Isomerization of Cyclohexyl Phenyl Ketoxime in Liquid Sulfur Dioxide[*]

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(Received May 16, 1962)

It has been shown by Waterman et al.[1] that the cis-trans isomerization of olefins is carried out by sulfur dioxide at 100～140°C. As to the elaidination of oleic acid by sulfur dioxide, many papers have been published[2] since the first paper on this subject appeared in 1894 by Saytzeff[3]. The carbon-carbon double bonds of steroids are also rearranged by liquid sulfur dioxide or by sulfur dioxide vapor[4]. Recent works by Cunneen et al.[5] are concerned with the cis-trans isomerization of polybutadiene and polyisoprene by sulfur dioxide at high temperatures.

The isomerization of a ketoxime in liquid sulfur dioxide was first found by Tada, Masubuchi and Tokura[6], the isomerization taking place even at low temperatures. According to their view[6], the rate of the Beckmann rearrangement of a ketoxime in liquid sulfur dioxide is so fast that the isomerization of the ketoxime is not competitive with the Beckmann rearrangement in liquid sulfur dioxide, the product of the reaction being a pure and single acidamide.

On the other hand, Brown et al.[7a] have reported on an ordinary case of Beckmann rearrangement in which the isomerization was predominant over the rearrangement, the product being a mixtue of the acidamides.

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[*] The Beckmann Rearrangement in Liquid Sulfur Dioxide. Part X.

[1] H. I. Waterman and C. Boelhower, "Advances in Catalyst", 9, Ed. by A. Farkas, Academic Press, New York (1957), p. 294.

[2] a) H. I. Waterman et al., *Chem. Abstr.*, **42**, 2787 (1948).
b) H. I. Waterman et al., ibid., **44**, 3884, (1950).
c) H. I. Waterman et al., *Chemie et Industrie*, **64**, 557 (1950).
d) H. I. Waterman et al., *Chem. Abstr.* **45**, 5946 (1951).
e) A. Kenzenkamp et al. *J. Am. Oil Chem. Assoc.*, **26**, 479 (1949).

[3] A. Saytzeff, *J. Prakt. Chem.*, **50**, 73, 81 (1894).

[4] a) C. D. Laubach, *J. Am. Chem. Soc.*, **78**, 4744 (1956).
b) A. W. D. Hudgell, J. H. Turnbull and W. Wilson, *J. Chem. Soc.*, **1954**, 814.

[5] a) J. I. Cunneen and F. W. Sirley, *J. Polymer Sci.*, **34**, 260 (1959); **36** 77 (1959).
b) J. I. Cunneen and H. F. Watson, ibid., **38**, 521, 533 (1959); **40**, 1 (1959).

[6] R. Tada, Y. Masubuchi and N. Tokura, This Bulletin, **34**, 209 (1961).

[7] a) R. F. Brown, M. van Gulic and C. H. Schmid, *J. Am. Chem. Soc.*, **77**, 1094 (1955).
b) Y. Yukawa, "Jikken Kagaku Koza", Vol. **18**, Ed. by the Chemical Society of Japan, Maruzen, Tokyo (1957), p. 426.

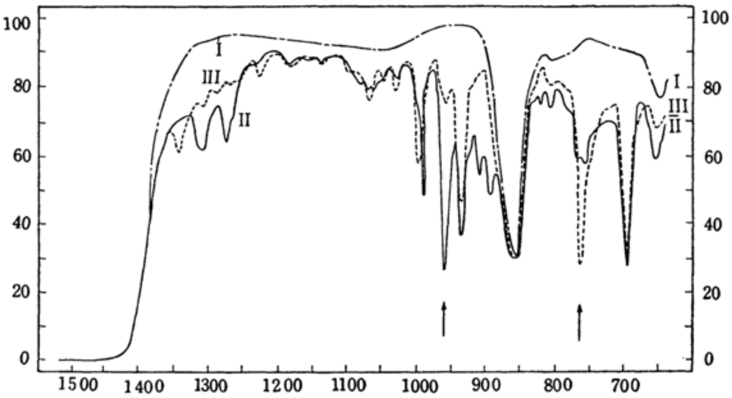
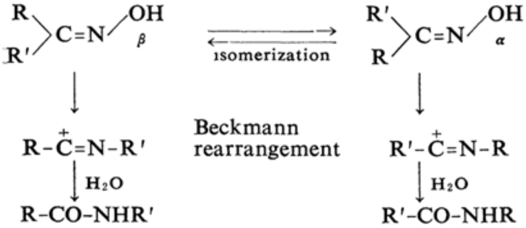


