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The Thermal Decompositions and Mass Spectral Studies of the Cyclic Anhydrides of Some β-Sulfocarboxylic Acids

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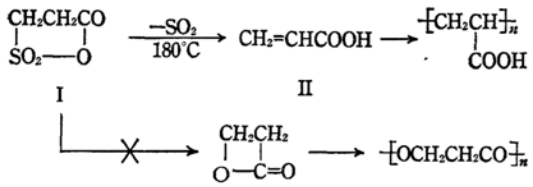
The thermal decompositions of the cyclic anhydrides of β-sulfopivalic acid (III) and β-sulfoisobutyric acid (IV) have been studied. The pyrolysis of III without a solvent gave pivalic acid, isobutene, isobutane, water, and a mixture of trimers of isobutene, while the pyrolysis of IV resulted in the formation of methacrylic acid and acetone. In the case of III, the evolution of sulfur dioxide and carbon dioxide occurred mainly. On the contrary, in the case of IV, the carboxylic acid derivative was the predominant product. These results might be interpreted in terms of a decomposition mechanism in which the compound (IV) having α-hydrogen to a carbonyl group undergoes thermal decomposition *via* a concerted mechanism. In the case of IV, it should be noted that acetone was formed. This paper will also be concerned with the mass spectra of III and IV and with the cyclic anhydride of β-sulfopropionic acid.

In a previous paper,[1] we reported the formation and decomposition mechanisms of cyclic anhydride of β-sulfopropionic acid (I); we found that acrylic acid (II) was formed intramolecularly in a 30.2% yield, and that the evolution of carbon dioxide was not detected, when I was heated at 180°C without a solvent.



No such a sterically unfavorable, intramolecular 1,3 hydrogen shift to oxygen as is described above has yet been reported so far as we know, while the 1,5 hydrogen transfer to oxygen[2-4] and the 1,3 hydrogen shift to carbon[5-7] have been reported. Thus, it was inferred that such a cyclic anhydride as I, with α-hydrogens to a carbonyl group, should exhibit interesting behavior upon thermal decomposition. Moreover, there have not yet been any reports about the 1,3 methyl shifts to oxygen in pyrolyses of saturated hydrocarbon systems. Therefore, we have examined the behavior of compounds similar to I upon heating. In the present paper, we wish to report on the behavior in thermal decomposition of the cyclic anhydrides of β-sulfopivalic acid (III) and β-sulfoisobutyric acid (IV). In these two systems, no 1,3 methyl shifts to oxygen were observed, through hydrogen shifts did occur in the case of IV. It was also found that the reaction courses of the pyrolyses were considerably affected with presence of the α-hydrogen to the carbonyl group; a possible mechanisms for this will be presented.

We will then deal further with the mass spectra of these three cyclic anhydrides (I, III and IV) in connection with pyrolysis studies of them.

