

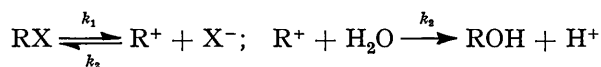
264. *The Second (Rapid) Step in the Nucleophilic Substitution of Alkyl Halides. Part I. Hydrolysis of Triphenylmethyl Chloride in Acetone of Low Water Content.*

By D. GOLOMB.

The hydrolysis of triphenylmethyl chloride in acetone of low water content follows the first-order kinetic law strictly. At first sight this appears to contradict the S_N1 scheme proposed by Hughes, Ingold, and their co-workers in which deviation from first-order kinetics is expected owing to accumulation of chloride ion. These ions will increase the reverse reaction of step (a) in: (a) $\text{Ph}_3\text{C-Cl} \rightleftharpoons \text{Ph}_3\text{C}^+ + \text{Cl}^-$; (b) $\text{Ph}_3\text{C}^+ + \text{H}_2\text{O} \longrightarrow \text{Ph}_3\text{C-OH} + \text{H}^+$. It was shown conductometrically that hydrochloric acid dissociates only slightly in acetone of low water content (K_a in water-acetone (3%—97%) $29.5^\circ \cong 2 \times 10^{-4}$); hence the increase of the reassociation in step (a) is almost negligible and no deviation from first-order kinetics is observed. On the other hand, addition of lithium chloride (a salt with a common ion) causes a large decrease in the first-order rate constant. It was shown that the dissociation of this salt is about 8 times that of hydrochloric acid; hence larger chloride-ion concentrations are present upon addition of lithium chloride, which retard hydrolysis.

Various additives and the ionizing power of the solvent affect differently the rates of the reactions in the above scheme. Perchloric acid and lithium perchlorate retard the reverse reaction in step (a) because of the primary salt effect and, therefore, increase the overall rate of hydrolysis. Silver nitrate diminishes the chloride concentration, thus accelerating the overall hydrolysis. Increase of the water content in acetone raises its ionizing power and enhances the dissociation in step (a). In heavy water the rate constant is depressed. Phenol has no marked consequences.

BATEMAN, CHURCH, HUGHES, INGOLD, and TAHER¹ discussed extensively the hydrolysis of the derivatives of diphenylmethyl halides in aqueous acetone in terms of the S_N1 scheme:



The detailed rate equation of this scheme, account being taken of the mass-law effect and ionic-strength effect as derived by Bateman *et al.*, is:

$$-\frac{d[\text{RX}]}{dt} = \frac{k_1^0[\text{RX}]}{\alpha^0[\text{X}^-] \text{antilog}(AI^{\frac{1}{2}}) + \text{antilog}(B\sigma I)} \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

where $A = -1.815 \times 10^6(DT)^{-3/2}$; $B = -0.912 \times 10^{16}(DT)^{-2}$; I = ionic strength; D is the dielectric constant of the solvent; k_1^0 is the rate constant of the dissociation of the carbon-halogen bond; $\alpha^0 = k_2^0/k_3^0$, where k_2^0 is the rate constant of the reaction between the carbonium ion and the halide and k_3^0 is the rate constant of the nucleophilic attack of a water molecule on the carbonium ion, all at zero ionic strength. k_2 and k_3 represent the rate constants of the fast steps in the nucleophilic substitution reactions. σ is a

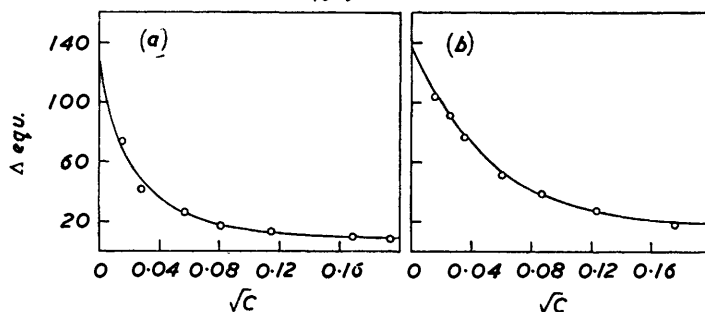
¹ Bateman, Church, Hughes, Ingold and Taher, *J.*, 1940, 979.

