Mercury Photosensitized Reaction of Deuterio-Propylene Studied by Microwave Spectroscopy

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The mercury photosensitized reaction of propylene-*cis*-1-d_1 and 1-butene-*cis*-1-d_1 was studied by means of microwave spectroscopy combined with gas chromatography and mass spectrometry. At pressures above 100 mmHg *cis-trans* isomerization was the main reaction for both the propylene and 1-butene. The number of the absorbed quanta of photons and the number of molecules reacted was almost equal. However, at lower pressures, this condition was not satisfied. At pressures less than 30 mmHg, substantial amounts of the 2-d_1 and 3-d_1 propylene species were detected in the reaction mixtures. Decomposition of propylene into an allylic radical and a hydrogen atom with subsequent "recombination," was proposed to account for this observation. Similar results were obtained with 1-butene-*cis*-1-d_1.

Several investigations on the mercury photosensitized reaction of simple olefins such as *cis*- or *trans*-dideuterioethylene,[1-3] 2-butene,[4,5] and 1-butene[6] have been reported. Usually the reaction was followed by means of gas chromatography, and in the reaction of dideuterioethylene infrared spectroscopy was employed to determine the extent of the reaction. Quite recently another application of infrared spectroscopy to this type of reactions, *e.g.*, photosensitized reaction propylene-1,3,3,3-d_4 has been reported by Hirokami and Sato.[7] In this paper an attempt has been made to apply microwave spectroscopy to the study of the mercury photosensitized reaction of propylene-*cis*-1-d_1 and 1-butene-*cis*-1-d_1.

Experimental

Methylacetylene was treated with weakly alkaline deuterium oxide to replace its acetylenic hydrogen with deuterium. By repeating this procedure several times, the concentration of methylacetylene-1-d_1 was made greater than 90%. The methylacetylene-1-d_1 thus obtained was selectively hydrogenated to propylene-*cis*-1-d_1 by the procedure developed by Rabinovitch and Looney.[8] 1-Butene-*cis*-d_1 was synthesized from ethylacetylene by a similar method. Deuterium contents in the synthesized olefins were determined by mass spectrometry, while the *cis-trans* distribution was analyzed by means of microwave spectroscopy.

Microwave spectra of propylene and its mono-deuterated species were observed by Lide and Christensen,[9] and applied to the quantitative determination of the deuterium contents at each hydrogen position of propylene-d_1 by Hirota and Morino.[10] Microwave spectra of 1-butene and its mono-deuterated species have been reported by Kondo, Hirota, and Morino[11] and were employed as a useful tool to study *n*-butene isomerization over solid acid catalysts.[12] Analysis by means of microwave spectroscopy revealed that more than 96% of the mono-deuterated species of both the propylene and the 1-butene was *cis*-1-d_1, the remainder was *trans*-1-d_1. Other mono-deuterated species such as 2-d_1 and 3-d_1 (and also 4-d_1 in the case of 1-butene) were not observed within the detection limits of the microwave spectroscopy. The prefixes *cis* and *trans* represent the configuration of deuterium relative to the methyl or ethyl group attached to the C_2 atom.

The 10 W low pressure mercury lamp and the quartz-made cylindrical reaction vessel employed in this work were of a conventional type. The light intensity of the 2537 Å resonance line was estimated by the amounts of hydrogen produced in the decomposition reaction of ethylene under the same reaction conditions. The quantum yield of this reaction was assumed to be 0.351 at an ethylene pressure of 13.3 mmHg.[13]

The reaction products were analyzed mainly by means of microwave spectroscopy and mass spectrometry. In some cases gas chromatography was employed in order to identify the reaction products of the decomposition process and also to determine their composition.

