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ION PAIRS, RACEMIZATION, CHLORIDE EXCHANGE AND THE MASS LAW EFFECT IN SOLVOLYSIS OF P-CHLOROBENZHYDRYL CHLORIDE[1]

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In the classic investigations of C. K. Ingold and his coworkers[2], solvolysis of benzhydryl type halides in aqueous acetone was interpreted with the aid of only one variety of carbonium ion intermediate, the dissociated cation, $R^{\oplus}$, as in equation (1). In the so-called mass law effect

$$\begin{tikzcd} RCl \arrow[r, shift left, "k_1"] & R^{\oplus} \arrow[l, shift left, "k_2"] \arrow[d, "k_3"] & + \; Cl^{\ominus} \\ & ROH & \end{tikzcd} \qquad (1)$$

(common ion rate depression[3]), chloride ion competes with water for $R^{\oplus}$, diverting it from benzhydrol (ROH) formation back to covalent benzhydryl chloride (RCl). This formulation leads to equation (2) for k_t, the first

$$k_t = \frac{-d(RCl)/d\,t}{(RCl)} = k_1/[1 + \alpha(Cl^{\ominus})] \qquad (2)$$

order titrimetric rate constant, α denoting (k_2/k_3).

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[1] Research supported by the National Science Foundation.

[2] C. K. Ingold, et.al., J. Chem. Soc. 979 (1940).

[3] (a) S. Winstein, E. Clippinger, A. H. Fainberg and G. C. Robinson, Chemistry and Industry 664 (1954); (b) S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, J. Am. Chem. Soc. 78, 328 (1956).

Evaluation of the magnitude of the mass law coefficient, α, is by no means straightforward, since k_1, k_2 and k_3 are all subject to salt effects. Treating the activity coefficients of $R^{\oplus}$ and $Cl^{\ominus}$ by the Debye-Hückel limiting law, that of the transition state in step 1 by an ion-atmosphere theory and those for RCl and the transition state in step 3 as though they remained unity, Hughes and Ingold[2] expressed the dependence of k_t on ionic strength, μ, and common ion concentration, $(Cl^{\ominus})$, in the form of equation (3). In this equation, k_1^o and α^o are values at zero μ

$$k_t = \frac{k_1^o}{10^{-\frac{0.912 \times 10^{16} \sigma \mu}{D^2 T^2}} + \alpha^o (Cl^{\ominus})\ 10^{-\frac{1.815 \times 10^6 \mu^{1/2}}{(DT)^{3/2}}}} \qquad (3)$$

and σ is a parameter related to the polarity of the transition state in step 1. Not only does equation (3) specify a logarithmic fit of salt effects in solvolysis, but it makes no provision for specificity of salt effects. The assessments of the mass law effect by Ingold[2] or Kohnstam[4] with equation (3) or with equation (2) at constant μ inevitably involve the assumption that the "ionic strength" effect of the common ion salt, e.g., HCl or NaCl, is the same as that of some non-common ion salt.

In his original formulation[2], Ingold did not consider ion pair intermediates in the solvolysis scheme. Even after such intervention of ion pair intermediates in solvolysis of other systems was recognized[5], the same formulation was continued[6]. On the other hand, Kohnstam[4], who

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[4] (a) B. Bensley and G. Kohnstam, *J. Chem. Soc*. 3408 (1955); (b) G. Kohnstam and B. Shillaker, *ibid*. 1915 (1959).

[5] W. G. Young, S. Winstein and H. L. Goering, *J. Am. Chem. Soc.* **73** 1958 (1951).

[6] (a) O. T. Benfey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.* 2488 (1952); (b) A. R. Hawdon, E. D. Hughes and C. K. Ingold, *ibid*. 2499 (1952).

has more recently interpreted the hydrolysis of diphenyldichloromethane in aqueous acetone on the basis of equations (1)-(3), concluded that his results would be consistent with intervention of ion pair intermediates if ROH arises only from dissociated $R^{\oplus}$. More insight into such matters can be provided by an optically active benzhydryl halide[7], and we have now measured rates of racemization, acid formation and radio-chloride exchange of p-chlorobenzhydryl chloride in 80% acetone. These show that it is important to distinguish between ionization and dissociation[3,5] and to recognize explicitly the intervention of ion pair intermediates[3,5] in solvolysis of benzhydryl halides even in solvents as dissociating as 80% acetone.