over solid potassium hydroxide–potassium permanganate, drying it twice over “Drierite” [CaSO₄], each time for 24 hr. with occasional shaking, and distilling it through a column. 0.05M-Triphenylmethyl chloride in such acetone gave about 0.02M-hydrochloric acid before any water was added, presumably owing to the water left. Lucchesi⁶ showed by infrared spectrometry that traces of water are usually present in acetone, even if purified by recrystallization of its addition compound with sodium iodide. Hudson and Saville⁷ dried acetone over phosphoric oxide, yet it contained 0.05% of water (0.03M).

Apparatus and Kinetic Measurement.—The rate was followed by measuring conductometrically the hydrochloric acid liberated in the reaction: Ph₃C·Cl + H₂O → Ph₃C·OH + HCl. The apparatus was described by Archer and Hudson.⁸ A conductance cell (cell constant = 0.65) containing triphenylmethyl chloride in dry acetone was kept in a thermostat until constant temperature was reached. A measured volume of water at the same temperature was quickly introduced with a syringe pipette while the solution was stirred by a magnetic stirrer. The decrease in resistance as a function of time was measured. Zero time reading could be taken usually 10–20 seconds after mixing.

Resistance readings were calibrated against hydrochloric acid concentrations for every acetone–water mixture employed and also in presence of added substances. Even at the

FIG. 1. Equivalent conductances of (a) hydrochloric acid and (b) lithium chloride in acetone containing 3% of water.



lowest water content (1%), the water concentration was more than ten times that of the triphenylmethyl chloride concentration, so the reaction should be at least pseudo-unimolecular, represented by:

$$\bar{k}t = \log (c_{\infty} - c_0)/(c_{\infty} - c_t) \quad (5)$$

where c_{∞} , c_0 , and c_t are hydrochloric acid concentrations, and \bar{k} is the observed rate constant. At very low water concentrations only part of the chloride hydrolyses and hence the rate constants obtained from eqn. (5) were multiplied by the fraction of reaction at equilibrium to obtain rate constants of the forward reaction (k). These fractions (% reaction) appear in Table 3.

Plots of eqn. (5) were always very good straight lines up to 2–3 half-times of reaction and \bar{k} was obtained from the slopes.

For the evaluation of the mass-law and ionic-strength effects (cf. Discussion), dissociation constants of HCl and LiCl in acetone with 3% of water at 29.5° were estimated from conductance curves at high dilutions by Fuoss's graphical successive-approximation method.⁹ The dielectric constant of this mixture¹⁰ is 20 and the viscosity¹¹ is 33×10^{-4} cp. Plots of equivalent conductance are given in Fig. 1. The estimated dissociation constants are:

$$K_{\text{HCl}} = [\text{H}^+][\text{Cl}^-]/[\text{HCl}] = 1.8 \times 10^{-4}; \quad K_{\text{LiCl}} = [\text{Li}^+][\text{Cl}^-]/[\text{LiCl}] = 1.4 \times 10^{-3}$$

⁶ Lucchesi, *J. Amer. Chem. Soc.*, 1956, **78**, 4229.
⁷ Hudson and Saville, *J.*, 1955, 4130.
⁸ Archer and Hudson, *J.*, 1950, 3259.
⁹ Fuoss, *J. Amer. Chem. Soc.*, 1935, **57**, 488.
¹⁰ Åkerlöf, *ibid.*, 1932, **54**, 4132.
¹¹ S. C. R. Hughes, *J.*, 1956, 998.