Results and Discussion

Table 1 shows some of the results obtained in the mercury photosensitized reaction of propylene-*cis*-1-d_1. The deuterium concentration of the starting propylene was about 80%, but it did not change appreciably in the course of the reaction. (The change in the deuterium content was less than 0.3%.) Table 1 shows the relative, not the absolute concentrations of each mono-deuterated species. The starting reactant listed at the top of the Table contained neither the 2-d_1 nor 3-d_1 species. Especially at pressures less than 15 mmHg, considerable amounts of both the 2-d_1 and 3-d_1 species were formed as the reaction progressed, as well as the *trans*-1-d_1

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TABLE 1. DEUTERIUM DISTRIBUTION IN PROPYLENE IN THE CASE OF Hg PHOTOSENSITIZED REACTION OF PROPYLENE-*cis*-1-d_1

Pressure mmHg	Photons absorbed μ einstein	d_0 %	d_1 %	*cis*-1-d_1 %	*trans*-1-d_1 %	2-d_1 %	3-d_1 %
		20.0	80.0	96.5	3.5	0.0	0.0
3.3	36	20.2	79.8	74.8	10.2	2.5	12.5
7.2	36			85.7	8.4	1.1	4.8
7.6	48	20.3	79.7	84.0	8.9	1.2	5.9
11.9	72	20.0	80.0	83.4	10.5	1.1	5.0
13.1	108	20.3	79.7	80.1	11.7	1.4	6.8
16.6	72	20.3	79.7	86.4	10.3	0.6	2.7
28.8	72			90.9	7.8	0.2	1.1
42.4	72			92.6	7.4	0.0	trace
76.3	216			90.2	9.4	0.0	0.4

species produced by the *cis-trans* isomerization. The fraction of the 2-d_1 species was always smaller than that of the 3-d_1 species, and both became negligible at pressures above 40 mmHg. The quantum yield of the *cis-trans* isomerization was calculated on the basis of the following reaction scheme (A), and the results are plotted against the pressure of propylene in Fig. 1:

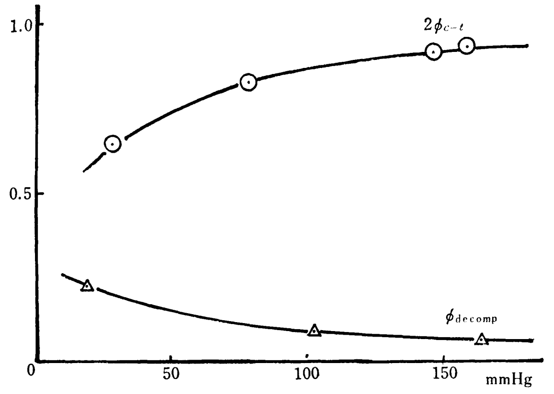


Fig. 1. Pressure dependence of quantum yield of Hg photosensitized *cis-trans* isomerization of propylene-*cis*-1-d_1. (ϕ_{decomp} is for C_3H_6.)

Scheme (A)

$$cis\text{-P} + \text{Hg}^* \longrightarrow \text{P}^* + \text{Hg}$$

$$trans\text{-P} + \text{Hg}^* \longrightarrow \text{P}^* + \text{Hg}$$

$$\text{P}^* + \text{M} \longrightarrow 1/2\, trans\text{-P} + 1/2\, cis\text{-P} + \text{M}$$

Here P* represents an excited state of propylene, possibly the lowest triplet state, and M a third body. The quantum yield of the decomposition reaction, ϕ_{decomp} was calculated for normal propylene after the method of Hirokami and Sato,[7] and the results are shown in Fig. 1 together with $2\phi_{c-t}$.

The pressure dependence of $2\phi_{c-t}$ and ϕ_{decomp} agrees rather well with the results reported by Hirokami and Sato,[7] and the balance between the number of the absorbed quanta of photons and the number of molecules which underwent either isomerization or decomposition is nearly satisfied above 100 mmHg. At pressures less than 100 mmHg, however, this balance can not hold owing to the significant decrease in the quantum yield of the *cis-trans* isomerization. This phenomenon was also observed in the mercury photosensitized reaction of 2-butene[5] and propylene-1,3,3,3-d_4.[7] The formation of vibrationally excited propylene or 2-butene, which could not contribute to the isomerization, was assumed in order to explain these observations. However, as is shown in Table 1, 3-d_1 and 2-d_1 species were formed in considerable amounts from propylene-*cis*-1-d_1 at pressures less than 30 mmHg. When the increase in the fraction of *trans*-1-d_1 species (Δ*trans*-1-d_1) to that of 3-d_1 (Δ3-d_1) was plotted against the pressure of propylene, the ratio Δ*trans*-1-d_1/Δ3-d_1 gave a *linear curve* with a zero intercept of about 0.2 (Fig. 2). On the other hand, the ratio Δ2-d_1/Δ3-d_1 was constant and equal to about 0.2 in the pressure region less than 30 mmHg, as shown in Fig. 3.