Optically active p-chlorobenzhydryl chloride was available from the action of hydrogen chloride on the p-chlorobenzhydrol in pentane[8] at -80°, this material being several times as active as the product of the reaction of carbinol with thionyl chloride[7a]. Fairly satisfactory first order rate constants for disappearance of optical activity, k_α , are obtained at 25° with ca. 0.1 M solutions of active RCl in 80% aqueous acetone with or without added lithium chloride or perchlorate (Table I and Fig. 1). The rotation of the final solution of chlorobenzhydrol is zero within experimental error.

First order titrimetric rate constants, k_t, for 0.01 M solutions of RCl are steady within a run. As illustrated in Table II and Fig. 1, k_t is increased by non-common ion salts and decreased by common ion salts. At an RCl concentration of 0.1 M, corresponding to the polarimetric work, k_t values are slightly lower than those at 0.01 M (Table I). They are still

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[7] (a) S. Winstein and J. S. Gall, Tetrahedron Letters 2, 31 (1960); (b) S. Winstein, J. S. Gall, M. Hojo and S. Smith, J. Am. Chem. Soc. 82, 1410 (1960).

[8] P. G. Stevens and N. L. McNiven, J. Am. Chem. Soc. 61, 1295 (1939).

Table I

Rate Constants for 0.10 M RCl in 80% Acetone at 25.0°

Salt	Concn. 10^2M	$10^5 k_\alpha$ Sec.$^{-1}$	$10^5 k_t$ Sec.$^{-1}$	$10^4 k_{e2}$ M^{-1}Sec.$^{-1}$	$10^5 k_t^u$ Sec.$^{-1}$
-	-	5.7 ± 0.3	2.31 ± 0.02	-	2.6
LiCl	1.02		2.34 ± 0.02	1.10 ± 0.03	2.7
LiCl	5.4		2.15 ± 0.02	0.97 ± 0.04	2.9
LiCl	9.0		1.97 ± 0.02	0.97 ± 0.02	3.1
LiCl	10.0	5.7 ± 0.2	1.94 ± 0.03		3.1
$LiClO_4$	5.0	6.8 ± 0.5			
$LiClO_4$	10.0	8.0 ± 0.4			

Table II

k_t Values for 0.010 M RCl in 80% Acetone at 25.0°

Salt	Concn. 10^2 M	$10^5 k_t$ Sec.$^{-1}$	**Salt**	Concn. 10^2 M	$10^5 k_t$ Sec.$^{-1}$
-	-	2.45 ± 0.02	Bu_4NBr	4.98	2.62 ± 0.03
LiCl	5.09	2.33 ± 0.02	Bu_4NBr	10.0	2.61 ± 0.03
LiCl	10.3	2.08 ± 0.02	$LiClO_4$	5.14	2.98 ± 0.02
Bu_4NCl	4.95	2.18 ± 0.05	$LiClO_4$	9.82	3.35 ± 0.02
Bu_4NCl	9.21	1.81 ± 0.02	LiBr	1.02	2.64 ± 0.03
Bu_4NClO_4	5.00	2.55 ± 0.01	LiBr	5.00	2.94 ± 0.01
Bu_4NClO_4	10.0	2.54 ± 0.01	LiBr	10.0	3.25 ± 0.01

