indicate that formation of the second complex through a base catalyzed path does not occur to a large extent. This would agree with Lister and Rivington's[5] estimate that the hydrolysis constant for hydrolysis of $FeNCS^{++}$ to $Fe(NCS)(OH)^+$ is about one hundred fold smaller than for hydrolysis of iron(III) ion.[13]

Acknowledgments.—The support of the Research Corporation and the National Science Foundation for this project is gratefully acknowledged. Thanks are also given to the following students who actively participated in the project: Merrit Birky, Philip Rule, Lewis Brubacher, Eldon Kreider, John Leffel, Daniel Driver, Eunice Steiner, Elmer Bowers and Glen Kauffman.

(13) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1216 (1955).

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PA.]

A Manometric Determination of the Solvolysis Rate of Gaseous *t*-Butyl Chloride in Aqueous Solution[1]

BY GEORGE A. CLARKE,[2] THEODORE R. WILLIAMS[3] AND ROBERT W. TAFT

RECEIVED OCTOBER 2, 1961

The rate of solvolysis of gaseous *t*-butyl chloride at unit pressure has been determined in a closed vessel from the rate of pressure drop of the vapor over the aqueous solution in which reaction occurs. Extrapolation of the vapor pressure measurements to zero time gives an approximate determination of the solubility of gaseous *t*-butyl chloride. From these measured quantities, the conventional rate of solvolysis at unit concentration is calculated and the values compared with those obtained by independent methods in the literature. Fair agreement is found. The activation energy for the solvolysis of dissolved *t*-butyl chloride agrees with literature values within the experimental error. The rate of solvolysis of gaseous *t*-butyl chloride at unit pressure is reduced in D_2O compared to H_2O by essentially the same factor ($\sim$0.72 at 15°) as is the conventional rate constant.

The rate of solvolysis of *t*-butyl chloride at unit concentration k_c in aqueous solution is so rapid that conventional techniques for rate measurement are applied with difficulty.[4] On the other hand, the vapor pressure and solubility of *t*-butyl chloride lend themselves to the precise determination of the rate of solvolysis at unit pressure k_p of the volatile reactant.

In the present paper we report the determination of the rate constant k_p using an experimental technique which has been previously employed to determine the rate of hydration of volatile olefins.[5] The rate of pressure drop of gaseous *t*-butyl chloride in a closed system is measured over the aqueous solution in which the solvolysis reaction occurs. Extrapolation of the vapor pressure measurements to zero time provides an approximate determination of the solubility, h, of gaseous *t*-butyl chloride. From values of h and k_p, the conventional rate constant k_c is obtained. The method has been successfully applied to measurements in ordinary water at 0.99°, 5.00° and 14.85°, to dioxane–water mixtures at 14.85° and to heavy water at 14.85°. Generally, satisfactory accord is obtained between the rate thermodynamic properties from the present and other investigations. In subsequent work,[6] the method is applied to an extensive study of the effects of aqueous electrolytes on the activity coefficient of *t*-butyl chloride and of its solvolysis transition state.

Experimental

Materials.—The *t*-butyl chloride was prepared by reaction of concentrated hydrochloric acid with *t*-butyl alcohol.[7a] The fraction used for the solvolysis experiments boiled at 48.9–49.0° (uncorr.) at 732 mm. A sample of the *t*-butyl chloride was passed through a gas chromatographic column containing 20% (wt.) paraffin oil on C-22 firebrick at 56°. Only a single fraction was obtained. The collected sample gave the same rate and distribution constants within experimental error as the original sample. Similar results were obtained with the sample of *t*-butyl chloride remaining in the filling vial (*cf.* section on rate measurement) after a series of solvolysis reactions.

