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. 1. 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 ± 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).

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# 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

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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 $f \cong f^{\mathrm{e.s.}} \cdot f^{\mathrm{i.p.}}$, where $f^{\mathrm{e.s.}}$ is the ion atmosphere (coulombic) contribution and $f^{\mathrm{i.p.}}$ 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).

in the electrolyte effect on the activity coefficients of methylal and the Hammett reference base.

In the present study, the salt effects of aqueous electrolyte solutions (up to 1 *M*) on the activity coefficients of *t*-butyl chloride and its solvolysis transition state have been determined. This has been accomplished by determining the electrolyte effect on the solubility and on the rate of solvolysis $k_p$ of gaseous *t*-butyl chloride at unit pressure. This rate constant gives a direct measure of the activity coefficient of the solvolysis transition state.

The solvolysis of *t*-butyl chloride was chosen for study because its vapor pressure and solubility in aqueous solution lend themselves to this type of investigation. Further, the mechanism for this reaction has been the subject of extensive scrutiny and is considered to be a prototype of a SN1[7] or limiting[8] solvolysis mechanism.

Our results permit a substantial test of the ion-atmosphere treatment proposed by Bateman, Church, Hughes, Ingold and Taher[9] for the activity coefficient of a highly dipolar transition state. This rather widely adopted theory, analogous to the Debye–Hückel theory for the activity coefficient of an ion,[10] was initially employed to account for the observed salt effects on the rate of solvolysis of *t*-butyl bromide at unit concentration in 90% acetone–water solvent.[9] The treatment was made possible by the assumption that there are no electrolyte effects on the ground state activity coefficient. The theory predicts that the rate will increase with the first power of the ionic strength with no specific electrolyte effects. The theory, however, was put to no stringent experimental tests.

Subsequent studies have consistently demonstrated that electrolyte effects on unimolecular reactions are generally quite unique for a given electrolyte.[11–16] In fact, some electrolytes were discovered to have a retarding effect on the reaction rate.[11] Further, the ordering of the electrolyte effects has been shown to be dependent upon the medium.[13] These observations together with the failure of electrostatic theories to account, even qualitatively, for salt effects on the activity coefficient of polar non-electrolytes[17] have cast strong doubt on the ability of the ion-atmosphere model to adequately describe salt effects in reaction kinetics.[13,14,16] Brönsted pointed out long ago[18] that two factors must be considered to act in the electrolyte effect on an activity coefficient: (1) The direct electrical (ion-atmosphere) interaction and (2) the indirect salt-induced medium effect (effect of the salt on the internal pressure of the solvent[19]). Recent investigations have made abundantly clear the importance of salt-induced medium effects.[20,21]

The present investigation was carried out in water as the solvent. This choice was dictated not only by practical considerations of the method of investigation but by the availability of detailed knowledge of salt effects in this medium.[17,22,23] Our results on the solubility of *t*-butyl chloride provide the first detailed examination of aqueous salt effects on a non-aromatic organic non-electrolyte. From the combined knowledge of the salt effect on the rate constant $k_p$ and on the solubility distribution constant *h* we are able to demonstrate (under our especially favorable conditions) the essential cancellation of inorganic salt induced solvent effects between ground and transition states. That is, the effects of inorganic salts on the conventional rate constant $k_c$ of aqueous *t*-butyl chloride at unit concentration do follow the predictions of the ion atmosphere model.

## Experimental

Materials.—Tetramethylammonium hydroxide (10% in water), tetraethylammoniumhydroxide (10% in water), tetramethylammonium bromide and chloride were Eastman Kodak Company "White Label" chemicals. Lithium sulfate (monohydrate), potassium sulfate, potassium fluoride (dihydrate), lithium nitrate, lithium chloride, potassium chloride and sodium thiocyanate were Fisher "Certified Reagent" chemicals. Sodium perchlorate (monohydrate) and sodium benzoate (U.S.P.) were Fisher Laboratory chemicals. Sodium trifluoroacetate was a Sapon Laboratories Inc. chemical. All other electrolytes were Baker Analyzed Reagents.

All electrolytes were used without further purification. The solids, with the exception of sodium thiosulfate, were heated in an oven at temperatures varying from 115-130° or dried in a vacuum desiccator to constant weight. The per cent. weight loss of the hydrated compounds dried by these methods agreed with the calculated water content to better than 1% with the exception of sodium dichromate. All salt solutions were made up by weight of the dried salts and the concentrations of the solutions of sodium thiosulfate and sodium dichromate were determined accurately by titration using standardized potassium iodate for sodium thiosulfate[24] and standardized sodium thiosulfate for sodium dichromate.[25] The concentration of the acid and base solutions were determined by titration with standardized reagents. The solutions of sodium thiosulfate and one of the solutions of sodium carbonate were made up with about 0.1 *M* base; potassium hydrogen sulfate was made up with a 1 *M* hydrochloric acid solution.

Procedure.—This has been previously described in detail.[26] The apparent olefin fraction,[26] $p_{ol}^{e}/p^{l}$, was generally

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(7) (a) J. L. Gleave, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 236 (1935). (b) E. D. Hughes and C. K. Ingold, *ibid.*, 244 (1935).

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(20) (a) W. F. McDevit and F. A. Long, *J. Am. Chem. Soc.*, **74**, 1773 (1952); (b) R. L. Bergen, Jr., and F. A. Long, *J. Phys. Chem.*, **60**, 1131 (1956).

(21) E. Grunwald and A. F. Butler, *J. Am. Chem. Soc.*, **82**, 5647 (1960).

(22) R. W. Gurney, "Ionic Processes in Solution," McGraw-Hill Book Co., Inc., New York, N. Y., 1953.

(23) Discussions of the Faraday Soc., "Interaction in Ionic Solutions," No. 24, 1957, Aberdeen University Press, Ltd., Great Britain, 1958.

(24) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1952, p. 594.

(25) Ref. 24, pp. 594–595.

(26) G. A. Clarke, T. R. Williams and Robert W. Taft, *J. Am. Chem. Soc.*, **84**, 2292 (1962).

