The Racemization of Optically Active α-Phenylethyl Alcohol in Liquid Sulfur Dioxide

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It has been reported that optically active α-phenylethyl alcohol is racemized in an aqueous solution by the catalysis of perchloric acid; carbonium ion is presumed to be formed during the reaction.[1] In the present communication we should like to report on the racemization of the alcohol in liquid sulfur dioxide in the absence of any proton donor; this is supposedly a somewhat different kind of racemization.

As may be seen in Fig. 1, the optical rotation of the solution first increases, reaches a maximum, and then tends to decrease very slowly, thus resulting in the complete racemization. Such a phenomenon may be presumed to be typical of the series of consecutive reactions involving an intermediate formation:

$$\underset{[A]}{ROH + SO_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{[C]}{\text{Intermediate}} \xrightarrow{k_2} \underset{[R]}{\text{Racemic ROH}}$$

There are three possible intermediates, I, II and III.

$$ROH + H^+ \rightarrow \underset{I}{ROH_2{}^+} \rightarrow R^+ + H_2O \qquad (1)$$

$$ROH + SO_2 \rightarrow \underset{II}{ROH\cdot SO_2} \rightarrow R^+ + {}^-OH\cdot SO_2 \qquad (2)$$

$$ROH + SO_2 \rightarrow \underset{III}{ROSO_2H} \rightarrow R^+ + {}^-HSO_3 \qquad (3)$$

They are a protonated alcohol (I), a SO_2–ROH complex (II), and an ester of sulfurous acid (III), respectively.

It might be considered that the trace of water present in liquid sulfur dioxide is the source of a proton which could combine with the alcohol as I and racemize via the route 1. This mechanism is unlikely, however, since the acid- or proton-catalyzed racemization ordinarily results in a smooth descending curve vs. the time plot, with no maximum of the rotation at all, as has been shown in the literature.[1] Moreover, the water content in dehydrated (by phosphorus(V) oxide) liquid sulfur dioxide is as low as 48 p. p. m., thus showing practically no effect of the catalyst.

As for the interaction between an alcohol and liquid sulfur dioxide, several papers have appeared lately. Hoyer[3] has observed that the sulfur dioxide molecule can neither permit hydrogen bonds among alcohol molecules themselves nor make hydrogen bridges with the hydrogen atoms of the alcohol by

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[1] E. Grunwald, A. Heller and F. S. Klein, *J. Chem. Soc.*, **1957**, 2604.

[2] N. Tokura and F. Akiyama, This Bulletin, **37**, 1723 (1964).

[3] H. Hoyer, *Angew. Chem.*, **72** 269 (1960).

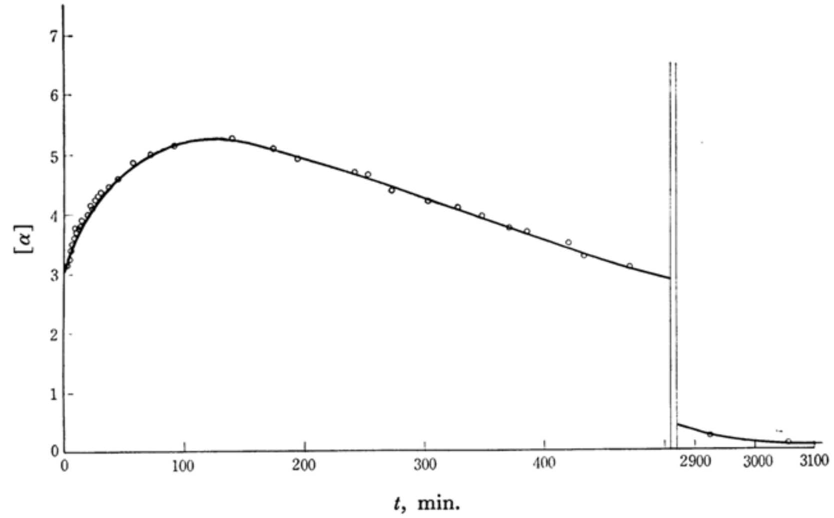

Fig. 1. Optical rotation of *l*-α-phenylethyl alcohol in liquid sulfur dioxide.

using oxygen atoms of the sulfur dioxide molecules. Only a very small amount of $RO \cdot SO_2H$ has been found in the mixture of ethyl alcohol and sulfur dioxide,4) and Guss5) has revealed that, by the colorimetric titration, a sulfite or an ester like III might partly be formed from the alcohol and sulfur dioxide.

