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CAPTURE OF BENZHYDRYL CHLORIDE ION PAIRS BY COBALT NITRATE[1,2]

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Abstract—A case is presented where a transition metal salt, $Co(NO_3)_2$, intervenes in the solvolysis of benzhydryl chloride, after the rate determining ionization step. This is in contrast to the behavior of other salts which intervene early and promote the ionization reaction. This novel behavior of $Co(NO_3)_2$ permits for the first time the detection of two ion pair intermediates in the solvolysis of an alkyl chloride which generates an open carbonium ion.

In our previous reports on metal salt promoted ionization reactions we presented cases where salts such as $HgCl_2$ assist in the bond breaking processes of various alkyl chlorides (RCl).[2] Thus, the $HgCl_2$-promoted solvolysis of RCl involves the active role of $R^+HgCl_3^-$ pairs which can give solvolysis products, k_t, racemize and regenerate racemic RCl, k_{rac}, or equilibrate the chlorine atoms and regenerate chlorine exchanged RCl, k_e. We recently obtained results that suggest that the metal salt can intervene late in the ionization reaction, i.e., after the slow bond breaking step, and now wish to present the results of this investigation.

$$\begin{array}{lll} \mathrm{RCl+SOH}\xrightarrow{\mathrm{HgCl_2}}\mathrm{ROS+H^+} & & (1)\\ \mathrm{d\text{-}RCl}\xrightarrow{\mathrm{HgCl_2}}\mathrm{dl\text{-}RCl} & \left.\begin{array}{l}k_t\\ \\ k_{rac}\end{array}\right\} k_\alpha & (2)\\ \mathrm{RCl+HgCl_2^{*}\rightarrow RCl^{*}+HgCl_2} & k_e & (3)\end{array}$$

RESULTS AND DISCUSSION

The rates of solvolysis of benzhydryl and *p*-chlorobenzhydryl chloride were measured in 80% acetone at 25·0° in the presence of various salts.[3] The reactions studied in the presence of $n\text{-}Bu_4NClO_4$, LiCl, $LiClO_4$ and KNO_3 proceeded to 99% infinity showing good first order kinetics with no apparent drift. The first order rate constants are listed in Table 1. The effects of adding the common ion salt LiCl is to produce a mild rate depression as was previously reported,[3] where the addition of 0·05*M* LiCl depresses k_t by *ca* 5% in the case of both RCl's.

The noncommon ion salts produce small normal salt effects. The $n\text{-}Bu_4NClO_4$ salt produces a very small effect in the solvolysis of benzhydryl chloride, where the 'b'-value is 1.[4] $LiClO_4$ and KNO_3 produce a larger rate enhancement and show comparable 'b' values, equal to 4·6 and 3·9, respectively.

The reactions carried out in the presence of $Co(NO_3)_2$, again showed good first order kinetics with no apparent drift. The k's were obtained up to 60% conversion of RCl. The addition of $Co(NO_3)_2$ enhances the solvolysis rate of the RCl much more than the other salts. As seen in Fig 1, the plot of k_t *vs* $[Co(NO_3)_2]$ shows an initial steep increase up to *ca* 0·04*M* salt followed by a shallow increase at higher concentrations. This behavior parallels the Winstein "special salt effect" curves observed in the acetolysis of various alkyl arenesulfonate esters.[4] Extrapolation of the shallow part of the curve provides k°_{ext} values equal to 3·25 and $9{\cdot}00\times10^{-5}$ sec^{-1} for *p*-chlorobenzhydryl chloride and benzhydryl chlorides respectively. These values are summarized in Table 1.

The polarimetric rate constants measured with p-chlorobenzhydryl chloride, which are a better measure of the ionization rate, do not show this special effect with Co(NO₃)2. Furthermore, the value of k°_{ext} $(3{\cdot}25\times10^{-5}\ sec^{-1})$ does not close the gap between k_t $(2{\cdot}36\times10^{-5}\,sec^{-1})$ and k_α $(5{\cdot}9\times10^{-5}\,sec^{-1})$, thus this solvolysis must involve two types of ion pairs plus dissociated ions as intermediates;[4] an intimate ion pair that regenerates racemic RCl and is not chemically captured (**2**), a solvent separated ion pair which can be captured by $Co(NO_3)_2$ (**3**) and dissociated ions that produce ROH product and can be returned to RCl by added common ion salt (**4**).[3]

$$\begin{array}{ccccc} \mathbf{2} & & \mathbf{3} & & \mathbf{4} \\ \left.\begin{array}{c}\mathrm{d\text{-}RCl}\rightleftarrows\mathrm{d\text{-}R^+Cl}\\ \downarrow\!\uparrow\\ \mathrm{l\text{-}RCl}\rightleftarrows\mathrm{l\text{-}R^+Cl}\end{array}\right\} & \rightleftarrows & \mathrm{dl\text{-}R^+\|Cl^-} & \rightleftarrows & \begin{array}{c}\mathrm{dl\text{-}R^+ + Cl^-}\\ \downarrow\\ \mathrm{ROH}\end{array} \end{array} \qquad (4)$$