Fig. 1. Infrared spectra of the oximes in carbon disulfide.
I —·— CS_2 II —— α-Oxime III - - - β-Oxime

derived from both the initial and the isomerized oximes. Yukawa et al. have tried the Beckmann rearrangement of cyclohexyl phenyl ketoxime in order to obtain various mixtures of the two acidamides, the proportions of which were dependent upon the reagents used for the rearrangement[7b].

Chart 1



In the present paper, the present authors should like to submit their findings on the kinetics of the liquid sulfur dioxide-catalyzed isomerization of β-cyclohexyl phenyl ketoxime ($R=C_6H_{11}$, $R'=C_6H_5$) to the α-isomer.

Experimental

Liquid Sulfur Dioxide.—Sulfur dioxide was dehydrated by phosphoric acid anhydride[6].

Preparation and Separation of Cyclohexyl Phenyl Ketoxime.—The method used in the preparation and separation of the α and β-oximes was that described in a preceding paper[6].

Experimental Procedure.—In a 200 ml. glass pressure vessel about 250 mg. of the β-oxime(m. p., 114.5°C) was dissolved into liquid sulfur dioxide to make up a 40 ml. solution of the reaction mixture, the temperature of which was kept constant throughout the preparation[8] and the runs by means of a thermostat. At definite time intervals 8 ml. portions of the solution were withdrawn from the mixture. The aliquot was mixed with ice water and neutralyzed with an ammonia solution, and the precipitate was filtered, dried and analyzed for the oxime content. The run in dark was also carried out to compare the photochemical effect on the isomerization.

Analysis of the Isomeric Oximes.—The infrared spectrophotometric method was employed for this analysis. A Perkin-Elmer double-beam model 21 type spectrometer was used. As may be seen in Fig. 1, the characteristic absorption curves of α and β-oximes in carbon disulfide (curves II and III respectively) offer absorption maxima at 762 and 957 cm^{-1} for use as key bands for the analysis of the oximes. The simultaneous Eqs. 1 and 2 were used to calculate the content of the oximes.

$$E_{\text{m}}^{762}=C_\alpha\cdot \text{E}_\alpha^{762}+C_\beta\cdot E_\beta^{762} \tag{1}$$

$$E_{\text{m}}^{957}=C_\alpha\cdot E_\alpha^{957}+C_\beta\cdot E_\beta^{957} \tag{2}$$

where, E_α^{762}, E_β^{762}, E_α^{957}, and E_β^{957} are the molecular extinction coefficients of α-oxime and of β-oxime at 762 and 957 cm^{-1} respectively, the upper suffixes corresponding to the wave numbers and the lower suffixes to the α- and β-oximes, E_{m}^{762} and E_{m}^{957} are the extinction coefficients of the sample at the respective wave numbers, and C_α and C_β are the contents of the oximes in the sample. Beer's law was obeyed throughout the experimental conditions, and the experimental error of this analytical method was within three percent.

Results and Discussion

The isomerization of the β-oxime to the α-oxime is a slow reaction, as was expected. The conversions, in percentages, were 27 at 48 hr. and 20 at 12 hr., the initial concentrations of the oxime being, 2.46×10^{-2} mol./l. and 4.31×10^{-2} mol./l. at 0°C in diffused-room daylight. The reaction was accelerated by light and retarded by the addition of hydroquinone (H.Q.) (Fig. 2). In Fig. 3 the effects of the degree of dehydration of the liquid sulfur dioxide and of the addition of

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[8] N. Tokura, M. Matsuda and F. Yazaki, *Makromol. Chem.*, **42**, 108 (1960).