Owen and Waters¹² obtained $K = 2.0 \times 10^{-4}$ for the dissociation of hydrochloric acid in 18% (w/w) water in dioxan ($D = 9.53$ at 25°). This constant is nearly the same as ours in 3%

TABLE 1. *Effect of the initial concentration of Ph₃C-Cl on the rate of hydrolysis.*

[Ph ₃ C-Cl] ₀	1.35M-H ₂ O	10 ³ k (sec. ⁻¹) 1.67M-H ₂ O	2.46M-H ₂ O
0.026	4.35	7.2	21.0
0.050	4.75	7.7	20.5
0.079	5.00	—	20.2
0.10	5.3	—	20.0

TABLE 2. *Rate constants (sec.⁻¹) of the forward reaction and activation energies (E_a, kcal./mole) in the hydrolysis of 0.05M-triphenylmethyl chloride in aqueous acetone.*

[H ₂ O] (M)	0.55	0.93 ₅	1.35	1.67	2.31	2.64	2.98	3.88
H ₂ O (% v/v)	1.00	1.68	2.44	3.01	4.15	4.76	5.36	6.98
10 ³ k	2.00	2.90	4.75	7.67	17.3	25.0	36.2	
	14.4°	0.61 ₅	1.00	1.72	2.50	5.50	8.35	11.9
	0.0°	0.14 ₃	0.23 ₄	0.42	0.66 ₅	1.47	2.17	3.42
E _a	15.0	14.3	13.6	13.8	14.0	13.7	13.0	12.6

TABLE 3. *Fraction of triphenylmethyl chloride hydrolysed at equilibrium.*

Initial concentration = 0.05M.				
[H ₂ O] (M)	0.55	0.93 ₅	1.36	1.67
H ₂ O (% v/v)	1.00	1.68	2.44	3.06
Reaction (%)	29.5°	75	85	100
	14.4°	81	93.5	100
	0.0°	85	100	

TABLE 4. *Effect of lithium chloride and perchlorate, silver nitrate, perchloric acid, hydrochloric acid, and phenol on the rate constants (sec.⁻¹) at 29.5°.*

[RCI] ₀ = 0.05M, [H ₂ O] = 1.67M (3% v/v) unless otherwise indicated. All concentrations mm.									
[LiCl]	[Cl ⁻]*	10 ³ k	[LiClO ₄]	10 ³ k	[HClO ₄]	10 ³ k	[Ph-OH]	[H ₂ O]	10 ³ k
0	2.40	7.67	0	7.67	0	7.67	0	830	2.5
6	2.84	6.41	3	9.85	2.5	9.35		1350	4.75
12	4.00	5.67	6	10.0	[HCl]	10 ³ k		1670	7.67
18	4.91	5.25	[AgNO ₃] [†]	10 ³ k	0	7.67		830	2.5
24	5.6	4.84	0	2.0	12	8.25	10	1350	4.75
			50	2.33	24	8.75		1670	7.67

* Mean free chloride-ion concns. calc. from dissociation constants.

† [H₂O] = 0.55M (1% v/v).

water in acetone and their equivalent conductance plot resembles ours closely. Results are given in Tables 1—4. The rate constants at 29.5° in 1.35M-H₂O and 1.35M-D₂O (isotopic enrichment 95%) are 4.75 and 3.66×10^{-3} sec.⁻¹ so $k_{D_2O}/k_{H_2O} = 0.77$.

DISCUSSION

Reaction Order.—The kinetics in aqueous acetone follow the first-order rate equation (eqn. 5) strictly. The rate constants depend to some extent on the initial concentration of the alkyl halide, especially at very low water contents (Table 1) where probably some bimolecular substitution also occurs. No definite dependence of order on water concentration can be established. Such a dependence would require a linear plot of $\log k - \log [H_2O]$ with a slope equal to n , the order with regard to water: $-d[RCI]/dt = k[RCI][H_2O]^n$. Even at 1% water in acetone, the water concentration exceeded ten times the alkyl halide concentration and can be assumed not to change effectively during a run: $-d[RCI]/dt = k'[RCI]$, where $k' = k[H_2O]^n$ and hence $\log k' = n \log [H_2O] + \text{const}$. Fig. 2 displays a parabola with no distinct linear parts. Consequently the "push-pull" mechanism proposed by Swain,¹³ according to which two water molecules participate actively (*i.e.*,

¹² Owen and Waters, *J. Amer. Chem. Soc.*, 1938, **60**, 2371.