TABLE I

SETSCHENOW SALT PARAMETERS $K_g$ FOR THE DISSOLVED *t*-BUTYL CHLORIDE IN VARIOUS ELECTROLYTE SOLUTIONS AT 14.85°

| Electrolyte | $K_g$ | Electrolyte | $K_g$ | Electrolyte | $K_g$ |
|---|---|---|---|---|---|
| HCl | $+0.04^a$ | NaOH | $+0.41^c$ | $NaClO_4$ | $+0.24^a$ |
| LiCl | $+\ .29^b$ | KOH | $+\ .43^a$ | $Na_2CO_3$ | $+\ .96^c$ |
| NaCl | $+\ .35^b$ | $(CH_3)_4NOH$ | $+\ .24^a$ | $NaCO_2H$ | $+\ .24^a$ |
| KCl | $+\ .26^e$ | $(C_2H_5)_4NOH$ | $+\ .24^a$ | $NaCO_2C_6H_5$ | $+\ .26^a$ |
| $NH_4Cl$ | $+\ .18^a$ | KF | $+\ .51^d$ | $NaCO_2CH_3$ | $+\ .29^a$ |
| $HNO_3$ | $-\ .10^a$ | KBr | $+\ .19^a$ | $NaCO_2CF_3$ | $+\ .17^a$ |
| $LiNO_3$ | $+\ .25^b$ | $(CH_3)_4NBr$ | $+\ .02^a$ | | |
| $H_2SO_4$ | $+\ .44^b$ | NaI | $+\ .25^b$ | $Na_2Cr_2O_7$ | $+\ .64^a$ |
| $Na_2SO_4$ | $+\ .88^b$ | $NH_4I$ | $.00^a$ | $Na_2S_2O_3$ | $+\ .87^{b,g}$ |
| $K_2SO_4$ | $+\ .98^c$ | $HClO_4$ | $.00^a$ | NaSCN | $+\ .16^a$ |
| $KHSO_4$ | $+\ .46^{a,e,f}$ | | | | |

[a] Estimated uncertainty in the parameter is ±0.03. [b] Estimated uncertainty in the parameter is ±0.05. [c] Estimated uncertainty in the parameter is ±0.08. [d] Estimated uncertainty in the parameter is ±0.10. [e] Estimated uncertainty in the parameter is ±0.15. [f] Corrected for the added acid (1 *M* HCl) by assuming an additive Setschenow relationship. [g] Corrected for the added base (0.1 *M* NaOH/KOH) by assuming an additive Setschenow relationship.

TABLE II

SETSCHENOW SALT PARAMETERS $K\ddagger$ FOR THE *t*-BUTYL CHLORIDE TRANSITION STATE IN VARIOUS ELECTROLYTE SOLUTIONS AT 14.85°

| Electrolyte | $K\ddagger$ | Electrolyte | $K\ddagger$ | Electrolyte | $K\ddagger$ |
|---|---|---|---|---|---|
| HCl | $-0.03^a$ | $KHSO_4$ | $+0.18^{b,d}$ | $HClO_4$ | $-0.14^a$ |
| LiCl | $+\ .03^a$ | NaOH | $+\ .20^b$ | $NaClO_4$ | $-\ .04^a$ |
| NaCl | $+\ .06^a$ | KOH | $+\ .19^a$ | $Na_2CO_3$ | $+\ .41^a$ |
| KCl | $+\ .06^b$ | $(CH_3)_4NOH$ | $+\ .22^b$ | $NaCO_2H$ | $+\ .14^a$ |
| $NH_4Cl$ | $+\ .02^a$ | $(C_2H_5)_4NOH$ | $+\ .24^b$ | $NaCO_2C_6H_5$ | $+\ .11^a$ |
| $HNO_3$ | $-\ .05^b$ | NaF | $+\ .22^b$ | $NaCO_2CH_3$ | $+\ .21^a$ |
| $LiNO_3$ | $+\ .01^b$ | KF | $+\ .20^b$ | $NaCO_2CF_3$ | $+\ .11^a$ |
| $NaNO_3$ | $+\ .03^b$ | KBr | $-\ .02^a$ | | |
| $H_2SO_4$ | $+\ .01^b$ | $(CH_3)_4NBr$ | $.00^a$ | $Na_2Cr_2O_7$ | $-\ .10^a$ |
| $Li_2SO_4$ | $+\ .29^b$ | NaI | $-\ .08^b$ | $Na_2S_2O_3$ | $+\ .25^{a,c,e}$ |
| $Na_2SO_4$ | $+\ .27^b$ | $NH_4I$ | $-\ .14^b$ | NaSCN | $-\ .10^a$ |
| $K_2SO_4$ | $+\ .33^b$ | $(CH_3)_4NI$ | $-\ .12^b$ | | |

[a] Estimated uncertainty in the parameter is ±0.02. [b] Estimated uncertainty in the parameter is ±0.03. [c] Estimated uncertainty in the parameter is ±0.04. [d] Corrected for the added acid (1 *M* HCl) assuming an additive Setschenow relationship. [e] Corrected for the added base (0.1 *M* NaOH/KOH) by assuming an additive Setschenow relationship.

unaffected (= 0.04 ± 0.01) by salt concentrations up to 1 *M*. Exceptions were noted for salts which strongly salt-out aqueous *t*-butyl chloride. The following values of $p_{\text{ol}}{}^{\text{e}}/p^{\text{i}}$ were obtained for the exceptional electrolytes at 1 *M*: KOH (0.08 ± 0.01), $(CH_3)_4NOH$(0.10 ± 0.01), KF(0.07 ± 0.01), $Li_2SO_4$(0.07 ± 0.01), $Na_2CO_3$(0.10 ± 0.01) and $Na_2S_2O_3$(0.14 ± 0.01). Since the salt effects on the olefin fraction tend to parallel (probably within the accuracy of the data) the electrolyte order for either $K\ddagger$ or $K_g$, it is probable that these effects are medium effects acting to a greater extent on the substitution than the elimination transition state. The intervention of a measureable E2 reaction does not appear to be indicated by the results of Table VII.

## Results

Electrolyte effects on $k_p$ and $h$ were obtained in each case at 14.85° for electrolyte concentrations from approximately 0.1 *M* to 1.0 *M*. The values obtained are recorded in Dr. Clarke's Ph.D. thesis.[27] The results may be summarized (as follows) in terms of Setschenow salt effect parameters.

Electrolyte effects on activity coefficients of nonelectrolytes generally follow the empirical Setschenow equation[17,21,28]

$$\log f = \log (h^0/h) = KC_s \qquad (1)$$

where $C_s$ is the molar electrolyte concentration and $K$ is the Setschenow salt effect parameter. The superscript$^0$ refers to the distribution constant for pure water.

The results for the distribution constant $h$ for *t*-butyl chloride follow this relationship within their precision measures. Typical results are illustrated in Fig. 1. The slope of these plots is denoted as the Setschenow parameter for dissolved *t*-butyl chloride, $K_g$.