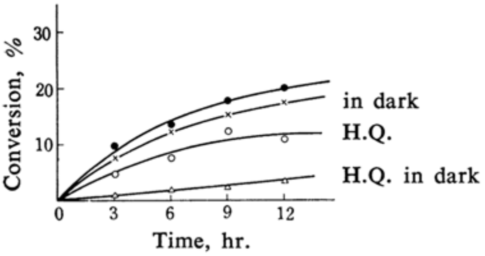

Fig. 2. Isomerization at 0°C in liquid sulfur Dioxide
[β-oxime] 4.31×10^{-2} mol./l.
[H. Q.] 1.0×10^{-2} mol./l.

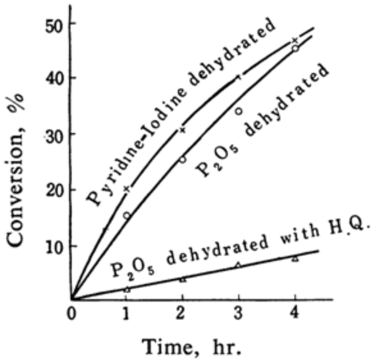

Fig. 3. Effect of degree of dehydration of liquid sulfur dioxide.
[β-oxime] 4.31×10^{-2} mol./l., Temp. 30°C

hydroquinone at 30°C in diffused daylight are visualized together. Liquid sulfur dioxide dried with phosphorus pentoxide (assuming the water content to be 100~50 p. p. m.)[9] or liquid sulfur dioxide dried with pyridine and iodine (estimating the water content as 30 p. p. m.)[10] has produced little difference in the rate of isomerization, whereas the addition of hydroquinone produced a marked depression of the rate at this temperature also.

These results are consistent with the radical nature of the isomerization reaction, as was shown in the cases of the cis-trans isomerization of olefins at higher temperatures[1−5]. However, acid catalysis by sulfur dioxide in part may not completely be ruled out since Tokura et al.[11] have found that a cationic polymerization by sulfur dioxide itself can be carried out in preference to a radical reaction in liquid sulfur dioxide.

To avoid the effect of light, all of the following kinetic runs were performed in the dark. The extent of the isomerization for the kinetical analysis was confined to a low conversion as much as possible. The reactions were carried out at 0, 10 and 20°C, the initial concentration of the β-oxime being 4.31×10^{-2} mol./l. The $\ln\{a/(a-x)\}$ vs. time plots are shown in Fig. 4. The results fit well with a first-order rate expression with respect to the concentration of the β-oxime. The rate constants, k, for the respective temperatures are listed in Table I.

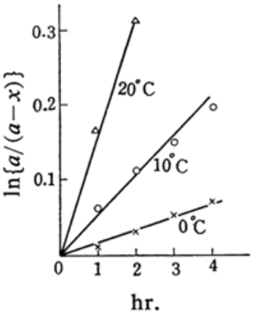

Fig. 4

TABLE I. THE RATE CONSTANTS OF THE ISOMERIZATION
Rate$=k\cdot$[oxime]

Temp., °C	Rate constant, k $\times10^{5}$ sec^{-1}
0 (dark)	0.41
10 (dark)	1.58
20 (dark)	4.66
0 (diffused daylight)	0.65

TABLE II. THE ARRHENIUS PARAMETERS

Activation energy:	E_a 19.1 kcal./mol.
Frequency factor:	A 6.3×10^{11} sec^{-1}
Rate constant:	$k=6.3\times10^{11}\times\exp[-19.1/\boldsymbol{RT}]$ sec^{-1}

TABLE III. ATTEMPTED ISOMERIZATION IN VARIOUS SOLVENTS
(In the dark at 0°C and over a 12-hr. period)

Solvent	Isomerization
Ethanol	None
Acetone	None
Benzene*	None
CCl_4	None
Acetic acid*	None
Dimethyl sulfoxide*	None
Dimethylformamide	None

* At room temperature

The Arrhenius parameters are obtained from the linear plot, $\log k$ vs. $1/T$, and are listed in Table II.

To compare these results with the catalytic action of the ordinary solvents with the syn-anti isomerization of the oxime, the β-oxime

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[9] D. Murakami and N. Tokura, This Bulletin, 31, 431 (1958).

