The observed ^{18}O content is in excellent agreement with values calculated for return with equal amounts of mixing in the two enantiomers (*i.e.*, return from III and IV). This means the observed equilibration to return ratio (k_{eq}/k_{rac}) applies for rebonding of the anion to the original carbon atom. In the present case only internal return is involved.[7] Thus it appears that, in secondary alkyl systems that do not rearrange, internal return will result in up to 50% sulfonate oxygen equilibration. In other work we are determining if external ion-pair return[8] results in complete equilibration.

It is not clear if one intermediate (a hybrid of III and IV) or if two or more intermediates are involved. Evidence for more than one intermediate in a similar case[3] suggests that ionization gives IV which is in equilibrium with III and it is the latter which is more capturable by lithium perchlorate (and solvent) and returns with equilibration.

---

(7) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956).

(8) S. Winstein, P. E. Klinedinst, Jr., and G. C. Robinson, *ibid.*, **83**, 885 (1961).

(9) National Institutes of Health Predoctoral Fellow.

Harlan L. Goering, Richard W. Thies[9]
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

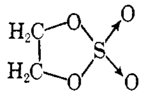
Received February 21, 1968

The Structure and Reactivity of Cyclic Esters. Ethylene Sulfate and Vinylene Sulfate

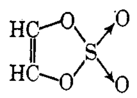
Sir:

Interest in five-membered cyclic esters of sulfur[1–4] and phosphorus[5–12] is keen because certain compounds of this class exhibit exceptional reactivity to solvolysis at the hetero atom when compared to their six-membered cyclic or acyclic analogs. For example, the rate enhancement has been estimated at 10^8 for alkaline hydrolysis of salts of ethylene phosphate over those of dimethyl phosphate.[5] This kind of kinetic acceleration has been attributed alternately to the effects of angle strain in five-membered rings and to 2p–3d π character in the oxygen–hetero atom bonds.[1,6,9] The search for a correlation between reactivity and structure has led to X-ray diffraction studies of two unsaturated phosphoric acid diesters, methyl ethylene phosphate[10] and methyl pinacol phosphate,[11] and more recently of an unsaturated cyclic diester, acetoinenediol cyclophosphate,[12] which is also known[12] to be highly reactive in solvolytic reactions.

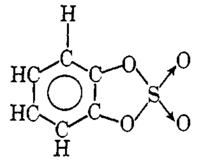
In the sulfur series, ethylene sulfate (I) hydrolyzes in base with about 14% S–O bond cleavage, while dimethyl sulfate is hydrolyzed exclusively at carbon. While highly indicative, this case unfortunately cannot permit comparison of relative rate constants for attack of hydroxide ion at the sulfur atom beyond establishing a lower limit (~300). However, more recent solvolytic studies[2] on catechol cyclic sulfate (III) have shown this compound to hydrolyze 2×10^7 times faster than its open-chain analog, diphenyl sulfate, and in fact considerably faster than ethylene sulfate. Studies described here show that vinylene sulfate (II) hydrolyzes in base nearly as rapidly as III.



I



II

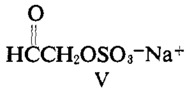


III

Structural studies of the cyclic esters of sulfuric acid have not hitherto been reported, although a comparison[4] has been made recently of the structures of five- and six-membered cyclic sulfonates. We now describe the molecular and crystal structures of ethylene sulfate (I) and vinylene sulfate (II).

Vinylene sulfate was prepared using the following reactions. Ethylene sulfate[13] was chlorinated in refluxing carbon tetrachloride (CCl_4) using chlorine and a GE sunlamp to give 1,2-dichloroethylene sulfate (IV) which was isolated by vacuum distillation and recrystallized from CCl_4–hexane as a white solid, mp 47–49°.[14] The dechlorination of V was effected by using magnesium in refluxing tetrahydrofuran. The solvent was subsequently removed and II was isolated in 50% yield by steam distillation. Recrystallization from CCl_4 and sublimation gave pure II, mp 51.5–52°.