Using the best measure of ionization, i.e., k_α, one calculates from the $(k_\alpha - k_t)/k_\alpha$ ratio that 60% of the

Table 1. Summary of k's in 80% acetone at 25·0°C

RCl, 10^3M	Salt	10^3M	$10^5 k_t$, sec^{-1}	'b'-Value[a]
Benzhydryl chloride				
11·01			6·70 ± 0·015[b]	
		(k°_{ext})	9·00[c]	
4·0	$Co(NO_3)_2$	2·00	6·68 ± 0·05	
4·7	$Co(NO_3)_2$	3·90	7·38 ± 0·32	
5·49	$Co(NO_3)_2$	8·58	8·12 ± 0·42	
	$Co(NO_3)_2$	11·91	7·59 ± 0·07	
5·93	$Co(NO_3)_2$	12·4	8·34 ± 0·18	
	$Co(NO_3)_2$	17·27	8·42 ± 0·1	
10·0	$Co(NO_3)_2$	20·0	8·56 ± 0·05	
9·23	$Co(NO_3)_2$	38·8	9·74 ± 0·30	
10·0	$Co(NO_3)_2$	50·0	10·07 ± 0·2	
10·01	$Co(NO_3)_2$	96·8	11·05 ± 0·3	2·3[d]
9·99	$Co(NO_3)_2$	100·0	10·96 ± 0·4	
11·2	$Co(NO_3)_2$ KNO_3	21·58 24·33	8·54 ± 0·03	
10·0	$LiClO_4$	20·0	7·33 ± 0·13	4·6
10·1	$LiClO_4$	50·0	8·08 ± 0·19	
9·05	$LiClO_4$	101·0	9·88 ± 0·06	
10·69	KNO_3	20·49	7·31 ± 0·02	3·9
10·24	KNO_3	50·66	7·91 ± 0·08	
13·44	$n\text{-}Bu_4NClO_4$	20·31	6·90 ± 0·03	1·0
10·16	$n\text{-}Bu_4NClO_4$	50·35	6·97 ± 0·04	
9·90	$n\text{-}Bu_4NClO_4$	99·0	7·38 ± 0·03	
9·82	LiCl	8·63	6·60 ± 0·16	
10·50	LiCl	9·67	6·60 ± 0·07	
9·37		25·6	6·47 ± 0·01	
9·95		34·5	6·52 ± 0·08	
9·40		38·9	6·44 ± 0·10	
p-*Chlorobenzhydryl chloride*				
76 to 106	$Co(NO_3)_2$ $Co(NO_3)_2$	44·7 (k_α) 72·5	5·88 ± 0·07[e] 6·9 ± 0·1 7·8 ± 0·2	4·3
11·36			2·36 ± 0·02[e]	
		(k°_{ext})	3·25[c]	
11·75	$Co(NO_3)_2$	15·52	2·77 ± 0·04	
13·90	$Co(NO_3)_2$	25·1	3·11 ± 0·05	
11·19	$Co(NO_3)_2$	50·0	3·31 ± 0·04	
10·67	$Co(NO_3)_2$	101·2	3·35 ± 0·10	0·34
10·0	$LiClO_4$	5·14	2·98 ± 0·02[f]	4·7
10·0	$LiClO_4$	9·82	3·35 ± 0·02[f]	
10·0	LiCl	5·09	2·33 ± 0·02[f]	
10·0	LiCl	10·3	2·08 ± 0·02[f]	

[a] Calculated using $k_{obs} = k_0(1 + b\ [salt])$.

[b] Compare to literature value[18] of $7{\cdot}27 \times 10^{-5}$ sec $^{-1}$.

[c] Extrapolated value from Fig 1.

[d] Calculated using $k^{\circ}_{ext} = 9{\cdot}00 \times 10^{-5}$ sec^{-1}.

