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The Benzene-photosensitized Isomerization of Butene-2 and Pentene-2

By Masahiro TANAKA, Masaaki KATO and Shin SATO

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Tokyo

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The benzene-photosensitized *cis-trans* isomerization of butene-2 has been reinvestigated, using 2537 Å as the light source. A comparative study with pentene-2 has also been carried out. In all experiments, pentene-2 behaved very similarly to butene-2. The quantum yield of the isomerization was estimated to be 0.27 ± 0.03, irrespective of the olefin used. The following photostationary ratios of the *cis* to the *trans* isomer were obtained: $1.0_5\pm0.1$ for butene-2, and $0.9_9\pm0.1$ for pentene-2. The ratio of the initial rates of isomerization was, for both olefins, $1.1_5\pm0.1_5$, in favor of the isomerization from the *cis* to the *trans* isomer. Both ratios are very close to unity; this finding is in agreement with our previous results (M. Tanaka, T. Terao and S. Sato, *Bull. Chem. Soc. Japan,* **38**, 1645 (1965)).

The benzene-photosensitized *cis-trans* isomerization of butene-2, first observed by Cundall and Palmer,[1] provides one of the simplest examples of intermolecular energy transfer in the gas phase. Cundall et al. recently carried out[2] a more detailed study of this reaction, using pyridine as well as benzene as the sensitizer; they concluded that the isomerization takes place through a triplet-triplet interchange. We have also studied this reaction[3,4] and have obtained similar results except for the *cis-trans* photostationary ratio, ours is about unity, while Cundall et al. reported it to be 1.37 in favor of *trans*-butene-2.

Some complications may arise in this system because the fate of the photoexcited benzene[5,6] depends on the experimental conditions, such as the wavelength of the irradiating light, the pressure of the reactants, the temperature, and so on.

In the present work, we have re-examined the butene-2 reaction in order to confirm the data previously obtained; we also attempted to find the reason for the discrepancy with the results of Cundall et al. At the same time, we have also carried out a comparative study with pentene-2.

Experimental

Materials.—The benzene and *cis*- and *trans*-butene-2 used were the same as those previously reported.[4] *Cis*- and *trans*- pentene-2 supplied by the Takachiho Shoji Co., which contained 3% of various pentene isomers, were purified gas chromatographically on a 30 m. column of dimethylsulfolane on celite. After the separation on this column, no impurities could be detected.

Apparatus.—The apparatus[4] was freshly reconstructed, with special attention paid to avoiding contamination by mercury. Since neither isomerization nor decomposition could be detected on prolonged irradiation in the absence of benzene, it was evident that competitive mercury photosensitization did not occur.

The pressure was measured roughly with an oil manometer (Silicone DC 704) which absorbed the reactants to some extent. More accurate values were calculated indirectly from the chromatographic peak areas of samples of the reacting mixture. The gas chromatograph was composed of two columns; one, packed with 30 to 50 mesh celite with Silicone DC 550 as the liquid phase (3 m. long; 80°C), was used for the separation of benzene and olefins, while the other, packed with 30 to 50 mesh celite with dimethylsulfolane (20 m. long; room temperature), was used for the separation of the *cis* and *trans* isomers.

The vacuum was checked with a Pirani gauge (supplied by The Japan Vacuum Engineering Co.), its filament being always kept below 200°C in order to avoid thermal reactions. The cylindrical quartz reaction vessel was 5 cm. in diameter and of nearly the same length. Metal valves were used in a few required places to prevent the reactants from being absorbed in the stopcock grease. The vessel was illuminated with a low-pressure mercury arc through a UV 25 filter (supplied by the Toshiba Denki Co.) which cut off the light of wavelengths shorter than 2000 Å. In order to determine the incident light intensity (I_0), the previously-described mercury-photosensitized decomposition of ethylene was employed.[7,8] The fraction of the light transmitted (I_t/I_0) at various benzene pressures (p) was found to be given by the empirical expression:

$$\log_{10}(I_0/I_t) = 0.0245\,p - 0.00014\,p^2$$

where I_t is the intensity of the transmitted light. The incident intensity, I_0, was occasionally redetermined

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[1] R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

[2] R. B. Cundall, F. J. Fletcher and D. G. Milne, ibid., **60**, 1146 (1964).

