Ion Pairs. II. Kinetics and Salt Effects in the Solvolysis of Acetyl Chloride in Glacial Acetic Acid[1]

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The solvolysis of acetyl chloride in glacial acetic acid has been studied by measuring the time required for the neutralization of a base (such as lithium acetate) after adding an excess of acetyl chloride. The reaction is predominantly first order with a rate constant of about $9 \times 10^8\, e^{-15,000/RT}$ sec.$^{-1}$. The detailed kinetics is complicated by the dependence of the rate on the concentrations of salts and acetates present. A number of acetates, chlorides, and perchlorates increase the solvolysis rate moderately, giving a twofold increase in rate at some point in the concentration range of 0.06 to 0.30 *N*. This effect is of the proper order of magnitude for the effect of the dipoles of the ion pairs present on the activity coefficient of an activated complex with appreciable charge separation. Zinc chloride and mercuric chloride have an additional catalytic effect.

In the course of work in this laboratory using countercurrent columns for isotopic separation,[3] it was necessary to analyze solutions of hydrogen chloride and acetyl chloride in glacial acetic acid. It was found that titration with a base such as lithium acetate gave a value for the sum, hydrogen chloride plus acetyl chloride concentrations, provided that the solution was allowed to stand for about ten minutes in the vicinity of the end point so that the acetyl chloride reacted completely. Whenever an insufficient amount of lithium acetate for complete titration was added rapidly, an indicator such as α-Naphtholbenzein was converted to its basic form, but it would change back on standing as hydrogen chloride was formed by the reaction:

$$CH_3COCl + CH_3COOH = (CH_3CO)_2O + HCl \qquad (1)$$

This suggested the possibility of obtaining both the hydrogen chloride and acetyl chloride concentrations from the time required for reaction with various amounts of base together with a knowledge of the kinetics of the reaction. Kinetic data sufficiently accurate for this purpose were readily obtained, and the salt effects clearly apparent in even the preliminary work justified further experimental and theoretical study.

The solvolysis reactions in glacial acetic acid of a large number of organic chlorides less reactive than acetyl chloride have been studied,[4] and the occurrence of relatively large salt effects similar to those reported here has been noted in a number of these papers.[5-9] It has been explicitly pointed out[10,11] that large salt effects are to be expected in polar reactions of this type in solvents of low dielectric constant such as acetic acid. Several relations have been proposed[12-14] for the correlation of these solvolysis rates in different solvents.

Data have been reported[15] for the solvolysis in glacial acetic acid of one chloride more reactive than acetyl chloride. The solvolysis of acetyl chloride itself has been studied in water,[16] and in mixtures of water with dioxane[17] and acetone.[18-20] The solvolysis in dimethylformamide is reported[21] to be instantaneous. In addition there are a number of studies[22] of the reactions of acetyl chloride with alcohols in a number of inert solvents. It is hoped that the data and ideas reported here will further the understanding of this important class of solvolytic reactions.

Experimental

Glacial acetic acid (duPont) and acetyl chloride (Gen. Chem. Div., Allied Chem., reagent grade) were used without further purification. Most of the inorganic salts and acetates used were standard C.P. or reagent grade materials, however the various perchlorates were prepared in solution by

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[3] R. A. Howald, *J. Am. Chem. Soc.*, **82**, 20 (1960).

[4] See for example, ref. 5–8, 13.

[5] G. Barbieri and A. Pignedoli, *Atti. Soc. nat. e mat. Modena*, **32–33**, 95 (1954–55) (publ. 1956).

[6] H. L. Goering, T. D. Nevitt, and E. F. Silversmith, *J. Am. Chem. Soc.*, **77**, 5026 (1955).

[7] A. H. Fainberg and S. Winstein, *ibid.*, **78**, 2770, 2763 (1956); **79**, 1597, 1608 (1957).

[8] K. D. McMichael and R. A. Clement, *J. Org. Chem.*, **26**, 620 (1961).

[9] L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 979 (1940).

[10] C. K. Ingold, *Proc. Chem. Soc.*, 279 (1957).

[11] S. Winstein, S. Smith, and D. Darwish, *J. Am. Chem. Soc.*, **81**, 5511 (1959).

[12] K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

[13] E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).