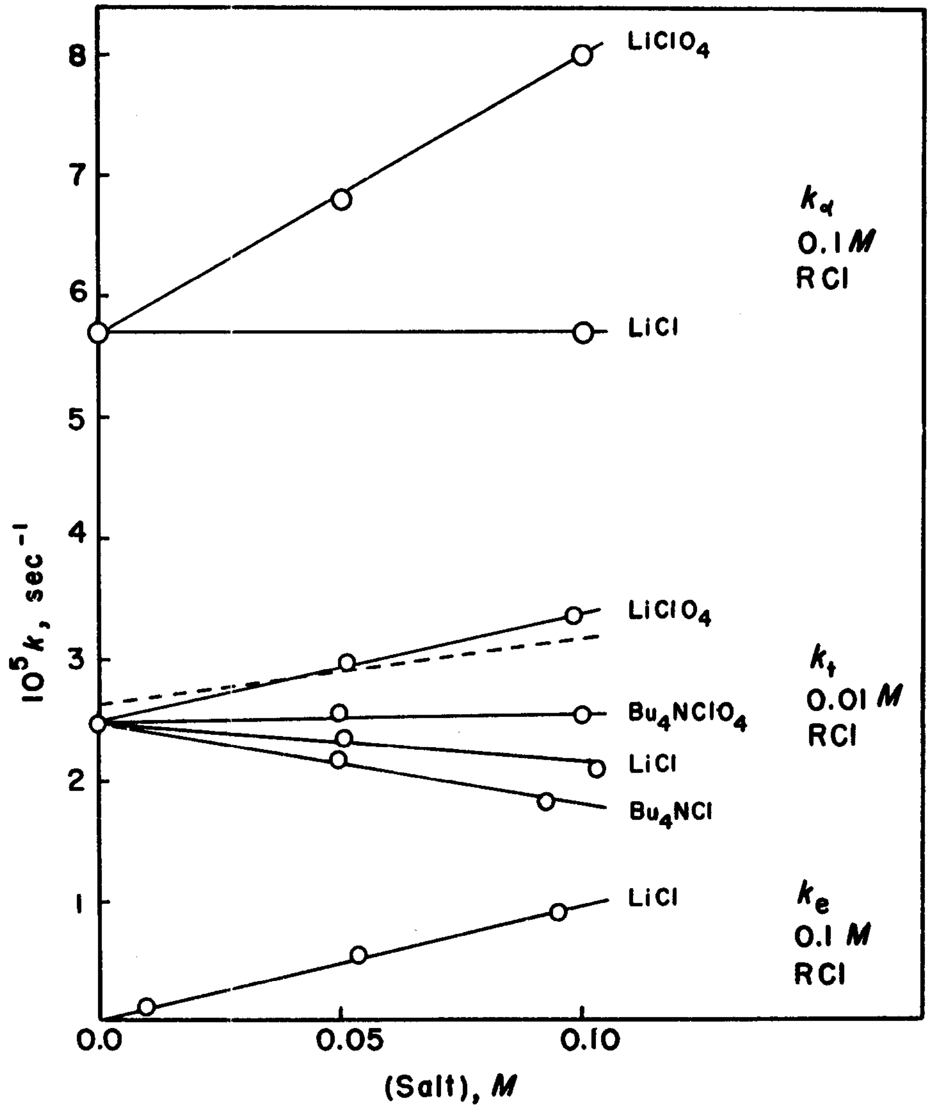

Fig. 1.- Effects of salts on k_α, k_t, and k_e.

quite steady in a run, acceleration of rate by accumulating electrolyte balancing common ion rate depression. The observed polarimetric rate constants are obviously 2.5 - 3 times as large as the titrimetric values[9].

With the pattern of salt effects on k_t as it is, it is difficult to assess what contribution the mass law effect makes to the gap between k_α and k_t without calling on independent evidence. It is evident from Table II and Fig. 1 that equation (3) fails to fit the observed pattern of salt effects on k_t. Instead of different non-common ion salts giving identical accelerated k_t values and different common ion salts leading to identical depressed rates, the observed effects depend on the salt. The specificity is especially marked for the change of cation from lithium to tetrabutylammonium. As pointed out previously[10], equation (3) was insufficiently tested, and it has become increasingly clear that there is very considerable specificity of salt effects on the various solvolysis steps even in solvents of relatively high dielectric constant[10,11]. Other recent evidence of such specificity pertains to t-butyl chloride hydrolysis in water[12] as solvent, ionization of neophyl and 3-phenyl-2-butyl toluenesulfonates in 50% dioxane[13] and α values in hydrolysis of trityl chloride in aqueous dioxane[14].

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[9] An erroneous preliminary (k_α/k_t) ratio of 4.9 was previously mentioned[7b].

[10] A. H. Fainberg and S. Winstein, J. Am. Chem. Soc. 78, 2763 (1956).