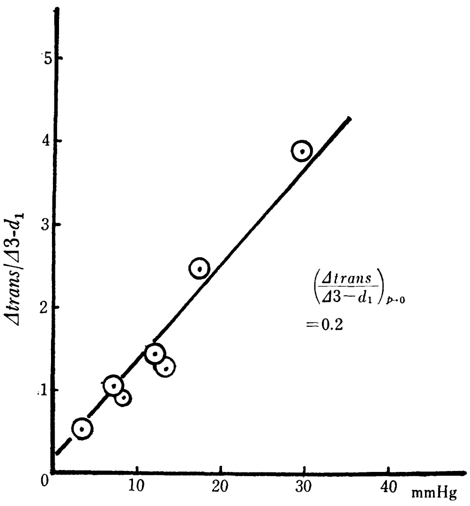


Fig. 2. Hg photosensitized isomerization of propylene-*cis*-1-d_1. Pressure dependence of the ratio (Δ*trans*-1-d_1/Δ3-d_1)

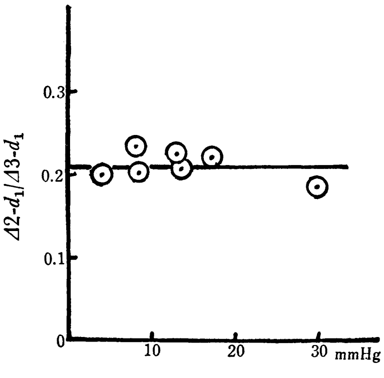
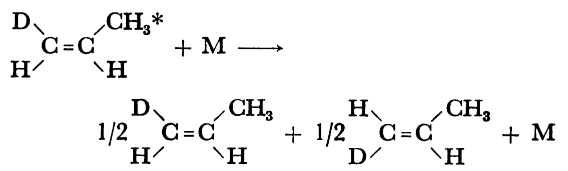


Fig. 3. Hg photosensitized isomerization of propylene-*cis*-1-d_1. Pressure dependence of the ratio (Δ2-d_1/Δ3-d_1)

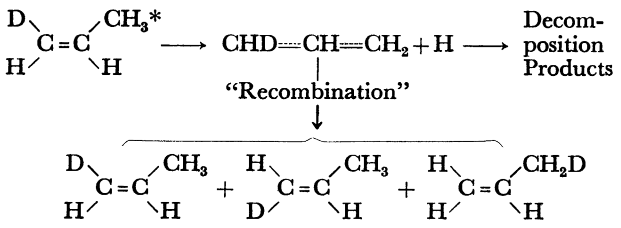
The results in Fig. 2 suggest that the calculation of the quantum yield of the *cis-trans* isomerization on the basis of scheme (A) is open to question at pressures less than 30 mmHg, where the fraction of 3-d_1 species is nearly comparable to that of *trans*-1-d_1. Due attention being paid to the considerable contributions of 2-d_1 and 3-d_1 species in the low pressure region, it was assumed that the mercury photosensitized reaction of propylene-*cis*-1-d_1 proceeds in the following way.

Scheme(B)

Main reaction at high pressures:



At low pressures:



In a rough approximation, the "recombination" reaction of an allylic radical and a hydrogen atom may be expected to yield *cis*-1-d_1, *trans*-1-d_1, and 3-d_1 species in the ratio of 1:1:2. Hydrogen abstraction by an allylic radical from another propylene molecule may also lead to similar results. As this reaction can not be ruled out completely, the term "recombination" is here rather tentatively employed to express the reaction of an allylic radical with a hydrogen atom either in the free or bound state in a hydrocarbon molecule.

The fraction of 3-d_1 species was 1.1% at a pressure of 28.8 mmHg. This suggests that the *trans*-1-d_1 fraction of 0.6% may have resulted from a "recombination" reaction. When this fraction and the original portion of *trans*-1-d_1 in the starting material were substracted, the fraction of *trans*-1-d_1 in the reaction mixture was found to be about 3.7%. In this case the contribution of *cis-trans* isomerization and "recombination" reaction was estimated to be approximately in the ratio of 3.4:1. The $2\phi_{c-t}$ under these conditions was about 0.65 (Fig. 1), and this gave rise to a value of about 0.19 for the quantum yield of the "recombination" reaction.