The rate quantity, $-\log (k_p/k_p{}^0)$, which is shown in the Discussion section to equal the logarithm of the activity coefficient for the *t*-butyl chloride solvolysis transition state, also follows the Setschenow relationship within the precision measures. Typical results are illustrated in Fig. 1. The slope of these plots is denoted as the Setschenow parameter for the *t*-butyl chloride transition state, $K\ddagger$.

Tables I and II summarize the results obtained. The former gives values of $K_g$ and the latter values of $K\ddagger$. In general, the $K\ddagger$ values are considerably more precise because of the experimental limitations in determination of precise values of $h$.[26]

## Discussion

According to the transition state theory, the electrolyte effects on $k_p$ may be attributed to the effects on the following hypothetical "equilibrium"

$$t\text{-BuCl}_{(g)} + (\text{aq.}) \rightleftharpoons t\text{-BuCl}_{(\text{aq.})}\ddagger \text{ (transition state)}$$

in terms of the rate equation:

$$\frac{\text{Rate}}{p} = k_p = \left(\frac{RT}{Nh}\right)(K\ddagger)\left(\frac{1}{f\ddagger}\right)$$

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(27) G. A. Clarke, Ph.D. Thesis, The Pennsylvania State University, June, 1960.

(28) J. Setschenow, *Ann. Chim. Phys.*, [6] **25**, 226 (1891).

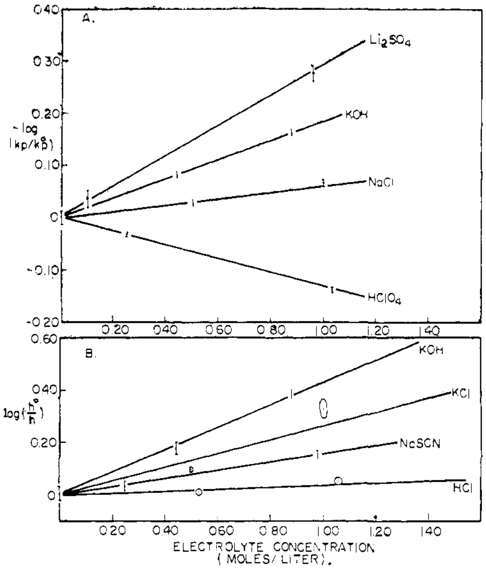


Fig. 1.—Typical Setschenow plots for the transition state (A) and the ground state (B) activity coefficients.

where $K\ddagger$ denotes the transition state theory "equilibrium constant" for the above reaction, and $f_\ddagger$ is the activity coefficient of the transition state (standard state-hypothetical one molal in pure water). No term in *t*-butyl chloride appears on the right hand side of this equation since at the low pressures involved the fugacity of the chloride may be taken as equal to its partial pressure. The salt effect on the solvolysis of gaseous *t*-butyl chloride, $k_p/k_p^0$ (where $^0$ refers to the reference state of pure water), is accordingly given as

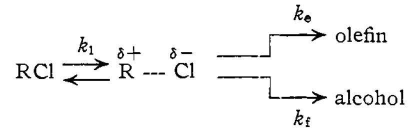
$$k_p/k_p^0 = \frac{1}{f_\ddagger} \qquad (2)$$

Further, combining equations 1 and 2 we have

$$\log (k_p^0/k_p) = \log f_\ddagger = K_\ddagger C_s \qquad (3)$$

A final consideration is necessary before the experimental results for the salt parameters $K_\ddagger$ and $K_g$ are considered.

According to the generally accepted mechanism for the solvolysis of *t*-butyl chloride in aqueous solution, the experimental rate constant $k_p$ (or $k_c$) is potentially a composite rate constant.[8]



Applying the steady state approximation to the intimate ion pair, $R^{\delta+} - - - Cl^{\delta-}$, one obtains the rate equation

$$\text{Rate} = -\frac{d(\mathrm{RCl})}{dt} = k_1\left[\frac{k_e + k_s}{k_2 + k_e + k_s}\right](\mathrm{RCl}),\ \text{and,}$$

$$\text{since}^{26}\ h = \frac{(\mathrm{RCl})}{p}$$

$$\frac{\text{Rate}}{p} = k_p = hk_1\left[\frac{k_e + k_s}{k_2 + k_e + k_s}\right] \qquad (4)$$

For the purposes of this discussion we shall assume that the quantity, $\frac{k_e + k_s}{k_2 + k_e + k_s}$, is approximately a constant, independent of electrolyte. The high concentration of the rather nucleophilic solvent employed, water, tends to justify this assumption since a high value of $k_s$ (by definition $k_s$ includes the concentration of water) will cause this quantity to approach unity. It may be noted too that the external return contribution (common ion effect) to $k_2$ has been found by recent tracer studies[29] to be small even in 80% methanol–20% water. Further, the condition of constancy of this quotient is satisfied if the individual ratios, $k_e/k_s$ and $k_2/k_s$, are both constant. The olefin fraction, $k_e/k_s$, is in fact found to be generally independent of electrolyte concentrations to 1 *M* (*cf.* Experimental for exceptions). Finally, the nature of the results in section 5 also appear to support the above assumption. With this assumption

$$\log (k_p^0/k_p) = \log\left(\frac{h^0k_1^0}{hk_1}\right) = \log f_\ddagger = K_\ddagger C_s \qquad (3')$$

where $f_\ddagger$ refers to the transition state for formation of the intermediate.

(1) **Effect of Electrolytes on the Dissolved Tertiary Butyl Chloride.**—From the results given in Table I, it is seen that the presence of an electrolyte generally salts-out (decreases the solubility or increases the activity coefficient) the dissolved *t*-butyl chloride. The effect is a characteristic one.[17] The only electrolyte which has a definite salting-in effect is nitric acid.

For purposes of comparison of cation and anion effects on *t*-butyl chloride, the salt parameters may be referred to arbitrary reference ions. Table III gives cation salt parameters for 1-1 electrolytes relative to the sodium ion. Table IV lists salt parameters for anions relative to the chloride or carbonate ions as the reference anion ion. It has been assumed throughout that the effect of the ions of the electrolyte are additive and the results appear to support this treatment.

Table III

Relative Cation Salt Parameters for *t*-Butyl Chloride in 1-1 Electrolyte Solutions

| Cation | $\Delta K_g$ |
|---|---|
| $Na^+$ | (0.00) |
| $H^+$ | − .28[a] |
| $Li^+$ | − .06[a] |
| $K^+$ | + .06[c] |
| $NH_4^+$ | − .21[b] |
| $(CH_3)_4N^+$ | − .17[a] |
| $(C_2H_5)_4N^+$ | − .17[b] |

[a] Estimated maximum uncertainty ±0.10. [b] Estimated maximum uncertainty ± 0.12. [c] Estimated maximum uncertainty ± 0.15.

