[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

The Influence of Inert Cations on the Reduction of Complex Anions. Polarography of the Cadmium EDTA Complex

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Kinetic waves of three different types were found in the polarographic reduction of the cadmium ethylenediaminetetraacetate complex (CdY^{--}). Between pH 1 and 4 a kinetic wave attributed to free cadmium ions, dissociated from the complex, occurs. In the pH region from 2 to 5 a second wave, from the reduction of the species $CdYH^-$, occurs; its height is controlled by the rate of recombination of CdY^{--} with hydrogen ions. In the pH region above 5 the wave height is independent of pH and yet is strongly dependent on kind, charge and concentration of "inert" cations present in solution. The cation effect may be attributed to the formation of an ion pair between CdY^{--} and the cation or to the formation of an activated bridge complex involving the surface of the mercury electrode, the cation, and the CdY^{--}. The ion pair or activated bridge complex is reducible, in contrast to the species CdY^{--}. The kinetics of the formation of such ion associates or complexes are discussed.

Although Koryta and Koessler[1] and Pecsok[2] observed no reduction wave for the cadmium EDTA complex, Heyrovsky[3] reported a doublet wave and Tanaka[4] found a singlet wave. These contradictory observations suggest some unrecognized factors whose influence depends strongly on the composition of the supporting electrolyte. The present study has revealed the kinetic character of the reduction wave and the factors which influence it have been identified as summarized in the abstract.

Polarograms.—The usual polarographic technique was employed in this study. The capillary had a m value of 2.3 mg. sec.$^{-1}$ and a drop time of 3.6 sec. in 0.1 M KCl at a height of the mercury reservior of 50 cm. (closed circuit). All measurements were made at 25.0 ± 0.1°, the potentials are referred to the SCE. Values reported for the limiting currents refer to a height of the mercury reservoir of 50 cm. No maxima were encountered and no maxima suppressors were added to the solutions.

Results and Discussion

I. Influence of pH on Limiting Currents.—Figure 1 demonstrates the influence of pH on the character of the reduction wave of the cadmium EDTA complex. The values for the limiting currents obtained between pH 1.5 and 4.6 are plotted in Fig. 2.

The limiting current of the first as well of the second wave becomes increasingly independent of the height of the mercury reservoir at the higher pH values, where the current diminishes to a small fraction of its maximum (diffusion-controlled) value. This behavior is characteristic of kinetic waves.

For the first wave, the rate-controlling step was found to be the dissociation of the cadmium EDTA complex and for the second wave the formation of the hydrogen complex, $CdYH^-$.

Kinetic Wave due to Free Cadmium Ions.—The half-wave potential of the first wave is practically independent of pH (−0.63 to −0.64 v.) and only slightly more negative than the half-wave potential of cadmium ions in potassium chloride (−0.62 v.). This indicates that the first kinetic wave is due to the reduction of free cadmium ions dissociated from the complex.

From the stability constants K_{CdY} and K_a where[5]

$$K_{CdY} = \frac{[CdY^{--}]}{[Cd^{++}][Y^{----}]} = 10^{16.5} \qquad (1)$$

$$K_a = \frac{[CdY^{--}][H^+]}{[CdYH^-]} = 10^{-2.9} \qquad (2)$$

and from the dissociation constants of EDTA,[6] the concentration of free cadmium ions in a 10^{-3} M solution of cadmium EDTA was calculated at various pH values. The diffusion current, which would result from the *equilibrium concentration* of dissociated cadmium ions is represented as a dotted line in Fig. 2. Experimentally, a higher limiting current is obtained, the difference corresponding to a kinetic contribution, according to

$$CdYH^- + (n-1)H^+ \underset{k_b}{\overset{k_f}{\rightleftarrows}} Cd^{++} + H_nY^{n-4} \qquad (3)$$

According to equation 3, the presence of an excess of EDTA would be expected to alter the limiting current. The calculated limiting current corresponding to the equilibrium concentration of free cadmium ions in the presence of a fourfold excess of EDTA is given in Fig. 2. Both the calculated and slightly higher experimental limiting currents are smaller with the excess of EDTA present.

The Koutecky[7] treatment was not applied for the calculation of the rate constants of equation 3 because the reaction was neither of first nor of pseudo first order. Furthermore, the requisite that the equilibrium concentration of the reducible species, Cd^{++}, be negligible under the solution conditions employed is not valid.

