The Benzene-Photosensitized cis-trans Isomerization of Butene-2

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Recently there have been a number of reports on the photochemical cis-trans isomerization of olefins by organic sensitizers.[1-3] Hammond et al.[1,2] have examined the photosensitized isomerization in the liquid phase, using mainly carbonyl compounds as sensitizers. Cundall and his co-workers[3] studied the gas-phase-photosensitized isomerization of butene-2, using several organic sensitizers. They showed that the photostationary trans-to-cis ratio was 1.37 when benzene and pyridine were used as sensitizers.

The photosensitization by organic substances seems to be of great importance not only in elucidating intermolecular energy transfer phenomena in general, but also in solving the problem of assimilation in plants.

This paper will describe the benzene-photosensitized cis-trans isomerization of butene-2 in the gas phase.[4]

Experimental

The benzene used was a special-grade reagent which had been fractionally distilled; the middle third was used. The *cis*- and *trans*-butene-2 were commercially available substances whose vapor-phase chromatography showed to be 99.9% pure. They were thus used without further purification.

Special care was taken to keep the vacuum line free of mercury. The light source used was a low-pressure mercury arc lamp. Between the lamp and the quartz reaction vessel, a UV25 filter (supplied by the Toshiba Denki Co.) which eliminated the light shorter than 2300 Å was placed.

The analysis was carried out gas chromatographically, using dimethylsulfolane on celite as a separation column.

In the course of the experiment, it was shown that the light absorbed by benzene did not obey Lambert-Beer's law. When necessary, the ratio of absorbed light and incident light, I_a/I_0, was obtained as follows: the light transmitted was measured by the mercury-photosensitized decomposition of ethylene[5,6] in a cell just behind the reaction cell, which contained various pressures of benzene. This procedure gave the relation $\log_{10}(I_0/I_t)=0.0205p-0.0000883p^2$, where I_0 and I_t are the intensities of transmitted light when the reaction cell contains no benzene and p mmHg benzene respectively. From this relation, I_a/I_0 ratio could be calculated at any benzene pressure.

All experiments were carried out at room temperature.

Results

The reaction was very clean, no products other than the isomerized butene-2 being detected.

Figure 1 shows the time dependence of the cis-to-trans ratio, both *cis*- and *trans*-butene-2 being used as starting materials. The photostationary cis-to-trans ratio may be seen from the figure to be about unity.

The effect of the benzene pressure on the cis-to-trans isomerization rate is summarized in Table I. It can be seen from the Table that the isomerization rate increases with the pressure of benzene. The rate tends to decrease, however, after the benzene pressure reaches a certain value. The ratio of the absorbed light to the isomerization rate is also seen to increase with the pressure of benzene.

The dependence of the isomerization rate on

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[1] G. S. Hammond and J. Saltiel, *J. Am. Chem. Soc.*, **84**, 4938 (1962).

[2] G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt and C. Dalton, ibid., **86**, 3197 (1964).

[3] R. B. Cundall, F. J. Fletcher and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1149 (1964).

[4] S. Sato, K. Kikuchi and M. Tanaka, *J. Chem. Phys.*, **39**, 239 (1963).

[5] A. B. Callear and R. J. Cvetanović, ibid., **24**, 873 (1956).

[6] Kang Yang, *J. Am. Chem. Soc.*. **86**, 3941 (1964).

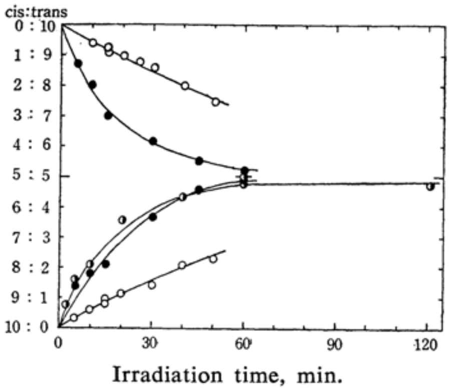

Fig. 1. The time dependence of the cis-trans isomerization.

○ Butene-2, 20 mmHg; benzene, 47.2 mmHg
● Butene-2, 5 mmHg; benzene, 47.2 mmHg
◑ Butene-2, 11 mmHg; benzene, 69 mmHg; The incident light intensity is not the same as the above two series.
-◑- Started from *trans*-butene-2. The other conditions are the same as just the above series.

TABLE I. BENZENE PRESSURE DEPENDENCE OF THE PHOTOSENSITIZED ISOMERIZATION

Initial *cis*-butene-2 pressure, 20.7±0.4 mmHg
Irradiation period, 15 min.

