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Mechanistic Aspects of the Formation and Decomposition of the Cyclic Anhydride of β-Sulfopropionic Acid. A Study of Radical Rearrangement Using a Labeled Compound

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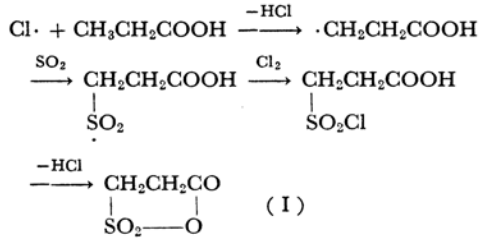
The photochemical sulfonation of propionic-α, α-d_2-acid-d_1 (83% isotopic purity at the α-position) with sulfuryl chloride to form the cyclic anhydride of the deuterated β-sulfopropionic acid was carried out. The isotopic purity of the resulting anhydride decreased to 55±2% at the α-position. This result indicates that an α-hydrogen is abstracted in a ratio of 67.5±5%, followed by the rearrangement of a β-hydrogen prior to the sulfonation at the β-carbon atom. The mechanism is somewhat different from that proposed by Kharasch *et al.* [M. S. Kharasch, T. H. Chao and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 2393 (1940)] for the photosulfonation of propionic acid. The present paper will also study the thermal decomposition of the cyclic anhydride to produce acrylic acid; its mechanistic aspects will be considered.

The photochemical sulfonation of propionic acid with sulfuryl chloride to form the cyclic anhydride of β-sulfopropionic acid (I) has been reported by Kharasch *et al.*:[1]

$$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

$$Cl_2 \xrightarrow{h\nu} 2Cl\cdot$$



$$Cl\cdot + CH_3CH_2COOH \xrightarrow{-HCl} \cdot CH_2CH_2COOH$$

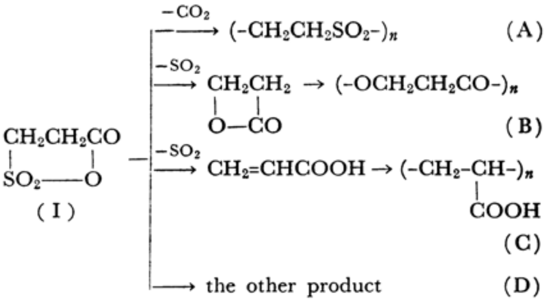
$$\xrightarrow{SO_2} \underset{\underset{\cdot}{SO_2}}{CH_2}CH_2COOH \xrightarrow{Cl_2} \underset{SO_2Cl}{CH_2}CH_2COOH$$

$$\xrightarrow{-HCl} \underset{SO_2-\!\!-O}{CH_2CH_2CO} \quad (I)$$

The mechanism they suggested for the photosulfonation reaction is that the abstraction of a β-hydrogen atom by the chlorine radical in the ratio of 55% is followed by sulfonation at the β-carbon atom, resulting in the exclusive formation of I, while the α-hydrogen is abstracted in the ratio of 45% to form the α-sulfonyl chloride of the acid momentarily, which decomposes into the α-chloride and sulfur dioxide. The mechanism involves no rearrangement of a hydrogen atom.

In the present paper, by using propionic acid containing deuterium as the starting material, we will deal with the possibility of the rearrangement of a β-hydrogen to the α-position, from which a hydrogen atom has been abstracted. This rearrangement is followed by sulfonation at the β-carbon atom.

No study of the thermal decomposition of I has yet appeared. We have now carried out such a study to see if the decomposition would result in the evolution of carbon dioxide, followed by the formation of a polysulfone (A); in the evolution of sulfur dioxide to give a polyester (B), or in the formation of other products (C or D):



In the present paper, we will also deal with the results of such a decomposition of I to form acrylic acid (C), together with its mechanistic aspects and with the formation of I.

