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MECHANISMS OF S_Ni REACTIONS. LACK OF O^{18}-EQUILIBRATION ACCOMPANYING THE DECOMPOSITION OF O^{18}-LABELLED α-PHENYLETHYL CHLOROCARBONATE[1a]

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The thermal decomposition of aralkyl thiocarbonates (eq. 1) has been shown to involve ion pair intermediates.[2] Subsequent studies[3,4] have demonstrated that the mechanism of the reaction

$$\underset{\underset{\textstyle 1}{}}{\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}}\mathrm{O}\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{C}}\mathrm{SR}} \longrightarrow \underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}}\mathrm{SR} + \mathrm{CO_2} \qquad (1)$$

is one (eq. 2) in which the aralkyl-oxygen and carbonyl-sulfur bonds are broken in two <u>successive</u> steps, with the cleavage of the carbonyl-sulfur bond being rate-determining ($k_b < k_{-a}$). This is shown by (a) the fact that optically active *p*-chlorobenzhydryl thiocarbonates (Ar = *p*-ClC_6H_4)

$$\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}}\mathrm{O}\overset{\substack{\mathrm{O}\\ \|}}{\mathrm{C}}\mathrm{SR} \underset{k_{-a}}{\overset{k_a}{\rightleftarrows}} \underset{\textstyle 2}{[\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}^+}\ {}^-\mathrm{O_2CSR}]} \xrightarrow{k_b} \mathrm{CO_2} + [\underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}^+}\ {}^-\mathrm{SR}] \longrightarrow \underset{\substack{|\\ \mathrm{Ph}}}{\mathrm{ArCH}}\mathrm{SR} \qquad (2)$$

$$k_b < k_{-a}$$

racemize faster than they decompose to sulfide and CO_2[3,4] and (b) the fact that ether-oxygen labelled *p*-chlorobenzhydryl thiocarbonates ($ArPhCHO^{18}C(O)SR$) undergo equilibration of the

O^{18}-label between ether and carbonyl oxygens more rapidly than they decompose to sulfide.[4] Both of these results can only be accounted for if ion pair return to reactants (step k_{-a}) is faster than loss of CO_2 from $RSCO_2^-$ in ion pair **2** (step k_b).

The unimolecular decomposition of chlorocarbonates (eq. 3) is one of the classic examples

$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \longrightarrow R\text{-}Cl + CO_2 \tag{3}$$

of an S_Ni reaction,[5,6] is known to involve ion pair intermediates,[5,6] and is clearly a process formally similar to the thiocarbonate decomposition in eq. 1. However, since Cl^- is presumably a more stable anion and better leaving group than RS^-, the possibility clearly exists that in the chlorocarbonate case decomposition will not be accompanied by ion pair return from $[R^+\ ^-O_2CCl]$ to ROC(O)Cl, because of the fact that in this instance loss of CO_2 from ^-O_2CCl (step k_b, eq. 4) will be faster than return to ROC(O)Cl (step k_{-a}, eq. 4).

$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} [R^+\ ^-O_2CCl] \xrightarrow{k_b} CO_2 + [R^+\ ^-Cl] \longrightarrow R\text{-}Cl \tag{4}$$

$$k_b > k_{-a}$$

In the present communication we report results which demonstrate that there is no appreciable ion pair return to ROC(O)Cl in the decomposition of a typical chlorocarbonate and that the mechanism for that decomposition is therefore either the one shown in eq. 4 with $k_b > k_{-a}$ or else one (eq. 5) in which cleavage of the R-O and C-Cl bonds is synchronous and one proceeds directly to the ion pair $[R^+\ Cl^-]$.

$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \longrightarrow CO_2 + [R^+\ ^-Cl] \longrightarrow R\text{-}Cl \tag{5}$$

O^{18}-labelled α-phenylethanol (1.46 atom % O^{18}) was converted to α-phenylethyl chlorocarbonate, $CH_3\underset{\underset{Ph}{|}}{C}HO^{18}C(O)Cl$, by the procedure described by Wiberg and Shryne[5] for the preparation of the unlabelled chlorocarbonate. That the label was present exclusively in the ether oxygen was shown by reduction of a sample of the chlorocarbonate with lithium aluminum hydride, and recovery of the resulting α-phenylethanol. Its O^{18} content (1.44 atom % O^{18}) was not significantly different from that of the alcohol used to make the chlorocarbonate.

The remainder of the labelled chlorocarbonate was partially decomposed by heating it at 60° in dioxane for a period of time sufficient to decompose half of the chlorocarbonate to α-phenylethyl chloride and CO_2. The reaction solution, containing, of course, the remaining undecomposed chlorocarbonate, was then immediately reduced with lithium aluminum hydride, and the α-phenylethanol resulting from reduction of the undecomposed chlorocarbonate was separated from the other materials present by glc. Its O^{18} content (1.46 atom % O^{18}) showed that during one decomposition half-life there had been <u>no detectable accompanying equilibration of O^{18} between the ether and carbonyl oxygens</u> of the remaining chlorocarbonate. This, of course, means that in the chlorocarbonate decomposition return from the ion pair [R^{+} $^{-}O_2CCl$] to ROC(O)Cl is unimportant, in marked contrast to the behavior of the otherwise closely analogous thiocarbonate decomposition. In the decomposition of *p*-chlorobenzhydryl S-methyl thiocarbonate (**1**, Ar = *p*-ClC_6H_4, R = CH_3), for example, at the end of one decomposition half-life O^{18}-equilibration is essentially complete (i.e., O^{18}-content of alcohol recovered after reduction, 0.83 atom % O^{18}).[4]

As indicated earlier, this marked difference in the behavior of two otherwise closely analogous reactions can most reasonably be ascribed to the fact that Cl^- represents a much better leaving group than RS^-, so that in the chlorocarbonate decomposition cleavage of $^{-}O_2CCl$ to CO_2 and Cl^- is faster than return of ion pair [R^{+} $^{-}O_2CCl$] to reactants, whereas in the thiocarbonate decomposition cleavage of $^{-}O_2CSR$ to RS^- and CO_2 is slower than return to reactants.

REFERENCES

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(2) J. L. Kice, R. A. Bartsch, M. A. Dankleff and S. L. Schwartz, *J. Amer. Chem. Soc.*, **87** 1734 (1965).

(3) J. L. Kice and M. A. Dankleff, Tetrahedron Letters, 1783 (1966).

(4) J. L. Kice, R. L. Scriven, E. Koubek, and M. Barnes, J. Amer. Chem. Soc., **92**, in press (1970).

(5) K. B. Wiberg and T. M. Shryne, ibid., **77**, 2774 (1955).

(6) K. L. Olivier and W. G. Young, ibid., **81**, 5811 (1959).