[11] (a) G. R. Lucas and L. P. Hammett, J. Am. Chem. Soc. 64, 1928 (1942); (b) O. T. Benfey, E. D. Hughes and C. K. Ingold, J. Chem. Soc. 2494 (1952); (c) F. Spieth and A. R. Olson, J. Am. Chem. Soc. 77, 1412 (1955).

[12] G. A. Clarke, R. W. Taft, Jr., and T. R. Williams, Page 8R of Abstracts of American Chemical Society Meeting, Boston, Mass., April 5-10, 1959.

[13] E. F. J. Duynstee, E. Grunwald and M. L. Kaplan, J. Am. Chem. Soc. in press.

[14] Y. Pocker, Chemistry and Industry 1599 (1957).

Independent evidence regarding the magnitude of the mass law effect or common ion rate depression is the rate of radio-chloride exchange accompanying hydrolysis of p-chlorobenzhydryl chloride. Second order rate constants[15] (k_{e2}) for such exchange accompanying hydrolysis of 0.1 M RCl are fairly constant within a run, and these are summarized in Table I. Since external ion return is inevitably associated with exchange[3], $k_{e2}(Cl^{\ominus})$, the first order rate constant for radio-chloride exchange at the prevailing chloride ion concentration, represents an upper limit to the decrease in k_t due to common ion rate depression. The reason that it is an upper limit is that exchange can also be visualized by way of undissociated ion pairs, and such exchange is not associated with common ion rate depression. Addition of $k_{e2}(Cl^{\ominus})$ to the observed k_t should yield an upper limit to the k_t value, k_t^u, which would be observed if external ion return and the corresponding common ion rate depression were absent. Table I lists these k_t^u values for 0.1 M RCl, $k_{e2}(Cl^{\ominus})$ being calculated for $(Cl^{\ominus})$ equal to the value at one polarimetric half-life of the optically active RCl. In Fig. 1 are plotted these k_t^u values as a dashed line, as well as initial first order radio-chloride exchange rate constants, k_e.

It is evident that the maximum correction for external ion return still leaves k_α twice as great as k_t^u. It is clear that ion pair intermediates play an important role in solvolysis of p-chlorobenzhydryl chloride even in 80% aqueous acetone. The minimum required elaboration of the solvolysis scheme is the following:

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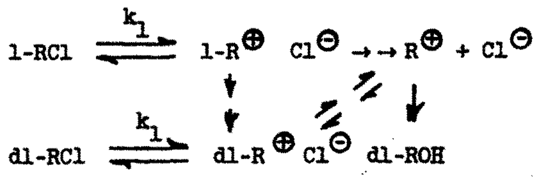
[15] E. R. Swart and L. J. le Roux, J. Chem. Soc. 2110 (1956).



In this scheme, solvolysis product is shown arising from dissociated R$^{\oplus}$ and not ion pairs, but it is really not clear that no variety of ion pair intermediate leads to product. At least for intimate ion pairs, it seems more likely that they do not lead to carbinol than that they do lead to this product which is, however, completely racemic.

With I denoting the fraction of ion pair intermediates which undergo ion pair return and R being the fraction which become racemic, equation (4) expresses the relation between k_1, k_α and k_t^u. A minimum value of I

$$k_\alpha - k_t^u = k_1 \, IR \qquad (4)$$

may be obtained by setting R equal to unity, this in turn making k_α equal to k_1. On this basis I has values of 0.46 - 0.54, at least half of the ion pair intermediates from ionization of RCl undergoing ion pair return. I may be considerably larger than the estimated minimum value since it seems very probable that R is substantially less than unity, much ion pair return occurring with retention of configuration of RCl.

The present work has disclosed that k_α for a benzhydryl chloride exceeds k_t or k_e, not only in acetic acid[7b] (D = 6) and acetone [7a] (D = 20.7), but even in 80% acetone (D = 29.6). Apparently, this is true also for the two non-hydroxylic solvents, sulfur dioxide[16] (D = 14) and nitromethane[16] (D = 36.7).

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[16] Unpublished work of Hughes, Ingold, Pocker and Swedlund, quoted by Y. Pocker, Trans. Faraday Soc. 55, 1266 (1959).