Results and Discussion

For the preparation of propionic-α, α-d_2-acid-d_1, the following method has been reported by Halevi *et al.*:[2] the reduction of ethyl di-(2-acetoxy-ethyl-) ether with $LiAlD_4$ to produce ethyl-α, α-d_2-alcohol is followed by conversion into the bromide, and the preparation of the Grignard reagent of the bromide is followed by carbonation to give propionic-α, α-d_2-acid-d_1.[3] The present authors

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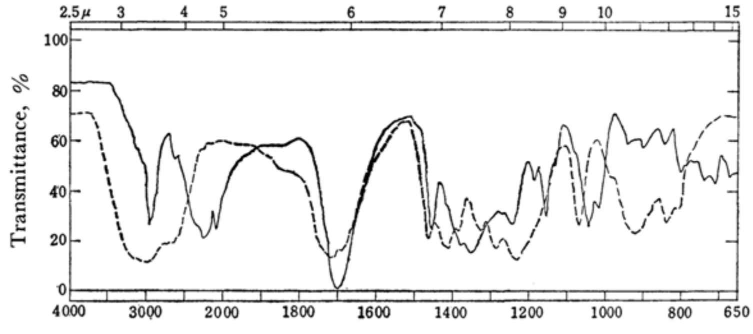
[1] M. S. Kharasch, T. H. Chao and H. C. Brown, *J. Am. Chem. Soc.*, **62**, 2393 (1940).

[2] E. A. Halevi, M. Nussim and A. Ron, *J. Chem. Soc.*, **1963**, 866.

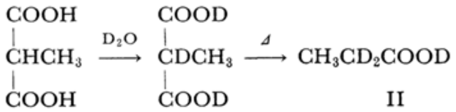
[3] The electrolysis of propionic acid in D_2O to produce propionic-α, α-d_2-acid-d_1 in a small yield has also been reported by A. Kruis and W. Schanzer, *Z. Physik. Chem.*, **191A**, 301 (1942).



Wave number, cm^{-1}

Fig. 1. Infrared spectra in liquid states.
---- Propionic acid, —— Propionic-α, α-d_2-acid-d_1 (83% isotopic purity at the α-position, II).

could obtain the compound by the easier method of the thermal decomposition of methylmalonic d_1-acid-d_2, which could be obtained by the liquid-phase exchange of methylmalonic acid.



$$\begin{array}{c}COOH\\ |\\ CHCH_3\\ |\\ COOH\end{array} \xrightarrow{D_2O} \begin{array}{c}COOD\\ |\\ CDCH_3\\ |\\ COOD\end{array} \xrightarrow{\Delta} \underset{\text{II}}{CH_3CD_2COOD}$$

The propionic-α, α-d_2-acid-d_1 (II) thus obtained displayed absorption peaks in its infrared spectrum at 2250, 1350, 1043 and 670 cm^{-1} (due to ν_{O-D}),[4] and at 2090 and 1150 cm^{-1} (due to ν_{C-D}), where the characteristic peaks at 2500—2800 and 930 cm^{-1} due to the ν_{O-H} of the –COOH of propionic acid essentially disappeared, as Fig. 1 shows. By NMR analysis (Fig. 2), it was found that the isotopic purity of the resulting II was 83% at the α-position.

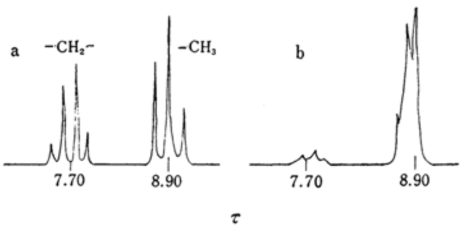


Fig. 2

a NMR spectra of propionic acid in CCl_4.

b NMR spectra of propionic-α, α-d_2-acid-d_1 (II) in CCl_4 (83% isotopic purity at the α-position).

