boxylate ion, there seems to be a difference in magnitude between the primary deuterium isotope effect (values greater than 2) and the secondary isotope effect (values less than 2). While these are subtle differences, they probably are real. It should be pointed out that part of the observed primary isotope effect may consist of a contribution from a secondary isotope effect. It may be concluded that the use of deuterium oxide solvent isotope effects as a criterion to distinguish between general base- and nucleophile-catalyzed reactions is ambiguous, but when applied in a restricted sense it may be empirically rewarding.

Acknowledgments.—The authors are pleased to acknowledge the use of unpublished material of Drs. C. A. Bunton and V. J. Shiner, Jr.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY, LAFAYETTE, IND.]

Hydrolysis of Ethylene and Dimethyl Sulfite and the Origin of Strain in Cyclic Esters[1]

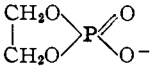
BY ROBERT EARL DAVIS

RECEIVED AUGUST 8, 1961

The aqueous alkaline hydrolysis of dimethyl sulfite and of ethylene sulfite has been compared. Ethylene sulfite reacts 360 times as fast at 25° as the dimethyl ester. The heats of hydrolysis have been measured and found to be nearly equal, indicating that there is no thermodynamic strain in the five-membered ring ester. The data have been interpreted with the aid of LCAO-MO calculations on the magnitude of 1,3-non-bonded interactions. The data are discussed in relationship to the behavior of phosphate esters.

Introduction

The mechanisms of reaction of carboxylic esters have received great attention for many years.[2-4] However, only within the past few years have systematic investigations of other types of esters received study. Phosphate esters[5,6] are of great interest as they are metabolites of ribonucleic acids, sugars and other hydroxylic compounds. Derivatives of ethylene phosphate (I) are known as important biological chemicals.[7,8] The tremendous reactivity of I compared to dimethyl phosphate (II) has been described.[9] Compound I hydrolyses about 10^7 times faster than II in alkaline solution. The tremendous kinetic acceleration is present only in the five-membered ring as trimethylene phosphate (III) is much more like II in its behavior.[10] Bunton[11-17] and co-workers have studied the hydrolysis of esters of sulfurous acid in detail as models for understanding phosphate esters. These authors determined the kinetic order and the position of bond cleavage in sulfites using O^{18}. The alkaline hydrolysis of ethylene sulfite was found to be extremely fast[12,14] and only recently has Tillett[17] given approximate values of the second-order rate constant. The authors conclude that 1,3-interelectronic repulsions are responsible for the very fast hydrolysis of the five-membered ring esters.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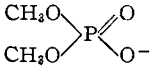
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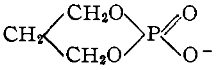
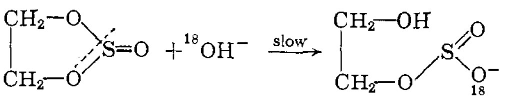

III

It is the purpose of the present investigation to establish accurate rate constants for the extremely fast hydrolysis reactions and to present thermochemical data. Rather unusual and non-conventional kinetic techniques have been used. The origins of strain in cyclic esters are also discussed.

Results

Kinetic Order.—The data are presented in Tables I–V. The reaction of hydroxide ion with the sulfite esters is strictly first order in hydroxide ion and first order in ester over a very wide variation of concentrations. The rate of production of one mole of sulfur dioxide as either bisulfite or sulfite ion is identical with the rate of consumption of two moles of hydroxide. Differential titration indicates that no monoester is present in greater than 1% concentration. These data are in agreement with those of Bunton[11-17] who also concluded that the reaction was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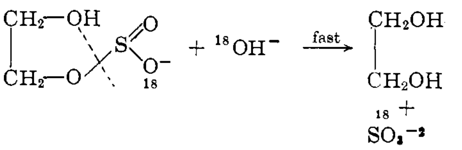
(2)

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(1) Paper II, Esters of Inorganic Acids; paper I, R. E. Davis, *Proc. Indiana Acad. Sci.*, **70**, 106 (1961). Presented in part at the 140th National American Chemical Society Meeting, Chicago, Ill., 1961.

(2) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 751–782.

(3) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, pp. 314–353.

(4) M. L. Bender, *Chem. Revs.*, **60**, 53 (1960).

(5) P. W. C. Barnard, C. A. Bunton, D. R. Llewellyn, K. G. Oldham, B. L. Silver and C. A. Vernon, *Chemistry & Industry*, 760 (1955).

(6) Chem. Soc. London Special Publ. No. 8, 1957.

(7) D. M. Brown and A. R. Todd, *J. Chem. Soc.*, 52 (1952).

(8) D. M. Brown, D. I. Magrath and A. R. Todd, *ibid.*, 2708 (1952).

(9) J. Kumamoto, J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **78**, 4858 (1956).

(10) L. Kéoy and E. M. Crook, *J. Chem. Soc.*, 710 (1961).

(11) C. A. Bunton, P. B. D. de la Mare, P. M. Greaseley, D. R. Llewellyn, N. H. Pratt and J. G. Tillett, *ibid.*, 4751 (1958).

