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MECHANISMS OF S_Ni REACTIONS.
THE DECOMPOSITION OF ARALKYL THIOCARBONATES

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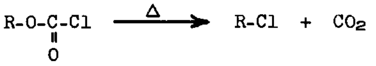
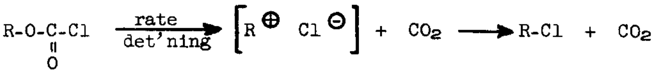
THE DECOMPOSITION of alkyl chlorocarbonates (equation 1) is one of the standard examples of an S_Ni reaction. The response of rate to structural

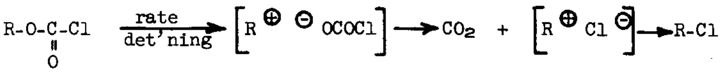


$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \xrightarrow{\Delta} R\text{-}Cl + CO_2 \tag{1}$$

variation of the alkyl group (1,2) and to solvent ionizing-power (1) leaves no doubt that the rate-determining step involves formation of the alkyl carbonium ion R^+ via heterolysis of the R-O bond. What has not been clear, however, is whether cleavage of the C-Cl bond is synchronous with (equation 2a), or alternatively, occurs subsequent to (equation 2b) breaking of the R-O bond.



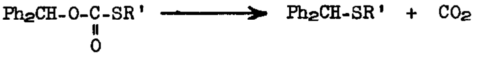
$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \xrightarrow[\text{det'ning}]{\text{rate}} \left[R^{\oplus} \quad Cl^{\ominus}\right] + CO_2 \longrightarrow R\text{-}Cl + CO_2 \tag{2a}$$



$$R\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}Cl \xrightarrow[\text{det'ning}]{\text{rate}} \left[R^{\oplus} \; {}^{\ominus}OCOCl\right] \longrightarrow CO_2 + \left[R^{\oplus} \, Cl^{\ominus}\right] \longrightarrow R\text{-}Cl \tag{2b}$$

We now present results obtained during the study of a new, closely related, internal substitution reaction -- the decomposition of aralkyl thiocarbonates -- which we feel provide at least a partial answer to this question.

A series of benzhydryl S-alkyl thiocarbonates, $Ph_2CHOCOSR'$, was prepared by reaction of benzhydrol with the appropriate chlorothiolformate, R'SCOCl.[1] On being heated in inert solvents they undergo decomposition according to equation 3, a reaction clearly analogous to equation 1. Also



$$Ph_2CH\text{-}O\text{-}\underset{\underset{O}{\parallel}}{C}\text{-}SR' \longrightarrow Ph_2CH\text{-}SR' + CO_2 \qquad (3)$$

analogous to the chlorocarbonate decomposition, the rate[2] of reaction 3 is notably dependent on solvent ionizing-power, benzhydryl S-phenyl thiocarbonate decomposing at 146° about 30 times faster in benzonitrile than it does in bromobenzene.

Determination of the decomposition rates of a series of aralkyl S-phenyl thiocarbonates (Table 1) shows that the variation of the rate with the

Table 1

Dependence of Rate on Aralkyl Group Structure

	Relative Rates		
Aralkyl Group, R	Decomp. of ROCOSPh in PhCN, 186°	Decomp. of ROCOCl in dioxane, 90° [a]	Solvolysis of RCl in HOAc, 25° [b]
$PhCH_2$-	(1.0)	(1.0)	(1.0)
$Ph\underset{CH_3}{C}H$-	---	450	370
Ph_2CH-	2.6×10^4	---	1.5×10^4
p-$ClC_6H_4\underset{Ph}{C}H$-	1.2×10^4	---	5.1×10^3

[a] Ref. 2. [b] Data for benzyl and 1-phenylethyl chlorides from A. Streitwieser, Chem. Revs., 56, 616 (1956). That for benzhydryl chloride from S. Winstein, A. H. Fainberg and E. Grunwald, J. Am. Chem. Soc., 79, 4146 (1957), and that for p-chlorobenzhydryl chloride from S. Winstein et al., ibid., 82, 1010 (1960).

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[1] Satisfactory analyses were obtained for all new compounds.

[2] The kinetics of the decompositions of the various thiocarbonates were followed by measuring the disappearance of the ester carbonyl absorption band between 1705 and 1720 cm.$^{-1}$. All reactions exhibited satisfactory first-order kinetics.

structure of the aralkyl group closely parallels that observed in the chlorocarbonate decomposition and in the solvolysis of the corresponding aralkyl halides. When combined with the pronounced solvent effect, these results seem to require that the rate-determining step of the aralkyl thiocarbonate decomposition, like the chlorocarbonate reaction, involve formation of the aralkyl carbonium ion by heterolysis of the aralkyl-oxygen bond.

The particularly interesting feature of the thiocarbonate decomposition is what kinetic study of the decomposition of a series of benzhydryl thiocarbonates, $Ph_2CHOCOSR'$, reveals concerning the dependence of the decomposition rate on the nature of the R'S group (Table 2). The key point is the behavior of the phenyl ester vis-à-vis that of the three S-alkyl esters. If the rate-determining step involved heterolysis of only the Ph_2CH-O bond, with formation of $R'SCO_2^-$, the phenyl group could stabilize the anion only by its inductive effect. In that case one might expect to find an excellent correlation between the rates for all four esters and the σ^* values for the respective R' groups. On the other hand, if both the aralkyl-oxygen and carbonyl-sulfur bonds were broken, with formation of $R'S^-$, the phenyl substituent could stabilize the anion not only inductively but also by resonance. The observed rate for the phenyl ester would then be faster than would be predicted from σ^* values and the rates for the other three esters.

