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MECHANISMS OF NUCLEOPHILIC SUBSTITUTION REACTIONS. THE REACTION OF METHYL CHLORODITHIOFORMATE WITH AZIDE IONS IN 70% AQUEOUS ACETONE.

A. Queen and T. C. Matts[1].

Parker Chemical Laboratory, University of Manitoba, Winnipeg, Manitoba, Canada.

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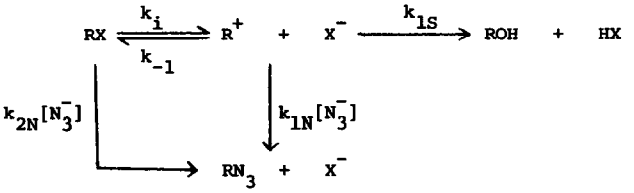
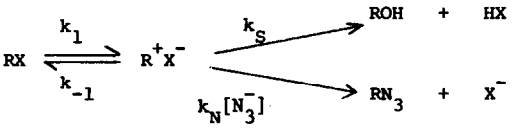
The reaction of 4-methoxybenzyl chloride with azide ions in 70% aqueous acetone, where solvolysis is a competing reaction, has been interpreted[2] in terms of parallel and distinct S_N1 and S_N2 pathways (mechanism I). Alternatively, Sneen[3] considers the same data to support his generalised ion-pair scheme (mechanism II) and a recent study[4] of the chlorine isotope effect for this reaction is claimed to provide support for this pathway, although the conclusion has been criticised[5]. Indeed, Sneen's mechanism has been opposed by a number of workers[6,7,8,9] and the data for the above reaction fit either mechanism equally well when allowances are made for salt effects[6a].

mechanism I



mechanism II



Proponents of mechanism II for this particular reaction overlook the fact that chloride

ions depress the rate of solvolysis[2,6], suggesting that free carbonium ions are kinetically significant intermediates. This effect cannot be due to attack of chloride ions on the ion-pair, since this would contradict the principle of microscopic reversibility. Hence, scheme II is only possible if the rate decrease is due to a negative salt effect. Previous studies[10] suggest that common ion rate depressions are not the result of negative salt effects and the retardations reported[11] for the solvolyses of substituted benzhydryl chlorides are far too large to be explained in this way. However, these systems are too sterically hindered to bimolecular attack to be useful in testing Sneen's mechanism and we have, therefore, looked for a more suitable reaction. Methyl chlorodithioformate reacts with water by the unimolecular mechanism[12] and chloride ions retard the rate (Table 1). Moreover, the reaction should not be subject to large steric effects and we have, therefore, measured the effect of azide ions on the rate of reaction in 70% aqueous acetone (Table 1). The slow reactions were measured at 325 nm with a Beckmann D.U. spectrophotometer and the fast ones with a Canterbury stopped-flow apparatus[13].

TABLE 1

The Effects of Added Salts on the Rate of Reaction of Methyl Chlorodithioformate with 70% Aqueous Acetone at 10.3° C.

Salt	10^4 x [CH_3SCSCl] mol l^{-1}	[Salt] mol l^{-1}	k_{obs} s^{-1}	k_{2N} s^{-1} mol^{-1} l	k_{obs}/k^o_{obs}
none	4		$2.11 \pm 0.03 \times 10^{-4}$		
$NaClO_4$	4	0.0496	$2.93 \pm 0.04 \times 10^{-4}$		1.39
NaCl	4	0.0608	$2.73 \pm 0.05 \times 10^{-5}$		0.129
NaN_3	0.1	0.0265	0.118 ± 0.002	4.45 ± 0.08	559
NaN_3	0.1	0.0530	0.233 ± 0.003	4.40 ± 0.06	1104
NaN_3	0.1	0.0870	0.382 ± 0.004	4.39 ± 0.05	1810

Although the reaction involves displacement of chloride from an sp^2 rather than an sp^3 centre, the present studies are considered to be a legitimate test of Sneen's mechanism because

he has applied scheme II to reactions of benzoyl chloride with amines in aqueous acetone[3,14] and has not subsequently excluded similar reactions from his general ion-pair mechanism. The kinetic consequences of this mechanism are summarised in Table 2 and compared with the corresponding equation for substitution by the S_N1 mechanism alone.

TABLE 2

Rate Equations for Solvolysis and Nucleophilic Attack.

	mechanism II			S_N1 mechanism
	Solvolysis; no salts present	Solvolysis; non-nucleophilic salts present	Solvolysis plus azide attack	Solvolysis plus azide attack
k_{obs}	$\frac{k_1^o}{1 + x^o}$	$\frac{k_1}{1 + x}$	$\frac{k_1(1 + m[N_3^-])}{1 + x + m[N_3^-]}$	$\frac{k_i(1 + \beta[N_3^-])}{1 + \alpha[Cl^-] + \beta[N_3^-]}$
	(3)	(4)	(5)	(6)

$x = k_{-1}/k_S$; $m = k_N/k_S$; $\alpha = k_{-1}/k_{1S}$; $\beta = k_{1N}/k_{1S}$

The rates of solvolysis of chlorodithioformate esters increase[12] with increasing electron donation by the alkyl group. This and the activation parameters for the methyl compound suggest an S_N1 like pathway for these reactions and for such cases, in the limit[3], $x \ll 1$. However, it is not inconceivable that similar results might be obtained for reactions where small values of $x > 1$ apply, but for such cases the large rate increase caused by azide ions would not be observed, unless an unusually large salt effect were to apply. This possibility is not supported by the small effect found for added sodium perchlorate. Assuming a similar effect for sodium azide, a positive value of m requires that x must be at least 770, leading to the unrealistic value of 1.2×10^7 for m. It follows that the azide results require a value for $x \gg 1$, so that the solvolytic reaction should be characterised by S_N2 like properties, rather than those observed. Hence, the results are not consistent with the

simple ion-pair scheme, mechanism II.

In agreement with this conclusion, the common ion rate depression (Table 1) is too large to be entirely due to a negative salt effect and can only be reasonably explained in terms of a mass-law effect on an S_N1 solvolysis. If the free carbocation can be captured by chloride ions, as this effect requires, it is reasonable to assume that azide ions will also react with the same intermediate. However, in the absence of a second pathway for azide attack, the observed rate constant is given by equation 6, which at the small substrate concentrations used, reduces to $k_{obs} = k_i$. Thus, the only observable effect of azide ions would be that due to a salt effect on k_i. The data in Table 1 indicate that the second pathway for azide attack is a bimolecular process, but the results do not permit any conclusions to be drawn concerning the actual mechanism. However, by analogy with results previously obtained for bimolecular reactions of chloroformate esters[14], it seems likely that a tetrahedral intermediate is formed and decomposes to the products. Further work on this problem is in progress.

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