(12) C. A. Bunton, P. B. D. de la Mare, D. R. Llewellyn, R. B. Pearson and J. G. Pritchard, *Chemistry & Industry*, 490 (1956).

(13) C. A. Bunton, P. B. D. de la Mare and J. G. Tillett, *J. Chem. Soc.*, 4754 (1958).

(14) C. A. Bunton, P. B. D. de la Mare, A. Lennard, D. R. Llewellyn, R. B. Pearson, J. G. Pritchard and J. G. Tillett, *ibid.*, 4761 (1958).

(15) E. D. Davies and J. G. Tillett, *ibid.*, 4766 (1958).

(16) C. A. Bunton, P. B. D. de la Mare and J. G. Tillett, *ibid.*, 1766 (1959).

(17) J. G. Tillett, *ibid.*, 37 (1960).

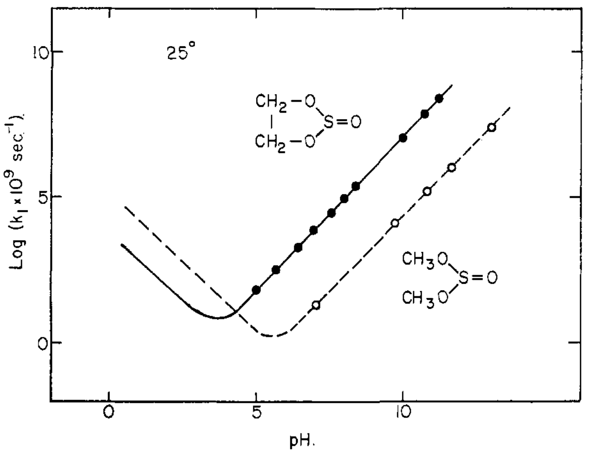

Fig. 1.—*p*H Profiles. Plot of first-order rate constant *vs.* *p*H for the hydrolysis of ethylene sulfite and dimethyl sulfite at 25°. Points represent data of this investigation.

The position of bond cleavage in both sulfite esters[11-17] is S–O in acid and base as determined by hydrolysis in H_2O^{18}.

Using the data of Bunton on the acidic hydrolysis[13,16] and the present data on alkaline hydrolysis, *p*H profiles have been constructed for ethylene sulfite (Fig. 1) from the equation

$$\frac{-d(\text{ethylene sulfite})}{dt} = 1.01 \times 10^{-5}(\text{ester})(H^+) + 106(\text{ester})(OH^-) = k_1(\text{ester}) \text{ moles/liter second} \quad (3)$$

The *p*H profile of the reaction of dimethyl sulfite is also given from the data of Voss[18] in acidic solution and from the data of Table IV:

$$\frac{-d(\text{dimethyl sulfite})}{dt} = 2.16 \times 10^{-4}(\text{ester})(H^+) + 0.30(\text{ester})(OH^-) \quad (4)$$

If a water term (k_{H_2O} (ester)(H_2O)) is present, it is certainly of very small importance in the hydrolysis of these sulfite esters. General acid and general base terms are also of small importance. The activation parameters are given in Tables VI and VII.

Salt Effects.—The rates of alkaline hydrolysis of these sulfite esters are nearly independent of the ionic strength (Tables III and V). This is in agreement with the suggestion that the reaction of the diester (a neutral molecule) with hydroxide ion is the rate-determining reaction. Had reaction 2, the attack of hydroxide on the monoester anion, been the rate-controlling step, then the Brönsted–Christiansen–Scatchard equation would have predicted a linear relationship between log k_2 and $\mu^{1/2}$ with a slope of +1 at low ionic strength. Potassium chloride increases the rate of hydrolysis of dimethyl sulfite but slows the rate of hydrolysis of ethylene sulfite. However, the effects do not follow the predictions of a uni-uni charge-type ionic reaction.

TABLE I

HYDROLYSIS OF ETHYLENE SULFITE, $T = 25.00 \pm 0.01°$

Conditions	μ, M^a	*p*H^b	Method^c	k_2, M^{-1} sec.$^{-1d}$
KH_2PO_4 buffer	0.05	5.01	SI	104 ± 3
KH_2PO_4–NaOH buffer	.05	5.88	SI	106 ± 4
KH_2PO_4–NaOH buffer	.05	6.79	SI	110 ± 4
0.10 *M* KCl	.10	7.00	TS	104 ± 3
KH_2PO_4–NaOH buffer	.05	7.40	SI	97 ± 5
0.10 *M* KCl	.10	8.00	TS, T	104 ± 4
.10 *M* KCl	.10	8.30	TS, T	105 ± 4
.10 *M* KCl	.10	8.50	TS, T	103 ± 4
.10 *M* KCl	.10	..	A	120 ± 25
.07 *M* KCl, 0.02 *M* NaOH	.09	..	I	110 ± 10
			Average	106 ± 5

^{a} Ionic strength. ^{b} ±0.01. ^{c} T, titrimetric method; SI, spectrophotometric–iodometric method; TS, titrimetric method at static *p*H; A, amperometric method; I, indicator method. ^{d} Specific second-order rate constant. Deviations are given in terms of σ; average of at least three runs. Ethylene sulfite concentration has been varied 90-fold.

