Reactivity of Vinyl Esters: Kinetic Evidence of a Unimolecular Reaction

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IT has been shown[1] that 1,2-diaryl-2-arylthiovinyl-2,4,6-trinitrobenzenesulphonates (I), dissolved in inert solvents, decompose spontaneously, or with BF_3 catalysis, to give trinitrobenzene sulphonic acid (TNBSA) and benzo[*b*]thiophen derivatives (II) as the main products. When weak nucleophiles are present in solution, however, substitution products (III) are obtained, while strong nucleophiles directly attack the TNBS group. The results of the kinetic investigation reported here support the suggestion that (II) and (III) are formed from a common cationic intermediate.

The kinetics of the spontaneous decomposition of vinyl esters (I) in inert and solvolytic solvents have been followed by conductometric† and spectrophotometric‡ techniques. The reaction is first-order up to at least 70% completion and is quite sensitive to solvent change. The solvent effect was determined (Table 1) for a substituted ester (I; X = H, Y = Me) in different solvents.

The increase of the rate with the polarity of the media and the magnitude of the effect observed are characteristic[2] of reactions in which ions are produced from neutral substrates.

The presence of small amounts of methanol has no appreciable effect on the reaction rate. For example for (I; X = Me, Y = H), the rate constants ($k \times 10^4$ sec.$^{-1}$) at 25° are: 7·06 in pure nitromethane, 7·58 in 19 : 1, and 7·75 in 9 : 1 (v/v)

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† Following the appearance of TNBSA. Calibration curves were determined in each solvent and used for the kinetic analysis.

‡ Determining the decrease of optical density at 414 mμ.

TABLE 1

Solvent effect on rate at 25°

Solvent	N	M	N–D 80–20%	N–D 20–80%	A	D
$k \times 10^4$ sec.$^{-1}$	42·4	14·5	10·5	3·27	3·10	0·34

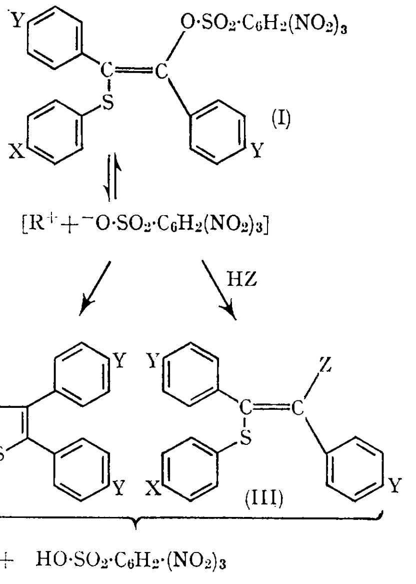
N = nitromethane, M = methanol, A = acetone, D = dioxan.

TABLE 2

Substituent effect for X-substituted esters (I; Y = H) *in nitromethane at* 25°

X		4-OMe	4-Me	H	4-Cl	3-Cl
$k \times 10^4$ sec.$^{-1}$	..	10·17	7·06	3·44	1·72	1·21

nitromethane–methanol. This small kinetic effect of added methanol is however accompanied by a dramatic change in the products. In the absence of methanol the main products, besides TNBSA, are benzo[*b*]thiophen derivatives (II);§ when methanol is present, even in small amounts, the main products are the 1,2-diaryl-2-arylthio-1-methoxyethylene derivatives (III; Z = OMe). This is typical of a S_N1-type reaction in which the product-determining step involves a common precursor which is consumed in a fast stage subsequent to the slow ionization process.



Tables 2 and 3 show kinetic data of the effects of substituent, (X), on the phenylthio-ring, and (Y) on the two phenyl rings. Electron-donating substituents in both X and Y increase the reaction rate, thus supporting the hypothesis of an electron-deficient intermediate. The data for X-substituents satisfactorily fit the Hammett equation with a ρ value of $-1·5$ (using Hammett's σ). Such an effect can be explained in terms either of an inductive–conjugative stabilization of a vinyl carbonium ion through the sulphur atom or of anchimeric assistance of the sulphide sulphur which would lead to a thiocyclopropenium ion as intermediate. The degree of sulphur participation is under current investigation.[3]

TABLE 3

Substituent effect for Y-substituted esters (I; X = H) *in nitromethane at* 25°

Y		4-Me	H	4-Cl
4×10^4 sec.$^{-1}$	..	42·4	3·44	1·03

The effect of the Y-substituents is quite large. Due to synthetic difficulties in obtaining the mono-Y-substituted esters it is not known whether the observed effect is due mainly to the Y-substituent on the phenyl ring near the reaction centre or to those on both rings, to comparable extents.¶ In any case, it certainly indicates that the reaction is largely facilitated by conjugation with the phenyl residues. This is also supported by the fact that when a phenyl group is not present at the ethylenic carbon linked to the TNBSA residue no reaction is observed under similar or more drastic conditions.[3]

The role of the leaving group is also under investigation. Qualitative results suggest that it is important in determining the high reactivity of the system since simple benzenesulphonic esters as well as mono- and dinitro-derivatives fail to react under similar or more forcing conditions except under BF_3 catalysis.

This preliminary kinetic investigation offers direct evidence that vinyltrinitrobenzenesulphonates (I) react, under the conditions used, *via* a

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§ In nitromethane at 25° when X is not an electron-donor substituent other products such as benzil, disulphides, and 1,2-diaryl-1,2-diarylthioethylene derivatives are formed along with only minor amounts of (II).

¶ Apparently the few available data can be correlated by the Hammett equation by use of Brown's σ^+ constants.

rate-determining fission of the carbon–oxygen bond,[4] and quite clearly shows that unsaturated cationic species may exist as true reaction intermediates. This is an independent confirmation of the mechanism proposed for some electrophilic additions to acetylenic derivatives.[5]

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[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry", Cornell University Press, Itacha, 1953, pp. 345–355.

[3] G. Capozzi and G. Modena, unpublished results.

[4] For reported S_N1-type reactions of olefinic compounds see: C. A. Grob and G. Cseh, *Helv. Chim. Acta*, 1964, **47**, 194; C. A. Grob, J. Csapilla, and G. Cseh, *ibid.*, p. 1590; S. J. Huang and M. V. Lessard, *J. Amer. Chem. Soc.*, 1968, **90**, 2432.

[5] See for instance: W. Drenth and H. Hogeveen, *Rec. Trav. chim.*, 1964, **83**, 167; D. S. Noyce and M. D. Schiavelli, *J. Amer. Chem. Soc.*, 1968, **90**, 1020; R. C. Fahey and Do-Jae Lee, *ibid.*, p. 2124, and references cited in these papers.