Benzene mmHg	I_a/I_0	Conversion %	Isomerization rate mmHg/min.
0	0	0.65	0
3.18	0.139	2.52	0.0258
4.48	0.187	2.76	0.0291
5.68	0.230	3.48	0.0391
6.6	0.261	3.78	0.0433
14.5	0.474	5.69	0.0696
14.5	0.474	5.70	0.0698
15.6	0.497	5.81	0.0712
18.7	0.556	7.01	0.0878
28.6	0.694	8.65	0.104
47.2	0.831	9.60	0.124
49.0	0.839	9.74	0.125
64.4	0.890	10.5	0.136
75.2	0.909	10.1	0.130
92.6	0.927	9.83	0.127
93.5	0.929	9.29	0.119

the butene-2 pressure was also examined. The results are summarized in Table II, which shows that the rate increases monotonously as the pressure increases, while at high pressures it tends to saturate.

TABLE II. BUTENE-2 PRESSURE DEPENDENCE OF PHOTOSENSITIZED ISOMERIZATION

Benzene pressure, 69 mmHg
Irradiation period, 2 min.

cis-Butene-2 mmHg	Isomerization rate mmHg/min.
3.16	0.0264
3.85	0.0283
6.05	0.0325
6.49	0.0464
9.08	0.0459
9.52	0.0461
14.9	0.0565
28.5	0.0596

Discussion

Table I clearly shows that scarcely any cis-trans isomerization of butene-2 occurs in the absence of benzene, but that the rate increases markedly as the pressure of benzene increased. It is evident from this fact that the energy transfer from excited benzene to butene-2 induces the ovserved isomerization. Among the excited states of benzene, the lowest-excited singlet ($^1B_{2u}$, 4.7 eV.)[7,8] and the lowest triplet ($^3B_{1u}$, 3.6 eV.)[8] are conceivably involved in the reaction when, as is the case in the present study, the 2537 Å mercury resonance line is employed. A possible reaction mechanism involving these excited states is

$$B + h\nu \longrightarrow {}^1B_n \qquad (1)$$

$$^1B_n + M \longrightarrow {}^1B_0 + M \qquad (2)$$

$$^1B_0 \longrightarrow B + h\nu' \qquad (3)$$

$$\longrightarrow {}^3B_n \qquad (4)$$

$$^1B_0 + B \longrightarrow B + B \qquad (5)$$

$$^3B_n + M \longrightarrow {}^3B_0 + M \qquad (6)$$

$$^3B_0 \longrightarrow B(+\ h\nu'') \qquad (7)$$

$$^3B_0 + B \longrightarrow B + B \qquad (8)$$

$$^1B_0 + C \longrightarrow B + {}^1C \qquad (9)$$

$$^3B_0 + C \longrightarrow B + {}^3C \qquad (10)$$

$$\left.\begin{aligned} {}^1C &\xrightarrow{1-\alpha} C \\ &\xrightarrow{\alpha} T \end{aligned}\right\} \qquad (11)$$

$$\left.\begin{aligned} {}^3C &\xrightarrow{1-\beta} C \\ &\xrightarrow{\beta} T \end{aligned}\right\} \qquad (12)$$

where B, C and T refer to benzene, *cis*- and *trans*-butene-2 respectively, where the superscripts and subscripts denote the electronic multiplicities and the vibrational quantum numbers respectively and where M indicates any third body carrying away the vibrational energy of excited benzene. The steady-state treatment gives the following equation:

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[7] M. Goeppert-Meiyer and A. L. Sklar, *J. Chem. Phys.*, 6, 645 (1938).

[8] R. Pariser, ibid., 24, 250 (1956).

$$R_T \equiv \frac{[\mathrm{dT}]}{\mathrm{d}t} = \frac{\alpha k_9[\mathrm{C}]I_a}{k_3+k_4+k_5[\mathrm{B}]+k_9[\mathrm{C}]} + \frac{\beta k_{10}[\mathrm{C}]}{k_7+k_8[\mathrm{B}]+k_{10}[\mathrm{C}]} \cdot \frac{k_4 I_a}{k_3+k_4+k_5[\mathrm{B}]+k_9[\mathrm{C}]} \tag{1}$$