Kinetic Wave due to Acid Recombination.—The half-wave potential and the limiting current of the second, more negative wave are strongly dependent on pH. This wave is attributed to the reduction of the species $CdHY^-$, which is the species predominantly present in the pH region from 2 to 3. Below pH 3.5 the height of the second wave is complementary to the first kinetic wave.

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(1) J. Koryta and I. Koessler, *Coll. Czech. Chem. Comm.*, **15**, 241 (1950).

(2) R. Pecsok, *J. Chem. Educ.*, **29**, 597 (1952).

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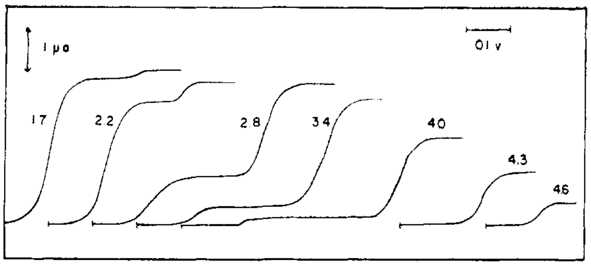

Fig. 1.—Polarographic waves of 0.001 *M* CdEDTA at various *p*H values. Polarograms start at −0.5 v. *vs.* SCE (*p*H 1.7–4.0), −0.9 v. (*p*H 4.3), −1.0 v. (*p*H 4.6).

Above *p*H 3.5 the wave height decreases (Fig. 2). The limiting current above *p*H 3.5 was found to depend not only on *p*H, but also on the sodium ion concentration. In order to evaluate the actual *p*H dependency, polarograms were obtained at various sodium ion concentrations (for a given *p*H value) and the limiting currents were linearly extrapolated to zero alkali ion concentration. The extrapolated values are plotted in Fig. 3 as a solid line.

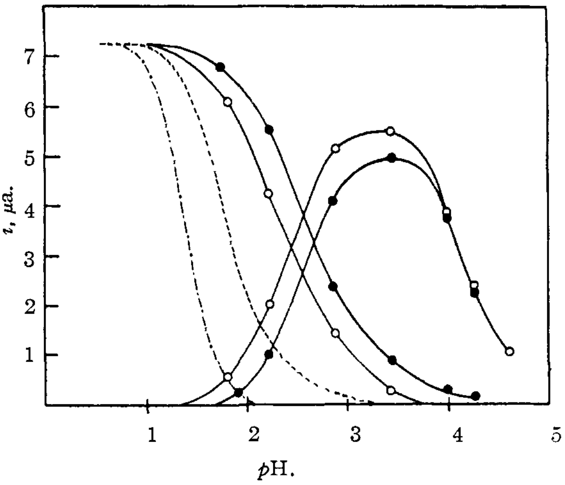

Fig. 2.—Solid lines: limiting current of first and second wave of CdEDTA as a function of *p*H: ●, 0.001 *M* CdEDTA; ○, 0.001 *M* CdEDTA + 0.004 *M* EDTA. Dashed lines, diffusion current corresponding to calculated equilibrium concentrations of Cd^{++}: ---------, 0.001 *M* CdETDA; —·—·—, 0.001 *M* CdEDTA + 0.004 *M* EDTA.

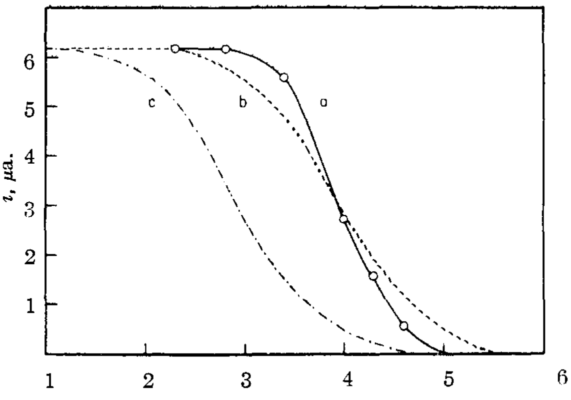

Fig. 3.———, limiting current of 0.001 *M* CdEDTA + 0.004 *M* EDTA as a function of *p*H. The points represent values extrapolated to zero Na^+-concentration: --------, kinetic limiting current as a function of *p*H according to the equation of Koutecky; —·—·—, diffusion current corresponding to the calculated equilibrium concentration of $CdYH^-$.