The propionic-α, α-d_2-acid-d_1 (II) was photosulfonated under the same conditions[*1] (50—60°C) as have been reported by Kharasch *et al.*[1] By

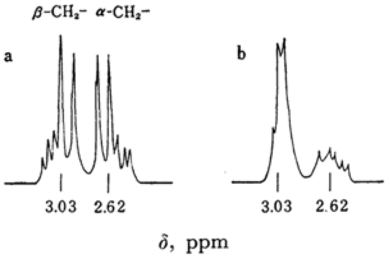


Fig. 3

a NMR spectra of β-sulfopropionic acid in H_2O (10 wt%) HO_3S-CH_2CH_2-COOH.

b NMR spectra of β-sulfopropionic-α, α-d_2-acid in H_2O (10 wt%) HO_3S-CH_2CD_2-COOH (isotopic purity 55%).
Dioxane was used as the internal reference, where the chemical shift relative to TMS of Dioxane was assumed to be $\delta=3.57$ (ppm).

NMR analysis (Fig. 3), it was found that the isotopic purity of the resulting cyclic anhydride (IV) of deuterated β-sulfopropionic acid had decreased to 55±2% at the α-position. Also, we observed that the H–D exchange of the methylene group in IV did not occur upon the dissolution of IV in water for 70 hr.

The accuracy was estimated by means of the integration of the peaks at a variety of concentrations in the NMR.

If the exclusive abstraction of β-hydrogen atoms occurs, followed by sulfonation at the β-carbon atom, the purity of the deuterium at the α-position should remain 83%, while if the exclusive abstraction of α-hydrogen atoms occurs, followed by the rearrangement of a β-hydrogen prior to sulfonation at the β-carbon atom, the isotopic purity of the α-position should decrease to 41.5%.

The ratio (x%) of the amount of the cyclic anhydride of β-sulfopropionic acid (IV) obtained through the β-hydrogen rearrangement mechanism to the resulting total amount of IV is expressed as follows:

$$x = 200(1 - a/p)$$

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4) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.*, **A216**, 247 (1953).

[*1] An examination of the recovered deuterated propionic acid (II) showed that the H–D exchange of methylene group in II did not occur in these conditions.

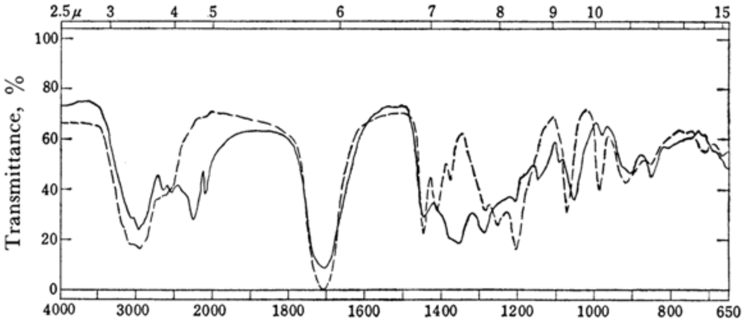


Fig. 4. Infrared spectra in liquid states.

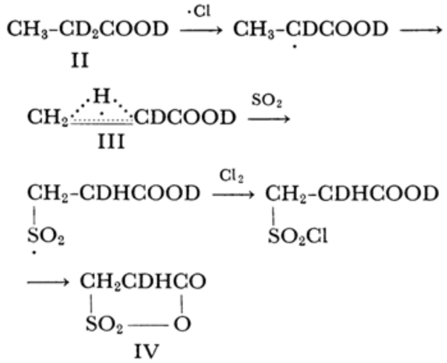
---- α-Chloropropionic acid.
—— α-Chloropropionic-α-d_1-β-d_1-acid-d_1 (83% and 25% isotopic purities at the α- and β-positions respectively, V).

where *a* and *p* are the isotopic purities of the resultant and of the reactant respectively (in the present case, *p* is 83).

The 55±2% isotopic purity obtained indicates that the α-hydrogen is abstracted in a ratio of 67.5±5%, while the β-hydrogen is abstracted in the ratio of 32.5±5%. The results also show that the relative reactivity of the α-C-H bond is nearly three times that of the β-C-H bond.