Distilled water was used in all experiments. Triply distilled water gave equivalent results. Deuterium oxide was obtained from Liquid Carbonic in greater than 99.5% purity. Dioxane was purified by the method of Vogel.[7b]

Measurements of Rate Constants.—The apparatus and methods used are basically those previously described.[5] The following modifications in the basic system (see Fig. 1–ref. 5a) have been made: (1) In place of the 50 ml. reaction flask (F) a 100 ml. or a 250 ml. flask was used; (2) Tube (G), the *t*-butyl chloride filling vial was sealed directly to the system with a precision stopcock (J′) placed at (J) and thereby eliminating the ground glass joint (J); (3) The two-way precision stopcock (S) was replaced by a one-way stopcock (S′).

This new arrangement of stopcocks was found to be quite satisfactory even though gaseous *t*-butyl chloride can attack the stopcock grease. The vapor which is contained in the section between (S′) and (J′) and that in the reaction system, however, was not observed to attack the stopcock (S′).

Solvent was introduced into the reaction flask (F) and the system degassed by evacuating *via* (O″) and (S′) and (J′) closed in a manner described in procedure B. The *t*-butyl chloride in (G) was degassed in a similar manner with (S′) closed and (J′) opened. The system was then completely immersed in a thermostat with regulation to within ± 0.02° as determined by a N.B.S. calibrated thermometer. The system was secured, the flask was shaken to attain tempera-

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(1) The work was supported in part by the Office of Naval Research.

(2) Taken in part from the Ph.D. thesis of G. A. Clarke, The Pennsylvania State University, June, 1960.

(3) Taken in part from the M.S. thesis of T. R. Williams, The Pennsylvania State University, June, 1954.

(4) (a) C. G. Swain and S. D. Ross, *J. Am. Chem. Soc.*, **68**, 658 (1946); (b) H. Kwart and W. C. Wilson, *ibid.*, **75**, 6147 (1953); (c) E. Tommila, M. Tiilikainen and A. Voipio, *Ann. Acad. Sci. Fennicae, Ser. A.*, II, No. 65 (1955); (d) P. W. Laughton and R. E. Robertson, *Can. J. Chem.*, **34**, 1714 (1956); (e) S. Winstein and A. H. Fainberg, *J. Am. Chem. Soc.*, **79**, 5937 (1957).

(5) (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, *ibid.*, **73**, 3972 (1951); (b) E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *ibid.*, **77**, 837 (1955).

(6) G. A. Clarke and R. W. Taft, *ibid.*, **84**, 2295 (1962).

(7) (a) A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1951, p. 275; (b) *ibid.*, p. 175.

ture equilibrium, (S') was then opened and the manometer reading P_{sp} due to solvent pressure noted. The stirrrer motor was shut-off to eliminate unnecessary motion and (J') was opened to allow 14–17 cm. of gaseous *t*-butyl chloride to vaporize into the system. (S') and (J') were then closed and the manometer pressure reading P_i noted. With the stirrer on and the bath at the calibrated temperature, shaking was commenced and manometer readings P were taken at regular intervals usually extending over about 4 half-lives. The reaction was allowed to continue for 10 half-lives and then the final (equilibrium) pressure reading, P_e was determined. For all measurements the shaking rate was maintained at about 330 r.p.m.

The rate equation for the solvolysis of gaseous *t*-butyl chloride is (*cf.* derivation below)

$$\frac{\mathrm{d}\ln(P - P_e)}{\mathrm{d}t} = \frac{k_p}{r/RT + h} = S, \text{ a constant} \quad (1)$$

where r = ratio of the vapor volume to the liquid volume in the reaction system; R = the gas constant in l. atm. (mole °K.)$^{-1}$; T = absolute temperature; P = pressure reading of manometer system at time t; P_e = equilibrium manometer reading; k_p = rate of conversion of gaseous reactant in units of moles-l.$^{-1}$ atm.$^{-1}$ sec.$^{-1}$; h = distribution constant of *t*-butyl chloride between solution and gaseous phase in units of moles^{-1} l.$^{-1}$ atm.$^{-1}$.

