The free energy of formation of chromate ion from its elements at 25° is, therefore, $\Delta F^0 = -171{,}400$ cal.

The free energies of formation of other substances whose equilibria with chromate ion have been measured, immediately follow, and their values will be included for the sake of completeness. The most recent determination of the second ionization constant of chromic acid[10] gives 3.2×10^{-7} at 25° or $\Delta F^0 = 8740$ cal. so that the free energy of formation of $HCrO_4^-$ ion is $-180{,}140$ cal. Neuss and Riemann[10] also have determined the equilibrium constant for the reaction

$$Cr_2O_7^{=} + H_2O = 2HCrO_4^-$$

finding $K = 0.023$ or $\Delta F = 2210$ cal. The free energy of formation of water[5] is $-56{,}690$ cal., so that the free energy of formation of dichromate ion at 25° is $-305{,}800$ cal. The free energy of formation of solid silver chromate involves the free energies of formation of silver ion,[11] 18,450 chromate ion and the free energy of solution of silver chromate.[2] It is found to be $-150{,}800$ cal.

Summary

The heat capacity of silver chromate has been measured from 15 to 300°K. and its entropy at 298.1°K. calculated to be 51.8 cal./deg. mole. Its heat of solution has been determined to be 14,450 cal. The entropy of chromate ion has been calculated to be 10.5 cal./deg. mole. The free energies of formation of chromate and several related ions and of solid silver chromate have been obtained.

(10) Neuss and Riemann, THIS JOURNAL, **56**, 2238 (1934).

(11) Gerke, *Chem. Rev.*, **1**, 377 (1925).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Rate and Mechanism of Hydrolysis and Alcoholysis of Tertiary Butyl Chloride. An Application to the Transition State Theory of Solvent Effects

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Ingold and his collaborators[2] have postulated that two types of mechanism may operate in typical organic substitution reactions. One of these is identical with the mechanism discussed by Polanyi[3] and Olson.[4] It can be characterized as a one-step bimolecular reaction, resulting in inversion of configuration. In the second mechanism, a primary ionization of one of the reactants would occur as the slow rate determining step and this would be followed by a rapid addition reaction. Such a reaction would be unimolecular, its rate would be independent of the substituting agent, and in the case of an optically active reactant, presumably would result in racemization. It was just this type of reaction which Olson and Voge[5] had in mind when they stated: "We therefore conclude that in the absence of large resonance effects any reaction mechanism which involves primary breaking of strong bonds at ordinary temperatures is erroneous."

Hughes[6] in studying the hydrolysis of *t*-butyl chloride in aqueous ethanol solvents found that the reaction was first order with respect to the halide and independent of the concentration of hydroxide ions. The specific reaction constant increased 750-fold as the solvent was changed from 90% ethanol by volume to 40% ethanol by volume. Since the reaction was not catalyzed by hydrogen or hydroxide ions, Hughes and Ingold[7] state that this reaction occurs by primary ionization and that water acts "as solvent alone." The tremendous change in rate constant which accompanied the change in composition of the solvent was ascribed to the superior properties of water over alcohol as an ionizing medium. It was decided therefore to reinvestigate this reaction, bearing in mind the role of nonionized water as the substituting agent. In general, Hughes' procedure was adopted. Aqueous methanol was employed as a solvent and methyl red was substituted for lacmoid as indicator.

A preliminary qualitative experiment, in which 25 cc. of *t*-butyl chloride was shaken for several

(1) Shell Research Fellow in Chemistry, 1937–1938.

(2) Hughes, Ingold and Patel, *J. Chem. Soc.*, 526 (1933).

(3) Polanyi, *Z. physik. Chem.*, **B19**, 164 (1932).

(4) Olson, *J. Chem. Phys.*, **1**, 418 (1933).

(5) Olson and Voge, THIS JOURNAL, **56**, 1690 (1934).

(6) Hughes, *J. Chem. Soc.*, 255 (1935).

(7) Hughes and Ingold, *ibid.*, 244 (1935).

days with 25 cc. of 50 mole per cent. methanol, yielded a product which remained as a separate phase. The non-aqueous layer was separated, washed several times with water, dried, and distilled. It was identified as methyl *t*-butyl ether by its physical properties.[8]

It was therefore evident that we were dealing with an alcoholysis as well as an hydrolysis. In spite of the fact that both hydrolysis and alcoholysis are occurring simultaneously, and that they may be bimolecular reactions, we still can express the over-all rate of disappearance of *t*-butyl chloride in the form of a first order rate equation. The constant so obtained changes markedly with the composition of the solvent, paralleling the similar observation of Hughes in aqueous ethanol.

