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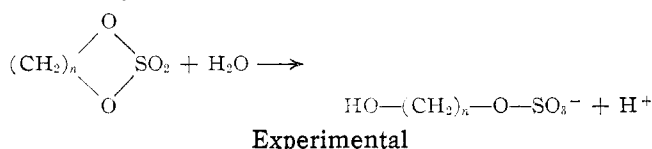
The Hydrolysis of Some Cyclic Esters of Sulfuric Acid<sup>1,2</sup>BY E. T. KAISER,<sup>3</sup> MANUEL PANAR AND F. H. WESTHEIMER

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Ethylene sulfate, trimethylene sulfate and dimethyl sulfate undergo first-order solvolysis to the corresponding monoesters in aqueous solution from pH 2 to 9 with relative rates of 12:1:6. In more alkaline solution, the dominant reaction is saponification, with second-order rate constants in the ratio 103:1:5.5. The first step in the solvolyses of all three esters in either neutral or alkaline solution is predominately carbon-oxygen cleavage; sulfur-oxygen fission (14%) was detected only for the saponification of ethylene sulfate. The heat of saponification of ethylene sulfate exceeds that of dimethyl sulfate by about 5.7 kcal./mole. (Similar calorimetric measurements are also reported herein for cyclic and non-cyclic esters of phosphoric acid.) The similarities and differences between cyclic esters of sulfuric and phosphoric acid are outlined.

The solvolysis of cyclic esters of phosphoric acid which contain a five-membered ring is extraordinarily rapid.<sup>4</sup> Kinetic studies<sup>5,6</sup> have shown that the rate of alkaline or acid hydrolysis of salts of ethylene phosphate exceeds that of salts of dimethyl phosphate by a factor of the order of 10<sup>7</sup>; the ratio of rates for attack at the phosphorus atom is even greater, since the hydrolysis of dimethyl phosphate,<sup>7,8</sup> in contrast to that of ethylene phosphate,<sup>8</sup> takes place primarily at carbon. Furthermore, the rate of saponification of methyl ethylene phosphate is similarly enhanced relative to that for trimethyl phosphate, and the heat of saponification of methyl ethylene phosphate exceeds that of methyl hydroxyethyl phosphate by about 5.5 kcal./mole.<sup>9</sup>

In order to help to elucidate the unusual thermochemical and kinetic behavior of cyclic phosphates, the rates of hydrolysis, position of bond cleavage and thermochemistry of ethylene sulfate and trimethylene sulfate have been investigated, and compared to those of dimethyl sulfate.



**Materials.**—Merck reagent grade solvents were used throughout. Acetone was dried over Drierite, xylene over sodium wire. Barium permanganate was obtained from the Carius Chemical Co., potassium permanganate (analytical reagent) and silver sulfate (analytical reagent) from Mallinckrodt Chemical Works, sodium chloride from Merck and Co., Inc. Sodium perchlorate (Fisher Scientific Co., C.P.) was recrystallized twice from water. Ethylene glycol (Jefferson Chemical Co.) and thionyl chloride (Eastman Kodak Co.) were used without further purification. Eastman Kodak Co. practical grade of trimethylene dibromide, and trimethylene glycol were purified by distillation. Dimethoxyethane was purified by distillation from calcium hydride. Sodium hydroxide solutions were prepared by the method of Kolthoff and Sandell.<sup>10</sup>

(1) Abstracted in part from the Thesis of E. T. Kaiser, Harvard University, 1959.

(2) Presented at the 140th Natl. Meeting of the American Chemical Society, Chicago, Ill., September, 1961 (Abstracts of Papers, p. 94 Q).

(3) National Science Foundation Fellow, 1956–1958; National Institutes of Health Fellow, 1958–1959.

(4) M. C. Bailly, *Compt. rend.*, **206**, 1902 (1938); **208**, 443 (1939); P. E. Verkade, J. C. Stoppelenburg and W. D. Cohen, *Rec. trav. chim.*, **69**, 886 (1940); G. R. Barker, M. D. Montague, R. J. Moss and M. A. Parsons, *J. Chem. Soc.*, 3786 (1957); D. M. Brown and A. R. Todd, *ibid.*, 52 (1952); D. M. Brown and H. M. Higson, *ibid.*, 2034 (1957).

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

(6) F. H. Westheimer, *8th Special Publication of the Chemical Society*, 1 (1957).

(7) C. A. Bunton, D. R. Llewellyn, K. G. Oldham and C. A. Vernon, *J. Chem. Soc.*, 3574 (1958).

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

(9) For an earlier, somewhat higher estimate of the difference in these heats of saponification, see J. R. Cox, Jr., R. E. Wall and F. H. Westheimer, *Chem. Ind. (London)*, 929 (1959).

(10) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Edition, The Macmillan Co., New York, N. Y., 1952, p. 326.

**Ethylene sulfite** was prepared by the method of Carlson and Cretcher<sup>11</sup>; a second sample was kindly donated to us by Associated Chemical Companies Ltd. The infrared spectrum of a sample of the latter, carefully fractionated, corresponded generally with that earlier reported by de la Mare, *et al.*,<sup>12</sup> but differed in that the strong bands were found about 0.1  $\mu$  higher than those previously reported, and some of the weak bands were missing. In solution in CS<sub>2</sub>, ethylene sulfite showed infrared bands of medium intensity at 3.37 and 3.45  $\mu$  and strong bands at 8.25, 10.0, 10.93 and 13.65  $\mu$ .

**Trimethylene sulfite**<sup>12,13</sup> was prepared following the procedure<sup>11</sup> for ethylene sulfite; yield 30–40%, b.p. 90–91° (40 mm.).

**Ethylene sulfate** has been prepared by the reaction of ethylene dibromide with silver sulfate in xylene.<sup>14,15</sup> Since the yields by this method, in our hands, were much less than those reported, a modification of the permanganate oxidation method of Garner and Lucas<sup>16</sup> was employed.