[14] C. G. Swain, D. C. Dittmer, and L. E. Kaiser, *ibid.*, **77**, 3737 (1955); C. G. Swain, R. B. Mosely, and D. E. Brown, *ibid.*, **77**, 3731 (1955). There is apparently a misprint in Table I of this reference, and the data given refer to $CH_3C_6H_4COCl$ instead of CH_3COCl.

[15] C. G. Swain and A. MacLachlan, *ibid.*, **82**, 6095 (1960).

[16] V. Gold and J. Hilton, *J. Chem. Soc.*, 838, 3303 (1955).

[17] Hudson and Macleod, cited in B. L. Archer and R. F. Hudson, *ibid.*, 3259 (1950).

[18] C. G. Swain and C. B. Scott, *J. Am. Chem. Soc.*, **75**, 246 (1953).

[19] G. Zimmerman and C. Yuan, *ibid.*, **77**, 332 (1955).

[20] E. J. Cairns and J. M. Prausnitz, *J. Chem. Phys.*, **32**, 169 (1960).

[21] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 2717 (1956).

[22] See for example, R. F. Hudson and I. Stelzer, *Trans. Farad. Soc.*, **54**, 213 (1958).

TABLE I[a]

Time,[b] Sec.	Temp., °C.	Concentrations, M				k, sec.$^{-1}$		
		$(AcCl)_0$	(H_2O)	(LiOAc)	$(LiCl)_0$	Exp.	Calcd.[c]	% Dev.
133	17	0.063	0.08	0.033	0	0.0057	0.0061	−7
186	18	.055	.1	.040	0	.0070	.0068	3
80	17	.10	.37	.055	0	.0098	.0093	5
24[d]	29.8	.020	.03	.0061	0.019	.015	.015	0
49[d]	27.4	.028	.07	.016	.035	.017	.014	18
44	28.5	.10	.06	.054	0	.017	.017	0
15	27.3	.065	.45	.017	0	.021	.022	−5
29	28.7	.062	.45	.033	0	.025	.025	0
25[d]	30.0	.14	.03	.064	0.13	.026	.026	0
28	28.3	.036	.16	.019	.35	.026	.030	−15
27	27.1	.035	.16	.018	.36	.027	.028	−4
20	28.5	.064	.33	.033	.31	.036	.035	3
19	43	.055	.1	.033	0	.048	.052	−8

[a] Typical runs, acetyl chloride solvolysis in the presence of lithium acetate. About one third of the runs are represented. [b] τ, time between the addition of acetyl chloride and the color change of the indicator. [c] Rate constants calculated from the equation:

$$k = [0.0085 + 0.018(H_2O) + 0.10(LiOAc) + 0.03(LiCl)] \exp\left[15{,}000\,\frac{T - 298}{298TR}\right]$$

[d] In these runs a solution of acetyl chloride and hydrogen chloride was added rather than a solution of acetyl chloride and acetic anhydride.

the reaction of perchloric acid with the various acetates. Hydrogen chloride was prepared by the reaction between sodium chloride and sulfuric acid in a Kipp generator or by the reaction of acetyl chloride and water. Some of the solutions were dried by refluxing with acetic anhydride. With mercuric acetate solutions, refluxing with acetic anhydride yielded an insoluble white compound, presumably polymeric $HgC_2H_2O_2$.[23] Thus the chemical form of the mercury remaining in solution is uncertain, however, it is undoubtedly converted to mercuric chloride in the initial stages of a solvolysis run. The water contents of the acetic acid and the various solutions were measured by Karl Fischer titration.