The photochemical cis-trans isomerization of olefins by organic sensitizers has been extensively studied in the liquid phase by Hammond et al.,[1,2] the results being best understood in terms of a triplet energy transfer from sensitizer to olefin. Since butene-2 has little absorption in the neighborhood of 2500 Å, and since the life-time of a singlet excited state is much shorter than that of a triplet, the excitation of butene-2 by an energy transfer from a singlet-excited benzene to butene-2 is unlikely; the intersystem crossing from an excited-singlet benzene to its lowest triplet would be much faster than the energy transfer to butene-2. Therefore, it may be safe to say that the isomerization we observed resulted from a triplet state of butene-2 formed by the energy transfer from the triplet benzene to butene-2. By applying $k_4 \gg k_9[\mathrm{C}]$ to Eq. 1, we obtain:

$$\frac{\beta I_a}{R_T} = \frac{k_3+k_4+k_5[\mathrm{B}]}{k_4}\left(1+\frac{k_7+k_8[\mathrm{B}]}{k_{10}[\mathrm{C}]}\right) \tag{2}$$

Equation 2 requires that, under a constant pressure of benzene, a linear relationship should hold between the reciprocal of the isomerization rate and that of the butene-2 pressure. As may be seen from Fig. 2, this is indeed the case. The ratio of the slope to the intercept gives $(k_7+k_8[\mathrm{B}])/k_{10}$. We may assume k_7 to be negligibly small compared with $k_8[\mathrm{B}]$, since the triplet benzene seems to have a rather long life-time, of the order of magnitude 10^{-4} to 10^{-5} sec., as has been found for other aromatic molecules,[9] and we obtain 11.2 as the value of k_{10}/k_8. That is, butene-2 quenches triplet benzene more efficiently than does benzene.

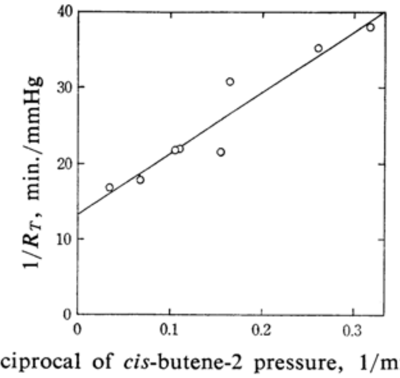

Fig. 2. The relation between the reciprocal of isomerization rate and that of butene-2 pressure.
Benzene, 69 mmHg; irradiation time, 2 min.

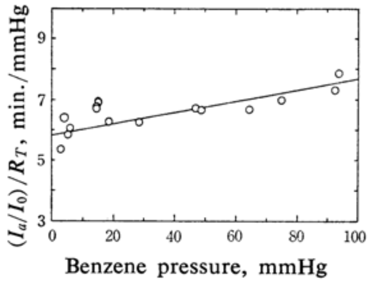

Fig. 3. The relation between the reciprocal of isomerization rate and the pressure of benzene.
cis-Butene-2, 20.7 mmHg; irradiation time, 15 min.

The relation between the reciplocal of the isomerization rate and the pressure of benzene is shown in Fig. 3. Although the plots show a considerable scatter a straight line may be drawn. This linear relationship[10] may be expected from Eq. 2 in two cases: (1) $k_3+k_4 \gg k_5[\mathrm{B}]$, or (2) $1 \gg (k_7+k_8[\mathrm{B}])/k_{10}[\mathrm{C}]$. In case 1, the ratio of the slope to the intercept gives $k_8/(k_7+k_{10}[\mathrm{C}])$. Neglecting k_7 compared with $k_{10}[\mathrm{C}]$, one obtains the value of k_{10}/k_8 as 12.8, which is comparable to the value (11.2) obtained from the relation between $1/R_T$ and the butene-2 pressure. Because our experiment was carried out below 100 mmHg of benzene, the condition $k_3+k_4 \gg k_5[\mathrm{B}]$ will be satisfied if we take 10 as the value of the ratio $(k_3+k_4)/k_5[\mathrm{B}]$ at 100 mmHg of benzene, which gives $(k_3+k_4)/k_5 = 1\times10^3$ mmHg. In case 2, the slope to intercept ratio gives $k_5/(k_3+k_4)$. The value of $(k_3+k_4)/k_5$ thus obtained is 3.05×10^2 mmHg. If we take the ratio $(k_7+k_8[\mathrm{B}])/k_{10}[\mathrm{C}]$ to be 1/10 at 100 mmHg of benzene, the highest pressure employed in our experiment, the condition $(k_7+k_8[\mathrm{B}])/k_{10}[\mathrm{C}] \ll 1$ will be satisfied. Neglecting k_7, we obtain from this relation 48.3 as the value of k_{10}/k_8.