A saturated solution of barium permanganate in acetone was added with shaking over a period of about 5 minutes to a solution of the equivalent quantity of the sulfite in acetone. The reaction was exothermic; when the reaction mixture had cooled, the precipitated manganese dioxide was removed by filtration, and the acetone was evaporated at reduced pressure. The residue, which contains the cyclic sulfate, was recrystallized from benzene-petroleum ether. The yield was about 25% of product, which melted at 97–98° (cor.; lit.<sup>11</sup> 99°). The thermochemical measurements were made with material recrystallized from benzene-petroleum ether and sublimed; m.p. 97.3–97.5°, cor. The infrared spectrum, in a KBr pellet, showed very weak bands at 3.35, 6.9, 10.5 and 10.7  $\mu$ , a weak band at 11.35  $\mu$ , medium bands at 9.45, 10.0 and 13.3  $\mu$  (broad), and a strong band at 8.15  $\mu$  (broad).

**Trimethylene sulfate** was prepared from barium permanganate and trimethylene sulfite by the same procedure as that given above for ethylene sulfate; the yield was comparable. The melting point of the compound was 62° (lit.<sup>11</sup> 63°). The infrared spectrum, in a KBr pellet, showed a very weak band at 3.35  $\mu$ , weak bands at 6.85, 7.03, 7.85, 8.82, 9.7 and 11.1  $\mu$ , medium bands at 8.12 and 13.2  $\mu$ , and strong maxima at 7.3, 8.42, 10.05, 10.82, 11.6 and 12.15  $\mu$ .

**Dimethyl sulfate** was purified by distillation through a 1.8  $\times$  30 cm. column packed with glass helices; the fraction boiling at 84.6–85.2° (25 mm.) was used for the kinetic and thermochemical experiments.

**Barium hydroxyethyl sulfate** was isolated from the hydrolysis of 51.2 mg. of ethylene sulfate in 10 cc. of water, in the presence of excess barium carbonate. The suspension was freed of insoluble salts by centrifugation, and the supernatant evaporated to dryness at reduced pressure in a rotary evaporator. The product, after drying over P<sub>2</sub>O<sub>5</sub> in a vacuum oven at 70°, weighed 89.4 mg.; this corresponds to a 98.7% yield of (HOCH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub>)<sub>2</sub>·Ba·H<sub>2</sub>O. The crude product was analyzed for carbon and hydrogen by the Schwartzkopf Microanalytical Laboratory, and its molecular weight determined by a titration procedure. A weighed sample of the compound was dissolved in water, and the solution passed through a column filled with Dowex 50 ion exchange resin in the acid form. The resulting acid was titrated with standard base.

*Anal.* Calcd. for C<sub>4</sub>H<sub>10</sub>S<sub>2</sub>O<sub>8</sub>·Ba·H<sub>2</sub>O: C, 10.97; H, 2.76; equiv. wt., 218.8. Found: C, 11.16; H, 2.85; equiv. wt., 216.

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

(12) P. B. de la Mare, W. Klyne, D. J. Millen, J. G. Pritchard and D. Watson, *J. Chem. Soc.*, 1813 (1956).

(13) R. Majima and H. Simanuki, *Proc. Imp. Acad. (Japan)*, **2**, 544 (1926); H. H. Szmant and W. Emerson, *J. Am. Chem. Soc.*, **78**, 454 (1956).

(14) W. Baker and F. B. Field, *J. Chem. Soc.*, 86 (1932).

(15) J. S. Brimacombe, A. B. Foster, E. B. Hancock, W. G. Overend and M. Stacey, *ibid.*, 201 (1960).

(16) H. K. Garner and H. J. Lucas, *J. Am. Chem. Soc.*, **72**, 5497 (1950).

When the hydrolysis of ethylene sulfate was carried out in solutions ten times as concentrated as that described above, the product obtained was impure, as measured by the equivalent weight from the ion-exchange method. Similarly, the product prepared from ethylene glycol and sulfuric acid<sup>17</sup> gave values for the equivalent weight which were about 7% low. The impure and pure samples gave very similar infrared spectra, with the principal bands at 3.38, 6.12 and 6.88  $\mu$  (weak), 12.82 (broad); 2.90, 9.40, 9.92 and 11.00  $\mu$  (broad, strong) and a very strong band at 8.15  $\mu$ .

The corresponding sodium salt, prepared by opening ethylene sulfate in NaHCO<sub>3</sub> solution, was analyzed by the ion exchange method; it proved to be a monohydrate.

Barium 3-hydroxypropyl sulfate was similarly obtained in essentially quantitative yield from trimethylene sulfate and water, either in the presence of barium carbonate or, alternatively, by neutralization of a hydrolysis mixture with barium carbonate.

*Anal.* Calcd. for C<sub>6</sub>H<sub>14</sub>S<sub>2</sub>O<sub>8</sub>Ba: C, 16.10; H, 3.15; equiv. wt., 223.8. Found: C, 15.93; H, 3.26; equiv. wt., 223, 224, 225, 226.

The infrared spectrum in KBr showed a weak band at 3.45  $\mu$ , medium bands at 2.90, 12.10 (broad) and 13.13  $\mu$  (broad), strong bands at 9.37, 9.80 and 10.65  $\mu$ , and a very strong band at 8.15  $\mu$  (broad). When the KBr salt mixture was dried before pressing the KBr pellet, the absorption around 6.15  $\mu$  was very weak. The spectra and analyses (and especially the neutralization equivalents on the solutions which had been passed through Dowex 50) suggest that barium hydroxyethyl sulfate but not the hydroxypropyl analog holds a molecule of water of crystallization.

Barium methyl sulfate<sup>18</sup> was prepared from dimethyl sulfate by hydrolysis in the presence of BaCO<sub>3</sub>. An equivalent weight of 195 was found by the ion exchange method; theory 197.8.

Methyl ethylene phosphate, which had previously been obtained as an oil by the oxidation of the corresponding phosphite with nitrogen tetroxide,<sup>19</sup> was induced to crystallize when the starting material was carefully vacuum fractionated with a Poddieniak spinning band column.<sup>20</sup> The pure ester boiled at 102° (2 mm.), and melted at -6 to -5°; recrystallization from methylene chloride in a deep-freeze did not raise the melting point. Dimethyl hydroxyethyl phosphate<sup>9</sup> had a neutralization equivalent (170.0, 169.9) in agreement with theory.