TABLE II

HYDROLYSIS OF ETHYLENE SULFITE AT 0°

Conditions^a	μ, *M*	*p*H^b	Method	k_2, M^{-1} sec.$^{-1}$
KH_2PO_4–NaOH	0.05	7.52	SI	26.2 ± 0.4
KH_2PO_4–NaOH	.05	7.05	SI	30.1 ± 0.5
0.08 *M* KCl–0.001 *M* NaOH	.08	...	I	20 ± 4
0.10 *M* KCl	.10	10.00	TS	25.7 ± 0.9
			Average	25.5 ± 2.5.

^{a} See Table I. ^{b} *p*H at 0°, pK_w = 14.94.

TABLE III

SALT EFFECTS ON THE HYDROLYSIS OF ETHYLENE SULFITE AT 25.00°

*p*H = 8.30	"*p*H Stat"	
Salt^a	μ, M^b	10^4 k_1, sec.$^{-1c}$
0.0091 *M* KCl	0.0095	2.25 ± 0.08
.046 *M* KCl	.046	2.30 ± .09
.0832 *M* KCl	.083	2.20 ± .05
.100 *M* KCl	.10	2.16 ± .05
.182 *M* KCl	.18	2.00 ± .07
.05 *M* $BaCl_2$	.12	2.50 ± .09
.10 *M* $BaCl_2$	.30	2.75 ± .10

^{a} In each solution 0.0001 *M* KH_2PO_4 has been used as an initial buffering solution. The *p*H is adjusted to 8.30 with sodium hydroxide and then the ester was added. ^{b} Ionic strength. ^{c} First-order rate constant as obtained using the Guggenheim procedure.

The hydrolysis of ethylene sulfite is increased slightly by the presence of barium chloride (Table III). A multi-valent cation would be expected to have an abnormally large effect if reaction 2 were the rate step. Barium chloride (0.167 *M*) increases[9,19] the rate of hydrolysis of ethylene phosphate monoanion by 8.4-fold at 25°. The effects of calcium and magnesium ions are very great on the hydrolysis of pyrophosphates.[19b]

Heats of Reactions.—The heats of alkaline hydrolysis of ethylene sulfite and dimethyl sulfite are the same within experimental error (Table VI). The heats of acidic hydrolysis are also the same as one would only need add the heat of neutralization of the sulfite ion and of the hydroxide ions. *Thus there is no strain in the ethylene sulfite ring.* Such a result suggested that a transesterification equilibrium might be readily obtained. Upon

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[18] W. Voss and E. Blanke, *Ann.*, **485**, 258 (1931).

[19] F. H. Westheimer, Chem. Soc. London, Special Publ. No. 8, 1957, p. 8-12; (b) p. 6.

TABLE IV

HYDROLYSIS OF DIMETHYL SULFITE

Conditions	μ, M	pH	Method	k_2, M^{-1} sec.$^{-1}$
		T = 25.00°		
KH_2PO_4–NaOH	0.10	7.00	SI	0.31 ± 0.01
Na_2HPO_4–NaOH	.40	9.90	T	.35 ± .01
Na_2HPO_4–NaOH	.40	10.70	T	.34 ± .02
Borax–NaOH	.08	11.41	T	.30 ± .02
Borax–NaOH	.10	11.40	T	.30 ± .01
0.10 M KCl	.10	11.40	TS	.31 ± .02
.04 M KCl	.05	11.40	TS	.29 ± .02
.01 M KCl	.02	11.40	TS	.27 ± .02
			Average	0.30 ± 0.02
0.01 M NaOH	.01	...	T	0.22[a]
Universal buffer	?	11.60	T	.15[b]
Universal buffer	?	11.79	T	.17[b]
		T = 0.00°		
0.10 M NaOH	0.10	...	T	0.0204
Borax–NaOH	.10	11.62	T	.0195
0.04 M NaOH	.04	...	T	.023[b]
			Average	0.021 ± 0.01

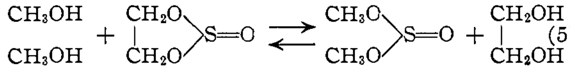
[a] Data of Voss, ref. 18. [b] Data of Tillett, ref. 17; see Table I for notes.

