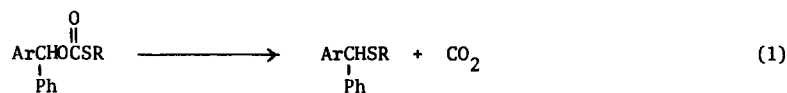


MECHANISMS OF  $S_N1$  REACTIONS. LACK OF  $O^{18}$ -EQUILIBRATION ACCOMPANYING  
THE DECOMPOSITION OF  $O^{18}$ -LABELLED  $\alpha$ -PHENYLETHYL CHLOROCARBONATE<sup>1a</sup>

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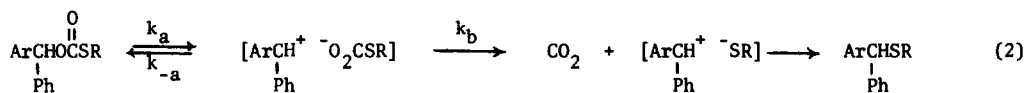
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The thermal decomposition of aralkyl thiocarbonates (eq. 1) has been shown to involve ion pair intermediates.<sup>2</sup> Subsequent studies<sup>3,4</sup> have demonstrated that the mechanism of the reaction

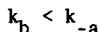


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is one (eq. 2) in which the aralkyl-oxygen and carbonyl-sulfur bonds are broken in two successive steps, with the cleavage of the carbonyl-sulfur bond being rate-determining ( $k_b < k_{-a}$ ). This is shown by (a) the fact that optically active *p*-chlorobenzhydryl thiocarbonates ( $\text{Ar} = \text{p-ClC}_6\text{H}_4$ )



2



racemize faster than they decompose to sulfide and  $\text{CO}_2$ <sup>3,4</sup> and (b) the fact that ether-oxygen labelled *p*-chlorobenzhydryl thiocarbonates ( $\text{ArPhCHO}^{18}\text{C(O)SR}$ ) undergo equilibration of the

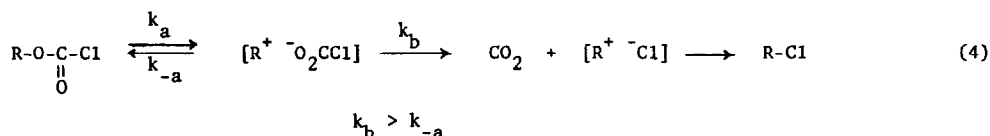
$O^{18}$ -label between ether and carbonyl oxygens more rapidly than they decompose to sulfide.<sup>4</sup>

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  $k_b$ ).

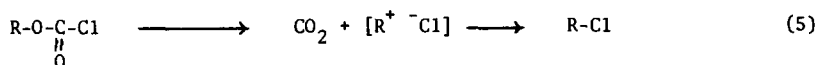
The unimolecular decomposition of chlorocarbonates (eq. 3) is one of the classic examples



of an  $S_Ni$  reaction,<sup>5,6</sup> is known to involve ion pair intermediates,<sup>5,6</sup> 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).



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  $[R^+ {}^-Cl]$ .



$O^{18}$ -labelled  $\alpha$ -phenylethanol (1.46 atom %  $O^{18}$ ) was converted to  $\alpha$ -phenylethyl chlorocarbonate,  $CH_3\underset{\text{Ph}}{\underset{|}{CH}}C(O^{18})Cl$ , by the procedure described by Wiberg and Shryne<sup>5</sup> 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  $\alpha$ -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  $60^\circ$  in dioxane for a period of time sufficient to decompose half of the chlorocarbonate to  $\alpha$ -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  $\alpha$ -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 no detectable accompanying equilibration of  $O^{18}$  between the ether and carbonyl oxygens of the remaining chlorocarbonate. This, of course, means that in the chlorocarbonate decomposition return from the ion pair  $[R^+ \text{ } ^-O_2CCl]$  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 =  $p\text{-ClC}_6\text{H}_4$ , 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 %  $O^{18}$ ).<sup>4</sup>

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  $[R^+ \text{ } ^-O_2CCl]$  to reactants, whereas in the thiocarbonate decomposition cleavage of  $^-O_2CSR$  to  $RS^-$  and  $CO_2$  is slower than return to reactants.

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