**Kinetic Methods.**—The solvolysis of the esters in the pH range from 1–10 was followed by two methods: (a) The pH of the solution was maintained at a constant value with a Beckman model K automatic titrator; the amount of alkali added by the titrator was then observed as a function of time. (b) The pH of the reacting solution was allowed to fall during the experiment; aliquots were removed from time to time, and the amount of acid which had been produced determined by titration, using a Beckman model G pH meter to determine the end-point.

For the saponification of the esters in alkali, aliquots were withdrawn and titrated rapidly with standard acid. After preliminary experiments had established the approximate rates, more accurate experiments could be performed in which aliquots were delivered from a syringe into the approximate amount of acid needed for neutralization; this minimized the time during which the sample was in contact with excess alkali.

**Kinetic Equations.**—The data for the solvolysis at pH less than 10 was fitted graphically to the simple first-order rate expression. In the alkaline solutions, eq. 1 represents the dif-

$$dx/dt = k_1(s - x) + k_2(s - x)(h - x) \quad (1)$$

ferential equation for the mixed first- and second-order reaction, where  $h$  is the initial hydroxide ion concentration,  $s$  is the initial sulfate ester concentration and  $x$  is the concentration of product at time  $t$ . On integration, 1 yields 2.

$$\ln \frac{s - x}{s} + \ln \frac{k_1 + k_2 h}{k_1 + k_2(h - x)} = [k_2(s - h) - k_1]t \quad (2)$$

Since the observations cannot easily be fitted to this equation, more convenient approximate treatments of 1 have been suggested.<sup>21,22</sup> In addition, a method of successive approximations for the direct solution of 2 was developed.<sup>1</sup>

**Thermochemistry.**—Although approximate values of the heats of saponification were obtained<sup>1</sup> with the crude apparatus used earlier,<sup>9</sup> those here reported, although still rough by modern standards,<sup>23</sup> were obtained with more refined equipment. An

isothermal calorimeter was patterned after that of Sunner and Wadsö,<sup>24</sup> except that the inner brass chamber was gold-plated, and the stirrer cage, which held a vial containing the sample, was machined from Teflon. The vacuum jacket for the calorimeter (the outer, brass chamber) was evacuated with a Consolidated Electrodynamics Inc. VMF oil diffusion pump, and the vacuum measured with a Veeco thermocouple gage, type GV; the system was used when the gage registered zero, i.e., a pressure of less than a micron. The calorimeter was immersed in a water-bath, maintained at a temperature of about 30° to  $\pm 0.002^\circ$ .

Temperature within the calorimeter was measured with a Vico 50 K $\Omega$  thermistor (Victory Engineering Corp., Union, N. J.) which formed one arm of a Wheatstone bridge; the remaining arms consisted of a 100 K $\Omega$  decade resistance box and two 40 K $\Omega$  precision resistors such that the two arms were equal to a precision of 0.01%. The imbalance of the bridge was amplified by a Philbrick USA-3 d.c. amplifier. A Varian G-10 recorder was used as a null detector, and time was measured as distance along the strip chart. Points on a resistance vs. time curve were obtained by selecting a setting on the decade box, and later determining the distance, and hence the time, when the recorder line crossed the zero. In this manner, resistance points could be taken as fast as the decade box could be switched, and the corresponding times read at leisure from the sawtooth curve on the chart. The system was sensitive to 1 ohm, or about 0.0005°.

The calorimeter was calibrated electrically by means of a 10-ohm Nichrome wire heater, which was wound on a glass tube and insulated by painting it with a solution of polystyrene in toluene. The heating wire was connected to heavy copper leads which passed through the solution in the calorimeter for a distance of 2 cm., in order that the excess heat from the heater be dissipated in the vessel, and not conducted out of the calorimeter. The coil was heated by a 4-volt storage battery, and the resistance determined by comparison with that of a General Radio Co. 500-D resistance of 100 ohms  $\pm 0.05\%$ , using a Leeds and Northrup Jones bridge, with a rated accuracy of 0.02%. The voltage (and hence the amperage) which passed through the heater was determined with a Leeds and Northrup type K potentiometer and a voltage divider which consisted of General Radio Co. resistances rated to  $\pm 0.05\%$ . The precision of the calorimetric measurements is much greater than their accuracy. The calibration of the calorimeter gave results with an average deviation of 0.3%. The absolute value of the specific heat of the vessel plus 200 ml. of water was 223 cal./degree, based on the manufacturer's specification of 4.5% change in resistance of the thermistor per degree. The calibration was checked by a determination of the heat of neutralization of hydrochloric acid. The value obtained, 12.8 kcal./mole, is almost 2% lower than the best literature values<sup>25</sup> when the latter are corrected for heats of dilution and to the temperature (31°) of our measurements.<sup>26</sup> Thus, although the precision of the values here reported is about 0.5%, the absolute values of the differences in heats of neutralization may be in error by as much as 0.3 kcal./mole.

The calorimeter was stirred with a synchronous speed motor at about 600 r.p.m. The heat of breaking of the ampoules used for the samples was negligible, although frictional heating, which resulted when the stirrer accidentally pressed against the vessel during the bulb-breaking, offers a possible source of error in individual runs. The major errors are introduced by the slow equilibration of the Teflon stirrer shaft with the solution in the calorimeter, and the leak through the glass collar which joins the inner and outer chambers<sup>24</sup> of the calorimeter. The rate of solution of dimethyl sulfate and of ethylene sulfate is too slow to permit easy measurement of the heat of reaction or solution, and experiments with these compounds were therefore conducted with water containing 4% by volume of purified dimethoxyethane. The specific heat of the calorimeter with this solvent was less than that with water by 0.4%.

**Isotopic Measurements.**—Ethylene sulfate, trimethylene sulfate and dimethyl sulfate were hydrolyzed in water enriched with O<sup>18</sup>. In some experiments, the diesters were hydrolyzed directly to inorganic sulfate by heating the acidic or basic solutions on a steam-cone. In others, the monoesters of sulfuric acid were isolated (as the barium or sodium salts). These were then either analyzed directly or further hydrolyzed in ordinary water. Inorganic carbon when obtained was precipitated as barium sulfate. Carbon dioxide was formed from the salts<sup>27</sup> (e.g.,

(17) M. Simpson, *Ann.*, **112**, 146 (1859).