The solvolysis reaction was studied by measuring the time required to neutralize a basic solution of known composition after adding a known quantity of a solution of acetyl chloride. Usually *p*-naphtholbenzein (Eastman 924) was used as a visual indicator for the neutralization, but a few determinations were made with other indicators such as Crystal Violet. The equilibrium solvolysis of the initial acetyl chloride solution was repressed by the addition of acetic anhydride or saturation of the solution with hydrogen chloride at a definite pressure. Runs of both these types are shown in Table I, and the agreement shown there indicates that excess acetic anhydride does not have an appreciable effect on the rate of solvolysis. The acetyl chloride solution was added rapidly (in about 3 sec.) from a pipet with a stopcock at the bottom. These pipets were filled through a three way stopcock at the top or by pouring from a suitable reservoir sealed to the top of the pipet. The indicator generally changed from its yellow basic form to green 10 to 90 sec. after the addition of acetyl chloride was started. Some heat is liberated by the reaction, and the temperature of the solution increased, sometimes by as much as 1°. Ordinarily the temperature of the solution was measured before adding the acetyl chloride and immediately after the color change, and the average of these two readings was used for further calculations. Several runs were made at about 17° and 40°. Although these were less accurate than the room temperature runs, they did yield a value for the activation energy, 15 ± 1 kcal./mole, sufficiently accurate to correct the room temperature (24–29°) runs to a standard temperature of 25°.

Results

To a first approximation the solvolysis reaction is first order, and the rate constants calculated from the expression $k_a = R/(AcCl) = (1/\tau) \ln (AcCl)_0/(AcCl)_\tau$ are reasonably constant. τ represents the time required for neutralization of the base and $(AcCl)_T$ is the concentration of unreacted acetyl chloride at this time. The concentration of water was varied from 0.065 to 0.51 M, and over this range its contribution to the rate of reaction can be represented within experimental error by a term proportional to the water concentration. Thus correcting for both the temperature and water effects one obtains:

$$k_c = k_a\, e^{-15000\Delta T/RT^2} - 0.018(H_2O) \qquad (2)$$

These corrected rate constants are shown in Fig. 1 plotted against the initial concentrations of sodium and lithium acetates used. The results show considerable experimental scatter, and they can be fitted by straight lines as well as by any other reasonable curves. The least squares fits of both sets of data yield values of close to 0.0085 for the solvolysis rate constant at 25° in the limit of negligible base and salt concentrations.

A rate expression of the form $R = k_0(AcCl) + k_1(MOAc)(AcCl)$ can be readily integrated to give:

$$k_a = \frac{k_0 - k_1(AcCl)_\tau}{1 - A \ln [1 + (k_1/k_0)(MOAc)_0]} \qquad (3)$$

where $1/A = \ln [(AcCl)_0/(AcCl)_\tau] = k_a\tau$. In the case where k_1 is sufficiently small that the terms in k_1^2 are negligible this expression simplifies to $k_a = k_0 + k_1[A(MOAc)_0 - (AcCl)_\tau]$. The increase in rate on increasing the initial concentration of lithium acetate is due partly to the lithium acetate and partly to the effect of the lithium chloride produced. The runs with added lithium chloride up to 0.63 M listed in Table I show that

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[23] A. E. Goddard and D. Goddard, "Organometallic Compounds," Vol. XI of J. N. Friend, "Text Book of Inorganic Chemistry," C. Griffin and Co., London, 1928, pp. 59, 60.

TABLE II[a]

Time,[b] Sec.	Temp., °C.	Concentrations, M					k, sec.$^{-1}$ (25°)	
		$(AcCl)_0$	(H_2O)	$(Sr(OAc)_2)$	$(SrCl_2)_0$	$(Sr(ClO_4)_2)$	Exp.[c]	Calcd.[d]
27	27.4	0.074	0.06	0.011	0	0	0.011	0.011
88	28.9	.071	.07	.027	0	0	.012	.0125
29	26.5	.057	.10	.010	0	0	.0125	.0115
20	26.6	.033	.13	.005	0.15	0	.015	.016
49	26.9	.088	.11	.029	.11	0	.019	.018
20	27.2	.037	.14	.055	0	.014	.015	.015
17	28.1	.060	.34	.013	0	.055	.027	.028

[a] Principal runs (7 out of 11) on the solvolysis of acetyl chloride in the presence of strontium acetate. [b] τ, the time between the addition of acetyl chloride and the color change of the indicator. [c] Experimental apparent first-order rate constants corrected to 25° using 15,000 cal for the activation energy. [d] Rate constants calculated from the equation:

$$k = 0.0085 + 0.018(H_2O) + 0.25(Sr(OAc)_2) + 0.03(SrCl_2) + 0.22(Sr(ClO_4)_2)$$

the lithium chloride effect can be represented within experimental error by the term 0.03(LiCl)(AcCl). Applying this correction to the other runs with lithium chloride initially present, one can evaluate the lithium acetate contribution making use of the value $A(LiOAc)_0 - (AcCl)_\tau$ for the average lithium acetate concentration during a run. The final complete empirical rate expression is:

$$R = [0.0085 + 0.018(H_2O) + 0.10(LiOAc) + 0.03(LiCl)]\,(AcCl) \quad (4)$$

at 25°. The rate constants calculated from this expression are compared with the individual experimental values in the last three columns of Table I.