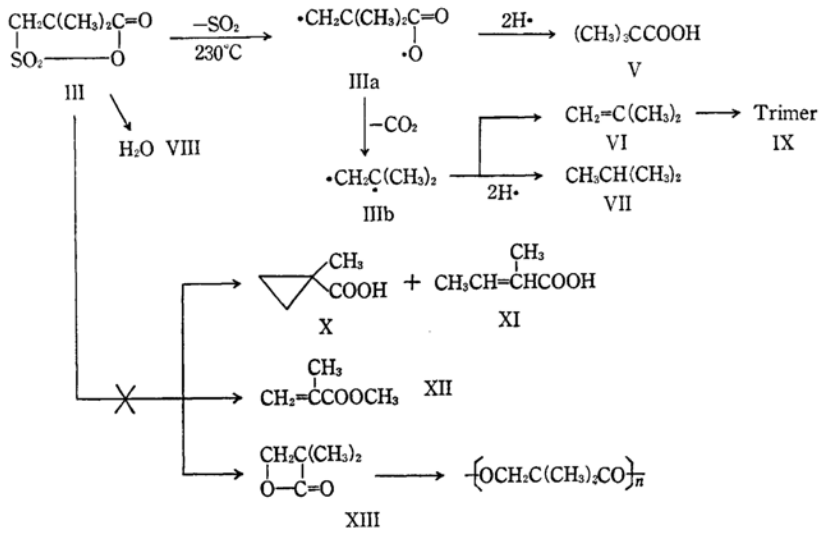
Results and Discussion

Thermal Decompositions. When cyclic anhydride of β-sulfopivalic acid (III) was heated at 230°C without a solvent, there were obtained pivalic acid (V, in a 1.4% yield*1), isobutene (VI, in a 17.7% yield), isobutane (VII, in a 20.0% yield), water (VIII, in a 69.0% yield), and some bad-smelling, dark yellow liquid (IX, in a 6.1% yield as isobutene trimer); at the same time, sulfur dioxide and carbon dioxide were evolved. The residue was a black and spongy material which was insoluble and non-melting.

The sulfur dioxide, isobutene, and isobutane were identified by comparing their retention times in vapor-phase chromatography with those of authentic samples. No *n*-butane or propylene was

1) T. Nagai, K. Nishitomi and N. Tokura, This Bulletin, **40**, 1183 (1967).
2) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961).
3) C. Walling and A. Padwa, *ibid.*, **83**, 2207 (1961).
4) M. Akhtar and D. H. R. Barton, *ibid.*, **83**, 2213 (1961).
5) J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.*, **1960**, 1602.
6) A. S. Gordon and J. R. McNesby, *J. Chem. Phys.*, **33**, 1882 (1960).
7) C. P. Quinn, *Trans. Faraday Soc.*, **59**, 2543 (1963).

*1 The yields described in this paper are in mole % based on the starting cyclic compounds used.



Scheme I

detected.

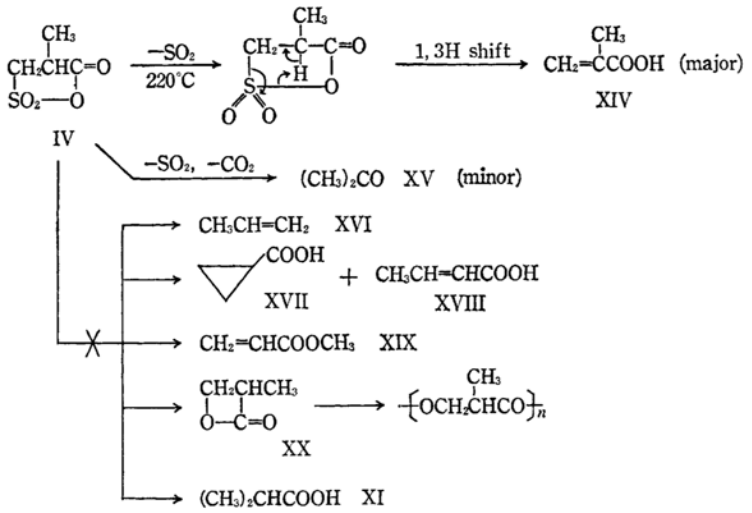
The pivalic acid (V) was identified by comparing its IR and NMR spectra with those of an authentic sample. The dark yellow liquid was confirmed to be a mixture of trimers of isobutene (IX) on the basis of the IR, UV, and NMR spectra, the boiling point, and chemical evidence. The IR spectrum showed absorptions at 2900 (methyl), 1365, 1380 (geminal dimethyl), and 800 cm^{-1}(C=C), among others. It also exhibited a moderate absorption at 1700 cm^{-1}, but this was not due to the carbonyl group, since authentic di-isobutylene showed a similar absorption at 1700 cm^{-1}. The NMR spectrum of IX showed multiplet peaks centered at τ 8.9, 7.9 and 3.4, the area ratio being 9 : 10 : 3. The UV spectrum of IX exhibited a very broad absorption at around 230 mμ ($\varepsilon = 3.0 \times 10^4$), with tailing up to 350 mμ. The multiplet at τ 3.4 and the broad absorption at near 230 mμ suggest the presence of a conjugated double bond in the IX molecule. The color of bromine in a carbon tetrachloride solution disappeared upon the addition of IX. The boiling point of IX was determined to be about 180°C. This boiling point coincided with that of the isobutene trimer which is obtainable from isobutene in the presence of sulfuric acid or by heating.[8] No further studies of the isomers or the structures of IX were carried out.