The alkaline hydrolysis of vinylene sulfate (II) was conducted in a thermostated cell at 25° in solutions maintained at constant pH values by means of a Radiometer automatic titrator and at an ionic strength of 0.5 by the addition of sodium perchlorate. The hydroxide ion concentrations employed ranged from 1.59×10^{-5} to 5.01×10^{-5} *M*, and the initial concentration of sulfate II ranged from 3.56×10^{-4} to 11.54×10^{-4} *M*. Calculation of the second-order rate constant for the hydroxide ion catalyzed hydrolysis of II from the pseudo-first-order constants measured in various runs gave a value of 8.33 M^{-1} sec^{-1}. The corresponding rate constant for III is 18.8 M^{-1} sec^{-1} (see ref 2). The product of the hydrolysis of II in sodium hydroxide solution was isolated and identified as sodium glycolaldehyde monosulfate (V), a hygroscopic solid.



$$\mathrm{H\overset{O}{\overset{\|}{C}}CH_2OSO_3^-Na^+}$$

V

Our X-ray studies indicated that I and II crystallize isomorphously in the space group F2dd with eight

---

(1) E. T. Kaiser, M. Panar, and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 602 (1963).

(2) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *ibid.*, **87**, 3781 (1965).

(3) O. R. Zaborsky and E. T. Kaiser, *ibid.*, **88**, 3084 (1966).

(4) E. B. Fleischer, E. T. Kaiser, P. Langford, S. Hawkinson, A. Stone, and R. Dewar, *Chem. Commun.*, 197 (1967).

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

(6) P. C. Haake and F. H. Westheimer, *ibid.*, **83**, 1102 (1961).

(7) J. R. Cox, Jr., R. E. Wall, and F. H. Westheimer, *Chem. Ind.* (London), 929 (1959).

(8) A Eberhard and F. H. Westheimer, *J. Am. Chem. Soc.*, **87**, 253 (1965).

(9) D. A. Usher, E. A. Dennis, and F. H. Westheimer, *ibid.*, **87**, 2320 (1965).

(10) T. A. Steitz and N. W. Lipscomb, *ibid.*, **87**, 2488 (1965).

(11) M. G. Newton, J. R. Cox, Jr., and J. A. Bertrand, *ibid.*, **88**, 1503 (1966).

(12) D. Swank, C. N. Caughlan, F. Ramirez, O. P. Madan, and C. P. Smith, *ibid.*, **89**, 6503 (1967).

(13) A modified procedure of J. Brunken (West German Patent 1,049,870 (1959)) was used.

(14) All new compounds exhibited satisfactory analytical and spectral properties.

Table I. Crystal Structure Parameters[a] for Ethylene Sulfate (I) and Vinylene Sulfate (II)

		I	II
	Unit cell parameters, Å		
	a	6.226 (6)	6.436 (6)
	b	9.685 (9)	9.414 (9)
	c	15.865 (15)	15.426 (15)
	Calculated density, g cm^{-3}		
	ρ	1.723	1.735
	Atomic coordinates[b]		
S	*X*	0	0
	Y	0	0
	Z	0	0
O(1)	*X*	−0.1147 (21)	−0.1186 (23)
	Y	0.0832 (6)	0.0797 (8)
	Z	0.0541 (4)	0.0527 (8)
O(2)	*X*	0.1609 (12)	0.1719 (19)
	Y	0.0835 (5)	0.0969 (6)
	Z	−0.0525 (3)	−0.0482 (5)
C	*X*	0.3790 (14)	0.3635 (19)
	Y	0.0693 (8)	0.0527 (11)
	Z	−0.0199 (5)	−0.0274 (7)

		I	II
Root-mean-square amplitudes of vibration, Å[c,d]			
Atom S	axis 1	0.209 (3)	0.258 (3)
	2	0.241 (2)	0.285 (2)
	3	0.257 (2)	0.319 (3)
O(1)	1	0.207 (9)	0.261 (14)
	2	0.364 (10)	0.437 (10)
	3	0.449 (10)	0.522 (15)
O(2)	1	0.207 (12)	0.264 (8)
	2	0.233 (10)	0.294 (9)
	3	0.396 (3)	0.452 (8)
C	1	0.203 (12)	0.254 (12)
	2	0.251 (13)	0.339 (12)
	3	0.349 (6)	0.360 (10)
Bond distances, Å[d,e]			
S–O(1)		1.377 (8)	1.344 (10)
S–O(2)		1.533 (7)	1.616 (10)
O(2)–C		1.459 (11)	1.341 (15)
C–C′		1.483 (18)	1.305 (21)
Bond angles,[d,e]			
O(1)–S–O(1)′		117.5 (1.0)	110.8 (1.4)
O(2)–S–O(2)′		98.4 (0.5)	93.6 (0.7)
S–O(2)–C		111.5 (0.5)	110.2 (0.6)
O(2)–C–C′		103.7 (0.3)	113.0 (0.6)