The species $CdHY^-$ dissociates according to

$$CdHY^- \underset{k_r}{\overset{k_f}{\rightleftarrows}} CdY^{--} + H^+ \tag{4}$$

The dissociation constant K_a is given in equation 2. The species $CdHY^-$ is reducible at the d.m.e., CdY^{--} is not reducible. The diffusion current which would result from the reduction of the species $CdHY^-$ in its equilibrium concentration is shown in Fig. 3, c. The kinetic contribution from the recombination of H^+ and CdY^{--} is evident in the limiting current. The acid recombination rate constant k_r, according to

$$\frac{d[CdYH^-]}{dt} = k_r[H^+][CdY^{--}] \tag{5}$$

was calculated by means of the formula developed by Koutecky.[7]

$$\frac{i_l}{i_d} = \frac{0.87[H^+]\sqrt{\frac{k_r\,\tau}{K_a}}}{1 + 0.87[H^+]\sqrt{\frac{k_r\,\tau}{K_a}}} \tag{6}$$

i_l is the average limiting current, i_d the average diffusion current, τ the drop time, K_a and k_r are defined by equation 2 and 5. From the point of curve a in Fig. 3, at which the experimental limiting current is equal to one-half of the diffusion current, *i.e.*, at *p*H 3.94, k_r was determined equal to 4.3×10^4 mole^{-1} liter sec.$^{-1}$. The limiting current which is obtained by reinserting this value into equation 6 is shown as curve b in Fig. 3. Equation 6 assumes that the kinetic controlled current appears in a *p*H range where the equilibrium concentration of the acid form is negligible and this condition is not quite fulfilled (Fig. 3). In addition, at *p*H values lower than 3.5 the kinetic current due to the dissociation of the complex into free cadmium ions contributes to the total limiting current. These circumstances give a reasonable explanation for the increase (with decreasing *p*H) of the experimental limiting current of $CdYH^-$ relative to the calculated current. For the same reason the value calculated for k_r is probably somewhat too high. Nevertheless the data show that k_r is of the order of magnitude 10^4 mole^{-1} liter sec.$^{-1}$ or smaller. This value is unusually small when compared to the rate constants reported[8] for acid recombination for substances whose rate constants range from 10^7 to 10^{13}. It appears that some steric rearrangement is involved in reaction 4, probably the breaking of a bond between a carboxyl group and the cadmium atom, and that this factor may be responsible for the low rate constant.

II. Influence of Cations on Limiting Current. Experimental Results.—In the *p*H region above 3.5 the addition of alkali or alkaline earth ions increases the limiting current of cadmium EDTA.

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TABLE I

LIMITING CURRENT OF 0.001 M CdEDTA + 0.004 M EDTA AT pH 4.6 IN THE PRESENCE OF VARIOUS Na AND K SALTS

Buffer	Additional alkali salt, moles/l.	Concn. of alkali ion, moles/l. Na	K	Limiting current, μa.
0.1 M Acetic acid–sodium acetate	....	0.06	..	1.12
.1 M Acetic acid–sodium acetate	0.05 NaCl	.11	..	1.65
.1 M Acetic acid–sodium acetate	.05 $NaNO_3$	.11	..	1.61
.2 M Acetic acid–sodium acetate	....	.11	..	1.57
.1 M Acetic acid–sodium acetate	.10 $NaClO_4$	.16	..	1.98
.1 M Monosodium citrate–disodium citrate	....	.16	..	1.95
.1 M Acetic acid–potassium acetate	....	.01	0.05	1.60
.1 M Acetic acid–potassium acetate	.05 KNO_3	.01	.10	2.30
.1 M Acetic acid–potassium acetate	.05 KCl	.01	.10	2.30
.2 M Acetic acid–potassium acetate	....	.01	.10	2.45
.1 M Acetic acid–potassium acetate	.10 KCl	.01	.15	2.95
.1 M Monopotassium citrate–dipotassium citrate	....	.01	.15	2.90

TABLE II

Cation	Li^+	Na^+	K^+	NH_4^+	Mg^{++}	Ca^{++}	Sr^{++}	Ba^{++}
Concn. at $i_l = i_d/2$, moles/l.	..	0.58	0.37	0.12	0.026	0.0035	0.0025	0.0018
Ionic radius	2.30	1.79	1.22	1.22	3.44	3.05	3.04	2.83
K_t, model 1	<4	1-6	3-7	3-7	60-90	70-100	70-100	80-110
K_t, model 2	0	0.25	0.63	0.63	6.5	7.7	7.7	8.5

The value of the limiting current depends only on kind and concentration of the added cation and is independent of the concentration and nature of the anion (see Table I). At pH values above 5 (where the kinetic current contribution of protons is negligible) the limiting current as a function of the cation concentration extrapolates to zero.