TABLE V

SALT EFFECTS ON THE HYDROLYSIS OF DIMETHYL SULFITE AT 25°, pH STAT

Ionic strength KCl	k_2, M^{-1} sec.$^{-1}$
0.01	0.24 ± 0.01
.02	.27
.05	.29
.08	.30
.10	.30
.40	.31

mixing pure methanol with ethylene sulfite in sealed ampules, a slow production of dimethyl sulfite and ethylene glycol was observed. The equilibrium was reached from both directions in twenty months. The compounds are easily separated and analyzed using gas chromatography. There was no indication that the mixed ester IV was present in any significant concentration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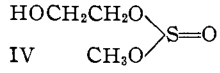
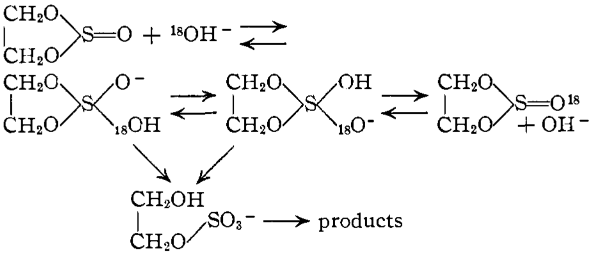

IV

It would be expected to undergo a facile unimolecular cyclization reaction, since there is no strain in the five-membered ring. It would also be conceivable that this ester would decompose to ethylene sulfite and methanol in the V.P.C. column. Because of this, the value of K = 0.028 M^{-1} of eq. 5 must be taken with some reserve. The value of ΔF is 2.1 kcal./mole. The important fact is that comparable amounts of the materials are present at equilibrium.

Discussion

Considering the data on phosphates and sulfites in Tables VI and VII, it is observed that the behaviors of these esters are markedly different, contrary to the earlier suggestions of Bunton and co-workers.[11–17] The five-membered ring phosphate is strained[20] while the five-membered sulfite is not. The five-membered ring phosphate is about 10^7 times more reactive than the dimethyl ester in both acidic and basic hydrolysis. Ethylene sulfite is 360 times more reactive in base than dimethyl sulfite, whereas in acid the dimethyl compound is now 22 times more reactive (Tables VI and VII and Fig. 1). In both series the trimethylene ester more closely resembles the dimethyl ester.

Position of Bond Cleavage and the Question of An Intermediate.—In both cyclic systems the attack of hydroxide ion occurs on the heteroatom, sulfur or phosphorus. Ethylene phosphate does not exchange O^{18} in alkaline solution[21] while ethylene sulfite exchanges to a small extent.[22]



Westheimer has provided a discussion of some possible geometric arrangements of the activated complexes for the acid-catalyzed hydrolysis and exchange in ethylene phosphate. In view of the problems of discussing the nature of the activated complex in any system, it is more profitable to consider the ground states and the origin of the strain. The origin of kinetic acceleration will be discussed in a forthcoming paper in this series.

The Magnitude of Steric Effects in Cyclic Esters.—The usual discussion of the magnitude of steric effects in organic structures[24] assumes that the strain energy, E_s, is the sum of three terms due to stretching the valence bonds, bending the valence angles and torsion about the dihedral angles. The stretching and bending energies usually are assumed to follow a quadratic potential and the torsional energies a cosine law.[25,26]

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(20) J. R. Cox, Jr., R. E. Wall and F. M. Westheimer, *Chemistry & Industry*, 929 (1959).

(21) P. C. Haake and F. H. Westheimer, *J. Am. Chem. Soc.*, **83**, 1102 (1961).

(22) Bunton[11] interpreted their data on ^{18}O exchange into the ethylene sulfite system to indicate that the exchange does not occur in significant competition with hydrolysis. In an experiment starting with H_2O^{18} enriched to 0.940 atom % excess and ethylene sulfite in alkaline solution, the recovered sulfite has 0.016 atom % excess of O^{18}. We interpret their data to indicate that there is some exchange and that there is an intermediate as there is in $B_{AC}2$ ester hydrolysis.[23]

(23) M. L. Bender, *J. Am. Chem. Soc.*, **73**, 1626 (1951).

(24) F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(25) That the cosine behavior is to be expected can be supported by an LCAO–MO treatment on adjacent non-bonded interactions. The quantum mechanical expression for a four-electron, two-orbital expression combining the atomic orbitals from atoms A and B contains an S, β and an S^2 term which is small and can be neglected. Consideration of the angular dependence of the integrals S and β gives an expression for the torsional energy, E_t

$$E_t = \frac{1}{2} V_r (1 - \cos n\Delta\theta_R)$$

where V_r is the torsional barrier height about the bond r, $\Delta\theta_R$ is the deviation from the normal dihedral angle and n is an integer dependent upon the character of the bond and the atoms forming the bond.

TABLE VI

BASIC HYDROLYSIS OF ESTERS

Phosphates	T, °C.	k_2, M^{-1} sec.$^{-1}$	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	ΔH^{c}	Cleavage
Ethylene[d]	25	4.6×10^{-4}				P–O
Dimethyl[d]	25	3×10^{-11}	27.5	−14		Some P–O
	115	2.2×10^{-6}				Major C–O
	125	6.1×10^{-6}				
Trimethyl[e]	0.4	1.24×10^{-5}	15.2	−26	−20 ± 2	
	35	3.39×10^{-4}				
Dimethyl β-hydroxyethyl[f]	30				−21.9 ± 0.4	
Methyl ethylene[f]	30				−29.5 ± 0.6	
Sulfites						
Ethylene	0	25.5				
	25	106	7.9	−23	−33.5 ± 0.5	S–O
Trimethylene[g]	0	8.0×10^{-2}				
	25	5.0×10^{-1}	11.3	− 8		S–O
Dimethyl	0	2.1×10^{-2}				
	25	3.0×10^{-1}	12.2	−21	−32.0 ± 0.6	S–O

[a] Kcal./mole at 25°. [b] Cal./mole degree at 25°. [c] Kcal./mole, heat of reaction. [d] Ref. 9. [e] Ref. 5. [f] Ref. 20. [g] Ref. 14.