According to the above rate equation, a plot of ln (P–P_e) *vs.* time should be linear (with slope, S) after saturation of the solution is achieved. This relationship was precisely obeyed in all experiments. A typical plot for the solvolysis in water at 14.85° is shown in Fig. 1. Linearity extends over four half-lines, corresponding to greater than 90% removal of the chloride from the gas phase to form products in solution. In general it has been found that the solution process attained "equilibrium" in less than one minute. (The open circles in Fig. 1 are assumed to represent the period in which solution equilibrium is being attained.) It can be seen from the plot (Fig. 1) that the half-time for the initial solution of the chloride is significantly smaller than that for the subsequent disappearance of the chloride by reaction—the former being on the order of 15 seconds and the latter on the order of seven minutes. The solution process, then, is a much more rapid one than the reaction process. This demonstration substantiates an implicit assumption made in the derivation (below) of the rate expression, namely, that the solution process occurs as a fast reversible equilibrium during the reaction process (*cf.* below). The following symbolism has been employed throughout:

P = pressure (total) reading on manometer at time, t
P_i = manometer reading after introduction of gaseous *t*-butyl chloride but before shaking (solution) has commenced (*cf.* Fig. 1)
P_{sp} = manometer reading due to solvent pressure only
P_e = manometer reading at equilibrium (t_∞)
P_0 = initial manometer reading due to *t*-butyl chloride in equilibrium with liquid phase (obtained by extrapolation to zero time (*cf.* Fig. 1)
p^i = $P_i - P_{sp}$ = initial partial pressure of *t*-butyl chloride introduced into system (before shaking)
p = partial pressure of *t*-butyl chloride at time t
p^0 = $P_0 - P_{sp}$ = initial partial pressure of *t*-butyl chloride (after solution saturation but at zero time in the solvolysis reaction)
p_{ol} = partial pressure of olefin at time, t
p_{ol}^e = $P_e - P_{sp}$ = equilibrium partial pressure of olefin

Values of k_p were calculated for individual experiments using the average value of h obtained from a series of experiments.[5] The reproducibility of the rate constant k_p was within ± 3%.

Distribution Constant *h*.—This constant was calculated from the results of a solvolysis experiment (as described above) by the equation[8]

$$h = \frac{r}{RT}\left(\frac{P_i - P_0}{P_0 - P_{sp}}\right) = \left(\frac{P_i - P_0}{p^0}\right)\frac{r}{RT} \quad (2)$$

where symbols are as previously defined.

The reproducibility of the most precise determination of h (experiments employing a 250 ml. flask) was on the order of ± 3–7%.

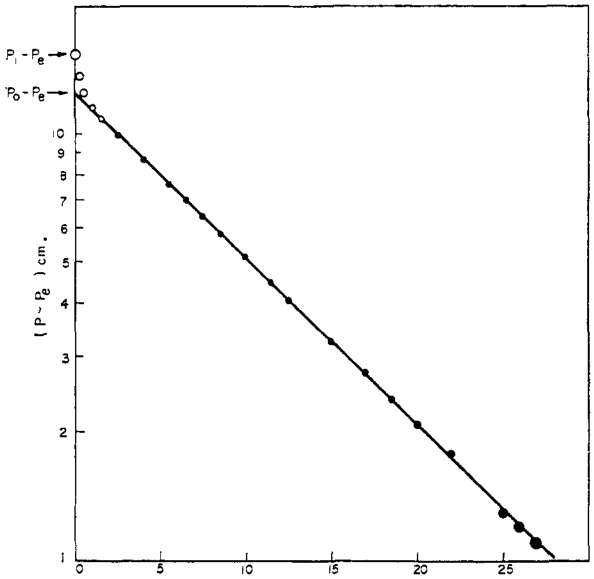

Fig. 1.—A typical first order plot for the solvolysis of gaseous tertiary butyl chloride in water at 14.85°.