¹³ Swain, *J. Amer. Chem. Soc.*, 1948, **70**, 1124.

changing their covalent bonds and thereby contributing to the order of reaction) in the transition state, does not fit this hydrolysis in aqueous acetone.

Effect of the Water Content in Acetone on the Rate of Hydrolysis.—The observed rate constants depend markedly on the water content in acetone (Table 2; Fig. 3). This must be related to the ionizing power of the solvent. The rate-determining step is the heterolysis of the carbon-halogen bond: $\text{RCl} \rightarrow \text{R}^+ + \text{Cl}^-$. In the gaseous phase the energy required for this fission equals the heat of ionization. In solution this energy is lowered considerably owing to the heat of solvation of the produced ions. The solvation of the ions is achieved mainly by water molecules and this process is easier the higher the water content in acetone. Therefore a rise in the rate constants and a decrease in activation energy with increased water content is observed.

In fact, E_a in Table 2 does not represent true activation energies, because they were calculated by means of the Arrhenius equation from the *observed* rate constants. As will be shown, these observed rate constants are composed of rate constants of several reactions,

FIG. 2. *Effect of water on the hydrolysis rate.*

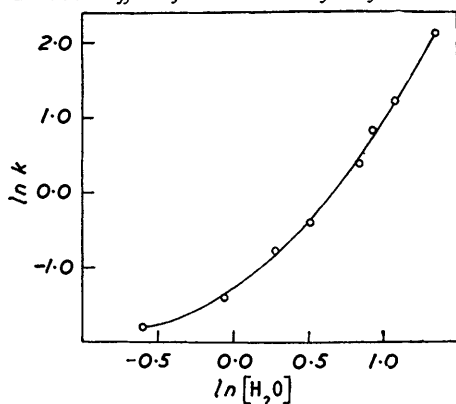
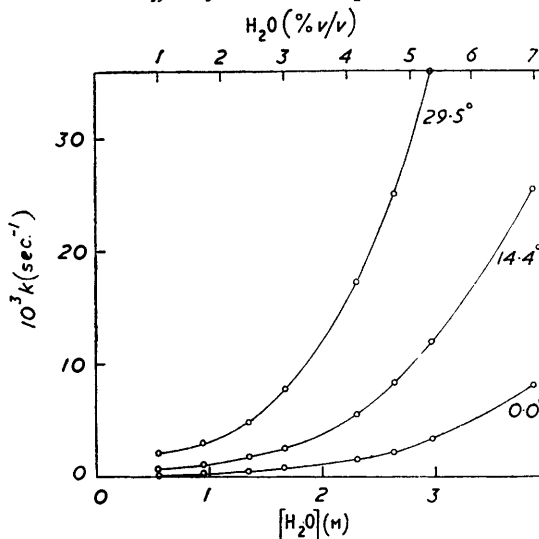


FIG. 3. *Effect of water and temperature on the rate.*



each of which is affected differently by varying the acetone-water ratio. Thus the term "temperature coefficient" would be more appropriate than activation energy.

Mass-law and Ionic-strength Effects.—The linearities of the kinetic plots appear at first sight to contradict the $\text{S}_{\text{N}}1$ scheme and its consequences. According to this scheme, deviation from first-order kinetics during a run is expected owing to the mass-law effect. Although the ionic-strength effect tends to neutralize it, in general they do not counteract one another exactly. Moreover, the addition of lithium chloride, a common-ion salt, causes a very significant decrease of the observed rate constant (Table 4) although it increases the ionic strength. Further, one cannot expect a small value for α , the mass-law constant, since even less stable ions have a value of tens for this constant.¹ This is clarified by consideration of the small dissociation of hydrochloric acid in acetone of low water content. The absolute increase of the free chloride-ion concentration during a run is so small that neither a marked mass-law effect nor an ionic-strength effect can be detected.

Table 5 gives the kinetics when the water content is the mean of the range investigated. The concentrations of the hydrochloric acid liberated in the hydrolysis are given in the third column. About half the triphenylmethyl chloride was already decomposed when measurements started owing to its decomposition in the stock solution and to the reaction which occurs before the first reading can be taken.