It is clear from Table III that salting-out by an electrolyte shows the familiar relation to the cation size—the larger cations reduce the observed salting-out with respect to the smaller reference cation, $Na^+$. The effect observed with hydronium or ammonium ions is a reasonable one in terms of well hydrated ions.

The influence of the anion (*cf.* Table IV) is qualitatively similar to that of the cation, *i.e.*, with increasing size of the anion *t*-butyl chloride is increasingly salted-in.

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[29] C. A. Bunton and B. Nayak, *J. Chem. Soc.*, 3854 (1959).

TABLE IV

RELATIVE ANION SALT PARAMETERS FOR *t*-BUTYL CHLORIDE

| Anion | $\Delta K_g$ | Anion | $\Delta K_g$ |
|---|---|---|---|
| $Cl^-$ | (0.00) | $CO_3^{=}$ | (0.00) |
| $F^-$ | + .25[d] | $SO_4^{=}$ | − .08[c] |
| $OH^-$ | + .12[d] | $S_2O_3^{=}$ | − .09[c] |
| $Br^-$ | − .07[b] | $Cr_2O_7^-$ | − .32[b] |
| $I^-$ | − .14[c] | | |
| $NO_3^-$ | − .04[b] | | |
| $HCO_2^-$ | − .11[a] | | |
| $ClO_4^-$ | − .08[b] | | |
| $SCN^-$ | − .18[a] | | |
| $CH_3CO_2^-$ | − .06[a] | | |
| $CH_3CO_2^-$ | − .18[a] | | |
| $C_6H_5CO_2^-$ | − .09[a] | | |

[a] Estimated max. uncertainty ± 0.08. [b] Estimated max. uncertainty ± 0.12. [c] Estimated max. uncertainty ± 0.14. [d] Estimated max. uncertainty ± 0.18.

**(2) Effect of Electrolytes on the Solvolysis Transition State.**—Tables V and VI, respectively, record the relative cation (standard, sodium ion) and anion (standard, chloride and carbonate ions) salt parameters for the *t*-butyl chloride transition state. It is apparent from Table V that, in contrast to the ground state, the transition state is nearly insensitive to differences in cation size. Of the cations studied, only the hydrogen ion (and probably $NH_4^+$) shows a salting-in effect which is outside of experimental error. For the inorganic anions of the same charge type, the qualitative trend of increasing salting-in by the larger ions is pronounced and clearly evident. However, for the organic acid anions, this trend is strikingly absent and is replaced by a variable salting-out effect (*cf.* Table VI).

TABLE V

RELATIVE CATION SALT PARAMETERS FOR THE SOLVOLYSIS TRANSITION STATE OF *t*-BUTYL CHLORIDE

| Cation | $\Delta K_{\ddagger}$[a] |
|---|---|
| $Na^+$ | 0.00 |
| $H^+$ | − .09 |
| $Li^+$ | − .03 |
| $K^+$ | − .01 |
| $NH_4^+$ | − .05 |
| $(CH_3)_4N^+$ | .00 |
| $(C_2H_5)_4N^+$ | + .04 |

[a] Estimated uncertainty ± 0.06.

**(3) The Ion-atmosphere Model Applied to the Ground and Transition States of Tertiary Butyl Chloride.**—Ingold and co-workers[9] have considered the effect of an electrical atmosphere of point-charge ions about a point dipole in a continuous dielectric medium. Their treatment was analogous to that of Debye–Hückel[10] for the activity coefficient of an ion. The expression obtained for the activity coefficient of the dipole is

$$\log f = -\frac{4\pi N e^4}{2.303(10^3)(DkT)^2} Z^2 d\mu \qquad (5)$$

$Z$ = the fraction of an electronic charge at each point-pole; $d$ = the fixed distance of separation of the point charges of the dipole; $\mu$ = the ionic strength of the electrolyte solution containing the point-dipole; $N$ = Avogadro's number; $e$ = electronic charge; $D$ = dielectric constant of the solution; $k$ = Boltzmann's constant; $T$ = absolute temperature.

TABLE VI

RELATIVE ANION SALT PARAMETERS FOR THE SOLVOLYSIS TRANSITION STATE OF *t*-BUTYL CHLORIDE

| Anion | $\Delta K_{\ddagger}$ | Anion | $\Delta K_{\ddagger}$ |
|---|---|---|---|
| $Cl^-$ | 0.00 | $Cl^-$ | 0.00 |
| $F^-$ | + .15[b] | $HCO_2^-$ | + .08[a] |
| $OH^-$ | + .14[b] | $CH_3CO_2^-$ | + .15[a] |
| $NO_3^-$ | − .02[b] | $CF_3CO_2^-$ | + .05[a] |
| $Br^-$ | − .07[b] | $C_6H_5CO_2^-$ | + .05[a] |
| $ClO_4^-$ | − .11[a] | | |
| $I^-$ | − .15[c] | | |
| $SCN^-$ | − .16[a] | | |
| $HSO_4^-$ | + .12[c] | | |
| Anion | $\Delta K_{\ddagger}$ | | |
| $CO_3^{=}$ | 0.00 | | |
| $SO_4^{=}$ | − .14[b] | | |
| $S_2O_3^{=}$ | − .16[a] | | |
| $Cr_2O_7^{=}$ | − .51[a] | | |

[a] Estimated uncertainty ± 0.04. [b] Estimated uncertainty ± 0.05. [c] Estimated uncertainty ± 0.06.

For sufficiently dilute solutions equation 5 may be written as

$$\log f = -\alpha\beta Z^2 d\mu \qquad (6)$$

where $\alpha$ and $\beta$ are the Debye–Hückel constants for water at a given temperature. At 14.85° the product $(\alpha\beta)$ is equal to $0.164 \times 10^8$.

According to the theory, the presence of ions in solution results in an ionic atmosphere about a dipole which lowers the free energy. The reduction in free energy is proportional to the ionic strength.

It will be noted that both the empirical eqn. 3 and the theoretical eq. 5 have a first power dependence on the concentration of 1–1 electrolytes. However, the latter equation anticipates that electrolytes of a given charge type will all give the same value of $K_{\ddagger}$. In this respect the results in Table II in no way conform to the predictions of equation 5. Specific electrolyte effects are observed—both accelerations and retardations (negative and positive Setschenow parameters, respectively) of the solvolysis rate at unit pressure are observed. It is clear, therefore that eqn. 5 applied directly to the *t*-butyl chloride transition state is totally inadequate in describing the nature of the observed salt effects.