Sodium chloride is practically insoluble in glacial acetic acid, and it was originally hoped that maintaining a constant activity of sodium chloride by allowing it to precipitate as it formed would simplify the kinetics. The large scatter shown in Fig. 1 for the runs with sodium acetate indicates on the contrary that the precipitation of sodium chloride acts as a further complication. Initial seeding with sodium chloride had no consistent effect on the rate. In addition sodium acetate has a larger effect on the rate than lithium acetate, and the expansion of the logarithm in the integrated rate expression is no longer justified. In view of the large experimental scatter, a considerable range of values for k_1 will fit the data almost equally well. A value of $k_1 = 0.3$ is a satisfactory mean value from the data shown in Fig. 1, but this value must be considered uncertain by about ±50%. Two runs were made with added sodium perchlorate. They indicated a small increase in rate in the presence of sodium perchlorate, however the increase (at 0.05 M $NaClO_4$) was smaller than the uncertainty of the rate.

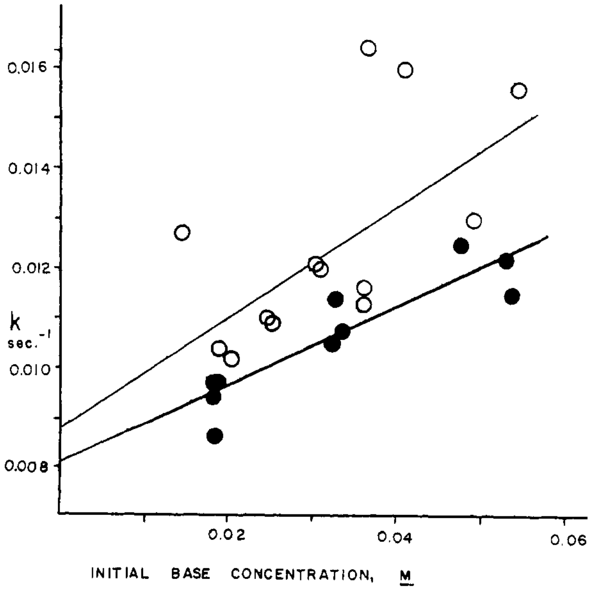

Fig. 1.—Plot of corrected rate constants, k_c, equation 2, vs. initial base concentration. ●, runs with lithium acetate; ○, runs with sodium acetate.

Runs in which strontium acetate was used as the base initially present are summarized in Table II. The data are quite similar to those with lithium acetate. As shown in Table II, they are fitted satisfactorily by the rate expression:

$$R = [0.0085 + 0.018(H_2O) + 0.25(Sr(OAc)_2) + 0.03(SrCl_2) + 0.22(Sr(ClO_4)_2)](AcCl) \quad (5)$$

The salt effects presented above are all of the same order of magnitude and are probably primarily due to a straightforward salt effect on the activity coefficient of a single activated complex as discussed below. The values for the soluble chlorides, lithium chloride, and strontium chloride are somewhat smaller than those for the various acetates and perchlorates, perhaps because of the possibility of the reverse reaction if a reaction intermediate reacts with a chloride (*i.e.*, "external return"[24]). In contrast to these results, considerably larger catalytic effects were observed with lead acetate, mercuric chloride, and zinc chloride. Certain selected runs with these materials present are summarized in Table III.

Lead chloride precipitates when lead acetate is used; however, the addition of freshly precipitated lead chloride had no detectable influence on the rate. The experimental values of τ for ten runs with lead acetate are duplicated within 17%

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[24] S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *J. Am. Chem. Soc.*, **83**, 885 (1961).

