Mercuric Chloride Promoted Reactions of *p*-Chlorobenzhydryl Chloride[1]

Sir:

The importance of carbonium ion pair intermediates in solvolysis of RX substrates was first recognized with rearranging allylic systems[2a] and substances that lead to bridged cations.[2b-e,3a] Their importance was later recognized in solvolysis of systems that lead to relatively stable classical cations, for example, *p*-chlorobenzhydryl[3-5] or trityl.[3a,6]

While ion pair return accompanying the solvolysis of benzhydryl derivatives can be efficiently eliminated by promoting the reaction with protonic acids,[4c,7a,8] the role of ion pair intermediates remains very important in the mercuric chloride promoted reactions. As was reported,[9] the first-order rate constants for racemization (k_{rac}) and radiochloride exchange (k_{e}) for the $\mathrm{HgCl_2}$-promoted ionization of *p*-chlorobenzhydryl chloride (RCl) provide a unique ($k_{\mathrm{rac}}/k_{\mathrm{e}}$) ratio of 1.50 in acetone (D = 20). The explanation offered was that RCl was regenerated from racemic $\mathrm{R^+HgCl_3^-}$ ion pairs (I) in which all three chlorine atoms on mercury are *equivalent* but still so constituted that two chlorine atoms are from the original labeled $\mathrm{HgCl_2}$ and one is from the RCl. The present communication deals with the effect of solvent variation on the ion pair intermediate produced in the $\mathrm{HgCl_2}$-promoted ionization.

Table I. Summary of k's for the $\mathrm{HgCl_2}$-Promoted Reactions of *p*-Chlorobenzhydryl Chloride[a]

		10^3k_2, M^{-1} sec^{-1} [b]				
Solvent	$\mathrm{HgCl_2}$, 10^3 M	k_α	k_{e}	k_{t}	$k_{\mathrm{rac}}/k_{\mathrm{e}}$	Ion pair dissociation, %
Acetone[c]	1.00–15.00	18.7	12.4		1.5	0
80% acetone	5.10–17.10	107 ± 7	30.0 ± 2	59.0 ± 1.0	1.6	55
Acetonitrile	1.54–13.50	110 ± 5.2	110 ± 5.6		1.0	100
Benzene	1.10–3.04	1.04[d]	4.37		0.24	

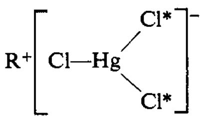
[a] RCl concentration *ca.* 0.01 M; at 25.0°. [b] Each k value represents an average of five measurements. [c] Reference 9. [d] One $\mathrm{HgCl_2}$ concentration.

$$\left.\begin{array}{ll} d\text{-RCl} \longrightarrow dl\text{-RCl} & k_{\mathrm{rac}} \\ d\text{-RCl} + \mathrm{H_2O} \longrightarrow dl\text{-ROH} + \mathrm{HCl} & k_{\mathrm{t}} \end{array}\right\} k_\alpha$$

$$\mathrm{HgCl_2^*} + \mathrm{RCl} \rightleftharpoons \mathrm{HgCl_2} + \mathrm{RCl^*} \qquad k_{\mathrm{e}}$$

Summarized in Table I are the second-order rate constants for the racemization and exchange of RCl in the presence of $\mathrm{HgCl_2}$. In 80% aqueous acetone, mercuric chloride does not enhance the reactions of RCl as dramatically as in acetone. The titrimetric rate of solvolysis showed good second-order kinetics, first order in RCl and first order in $\mathrm{HgCl_2}$, where the infinity titers were 100 ± 1.2%. The first-order titrimetric rate constants, k_{t}, given by the product of the measured second-order rate constant and the initial mercuric chloride concentration show a linear dependence on $[\mathrm{HgCl_2}]$. The increase in k_{t} due to added $\mathrm{HgCl_2}$ is fit by a least-squares line with slope $59 \pm 1 \times 10^{-3}$ M^{-1} sec^{-1} and intercept 2.5×10^{-5} sec^{-1}.[3d] Similarly, the k_{e} values show a linear dependence on $[\mathrm{HgCl_2}]$ for the concentration range 0.0050–0.0160 M where the slope for the least-squares line through the origin provides a second-order rate constant equal to $30 \pm 2 \times 10^{-3}$ M^{-1} sec^{-1}.