Since the optical rotaion of an alcohol is generally enhanced when it is converted to an ester, as is the case in *l*-menthol,2) the rise in the rotation might be suspected to result from an ester-formation such as III. The recovered residue of the racemization was not the sulfurous acid ester of the α-phenylethyl alcohol, but the racemized alcohol itself. However, the present authors are not sure whether the intermediate of the reaction is the complex II or the sulfite III, the stoichiometry of the two being the same. A complex formation like II has already been indicated by Dietzel and Galanos.6) However, we cannot distinguish the complex from the ester like III, since the ester is also very unstable, as was reported by Zimmermann.7)

The over-all racemization process may be deemed to be the result of the consecutive reactions, the reversible formation of the intermediate and the dissociative racemization of the intermediate, II or III.

Actually, the experimental curve in Fig. 1 has a maximum of rotation, α_{max}; this fact may be fairly reconciled with the consecutive (series) reaction mechanism consisting of intermediate formation and racemization, where $k_2 \gg k_{-1}$. The alternative route, viz., a preliminary reversible formation of the intermediate C, $k_2 \ll k_{-1}$, may thus be ruled out, as will be elucidated below. I $k_2 \gg k_{-1}$, for the $A \rightarrow C \rightarrow R$ series,

$$-\mathrm{d(A)}/\mathrm{d}t = k_1\mathrm{(A)} \tag{4}$$

$$\mathrm{d(C)}/\mathrm{d}t = k_1\mathrm{(A)} - k_2\mathrm{(C)} \tag{5}$$

$$\mathrm{d(R)}/\mathrm{d}t = k_2\mathrm{(C)} \tag{6}$$

and $\mathrm{(C)}_0$ and $\mathrm{(R)}_0$ are zero, where the suffix zero indicates the initial concentration. The solution of the series reactions is:

$$\mathrm{(C)} = \frac{\mathrm{(A)}_0 k_1}{k_2 - k_1}\,(\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}) \text{ and } \mathrm{(A)} = \mathrm{(A)}_0 \mathrm{e}^{-k_1 t} \tag{7}$$

and a variable vs. time plot should be a curve with a maximum.8) Since $\alpha = [\alpha]_A \cdot \mathrm{(A)} + [\alpha]_C \cdot \mathrm{(C)}$, where $[\alpha]_A$ and $[\alpha]_C$ are the specific rotations of the alcohol and the intermediate, respecively, in liquid sulfur dioxide at the temperature, by rearranging and substituting Eq. 8 one gets:

$$\alpha = \mathrm{(A)}_0 \left\{ [\alpha]_A \mathrm{e}^{-k_1 t} + [\alpha]_C \frac{k_1}{k_2 - k_1} (\mathrm{e}^{-k_1 t} - \mathrm{e}^{-k_2 t}) \right\} \tag{8}$$

By differentiating Eq. 8 and putting $\mathrm{d}\alpha/\mathrm{d}t = 0$ at α_{max} and t_{max} on the curve in Fig. 1, the value of $[\alpha]_C$ can be estimated; this will give the ultimate equation with regard to α.

As a first approximation, the complication of the calculation may be alleviated by the following procedures. The expressions are derived from the above discussion as:

$$\mathrm{d(C)}/\mathrm{d}t = k_1\mathrm{(A)}_0 \left\{ e^{-k_1 t} - \frac{1}{1 - k_1/k_2} \mathrm{e}^{-k_1 t} (1 - \mathrm{e}^{(k_1 - k_2)t}) \right\} \tag{9}$$

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4) A. Simon and R. Paetzold, *Z. anorg. und allgem Chem.*, **303**, 53 (1960).

5) L. S. Guss, *Chem. Abstr.*, **39**, 4278 (1945).

6) R. Dietzel and S. Galans, *Z. Elektrochem.*, **31**, 466 (1925).

7) M. R. Zimmermann, *Angew. Chem.*, **15**, 898 (1902).

8) A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, John Wiley, New York (1953), pp. 153—154.

and:

$$d(R)/dt = k_2 \frac{(A)_0}{k_2/k_1 - 1} e^{-k_1 t}(e^{(k_2-k_1)t} - 1) \quad (10)$$

where (R) is the concentration of the racemized alcohol. In the region where t is zero to t_{max}, especially when t is very small, i. e. at the initial stage of the reaction, $e^{(k_1-k_2)t}$ is approximately unity and $1/e^{k_1 t} < 1$, so the second term in parentheses in Eq. 9 may be eliminated;

$$d(C)/dt = k_1(A)_0 e^{-k_1 t} \quad (11)$$

Since, in the reaction stage from t_{max} to t, $k_2/k_1 \fallingdotseq 0$, and $e^{(k_2-k_1)t} = 0$, Eq. 10 reduces to:

$$d(R)/dt = k_2(A)_0 e^{-k_2 t} \quad (12)$$

Consequently, the rate constants, k_1 and k_2, can be estimated from the ascending and the descending parts of the curves in Fig. 1 respectively:

$$\ln \frac{\alpha_{max} - \alpha_0}{\alpha_{max} - \alpha} = k_1 \cdot t \quad (13)$$

$$\ln \frac{\alpha_{max}}{\alpha} = k_2 \cdot t \quad (14)$$

where α, α_0 and α_{max} are the optical rotations of the reaction mixture at time t, at time zero, and at the time when the rotation was at the maximum respectively. Both plots were linear, as may be seen in Figs. 2 and 3, and both obey the first-order rate law derived in the above discussion.