In the quantitative kinetic experiments duplicate runs were made in each solvent. Checks within 2% were obtained. The rate measurements are summarized in Table I, in the column headed "*k* experimental."

If we attempt to account for the variation in the first order rate constant by considering two bimolecular reactions represented by the rate equation

$$\mathrm{d(RCl)}/\mathrm{d}t = -[k_1(\mathrm{H_2O}) + k_2(\mathrm{ROH})](\mathrm{RCl})$$

we fail completely, the measured constant changing much more rapidly than can be accounted for by changes in the concentrations of alcohol and water. We could, of course, dismiss this failure by ascribing the variation to some loosely defined solvent effect. However, this would not enable us to decide unequivocally between the unimolecular and bimolecular mechanisms. We must, rather, regard a reaction as a mode of escape by the reactants. The rate of a reaction should therefore be determined by the escaping tendencies of the reactants. Rate laws based upon these considerations have been advocated for the past fifty years. The success of such a rate law in describing experimental facts will depend upon the extent to which we can correlate the escaping tendency by means of one process with the escaping tendency by means of another process (*i. e.*, vapor pressure, solubility, distribution, etc.). The success of a rate law based upon concentration as a variable is then due to the existence of a constant proportionality between escaping tendency and concentration. As we pass from one environment to another, this proportionality factor will, in general, change in magnitude to such an extent that the concentration law fails completely even though the fugacity law may still be valid. We have, therefore, attempted to interpret our data by the expression

$$\text{Rate} = -[k_\mathrm{w}^0 p_\mathrm{w} + k_\mathrm{a}^0 p_\mathrm{a}]p_\mathrm{RCl} \qquad (1)$$

where the escaping tendency of each reactant is set equal to its partial vapor pressure.

Two courses are now open to us. For simplicity we consider a unimolecular reaction. Starting with the expression

$$\text{Rate} = -kp$$

we can then write

$$\mathrm{d}c/\mathrm{d}t = -k_c(p/c)c \qquad (2)$$

or

$$\mathrm{d}N/\mathrm{d}t = -k_N(p/N)N \qquad (3)$$

Integration of (2) and (3) leads to

$$\ln c_0/c = k_c(p/c)t$$
$$\ln N_0/N = k_N(p/N)t$$

assuming that (p/c) and (p/N) are constants. If we are dealing with sufficiently dilute solutions, the concentration of the solute will be proportional to its mole fraction. Let us call the constant of proportionality, α. Then since

$$(p/c)c = (p/N)N = p$$

it follows that

$$1/\alpha(p/c) = p/N$$

and since

$$k_c(p/c) = k_N(p/N)$$

we obtain

$$k_c\alpha = k_N \qquad (4)$$

If, now, we change from one solvent of molal volume, V_1, to a second solvent of molal volume, V_2, the value of α necessarily changes. Therefore, k_c does not bear a constant relationship to k_N. Consider again equation (3). If we set $N = 1$ we see that k_N is the rate which we would observe if the pure substance were present at unit fugacity. It is, therefore, a characteristic property of the solute alone, and so at constant temperature is a true constant. From this and (4) it follows that k_c is a property not only of the solute, but of the solvent as well. We shall therefore choose the equivalent of expression (3) for formulating our rate equations. With this in mind expression (1) becomes

$$\mathrm{d}N_\mathrm{RCl}/\mathrm{d}t = -(k_\mathrm{w}^0 p_\mathrm{w} + k_\mathrm{a}^0 p_\mathrm{a})P_\mathrm{RCl} = -[(k_\mathrm{w}^0 p_\mathrm{w} + k_\mathrm{a}^0 p_\mathrm{a})(p/N)_\mathrm{RCl}]N_\mathrm{RCl}$$

In any one solvent, the expression enclosed within brackets is a constant if Henry's law is

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(8) In connection with this experiment it was noted that methyl *t*-butyl ether forms a minimum boiling mixture with methyl alcohol, boiling at about 51°.

obeyed by the *t*-butyl chloride, and, therefore

$$\ln N_0/N = k_m t$$

where the value for k_m can be calculated for each solvent if we know the partial pressures of alcohol and of water, the value of p/N for the halide, and the values of K^0_w and k^0_a. k^0_w is a constant determined solely by the properties of pure water and pure *t*-butyl chloride and k^0_a likewise is determined solely by the properties of pure alcohol and pure *t*-butyl chloride.