Aqueous *t*-butyl chloride may also be regarded as a dipole. The $K_g$ parameters therefore provide a further test of eq. 5. The complete failure of this equation to account for the observed behavior of *t*-butyl chloride in the ground state is obvious from the results given in Table I.

It appears that the principal reason for the failure of eq. 5 to reproduce the observed effects of electrolytes on the activity coefficient of dipolar molecules arises because of the assumption that the only effect of the electrolyte is the ion atmosphere effect (*cf.* subsequent section).

A second potential source of difficulty is the fact that the concentration range over which a Debye–Hückel type ion-atmosphere treatment can be expected to apply is a very limited one. Fuoss

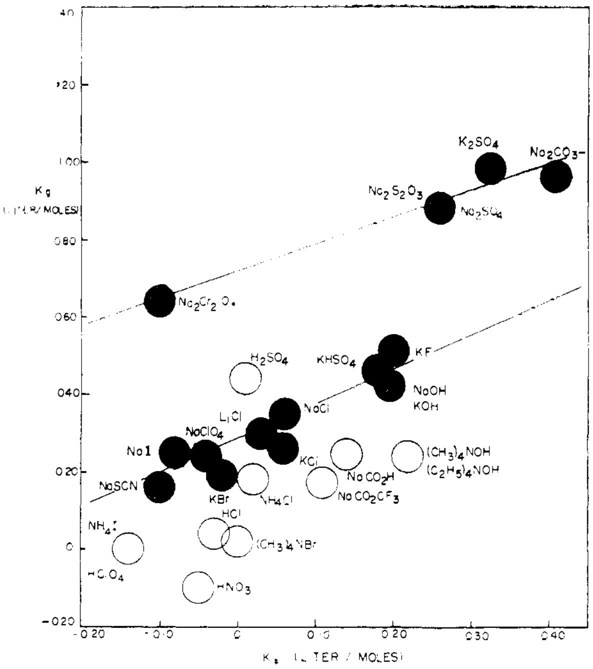

Fig. 2.—The relationship between the ground state parameter $K_g$ and the transition state parameter $K_\ddagger$.

and Onsager[30] consider the region of reliability for the Debye-Hückel theory to extend to no more than 0.01 *M*. However, Ingold and co-workers[9] anticipated that eq. 5 for dipoles should be valid over a more extensive range because of the smaller density variation of the ionic atmosphere around dipoles. In reaching the conclusions above, we have assumed that the ion-atmosphere theory for dipoles is at least approximately valid over the entire concentration range of the present investigation. The results in a subsequent section appear to justify this assumption.

**(4) Comparison of Ground and Transition State Salt Parameters–Evidence of Salt Induced Medium Effects.**—A plot of corresponding $K_g$ *vs.* $K_\ddagger$ parameters (Fig. 2) does not reveal any general relationship between the ground and transition state salt effects. However, if one considers only the inorganic salts (*i.e.* excludes organic cations and anions and the acidic cations $H_3O^+$ and $NH_4^+$), distinctly linear relationships of near unit slope are apparent (dark circles in Fig. 2) which separate accordingly to the charge type of the anion. In this section and the following one, we shall confine our attention to this orderly behavior exhibited by the inorganic salts. In a subsequent section, the behavior of the organic cations and anions and the acidic cations will be considered.

The separation of inorganic salts according to charge type in Fig. 2 provides clear evidence of the operation (at least qualitatively) of the ion atmosphere effect. However, it is equally clear that there is at least one other important contribution to the activity coefficients. According to the ion atmosphere model, one should obtain the same salt parameter for all electrolytes of a given charge type (so that Fig. 2 would consist of two points, one for all 2–1 electrolytes and another for all 1–1 electrolytes). Instead, there is ordering of 2–1 and 1–1 electrolytes along separate approximately parallel lines. The order of anions along these lines is a common one which has been frequently observed in a number of phenomena associated with aqueous electrolyte solutions. Namely, it is that associated with increased internal pressure of the water structure[20,31] resulting from decreased ion size.

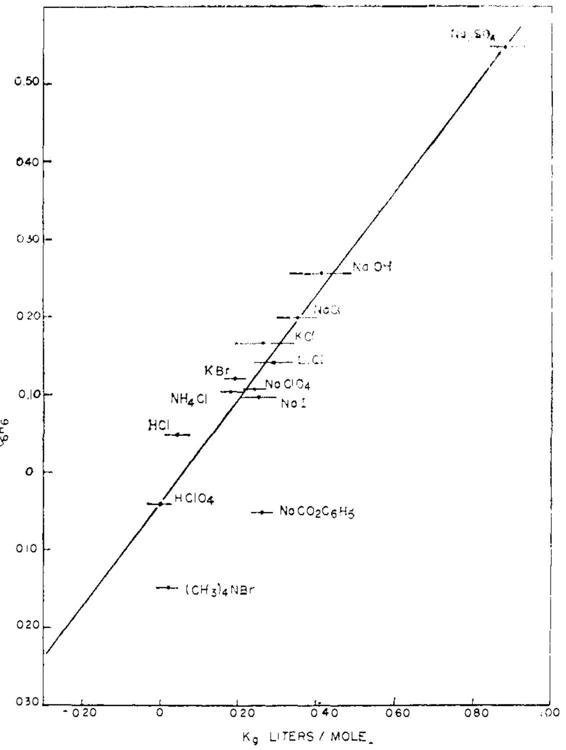

Fig. 3.—The relationship between the salt parameters for benzene and dissolved tertiary butyl chloride.

Nearly the same quantitative order of anion effects has been observed in all previous studies[17,20] of aqueous electrolyte effects on the activity coefficients of non-electrolytes. This is illustrated in Fig. 3 which shows a typical correlation (of nearly unit slope) between the Setschenow parameters for benzene ($K_{C_6H_6}$) and *t*-butyl chloride ($K_g$). Deviations from this correlation are again to be noted for organic anions and cations. Similar plots are obtained for the less abundant data on the salt parameters for any pair of the non-electrolytes: nitrous oxide, benzoic acid, aniline and *t*-butyl chloride.

Linear correlations resembling Fig. 3 are also obtained in plots of $K_g$ (or $K_\ddagger$) *vs.* partial molal absolute entropies,[32] $\bar{S}^0$, viscosity $\beta$-coefficients[33] and shifts of the NMR proton resonance frequencies of electrolyte solutions.[34] In the correlation of $K_\ddagger$ parameters and partial molal

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(30) R. M. Fuoss and L. Onsager, *J. Phys. Chem.*, **61**, 668 (1951).

(31) H. S. Frank and W. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

(32) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1952, p. 368.

(33) R. W. Gurney, ref. 25, Chapter 10.