[a] With standard errors in parentheses. [b] In fractions of the unit cell lengths. [c] Ordered on increasing amplitude. [d] Standard errors are calculated from the variance–covariance matrix obtained in the final cycle of least-squares refinement. [e] Primes refer to atoms related by the twofold axis.

molecules per unit cell (molecular C_2 symmetry is thus implied). The lattice parameters are compared in Table I. The intensity data were measured visually from reciprocal lattice levels *Hkl* obtained by the multiple-film Weissenberg method (Cu Kα radiation) and from timed exposures of levels perpendicular to 010, 001, and 011 taken on a precession camera (Mo Kα radiation). The crystal structures were solved from a Patterson function and refined by full-matrix least squares to final disagreement factors $R_F = 0.072$ for I (271 observed reflections) and $R_F = 0.064$ for II (204 reflections). Hydrogen atoms were not located. Final atomic coordinates, amplitudes of thermal motion, bond distances, and bond angles (along with their standard deviations) for I and II are compared in Table I.

Comparison of the structures of ethylene and vinylene sulfates with their phosphate analogs is revealing. The O–S–O bond angle of the five-membered ring in I has a value of 98.4° which, while substantially below the tetrahedral angle of 109.5°, is nearly the same as the analogous O–P–O angle of 99.1° reported for methyl ethylene phosphate (VI). However, the corresponding O–S–O angle in vinylene sulfate has an extremely low value, 93.6°, very close to the 90° required to achieve a possible trigonal-bipyramid structure in the transition state for its alkaline hydrolysis. This low value appears to be unique to II; the O–P–O angle in the unsaturated ester acetoinediol cyclophosphate (VII) has a somewhat larger value, 98.5°.

The degree of nonplanarity in the five-membered rings may be measured by the angle formed by the C–C′ bond with the O(2)–S–O(2)′ plane.[15] Vinylene sulfate, as expected, is planar within experimental error (1.3 ± 0.9°). The angle found in ethylene sulfate, 20.6 ± 0.5°, is about as large as the 20° reported for ethylene carbonate[16] and substantially greater than the 11° found in VI.

The most remarkable difference between the structures of I and II is the decrease in the O(2)–C bond distance from an essentially normal figure of 1.46 Å in I to a very short value of 1.34 Å in the unsaturated ester II. A similar but smaller effect was observed[10,12] in phosphates VI and VII. At the same time, the S–O(2) bond distance *increases* significantly with unsaturation, from 1.53 Å in I to 1.62 Å in II. Again, a similar but smaller effect appears to occur in VI and VII, although in this case the evidence[12] is less clear. The exocyclic S–O(1) distances, 1.38 Å in I and 1.34 Å in II, again parallel the behavior reported for the correspondind bonds in the phosphates, *e.g.*, 1.44 Å in VI and 1.38 Å in VII.

Further X-ray studies on these cyclic sulfate systems at cryogenic temperatures and theoretical investigations of the structural and rate data are in progress.

---

(15) O(1) refers to exocyclic oxygen, O(2) to oxygen in the five-membered rings; primes indicate atoms related by the molecular twofold axis.

(16) C. J. Brown, *Acta Cryst.*, 7, 92 (1954).

(17) The studies at the University of Chicago were supported in part by the National Science Foundation.

(18) Predoctoral Fellow of the National Institutes of Health.

F. P. Boer, J. J. Flynn
The Dow Chemical Company, Eastern Research Laboratory
Wayland, Massachusetts 01778

E. T. Kaiser,[17] O. R. Zaborsky[18]
Department of Chemistry, University of Chicago
Chicago, Illinois 60637

D. A. Tomalia, A. E. Young, Y. C. Tong
The Dow Chemical Company, E. C. Britton Research Laboratory
Midland, Michigan 48640

Received March 2, 1968