The quantum yields of *cis-trans* isomerization, "recombination" and decomposition were summed and gave a value of about 1.0, showing that the balance between the number of the absorbed quanta and the number of the reacted molecules was nearly satisfied. Similar results were obtained for reaction at 16.6 mmHg, with a quantum yield of *cis-trans* isomerization being taken from Fig. 1 as 0.55. At pressures less than 15 mmHg the fraction of Δ3-d_1 may become comparable to, or even exceed that of Δ*trans*-1-d_1, as can be seen in Fig. 2. In this pressure region even such very qualitative discussions as described above may not hold.

The above mentioned discussions are rather crude in nature, but they still serve to elucidate the reaction paths involved in the mercury photosensitized reaction of propylene-*cis*-1-d_1. Decomposition of propylene into an allylic radical and a hydrogen atom with subsequent "recombination" to yield the 3-d_1 species of propylene as well as the *cis*- and *trans*-1-d_1 species can not be neglected in the low pressure regions. The formation of 2-d_1 species was tentatively explained by an intramolecular hydrogen shift within the allylic radical resulting in $CH_2 \cdots CD \cdots CH_2$, which then reacted with a hydrogen atom to yield CH_2=CD–CH_3.

Table 2. Deuterium distribution in 1-butene in the case of Hg photosensitized reaction of 1-butene-*cis*-1-*d*

Pressure mmHg	Photons absorbed μ eistein	*cis*-1-d_1 %	*trans*-1-d_1 %	3-d_1 %	d_0 %	d_2 %
		87.2	2.7	0.0	9.1	1.0
6.1	43	75.7	10.3	3.5	10.3	1.6
13.2	64	79.1	8.5	2.0	9.5	0.9
22.7	64	80.9	7.7	1.3	9.3	0.8
34.3	86	83.9	6.7	0.0	9.1	0.9
62.4	143	83.2	6.8	0.0	9.2	1.0
		83.5	1.7	0.0	14.1	0.7
5.0	72	70.1	9.3	3.8	15.3	1.5
7.8	72	75.9	7.1	2.5	14.1	0.4
15.2	110	73.9	8.9	1.9	14.7	0.6
19.8	120	73.5	10.0	1.6	14.3	0.6

Some of the results obtained in the mercury photosensitized reaction of 1-butene-*cis*-1-d_1, especially those

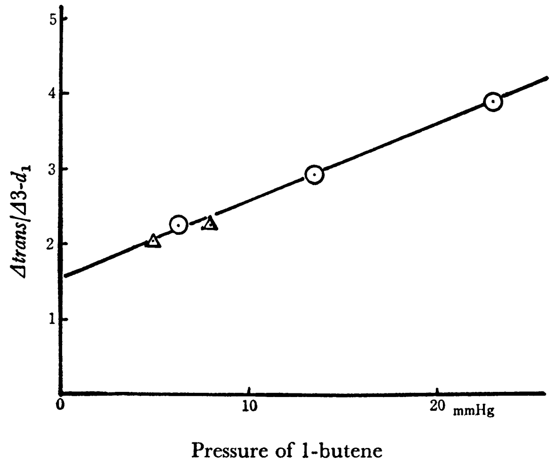


Fig. 4. Hg photosensitized reaction of 1-butene-*cis*-1-d_1. Pressure dependence of the ratio (Δ*trans*/Δ3-d_1)