The isotope effect in the reaction of hydrogen abstraction by chlorine radicals is known⁵⁾ to be $k_H/k_D=1.5$—2. This kind of effect being corrected for, the possibility of α-hydrogen abstraction would be much greater than that described above. However, the effect would not necessarily apply under such conditions as in the present over-all reaction.

The mechanism we suggest for this photochemical reaction is that an α-hydrogen may be abstracted predominantly, resulting in a β-hydrogen rearrangement through the intermediate III. The formation of IV follows. The fact that the formation ratio of cyclic anhydride to α-chloride is nearly 1 : 1 may well be interpreted in terms of the existence of III as an intermediate:



$$\underset{\text{II}}{CH_3\text{-}CD_2COOD} \xrightarrow{\cdot Cl} CH_3\text{-}\underset{\cdot}{C}DCOOD \longrightarrow$$

$$\underset{\text{III}}{CH_2\overset{\cdot H\cdot}{\cdots\cdots}CDCOOD} \xrightarrow{SO_2}$$

$$\begin{matrix} CH_2\text{-}CDHCOOD \\ | \\ \underset{\cdot}{SO_2} \end{matrix} \xrightarrow{Cl_2} \begin{matrix} CH_2\text{-}CDHCOOD \\ | \\ SO_2Cl \end{matrix}$$

$$\longrightarrow \begin{matrix} CH_2CDHCO \\ |\qquad | \\ SO_2\text{—}O \end{matrix}$$

IV

The possibility of the interconversion of the β-H and the α-D due to H-D exchange in the intermediate III′ prior to the sulfonation of III′ was omitted, since it was estimated that no deuterium atom would be observed at the β-position by a comparison of the area of the β-methylene peak with that of a definite amount of dioxan added as an internal reference.

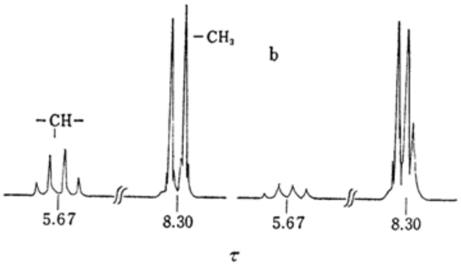
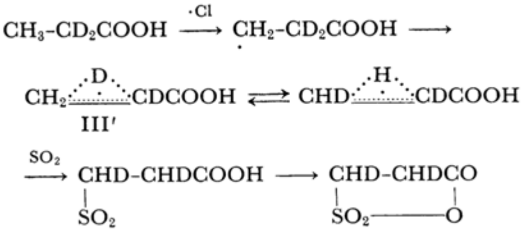


Fig. 5

a NMR spectra of α-chloropropionic acid in CCl_4.
b NMR spectra of α-chloropropionic-α-d_1-β-d_1-acid-d_1 in CCl_4 (83% and 25% isotopic purities at the α- and β-positions respectively, V).



$$CH_3\text{-}CD_2COOH \xrightarrow{\cdot Cl} \underset{\cdot}{C}H_2\text{-}CD_2COOH \longrightarrow$$

$$\underset{\text{III}'}{CH_2\overset{\cdot D\cdot}{\cdots\cdots}CDCOOH} \rightleftarrows CHD\overset{\cdot H\cdot}{\cdots\cdots}CDCOOH$$

$$\xrightarrow{SO_2} \begin{matrix} CHD\text{-}CHDCOOH \\ | \\ SO_2 \end{matrix} \longrightarrow \begin{matrix} CHD\text{-}CHDCO \\ |\qquad\quad | \\ SO_2\text{———}O \end{matrix}$$

Thus, the suggestion may be made that the III intermediate is perhaps not a classical radical in which the hydrogen atom migrates rapidly between the two carbon atoms (IIIa and b), but a bridged radical⁶⁾ such as IIIc:

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5) H. C. Brown and G. A. Russell, *J. Am. Chem. Soc.*, **74**, 3995 (1952); K. B. Wiberg and L. H. Slaugh, *ibid.*, **80**, 3033 (1958).