Measurement of Per Cent Olefin.—The apparent fraction of isobutene formed was taken as p^e_{ol}/p^i. This procedure neglects the olefin which was dissolved in solution. The solubility of isobutene in water is known[8] and the solubility corrections would be on the order of the (relatively large) experimental uncertainty of the above quantity. Consequently, this simplification was assumed adequate.

The residual vapor left at the completion of a solvolysis reaction was removed and its infrared spectrum taken. The spectrum was the same within the precision of measurement as that of a sample of pure isobutene. None of the peaks of *t*-butyl chloride appeared in the spectrum of the residual vapor, showing that the solvolysis proceeds to essential completion under these conditions of high dilution.

Derivation of Basic Rate Equation.—We first demonstrate that

$$\frac{\mathrm{d}\ln(P - P_e)}{\mathrm{d}t} = \frac{\mathrm{d}\ln p}{\mathrm{d}t}$$

where all symbols are as defined above. From material balance considerations we have

$$\text{moles RCl reacted at time, } t = (p^0 - p)\left[\frac{V_g}{RT} + V_l h\right] \quad (3)$$

where V_g and V_l are the volumes of the gas and liquid phases of the solvolysis apparatus.

$$\text{Further, let } \frac{\text{moles alcohol formed at time } t}{\text{moles olefin formed at time } t} = \frac{k_s}{k_e}$$

Then, moles olefin formed at time,

$$t = p_{ol}\left[\frac{V_g}{RT} + V_l h_{ol}\right] \quad (4)$$

$$= (\text{moles RCl reacted at time, } t)\left(\frac{k_e}{k_e + k_s}\right) \quad (5)$$

where h_{ol} is the distribution (solubility) constant for isobutene. From (3), (4) and (5) we obtain, on rearrangement,

$$p_{ol} = \frac{(p^0 - p)\left[\frac{V_g}{RT} + V_l h\right]\left(\frac{k_e}{k_s + k_s}\right)}{\left[\frac{V_g}{RT} + V h_{ol}\right]} \quad (6)$$

From this and the equilibrium condition ($p \cong 0$), we obtain,

$$p_{ol} - p_{ol}^e = -\left[\frac{\left(\frac{V_g}{RT} + V_l h\right)\left(\frac{k_e}{k_e + k_s}\right)}{\left(\frac{V_g}{RT} + V_l h_{ol}\right)}\right] p \quad (7)$$

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(8) R. W. Taft, Jr., E. L. Purlee and P. Riesz, *J. Am. Chem. Soc.*, **77**, 899 (1955).

therefore, $P - P_e = p + (p_{ol} - p_{ol}^e) = ap$ (8)

where a is a constant. Differentiation gives

$$\frac{d \ln (P - P_e)}{dt} = \left(\frac{a}{P - P_e}\right) \frac{dp}{dt} = \frac{d \ln p}{dt} \quad (9)$$

The rate equation for the first order solvolysis reaction is

$$-\frac{d(RCl)}{dt} = k_c(RCl) = k_c hp = k_p p \quad (10)$$

differentiation of (3) gives

$$-\frac{d(RCl)}{dt} = -\left(\frac{r}{RT} + h\right) \frac{dp}{dt} \quad (11)$$

from (10) and (11) we obtain

$$k_p = -\left[\frac{d \ln (P - P_e)}{dt}\right]\left(\frac{r}{RT} + h\right) = (S)\left(\frac{r}{RT} + h\right) \quad (1)$$

$$\text{where } S = -\frac{d \ln(P - P_e)}{dt}$$

Verification of the Method.—The expression for the rate constant, k_p, eq. 1, requires that the value of this constant be independent of variations made in the ratio of vapor to liquid volume of the reaction system, r. The results given in Table I show that variations in r by a factor of about 7 produces no apparent trends, and, the precision of k_p and h values obtained in these experiments with variable r/RT is the same within the experimental error as that based upon a series of experiments at nearly constant r/RT. These results therefore confirm the basic assumption made in the derivation of rate eq. 1, namely, that all of the solvolysis reaction occurs in solution (none in the vapor).