Table 2

Rates of Decomposition of $Ph_2CHOCOSR'$ in Benzonitrile at 166°

R'	$k_1 \times 10^4$, sec.$^{-1}$	relative rate
CH_3CH_2-	0.66	0.60
CH_3-	1.1	(1.0)
$PhCH_2$-	2.4	2.2
Ph-	25	23

However, since similar resonance stabilization of the mercaptide ion enhances the acidity of thiophenol over that predicted by purely inductive considerations (3), one might expect to find instead in this second case a linear relation between decomposition rates and the pK_a's of the mercaptans R'SH.

As can be seen from Fig. 1, the actual situation is somewhere between these two extremes. Thus, the best straight line through a log k_1 vs. σ^* plot for the three S-alkyl esters predicts a rate for the phenyl ester which is significantly lower than is actually observed. On the other hand, in the log k_1 vs. pK_a plot the best line through the S-alkyl ester data predicts a rate for the phenyl ester which is significantly larger than that observed.

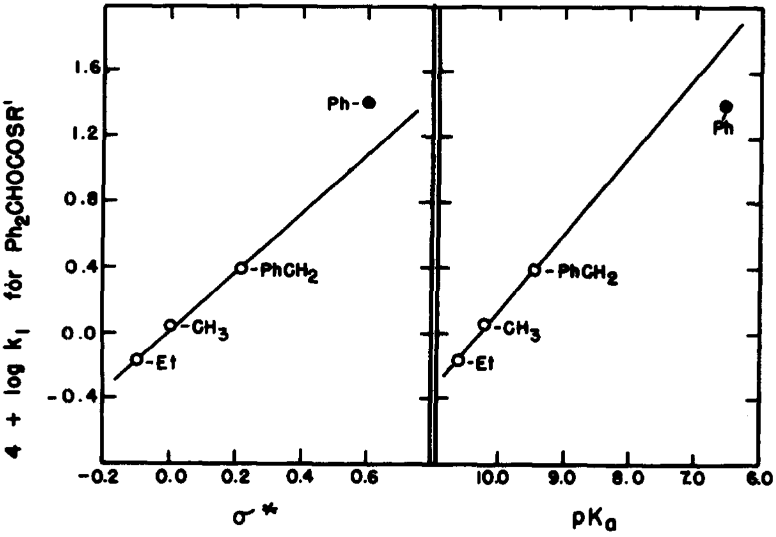
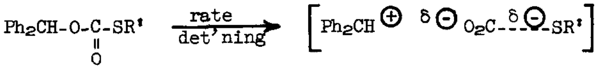


Fig. 1

Plot of log k_1 for $Ph_2CHOCOSR'$ (Table 2) vs. (1) σ^* for R' and (2) pK_a for R'SH.

The simplest explanation for this behavior is that the rate-determining step should be pictured as shown in equation 4. In the transition state of this reaction the carbon-sulfur bond has been substantially weakened, but the



$$Ph_2CH\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}SR' \xrightarrow[\text{det'ning}]{\text{rate}} \left[Ph_2CH^{\oplus} \quad {}^{\delta\ominus}O_2C\text{-}\overset{\delta}{-}\text{-}{}^{\ominus}\text{-}SR' \right] \qquad (4)$$

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breaking of this bond has lagged significantly behind the cleavage of the aralkyl-oxygen bond, with the result that an appreciable fraction of the developing negative charge resides on the oxygens. The ion pair (I) produced by this reaction is intermediate in structure between the two extremes represented in equations 2a and 2b.[3]

This does not mean, of course, that exactly the same degree of weakening of the C-Cl bond occurs in the rate-determining step of the chlorocarbonate decomposition, but it does strongly suggest at least some involvement of the carbon-chlorine bond in that step. When taken together with the recent data of Rhoads and Michel (4) on alkyl chloroglyoxalate decomposition, these results make it tempting to suggest that mechanisms involving at least partial heterolysis of more than one bond in the rate-determining step may be the rule rather than the exception for S_Ni reactions.

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[3] Naturally, the correctness of this interpretation cannot be said to be rigorously established until investigation of a wider range of R' groups has demonstrated that variations in the steric requirements of R' have essentially no effect on the decomposition rates of the thiocarbonates. However, the considerable distance of separation of R' and Ph_2CH and the unimolecular nature of the reaction make it extremely likely that for the esters in Table 2 the moderate variations in the steric requirements of the R' groups have no significant influence on their relative rates of decomposition.

REFERENCES

(1) K. L. Olivier and W. G. Young, J. Am. Chem. Soc., 81, 5813 (1959).

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

(3) M. M. Kreevoy, E. T. Harper, R. E. Duvall, H. S. Wilgus, III, and L. T. Ditsch, ibid., 82, 4899 (1960).

(4) S. J. Rhoads and R. E. Michel, ibid., 85, 585 (1963).