TABLE VII

ACIDIC HYDROLYSIS OF ESTERS

Phosphates	T, °C.	k, M^{-1} sec.$^{-1}$	$\Delta H^{\ddagger a}$	$\Delta S^{\ddagger b}$	Cleavage
Ethylene[c]	0	1.1×10^{-3}			P–O
	30	1.7×10^{-1}			
	37[d]	1.5×10^{-2}			
Trimethylene[d]	100	6.9×10^{-5}			
Dimethyl	118	2.2×10^{-4}			P–O C–O
Sulfites					
Ethylene[e]	0	4.1×10^{-7}			
	25	1.01×10^{-5}	20.2	−16	S–O
	45	7.5×10^{-5}			
	73	1.27×10^{-4}			
Trimethylene[e]	35	1.41×10^{-5}			
	60	1.57×10^{-4}	20.2	−13	S–O
Dimethyl	0	1.0×10^{-5}[e]			
	25	2.16×10^{-4}[f]	19.3	−10.6	S–O

[a] Kcal./mole at 25°. [b] Cal./mole degree at 25°. [c] Barium salt, $[H^+] = 0.10\ M$, data calculated from results of Westheimer *assuming* a second-order reaction; $\Delta H^\ddagger$ and $\Delta S^\ddagger$ have not been calculated due to the experimental uncertainties; ref. 19. [d] Guanidinium salt, $[H^+] = 0.05\ M$, second-order rate constant calculated from the data of Keoy, ref. 10. [e] Refs. 11–17. [f] Ref. 18.

To apply the equation[26] the parameters must either be known or judicious estimates be made. Unfortunately the molecular dimensions of none of the molecules under discussion have been measured using the techniques of X-ray or electron diffraction. Molecular models have been constructed using average bond distances and angles.

Sulfite Esters.—It is well-known that three-bonded sulfur forms a shallow pyramid.[27] If the five ring atoms of ethylene sulfite defined a plane, then the exocyclic oxygen would be definitely above or below this plane. Allowing the ring to pucker,[28] as does cyclopentane, still does not allow complete symmetry about the sulfur. In agreement with these expectations it has been found that the n.m.r. spectrum of ethylene sulfite is very rich in fine structure indicating that the two pairs of hydrogens are not completely equivalent.[29]

Of the various parameters, the choice of k_r and V_r for the –O–SO bond and the k_α's for the SO_3 unit are the most uncertain due to the paucity of data.[30] Average values were chosen using structural data reviewed by Abrahams.[27] Nevertheless, the conclusion is interesting in that estimates of the strain in ethylene sulfite are less than 2 kcal./mole. *Thus there should be no strain in the ethylene sulfite ring.* This agrees with the thermochemical results.

Phosphates.—Westheimer[31] has estimated from theory that the strain in the ethylene phosphate ring would be 3 to 4 kcal./mole. Experimentally there is about 9 kcal. of strain. In re-examining this calculation we find that the most serious uncertainty arises in assigning values of k_r, k_α and V_r to the bonds and angles in the phosphate group. Westheimer has suggested that 1,3-non-bonded interactions between the oxygen atoms may give rise to the strain. Bunton and co-workers have accepted this explanation for all cyclic esters. Westheimer has also stated that a cyclic five-membered ring phosphate may have unfavorable dihedral angles. The first of these suggestions has been considered in this present study. Theoretical discussion of dihedral angle effects and partial double bond character as caused by strong 1,2-interaction will be debated in a forthcoming paper.

Estimate of 1,3-Non-bonded Interactions. The model chosen for calculation is a two electron

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(26) The complete expression for E_s in kcal./mole is given as

$$E_s = 7.21 \times 10^{-8} \sum_{r} k_r(\Delta X_r)^2 + 2.18 \times 10^9 \sum k\alpha(\Delta\omega_\alpha)^2 + \frac{1}{2} V_r (1 - \cos n\Delta\theta_R)$$

where k_r is the stretching force constant for bond r in dyne/cm. ΔX_r is the deviation from normal bond length in cm. × 10^8, $k\alpha$ is the bending force constant for the angle in erg/radians^2, $\Delta\omega\alpha$ is the deviation from the normal bond angle in degrees.

(27) S. C. Abrahams, *Quart. Revs.*, **10**, 407 (1956).

(28) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

(29) J. G. Pritchard and P. C. Lauterbur, *ibid.*, **83**, 2105 (1961). The authors have observed this asymmetry in the ethylene sulfite ring and have used this information to prepare the two isomeric forms of propylene 1,2-sulfite. They also concluded that the ethylene sulfite ring system is not strained.