1-Methyl-1-carboxylcyclopropane (X) and its isomer, α-methylcrotonic acid (XI), were prepared by ordinary methods.[9] A comparison of their NMR spectra with that of the mixture of liquid products obtained in the present study showed that X and XI were not the products in the present case. Neither methyl methacrylate (XII), which should be formed if a 1,3 methyl shift to oxygen occurred, nor β-lactone (XIII), which might be obtained from IIIa, was detected in NMR analyses. From these results, it seems that the reaction products might be formed through a pathway such as that described in Scheme I. In this case, the fact that V and VII, which should be formed by intermolecular hydrogen abstraction, were obtained suggests that III undergoes thermal decomposition *via* a radical mechanism rather than *via* a concerted one.

Sulfur dioxide evolves first; the resulting diradical (IIIa) partly abstracts hydrogens intermolecularly to form V, and then mostly loses carbon dioxide to give another diradical (IIIb). Thus, IIIb, in one part, abstracts hydrogens intermolecularly to form VII and, in another part, converts to VI. Further, VI may be changed to IX. The formation of IX may be caused by heating under the experimental conditions or by the action of sulfuric acid, for the system evolves sulfur dioxide and water, and contains oxygen under an atmosphere. These results obviously indicate that no 1,4 hydrogen shift or 1,3 methyl shift occurs under these conditions. The formation of VIII should be noted, although the pathway to VIII is not clear.

Next, we examined the behavior of the cyclic anhydride of β-sulfoisobutyric acid (VI), with one α-hydrogen to a carbonyl group. When IV was heated at 220°C without a solvent, there were obtained methacrylic acid (XIV, in a 66.9% yield) and acetone (XV, in a 6.1% yield); at the same time sulfur dioxide and a small amount of carbon dioxide were evolved. In this case no gaseous compounds other than sulfur dioxide and carbon dioxide were detected by vapor-phase chromatography. The residue was a black and

8) S. W. Lebedew and G. G. Kobliansky, *Ber.*, **63**, 103 (1930).
9) S. Siegel and C. G. Bergstrom, *J. Am. Chem. Soc.*, **72**, 3815 (1950).



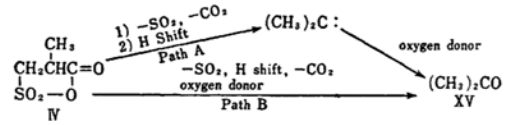
Scheme II

spongy material which was insoluble and non-melting.

Methacrylic acid (XIV) was identified by comparing its IR and NMR spectra with those of an authentic sample. Acetone (XV) was identified by comparing its NMR spectrum and the melting point of its 2,4-dinitrophenylhydrazone (mp 123.5—124°C) with those of an authentic sample. Propylene (XVI) was not detected by vapor-phase chromatography. There were none of the peaks at fields higher than 9.0 τ in the NMR spectrum which are characteristic of the methylene protons of 1-carboxylcyclopropane (XVII). Moreover, there were no peaks assignable to crotonic acid (XVIII), the isomer of XVII.[10] Neither methyl acrylate (XIX) nor β-lactone (XX) was detected in NMR analyses. Moreover, isobutyric acid (XXI), which should be formed by intermolecular hydrogen abstraction if the thermal decomposition proceeds, *via* such a radical mechanism as was observed in the case of III, was not detected in NMR analyses of the reaction mixture.

These results are presented in Scheme II. In this case, the fact that XXI, which should be formed by intermolecular hydrogen abstraction in a radical mechanism, was not obtained suggests that XIV is formed *via* a concerted mechanism rather than *via* a radical one. Moreover, no 1,4 hydrogen shift or 1,3 methyl shift occurred under these conditions, either.