[e] Compare to literature values $5{\cdot}7 \times 10^{-5}$ sec^{-1} for k_α and $2{\cdot}45 \times 10^{5}$ sec^{-1} for k_t (Ref 3).

[f] Ref 3.

intermediates generated in the reaction racemize and return to RCl. One informative aspect of these results is that only *ca* 1/4 of these intermediates can be chemically captured (from $(k_\alpha - k^{\circ}_{ext})/(k_\alpha - k_t)$) indicating that racemization can occur quite efficiently at the intimate ion pair stage with open carbonium ions when the counter ion is chloride.

The stereochemistry of the return from the ion pair **2** seems to depend very much on the stability of the intermediate. Thus, return from ion pair **2** in the cases of *p*-methylbenzhydryl and α-anisylethyl *p*-nitrobenzoate[5a] occurs with considerable racemization while in the cases of *p*-chlorobenzhydryl[6] and α-phenylethyl[5a] *p*-nitrobenzoate, which produces less stable ions, return occurs without racemization. In line with this trend, return from **2** in the solvolysis of the less endothermic *p*-chlorobenzhydryl chloride occurs with racemization.

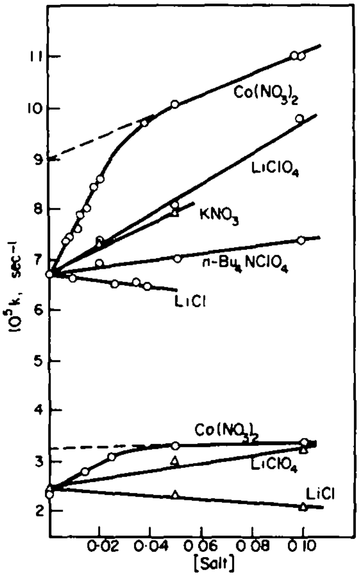

Fig 1.

From the special salt effect curve, a measure of the efficiency of the salt to capture the intermediate is provided by $[\text{salt}]_{1/2}$, the salt concentration where k_t is raised to a value halfway between k_t° and k_{ext}°. The $[\text{Co(NO}_3)_2]_{1/2}$ value for this system is 0·015*M* which is 10 to 100 times larger than the values observed using $LiClO_4$ in the acetolysis of various β-aryl alkyl esters.[7] Thus $Co(NO_3)_2$ in this system is 10 to 100 less efficient than $LiClO_4$ in those cases. On the other hand, it is *ca* 4 times more efficient than NaN_3 in the reactions of α-*p*-anisylethyl[5a] and *p*-methylbenzhydryl *p*-nitrobenzoates[5a] in 90% acetone where $[N_3^-]_{1/2}$ is *ca* 0·06M.

Spectral measurements were made on the $Co(NO_3)_2$ solutions in an attempt to determine the role of the salt in the reaction. The visible spectrum for 0·01M $Co(NO_3)_2$ in 80% acetone shows a broad peak with λ_{max} at 510 nm and $\epsilon = 5{\cdot}50$, resembling spectra previously reported,[8a] and increases to 5·90 with the presence of 0·0095 M KNO_3. This spectral information[9a,b,10] suggests that the salt is a medium dissociated ion triplet with an octahedral arrangement by six H_2O molecules and with the two NO_3^- anions in the outer-solvation shell, thus $[CO(H_2O)_6](NO_3)_2$.[9a,b,11] This is reasonable since H_2O is a better electron donor than acetone by a factor of *ca.* 10.[8b,9c] These results plus the fact that k_t measured in the presence of 0·021 M $Co(NO_3)_2$ is not affected by the presence of the common ion salt, 0·02433 M KNO_3, is in line with having the dissociated cobalt cation be the active species in the reaction which does not form a cobalt nitrate salt such as **5**. Also in line with this conclusion is the estimate of unity[12] for the value of K for an equilibrium such as shown in Equation 5

$$\underset{\mathbf{5}}{Co(NO_3)_2(H_2O)_4} + 2H_2O \rightleftarrows Co(H_2O)_6^{++} + 2NO_3^- \quad (5)$$

The absence of a significant downward drift in the k_t's indicates that the chloride ion probably does not remain affiliated with the cobalt ion. Since cobalt chloride shows no apparent reactivity,[13] where k_t for benzhydryl chloride in the presence of 0·05 M $CoCl_2$ is $6{\cdot}12 \pm 0{\cdot}01 \times 10^{-5}\ sec^{-1}$, a downward drift in k_t is expected if the cobalt ion became deactivated by the formation of cobalt chloride complexes.[14]

In conclusion, $Co(NO_3)_2$ does intervene actively in the solvolysis of benzhydryl chloride in 80% acetone. However, in contrast to the role of the mercury salts, where $HgCl_2$[2] and $Hg(NO_3)_2$[15] facilitate the bond breaking process by providing electrophilic assistance, $Co(NO_3)_2$ intervenes late in the reaction. Thus, the cobalt salt does not affiliate the chlorine atom until after it has fully developed a negative charge. This particular behavior of the cobalt salt helps demonstrate for the first time that the solvolysis of benzhydryl chloride proceeds via two ion pair intermediates where only the more dissociated one is captured by the cobalt salt.