6) W. Thaler, *ibid.*, **85**, 2607 (1963); P. I. Abell and L. H. Piette, *ibid.*, **84**, 916 (1962).

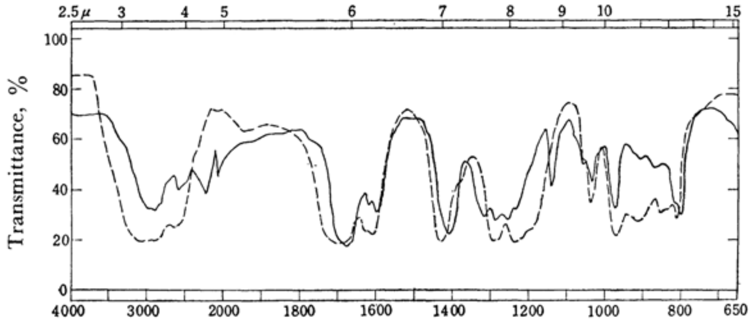
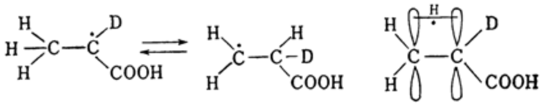
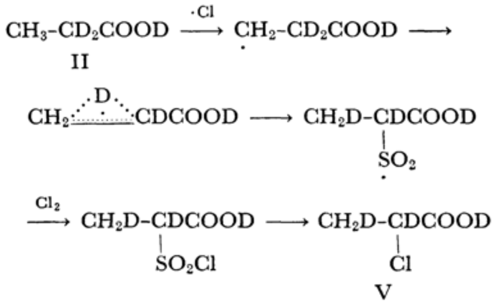


Fig. 6 Infrared spectra in liquid states.
- - - - Acrylic acid. —— Acrylic-α-d_1-acid-d_1 (XI).



IIIa IIIb IIIc

Another support for the rearrangement of a hydrogen is the fact that the resulting α-chloropropionic acid (V) (the NMR spectrum of which is shown in Fig. 5b) is found to have a $8.2\pm4\%$[7] isotopic purity at the β-position, indicating the abstraction of the β-hydrogen in the ratio of $30\pm14\%$,[7] followed by the rearrangement of an α-hydrogen prior to sulfonation at the α-carbon atom:



$$\underset{\text{II}}{CH_3\text{-}CD_2COOD} \xrightarrow{\cdot Cl} \underset{\cdot}{C}H_2\text{-}CD_2COOD \longrightarrow$$

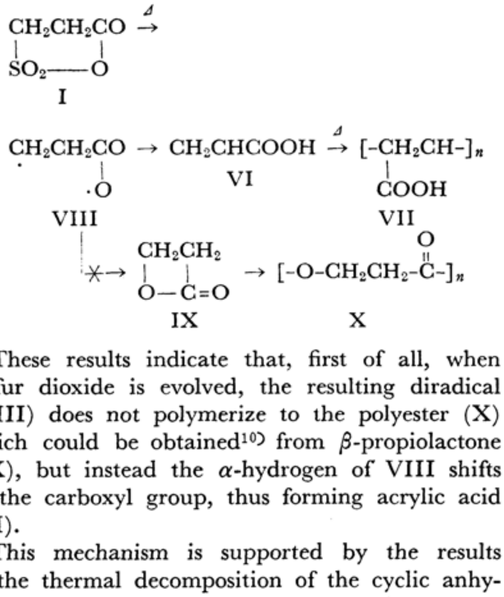
$$CH_2\overset{\cdot D \cdot}{\cdots\cdots}CDCOOD \longrightarrow CH_2D\text{-}\underset{\underset{\cdot}{SO_2}}{\underset{|}{C}}DCOOD$$

$$\xrightarrow{Cl_2} CH_2D\text{-}\underset{SO_2Cl}{\underset{|}{C}}DCOOD \longrightarrow \underset{\text{V}}{CH_2D\text{-}\underset{Cl}{\underset{|}{C}}DCOOD}$$

The infrared spectrum of V is shown in Fig. 4.