Values for the limiting currents were obtained at various Li^+, Na^+, K^+ and NH_4^+ ion concentrations in several buffers in the pH range from 5 to 9. The polarograms obtained in the presence of lithium salts were poorly defined and the limiting currents are evaluated with less accuracy. For a given alkali ion, the points fall approximately on the same line and extrapolate to zero regardless of the buffer type and pH (Fig. 4). The effect of the alkali ion increases in the order $Li^+ \simeq Na^+ < K^+ < NH_4^+$.

The limiting current increases linearly with the concentration of cadmium EDTA in the presence of a fixed amount of cation. On the other hand, the addition of an excess of EDTA has no influence.

The effect of alkaline earth ions is much larger and increases in the order $Mg^{++} < Ca^{++} < Sr^{++} < Ba^{++}$. Investigation of this effect in a buffer containing only the alkaline earth cation was not possible because the alkaline earth concentrations required for a proper background electrolyte were already sufficient to give a diffusion controlled reduction of the cadmium EDTA complex. This difficulty was circumvented by operating in a sodium acetate buffer (pH 5.4) and employing small concentration increments of added alkaline earth ions. The small blank limiting current resulting from the effect of the sodium ions was subtracted from the total current obtained in the presence of the alkaline earth ion. This correction method is only approximately valid. To avoid complexation of the alkaline earth ion, no excess EDTA was present in these experiments.

In Table II are listed the cation concentrations required to obtain a limiting current equal to one-half of the diffusion current for solutions of 0.001 M CdEDTA at pH 5.4. Although the values for the alkaline earth ions are only approximate, the order of the effect is evident. The effect produced by the alkaline earth ions is remarkably large. A strontium or barium concentration which is only twice that of the CdY^{--} is sufficient to give a limiting current equal to one-half of the diffusion current for the reduction of CdY^{--}.

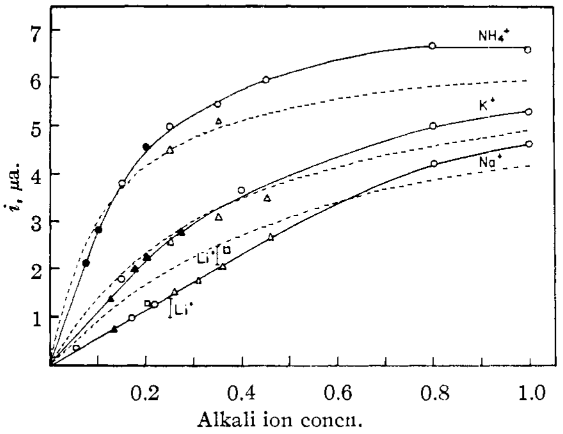

Fig. 4.—Solid lines: limiting current of 0.001 M CdEDTA + 0.004 M EDTA as a function of the alkali ion concentration for various alkali ions. ▲, 0.05 M citrate buffer (pH 5.2–5.5); △, 0.10 M citrate buffer (pH 5.2–5.5); ●, 0.05 M phosphate buffer (pH 6.5–7.0); ○, 0.10 M phosphate buffer (pH 6.5–7.0); □, 0.10 M borate buffer (pH 8.8–9.2). Dashed lines: kinetic limiting current calculated according to the equation of Koutecky.

Discussion

The cation effect cannot be attributed to a usual salt effect, *i.e.*, that the recombination rate of the

CdY^{--} anion with the hydrogen ions is changed with ionic strength. First, the independence of the effect on *p*H is not compatible with this concept. Second, according to the equations of Brønsted–Bjerrum and Debye–Hückel[9]

$$\ln k = \ln k^0 + 2AZ_AZ_B\sqrt{\mu} \qquad (7)$$

the logarithm of the rate constant *k* would be proportional to the product of the charges Z_AZ_B of the reacting ions. In the case of CdY^{--} and H^+, this product is -2 and a rate *decrease*, and not an increase as observed, would be expected with increasing ionic strength μ. The specificity of the alkali ion type and the independence of the type, charge and concentration of anion also point to a different explanation.