It is very interesting that XV was formed in a 6.1% yield in this system, for the formation of XV involves the possibility of a 1,2 hydrogen shift in the thermal process, though there have hitherto been few examples of 1,2 hydrogen shifts in pyrolyses[11-15] (below 300°C). The fact that carbon dioxide was detected must be related to the formation of XV. In this case, it seems that XV is not formed *via* a free dimethylcarbene, for if this were the case, propylene (XVI) should be formed,[16] while XVI was not detected by vapor-phase chromatography. Also, it may be very difficult to consider the intermolecular hydrogen shift upon the formation of XV. Thus, Path B below may be more plausible than Path A, although the details of the process are obscure:



Scheme III

There exist two possibilities in this system as to the oxygen donor. One is atmospheric oxygen, and the other is sulfur dioxide. The former can be neglected from the fact that, in the experiment on the thermal decomposition of IV under a nitrogen stream, the yield of XV was essentially

10) Crotonic acid, CH_3^a H_b $C=C$ H^c $COOH$, exhibited peaks at τ 8.10 (a), 2.90 (b), and 4.17 (c), while methacrylic acid, H^b H_c $C=C$ CH_3^a $COOH$, showed peaks at τ 8.03 (a), 4.28 (b), and 3.70 (c).

11) D. Y. Curtin and M. J. Hurwitz, *J. Am. Chem. Soc.*, **74**, 5381 (1952).
12) M. S. Kharasch, F. L. Lambert and W. H. Urry, *J. Org. Chem.*, **10**, 298 (1945).
13) H. C. Brown and G. A. Russell, *J. Am. Chem. Soc.*, **74**, 3995 (1952).
14) L. H. Slaugh, *ibid.*, **81**, 2262 (1959).
15) N. Kornblum and H. E. De LaMare, *ibid.*, **74**, 3079 (1952).
16) W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y. (1964), p. 47ff.

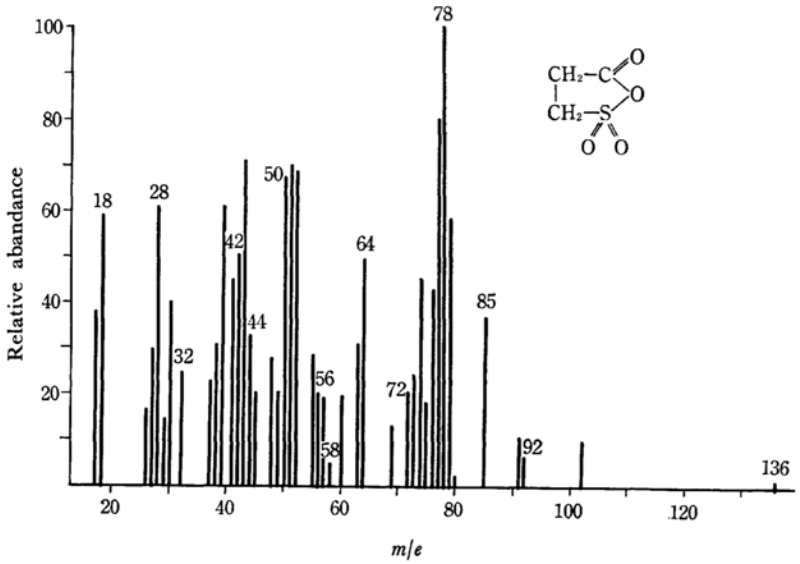


Fig. 1. Mass spectrum of cyclic anhydride of β-sulfopropionic acid (I). (Weaker peaks are omitted here.)

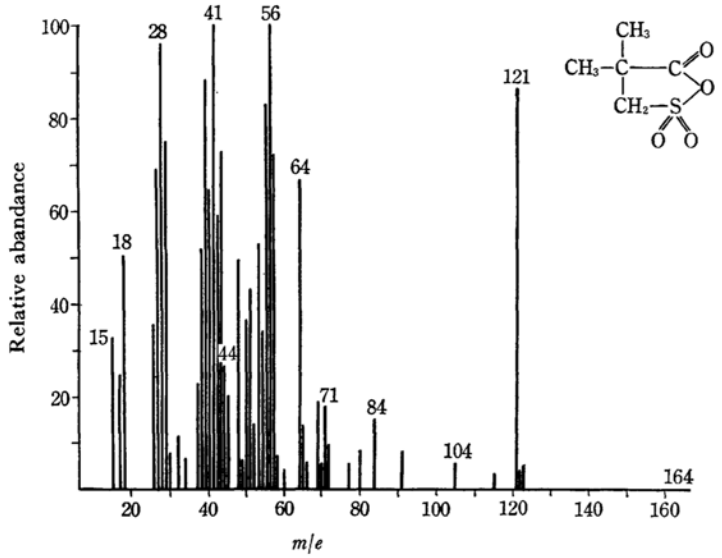


Fig. 2. Mass spectrum of cyclic anhydride of β-sulfopivalic acid (III). (Weaker peaks are omitted here.)