TABLE I

EFFECTS OF VARIATIONS OF r/RT ON THE RATE CONSTANT k_p, THE DISTRIBUTION CONSTANT h AND THE SLOPE S FOR THE SOLVOLYSIS OF TERTIARY BUTYL CHLORIDE IN PURE WATER AT 14.85°

r/RT[a]	S[b]	$h \times 10^2$[a]	$k_p \times 10^2$[c]
0.0476	0.2128	3.44	1.66
.0590	.1841	3.02	1.64
.0590	.1899	3.02	1.69
.1400	.1033	2.99	1.76
.1400	.1016	3.39	1.73
.1806	.0864	2.58	1.82
.1856	.0831	2.76	1.79
.3245	.0482	2.95	1.71
	Av.	3.02 ± 0.20	1.73 ± 0.05

[a] (mole $l.^{-1}$ $atm.^{-1}$). [b] ($min.^{-1}$). [c] (mole $l.^{-1}$ $atm.^{-1}$ $min.^{-1}$).

TABLE II

THE RATE OF SOLVOLYSIS AT UNIT PRESSURE (k_p) AND THE DISTRIBUTION CONSTANT (h) FOR GASEOUS t-BUTYL CHLORIDE

Solvent	Temp., °C.	$10^4 k_p$[a]	$10^2 h$[b]	$10^3 k_c = k_p/h$, $sec.^{-1}$	Fraction olefin
H_2O	0.99	0.778 ± 0.007	8.18 ± 0.35	0.95	0.023 ± 0.006
H_2O	5.00	1.18 ± .03	6.62 ± .25	1.78	.046 ± .012
H_2O	14.85	2.90 ± .07	3.11 ± .17	9.32	.041 ± .010
D_2O	14.85	2.07 ± .02	3.18 ± .11	6.51	.044 ± .008
0.200 M aq. dioxane	14.85	2.72 ± .03	3.37 ± .01	8.07	.050 ± .014
1.00 M aq. dioxane	14.85	2.33 ± .05	4.40 ± .09	5.30	.056 ± .012
2.01 M aq. dioxane	14.85	1.80 ± .03	5.4 ± .8	3.3	.076 ± .015

[a] (M-$l.^{-1}$ $atm.^{-1}$ $sec.^{-1}$.) [b] (M-$l.^{-1}$ $atm.^{-1}$.)

Results

Table II lists the best values of the rate constant k_p and their precision measures. Also given is the calculated value of the conventional rate constant k_c for the solvolysis rate at unit concentration and the fraction of olefin formed in the solvolysis reaction.

TABLE III

COMPARISON OF THE CALCULATED RATE CONSTANT k_c WITH LITERATURE VALUES AT 14.85°

Solvent	Method	Ref.	$10^2 k_c$, $sec.^{-1}$
H_2O	Titrimetric	4e	0.70
H_2O	Conductivity	4d	.72
H_2O	Conductivity	4c	.78
H_2O	$k_{p/h}$	This work	.93 ± 0.07
D_2O	Conductivity	4d	.54
D_2O	$k_{p/h}$	This work	.65 ± .04
1.30 M aq. dioxane	Titrimetric	4e	.39
1.30 M aq. dioxane	$k_{p/h}$	This work	.45 ± .05

The validity of the present method is additionally confirmed by the fair agreement between the calculated k_c values ($k_c = k_p/h$) and the values which have been obtained by other methods. Comparative values at 14.85° are shown in Table III. A similar comparison of the energy of activation, $\Delta H_c^{\ddagger}$, at 8° is given in Table IV. The calculated k_c values are consistently 15 to 25% higher than the literature values. On the other hand, the calculated energy of activation $\Delta H_c^{\ddagger}$ agrees with literature values within the experimental error. These results are considered satisfactory in view of the relatively poor precision of the determination of the distribution constant, h, and a known source of error in the determination of the distribution constant. Relatively soluble inert gases (*e.g.* CO_2) give h values which are too low, presumably because of pre-solution[8] (*i.e.* low-values of p^i are obtained *cf.* Experimental). The agreement of the values for the activation energy $\Delta H_c^{\ddagger}$ implies, however, that relative values of the distribution constant h are accurate within their precision measures. This point is of importance in connection with the accuracy of the salt effects on h reported in the following paper.[6]

