstraction of hydrogen from various donors. The latter reaction has a smaller activation volume; the difference amounts to about 15 cm³/mol. In other work, Zhulin reports the trimerization of acetonitrile at 15 kbars.[441]

Finally, Table VIII contains among other data Ishihara's interesting result that the dissociation of lithium bromide ion pairs in acetone causes a volume diminution of 25 cm³/mol. Once again, therefore, caution is clearly necessary in the interpretation of rate data under pressure if ionic reactions in relatively nonpolar media are under study.

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IX. References and Notes

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