TABLE III[a]

Time,[b] Sec.	Temp., °C.	Concentrations, M: $(AcCl)_0$	(H_2O)	Other			k,[c] Sec.$^{-1}$
				$(Pb(OAc)_2)_0$			
31	27	0.023	0.13	0.007			0.030
15	29	.071	.12	.024			.077
				$(Hg(OAc)_2)_0$	$(Sr(OAc)_2)_0$	$(SrCl_2)$	
45	26.7	.031	.13	0.006	0.005	0.15	.026
				$(Hg(OAc)_2)_0$	$(LiOAc)$		
64	26.3	.055	.07	0.011	0.022		.025
				$(Sr(OAc)_2)_0$	$(Zn(ClO_4)_2)_0$	$(Sr(ClO_4)_2)$	
18	28.8	.073	.12	0.028	0.0090	0	.08
16	28.8	.052	.21	.020	.0064	0.020	.09
10	28.8	.034	.12	.006	.0023	.008	.04
				$(NaOAc)_0$	$(ZnCl_2)$		
19	27.5	.033	.06	0.015	0.007		.03
20	27.2	.059	.25	.036	.011		.05
				$(LiOAc)_0$	$(ZnCl_2)$	$(LiCl)$	
20	27.9	.059	.22	0.032	0.007	0	.040
23	27.8	.059	.15	.033	.007	0.32	.035

[a] Selected runs on the solvolysis of acetyl chloride in the presence of lead, mercury, and zinc compounds. [b] τ, the time between the addition of acetyl chloride and the color change of the indicator. [c] Apparent first-order rate constant, $k = (1/\tau) \ln [(AcCl)_0/(AcCl)_\tau]$.

(maximum absolute discrepancy, 3 sec.) by calculations using the integrated form (equation 3) of the rate expression

$$R = [0.0085 + 7.0(Pb(OAc)_2)](AcCl)$$

Runs were made with mercuric acetate alone and in combination with lithium acetate or strontium acetate. Details of two of the six runs are given in Table III including one run in which strontium chloride was added initially so that the mercury was in the form of mercuric chloride throughout the run. All the data are consistent with a contribution to the rate of $1.2(HgCl_2)(AcCl)$.

The data on the rate in the presence of zinc are more complex. Zinc chloride is a very effective catalyst. A concentration as low as 0.007 M is sufficient to more than double the rate of reaction. Zinc perchlorate is equally effective, presumably because it is readily converted to zinc chloride. However the zinc chloride catalysis is strongly inhibited by the addition of lithium chloride. Two runs from a series of 16 illustrating this effect are presented in Table III. The inhibition is probably due to removal of the catalyst by the formation of a complex such as $LiZnCl_3$; however, the kinetic data alone are not sufficient to establish the formula of the complex or its dissociation constant. Sodium acetate shows a similar inhibition of the zinc chloride catalysis. Thus only with strontium acetate are the increases in rate on adding zinc salts directly proportional to the total zinc concentration within experimental error. For these runs the experimental data is satisfactorily fitted by equation 5 with the additional term $6(ZnCl_2)(AcCl)$.

The various rate constants proposed above are listed, with their respective uncertainties, in Table IV.

TABLE IV

SUMMARY OF THE RATE CONSTANT DATA FOR THE SOLVOLYSIS OF ACETYL CHLORIDE IN GLACIAL ACETIC ACID AT 25°

The rate = k (AcCl) with the rate constant given by:

$$\begin{aligned} k = \; & (0.0085 \pm 0.0008) \\ & +(0.018 \pm 0.009)(H_2O) \\ & +(0.10 \pm 0.03)(LiOAc) \\ & +(0.03 \pm 0.01)(LiCl) \\ & +(0.3 \pm 0.15)(NaOAc) \\ & +(0.25 \pm 0.12)(Sr(OAc)_2) \\ & +(0.03 \pm 0.015)(SrCl_2) \\ & +(0.22 \pm 0.04)(Sr(ClO_4)_2) \\ & +(7 \pm 1.5)(Pb(OAc)_2) \\ & +(1.2 \pm 0.5)(HgCl_2) \\ & +(6 \pm 1.5)(ZnCl_2) \end{aligned}$$