(18) R. Kremann, *Monatsh.*, **28**, 13 (1907); A. Klemenc, *ibid.*, **38**, 553 (1917).

(19) J. R. Cox, Jr., and F. H. Westheimer, *J. Am. Chem. Soc.*, **80**, 5441 (1958).

(20) F. Covitz, unpublished.

(21) W. G. Young and L. J. Andrews, *J. Am. Chem. Soc.*, **66**, 421 (1944).

(22) E. D. Hughes, C. K. Ingold and W. G. Shapiro, *J. Chem. Soc.*, 225 (1936).

(23) "Experimental Thermochemistry," H. A. Skinner, Ed., Interscience Publishers, Inc., New York, N. Y., 1962.

(24) S. Sunner and I. Wadsö, *Acta Chem. Scand.*, **13**, 97 (1959).

(25) H. M. Papee, W. J. Canady and K. J. Laidler, *Can. J. Chem.*, **34**, 1677 (1956).

(26) F. Daniels, J. H. Mathews, J. W. Williams, P. Bender and R. A. Alberty, "Experimental Physical Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 5th Edition, 1956, p. 36.

(27) M. Anbar and S. Guttman, *Int. J. Appl. Rad. and Isotopes*, **4**, 233 (1959); F. R. Williams and L. P. Hager, *Science*, **128**, 1434 (1958).

barium sulfate) by heating the sample with a mixture of mercuric cyanide and mercuric chloride in a break-seal tube at 400°. Not much cyanogen was formed in the reaction. About 80% of the cyanogen could be removed by passing the gas through a trap immersed in a mixture of isohexane and Dry Ice. The mass spectrometric determination of the isotopic ratio in CO<sub>2</sub> was not appreciably affected by removing the cyanogen in this way. The samples of water in which the various hydrolyses were analyzed for O<sup>18</sup> by sealing 1 ml. with 1 or 2 ml. of CO<sub>2</sub> and allowing the mixture to equilibrate at 80° overnight. The ratio of the masses 46 to 44 was obtained using a recording Consolidated mass spectrometer, type 21-103 C.

### Results

**Kinetics.**—The rates for the first-order (uncatalyzed) hydrolysis of ethylene sulfate, trimethylene sulfate and dimethyl sulfate are given in Tables I, II and III.

TABLE I  
HYDROLYSIS OF ETHYLENE SULFATE

Initial concn. sulfate, <i>M</i>	Method	pH	<i>T</i> , °C.	10 <sup>3</sup> <i>k</i> <sub>1</sub> , sec. <sup>-1</sup>
0.00948	<sup>a</sup>	<sup>b</sup>	0.4	1.73
.0139	<sup>a</sup>		0.4	1.78
.0353	<sup>a</sup>	<sup>c</sup>	9.97	7.25
.00175	<sup>e</sup>	7 <sup>d</sup>	9.97	7.25
.00186	<sup>e</sup>	7	9.97	7.24
.00202	<sup>e</sup>	7	9.97	7.25
.00251	<sup>e</sup>	5	9.97	7.23
.00460	<sup>e</sup>	7	9.97	7.23
.00184	<sup>e</sup>	3.7	30.00	76
.00141	<sup>e</sup>	6.2	30.00	77
.00113	<sup>e</sup>	7.0	30.00	76
.00133	<sup>e</sup>	8	30.00	77
.00280	<sup>e</sup>	8	30.00	76
.00205	<sup>e</sup>	9.5	30.00	75

<sup>a</sup> Manual titration; pH falls during "run." <sup>b</sup> 0.256 *M* NaClO<sub>4</sub> present. <sup>c</sup> 0.0265 *M* HClO<sub>4</sub> added initially. <sup>d</sup> 0.0968 *M* NaClO<sub>4</sub> present. <sup>e</sup> Automatic titration.

TABLE II  
HYDROLYSIS OF TRIMETHYLENE SULFATE

Initial concn. sulfate, <i>M</i>	Method	pH	<i>T</i> , °C.	10 <sup>3</sup> <i>k</i> <sub>1</sub> , sec. <sup>-1</sup>
0.00234	<sup>a</sup>	<sup>b</sup>	30.00	6.25
.0122	<sup>a</sup>	<sup>c</sup>	30.00	6.25
.0123	<sup>a</sup>	<sup>d</sup>	30.00	6.35
.00422	<sup>e</sup>	4.0	30.00	6.25
.00296	<sup>e</sup>	4.0	30.00	6.33
.00180	<sup>e</sup>	4.9	30.00	6.33
.00823	<sup>e</sup>	4.9	30.00	6.25
.00248	<sup>e</sup>	7.0	30.00	6.20
.00356	<sup>e</sup>	7.0 <sup>f</sup>	30.00	6.25
.00224	<sup>e</sup>	8.8	30.00	6.35
.00357	<sup>e</sup>	8.8	30.00	6.30
.00699	<sup>a</sup>	<sup>g</sup>	40.02	18.5
.01658	<sup>a</sup>		40.02	19.0
.02397	<sup>a</sup>	<sup>h</sup>	40.02	18.2

<sup>a</sup> Manual titration; pH falls during "run." <sup>b</sup> 0.00181 *M* HCl added initially. <sup>c</sup> 0.00867 *M* HCl added initially. <sup>d</sup> 0.00850 *M* HCl added initially. <sup>e</sup> Automatic titration. <sup>f</sup> 0.0624 *M* NaCl present. <sup>g</sup> 0.415 *M* NaClO<sub>4</sub> present. <sup>h</sup> 0.161 *M* LiClO<sub>4</sub> present.