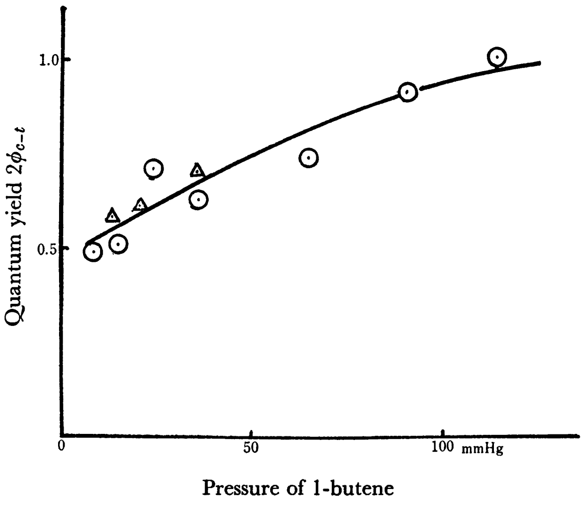


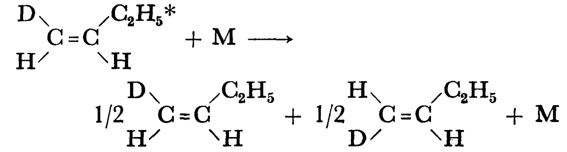
Fig. 5. Pressure dependence of quantum yield of Hg photosensitized *cis-trans* isomerization of 1-butene-*cis*-1-d_1.

in the low pressure regions, are given in Table 2. The 3-d_1 species of 1-butene ($CH_2{=}CHCHDCH_3$) was formed in appreciable amounts after reaction at lower pressures. The 2-d_1 species ($CH_2{=}CDCH_2CH_3$) was not detected within the limits of the microwave spectroscopy. When the ratio Δ*trans*-1-d_1/Δ3-d_1 was plotted against the pressure of 1-butene, a *linear curve* with a zero intercept of about 1.5 was obtained (Fig. 4).

The pressure dependence of the quantum yield of *cis-trans* isomerization, $2\phi_{c-t}$, gave a curve which is shown in Fig. 5; the quantum yield was calculated with a reaction scheme similar to scheme (A) for the reaction of propylene. Owing to the considerable inherent difficulties in the analyses of 1-butene and its mono-deuterated species by microwave spectroscopy, the experimental data showed considerable scattering. Nevertheless Fig. 5 clearly showsed that $2\phi_{c-t}$ continuously decreasesed with decreasing pressure and attains a value of 0.45 at the zero pressure intercept. The results in Fig. 4 and Table 2 lead to the conclusion that the mercury photosensitized reaction of 1-butene-*cis*-1-d_1 proceeds *via* scheme (C) which is quite similar to scheme (B) for the reaction of propylene-*cis*-1-d_1.

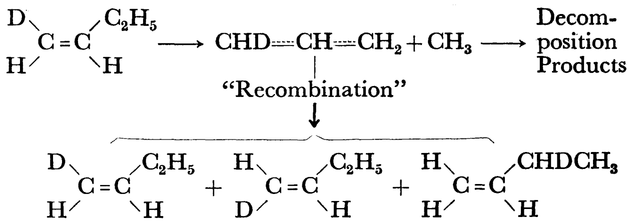
Scheme(C)

Main reaction at high pressure:



$$\begin{matrix}D & & C_2H_5^*\\ & C{=}C & \\ H & & H\end{matrix} + M \longrightarrow \frac{1}{2}\begin{matrix}D & & C_2H_5\\ & C{=}C & \\ H & & H\end{matrix} + \frac{1}{2}\begin{matrix}H & & C_2H_5\\ & C{=}C & \\ D & & H\end{matrix} + M$$

At low pressure:



$$\begin{matrix}D & & C_2H_5\\ & C{=}C & \\ H & & H\end{matrix} \longrightarrow CHD\cdots CH\cdots CH_2 + CH_3 \longrightarrow \text{Decomposition Products}$$

$$\text{“Recombination”} \downarrow$$

$$\begin{matrix}D & & C_2H_5\\ & C{=}C & \\ H & & H\end{matrix} + \begin{matrix}H & & C_2H_5\\ & C{=}C & \\ D & & H\end{matrix} + \begin{matrix}H & & CHDCH_3\\ & C{=}C & \\ H & & H\end{matrix}$$

In the reaction of 1-butene-*cis*-1-d_1 the decomposition products were not analyzed accurately, and the pressure dependence of ϕ_{decomp} or an estimation of the quantum yield of the "recombination" reaction was not available for discussion. However, when the data for the deuterium distribution within 1-butene was compared with that for propylene, their similarity strongly suggested that the same conclusion concerning the balance between the number of the reacted molecules and the absorbed photons may also be derived for 1-butene-*cis*-1-d_1.

Thus, microwave spectroscopy was applied to the study of the mercury photosensitized reactions of propylene-*cis*-1-d_1 and 1-butene-*cis*-1-d_1, and some of the reaction paths involved in these reactions were revealed.

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