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A MECHANISTIC ASPECT ON THE FORMATION AND DECOMPOSITION OF THE CYCLIC ANHYDRIDE OF β-SULFOPROPIONIC ACID

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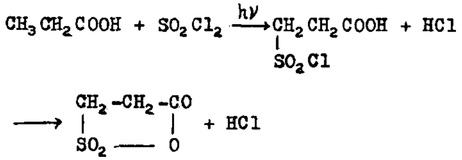
The photochemical sulfonation of propionic acid with sulfuryl chloride to form the cyclic anhydride of β-sulfopropionic acid (I) has been reported by Kharasch et al.[1]



I

$$CH_3CH_2COOH + SO_2Cl_2 \xrightarrow{h\nu} \underset{SO_2Cl}{\underset{|}{CH_2}}CH_2COOH + HCl$$

$$\longrightarrow \begin{array}{l} CH_2-CH_2-CO \\ |\qquad\qquad\quad | \\ SO_2 —— O \end{array} + HCl$$

The mechanism they suggested for the photosulfonation reaction is that the abstraction of a β-hydrogen atom by chlorine radical ($SO_2Cl_2 \longrightarrow SO_2 + Cl_2$, $Cl_2 \xrightarrow{h\nu} 2Cl\cdot$) in the ratio of 55% is followed by sulfonation at the β-carbon atom results 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 which momentarily decomposes into the α-chloride and sulfur dioxide. This mechanism involves no rearrangement of a hydrogen atom.

In the present paper, we 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.

The **propionic-α,α-$\underline{d_2}$**-acid-$\underline{d_1}$ of 83% isotopic purity at the α-position, prepared by the thermal decomposition of methylmalonic-$\underline{d}_1$-acid-$\underline{d}_2$*, was photosulfonated under the same conditions (50-60°C) as were reported by Kharash et al.[1] By NMR analysis (FIG I), it was found that the isotopic purity of the resulting cyclic anhydride of deuterated β-sulfopropionic acid had decreased to 55% at the α-position.

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

The 55% isotopic purity obtained indicates that the α-hydrogen is abstracted in a ratio of 67.5%, while the β-hydrogen is abstracted in the ratio of 32.5%. The result also shows that the relative reactivity of the α-C-H bond is nearly three times greater than that of the β-C-H bond.

The isotope effect in the reaction of hydrogen abstraction by chlorine radicals is known[2] to be $\underline{k}_H/\underline{k}_D = 1.5\text{-}2$. 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 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,

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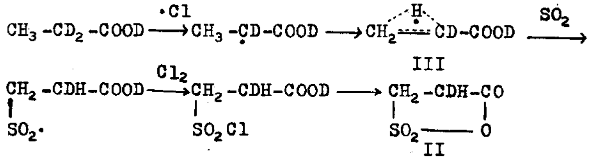
* Obtained by a method of liquid-phase exchange of methylmalonic acid.

where the π electrons, having double bond character, may be resonance-stabilized with the carbonyl group. Then the formation of II follows. The fact, that the formation ratio of cyclic anhydride to α-chloride is nearly 1:1, is well interpreted by the existence of III as an intermediate.

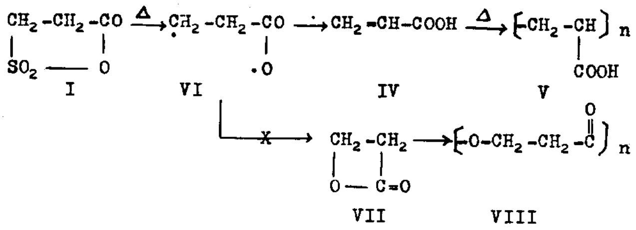


$$CH_3\text{-}CD_2\text{-}COOD \xrightarrow{\cdot Cl} CH_3\text{-}\dot{C}D\text{-}COOD \longrightarrow \overset{\cdot H}{CH_2 \text{=} CD}\text{-}COOD \xrightarrow{SO_2}$$

$$\underset{SO_2\cdot}{CH_2}\text{-}CDH\text{-}COOD \xrightarrow{Cl_2} \underset{SO_2Cl}{CH_2}\text{-}CDH\text{-}COOD \longrightarrow \underset{SO_2 - O}{CH_2\text{-}CDH\text{-}CO}$$

Next, we have carried out a study of the thermal decomposition of the cyclic anhydride (I). Such a study has not been reported previously. When (I) was heated at 180° without solvent, sulfur dioxide evolved gradually, and at the same time a colourless liquid (IV) was distilled out in 30% yield. Also obtained were a small amount of polymer (V) and some insoluble, non-melting, black residue. Neither β-propiolactone nor polyester was produced.