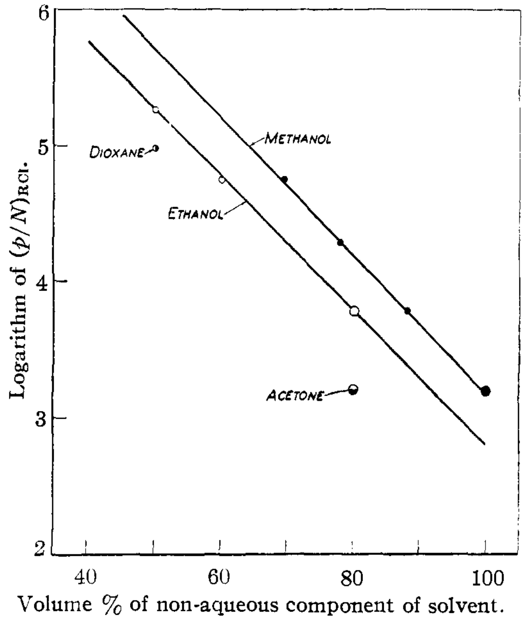

Fig. 1.

Fortunately, the partial pressures of the methanol–water system have been carefully determined at 25°.[9] In our kinetic experiments the concentrations of tertiary butyl chloride always were small. We therefore can neglect any change in the partial pressures of the methanol–water system which might be caused by the addition of the *t*-butyl chloride. The Henry's law constants for *t*-butyl chloride in these solutions were determined in the following manner. A known volume of the solvent was enclosed in a flask and partially evacuated. A small, known quantity of *t*-butyl chloride was added and the increase in pressure read as equilibrium was established. Another portion of the halide was then added and the new pressure recorded. This process was repeated a sufficient number of times so that a curve could be constructed showing the total pressure as a function of the amount of halide added. Curves were obtained for several solvents in the range from 50 to 100 mole per cent. methanol. When a blank run was tried, in which pure liquid *t*-butyl chloride was present initially in the flask the total pressure increased slightly. This was assumed to be due to some gas, which was dissolved in the *t*-butyl chloride that was being added, which then was released at the lower pressure. The recorded pressures, therefore, were slightly too high, but the correction could be neglected in all solvents except pure methanol. These plots showed some curvature, even in the dilute solutions which we used. This is in accord with Hughes' observation that the first order rate constant decreased as the initial concentration of the halide increased. For our calculations we have used an average value for the Henry's law constant which is about 5% less than the value for infinite dilution. On plotting the logarithms of these constants against the volume per cent. of methanol it was found that they lay on a straight line, as shown in Fig. 1. The values in Table I were taken from this straight line. Similar measurements were made for aqueous ethanol, dioxane, and acetone.

We are now in a position to determine k^0_a from the measured rate in pure methanol, the Henry's law constant for *t*-butyl chloride, and the vapor pressure of pure alcohol. This value of k^0_a when combined with the necessary pressures enables us to determine k^0_w from the measurement in the 50 mole per cent. solvent. We now have sufficient data for the calculation of the rates in all other methanol–water solvents. The data and calculations are collected in Table I.

TABLE I

Summary of data and calculations for methanol–water solvents. p_w and p_a are the partial pressures of water and of methanol, respectively. The Henry's law constants, $(p/N)_{RCl}$, are taken from Fig. 1 and k_m is the over-all first order rate constant for the disappearance of *t*-butyl chloride. The data in parentheses have been used to obtain $k^0_w = 3.93 \times 10^{-4}$ hr.$^{-1}$ and $k^0_a = 1.56 \times 10^{-5}$ hr.$^{-1}$. A 5% uncertainty in the $(p/N)_{RCl}$ values introduces corresponding uncertainties in k_m calcd. and in the calculated percentage of butyl alcohol.

Compn. of solvent as mole % of water	p_w, mm.	p_a, mm.	$(p/N)_{RCl} \times 10^{-3}$, mm.	$k_m \times 10^3$, calcd. hr.$^{-1}$	$k_m \times 10^3$ exptl. hr.$^{-1}$	% *t*-BuOH formed calcd.
49.7	13.7	70.2	53.5	(347)	(347)	83
43.2	12.5	76.7	29.8	182	188	81
38.3	11.5	81.9	19.8	115	110	78
34.6	10.7	84.9	13.8	76.5	75.4	76
28.2	9.10	92.5	8.6	43.4	40.7	71
23.0	7.63	98.0	6.0	27.2	25.4	66
17.5	5.92	105	4.1	16.3	15.4	59
7.0	2.46	118	2.1	5.9	6.24	34
0.0	0.00	126.6	1.48	(2.92)	(2.92)	0

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(9) Butler, Thompson and McLennan, *J. Chem. Soc.*, 674 (1933).