Brimacombe, *et al.*,<sup>15</sup> carried out the hydrolysis of the sulfates of *cis*- and *trans*-cyclohexane-1,2-diols in acid solution, and the alkaline hydrolysis of ethylene sulfate. The legend of Fig. 3 in their article implies that the first and second steps in the hydrolysis of ethylene sulfate in acid solution occur with comparable rates, *i.e.*, there is no break in their curve for the generation of acid with time at the point corresponding to the formation of one equivalent of acid. From the discussion in their paper, however, it appears that the curves in Fig. 3 have been mislabeled, and that no data on ethylene sulfate in acid solution have been submitted. In any event, no difficulty with ethylene sulfate was observed in the

TABLE III  
HYDROLYSIS OF DIMETHYL SULFATE

Initial concn. sulfate, <i>M</i>	Method	pH	<i>T</i> , °C.	10 <sup>3</sup> <i>k</i> <sub>1</sub> , sec. <sup>-1</sup>
0.077	<sup>a</sup>	<sup>b</sup>	9.97	2.1
.141	<sup>a</sup>	<sup>c</sup>	9.97	2.1
.0316	<sup>a</sup>		9.97	2.3
.0325	<sup>a</sup>	<sup>d</sup>	9.97	2.3
.00338	<sup>e</sup>	7.0	30.00	34.8
.00362	<sup>e</sup>	7.0	30.00	34.5
.00214	<sup>e</sup>	7.8 <sup>f</sup>	30.00	34.2
.00378	<sup>e</sup>	9.5	30.00	34.6

<sup>a</sup> Manual titration; pH falls during "run." <sup>b</sup> 0.356 *M* HCl added initially. <sup>c</sup> 0.712 *M* HCl added initially. <sup>d</sup> 0.170 *M* NaClO<sub>4</sub> present. <sup>e</sup> Automatic titration. <sup>f</sup> 0.146 *M* NaClO<sub>4</sub> present.

course of the present work, and the end of the reaction, determined after seven or more half-lives by titration, corresponded quite well with that calculated for the hydrolysis of ethylene sulfate to hydroxyethyl hydrogen sulfate.

The rates for the second-order hydrolyses (saponification) of ethylene sulfate, trimethylene sulfate and dimethyl sulfate are presented in Tables IV, V and VI. The second-order constants were calculated by one or more of the methods discussed in the section on kinetic equations. Since the reaction as measured was a mixed first- and second-order process, the accuracy of *k*<sub>2</sub> is not high.

TABLE IV  
SAPONIFICATION OF ETHYLENE SULFATE

Initial concn. sulfate, <i>M</i>	Initial concn. NaOH, <i>M</i>	<i>T</i> , °C.	10 <sup>3</sup> <i>k</i> <sub>2</sub> , l./m. sec.
0.00463	0.0128	0.4	1.49
.00825	.0128 <sup>a</sup>	.4	1.47
.0136	.0232	.4	1.53
.0166	.0423	.4	1.36
.00332	.00998	9.97	3.80
.00453	.00998	9.97	4.04
.0534	.00998	9.97	4.06
.00813	.0196	9.97	4.22

<sup>a</sup> 0.433 *M* NaClO<sub>4</sub> present.

TABLE V  
SAPONIFICATION OF TRIMETHYLENE SULFATE

Initial concn. sulfate, <i>M</i>	Initial concn. NaOH, <i>M</i>	<i>T</i> , °C.	10 <sup>3</sup> <i>k</i> <sub>2</sub> , l./m. sec.
0.0202	0.0423	30.00	0.275
.0307	.0993	30.00	.263
.0331	.0993	30.00	.285
.0432	.0993	30.00	.286
.0448	.0993	30.00	.258
.00458	.0128	40.00	.625
.0153	.0128	40.00	.635
.0192	.0423	40.00	.610

TABLE VI  
SAPONIFICATION OF DIMETHYL SULFATE

Initial concn. sulfate, <i>M</i>	Initial concn. NaOH, <i>M</i>	<i>T</i> , °C.	10 <sup>3</sup> <i>k</i> <sub>2</sub> , l./m. sec.
0.0204	0.0204	9.97	0.200
.0538	.0993	9.97	.217
.0740	.0993	9.97	.224
.00515	.0204	30.00	1.48
.0772	.0913	30.00	1.58
.1475	.0993	30.00	1.74

The essential data of Tables I-VI are presented in Table VII.

**Heat of Hydrolysis.**—The heats of alkaline hydrolysis of ethylene sulfate, dimethyl sulfate methyl ethyl-

TABLE VII  
SUMMARY OF KINETIC RESULTS

Compound, sulfate	T, °C.	10 <sup>3</sup> k <sub>1</sub> , sec. <sup>-1</sup>	10 <sup>3</sup> k <sub>2</sub> , l./m. sec.
Ethylene	0.40	1.75	1.46
	9.97	7.24	4.03
	30.00	76	
Trimethylene	30.00	6.28	0.273
	40.02	18.6	.623
Dimethyl	9.97	2.2	.214
	30.00	34.5	1.57

TABLE VIII

Sulfates	ΔH, kcal./mole			
	Reaction	Solution	Hydrolysis	Δ(ΔH)
Ethylene	28.0	-5.0	33.0	
Dimethyl	25.4	-1.9	27.3	5.7
Phosphates				
Methyl ethylene	28.9	0.4	28.5	
Dimethyl hydroxyethyl	25.6	2.6	23.0	5.5

TABLE IX

## POSITION OF CLEAVAGE IN SULFATES

Sulfate	Experimental conditions		Excess O <sup>18</sup> in H <sub>2</sub> O, %	Excess O <sup>18</sup> in sulfate, %	Atom O <sup>18</sup> introduced	Position of bond fission
	1st step	2nd step				
Ethylene	H <sub>2</sub> O	<sup>a</sup>	1.223	0.199	0.97	...
	H <sub>2</sub> O	4.95 N NaOH	1.400	.002	.00	C-O
	1.89 N NaOH	1.89 N NaOH <sup>b</sup>	1.203	.047	.156	14% S-O, 86% C-O
	3.08 N NaOH	3.08 N NaOH <sup>b</sup>	1.115	.037	.133	
Trimethylene	H <sub>2</sub> O	1.31 N NaOH	1.250	-.007	.00	C-O
	1.72 N NaOH	1.72 N NaOH <sup>b</sup>	1.222	.000	.00	
	1.18 N NaOH	1.18 N NaOH <sup>b</sup>	1.064	-.003	.00	
Dimethyl	H <sub>2</sub> O	1.56 N NaOH	1.322	.000	.00	C-O
	1.40 N NaOH	1.40 N NaOH <sup>b</sup>	1.197	.002	.00	
	1.40 N NaOH	<sup>c</sup>	1.197	-.004	.00	
Sodium hydroxyethyl	...	1.68 N NaOH	1.171	.004	.00	C-O
Trimethylene	H <sub>2</sub> O	{ 0.358 N HClO <sub>4</sub> }	1.248	.269	.86	S-O
		{ +0.384 N BaCl <sub>2</sub> }				
	H <sub>2</sub> O	{ 5.39 N HCl }	1.151	.286	.99	
		{ +0.500 N BaCl <sub>2</sub> }				

<sup>a</sup> Product isolated and analyzed as barium hydroxyethyl sulfate monohydrate. <sup>b</sup> Two steps carried out in same solution, without isolating intermediate. <sup>c</sup> Product isolated and analyzed as barium methyl sulfate.

ene phosphate and dimethyl hydroxyethyl phosphate are given in Table VIII.