Ishikawa and Noyes[11] have obtained the value of k_5 of 4.6×10^{-3} ml./molec./sec. $=1.5\times10^4$/mmHg/sec., taking $k_3+k_4=1.7\times10^6$ sec^{-1}. The value of $(k_3+k_4)/k_5$ calculated from these values is 1.2×10^2 mmHg, which is smaller than the values estimated above in both cases. The true value of $(k_3+k_4)/k_5$ might somewhat larger than the value given by Ishikawa and Noyes,

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[9] G. Porter and F. G. Wright, *Trans. Faraday Soc.*, **51**, 1205 (1955).

[10] The linear relationship between the ratio of the benzene pressure to the rate of isomerization ([B]/R_T) and the benzene pressure has been discarded in the previous note,[4] in which the correction to light absorption was not made.

[11] H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).

although the considerable scatter of our data makes questionable the accuracy of our value. It cannot be decided at this stage whether case 1 or case 2 is actually operative under our experimental conditions; more precise experiments must be carried out before further discussions can be made.

A crude estimation of the quantum yield can be made. Behind the reaction cell another quartz cell was placed; in this cell the mercury-photosensitized decomposition of ethylene was carried out. Using 0.502 as the quantum yield of hydrogen production in the mercury-photosensitized decomposition of ethylene,(6) the light quanta transmitted through a cell containing various pressures of benzene were obtained. On the basis of these measurements the quantum yield of the formation of *trans*-butene-2 in the benzene-photosensitized isomerization was calculated to be 1.5. Since the incident light beam was not a parallel one and since the light was reflected on the surfaces of the reaction vessels, the light absorbed by benzene must have been estimated too low by a factor of about 3. The true quantum yield seems to be nearly 0.5, the value which is to be expected from a full utilization of the light absorbed by benzene in the isomerization and from $\beta=0.5$. The isomerization observed in the present experiment, therefore, can be said to have proceeded very efficiently.

The observed photostationary cis-to-trans ratio was about 1.0 in our experiment. The value obtained by Cundall and his co-workers(3) was 0.73 in the benzene and pyridine sensitizations. The reason for this discrepancy is not clear, but the difference in the light sources employed by them (possibly a medium-pressure mercury arc lamp) and by us (a low-pressure mercury arc lamp) might be responsible for it.

The energy curve of the ground singlet state as a function of the relative angle of the rotation of two methyl groups around the axis passing through the two central carbon atoms of butene-2 would have its maximum at 90°. On the other hand, the energy of the lowest-triplet butene-2 would go down from 4.2 eV.(12) at 0° to a minimum at 90°. Thereby the two energy curves are very likely to intersect each other. That the triplet benzene sensitizes the isomerization implies that the energy of the crossing point is smaller than 3.6 eV., the energy of triplet benzene. The cis-to-trans ratio at the photostationary state may depend, according to Landau and Zener,(16) on the angle of the crossing of singlet and triplet energy curves and on the speed at the crossing point. Accordingly, the cis-to-trans ratio may depend on the energy of the sensitizers and on the pressure of the system. A detailed study along these lines is now in progress in this laboratory.

Summary

The benzene-photosensitized cis-trans isomerization of butene-2 has been investigated in the gas phase. The results have been discussed on the basis of a mechanism involving triplet-energy transfer from benzene to butene-2.

The quantum yield measurements indicate that the reaction occurs at a very high efficiency. The triplet-benzene quenching efficiency of butene-2 has been shown to be considerably greater than that of the ground-state benzene.

The photostationary cis-to-trans ratio has been about unity, unlike the value obtained by Cundall et al. A mechanism which may explain the dependence of the ratio on the pressure and on the energy of the sensitizer has been suggested.

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12) Although the energy of the triplet butene-2 has not been measured, this value was estimated as follows: The energy of triplet ethylene has been measured by Kupperman and Raff(13) by electron diffraction method and by Evans(14) spectroscopically. Kupperman and Raff gave the value of 4.8 eV., possibly a vertical one. Comparing the excitation energies of ethylene and butene-2 calculated by Sato and Cvetanović,(15) together with the above measured value of the triplet energy of ethylene, we obtain 4.2e V. as the value of the triplet energy of butene-2.

13) A. Kupperman and L. M. Raff, *J. Chem. Phys.* **37**, 2497 (1962).

14) D. F. Evans, *J. Chem. Soc.*, **1960**, 1735.

15) S. Sato and R. J. Cvetanović, *J. Am. Chem. Soc.*, **81**, 3223 (1959).

16) L. Landau, *Physik. Z. Sowjetunion*, **2**, 46 (1932); C. Zener, *Proc. Royal Soc.*, **A137**, 696 (1932).