the same as that in the experiment under an atmosphere (see Experimental Section). Sulfur dioxide can be used as the source of oxygen at a high temperature,[17] so the oxygen donor to XXII seems to be sulfur dioxide.

Mass Spectral Studies. There have been no reports on mass spectral studies of such compounds as cyclic anhydrides of β-sulfocarboxylic acids (I, III and IV) except that by Meyerson *et al.*[18] about benzyne formation. In the present work, we are going to compare the behavior of the compounds under electron impact with those under thermal decomposition. The mass spectra of I, III, and IV are shown in Figs. 1, 2, and 3 respectively. They display different features, although the parent peaks are all very weak. The intense peak at *m/e* 78 in Fig. 1 may be assigned as $CH_2SO_2^+$. The other peaks may be understood

17) T. H. Strickland and A. Bell, *Ind. Eng. Chem.*, **53**, 7 (1961).
18) S. Meyerson and E. K. Fields, *Chem. Commun.*, **1966**, 275.

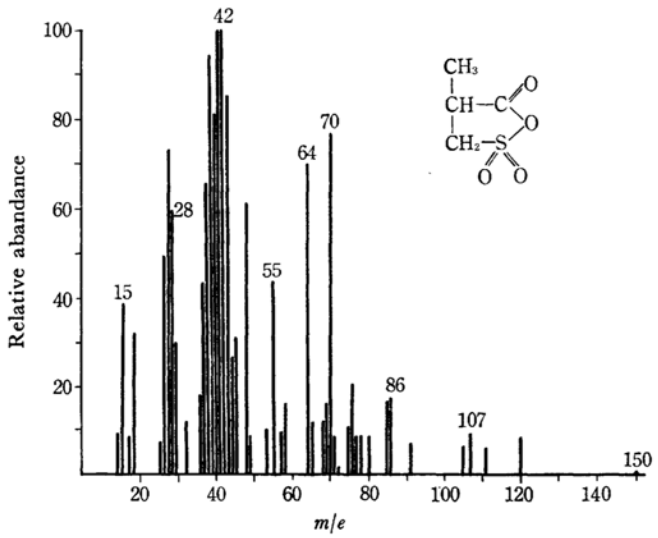
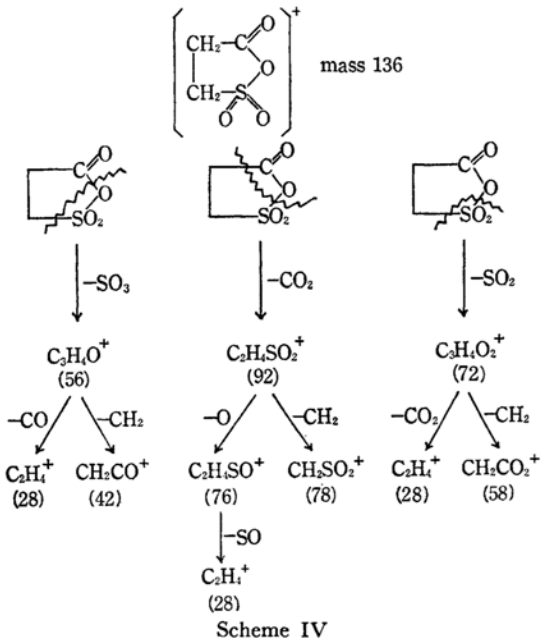


Fig. 3. Mass spectrum of cyclic anhydride of β-sulfoisobutyric acid (IV). (Weaker peaks are omitted here.)



