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INTERNAL-RETURN REARRANGEMENT IN SOLVOLYSIS OF CYCLOPROPYLCARBINYL DERIVATIVES

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The unusual reactivities of cyclopropylcarbinyl derivatives in solvolytic reactions have led to a continuing interest in the details of the reaction mechanism and the structures of the intermediates (1). Conductimetric (2) and titrimetric (3) methods for the rate determinations have increased the precision of the measured rate constants but reliance on kinetic data alone has led to some interpretative oversights.

The results of the first studies of the solvolysis of cyclopropylcarbinyl chloride (I) indicated that both ethanolysis and acetolysis were attended by substantial rearrangement to cyclobutyl chloride and allylcarbinyl chloride (4). Evidence was cited later against internal-return isomerization of I in 80% ethanol (5) but this was later shown to be incorrect (6). More recent studies have been interpreted as both favoring (7) and arguing against (8) internal-return isomerization in solvolyses of cyclopropylcarbinyl chlorides and sulfonate esters.

Clearly, the strongest evidence for the occurrence of internal-return isomerization is provided by actual detection of the formation of rearranged halide or sulfonate. However, the usual argument cited against internal return has been the observation of first-order rates of appearance of acid (5, 8). Although it may seem an obvious point to make, we wish to emphasize that first-order appearance of acid in no way argues against internal-return isomerization if the first-order rate is computed on the basis of an acid infinity titer which does not take account of rearrangement.

Consider the following system.

$$\begin{tikzcd}
 & ROH + HX \\
RX \arrow[ur, "k_1"] \arrow[dr, "k_2"'] & \\
 & R'X \arrow[uu, "k_3"']
\end{tikzcd} \qquad (1)$$

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$$\text{If } k_1 >> k_3 \text{ then } \frac{d[HX]}{dt} = k_1 [RX] \qquad (2)$$

which leads to

$$-\log \frac{([HX]_\infty - [HX]_t)}{[HX]_\infty} = (k_1 + k_2)t \qquad (3)$$

The apparent first-order rate constant will then be a sum of the rearrangement and the solvolytic rate constants. For the cyclopropylcarbinyl chloride-cyclobutyl chloride system, k_1 is known to be 35 to 100 times k_3 and the assumption in the derivation is justified. For 1-methylcyclopropylcarbinyl derivatives, k_1 is approximately equal to k_3 and a drifting rate constant is observed (3, 7e). For 1-phenylcyclopropylcarbinyl derivatives (9), k_3 is undoubtedly much larger than k_1 (or k_2) and the rate of acid production will equal the rate of disappearance of starting material.

To illustrate how this works out, some typical rate data obtained for the solvolysis of cyclopropylcarbinyl chloride in 50% ethanol given in Table I are shown graphically in Figure 1.

Table I

Rate of Solvolysis of Cyclopropylcarbinylchloride in 50% (v:v) Ethanol-Water at 50°[a]

Time, min.	Ml., base[b]	100-% Solv.[c]	$\frac{HA_\infty - HA}{HA_\infty} \times 10^2$
30	1.58	81.86	77.4
60	2.80	67.86	59.9
90	3.75	56.96	46.3
150	5.04	42.16	27.8
210	5.69	34.70	18.5
270	6.11	29.88	12.5
390	6.48	25.63	7.2
1440	6.98	19.89	0

[a] Samples were 5.00 ml aliquots from 0.6241 g of C_4H_7Cl made up to 50.00 ml with 50% ethanol.

[b] Using 0.07906 M sodium hydroxide, titrated to the phenolphthalein end-point.

[c] Based on starting chloride.

[d] Based on acid titer after 1440 min.

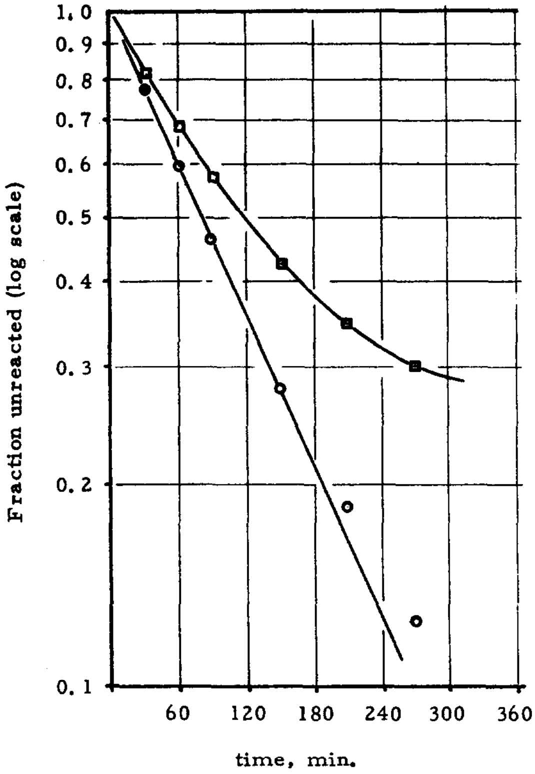

FIG. 1.

Fraction unreacted in solvolysis of cyclopropylcarbinyl chloride at 50° in 50% (v:v) ethanol-water at 50°, ○ based on "infinity" acid titer after 1440 min., □ based on concentration of starting chloride.

To avoid the difficulty in the analysis of solvolyses complicated by internal return, it is clearly desirable to analyze the reaction product after one or two half-lives and find out the degree to which the rearranged halide or sulfonate has actually been formed. This precaution has not always been taken in assessing the importance of internal return (5, 8).

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