The infrared spectra (2660, 2540, 1700, 1295 and 1240 cm^{-1})[3], NMR spectra (FIG 2A) and other physical properties of IV coincided with those of authentic acrylic acid. When IV was heated at 130°C, it was converted to a polymer (V). The properties and infrared spectra of the polymer (V) thus obtained were identical to those of authentic poly-acrylic acid.[4]



$$\underset{SO_2 - O}{CH_2\text{-}CH_2\text{-}CO} \xrightarrow{\Delta} \underset{\cdot O}{\dot{C}H_2\text{-}CH_2\text{-}CO} \longrightarrow CH_2\text{=}CH\text{-}COOH \xrightarrow{\Delta} \left[\text{-}CH_2\text{-}\underset{COOH}{CH}\right]_n$$

$$\xrightarrow{\times} \underset{O - C\text{=}O}{CH_2\text{-}CH_2} \longrightarrow \left[\text{-}O\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\right]_n$$

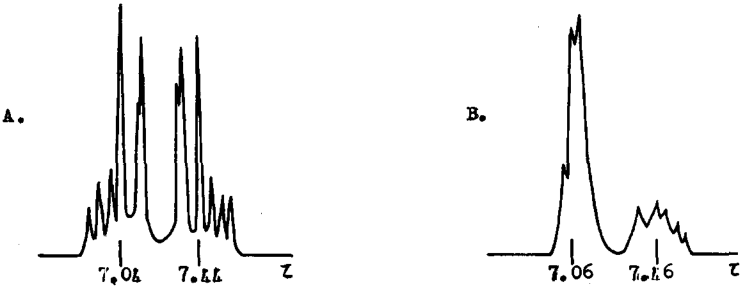
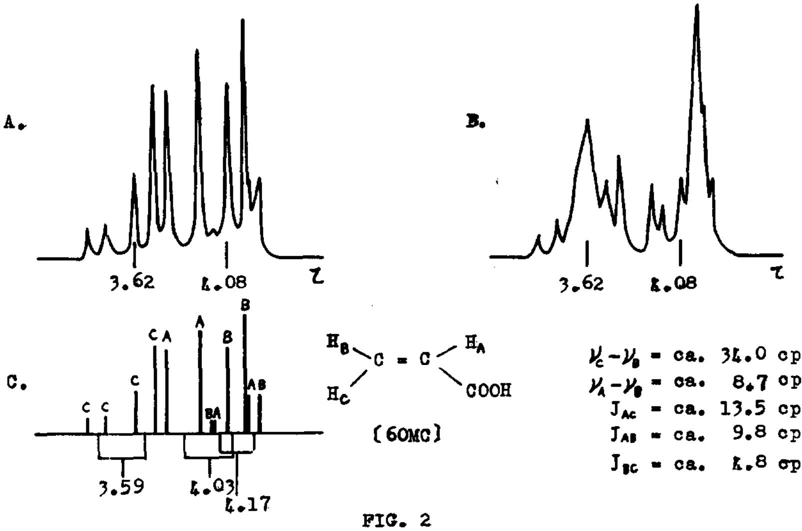


FIG. 1

A. NMR spectra of (I) in H_2O (10wt%) $HO_3S-CH_2CH_2-COOH$

B. NMR spectra of (II) in H_2O (10wt%) $HO_3S-CH_2CD_2-COOH$
(isotopic purity 55%)



$\nu_C - \nu_B$ = ca. 34.0 cps
$\nu_A - \nu_B$ = ca. 8.7 cps
J_{AC} = ca. 13.5 cps
J_{AB} = ca. 9.8 cps
J_{BC} = ca. 4.8 cps

FIG. 2

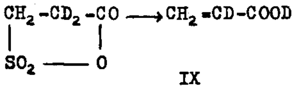
A. NMR spectra of acrylic acid in CCl_4

B. NMR spectra of acrylic-α-d_1-acid-d_1 (IX) in CCl_4
(isotopic purity 54%)

C. assignment of A

These results indicate that, first of all, when sulfur dioxide is evolved, the resulting diradical (VI) does not polymerize to a polyester (VIII) which would be obtainable[5] from β-propiolactone (VII), but instead the α-hydrogen of VI shifts to the carboxyl group to form acrylic acid (IV).

This mechanism is supported by the results of the thermal decomposition of the cyclic anhydride of β-propionic-α,α-d_2-acid-d_1 (isotopic purity 55%). The acrylic acid (IX) thus produced indicated the same purity (56%) of ionizable deuterium as was in the α-position of the reactant, anhydride.



IX

The structure of IX was confirmed by infrared spectra (2250, 2090, 1320 and 1140 cm^{-1}) and NMR studies (FIG 2B).

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