(34) J. N. Shoolery and B. Alder, *J. Chem. Phys.*, **23**, 805 (1955).

entropies separate lines appear for monatomic and oxyanions. It is of interest to note in connection with these various correlations that the order of anion effects on $K_\ddagger$ clearly does not parallel the order of nucleophilicities observed in alkyl halide displacement reactions.

As shown by the correlation of Fig. 3, the salt order for *t*-butyl chloride follows that anticipated by the theory of McDevit and Long for the salt induced internal pressure effects on non-polar non-electrolytes. Important contributions of salt induced medium effects to the activity coefficient of *t*-butyl chloride and its solvolysis transition state are therefore clearly established by the present results.

The fact that the correlation lines of Fig. 2 ($K_g$ *vs.* $K_\ddagger$) are approximately of unit slopes indicates that the salt induced solvent effects on the activity coefficients of *t*-butyl chloride and its solvolysis transition state are nearly equivalent. Accordingly, the medium effect should nearly disappear in the ratio of these activity coefficients, $f_g/f_\ddagger$. (A referee has pointed out that for perfect cancellation, $\Delta V^\ddagger = 0$ is implied. Since this is unlikely, the cancellation is an approximation, but one which is clearly useful (*cf.* section 5) in most practical applications.) This ratio of activity coefficients gives the salt effect on the conventional rate constant $k_c$ for solvolysis of dissolved *t*-butyl chloride at unit concentration. That is $k_c = k_c^0(f_g/f_\ddagger)$ and $\log (k_c/k_c^0) = \log f_g - \log f_\ddagger$, or $\log (k_c/k_c^0) = (K_g - K_\ddagger)C_s$, where the superscript $^0$ refers to the reference state pure water. The values of $K_g - K_\ddagger$ are examined in the following section.

**(5) The Ion-Atmosphere Model and ($K_g - K_\ddagger$) Values.**—Table VII summarizes the values of $K_g - K_\ddagger$ obtained for the various inorganic salts. The positive values of $K_g - K_\ddagger$ denote the logarithm of the rate acceleration in one molar salt solution.

TABLE VII

SALT EFFECT PARAMETERS ($K_g - K_\ddagger$) FOR THE RATE OF SOLVOLYSIS OF DISSOLVED *t*-BUTYL CHLORIDE AT UNIT CONCENTRATION, WATER 15°

| | | | |
|---|---|---|---|
| | 1–1 Salts | | |
| KBr | $+0.21^a = (0.19 + 0.02)$ | $LiNO_3$ | $0.24^b = (0.25 - 0.01)$ |
| KOH | $.24^a = (.43 - .19)$ | NaF | $.29^c = (.51 - .22)$ |
| $NaClO_4$ | $.28^a = (.24 + .04)$ | NaI | $.33^c = (.25 + .08)$ |
| NaSCN | $.26^a = (.16 + .10)$ | KCl | $.20^c = (.26 - .06)$ |
| LiCl | $.26^b = (.29 - .03)$ | NaOH | $.21^c = (.41 - .20)$ |
| NaCl | $.29^b = (.35 - .06)$ | KF | $.31^c = (.51 - .20)$ |
| | Av. $0.25 \pm 0.02^d$ | | |
| | 2–1 Salts | | |
| $Na_2Cr_2O_7$ | $+0.74^a = (0.64 + 0.10)$ | | |
| $Na_2SO_4$ | $.61^b = (.88 - .27)$ | | |
| $Na_2S_2O_4$ | $.62^b = (.87 - .25)$ | | |
| $K_2SO_4$ | $.65^c = (.98 - .33)$ | | |
| $Na_2CO_3$ | $.55^c = (.96 - .41)$ | | |
| | Av. $+0.66 \pm 0.05^d$ | | |

[a] Estimated max. uncertainty ± 0.06. [b] Estimated max. uncertainty ± 0.08. [c] Estimated max. uncertainty ± 0.13. [d] Based upon (a) and (b) only.

It is clear from Table VII that the specificities in $K_g$ and $K_\ddagger$ essentially disappear and all of the values $K_g - K_\ddagger$ collect into two distinct groups, one for 1–1 salts (avg. value + 0.25) and the other for 2–1 salts (avg. value + 0.66). This result is (within experimental error) in quantitative agreement with the expectations of the ion atmosphere model.

Eqn. 5 may be applied to both the ground and transition states for the *t*-butyl chloride solvolysis, giving

$$\log (k_c/k_c^0) = \log (f_g/f_\ddagger) = \left[\frac{4\pi N e^4}{2.303(DkT)^2(10^3)} (Z_\ddagger^2 d_\ddagger - Z_g^2 d_g)\right] nC_s \quad (7)$$

where $nC_s = \mu =$ ionic strength; $n = 1$ for 1–1 salt; $n = 3$ for 2–1 salts.

$Z_\ddagger, Z_g$ = fractional charges of the dipole of the transition and ground states, respectively

$d_\ddagger, d_g$ = distance of charge separation in the transition and ground states, respectively

Equating $n$ times the quantity in brackets on the right hand side of eq. 7 with the quantity $K_g - K_\ddagger$ gives

$$\frac{(K_g - K_\ddagger)_{2-1 \text{ salt}}}{(K_g - K_\ddagger)_{1-1 \text{ salt}}} = \frac{3}{1}$$

The ratio of the average values of ($K_g - K_\ddagger$) is 2.6 ± 0.2, in striking agreement with the theoretical ratio.

One may conclude (in accord with Brönsted[18]) that the effects of the aqueous inorganic salts (of Table VII) on the activity coefficient of the aqueous *t*-butyl chloride transition state are due primarily to two causes: the ion atmosphere effect and the salt induced medium effect. That is, $f_\ddagger \cong f_\ddagger^{\text{e.s.}} \cdot f_\ddagger^{\text{i.p.}}$, where $f_\ddagger^{\text{e.s.}}$ is the coulombic ion atmosphere contribution and $f_\ddagger^{\text{i.p.}}$ is the salt induced internal pressure contribution. Similarly, for dissolved *t*-butyl chloride, $f_g \cong f_g^{\text{e.s.}} f_g^{\text{i.p.}}$ (the fact that a salt of the 2–1 as well as the 1–1 type apparently falls on the correlation line of Fig. 3 suggests that $f_g^{\text{e.s.}}$ is rather inconsequential). Since we deduce from Figs. 2 and 3 that $f_g^{\text{i.p.}} \cong f_\ddagger^{\text{i.p.}}$, it follows that $f_g/f_\ddagger \cong f_g^{\text{e.s.}}/f_\ddagger^{\text{e.s.}}$, for most practical purposes a purely coulombic ion atmosphere quantity appropriate to treatment by the theoretical eq. 7.