EXPERIMENTAL

Benzhydryl chloride and *p*-chlorobenzhydryl chloride were prepared by treatment of the carbinols with HCl in pentane at 0°. The crude alkyl chlorides were distilled at 132° (4·2 mm); n_D^{25} 1·5937 (Lit[16] 137° (5·0 mm); n_D^{25} 1·5937) for benzhydryl chloride and 138° (3·6 mm); n_D^{25} 1·6002 (Lit[17] 172–173° (6 mm)) for *p*-chlorobenzhydryl chloride.

Anhydrous acetone prepared as previously described[18] was mixed with water in a 4 to 1 volume ratio. Dry $LiClO_4$, $CoCl_2$ and $Co(NO_3)_2$ were obtained by heating the hydrates $LiClO_4{\cdot}3H_2O$, $CoCl_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$, respectively, at 110° in an Abderhalder drying apparatus under 0·1 mm pressure for 6 h.

The solvolytic reactions measured in 80% acetone at 25·0° were followed by titrating the produced acid with 0·009819 *M* sodium methoxide to a brom phenol blue end point.[19] The polarimetric rate measurements were carried out in an all glass 1 decimeter thermostated cell using a Perkin Elmer Polarimeter Model 141.

The visible spectra were measured on freshly prepared solutions in a 2 dm cell using a Cary 14 recording spectrophotometer. The prepared solutions were gravity filtered directly into the cell in order to remove a faintly visible suspension. Analysis of the cobalt solution after filtration by titrating with 0·000990 *M* EDTA to a Murixide in NaCl end point[20] demonstrated the presence of 98·8% cobalt salt based on the initially weighed amount.

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[7] [Salt]$_{1/2}$ values for these esters vary in the range 8×10^{-5} to 3×10^{-3} *M*; see S. Winstein, *et al.*: [a] *J. Am. Chem. Soc.*, **78**, 328 (1956); [b] *ibid*, **78**, 2784 (1956); [c] *ibid*, **80**, 459 (1958); [d] *ibid*, **83**, 885 (1961); [e] *ibid*, **94**, 2256 (1972)

[8a] L. I. Katzin and E. Gerbert, *Ibid.* **72**, 5455 (1950); [b] L. I. Katzin and E. Gerbert, *Nature* **4453**, 425 (1955)

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[10] The small increase in ϵ from 5·50 to 5·90 is appropriate for a salt effect. See references 9a and 9b. The reaction solutions after 10 reaction half-lives show a comparable change, where ϵ equals 5·15, probably due to the presence of *ca.* 0·01 M HCl.

[11] C. C. Addison and D. Sutton, *J. Chem. Soc.*, 5553 (1964)

[12] The value of K is estimated using the extrapolated value for $Co(NO_3)_2$ in 80% t-butanol where ϵ for the cobalt salt is similar to that in 80% acetone.[8a]

[13] In contrast $CoCl_2$ promotes the ionization reaction of 1-phenylethyl chloride in anhydrous acetone very effectively (J. Palmer and A. Diaz, unpublished results).

[14] Since in a normal run the solvolysis of 0·01M RCl was followed to *ca.* 60% reaction, the average [Cl$^-$] produced is 0·003M which could produce 0·0015M $CoCl_2$. Therefore at 0·02M $Co(NO_3)_2$ only 7·5% of the salt would become inactive producing a mild downward drift in the run.

[15] See: I. Roberts and L. P. Hammett, *J. Am. Chem. Soc.*, **59**, 1063 (1937) and O. T. Benfey, *ibid*, **70**, 2165 (1948)

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[19] In those reactions containing $Co(NO_3)_2$ the pink to blue color change corresponds to the conductance equivalence point. The titrametric analyses were straightforward except with solutions containing 0·1*M* $Co(NO_3)_2$ where the end point was sometimes difficult to work with

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