Discussion

Specific Friedel-Crafts-type Catalysis.—The catalytic effect of the lead, mercury, and zinc salts described above is too large to be explained in terms of a salt effect on the activity coefficient of the activated complex for the uncatalyzed reaction. These metals must be incorporated directly into the activated complex. This behavior is not unexpected in view of the tendency of these metals to form coordinate covalent bonds with chlorine atoms, which is so great that their chlorides are not completely dissociated in aqueous solution. The catalysis by zinc chloride is particularly interesting since zinc chloride is generally recognized as a Friedel-Crafts catalyst. Thus this work provides a direct experimental link between the two classes of reactions, solvolysis reactions and Friedel-Crafts-type reactions, both of which are considered to involve carbonium ions or carbonium ion pairs as intermediates. Friedel-Crafts catalysis of solvolysis reactions would presumably be a common phenomenon except for the fact that most Friedel-Crafts catalysts are inactivated by reaction with the common solvolysis solvents.

Thus ferric chloride is itself extensively solvolyzed in glacial acetic acid.[25]

Zinc chloride has been shown to be a catalyst for the acetylation of toluene,[26] although it is one of the weaker catalysts studied. The importance of complexes between the catalyst and reacting chloride, $AcCl \cdot ZnCl_2$ in this case, was emphasized many years ago by Meerwein,[27] who pointed out at the same time that such complex formation increases the ability of weak electrolytes to ionize. This is an adequate picture of the mechanism of the zinc chloride catalysis of the solvolysis, with only the additional recognition that ionization does not necessarily imply dissociation, but that various ion pairs are involved in the mechanism.

The Normal Salt Effect.—The evaluation of thermodynamic properties including activity coefficients of solute molecules in terms of the potentials of average force between these molecules has been discussed by McMillan and Mayer.[28] The principal part of this potential between two ion pairs will be the dipole-dipole potential in a medium of dielectric constant D:

$$\Phi = -(\mu_1\mu_2/r^3D)\,g(\theta_1,\theta_2,\varphi_2-\varphi_1). \quad (6)$$

The appropriate integrals for second virial coefficients are available for this potential combined with hard sphere repulsion[29] and for the Stockmayer potential:[30,31]

$$\Phi = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] - (\mu_1\mu_2/r^3D)\,g(\theta_1,\theta_2,\varphi_2-\varphi_1) \quad (7)$$

The quantity σ is a measure of the size of the ion pairs, and is probably approximately 3 Å. However ϵ is somewhat more difficult to estimate. The r^{-6} term represents principally dispersion and induction energies, both of which are electrical in origin and should be decreased by a dielectric, although for the dispersion energy a high frequency dielectric constant should be used. The expression for the inductive contribution is $\epsilon = 2\mu_1\mu_2\bar{\alpha}/4\sigma^6D$, where $\bar{\alpha}$ is an average polarizability. The polarizabilities of ion pairs and carbonium ion activated complexes are probably quite high, and a reasonable estimate is the highest values listed for simple molecules in Landolt-Börnstein[32] which lie near 140×10^{-25} cm.^{3}. Then, neglecting the dispersion contribution, one obtains for the reduced parameters defined in Hirschfelder, Curtiss, and Bird:[31]

$$T^* = kT/\epsilon \text{ and } t^* = \mu_1\mu_2/\epsilon\sigma^3D\sqrt{8} = 2\sigma^3/(\sqrt{8}\,140 \times 10^{-25}) = 1.36$$

For a twofold increase in rate in the presence of ion pairs at 0.28 M, such as occurs for lithium chloride, we need a second virial coefficient of about -2500 cm.^{3} moles^{-1}, since $\ln \gamma_2 = \ln 0.5 = B_{12}C_1 = B_{12}\ 2.8 \times 10^{-4}$. This corresponds to a value of $B^* = 3B_{12}/2\pi N\sigma^3 = -73$. This is somewhat beyond the range of the published table,[31] but a reasonable estimate can be made from the closest entry: $t^* = 1.4$, $T^* = 0.9$, $B^* = -50.3$. This gives $\epsilon = 330k$ and $\mu_1\mu_2/D = \sqrt{8}\sigma^3kT\ t^*/T^* = 4.9 \times 10^{-36} = 4.9$ debye^2. Using 6.2 for the dielectric constant of acetic acid,[33] and assuming $\mu_1 = \mu_2$, one obtains $\mu_1 = 5.5$ debye. This corresponds to single charges separated by 1.15 Å, and so is certainly of the proper order of magnitude. The other salts which have a larger effect than LiCl presumably have a larger dipole moment or a smaller value of $\sigma = {}^1/_2(\sigma_1 + \sigma_2)$.