The polarographic waves of CdY^{--} observed in the presence of *low* concentrations of alkali or alkaline earth cations exhibit a limiting current which is less than the computed diffusion controlled value. With decreasing wave height (smaller cation concentration) the limiting current becomes more independent of the height of the mercury reservoir. The limiting current under these conditions is thus not controlled by the rate of diffusion of some reaction component but by the rate of some other process taking place prior to the electron transfer. This process is discussed from the standpoint of (1) the formation of an ion pair between cation and CdY^{--} in solution and (2) the formation of some activated bridge complex between the electrode, cation and CdY^{--}.

Formation of an Ion Pair in Solution.—A possible explanation is that the cation combines in solution with the CdY^{--} to an ion pair similar to

$$CdY^{--} + M^{+n} \xrightarrow{k} [M^{+n}, CdY^{--}]^{n-2} \qquad (8)$$

the way protons combine with CdY^{--} to form $CdYH^-$. Such an ion pair, like the $CdYH^-$ ion, would then be reducible at the dropping mercury electrode at an observable potential.

Spectrophotometrically no evidence could be found for the formation of ion pairs in solution.

On the other hand, an application of the equation of Bjerrum and Brønsted[10] gives evidence of considerable ion pair formation, in particular with the bivalent cations. The ion pair formation constant

$$K_f = \frac{[M^{+n}, CdY^{--}]^{n-2}}{[M^{+n}][CdY^{--}]} \qquad (9)$$

was computed under the assumption that the cation is electrostatically bound either to the double negative charged CdY^{--} particle as a whole (model 1) or to the oxygen atom of one carboxyl group of the complex, detached from the central metal atom (model 2). Ion pair formation constants K_f in water for 25° calculated according to these two models are listed in Table II. The atomic radii employed for the hydrated cations are values[11] derived from ionic mobilities. The ionic radius of the non-hydrated CdY^{-2} ion was estimated from Stuart models as between 3.4 and 5.0 Å., the shape being a flat ellipsoid. The atomic radius of oxygen in a carboxyl group was taken as 1.40 Å.[12] Table II illustrates an obvious *parallelism between the strength of the cation effect and the ion pair formation constants* K_f.

Under the assumption that the rate of formation of such an ion pair in solution is the step limiting the current, the Koutecky equation was applied to estimate the rate constant *k* (equation 8). The values for K_fk were obtained from the point at which the limiting current, i_l was one-half of the diffusion current i_d. The K_fk values are 1.30 (Na^+), 3.28 (K^+) and 10.1 (NH_4^+) mole^{-2} liter^2 sec.$^{-1}$.

From these values the limiting kinetic current corresponding to Koutecky's theory was calculated as a function of the alkali ion concentration and plotted as a dotted line in Fig. 4. The deviation between the experimental and the calculated curves might be attributed to the fact that the analytical equilibrium concentration of the ion pair is not negligible under the given conditions.

The rate constant *k* of ion pair formation is of the order of magnitude of 1 mole^{-1} liter sec.$^{-1}$ in the case of the alkali ions when the K_f values according to model 1 are used. With model 2, the rate constant is about 5 for Na^+ and K^+, about 15 for NH_4^+. For the alkaline earth ions, Koutecky's pseudomonomoleuclar treatment cannot be applied.

It is difficult to conceive that the formation of the ion pair should proceed at such low rates, because this reaction is purely electrostatic and does not involve the breakage or formation of chemical bonds.

Formation of an Activated Bridge Complex.—A model of an activated bridge complex[13–15] may be employed to explain the enhanced reduction rate of CdY^{--} caused by the presence of cations: the activation energy required for direct reduction of CdY^{--} is too high to give a polarographic wave at an observable potential. The electron transfer through an activated bridge complex between the negatively charged mercury surface, the cation and the CdY^{--}, ($Hg. . .M^{+n}. . .CdY^{--}$), may take place easier and a reduction wave thereby occurs at an observable potential.

Two rate factors should be distinguished in this model, *i.e.*, the rate of formation of the bridge complex and the rate of the electron transfer. It is possible to investigate these two rate factors separately, at least in a qualitative way.

