Anchimeric Assistance Effects due to the β-Sulphur Atom in Solvolytic Reactions of Dialkyl-β-thiovinyl Sulphonates

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Summary Large rate enhancements (10^4—10^5) due to anchimeric assistance by the β-sulphur have been observed in S_N1-type reactions of 1,2-dialkyl-2-alkylthiovinyl sulphonates.

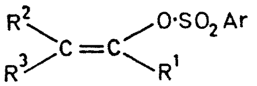
WE have recently reported[1] kinetic and stereochemical evidence of β-sulphur participation in S_N1-type reactions of *trans*-β-thiovinyl sulphonates (I). The small rate enhancements estimated when R^1 is an aryl group (rate factors of 1—35, depending on the nature of R^2, solvent, and temperature conditions[2]) as well as the rather large negative ρ values[1,2] measured for substituents on the α-aryl residue have been interpreted in terms of a "late" participation of the β-sulphur along the reaction path. It has been argued that the two possible intermediates, the open vinyl cation (II) and the bridged thiirenium ion (III) could be of comparable stability when R^1 is an aromatic residue capable of delocalizing the positive charge formally at the α-carbon of (II). Substitution of an α-alkyl group for the α-aryl group should destabilize the open ion (II) more than the bridged ion (III) and hence magnify the kinetic effects of anchimeric assistance in the reactivity of esters of type (I).

Rate coefficients and activation parameters for the esters (IV) *and* (I) ($R^1 = R^2 =$ alkyl)

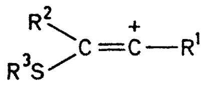
Ester[a,b]		Solvent[c] ratio	T/°C	k/s^{-1}[d]	E_a/kcal mol^{-1}	$\Delta S^\ddagger$/cal mol^{-1} K^{-1}[f]
(IV)	$Me_2C:C(tnbs)Me$	9:1	25	($1{\cdot}1 \times 10^{-8}$)[g]	—	−12
		9:1	100	$5{\cdot}55 \times 10^{-5}$	25·3[h]	−13
(Ia)	$Me(MeS)C:C(tnbs)Me$	9:1	25	$4{\cdot}07 \times 10^{-4}$	22·3[i]	− 1
(Ib)	$Me(PhS)C:C(tnbs)Me$	9:1	25	$4{\cdot}70 \times 10^{-5}$	—	—
		19:1	25	$4{\cdot}31 \times 10^{-5}$	—	—
(Ic)	$Pr^n(MeS)C:C(tnbs)Pr^n$	19:1	25	$6{\cdot}53 \times 10^{-3}$	—	—
(Id)	$Pr^n(PhS)C:C(tnbs)Pr^n$	19:1	25	$6{\cdot}32 \times 10^{-4}$	21·6[i]	− 3

[a] tnbs = 2,4,6-trinitrobenzenesulphonate. [b] All new compounds gave satisfactory elemental analysis and displayed spectroscopic characteristics in agreement with the assigned structure. [c] Nitromethane : methanol. [d] Average of at least two kinetic runs; mean deviation ±3%. [e] Estimated error ±1 kcal mol^{-1}. [f] Estimated error ±2 cal mol^{-1} K^{-1}. [g] Value extrapolated from higher temperature measurements. [h] From measurements in the range 80—110°. [i] From measurements in the range 15—35°.

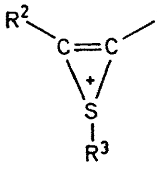
This communication reports the rates of solvolysis of the 1,2-dialkyl-2-alkylthio- and 1,2-dialkyl-2-arylthio-vinyl 2,4,6-trinitrobenzenesulphonates listed in the Table together with those of the trimethylvinyl analogue (IV) chosen as a model compound for unassisted unimolecular reactivity.[3] Compounds (Ia)—(Id) were prepared by a described method[4] and compound (IV) was obtained by decomposition of 3-phenyl-1-trimethylvinyltriazene in the presence of trinitrobenzenesulphonic acid following a method first described by Jones and Maness.[5] The rates of solvolysis of the esters here considered were measured in nitromethane–methanol mixtures in which the reaction mechanism of esters (I; R^1 = Ar) has been investigated in detail[1,2] and the rate coefficients (the first-order rate law was well obeyed up to at least 80%) together with the available activation parameters are shown in the Tabe.



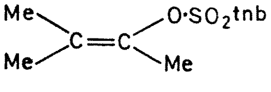
(I)



(II)



(III)



(IV)

tnb = 2,4,6-trinitrobenzene.

The data of the Table allow the following c onsiderations: (a) 1,2-Dialkyl-2-methylthiovinyl derivativesl (Ia) and (Ic) react 4×10^4 and 6×10^5 times faster than the trimethylvinyl analogue. Since steric and inductive effects only play a minor role,[2] the rate enhancements here observed are certainly to be ascribed to anchimeric assistance by the β-sulphur. The values of activation entropy for (IV) and (Ia) are significantly different and shifted in the expected direction.[6] (b) 1,2-Dialkyl-2-phenylthiovinyl derivatives (Ib) and (Ie) react *ca.* 10 times slower than the corresponding 2-methylthio-compounds (Ia) and (Ic). This effect of substituents bound to the β-sulphur is consistent with the nucleophilic participation of the β-sulphur atom in the transition state. It is noteworthy that a similar substitution in the α-phenyl derivatives of (I) results in a much smaller retardation[1] (by *ca.* 2—3 times). (c) The 1,2-di-n-propyl derivatives (Ic) and (Id) react *ca.* 15 times faster than the corresponding 1,2-dimethyl compounds (Ia) and (Ib), respectively. The rate increase is larger than expected on the basis of an increased inductive effect of the alkyl chain. The reasons for such an effect are obscure although relief of steric strain[7] on going to the transition state may be suggested as one of the factors involved in the enhanced reactivity of the di-n-propyl derivatives.

The present results, therefore, verify the expectation that the bridged ion (III) is actually much more stable than the open vinyl cation (II) when R^1 = alkyl. Our conclusions parallel those recently reached by Pincock and Yates[8] indicating that the bromination of 1-phenylpropynes occurs *via* an open vinyl cation, whereas that of hex-3-yne proceeds through a bridged bromonium ion. Finally, it is emphasised that the fact that the rate enhancements here recorded for anchimeric assistance in vinylic solvolyses are even greater than those usually observed for β-thioethyl derivatives.[9]

(*Received, July 12th,* 1971; *Com.* 1182.)

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