[10] T. Hata and T. Asano, *Bull. of Res. Inst. of Non-Aqueous. Solns.* (*Hisuiken Hokoku*), 9, 79 (1960).

[11] N. Tokura, M. Matsuda, I. Shirai, K. Shiina, Y. Ogawa and Y. Kondo, This Bulletin, 35, 1043 (1962).

was dissolved in a number of solvents and the mixtures were allowed to stand for 12 hr. at 0°C in the dark. As is shown in Table III, no isomerization was observed.

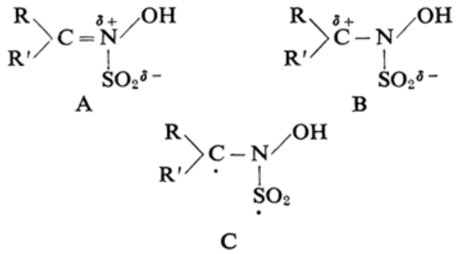
Tada, Shoji and Tokura[12] have shown that oxime is liable to form a 1 : 1 complex with sulfur dioxide:

$$\text{Oxime} + SO_2 \rightleftharpoons \text{Oxime}\cdot SO_2 \text{ (complex)} \qquad (3)$$

The postulated dual (radical and ionic) nature of sulfur dioxide catalysis upon isomerization may well be elucidated by such a complex formation as an intermediate, as such is often the case in sulfur dioxide catalyses[1-5].

In the absence of light, the isomerization may be subject to acid catalysis via form B in Chart 2 through a rotating of the C–N axis conducted by a carbonium ion mechanism.

Chart 2



On the other hand, in the presence of light complex A may be excited to make easy the formation of the carbon radical, as is seen in form C in Chart 2, the rotation of the C–N axis being carried out through this radical form. That sulfur dioxide is an excellent radical acceptor by using the expanded orbital (3d orbital) of the sulfur atom has already been recognized in many instances.

For the early stage of the oxime conversion and in the case of a large excess of liquid sulfur dioxide, the rate of the isomerization, R, may be expressed as Eq. 4, the rate-determining step being assumed as the isomerization of the complex.

$$R = k_0\,[\text{complex}] = k_0 K\,[\beta\text{-oxime}]\,[SO_2]$$
$$= k\,[\beta\text{-oxime}] \qquad (4)$$

where K is an equilibrium constant for Eq. 3, k_0 and k are the rate constants of the isomerization for the second order and the pseudo-first order reactions respectively, and the brackets indicate the concentrations of the respective components.

As has been described above, the isomerization of the oxime in liquid sulfur dioxide is a very slow reaction in comparison with the fast Beckmann rearrangement, the latter reaction being much too fast to be measured accurately and the rearrangement being completed within 5 min. at 0°C[6].

However, the conclusion that liquid sulfur dioxide is an excellent solvent for such a Beckmann rearrangement should be taken with many reservations, since there remains another possibility of the isomerization during the Beckmann rearrangement, viz., an acid-catalyzed isomerization accompanied by this rearrangement. The acid may be either the acid (Lewis acid) itself used as the reagent for the Beckmann rearrangement or a Brφnsted acid derived from Lewis acid. Experiments on an acid-catalyzed isomerization in liquid sulfur dioxide are now in progress; and the results will be published in a following article.

Summary

1. The syn-anti isomerization of β-cyclohexyl phenyl ketoxime is carried out in liquid sulfur dioxide.

2. The isomerization is accerelated by light and retarded by hydroquinone. The degree of the dehydration of liquid sulfur dioxide has little effect on the rate of isomerization.

3. The kinetic result has shown that the reaction is of the first order with respect to the concentration of the oxime and that the rate constant, k for $R = k\,[\beta\text{-oxime}]$, may be expressed as:

$$k = 6.3 \times 10^{11} \exp\,[-19.1/RT]$$

4. A complex between the oxime and sulfur dioxide is assumed as the intermediate step, the isomerization of the complex being the rate-determining step. The dual (radical and ionic) nature of the isomerization in liquid sulfur dioxide may well be elucidated by such an assumption.

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[12] R. Tada, K. Shoji and N. Tokura, unpublished.