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CONFORMATIONAL STUDIES OF TRIMETHYLENE SULFITE AND RELATED COMPOUNDS II*

EVIDENCE FROM THE RATE OF ALKALINE HYDROLYSIS

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The conformation of trimethylene sulfite and a number of 2-substituted derivatives has been studied by investigating the dipole moments, IR spectra and rates of alkaline hydrolysis of these compounds (1). Simultaneously and closely linked up with the work in our laboratory, NMR- and IR-spectroscopic studies on these and related systems have been carried out in London (2, 3, 4).

From a comparison of the dipole moments of the six-membered cyclic sulfites (on which we hope to report in detail, before long) we concluded that the S=O bond takes up preferentially an axial position. In fact it was concluded that an equatorial S=O bond is several Kcalories/mole less stable than an axial bond.

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* Reference 2 is considered as part I

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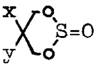
In the present paper an account is given of the kinetic investigation.

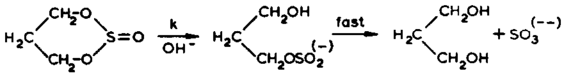
The rates of hydrolysis of the cyclic sulfites have been measured at 25°C, in aqueous solutions containing 1% dioxan. Use was made of an automatic titrator technique in a similar way as described earlier (5). From the pseudo-first order kinetics observed at constant pH, the second order rate coefficients of the alkali-catalysed reaction could be evaluated, for each compound by suitable variation of the pH. The result is shown in Table 1.

TABLE 1

Bimolecular Rates of Alkaline Hydrolysis of 2-Substituted Trimethylene Sulfite at 25°.

	mp./bp.	k (l.mole^{-1}min.$^{-1}$)
Bu^t > H	47 - 47.5° 37.5 - 38.5°	14 80
H > H	66 - 67°/14 mm	31
NH_2 > CH_3	(HCl-salt 180 - 181°)	95
$HOCH_2$ > $HOCH_2$	104 - 105°	1.6×10^2
$O=S<^{O-CH_2}_{O-CH_2}>$	149.5 - 150°.5	15×10^2
Cl > CH_3	70 - 71°	18×10^2
NO_2 > CH_3	112° 59 - 60°	6.0×10^3 29×10^3
NH+ > CH_3		9.0×10^3

It has previously been established by Bunton, de la Mare, Tillett and others (6, 7) that in the alkaline hydrolysis of cyclic and open-chain sulfites, hydroxide ions attack the sulfur atom in a first, rate-determining step. This is followed by a fast step, in which the intermediate half-ester decomposes under liberation of sulfite ions:



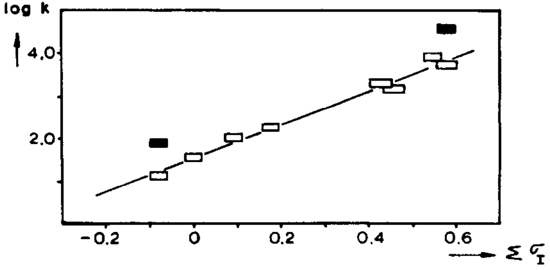
It may be assumed that the mechanism adopted by the presently investigated compounds is essentially similar.

Now, if these cyclic esters are conformationally analogous in that the sulfite group has a constant orientation relative to the remainder of the ring, and if the hydrolyses proceed via similar transition-states, then steric effects should be absent in the relative rate constants of these compounds. We may try, therefore, whether our rate constants follow a correlation of the type (9):

$$\log k/k_0 = \rho_I \Sigma \sigma_I$$

where $\Sigma\sigma_I$ is the sum of the inductive constants for the substituents at carbon atom 2, and ρ_I is a characteristic constant for the reaction.

Fig. 1



The result is shown in Fig 1. The values of $\Sigma\sigma_I$ have been calculated from recent compilation of σ_I values (10). A statistical factor of two was applied to the bimolecular rate constant of pentaerythrityl disulfite. The σ_I value of the sulfite ring itself was estimated from the pK_A value 6,83 of 2-amino-2-methylpropylene-1,3-sulfite, by correlating the pK_A values of some amines of the type $R_1R_2(CH_3)CNH_2$ with the quantity $\Sigma\sigma_I$ for the groups R_1 and R_2, and assuming a linear relationship (cf. 11).

If allowance is made for the estimated standard error in σ_I of ± 0.03 and the somewhat larger uncertainty in the case of the ammonium group, it can be inferred that a linear relationship holds for all compounds investigated except two. From the slope ρ_I is found to be 4.0. The two deviating compounds both have a five- to sixfold increased rate of hydrolysis compared to their respective isomers. It can be shown by other physical means that the two sulfites in question exist in the dissolved state as conformational equilibria (8).

It is seen that the low pK_A value of 2-amino-2-methylpropylene-1,3-sulfite correlates well with the high rate of hydrolysis of pentaerythrityl disulfite. From this we conclude that the sulfite group is strongly electronegative. Taking into account that the interposition of a methylene grouping reduces the inductive effect of a substituent to about 30%, it follows from the foregoing that a sulfite group exerts by means of each of its two σ-bonds a -I effect comparable to that of a nitro-group.

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