Next, we have studied the thermal decomposition of the cyclic anhydride (I). No such study has been reported previously. When I was heated at 180°C without a solvent, sulfur dioxide evolved gradually, and at the same time a colorless liquid (VI) was distilled out in a 30% (28.7—33.5%, average value for six experiments) yield. Also obtained were a small amount of a polymer (VII) and an insoluble, non-melting, black residue. Neither β-propiolactone nor polyester was produced, nor was any evolution of carbon dioxide observed.

The infrared spectra (2660, 2540, 1700, 1295, and 1240 cm⁻¹, Fig. 6),[8] NMR spectra (Fig. 7a), and other physical properties of VI coincided with those of authentic acrylic acid. When VI was heated at 130°C, it was converted to a polymer (VII). The properties and infrared spectra of the polymer (VII) thus obtained were identical with those of authentic poly-acrylic acid.[9]



$$\underset{\text{I}}{\underset{SO_2\text{——}O}{\overset{|\qquad\quad|}{CH_2CH_2CO}}} \xrightarrow{\Delta}$$

$$\underset{\text{VIII}}{\underset{\cdot}{C}H_2CH_2\underset{\cdot O}{\underset{|}{C}O}} \rightarrow \underset{\text{VI}}{CH_2CHCOOH} \xrightarrow{\Delta} \underset{\text{VII}}{[\text{-}CH_2\underset{COOH}{\underset{|}{C}}H\text{-}]_n}$$

$$\text{VIII} \not\rightarrow \underset{\text{IX}}{\underset{O-C=O}{\overset{|\qquad|}{CH_2CH_2}}} \rightarrow \underset{\text{X}}{[\text{-}O\text{-}CH_2CH_2\text{-}\overset{\overset{O}{\|}}{C}\text{-}]_n}$$

These results indicate that, first of all, when sulfur dioxide is evolved, the resulting diradical (VIII) does not polymerize to the polyester (X) which could be obtained[10] from β-propiolactone (IX), but instead the α-hydrogen of VIII shifts to the carboxyl group, thus forming acrylic acid (VI).

This mechanism is supported by the results of the thermal decomposition of the cyclic anhydride of β-sulfopropionic-α, α-d_2-acid-d_1 (isotopic

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[7] The isotopic purity (c) at the β-position and the degree (y) of the rearrangement of the α-hydrogen are estimated from the following equations:

$$c = 100 - (17b)/3$$

b: integration ratio of the peaks ($CH_3\text{-} : \text{-}\overset{|}{\underset{|}{C}}H$) in the NMR.

$$y = 300\,c/p$$

p: isotopic purity of the reactant

The accuracies of c and y are poor, because the value of b is large and does not change very greatly (12.8—17.6) regardless of the rearrangement.

[8] M. St. C. Flett, *J. Chem. Soc.*, **1951**, 962.

[9] H. Staudinger and H. W. Kohlschütter, *Ber.*, **64**, 2091 (1931).

[10] T. L. Gresham, J. E. Jansen and F. W. Shaver, *J. Am. Chem. Soc.*, **70**, 998 (1948).

purity, 55±2%). The infrared spectra (Fig. 6) of the resulting acrylic acid (XI) exhibited characteristic peaks at 2250 and 1320 cm^{-1} due to ν_{O-D}, and at 2090 and 1140 cm^{-1} due to ν_{C-D}; these peaks were assigned by a comparison of the spectra of XI with those of acrylic acid-d_1.

The NMR spectrum of acrylic acid is complicated because of the ABC system. In this complicated spectrum, it is not easy to obtain the chemical shifts and the coupling constants; however, theoretical studies by other investigators[11] have indicated that we can make an approximate assignment of the multiplet lines as in Fig. 7a. The NMR spectra (Fig. 7b) of the resulting deuterated acrylic acid can then be interpreted by assuming that the quartet of H_A has 0.5—0.6 atoms of D.