Unquestionably the most reliable values of the distribution constant h and of the heat of solution ΔH_s^0 at 8° are those obtained from our precise rate constants k_p and the correspondingly precise values of the rate constants k_c from the literature. In this manner one obtains for water at 14.85°, $10^2 h = 4.03 \pm 0.10$ M $l.^{-1}$ $atm.^{-1}$ [8a] and $\Delta H_s^0 = 10.0 \pm 0.3$ kcal./mole (at 8°). Robertson, Heppolette and Scott, have predicted the heat solution

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(8a) NOTE ADDED IN PROOF.—This value (and the pre-solution hypothesis) have been confirmed by direct measurements carried out by Mr. Gary Ceska, who has obtained the result $10^2 h = 4.11 \pm 0.13$ m.-$l.^{-1}$-$atm.^{-1}$. The method used avoids pre-solution by weight determination of the t-butyl chloride introduced—*cf.* R. R. Beishline, Ph.D. Thesis, The Pennsylvania State University, June, 1962, p. 25.

of gaseous *t*-butyl chloride in water to be 8.2 kcal./mole at 25°, in quite reasonable accord with the above value.[10b]

TABLE IV

COMPARISON OF THE CALCULATED ENERGY OF ACTIVATION (8°), $\Delta H_c^{\ddagger}$, WITH LITERATURE VALUES FOR SOLVOLYSIS OF *t*-BUTYL CHLORIDE IN WATER

Method	Ref.	$\Delta H_c^{\ddagger}$, k, cal. l. mole
Titration	4e, 9	24.1 ± 0.2
Conductivity	10	24.4 ± 0.2
$k_{p/h}$	This work	25.2 ± 1.1

A plot of log k_p *vs.* $1/T$ is linear within the experimental error for the temperature range measured, 1–15°. Thus the value of $10^4\ k_p$ calculated at 5.00° by the Arrhenius equation from measurements at 0.99° and 14.85° is 1.15 ± 0.04 compared to the experimental value of 1.18 ± 0.03. The energy of activation $\Delta H_p^{\ddagger}$ and the entropy of activation $\Delta S_p^{\ddagger}$ for the aqueous solvolysis of gaseous *t*-butyl chloride derived from this result are $+14.3 \pm 0.3$ kcal./mole and 24.9 ± 1.0 e.u., respectively, at 8°.

The solvent isotope effect, k_{D_2O}/k_{H_2O}, for the rate of solvolysis of gaseous *t*-butyl chloride at unit pressure at 14.85° is 0.71. This figure may be compared with the solvent isotope effect for the rate of solvolysis of dissolved *t*-butyl chloride at unit concentration at 14.03° of 0.74.[4d,11] The essential agreement of these two figures (which is consistent with the fact that the distribution constant for *t*-butyl chloride is the same within experimental error in D_2O as H_2O *cf.* Table II) does not support the suggestion of Heppolette and Robertson[12] that the solvent isotope effect resides primarily in the isotope effect on the initial state (dissolved *t*-butyl chloride). Instead, in the present instance at least, our results require the effect to apply primarily to the solvolysis reaction transition state.[11]

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[9] Calculated from the value given for 25° using $\Delta Cp^{\ddagger} = -50$ cal./deg., *cf.* ref. 4d and e.

[10] (a) Private communication from Dr. R. E. Robertson; (b) R. E. Robertson, R. L. Heppolette and J. M. W. Scott, *Can. J. Chem.*, **37**, 803 (1959).