Scheme IV

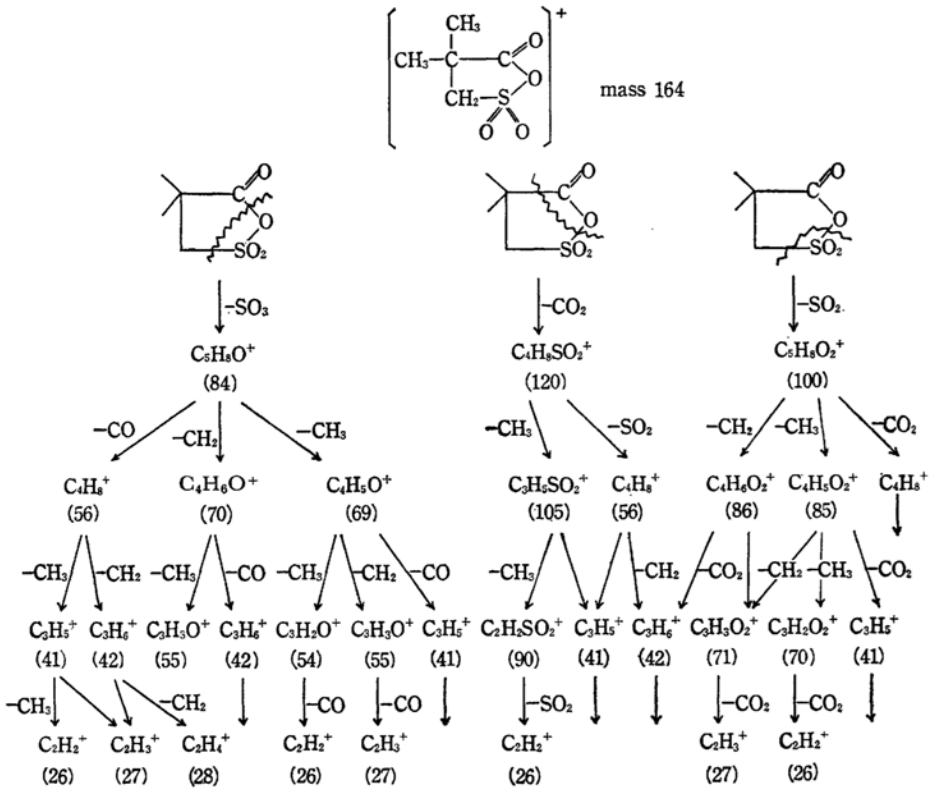
in such a manner as in Scheme IV. The peak at *m/e* 28, which may be assigned to $C_2H_4^+$ (=I−SO_2−CO_2) and CO^+, is not so intense. This tendency is similar to that in thermal decomposition. The intense peaks at *m/e* 28, 41, 56 and 121 in Fig. 2 may be assigned to $C_2H_4^+$, $C_3H_5^+$, $C_4H_8^+$, and $C_4H_8SO_2^+ + 1$ (=III−CO_2+1) respectively. The other peaks may be understood in such a manner as in Scheme V. The intense peaks at *m/e* 28, 41, and 56 may correspond to olefins; this tendency is similar to that in thermal decomposition. The intense peaks at *m/e* 27, 42, and 70 in Fig. 3 may be assigned to $C_2H_3^+$, $C_3H_6^+$, and $C_4H_6^+$ (=IV−SO_3) respectively. The other peaks may be understood in such a manner as in Scheme VI. The intense peaks near *m/e* 42 may correspond to propylene or dimethylcarbene; this tendency is different from that in the thermal decomposition.