The polarographic waves of CdY^{--} caused by the presence of "inert" cations have the drawn-out shape of irreversible waves, especially at low cation concentrations. These features indicate a slow electron transfer reaction in the potential region of the rise of the wave. The half-wave potentials above *p*H 5 are independent of *p*H and lie between -1.25 and -1.40 v. *vs.* SCE. They depend essentially only on the concentration of the cations

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(more positive at higher concentrations) and are independent of the type or charge of the cation. The rate of the electron transfer does not therefore vary significantly with the type and charge of the cation. The findings are in contrast to the observations in the reduction of the nitrate ion,[16] whose reduction potential depends strongly on the charge of the cations present.

On the other hand, the kinetic limiting current is a measure for the rate of the formation of the activated bridge complex. "Adsorption" processes such as movement of the inert cations into the Helmholtz layer are probably involved in the formation of the bridge complex and it does not seem unreasonable that the over-all rate of formation is slow. The assumption that the mercury surface is involved in the rate-determining chemical step is partially supported by the great ease with which this limiting current is suppressed by surface active material.

The rate of formation of the bridge complex increases with decreasing size and increasing charge of the hydrated cation involved. Sheppard and Wahl[14] found a similar order in the effect of inert cations on the electron exchange rate in the manganate–permanganate system.

Effect of Cations on the Reduction of Other Anions.—With the lead EDTA complex, a similar cation effect was found, but not further investigated, because of the ill-defined shape of the polarograms. Pecsok[17] reports that the wave of molybdenum(VI)–EDTA increases with electrolyte concentration and attributes the effect to the change in ionic strength. The effect is of similar order of magnitude as the one observed in the case of the CdY^{--}. By analogy, the cation effects observed with the lead and molybdenum EDTA complexes also may be the result of the formation of an ion pair or an activated bridge complex.

Minima appearing in the polarographic reduction waves of certain anions, such as $S_2O_8^{--}$, are eliminated by the addition of cations.[18,19] The effectiveness of the cations increases with their charge. Alkali ions are increasingly effective in the order Li < Na < K < Pb < Cs. Frumkin[18,19] attributed these minima to a retarded electron discharge in the potential region of the minima. The presence of cations was believed to cause changes in the structure of the double layer in such a way that the electron transfer is reaccelerated. The effect of cations on the reduction waves of this and other complex anions, such as NO_3^-,[16] $Cd(CN)_4^{--}$,[20,22] $Hg(CN)_4^{--}$ [21] can be explained by a slow formation of an activated bridge complex $Hg.^{\delta-}\ldots M^{+n}\ldots X^{-m}$ rather than by electron transfer rates only. Actually, an application of Frumkin's formula for electron transfer rates was in many cases not in concordance with the experimental results.[18,22]

Acknowledgment.—This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW MEXICO INSTITUTE OF MINING AND TECHNOLOGY]

Kinetic Study of Aromatic Nucleophilic Substitution under High Pressure: Bromoquinolines and Bromonaphthalenes

BY K. R. BROWER

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The displacement reactions of bromoquinolines and bromonaphthalenes with piperidine are accelerated several-fold by hydrostatic pressures up to 1300 atm. The volume changes of activation decrease throughout the sequence of increasing reactivities in accordance with the view that the faster reactions involve transition states more nearly resembling the separate reactants. Comparison of systems studied at different temperatures is justified by the absence of any measurable effect of pressure on the activation energies.

Introduction

The effect of pressure on the rates of homogeneous liquid-phase reactions has been given a theoretical explanation by Stearn and Eyring,[1] who derived from the Absolute Reaction Rate Theory the equation

$$RT(\partial \ln k/dP)_T = -\Delta V^{\pm} \qquad (1)$$

in which k is the reaction rate constant and $V^{\pm}$ is the change in molar volume resulting from the transformation of the reactant or reactants into activated complex. The volume changes of activation calculated from kinetic data on bimolecular reactions were found to be consistent with values estimated from equation 2

$$-\Delta V^{\pm} = \frac{1\ \text{Å.} \times \Sigma V}{\sum_i l_i + \sum_i r_i + 2\ \text{Å.}} \qquad (2)$$

in which ΣV is the sum of the molar volumes of the reactants, l_i is the component of length of the ith bond along the reaction coördinate, and r_1 and r_2 are the covalent radii of the terminal atoms. It is assumed that the average separation of reactant molecules is reduced by 1 Å. as the activated complex is formed. In recent years it has been found

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