(30) The high-resolution infrared spectra of the sulfite esters are being considered by D. Mayo of M.I.T. In private communications he claims that the spectra are not abnormal.

(31) Ref. 19, pp. 13–15.

atom approaching another two electron atom. Slater nodeless AO orbitals[32] have been used for this homopolar LCAO–MO molecule. The screening factor has been kept constant. The energy difference between the bonding ($\psi_a + \psi_b$) state (as the $2s\sigma_g$) and the ($\psi_a - \psi_b$) anti-bonding state (as the $2s\sigma_u{}^*$) has been used as an estimate of the repulsion forces. Calculations have been made for the $2s\sigma$ orbitals, the $2p\sigma$ orbitals and the $2p\pi$ orbitals (Fig. 2). The repulsion, *V*, in kcal. is the largest for $2p\sigma$ interaction and least for the $2p\pi$ interaction. This is the expected order. The oxygen atoms in ethylene sulfite are about 2.8 to 2.9 Å. apart. The repulsion forces at these distances are quite low, being about 0.8 kcal. for $2p\sigma$, 0.3 kcal. for $2s\sigma$ and less than 0.1 kcal. for $2p\pi$ interactions.[33] These values are probably correct within a factor of two and probably the true values are more nearly twice as large.

Two conclusions are evident: 1. *The 1,3-non-bonded interactions are moderately small between two oxygen atoms.* In the LCAO–MO approximation as applied to molecules, 1,3-interactions are usually set equal to zero. The small magnitude of the energies calculated when one considers these interactions validates this approximation.

The hybridization of the endocyclic oxygens is probably sp^2 leaving a filled $2p_z$ non-bonding orbital and one sp^2. The non-bonded sp^2 orbitals will not interact across the ring to any extent. The $2p\pi$ interaction (formed from two $2p_z$ orbitals) is very weak. The exocyclic oxygen has filled $2p_z$ and 2s orbitals in the first approximation. The $2p\pi$ interaction between the exocyclic oxygen and an endocyclic oxygen will be small. The 2s orbital is spherical symmetric and has no geometric requirements.

2. *If* the strain is caused by these 1,3-non-bonded interactions, then the strain energy should only be of any magnitude if there are at least four oxygen atoms about the sulfur or phosphorus. Non-bonded interactions could give rise to the thermochemical strain in the five-membered ring compounds.

The question of strong 1,2-sulfur–oxygen or phosphorus–oxygen interaction is currently being estimated. The non-bonded interactions would now involve back-bonding. There may also be partial double bond character between the ring oxygens and the heteroatom. Such terms presently can be seen to be larger and sensitive to the geometry.

Predictions

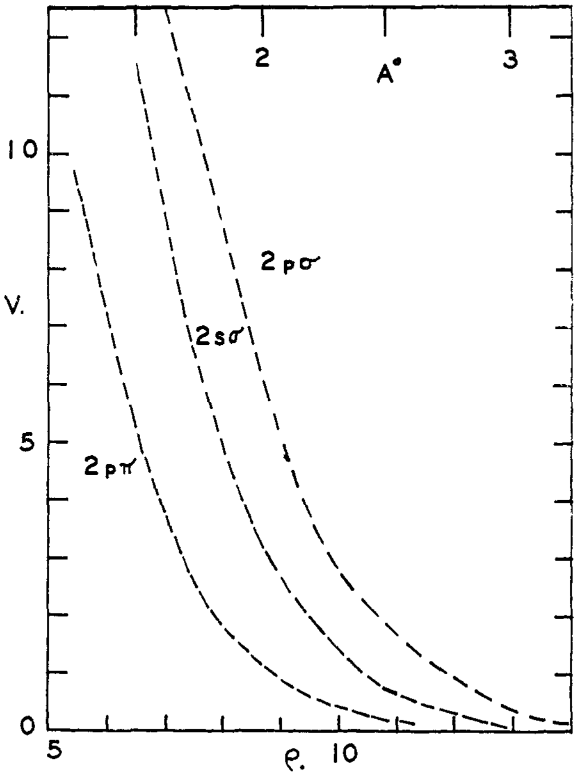

Fig. 2.—Repulsion potentials, *V*, in kcal./mole, between two two-electron oxygen atoms *versus* $\rho = \mu$ Å$/a_H$. The value of $\mu = 2.275$. The distance scale at the top is in Å. The most probable distance of 0—0 interaction in ethylene sulfite is between 2.7 and 2.9 Å.

As a result of data on the sulfite and phosphate esters and the theoretical considerations, two predictions will be made concerning the behavior of sulfite, sulfate, phosphite and phosphate esters: I. Kinetic acceleration (five membered >> open) will be observed if the attack of nucleophile (as hydroxide) occurs on the sulfur or phosphorus atom. The sulfur and phosphorus atom can form tetra- and pentavalent transition states more readily than does carbon. II. Thermodynamic strain will result upon closure of the five-membered ring only if the extra oxygen atom is present. Thus we predict that ethylene sulfate will be strained compared to dimethyl sulfate. The magnitude of strain should be at least 5 kcal./mole.