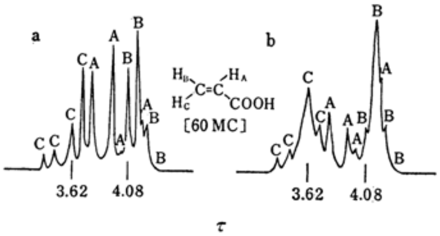
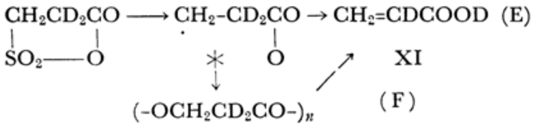


Fig. 7

a NMR spectra of acrylic acid in CCl_4.
b NMR spectra of acrylic-α-d_1-acid-d_1 (XI) in CCl_4.

These observations of the proton resonance and the infrared spectra should indicate that the structure of the resulting acid is acrylic-α-d_1-acid-d_1 (XI), as is shown in scheme E. The fact that no polyester is produced suggests that Route F of the formation[10] of acrylic acid due to the decomposition of polyester can be omitted here:



$$\underset{\displaystyle SO_2\text{——}O}{CH_2CD_2CO} \longrightarrow \dot{C}H_2\text{-}\underset{\displaystyle O}{CD_2CO} \rightarrow CH_2{=}CDCOOD \ \text{(E)} \quad \text{XI}$$

$$\ast \downarrow \quad (\text{-}OCH_2CD_2CO\text{-})_n \nearrow \quad \text{(F)}$$

Experimental

Ethyl Methylmalonate (XII). This was prepared from ethyl malonate and methyl bromide through the sodium salt of ethyl malonate in the same manner as has been described in the literature.[12]

Methylmalonic Acid (XIII). A sample (80 g) of XII was added to a 50% aqueous solution of potassium hydroxide (80 g) in a 500-m*l* flask equipped with a reflux condenser. The reaction temperature was maintained at 110—120°C for 3 hr, during which time the volume of the ester layer upon the aqueous one decreased, forming a uniform solution. The reaction mixtures were then cooled to room temperature, acidified with concentrated hydrochloric acid, and extracted with ether more than ten times, thus yielding, after the removal of the solvent, crude methylmalonic acid (42 g, 77.4%). Recrystallization from ethyl acetate - petroleum ether (8 : 2) gave colorless crystals, mp 120°C.[13]

Liquid-phase Exchange of XIII in D_2O (Formation of Methylmalonic-d_1-acid-d_2, XIV). XIII (33.6 g, 0.285 mol) was dissolved in D_2O (56.2 g, 2.8 mol). The solution was kept standing in a dry box 24 hr, and then frozen; the frozen content was submitted to evaporation to dryness under reduced pressure.

Thermal Decomposition of XIV (Preparation of Propionic-α, α-d_2-acid-d_1, II). The XIV obtained above was thermally decomposed at 140—150°C for 3 hr to yield a colorless liquid, which was then dried (Na_2SO_4) and distilled to give propionic-α, α-d_2-acid-d_1 (II), bp 141°C (yield 83.1%). The NMR spectrum of II is shown as Fig. 2; it is centered at τ 7.70 (quartet, methylene) and 8.90 (triplet, methyl). The ratio of the areas for the two peaks was 0.113 : 1.00; hence, the isotopic purity of II at the α-position was determined to be 83±2%.

IR Spectra. The infrared spectra were recorded on a EPI-S2-type Hitachi spectrometer.