Each datum for the phosphates is within the experimental error of the earlier, cruder measurements,<sup>9</sup> but the direction of the errors is such as to reduce the overall difference in heat of saponification from 7.6 to 5.5 kcal./mole.

**Point of Cleavage.**—The experiments with heavy oxygen which delineate the point of cleavage in the sulfate esters are summarized in Table IX.

The data for dimethyl sulfate are in agreement with those of Kursanov, *et al.*,<sup>28</sup> who have reported that dimethyl sulfate, in alkali, is cleaved exclusively with C-O fission.

### Discussion

**Summary of Results.**—(1) Ethylene sulfate, trimethylene sulfate and dimethyl sulfate hydrolyze by two distinct processes: (a) first-order solvolysis, which is dominant from pH 2 to the region around pH 10, and (b) a second-order reaction between the sulfate and hydroxide ion, which is dominant in the region where the concentration of base exceeds 0.01 M. (2) The rates of solvolysis of ethylene sulfate, trimethylene sulfate and dimethyl sulfate stand in the ratio 12:1:6. The rates of reaction with hydroxide ion stand in the ratio 103:1:5.5. (3) The hydrolyses of the diesters occur with C-O fission, except for the reac-

tion of ethylene sulfate with alkali, which is accompanied by 14% S-O fission. Since not more than 1% (and probably much less than 1%) of S-O fission accompanies the saponification of dimethyl sulfate, the rate of attack at sulfur is at least 300 times as great for the cyclic ester as for its open-chain analog. (4) The heats of reaction, summarized in Table VIII, show that the five-membered cyclic sulfate, like the five-membered cyclic phosphate, is less stable than its noncyclic analog by about 5-6 kcal./mole.

From these facts, it appears that the attack of water at carbon is almost unaffected by the thermochemical destabilization of the ring, but the attack of hydroxide on sulfur is accelerated (as is the attack on phosphorus in the analogous phosphate esters) in the five-membered cyclic ester. The six-membered ring, trimethylene sulfate, is opened in neutral solution or in base with C-O cleavage and reacts more slowly than

either ethylene sulfate or dimethyl sulfate. It therefore resembles the six-membered cyclic phosphate esters.<sup>29,30</sup>

Although the comparisons of rates of reaction, heats of hydrolysis and points of cleavage are available only for the compounds discussed above, other work in the field is consistent with that presented above. Brimacombe, *et al.*,<sup>15,31</sup> showed that cyclohexane-*cis*-1,2-diol sulfate is hydrolyzed with C-O cleavage in acid solution, but with S-O cleavage in alkali. Here again the cyclic sulfate is cleaved at sulfur in base; the repression of second-order reaction at carbon in the cyclohexane series probably accounts for the larger percentage of attack at the heteroatom. Comparable results were also obtained with the sulfate of *trans*-cyclohexane-1,2-diol<sup>15</sup> and with the sulfates of *meso* and optically active butane-2,3-diols.<sup>16</sup>

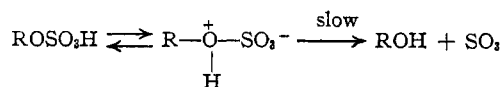
**Half-esters.**—The hydrolysis of the half-esters occurs at carbon in basic solution, but at sulfur in acid; this statement applies both to our own data (Table IX) and to the earlier work of Brimacombe<sup>15</sup> and of Lucas.<sup>16</sup> However, the mechanism of the hydrolysis of these half-esters may reasonably be expected to differ from that of the diesters. One possible mechanism would involve the ejection of SO<sub>3</sub>, as shown in the equation.

(29) H. G. Khorana, G. M. Tener, R. S. Wright and J. G. Moffatt, *J. Am. Chem. Soc.*, **79**, 430 (1957); E. Cherbuliez, H. Probst and J. Rabinowitz, *Helv. Chim. Acta*, **42**, 1377 (1959).

(30) R. E. Wall, Thesis, Harvard University, 1960.

(31) J. S. Brimacombe, A. B. Foster and M. Stacey, *Chem. Ind. (London)*, 262 (1959).

(28) D. N. Kursanov and R. V. Kudryavtsev, *J. Gen. Chem. U.S.S.R.*, **26**, 3323 (1956), English translation, Consultants Bureau, Inc., N. Y.



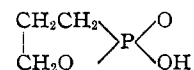
followed by the rapid hydration of the  $\text{SO}_2$ . Presumably the hydrolysis of these half-esters is simply the reverse of the esterification of alcohols in sulfuric acid.<sup>32</sup> The change in rate of these esterifications with changes in the concentration of sulfuric acid parallels that of aromatic sulfonation and the latter reaction has been shown with considerable probability to take place by way of  $\text{SO}_3$  as the active intermediate.<sup>33</sup> If this mechanism is correct, it resembles that suggested, in an equation, for the decomposition of monoesters of sulfurous acid,<sup>34</sup> where  $\text{SO}_2$  may be ejected. Furthermore, a somewhat similar scheme has been postulated for the solvolysis of the monoester monoanion,  $\text{RO-PO}_3\text{H}^-$ , of phosphoric acid,<sup>35,36</sup> with loss of monomeric metaphosphate ion,  $\text{PO}_3^-$ , instead of  $\text{SO}_3$ . And, finally, a parallel mechanism could account for the extraordinarily rapid alkaline hydrolysis of the diesters of phosphorous acid,<sup>37</sup> relative to that of the diethyl ester of ethylphosphonic acid.<sup>38</sup> The details of this example are somewhat obscure; although the reaction is general base catalyzed,<sup>39</sup> the rates are much less than those for the ionization of the P-H bond of the ester.<sup>40</sup> Nevertheless, the hydrolysis (by analogy with that of di-(2-octyl) phosphite<sup>41</sup>) presumably takes place with P-O fission, and so could involve a monomeric metaphosphite as an intermediate. If such proves to be correct, then the four hydrolyses (those of  $\text{ROSO}_2\text{H}$ ,  $\text{ROSO}_2\text{H}$ ,  $\text{ROPO}_3\text{H}^-$  and  $(\text{RO})_2\text{PHO}$ ) occur by comparable mechanisms.