The principal limitations of this type of calculation as outlined (other than the problem of evaluation of the integrals in the region beyond the current tabulations) are the neglect of dipole-quadrupole interactions and the neglect of free ions. The quadrupole contribution must be quite large to account for the effect shown by strontium salts which are presumably symmetrical with zero dipole moment. Since ion pair dissociation constants in glacial acetic acid[34] are of the order of 10^{-7}, the neglect of free ions limits one to concentrations above 10^{-3} M, at which point the ion pairs will be about 1% dissociated.

The electrostatic interaction between ion pairs is certainly of sufficient magnitude that it must be considered along with other effects in interpreting data on the effects of salts on the solubility and activity coefficients of other salts in glacial acetic acid.[35,36] It may be significant that sodium acetate which appears to have a larger effect on the activity coefficient of the activated complex for solvolysis than lithium acetate also produces a larger enhancement of the solubility of potassium bromide in acetic acid.[36]

Special Salt Effect.—Earlier studies of solvolysis reactions have distinguished a type of salt effect clearly distinct from the two described above, which has been designated the special salt effect.[24] This effect arises from competition between "external ion-pair return" and exchange reactions changing the anion of solvent separated ion pairs. It is distinguished kinetically by its steepness, nonlinearity, and saturation at relatively low concentrations of added salt. This type of salt effect

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(25) P. Walden, "Molekulargrössen von Elektrolyten in Nichtwässerigen Lösungmitteln," verlag T. Steinkopff, Dresden, Leipzig, 1923.

(26) O. C. Dermer, D. M. Wilson, F. M. Johnson, and V. H. Dermer, *J. Am. Chem. Soc.*, **63**, 2881 (1941); O. C. Dermer and R. A. Billmeier, *ibid.*, **64**, 465 (1942).

(27) H. Meerwein, *Ann.*, **455**, 227 (1927).

(28) W. G. McMillan, Jr., and J. E. Mayer, *J. Chem. Phys.*, **13**, 276 (1945); J. E. Mayer, *ibid.*, **18**, 1426 (1950).

(29) W. H. Keesom, *Comm. Phys. Lab. Leiden*, **Suppl. 24b**, sec. 6 (1912); **Suppl. 39a** (1915).

(30) W. H. Stockmayer, *J. Chem. Phys.*, **9**, 398 (1941).

(31) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, 1954, pp. 211, 1147.

(32) Landold-Börnstein, "Zahlenwerte und Functionen," Vol. I, part 3. Springer Verlag, Berlin, 1951, p. 510.

(33) C. P. Smyth and H. E. Rogers, *J. Am. Chem. Soc.*, **52**, 1824 (1930).

(34) M. M. Jones and E. Griswold, *ibid.*, **76**, 3247 (1954).

(35) R. K. Birdwhistell and E. Griswold, *ibid.*, **77**, 873 (1955); see also the references listed here and in ref. 36.

(36) E. Griswold, M. M. Jones, and R. K. Birdwhistell, *ibid.*, **75**, 5701 (1953).

is not evident with the acetates and perchlorates used in this work. Apparently the "special salt effect" is negligibly small in the solvolysis of acetyl chloride in glacial acetic acid.

The Effect of Solvent.—The work reported here extends the range of solvents in which the solvolysis of acetyl chloride has been measured. The plot of log *k* *vs.* *Y*, Fig. 2, shows some major deviations from Winstein's *mY* relation.[13] Thus the acetic acid points do not lie on the acetone–water line, and both lines apparently show a large curvature in the region of high water concentration. These deviations are of the same types commonly shown in the solvolysis of other compounds,[37] but they are unusually large. The deviations at high water concentrations are probably due more to differences between the reactants, acetyl chloride and *t*-butyl chloride, than to differences in the transition states for solvolysis. Thus acetyl chloride probably does not show a large increase in activity coefficient over the range from pure acetic acid to pure water whereas *t*-butyl chloride shows a 4000-fold increase in its Henry's law constant[13] over this range of solvents.