Experimental[35]

Materials.—Ethylene sulfite was prepared in high yield from ethylene glycol and thionyl chloride.[36] The material was purified by repeated vacuum distillations; b.p. 84° at 38 mm., 94° at 43 mm.; reported 86° at 52 mm., 88° at 52 mm.; $n^{25}D$ 1.4448, reported $n^{25}D$ 1.4450. The material was free from sulfur dioxide and was 99.8 to 99.9% pure as judged by hydrolysis and titration with iodine. The retention time on a Perkin–Elmer 2-meter R column at 25 p.s.i. of helium at 102° was 25.7 ± 0.2 minutes. No volatile impurities were detected. Upon standing several months on a laboratory shelf, sulfur dioxide and ethylene glycol were detected. Thus samples were redistilled before use.

Dimethyl sulfite was prepared from methanol and thionyl chloride, b.p. 126° at 758 mm., reported 126° at 760 mm.; $n^{25}D$ 1.4072, reported[16] b.p. 124° at 742 mm., $n^{25}D$ 1.4070.

The retention time was 7.8 ± 0.2 minutes on the R column at 102°. No other volatile material was detected.

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[32] The choice of Slater orbitals is the simplest for calculation. The use of Hartree-Fock SCF modified orbitals would give a better approximation to the interaction at greater distances, but the labor involved now becomes inordinate.

[33] As a check upon the wave functions, the data have been used to estimate the interaction between two oxygen *molecules*. The results were reported in more detail in Paper 1.[1] Recently the potential functions have been used to estimate the N_2–N_2 potential. The results are low by about fifty per cent. compared to the experimentally determined potential.[34] On these bases we feel that the curves of Figure 2 are correct within a factor of two. Several helpful discussions with Prof. Amdur are gratefully acknowledged.

[34] I. Amdur, E. A. Mason and J. E. Jordan, *J. Chem. Phys.*, **27**, 527 (1957).

[35] All temperature readings are taken from calibrated thermometers.

[36] W. W. Carlson and L. H. Cretcher, *J. Am. Chem. Soc.*, **69**, 1952 (1947).

Hydrolysis yielded 99.7% of the theoretical amount of sulfur dioxide.

All salts were of high purity and were dried to constant weight at 120°. Triply distilled water was used to prepare solutions.

Kinetic Methods.—During the basic hydrolysis of sulfite esters, hydroxide ion is consumed and sulfite or bisulfite ion produced. Therefore, several methods have been used to study the reaction. All solutions were oxygen free and protected by pure nitrogen.

The amperometric method (**method A**) is based upon the electrolytic generation of hydroxide ion at an electrode and then measuring the steady-state hydroxide ion concentration with a *p*H meter.[37] A measured volume of an oxygen-free solution of ethylene sulfite (about 1 to 5×10^{-2} *M*) in aqueous 0.1 *M* potassium chloride is placed in a jacketed beaker. Through a large, tight-fitting rubber stopper is passed a centrally located glass tube allowing nitrogen to be bubbled into the solution. The glass electrode and calomel electrode of a Beckman model G *p*H meter are placed near one side of the beaker. The generating electrode assembly is placed on the opposite side. The platinum cathode is placed directly into the solution. The anode compartment is constructed from a 10 × 1.5 cm. glass tube covered on one end by a Nepton CR-61 cation exchange membrane cut in a circle. The membrane is slanted slightly to prevent gas bubbles from collecting under the anode and changing the electrode resistance. The glass tube is then filled with a slurry of Dowex 50, 50–100 mesh, in 0.10 *M* potassium chloride. A platinum wire inserted into this slurry forms the complete anode. The generating electrodes are very firmly mounted as this detail and a slanting membrane give good electrode stability. The cation ion resin and membrane thus prevent the diffusion of hydrogen ions into the solution. After each electrolysis the resins are reconverted into the potassium form. A voltage of 1 to 16 volts d.c. is applied across the generating electrodes. An accurate d.c. milliammeter in series with the cell measures the current which is between 2.5 and 40 ma. By adjusting the voltage slightly during electrolysis, a steady state is soon reached where both the *p*H and current remain constant. When a new voltage is selected a new pair of steady-state values are recorded, yielding another estimate of the rate of reaction. The apparatus was checked at 25° by measuring the rate of ionization of nitroethane.[38,39] The rate constant reported is 5.8 M^{-1} sec.$^{-1}$ at 25°. The value obtained in the present study was 6.6 ± 0.6 M^{-1} sec.$^{-1}$ at 25°.

The Titrimetric Method at Static *p*H (**Method** *TS*).—The solution of ester is prepared in a very dilute buffer solution of a specific *p*H. The *p*H is then maintained constant by the addition of hydroxide from a micro buret driven by a *p*H Stat. A type SRR2-SBU1-TTA2 titration apparatus (Radiometer, Copenhagen, Denmark) was used with type B electrodes. The *p*H control and *p*H reproducibility is probably ±0.03. Thus the data are consistent within 5 to 7%.