**The Kinetic Acceleration.**—The central problem of the five-membered cyclic esters of phosphorus and sulfur concerns the high rates of hydrolysis with attack on the heteroatom. The phenomenon is to be distinguished from the rapid rates of hydrolysis of lactones.<sup>42</sup> The latter is presumably related to their large dipole moments, and not to some general property of rings, since lactams react at rates quite similar to those for amides.<sup>43</sup> Furthermore, the acceleration in lactones, as differentiated from those in cyclic phosphates and sulfates, is greater with the six- than with the five-membered rings.

The rates of hydrolysis of sulfites and phosphites fall in an intermediate class. In acid solution, ethylene sulfite actually reacts less rapidly than dimethyl sulfite,<sup>34</sup> but in alkali it reacts a hundred times as fast as trimethylene sulfite<sup>44</sup> and several hundred times as fast as dimethyl sulfite.<sup>44,45</sup> Preliminary measure-

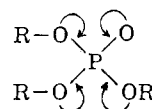
ments<sup>46</sup> suggest that similar comparisons, in both acid and base, may be made for the rates of hydrolysis of methyl ethylene phosphite and trimethyl phosphite. In sharp contrast, however, to the cyclic sulfates and phosphates, the cyclic sulfites<sup>45</sup> and selenites<sup>47</sup> give off no more heat on hydrolysis than do the corresponding non-cyclic derivatives. Thus the cyclic sulfites, selenites and phosphites are much more nearly normal than the analogous sulfates and phosphates.

Finally, it should be noted that the rate of acid-catalyzed hydrolysis<sup>2,48</sup> of the cyclic "phostonic acid,"



exceeds that of the monoethyl ester of ethylphosphonic acid by a factor of about  $10^5$ .

These data permit us to discard some of the explanations for the kinetic acceleration which had previously been considered. In particular, the large difference in rate of hydrolysis between the "phostonic acid" and the monoethyl ester of ethylphosphonic acid makes it improbable that the phosphorus atom imposes a sharp torsional angle upon the ring atoms<sup>5</sup>; such an explanation demands the presence of *two* C-O-P bonds in the ester. Furthermore, the possibility that the eclipsing of the hydrogen atoms or unpaired electrons on the ester oxygen atoms creates strain<sup>6</sup> (or, at least, that it creates *all* the strain) is improbable, in the light of the thermochemical data for the sulfites<sup>45</sup> and selenites,<sup>47</sup> and in the light of the lack of kinetic acceleration, in acid solution, for the hydrolysis of cyclic sulfites<sup>34</sup> and phosphites<sup>46</sup>; even the kinetic acceleration in alkaline solution,<sup>44-46</sup> although large, is dwarfed by that for the cyclic phosphates, and for the phostonic acid.<sup>48</sup> The results may, however, still prove consistent with the hypothesis<sup>8</sup> that partial double-bonding between the ester oxygen atoms and the heteroatom in the five-membered rings is essential to the kinetic acceleration. This explanation requires that, with phosphites and sulfites, the presence of an unshared pair of electrons on phosphorus or sulfur partially represses the formation of a double bond between the heteroatom and the ester oxygen atoms.



Such partial double-bonding in phosphates is generally accepted.<sup>49</sup> The X-ray crystallographic demonstration of short phosphorus-to-oxygen bonds in dibenzyl hydrogen phosphate<sup>50</sup> strongly supports the hypothesis. The evidence that double-bonding is less important in phosphites is not so satisfactory, and depends in part on the small differences in P-O bond lengths as determined by electron diffraction measurements<sup>49,51</sup> on  $\text{P}_4\text{O}_6$  and  $\text{P}_4\text{O}_{10}$ . The chemical shifts for phosphorus in n.m.r. spectra suggest greater shielding for phosphates than for phosphites,<sup>52,53</sup> and this observation has been interpreted<sup>52</sup> as showing that the

see "Additions and Corrections" by R. E. Davis, *ibid.*, **84**, 5001 (1962); and 1 and 2 of this paper.

(46) M. Panar and F. Covitz, unpublished.

(47) C. A. Bunton, private communication.

(48) A. Eberhard, unpublished.

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

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(37) P. Nylen, *Svensk. Kem. Tid.*, **49**, 29 (1937); P. R. Hammond, *J. Chem. Soc.*, 2521 (1962).

(38) R. F. Hudson and L. Keay, *ibid.*, 2463 (1956).

(39) P. Nylen, *Svensk. Kem. Tid.*, **49**, 79 (1937).

(40) P. R. Hammond, *J. Chem. Soc.*, 1365 (1962); P. Nylen, *Z. anorg. allgem. Chem.*, **235**, 161 (1938).

(41) W. Gerrard, W. J. Green and R. A. Nutkins, *J. Chem. Soc.*, 4076 (1952).

(42) R. Huisgen and H. Ott, *Tetrahedron*, **6**, 253 (1959).

(43) H. K. Hall, M. K. Brandt and R. M. Mason, *J. Am. Chem. Soc.*, **80**, 6420 (1958).

(44) J. G. Tillett, *J. Chem. Soc.*, 37 (1960); P. B. D. de la Mare, J. G. Tillett and H. F. van Woerden, *Chem. Ind.* (London), 1533 (1961).

