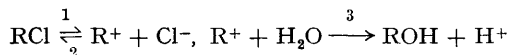


## Mass-law Constants in the Hydrolysis of Substituted Diphenylmethyl Chlorides

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UNIMOLECULAR ( $S_N1$ ) reactions of organic esters often proceed *via* intermediate ion-pairs,<sup>1</sup> but ion-pairs derived from the chlorides (RCl) do not appear to react significantly with the solvent or other nucleophiles in aqueous media.<sup>2</sup> This conclusion is confirmed by a detailed examination of the present results in 70% acetone, and the original reaction scheme for  $S_N1$  hydrolysis<sup>3</sup> can therefore be retained: *viz.*,



The mass-law constant,  $\alpha (=k_2/k_3)$ , provides information about the competition of water and chloride ions for the reactive carbonium ion, but changes in  $\alpha$  resulting from structural changes in the substrate have rarely been studied under constant reaction conditions. Results for some diphenylmethyl chlorides are now reported.

The determination of  $\alpha$  solely from the observed rate coefficients for hydrolysis

$$k_h = k_1 / (1 + \alpha[\text{Cl}^-]) \quad (1)$$

requires a knowledge of the effect of the electrolyte on  $k_1$ , an effect which may not be independent of its nature.<sup>4</sup> More reliable values of  $\alpha$  have now been obtained with substrates containing  $\text{R}^{36}\text{Cl}$  (see Table, Section A) by measuring  $k_h$  and the first-order rate coefficient for the formation of  $^{36}\text{Cl}^-$  ( $k_r$ ) at the same stage of reaction, when

$$k_r = k_h \{1 + \alpha([\text{Cl}^-] - [\text{RCl}] \times [^{36}\text{Cl}^-]/[\text{R}^{36}\text{Cl}])\} \quad (2)^*$$

Within the limits of the experimental error (<5%),  $\alpha$  was independent of the nature of the added electrolyte (HCl or NaCl) and of its concentration in the range 0.025–0.10M. The ratio of the activity coefficients in the Brønsted equations for  $k_2$  and  $k_3$  therefore appears to be virtually constant under these conditions.

Less accurate results were obtained with the more reactive substrates (see Table, Section B). Here Equation (2) could not be employed and  $\alpha$  was therefore obtained from the decrease of  $k_h$  as reaction proceeded in initially 0.001M solution by assuming that  $k_h$  and  $\alpha$  remained constant. Other assumptions led to slightly different values of  $\alpha$  and it is estimated that this parameter is only reliable to *ca.* 20%.

The Table shows that structural changes which enhance the stability of the intermediate carbonium ion (and therefore accelerate hydrolysis) also increase  $\alpha$ , as pointed out by previous workers.<sup>3</sup> However, compound (IV) shows a much larger  $\alpha$  than is indicated by the relation between  $\alpha$  and  $k_h$  for the other chlorides studied in 70% acetone, and this also applies to compound (II) (though to a smaller extent) if (I) and (III) can be regarded as "normal". Similarly, the results in the 85% solvent show an "abnormal"  $\alpha$  for compound (VIII) and, possibly, for (VI) and (VII). These anomalous chlorides contain substituents (Ph, Me,  $\text{MeO}\cdot\text{C}_6\text{H}_4$ ) which are polarisable with respect to an electron-demanding centre but which, nevertheless, do not greatly accelerate  $S_N1$  reactions.

\* The instantaneous rate coefficients ( $k$ ) in Equation (2) were obtained by equating their value at a time  $t$  (say) to that of the more accurate integrated parameters for the time interval 0–2t. This introduces a negligibly small error when  $k_h$  only decreases slightly as reaction proceeds; *i.e.*, when  $\alpha$  and the initial concentration of RCl are small.

The observations may therefore arise from an enhanced stabilisation of the fully developed carbonium ion which is not accompanied by a similar stabilisation of the partially ionic transition state (*cf.* ref. 2a). Analogous considerations may

explain the fact that  $\alpha = 140$  for the hydrolysis of 4-phenoxydiphenylmethyl chloride (not shown) which occurs more rapidly than that of compound (V) where  $\alpha = 350$ .

TABLE  
Mass-law constants for the hydrolysis of RCl at 0°

		Substituent	$\alpha^*$	$k_h$ (rel). <sup>†</sup>
A. 70% aq. acetone .. .. .	.. .. .	4-NO <sub>2</sub> (I)	0.71	0.00045
	RCl = Ph <sub>2</sub> CHCl .. .. .	4-Ph, 4-NO <sub>2</sub> (II)	1.52	0.0101
		H (III)	2.08	1.00
		4-Ph (IV)	8.43	8.15
B. 85% aq. acetone .. .. .	.. .. .	4-NO <sub>2</sub> (V)	350	0.095
	RCl = 4'-MeO-C <sub>6</sub> H <sub>4</sub> CHPhCl ..	H	700	1.00
		4-Ph (VI)	1100	3.04
		4-Bu <sup>‡</sup>	1000	4.68
		4-Me (VII)	1500	7.33
		4-An <sup>‡</sup> (VIII)	2300	10.3
		4-PhO	2300	25.2
	4-MeO	3700	252	

\* In mole<sup>-1</sup>l. † At zero ionic strength. ‡ An = 4-MeO-C<sub>6</sub>H<sub>4</sub>.

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<sup>1</sup> S. Winstein, B. Appel, R. Baker, and A. Diaz, "Organic Reaction Mechanisms", Chem. Soc. Special Publ. No. 19, 1965, p. 109.

<sup>2</sup> (a) B. Bensley and G. Kohnstam, *J. Chem. Soc.*, 1955, 3408; (b) G. Kohnstam and B. Shillaker, *ibid.*, 1959, 1915, and references there cited.

<sup>3</sup> L. C. Bateman, M. G. Church, E. D. Hughes, C. K. Ingold, and N. A. Taher, *J. Chem. Soc.*, 1940, 979.

<sup>4</sup> E. Jackson and G. Kohnstam, *Chem. Comm.*, 1965, 279, and references there cited.