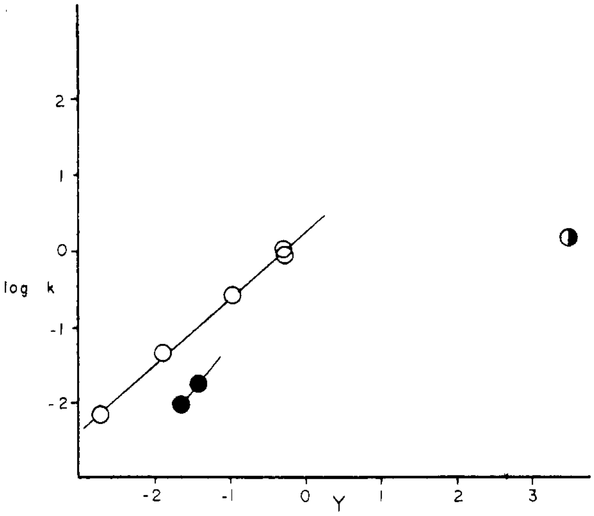

Fig. 2.—Rate constants at 25° for the solvolysis of acetyl chloride *vs.* Wintsein's *Y* values.[7] ●, this work; ◑, pure water, Gold and Hilton[16] corrected to 25°; ○, acetone–water mixtures, data from ref. 18, 19, and 20.

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[37] S. Winstein, A. H. Fainberg, and E. Grunwald, *J. Am. Chem. Soc.*, **79**, 4146 (1957).

Kinetics of the Sodium Alkoxide Reduction of Nitrobenzenes

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The rates of the reduction of nitrobenzene by sodium methoxide in methanol in a nitrogen atmosphere to form azoxybenzene were followed by the acidimetry of methoxide and by spectrophotometry of the aromatic compounds. The rates were expressed as $v = k[PhNO_2][CH_3ONa]^2$. Methanol was oxidized to formic acid and formaldehyde, formaldehyde then being gradually transformed to methyl formate and other products. Gaseous oxygen, hydrogen peroxide, benzoyl peroxide, and water retarded the reduction, while 9-fluorenone accelerated it. A mechanism (equations 1, 2, 5, and 7) was postulated, which involves simultaneous rate-determining attacks of two molecules of sodium methoxide to nitrobenzene, followed by a rapid condensation of the products, nitrosobenzene and phenylhydroxylamine. The rates of reduction of nitrobenzene by some other sodium alkoxides increased in the order: $CH_3ONa < C_2H_5ONa < n\text{-}C_3H_7ONa$. The electron-releasing group (p-CH_3O) in nitrobenzene retarded the reduction, while the electron-attracting group (m-NO_2) accelerated it.

It is well known that nitrobenzene is reduced to azoxybenzene by sodium alkoxide according to the stoichiometric equation[1]

$$4C_6H_5NO_2 + 3NaOCH_3 \longrightarrow 2C_6H_5\underset{\overset{\downarrow}{O}}{N}{=}NC_6H_5 + 3HCOONa + 3H_2O$$

It is probable that the reaction involves the condensation of phenylhydroxylamine and nitrosobenzene both produced by the reduction of nitrobenzene.[2,3] However, very little is known about the kinetics and mechanism of this reaction.

The present paper summarizes our data on the kinetic investigation on the reduction of nitrobenzene and ring-substituted nitrobenzenes by sodium methoxide, ethoxide, or propoxide. The rates of the consumption of alkoxide were followed by acidimetry and those of aromatic compounds by ultraviolet spectrophotometry. It was found that formaldehyde as well as formic acid was produced during the reaction, formaldehyde being then converted to methyl formate and other products in the presence of sodium methoxide. The concentration of formaldehyde was determined by the sulfite method.

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[1] H. S. Fry and J. L. Cameron, *J. Am. Chem. Soc.*, **49**, 864 (1927).

[2] E. Bamberger and E. Renauld, *Ber.*, **30**, 2278 (1897); E. Bamberger and A. Rising, *Ann.*, **316**, 257 (1901).

[3] Y. Ogata, M. Tsuchida, and Y. Takagi, *J. Am. Chem. Soc.*, **79**, 3397 (1957).