(45) R. E. Davis, *J. Am. Chem. Soc.*, **84**, 599 (1962). The thermochemical data reported in the reference above were obtained in collaboration with R. E. Wall and E. T. K. at Harvard. The last paragraph of Davis' discussion erroneously confused some of our earlier data with his predictions;

oxygen atoms in phosphates (but presumably particularly the phosphoryl oxygen atoms) contribute to shielding by partial bonding with the d-orbitals of phosphorus. However, the greater double-bond character in the P-O bonds of phosphates, as compared to those of phosphites, should also be apparent in infrared spectra, but here the situation is confused. No agreement has even been reached as to the correct assignments of individual frequencies to C-O and to P-O stretching motions.<sup>64</sup> Simple inspection, however, does not reveal much difference between the P-O-C vibrations in phosphates and phosphites.

If, indeed, p-d double-bonding is greater in the ester bonds of phosphates as compared to phosphites (and of sulfates as compared to sulfites), then such double-bonding could stiffen the P-O or S-O bonds, with concomitant stabilization of the esters. Since the bond lengths and angles do not exactly fit the five-membered rings of ethylene phosphate and sulfate, the stiffening and flattening of the rings caused by partial double-bonding might produce strain in excess of that previously<sup>6</sup> estimated. At the same time, the resistance of the ring could result in less double-bond character for the P-O and S-O bonds of the cyclic compounds. To the extent that double-bonding is diminished, the five-membered cyclic esters are less stabilized than their open-chain analogs; to the extent that the P-O and S-O bonds are stiffened, they increase the strain in the ring. This explanation places more emphasis on the stabilization of the non-cyclic esters, and less emphasis on ring strain than did our earlier discussions,<sup>6,9</sup> and perhaps makes it easier to understand why ethylene phosphate undergoes oxygen exchange with the solvent at a rate comparable to that of ring opening.<sup>8</sup> If the

(54) L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958, p. 316.

present view is correct, then the formation of the transition state for either hydrolysis or exchange of five-membered cyclic esters is preferred over that for the non-cyclic esters in part because less energy is required to overcome the stabilization supplied by the partial double bonds. The difference in heat of saponification between the cyclic and non-cyclic esters is of course unaffected by this somewhat different division of the energy, but perhaps this thermochemical quantity should not be regarded exclusively as strain. Presumably the double bond character of the S-O or P-O bonds is lost in the pentavalent transition state<sup>8</sup> when attack occurs at sulfur or phosphorus, but not when it occurs at carbon. In this way, it may be possible to account for the major part of the kinetic acceleration in the hydrolysis of five-membered cyclic sulfates and phosphates, and to understand why this acceleration is largely absent in the six-membered rings or when attack occurs at carbon. However, it must still be noted that on the one hand the thermochemical "strain" which has been measured (see Table VIII) is inadequate to account fully for the kinetic acceleration in phosphates, and on the other that kinetic acceleration, in alkaline solution, is moderately large for sulfites, where no thermochemical strain has been found. Further, although kinetic acceleration at sulfur may be very large in the cyclic sulfates, this point has not been proved, and at present one can only say that the factor exceeds 300. The difficulties with infrared spectra, noted above, also stand in the way of a complete understanding of the problem. Nevertheless, the role of p-d double-bonding in the kinetic acceleration seems reasonably probable.

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## Organic Reactions under High Pressure. VII. Volumes of Activation for Some Diels-Alder Reactions<sup>1</sup>

BY CHEVES WALLING AND HARVEY J. SCHUGAR

RECEIVED JULY 18, 1962

The effect of pressure on the dimerization of cyclopentadiene has been reinvestigated, yielding values of  $\Delta V^*$  near atmospheric pressure of  $-20.2$  to  $-22.5$  cc./mole at  $20-40^\circ$ . Similarly, a value of  $\Delta V^* = -22.6$  cc./mole at  $80^\circ$  has been obtained for the reaction of 2,3-dimethylbutadiene with butyl acrylate. The rearrangement of  $\beta$ -1-hydroxydicyclopentadiene is pressure retarded, consistent with its representing a partial retro-Diels-Alder reaction. These results further support the idea that Diels-Alder reactions of non-cyclic dienes are probably two-step processes involving an open chain intermediate, and that the transition states in reactions of cyclopentadiene are at least highly unsymmetric.

The pronounced increase in rate of Diels-Alder reactions at high pressure was first noted by Raistrick, Sapiro and Newitt in the dimerization of cyclopentadiene,<sup>2</sup> and the phenomenon has been studied further by Walling and Peisach for the case of isoprene dimerization.<sup>3</sup> Since the pressure coefficient of the reaction provides a criterion of mechanism, we have been interested in examining additional systems, particularly since the cyclopentadiene data appear dubious, and the isoprene results have recently been questioned.<sup>4</sup> This paper reports a reinvestigation of the cyclopentadiene dimerization, a study of the reaction between 2,3-dimethylbutadiene and butyl acrylate, and an investi-

gation of the effect of pressure on the rearrangement of  $\beta$ -1-hydroxydicyclopentadiene to *anti*-8-hydroxydicyclopentadiene which has been interpreted by Woodward and Katz<sup>5</sup> as a partial retro-Diels-Alder reaction.

### Results

**Cyclopentadiene.**—The dimerization of cyclopentadiene was studied by Raistrick, *et al.*,<sup>2</sup> at pressures up to 3000 kg./cm.<sup>2</sup> and temperatures from  $0-40^\circ$  in the absence of solvent. Although the reaction was accelerated by pressure over the whole range studied, their results are peculiar in that  $\Delta V^*$ , defined by the equation

$$d \ln k/dP = -\Delta V^*/RT \quad (1)$$

changes markedly with temperature.<sup>6</sup> In fact, a moderate extrapolation indicates that at higher temperatures  $\Delta V^*$  would become larger than  $\Delta V$  for the

(1) Taken from the Ph.D. thesis of Harvey J. Schugar, Columbia University, 1962. Support of this work by a grant from the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

(2) B. Raistrick, R. H. Sapiro and D. M. Newitt, *J. Chem. Soc.*, 1761 (1939).

(3) C. Walling and J. Peisach, *J. Am. Chem. Soc.*, **80**, 5819 (1958).

(4) S. W. Benson and J. A. Berson, *ibid.*, **84**, 152 (1962).

(5) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

(6) This peculiarity was pointed out to us by M. G. Gonikberg in 1960.