In the fourth column of Table 5 the free chloride-ion concentrations are listed, calculated from the dissociation constant. d_1 is the value of the denominator of eqn. (4), α^0 being taken as 6×10^3 (the estimation of the mass-law constant is given below). We applied the reduced eqn. (4) because the antilogarithmic factors of eqn. (3) containing the ionic strength in the first power do not differ much from unity. In 3% water in acetone,¹⁰ D is 20 at 302.7°K, and taking the mean ionic strength = 2.4×10^{-4} , one obtains antilog $(-CI) = 0.99$. The ionic-strength constants, σ , estimated by Hughes, Ingold, and co-workers for various alkyl halides are $1-3 \times 10^{-8}$. Assuming for triphenylmethyl chloride a mean value of 2×10^{-8} , we get antilog $(B\sigma I) = 0.97$.

TABLE 5. *Detailed kinetics of the hydrolysis of 0.05M-triphenylmethyl chloride in 1.67M-water (3% v/v) in acetone at 29.5°*

Time (min.)	$\log \frac{c_\infty - c_0}{c_\infty - c_t}$	$10^3[\text{HCl}]$ (M)	$10^3[\text{Cl}^-]$ (M)	d_1	d_2	Time (min.)	$\log \frac{c_\infty - c_0}{c_\infty - c_t}$	$10^3[\text{HCl}]$ (M)	$10^3[\text{Cl}^-]$ (M)	d_1	d_2
0.00	0.00	26.6	2.16	6.70	2780	1.01	0.46	33.8	2.44	7.15	5100
0.18	0.08 ₅	28.2	2.24	6.85	3220	1.46	0.67	36.0	2.52	7.25	5950
0.40	0.18	29.9	2.30	6.95	3750	2.12	0.96 ₅	38.5	2.60	7.38	7150
0.67	0.31	31.7	2.36	7.04	4250	2.57	1.17	39.9	2.66	7.45	7930

$$k = 7.67 \times 10^{-3} \text{ sec.}^{-1}; t_{\frac{1}{2}} = 1.5 \text{ min.}$$

The denominator (d_1) varies by *ca.* 5% about the mean value during the measurements. It should be noted that the free chloride-ion concentrations are calculated from the dissociation constant of HCl which is valid only in very dilute solutions. At the centimolar concentrations applied in the kinetics, the accumulation of the ions and consequently the deviation of the denominator from the mean during a run are probably even smaller. Therefore one may write:

$$\frac{k_1^0}{\alpha^0 [\text{Cl}^-] \text{antilog}(AI^{\frac{1}{2}}) + 1} \simeq \text{const.} = k \quad \dots \quad (6)$$

where k is the observed forward rate constant. Introducing eqn. (6) into (5) we get:

$$kt = \frac{k_1^0 t}{\alpha^0 [\text{Cl}^-] \text{antilog}(AI^{\frac{1}{2}}) + 1} = \log \frac{c_\infty - c_0}{c_\infty - c_t} \quad \dots \quad (7)$$

Thus the linearity of the kinetic plots is understandable. The observed rate constants obtained from the slopes of the plots have a very complex meaning.

For comparison, the fifth column of Table 5 (d_2) lists the values of the denominator of eqn. (3) by assuming that all the hydrochloric acid dissociates into ions. In this hypothetical case the deviation from the mean is immense and obviously the kinetic plots would not be linear.

The mass-law constant is estimated from the rate constants in presence of lithium chloride. The estimate is approximate, because we do not know exactly the chloride-ion concentration in the presence of one salt, let alone in a mixture of lithium chloride and hydrochloric acid. Assuming, however, that only the former contributes the ions (its dissociation constant is 8 times that of the acid) and that the dissociation constant calculated for infinite dilution is valid also for the concentrations used, and disregarding the antilogarithmic factors containing the ionic strength in the first power, one obtains, according to eqn. (6),

$$\frac{k_a}{k_b} = \frac{\alpha^0 [\text{Cl}^-]_b \text{antilog}(AI_b^{\frac{1}{2}}) + 1}{\alpha^0 [\text{Cl}^-]_a \text{antilog}(AI_a^{\frac{1}{2}}) + 1} \quad \dots \quad (8)$$

where k_a and k_b are the observed rate constants in presence of chloride-ion concentrations $[\text{Cl}^-]_a$ and $[\text{Cl}^-]_b$ respectively. If pairs of the ion concentrations and rate constants listed in Table 4 are introduced successively in eqn. (8), the following average is obtained for the mass-law constant: $\alpha^0 = (6 \pm 3) \times 10^3$. The accuracy is very low, which is not surprising in view of the many approximations.