The polarimetric rate constants (k_α) provided by the product of the measured second-order rate constant $k_{2\alpha}$ and the initial mercuric chloride concentration ($[\mathrm{HgCl_2}]_0$) show a linear dependence on $[\mathrm{HgCl_2}]_0$. The plot of k_α *vs.* $[\mathrm{HgCl_2}]_0$ is fit by a least-squares line through the fixed intercept of 5.8×10^{-5} sec^{-1}[3d] where the slope provides $k_{2\alpha}$ equal to $107.2 \pm 7.2 \times 10^{-3}$ M^{-1} sec^{-1}. The final reaction solutions were 98.4 ± 1.3% racemic.[10] In interpreting the results the $\mathrm{HgCl_2}$-promoted reaction, "the slope reaction," is assumed to proceed independently of the unpromoted reaction with little or no crossover between the two reactions.[12] Since k_α provides the best measure of ionization the k_{t}/k_α ratio shows that only 55% of the $\mathrm{R^+HgCl_3^-}$ pairs give rise to product. To the extent that the unpromoted reaction can be used as a model for the promoted reaction, k_{t}/k_α is a measure of the amount of ion pair dissociation accompanying the reaction.[13] The ion pairs that return and regenerate RCl still have the same constitution as in acetone since the $k_{\mathrm{rac}}/k_{\mathrm{e}}$ $((k_\alpha - k_{\mathrm{t}})/k_{\mathrm{e}})$ ratio again provides the unique value 1.5 (1.6 ± 0.16).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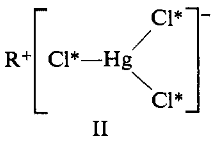
II

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[1] Research supported by the National Science Foundation.

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[10] Since the specific rotation of the carbinol is *ca.* twice that of the alkyl chloride,[11] *ca.* <0.8% of the carbinol could be produced with retention of configuration.

[11] A. Diaz, unpublished results.

[12] Normal salt effects on the solvolysis of RCl in 80% acetone are small[3d] and are ignored for the present treatment.

[13] Kinetic analysis of the solvolysis of RCl in 80% acetone indicates that solvolysis product arises almost completely from dissociated carbonium ions, while return to RCl is very inefficient.[3d,11]

The behavior in acetonitrile is quite different. Added $HgCl_2$ increases k_α and k_e enormously, rates being followed conveniently at 25.0°. The value of k_α is increased from *ca.* 1×10^{-7} sec^{-1} at 25.0° in the absence of salt[7b] to 1.1×10^{-3} sec^{-1} in the presence of 0.01 *M* $HgCl_2$. Both k_α and k_e are linear in $[HgCl_2]$ in the concentration range 0.0015–0.0135 *M*, leading to the second-order rate constants 0.110 and 0.110 M^{-1} sec^{-1}, respectively. This provides a k_{rac}/k_e ratio of 1.00 in line with return to RCl from a racemic ion pair intermediate II where all the chlorine atoms on $HgCl_3^-$ are equivalently labeled.

p-Chlorobenzhydryl chloride racemizes slowly in benzene ($D = 2$) at 25.0° even in the presence of $HgCl_2$. The racemization proceeds to completion (99 ± 5%) with good first-order kinetics as sampled up to 90% reaction, providing the second-order rate constant 1.04×10^{-3} M^{-1} sec^{-1}. Similarly, the rate of exchange between RCl and $HgCl_2$ is slow in benzene where the dependence of k_e on $[HgCl_2]$ in the concentration range reported is 4.37×10^{-3} M^{-1} sec^{-1}. The effect of going to this poorly ionizing solvent where the reaction intermediate stability is reduced, is to preferentially reduce that equilibration process in the ion pair which is of higher energy. Since k_α is smaller than k_e, equilibrating the faces of the benzhydryl cation must be more difficult than equilibrating chlorine atoms of $HgCl_3^-$ in the $R^+HgCl_3^-$ pair. If the ion pairs in benzene have the same constitution as in acetone, the rate of ionization is $^3/_2k_e$; thus only 16% of the ionization reactions which give rise to chlorine exchange is accompanied by racemization, providing a *ca.* 1 kcal/mol free energy difference between the two equilibration processes.