[11] *Cf.* also C. G. Swain, R. Cardinaud and A. D. Ketley, *J. Am. Chem. Soc.*, **77**, 934 (1955).

[12] R. L. Heppolette and R. E. Robertson, *ibid.*, **83**, 1834 (1961).

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PA.]

The Effects of Aqueous Electrolytes on the Activity Coefficient of *t*-Butyl Chloride and of its Solvolysis Transition State[1]

BY GEORGE A. CLARKE AND ROBERT W. TAFT

RECEIVED OCTOBER 2, 1961

An extensive study has been made of the effects of aqueous electrolytes (up to 1 *M*) on the rate of solvolysis of gaseous *t*-butyl chloride at unit pressure k_p and on the solubility distribution constant h, for gaseous *t*-butyl chloride. From the former measurement, the relationship, $\log f \ddagger = K \ddagger C_s$ (where $f \ddagger$ is the activity coefficient of the aqueous *t*-butyl chloride solvolysis transition state, $K \ddagger$ is the transition state salt parameter and C_s is the electrolyte concentration), is demonstrated. From the latter measurement the following relation holds, $\log f_g = K_g C_s$, (where f_g is the activity coefficient for dissolved *t*-butyl chloride and K_g is the salt parameter for the reaction ground state). Neither $\log f_g$ nor $\log f \ddagger$ obey the expression obtained by Ingold and co-workers based upon the ion atmosphere model. Instead, quite specific salt effects are found due to important contributions to the activity coefficient from salt induced effects upon the internal pressure of the solvent. For inorganic salts, it is shown that $f \cong f^{e.s.} \cdot f^{i.p.}$, where $f^{e.s.}$ is the ion atmosphere (coulombic) contribution and $f^{i.p.}$ is the salt induced internal pressure (non-coulombic) contribution. However, Ingold's ion atmosphere treatment of kinetic salt effects is shown to be applicable. This demonstration is made possible in the present instance by the essential cancellation between ground and transition state of the specific salt induced solvent effects. Thus, the inorganic salt parameters for the conventional rate constant k_c at unit concentration are the same (as predicted by the theory) for all salts of a given charge type. In terms of Ingold's equation a charge separation in the aqueous *t*-butyl chloride transition state of about 0.8 electronic units is indicated. Specific effects have been obtained for organic electrolytes and for the acidic cations, H_3O^+ and NH_4^+, and these results are discussed. The distinct contrast of present results in water with that of previous studies in mixed solvents is attributed to the greater complexity of salt induced medium effects in the latter solvents with the attendant non-cancellation of these effects between the ground and transition states for solvolysis reactions.

Electrolyte effects on reaction rates have played an important role in the investigation of mechanism.[2] However, the validity of theoretical treatment of salt effects has remained uncertain (*cf.* following Discussion.)

Several investigations have been made recently in which the effects of electrolytes on a reaction rate and on the activity coefficient of the reaction substrate have been independently determined. The results of such studies have been especially enlightening. By this procedure Long, McDevit and Dunkle showed that the direction of the effects of several salts in moderately concentrated electrolyte solutions on the rate of the acid-catalyzed hydrolysis of γ-butyrolactone to γ-hydroxybutyric acid was the direction of the electrolyte effect on the activity coefficient of the lactone.[3] Paul[4] and Long and McIntyre[5,6] have shown that the markedly different electrolyte effects on the acid-catalyzed hydrolysis rate of methylal and on the acidity function H_0 is largely a question of the difference

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[1] The work was supported in part by the Office of Naval Research.

[2] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, Chapter 7; also *cf.* ref. 35.

[3] F. A. Long, W. F. McDevit and F. Dunkle, *J. Phys. Chem.*, **55**, 829 (1951).

[4] M. A. Paul, *J. Am. Chem. Soc.*, **76**, 3236 (1954).

[5] D. McIntyre and F. A. Long, *ibid.*, **76**, 3240 (1954).

[6] F. A. Long and D. McIntyre, *ibid.*, **76**, 3243 (1954).