The spectrophotometric–iodometric method (**method SI**) involves the addition of a very dilute potassium triiodide (10^{-5} *M*) to buffer solutions (*p*H 5.0–7.4) containing ethylene sulfite. Only sulfite or bisulfite ion react with iodine and this reaction is very fast. Therefore, the rate of disappearance of the iodine color measured at 353 mμ in a Beckman DU spectrophotometer equals the rate of production of sulfur dioxide. As the ester concentration is 10^{-3} to 10^{-1} *M* and the solution buffered, the disappearance of iodine occurs in a zero-order reaction. The extinction coefficient has been found to be 2.60 ± 0.06 × 10^4 in agreement with the value of 2.64 × 10^4 reported by Autrey and Connick.[40] In neutral or mildly acidic solution triiodide ion is very stable. However, as the *p*H is raised to about 9, hypoiodite is formed, with a decrease in the optical density of the solution. This method, therefore, cannot be applied to the sulfite esters about *p*H 9.

The indicator method (**method I**) involves the addition of a *p*H indicator which changes color as a function of *p*H. Dilute solutions of ester (10^{-2} to 10^{-3} *M*) and sodium hydroxide are rapidly mixed and the time of the color change of the indicator is measured visually with a stop watch. This time then gives a two-point kinetic curve: the initial time, $t = 0$, with known concentration of reactants and the time *t*, of the color change which occurs at a known *p*H. Indicators which are useful for this type of kinetic experiments are phenolphthalein (*p*H 9.7), *m*-cresol purple (*p*H 8.3) and cresol red (*p*H 8.1). If a rapid mixer is used and if a spectrophotometer is fitted to record rapidly the color change, the method becomes a much more general and useful tool to study rapid reactions with a *p*H change.

A conventional technique was a **titrimetric method** (**method** *T*) in deoxygenated aqueous buffer solutions based on the rate of appearance of sulfite ion. Aliquots of the solution were run into excess acid and back titrated with standard thiosulfate. This method has been used to study the alkaline hydrolysis of trimethylene sulfite and ethylene sulfite.[17]

Product Study.—The products of the basic hydrolysis of ethylene sulfite in sodium hydroxide are ethylene glycol and sodium sulfite. These compounds were determined to be the only products within 1–2% uncertainties of the analytical procedures of titration, spectral analysis and isolation. Solutions of esters in base were allowed to hydrolyze only for the first half-time. Electrometric titration with dilute perchloric acid showed breaks for neutralization of the hydroxide ion, the sulfite and the bisulfite ion. Derivative curves showed no other component present to within 1–2% uncertainty. Thus no evidence has been obtained for the accumulation of the monoesters ($ROSO_2H$ or $ROSO_2^-$). Likewise the sole products of hydrolysis of dimethyl sulfite are methanol and sodium sulfite.

Temperature Control.—For methods *A* and *TS*, water from a constant temperature bath (±0.01°) was circulated rapidly through the jacketed beaker. For method SI a Westheimer brass jacket was used as the cell compartment of the DU spectrophotometer. Circulating water maintained the temperature to ±0.02°. All temperatures were referred to NBS certified thermometers. Method I was studied in an ice-bath at ±0.005°. Method T was studied in Pyrex flasks, thermostated under nitrogen in water-baths ±0.01°.

Thermochemistry.—The heats of hydrolysis were determined in a calorimeter constructed from a small Dewar flask and Beckmann thermometer within a submergible copper can. Calibration was performed using the heat of dilution of sulfuric acid and electrical measurements. An ampule of about 0.1 g. of the ester was crushed under 50.00 ml. of 0.1 *N* sodium hydroxide at 30.00°. The results were averaged over several runs.

$$(C_2H_4SO_3)_l \longrightarrow (C_2H_4SO_3)_{\text{aq. soln. }(0.02\ M)} \qquad \Delta H = +0.64 \pm 0.07 \text{ kcal.}$$

$$(C_2H_6SO_3)_l \longrightarrow (C_2H_6SO_3)_{(0.02\ M\text{ aq. soln.})} \qquad \Delta H = -0.17 \pm 0.02 \text{ kcal.}$$

$$(C_2H_4SO_3)_{(0.02\ M\text{ aq.})} + 2NaOH_{(0.1\ M)} \longrightarrow C_2H_4(OH)_{2(\text{aq.})} + Na_2SO_3 \qquad \Delta H = -33.5 \pm 0.5 \text{ kcal.}$$

$$(C_2H_6SO_3)_{(0.02\ M\text{ aq.})} + 2NaOH_{(0.1\ M)} \longrightarrow 2CH_3OH_{(\text{aq.})} + Na_2SO_3 \qquad \Delta H = -32.8 \pm 0.6 \text{ kcal.}$$

Equilibria Studies.—The equilibrium between ethylene sulfite, methanol, dimethyl sulfite and ethylene glycol has been measured using V.P.C. analysis of the materials on a Perkin–Elmer 2-meter (R) polypropylene glycol column at 100°. An F and M model 609 temperature programmed unit equipped with a Texas Instrument millivolt recorder with integrator was also used.

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