The $HgCl_2$-promoted ionization of *d*-RCl in acetone ($D = 20$) gives rise to ion pairs so constituted that two chlorine atoms are from the labeled $HgCl_2$ and one from RCl and only when the ion pair racemizes do all three chlorine atoms become equivalent in the ion pair I thus providing the unique k_{rac}/k_e ratio of 3/2. The reaction in this solvent of low dielectric constant is accompanied with efficient ion pair return and no detectable dissociation.[14] In the more dissociating solvent, 80% acetone ($D = 26$), the ion pair intermediates still maintain the same constitution observed in acetone, providing the unique k_{rac}/k_e ratio of 3/2 (1.6 ± 0.16). However, ion pair return is now reduced to 45% and is accompanied by 55% dissociation. Finally, in acetonitrile ($D = 36$) ion pair dissociation is very efficient compared to ion pair return producing a racemic cation which is no longer affiliated with the original $HgCl_3^-$. Thus, racemic RCl is regenerated by $HgCl_3^-$ which has fully equilibrated the original chlorine atom from RCl with the *total* chlorine atom pool II providing a k_{rac}/k_e ratio of unity.

The unique k_{rac}/k_e ratio of 1.5 observed in acetone[9] was assigned to a single mechanism and not to fortuitous balancing of two independent reactions with different statistics. The results in 80% acetone indicated that a single mechanism must be involved in anhydrous acetone and 80% acetone because it seems unlikely that the two independent reactions would show the same solvent sensitivity.

That the transition from acetone to acetonitrile effects the ion pair dissociation constants (k_2) primarily can be demonstrated using $Ph_3C^+HgCl_3^-$ ion pair dissociation (K_{diss}) information as model system. Since ion pair recombination (k_{-2}) is approximately diffusion control, the value of k_2 (sec^{-1}) can be estimated at 140 for acetone and 410,000 for CH_3CN. The *ca.* 5% average deviation in the measured results provides estimates for the k_2/k_{-1} ratio of $\gtrsim 1/20$ in acetone and $\gtrsim 20$ in CH_3CN. It follows then that the rate of ion pair return (k_{-1}) is quite insensitive to solvent variation, increasing from 2800 in acetone to 20,000 in CH_3CN. By comparison, k_2 increases by three orders of magnitude.

$$RCl + HgCl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R^+HgCl_3^- \underset{k_{-2}}{\overset{\overset{K_{diss}}{k_2}}{\rightleftharpoons}} R^+ + HgCl_3^-$$

Solvent	10^6K_{diss}, M^{15}	k_2, sec^{-1}	k_{-1}, sec^{-1}
Acetone	0.14	140	$\gtrsim 2,800$
CH_3CN	410.0	410,000	$\lesssim 20,000$

While the earlier literature contains some indications of ion pair phenomena in the salt-promoted reactions of alkyl chlorides,[16] a study directed toward the elucidation of the intrigued mechanism has not been reported. This paper is the second in a series on the study of ion pair behavior in salt-promoted reactions.

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[14] The k_α/k_e ratio is not changed to unity by the presence of added $LiHgCl_3$, suggesting the absence of significant ion pair dissociation. Ion pair dissociation will inevitably give rise to $HgCl_3^-$ exchange providing a k_α/k_e ratio of 1.

(15) The dissociation constants for the solutions of trityl chloride plus mercuric chloride were measured spectrophotometrically as described by J. W. Bayles, A. G. Evans, and J. R. Jones, *J. Chem. Soc.*, 1020 (1953).

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(17) Deceased, Nov 23, 1969.

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Pure Chromium(VI) Oxidations. The Effective Removal of Chromium(IV) from Interference in Oxidations by Chromic Acid

Sir:

The chromic acid oxidation of alcohols is a multistep process involving the formation of chromium(IV) and chromium(V) intermediates.[1] We have recently shown that reaction Scheme I best explains all data available

Scheme I

$$\text{Cr(VI)} + \text{S} \xrightarrow[\text{rate limiting}]{k_1} \text{Cr(IV)} + P_6 \qquad (1)$$

$$\text{Cr(IV)} + \text{S} \longrightarrow \text{Cr(III)} + \text{R}\cdot \qquad (2)$$

$$\text{Cr(VI)} + \text{R}\cdot \longrightarrow \text{Cr(V)} + P_4 \qquad (3)$$

$$\text{Cr(V)} + \text{S} \longrightarrow \text{Cr(III)} + P_5 \qquad (4)$$

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(1) (a) For extensive reviews of chromic acid oxidations, see K. B. Wiberg, "Oxidation in Organic Chemistry," Part A, Academic Press, New York, N. Y., 1965; R. Stewart, "Oxidation Mechanisms: Application to Organic Chemistry," W. A. Benjamin, New York, N. Y., 1964; (b) K. B. Wiberg and H. Schäfer, *J. Amer. Chem. Soc.*, 91, 927, 933 (1969).