Substituting the average values of $K_g - K_\ddagger$ from Table VII eq. 7 gives the average value of $1.44 \times 10^{-8}$ for the quantity ($Z_\ddagger^2 d_\ddagger - Z_g^2 d_g$). If the transition state charge separation is taken to be about 0.5 Å. greater[35] than the equilibrium carbon chlorine bond distance[36] of 1.76 Å., and the fractional charge $Z_g$ for the ground state is taken to be about 0.2 of an electronic charge,[37] the *t*-butyl chloride transition state is found to behave (in terms of eq. 7) as if about *0.8 of an electronic charge* is localized on the carbon and chlorine atoms. This result is relatively insensitive to small values chosen for $Z_g$. The result is, of course, only of qualitative significance in view of the delocalization of positive charge into the methyl groups of the *t*-butyl "cation" and accompanying uncertainty of the significance of the $d_\ddagger$ distance. (A referee has appropriately pointed out that a theoretical treatment more rigorous than that of the point dipole, such as the cavity model treatment of

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[35] A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956).

[36] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1956, p. 30.

[37] R. W. Taft, Jr., *J. Chem. Phys.*, **26**, 93 (1957).

Kirkwood (*J. Chem. Phys.*, 2, 351 (1934)), would also undoubtedly give a somewhat different figure.) The reaction constant,[38] $\rho^*$, for the solvolysis in water of *t*-carbinyl chlorides, $XCH_2CCl(CH_3)_2$ (X is a polar substituent[39]) has been found to be $-3.8$. Apparently $\rho^*$ values of this sign and magnitude may be associated (in water) with the kind of charge separation process indicated by the kinetic salt effect.

(6) **Specific Electrolyte Effects.**—A series of electrolytes has been investigated which give $(K_g - K_{\ddagger})$ values which do not conform to the ion atmosphere behavior exemplified by the salts of Table VII. The deviant behavior was found for the acidic cations, ammonium and hydronium, and for organic electrolytes. These results are listed in Table VIII.

All of the electrolytes of Table VIII show appreciably smaller rate accelerations ($HNO_3$ apparently produces a small rate retardation) than the inorganic salts of the same charge type in Table VII. The $(K_g - K_{\ddagger})$ values for the ammonium and alkylammonium salts are apparently independent of the anion (avg. value for the former is + 0.15 and for the latter + 0.01). The carboxylate ions as a class also appear to give approximately the same value (avg. + 0.10). The values for mineral acids, on the other hand, show an apparent dependence on the anion.

TABLE VIII

ELECTROLYTE EFFECTS $(K_g - K_{\ddagger})$ ON THE RATE OF SOLVOLYSIS OF DISSOLVED *t*-BUTYL CHLORIDE AT UNIT CONCENTRATION, WATER, 15°[a]

| Mineral acids | | Carboxylate salts | | Ammonium salts | |
|---|---|---|---|---|---|
| $HNO_3$ | −0.05 | $NaO_2CH$ | +0.10 | $NH_4Cl$ | +0.16 |
| HCl | + .07 | $NaO_2CC_6H_5$ | + .15 | $NH_4I$ | + .14 |
| $HClO_4$ | + .14 | $NaO_2CCH_3$ | + .08 | $(CH_3)_4NOH$ | + .02 |
| $H_2SO_4$ | + .43[b] | $NaO_2CCF_3$ | + .06 | $(CH_3)_4NBr$ | + .02 |
| | | | | $(C_2H_5)_4NOH$ | .00 |

[a] Estimated maximum uncertainty ± 0.06 unless otherwise indicated. [b] Estimated maximum uncertainty ± 0.08.

We shall consider first the possible cause of the deviant behavior of the organic electrolytes. In Fig. 3 and similar plots, these electrolytes deviate substantially from the linear correlation shown by inorganic electrolytes (including, incidentally, the acidic cations, $H_3O^+$ and $NH_4^+$). Benzene is substantially more salted-in by these organic electrolytes than is *t*-butyl chloride. Further, on the one hand, the *t*-butyl chloride transition state is virtually unaffected by the alkyl ammonium ions relative to the $Na^+$ (*cf.* Table V) and the $K_{\ddagger}$ salt parameters for the carboxylate anions (*cf.* Table VI) also tend to be small, whereas, on the other hand, Bergen and Long[20a] have found that phthalic acid and salicylic acid, for example, are even more strongly salted-in solution by organic electrolytes than is benzene. It is thus abundantly clear that the susceptibility to salting-in by the organic electrolytes varies enormously more among various non-electrolytes than does that for the salt effects of inorganic electrolytes. Further, Grunwald and Butler[21] have noted that although the inorganic salt order for naphthalene is dramatically inverted between water and 50% (wt.) dioxane-water as solvent, organic electrolytes salt-in in both media. They conclude that specific short-range (direct) dispersive interactions take place between non-electrolyte and organic electrolytes. Our results are consistent with this interpretation. Since these interactions are apparently less important for the *t*-butyl chloride transition than ground state, it is clear that quotient $f_g/f_{\ddagger}$ for organic electrolytes cannot be a purely coulombic ion atmosphere quantity.

We turn now to a consideration of the acidic cations, $H_3O^+$ and $NH_4^+$. The electrolytes of these cations do not show notable deviations from plots such as that shown in Fig. 3. One may infer then that there is no special effect of these cations (either direct or indirect) on dissolved *t*-butyl chloride. On the other hand, the only notable cation effects on the *t*-butyl chloride transition state (*cf.* Table V) are those for the *salting-in* exhibited by these ions, especially $H_3O^+$. The importance of front-side participation by hydroxylic solvents as a driving force in the solvolysis of *t*-butyl halides has been recognized since the conception of the $S_N1$ mechanism.[7] Hydrogen bonding by water to the incipient chloride ion in the transition state is definitely indicated by the finding[26] that the solvolysis rate $k_p$ gaseous *t*-butyl chloride at unit pressure is reduced in $D_2O$ compared to $H_2O$ by essentially the same factor (0.72) as is the conventional rate constant $k_c$. Thus the enhancement in the rate constant $k_p$ exerted by the acidic cations may be associated with the transition state hydrogen bonding effect.[40] Since these cations do not enter the rate equation, their effect is presumably an indirect one in which an increase in the concentration of the acidic cations increases the ability of the solvent to enter into the hydrogen bonding interaction. Since the proposed effect is specific to the *t*-butyl chloride transition state, it must also follow for the acidic cations that $f_g/f_{\ddagger}$ cannot be a purely coulombic ion atmosphere quantity.