Experimental

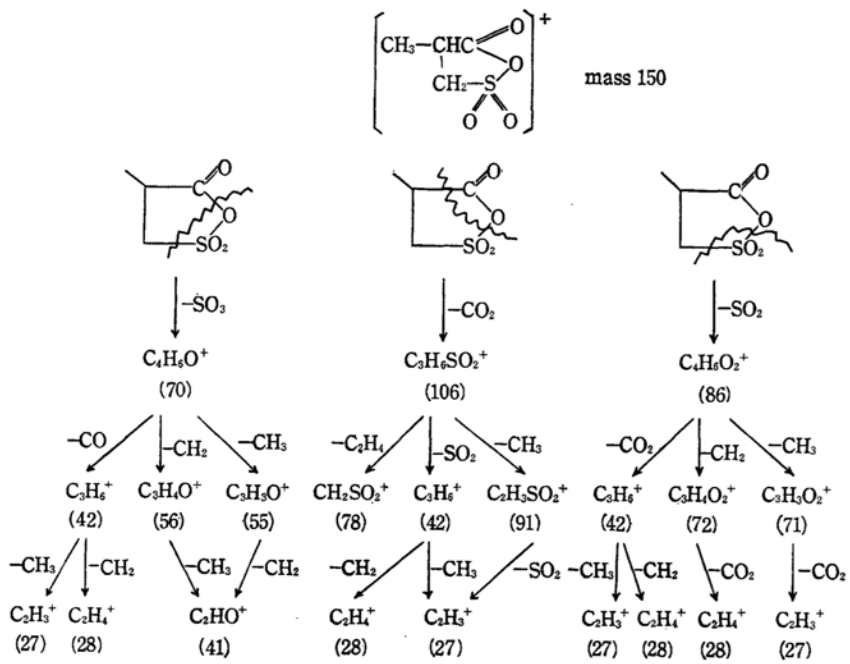
Cyclic Anhydride of β-Sulfopivalic Acid (III). This was prepared by the photosulfonation of pivalic acid, which had been synthesized in the same manner as has been described in the literature,[19] with sulfuryl chloride in a manner similar to that described by Kharasch *et al.*[20] In this case, we added one or two drops of pyridine as a catalyst. The product was separated as a white solid. It was dried *in vacuo* in a desiccator containing phosphorus pentoxide and paraffin wax. The yield was about 17%. The melting point of this material (III) was 62—63°C (lit.[21,22] 62—64°C), which did not change upon crystallization from thionyl chloride. The NMR spectrum of III in water (10 wt%) showed two singlets at δ(ppm) 3.30 (β-methylene, 2H) and 1.40 (α-methyl, 6H), where water was used as the internal reference (its chemical shift relative to TMS was assumed to be δ=5.05 (ppm)).

Cyclic Anhydride of β-Sulfoisobutyric Acid (IV). This was prepared by the photosulfonation of isobutyric acid with sulfuryl chloride in the same manner as was described by Kharasch *et al.*[20] The boiling point of IV was 134—135°C/3 mmHg. The NMR spectrum

19) L. T. Sandborn and E. W. Bousquet, "Organic Syntheses," Coll. Vol. I, p. 526 (1948).
20) M. S. Kharasch, T. H. Chao and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 2393 (1940).
21) J. L. Greene, Jr., and H. J. Hagemeyer, Jr., *ibid.*, **77**, 6065 (1955).
22) A. G. Schering, B. P. 1012325 (1965); *Chem. Abstr.*, **64**, 6503 (1966).



Scheme V



Scheme VI

of IV in water (11.76 wt%) showed a doublet at δ (ppm) 1.07 (α-methyl, 3H), and a doublet and a multiplet centered at δ 2.90 (β-methylene, 2H and α-methyne, 1H), where 1,4-dioxane was used as the internal reference (its chemical shift relative to TMS was assumed to be δ=3.57 (ppm)).

Thermal Decomposition of III. *A Typical Experiment.* In a 50 m*l*, round-bottomed flask fitted with an outlet tube leading to a cooler equipped with a receiving vessel and a calcium chloride tube, 10.6 g of III without a solvent were placed. The calcium chloride tube led to a trap dipped in dry ice and trichloroethylene bath equipped with a rubber tube. The trap further led to a 100 m*l* flask in which an aqueous calcium hydroxide solution was placed in order to remove carbon dioxide; the outlet gas was collected on the water. The round-bottomed flask was placed in an oil bath equipped with a thermometer, and heated gradually. When the temperature reached 65°C, the solid in the flask melted; upon further heating, to 220°C, sulfur dioxide gas evolved. The temperature was maintained at about 230°C for 3 hr, until the liquid in the flask changed to a black, spongy matter. During the heating, a mixture of a dark yellow liquid (IX) and a colorless liquid (VIII) was distilled out, and another mixture of sulfur dioxide and VI was trapped, while VII was collected on the water. Further calcium carbonate was also found to be deposited. The gaseous products were analysed by vapor-phase chromatography. As a result, VI and VII were identified by comparing their retention times with those of authentic samples. *n*-Butane and propylene were not detected.