The constants, k_1 and k_2, are estimated to be as in Table I.

TABLE I

Concn. of the alcohol mol./l.	$k_1 \times 10^4 \text{sec}^{-1}$	$k_2 \times 10^5 \text{sec}^{-1}$
0.327	6.26	2.89
0.223	6.41	2.86
Mean	6.34	2.88

Experimental

Materials.—Liquid sulfur dioxide was dehydrated by phosphorus(V) oxide and distilled. Optically active α-phenylethyl alcohol was prepared by the fractional crystallization of the brucine-complex salt of hydrogen monophthalate of the alcohol; b. p. 76.5°C/6 mmHg, $[\alpha]_D^{25} = -45°$ degree. $dm^{-1}g^{-1}$ml. in benzene.1)

Polarimetry.—A Shimadzu-Lippich type, model II, polarimeter equipped with a glass pressure cell coupled with an inlet joint was used.6)

A Typical Run of the Racemization of α-Phenylethyl Alcohol in Liquid Sulfur Dioxide.—Into 18.2 ml. of liquid sulfur dioxide in a pressure cell (the length of which was 22 cm.2)) there was dissolved 0.503 g. of optically-active l-α-phenylethyl aclohol; the solution was then allowed to stand for over 10 hr.

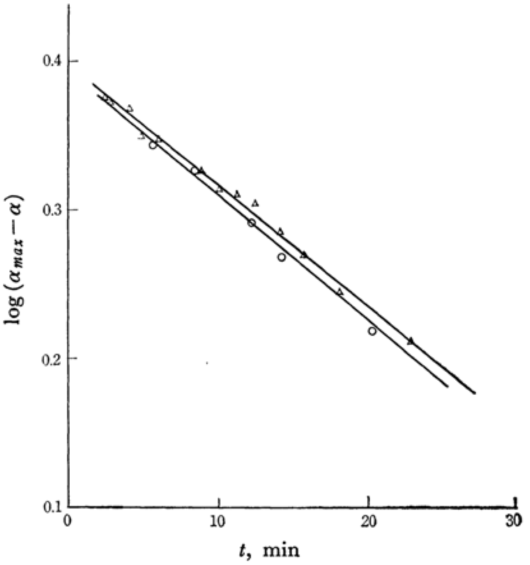

Fig. 2

△ 0.327 mol./l ○ 0.233 mol./l

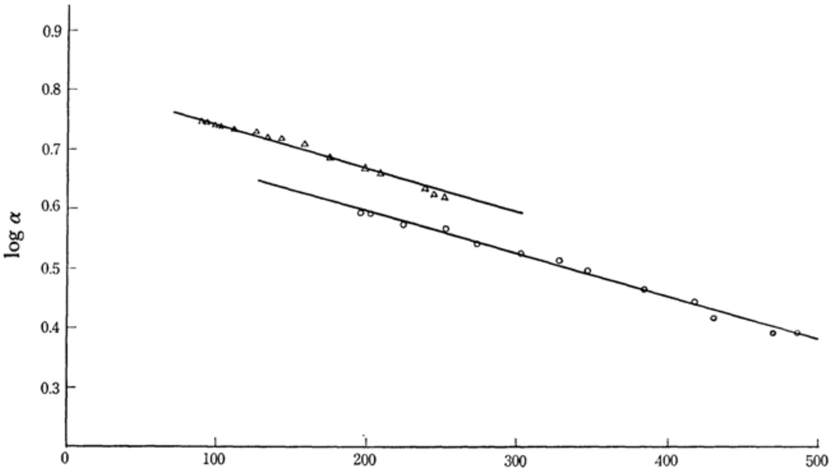

Fig. 3

△ 0.327 mol./l. ○ 0.223 mol./l.

in a thermostat the temperature of which was kept at 25± 0.2°C.

The plot of the change in the optical rotation, α, of the solution vs. the time is visualized in Fig. 1.

The Recovery of the Racemized Material from the Solution.—The sulfur dioxide solution, consisting of optically active α-phenylethyl alcohol (2.9 g.) in liquid sulfur dioxide (50 ml.), was allowed to stand for 60 hr. at 25°C. The residue was then further aerated with dried nitrogen, leaving a transparent oil (2.6 g.) which showed no reaction as an acid. The oil was the racemic α-phenylethyl alcohol; b. p. 76.5°C/6 mmHg, $[\alpha]_D^{25}=0$, benzene.

Found; C, 78.46; H, 8.23. Calcd. for $C_8H_{10}O$: C, 78.65; H, 8.25%.

The infrared spectrum of the sample was superimposable upon that of a synthetic specimen.