In every case, the agreement between the calculated and observed first order constants exceeds the predicted accuracy of our calculations. k^0_w, by our definition, involves only the properties of pure water and pure *t*-butyl chloride. Since it is independent of the solvent we can calculate the rate of hydrolysis in any other environment. But, in order to compare our calculations with Hughes' data in aqueous ethanol, we must first determine the new constant k^0_a for alcoholysis by ethanol. This we have done by extrapolating Hughes' measurements to pure ethanol. In Table II we have collected the fugacity data and results of our calculations of the over-all rates of disappearance of *t*-butyl chloride in aqueous ethanol. Hughes' experimental rate data are included for comparison. The agreement again is excellent.

TABLE II

Summary of data and calculations for ethanol–water solvents. p_w and p_a, the partial vapor pressures of water and of ethanol, were obtained from the data of Dobson.[10] The values of $(p/N)_{RCl}$ were taken from Fig. 1. From the value of k_m enclosed in parentheses, which was obtained from a rough extrapolation of Hughes' data as shown in the sixth column, we obtain the result k^0_a = 2.1 × 10^{-5} hr.$^{-1}$. k^0_w was taken from Table I. An uncertainty again is introduced by the $(p/N)_{RCl}$ values.

Compn. of solvent as mole % of water	p_w, mm.	p_a, mm.	$(p/N)_{RCl}$ × 10^{-3} mm.	k_m × 10^3 calcd. hr.$^{-1}$	k_m × 10^3 exptl. hr.$^{-1}$	% *t*-BuOH formed calcd.
82.9	20.5	25.4	*577*	4950	4660	94
76.4	19.9	28.6	*182*	1530	1320	93
68.4	19.2	31.4	*59.2*	487	453	92
58.1	17.9	34.5	*16.2*	126	145	91
44.8	16.6	38.4	*6.0*	44.4	32.9	89
26.2	11.5	45.5	*1.68*	9.2	6.16	82
0.0	0.0	59.0	0.65	(0.8)	(0.8)	0

Since, in aqueous acetone, we expect only hydrolysis to occur, we can use our constant k^0_w for the calculation of the rate. In Table III we show a comparison between our calculated value and a value obtained by extrapolating Hughes' data at higher temperatures, as well as a calculated rate and measured rate for an aqueous dioxane solvent.

Generalizing from our experimental results, we would write for any bimolecular reaction

$$\text{Rate} = k^0 f_a f_b$$

This equation is in disagreement with the one obtained from transition state theory by Wynne-Jones and Eyring,[12] unless we assume that the fugacity coefficient of each of the three complexes which we studied remains constant throughout the whole range of experimental conditions. This appears to us highly improbable.

TABLE III

Summary of data and calculations for aqueous dioxane and aqueous acetone. p_w is the partial vapor pressure of water. In dioxane, we have assumed the ideal value, however, the value in aqueous acetone was taken from data in the literature.[11] k^0_w was taken from Table I. The experimental k_m in dioxane is the result of our measurement, while that for aqueous acetone was extrapolated from Hughes' measurements at higher temperatures. The values for $(p/N)_{RCl}$ are the results of our measurements.

Compn. of solvent, mole % of water	p_w, mm.	$(p/N)_{RCl}$ × 10^{-3}, mm.	k_m × 10^3 calcd. hr.$^{-1}$	k_m × 10^3 exptl. hr.$^{-1}$
83.2 in dioxane	19.7	*96.5*	745	644
50.3 in acetone	17.8	*1.65*	11.6	6.90

Our equation, however, can be derived from transition state theory by assuming that the rate of the reaction in any solvent is proportional to the fugacity of the transition state in that solvent—rather than to its concentration as assumed by Wynne-Jones and Eyring. If we do this we fail to obtain the Brönsted equation.

Conclusions

1. It has been shown that *t*-butyl chloride undergoes both hydrolysis and alcoholysis in aqueous alcohol solvents.
2. The rates of hydrolysis and of alcoholysis have been shown to be bimolecular, and therefore do not involve the primary breaking of a strong bond.
3. It has been shown that the rate of hydrolysis is proportional to the product of the fugacities of *t*-butyl chloride and water, as measured by their vapor pressures. The proportionality constant is independent of the solvent employed. Similar conclusions hold for the alcoholysis reactions.
4. It has been shown that in terms of transition state theory the rate of the reaction must be determined by the fugacity of the transition state, and not by its concentration.

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[10] Dobson, *J. Chem. Soc.*, **127**, 2866 (1925).

[11] Beare, McVicar and Ferguson, *J. Phys. Chem.*, **34**, 1310 (1930).

[12] Wynne-Jones and Eyring, *J. Chem. Phys.*, **3**, 492 (1935).