The mixture of IX and VIII was treated as follows. It was mixed with anhydrous ether in a separate funnel, and the lower layer was removed. This lower layer was identified as water (0.802 g). The upper layer was further extracted with an alkali solution. The extract was acidified with hydrochloric acid and extracted with ether. The ether extract was dried over anhydrous sodium sulfate, and then the ether was distilled out. The resulting solid was identified as pivalic acid (V) by comparing its IR and NMR spectra with those of an authentic sample (0.124 g). The other ether extract, which was not extracted with the alkali solution, was dried over anhydrous sodium sulfate. Then the ether was distilled out. The resulting dark yellow liquid was confirmed to be isobutene trimer (0.591 g) by comparing its boiling point with that reported in the literature[8] and its IR spectrum with that of authentic di-isobutylene, and by considering the NMR spectrum and chemical evidence. The yield of VII was calculated from the volume of the collected gas by considering the dead volume. The yield of VII was 20.0%. The yield of VI was calculated from the weight of the mixture of sulfur dioxide and VI, and from their relative areas in vapor-phase chromatography. The yield of VI was 17.7%. The black, spongy residue was treated with anhydrous ether, and then the ether was distilled out from the ether extract. The resulting material was dissolved in chloroform, and the undissolved part was treated with aniline in a benzene solution. A white solid, which was supposed to be a monoaniline salt of β-sulfopivalic acid, was deposited, although it was only a trace. The dissolved part in chloroform was chromatographed over alumina. The resulting material (0.094 g) was identified as IX by its IR spectrum.

Thermal Decomposition of IV. *A Typical Experiment.* In a 50 m*l*, round-bottomed flask fitted with equipment in the same manner as has been described above in the case of III, 7.25 g of IV without a solvent were placed. The flask was placed in an oil bath equipped with a thermometer, and heated gradually. When the temperature reached 215—220°C, sulfur dioxide gas evolved. The temperature was maintained at about 220°C for 3 hr, by which time the liquid in the flask had changed to a black, spongy matter. During the heating, a colorless liquid (2.95 g) was distilled out. Most of it was identified as XIV by comparing its NMR and IR spectra with those of an authentic sample; the rest was identified as XV by comparing its NMR spectrum and the melting point of its 2,4-dinitrophenylhydrazone with those of an authentic sample. The yields of XIV and XV were caluclated from the total weight of the mixture and from their relative NMR areas. The yields were thus determined to be 66.9% (XIV) and 6.1% (XV). In this system no gaseous products except sulfur dioxide were detected by vapor-phase chromatography analyses. Calcium carbonate was also deposited, but its quantity was small. The black, spongy residue was treated in the same manner as has been described above in the case of III. The resulting liquid was identified as XIV (0.05 g) by means of its IR spectrum. In an experiment under a nitrogen stream, the yields of XIV and XV were 66.1% and 6.9% respectively.

IR Spectra. The infrared spectra were recorded on an EPI-S2-TYPE Hitachi spectrometer.

NMR Spectra. The proton resonance spectra were run on a Nihondenshi spectrometer at 60 Mc.

Vapor-phase Chromatography. Routine separations were carried out on a Yanagimoto Model GCS-100 gas chromatograph. A 3 m×0.25 in. stainless steel column packed with liquid paraffin (Column A) and a 4 m×0.25 in. stainless steel column packed with silicone hivac grease (Column B) were used. The column temperature was room temperature (31—33°C) for all fractions. Hydrogen (48 m*l*/min in Column A and 50 m*l*/min in Column B) was used as the carrier gas. The retention times in minutes were as follows: 1.4 (sulfur dioxide), 2.85 (VII), 3.45 (VI), 1.45 (propylene) and 3.75 (*n*-butane) in Column A; 3.0 (sulfur dioxide), 2.5 (VII), 3.15 (VI), 1.85 (propylene) and 3.2 (*n*-butane) in Column B.

Mass Spectra. The mass spectra were run on a VD-10001-A Hitachi spectrometer.