(7) **Regarding the General Cancellation of Salt-induced Medium Effects.**—The results of Table VII are in distinct contrast to those reported[11–16] in which quite specific salt effects have been observed on the rates of solvolysis of dissolved substrate at unit concentration. The later results all have the common feature that a mixed aqueous organic solvent was employed. It is perfectly clear from the detailed treatment of Grunwald and Butler[21] that salt induced medium effects are distinctly more complex in mixed than pure solvents of high dielectric constant. These authors show that at least one more term (and probably others) must contribute to the salt induced medium effects in mixed solvents. It is therefore expected that in mixed solvents the salt induced medium effects will not cancel between ground and solvolysis

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[38] R. W. Taft, Jr., in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, New York, N. Y., 1956, Chapt. 13.

[39] R. H. Boyd, Ph.D. Thesis, The Pennsylvania State University, 1959.

[40] For recent evidence of the importance of hydrogen bonding interactions on activity coefficient behavior *cf.* (a) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960); (b) N. C. Deno and H. Berkheimer, *J. Chem. Eng. Data*, **5**, 1 (1960).

transition states (because the salt effect on preferential solution will differ for these two states). It is in fact quite interesting that the 1-1 electrolyte effects for the rate of solvolysis of neophyl *p*-toluenesulfonate in 50% (wt.) dioxane-water[16] parallel quite closely (a roughly linear plot results) corresponding salt effects, $K_{\ddagger}$ (or $K_g$ but not $K_g - K_{\ddagger}$) for *t*-butyl chloride solvolysis in water.

(8) **A Comment on Pure Medium Effects.**—Smith, Fainberg and Winstein[41] have recently utilized the conventional rate constant for solvolysis of *p*-methoxy-neophyl *p*-toluenesulfonate as a measure of the ionizing power of a solvent. A close correspondence of the logarithm of the rate constant of pure polar non-hydroxylic solvents with other independent measures of ionizing power is found. The results support the notion that these rates are governed by the ability of the solvent to support a charge separation through non-specific induced polarization of the effective dielectric constant of the medium by the local electric fields of the dipolar transition state (*i.e.*, through coulombic interactions). Since the internal pressures of the solvents investigated vary widely, the partial molal free energy of the dissolved reaction substrate must also vary widely.[42] The success of the treatment implies at least substantial cancellation between ground and transition states of the non-coulombic contributions to the partial molal free energy of these two states. That is, there is apparently involved a cancellation of internal pressure effects between ground and transition states which leaves (for most practical purposes) the rate constant as a coulombic quantity, a situation analogous to the cancellation reported in this paper for kinetic salt effects in pure water. The complication of kinetic salt effects in mixed solvents appears to support the conclusion of the above authors that it can be less certainly accepted that the effects of mixed solvents on the solvolysis rates are purely coulombic quantities.

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[41] S. G. Smith, A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **83**, 618 (1961).

[42] J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd Ed., Reinhold Publishing Co., New York, N. Y., 1950, pp. 46, 94, 129, 435.

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[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

# Coördination Compounds of Trivalent Metals with Unsymmetrical Bidentate Ligands. I. Benzoylacetonates[1]

BY ROBERT C. FAY[2] AND T. S. PIPER

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The preparation of benzoylacetonates of a number of trivalent metals is described (M = Cr, Co, Rh, Al, Mn, Fe). *cis* and *trans* isomers of the inert complexes (M = Cr, Co, Rh) were separated by utilizing solubility differences in ethanol and column chromatography on alumina. Somewhat less than the statistical amount of *cis* isomer was obtained. In the case of the labile complexes (M = Al, Mn, Fe), only the more stable *trans* isomer could be isolated. The configuration of the diamagnetic complexes was determined by nuclear magnetic resonance; the configuration of the paramagnetic complexes was established on the basis of isomorphism of crystals of the diamagnetic and paramagnetic complexes. Small intensity differences in the electronic spectra suggest that the forbidden d-d transitions obtain intensity by mixing in odd molecular orbitals rather than odd atomic orbitals. *Cis* to *trans* isomerization of the cobalt and chromium complexes takes place at elevated temperatures. The potential importance of n.m.r. in stereochemical studies of metal coördination complexes is emphasized.

## Introduction

Coördination compounds in which the central atom is bound to three unsymmetrical bidentate ligands may exist in two geometrically isomeric forms. If the distinguishable ends of an unsymmetrical bidentate ligand are represented by X and Y (see Fig. 1), the X groups may be in the 1,2,3- or 1,2,6-positions. We shall refer to the isomer with X groups in the 1,2,3-positions as the *cis* isomer and the isomer with X groups in the 1,2,6-positions as the *trans* isomer.[3]

The majority of the work reported on isomeric tris-complexes has been concerned with the tris-amino acid chelates of cobalt(III). The glycine and alanine complexes have been known for a long time,[4] but only recently has the configuration of the two isomeric glycine complexes been determined on the basis of visible absorption spectra.[5] Carassiti and co-workers[6,7] using the same technique have determined the configuration of the alanine complexes and also a number of other amino acid chelates of cobalt(III). A tris-(ethanolamine)-cobalt(III) complex has been isolated and assigned the *cis* configuration, also on the basis of absorption spectra.[8] Very recently two tris-(8-quinolinolo)-chromium(III) complexes (one solvated) have been assigned *cis* and *trans* structures.[9] The assignment, however, must be viewed as only tentative because of the lack of experimental evidence.

One class of compounds which ought to give geometric isomers and which has not been previously investigated are tris-complexes of trivalent

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[1] Presented in part at the Symposium on Magnetic Phenomena in Inorganic Chemistry, 140th National Meeting, American Chemical Society, September, 1961, Chicago, Illinois.

[2] National Science Foundation Fellow, 1960–1962.

[3] W. C. Fernelius, *Adv. in Chem. Series*, **8**, 9 (1953).

[4] H. Ley and H. Winkler, *Ber.*, **42**, 3894 (1909); *ibid.*, **45**, 372 (1912); H. Ley and K. Ficken, *ibid.*, **50**, 1123 (1917).

[5] F. Basolo, C. J. Ballhausen and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).

[6] V. Carassiti and M. Claudi, *Ann. Chim. (Rome)*, **50**, 581 (1960).

[7] V. Carassiti and A. M. Marinangeli, *ibid.*, **50**, 593 (1960).

[8] H. Yoneda and S. Kida, *J. Am. Chem. Soc.*, **82**, 2139 (1960).

[9] F. Umland, G. H. Gudmundsson and K. Adam, *Naturwissenschaften*, **48**, 49 (1961).