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

Photosulfonation. The photosulfonation of propionic acid with sulfuryl chloride to produce the cyclic anhydride of β-sulfopropionic acid (I, mp 76—77°C) was carried out in the manner described by Kharasch *et al.*[1] The same method was also applied to the photosulfonation of propionic-α, α-d_2-acid-d_1 (II, isotopic purity 83% at the α-position) to produce the cyclic anhydride (IV), the reaction temperature being maintained at 50—60°C under irradiation by a tungsten filament lamp (300 W). The NMR spectra of IV, together with that of I in water[*2] are shown in Fig. 3, they are centered at δ (ppm) 2.62 (sextet, α-methylene) and 3.03 (sextet, β-methylene). The relative area was 1 : 1 for I and 0.45 : 1 for IV, and no deuterium atom at the β-position in IV was observed upon a comparison of the area of the peak with that of a definite amount of dioxan added as an internal reference (Fig. 3). Thus, a 55% isotopic purity of IV at the α-position was indicated.

The infrared spectrum of the resulting deuterated α-chloropropionic acid (V, bp 63°C/5 mmHg) showed characteristic peaks at 2250 and 1360 cm^{-1} (due to ν_{O-D}) and at 2100 and 1150 cm^{-1} (due to ν_{C-D}). The spectrum is shown in Fig. 4, together with that of α-chloropropionic acid. The NMR spectrum of V is shown in Fig. 5. The integration ratio of the peaks (CH_3– : –$\overset{|}{\underset{|}{C}}H$) in V was observed to be 16.2.

Thermal Decomposition of I. *A Typical Experiment.* In a 50-m*l* round-bottomed flask, fitted with a thermometer, an outlet tube leading to a receiving vessel, and a calcium chloride tube, 6.2 g of I without a solvent were placed. The flask was surrounded by an oil bath equipped with a thermometer and heated

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[11] S. Castellano and J. S. Waugh, *J. Chem. Phys.*, **34**, 295 (1961); Y. Arata, H. Shimizu and S. Fujiwara, *ibid.*, **36**, 1951 (1962); T. Yamamoto and S. Fujiwara, This Bulletin, **39**, 333 (1966).

[12] N. Weiner, "Organic Syntheses," Coll. Vol., II, ed. by A. H. Blatt (1948), p. 279.

[13] J. F. Norris and H. F. Tucker, *J. Am. Chem. Soc.*, **55**, 4697 (1933).

[*2] The cyclic anhydride is readily transformed by hydration into β-sulfopropionic acid.[1]

gradually. When the temperature reached at 80°C, the solid in the flask melted, upon further heating to 180°C, sulfur dioxide gas evolved. The temperature was maintained at nearly 190°C for 2.5 hr, until the liquid in the flask changed to a black, spongy matter (XV). During the heating, a colorless liquid (VI, 0.95 g, 28.7%) was distilled out. Also obtained was 0.15 g of the polymer VII. The infrared spectra[8] (Fig. 6) and NMR spectra (Fig. 7a) of VI coincided with those of authentic acrylic acid. When VI was heated at 130°C without a solvent, it was converted into a polymer (VII). The polymer VII thus obtained was soluble in water, forming a viscous liquid. The infrared spectrum (3420 cm^{-1} due to ν_{O-H} and 1710 cm^{-1} due to $\nu_{C=O}$, in dimethylformamide) was identical to that of authentic poly-acrylic acid.[9] The sulfur dioxide evolved was identified by its characteristic odor and by its ability to decolor a Fuchsin solution. The black spongy residue (XVII) was an insoluble, non-melting matter. Neither α-propiolactone nor polyester was produced. Moreover, at no time during the reaction, was the evolution of carbon dioxide by the action of an aqueous solution of calcium hydroxide detected.

Thermal Decomposition of the Cyclic Anhydride of β-Sulfopropionic-α, α-d_2-acid-d_1 (IV). The thermal decomposition of the deuterated cyclic anhydride (IV, isotopic purity 55±2%) was carried out in the manner described above, and similar results were obtained. The infrared spectrum of the resulting acrylic acid (XI) showed peaks at 2250, 2090, 1320, and 1140 cm^{-1} (Fig. 6). The NMR spectrum (Fig. 7b) of XI showed that the ratio of the area of the peaks due to hydrogens at the β-position to that due to those at the α-position was 2 : 0.48.