The above mass-law constant relates to 97% acetone. In other acetone-water mixtures different constants are to be expected, because the specific rates, k_2^0 and k_3^0 , constituting α^0 , are not affected to the same degree by the change of the medium. For instance, Bensley and Kohnstam¹⁴ found that the mass-law constant for dichlorodiphenylmethane in 85% acetone is 126 and in 75% acetone 79. (On the effect of the medium on rate constants, see following paper.)

Using the above value of α^0 , one may obtain for the rate of dissociation of triphenylmethyl chloride in 97% acetone at 29.5°:

$$k_1^0 = k \alpha^0 [\text{Cl}^-] \text{antilog}(AI^\ddagger) + k = 5.5 \times 10^{-2} \text{ sec.}^{-1}$$

where $k = 0.00767 \text{ sec.}^{-1}$ (observed rate constant) and $[\text{Cl}^-] = I = 0.0024$ (the mean free chloride concentration during a run).

Thus the rate of dissociation at zero ionic strength of such a rapid reaction can be calculated. The measurement of this rate by ordinary means seems almost impossible.

Effect of Additives on the Rate of Hydrolysis.—Lithium perchlorate increases notably the observed rate constant (Table 4), in accordance with the ionic-strength effect. The ionic strength decreases the rate of the reassociation of the ions and consequently the overall rate of hydrolysis increases.

Added silver nitrate accelerates the reaction (Table 4). Almost no reassociation occurs and the observed rate should nearly equal the rate of the dissociation of triphenylmethyl chloride. But since a precipitate is formed, the medium is not homogeneous and no quantitative conclusions should be drawn. Indeed, no linear kinetic plot is obtained in this case: the slope increases toward the end of the reaction.

Perchloric acid (Table 4) increases the rate noticeably, in conformity with the ionic-strength effect. Here some hydrogen bonding between the leaving halogen atom and the perchloric acid may play some rôle. Furthermore, because of the high degree of dissociation of this acid, a depression of the dissociation of the hydrochloric acid is to be expected and this also decelerates the reassociation.

Hydrochloric acid has little effect, only slightly accelerating the hydrolysis. It is, in any case, liberated during reaction.

Of special interest is the effect of a non-ionic additive on the rate of hydrolysis. In its presence the solvation process may be affected. Phenol is generally employed as a "solvation agent" in unimolecular reactions. Hudson and Saville⁷ noted an acceleration of the alcoholysis of triphenylmethyl chloride in carbon tetrachloride in the presence of phenol and similar results were obtained by Swain and Kreevoy¹⁵ in the radiochloride exchange of triphenylmethyl chloride in benzene. The rate of hydrolysis of this chloride in aqueous acetone is not changed by the presence of phenol (Table 4). Probably phenol is an excellent solvating agent compared with carbon tetrachloride and benzene, but it is a poor competitor compared with water or acetone.

The rate of hydrolysis in presence of heavy water also indicates the importance of the solvation, the rate being markedly depressed. It is well known that hydrogen bonds between the leaving halide ion and deuterium are weak compared with those with ordinary hydrogen.^{16,17,18} The rates of hydrolysis of typical unimolecular reactions in heavy water are usually only 0.7—0.8 of those in ordinary water, as is observed here. The rates of bimolecular reactions are generally not affected by interchanging the two kinds of water.¹⁸

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¹⁶ Streitwieser, *Chem. Reviews*, 1956, 56, 655.

¹⁷ Olivier, *Rec. Trav. chim.*, 1937, 56, 247.

¹⁸ Swain, Cardinaud, and Ketley, *J. Amer. Chem. Soc.*, 1955, 77, 934.