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

[4] M. Tanaka, T. Terao and S. Sato, This Bulletin, **38**, 1645 (1965).

[5] P. Sigal, *J. Chem. Phys.*, **42**, 1953 (1965).

[6] G. B. Kistiakowsky and C. S. Parmenter, ibid., **42**, 2942 (1965).

[7] D. J. LeRoy and E. W. R. Steacie, ibid., **9**, 829 (1941).

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

TABLE I. ISOMERIZATION RATES AT VARIOUS PRESSURES OF OLEFINS
(Benzene pressure: 47.0 mmHg. Light intensity has not been measured.)

Starting compound *cis*-Butene-2		*trans*-Butene-2		*cis*-Pentene-2		*trans*-Pentene-2	
P	R_{isom}	P	R_{isom}	P	R_{isom}	P	R_{isom}
1.6	0.43	1.6	0.36	2.0	0.44	1.6	0.37
2.1	0.41	1.9	0.44	2.3	0.49	1.9	0.35
2.3	0.50	2.4	0.48	3.1	0.48	2.4	0.38
3.1	0.45	3.2	0.37	4.7	0.47	3.1	0.47
4.7	0.39	4.7	0.38	7.8	0.43	4.7	0.40
7.8	0.51	7.9	0.34	15.8	0.47	7.8	0.44
15.7	0.51	15.7	0.39	31.2	0.50	15.7	0.40
31.3	0.49	31.2	0.51	62.4	0.48	31.2	0.47
62.4	0.48						
Ave.	0.46	Ave.	0.41	Ave.	0.47	Ave.	0.41

P=mmHg $R_{\text{isom}}=\mu$ mol./min.

in order to check the stability of the low-pressure mercury arc.

Results

As expected, the behavior of pentene-2 was found to be very similar to that of butene-2. Table I summarizes the initial rates of isomerization at a constant benzene pressure and at varying olefin pressures. The conversion was always kept below 5%. There is a tendency for the rate to increase slightly with an increase in the pressure. Another trend observed is that *R(cis→trans)*, the rate of isomerization from *cis* to *trans*, seems to be slightly larger than *R*(*trans*→*cis*) in both olefins. The ratio is $1.1_5 \pm 0.1_5$.

TABLE II. EFFECT OF BENZENE PRESSURE ON THE ISOMERIZATION RATE
(Olefin pressure: 7.8 mmHg, $I_0=2.6\times10^{-6}$ Einstein/min.)

Benzene pressure mmHg	I_a/I_0	R_{isom} μ mol./min.	Quantum yield
		cis-Butene-2	
2.0	0.097	0.07	0.28
3.9	0.191	0.12	0.24
7.1	0.298	0.23	0.30
7.1	0.298	0.22	0.29
11.7	0.467	0.28	0.23
15.0	0.541	0.35	0.25
24.6	0.698	0.41	0.23
31.3	0.776	0.53	0.26
40.5	0.831	0.55	0.25
			Ave. 0.26
		cis-Pentene-2	
2.0	0.097	0.10	(0.40)*
3.7	0.182	0.21	(0.45)*
7.6	0.338	0.24	0.27
11.9	0.469	0.34	0.28
15.5	0.552	0.48	0.33
15.7	0.554	0.44	0.31
19.0	0.616	0.36	0.23
23.4	0.681	0.43	0.24
24.2	0.692	0.48	0.27
31.5	0.722	0.57	0.30
39.0	0.823	0.59	0.28
			Ave. 0.28

* The values in parentheses are not used for averaging.

The effect of the variation in benzene pressure on the isomerization has also been examined, using the *cis* isomers of the two olefins as the starting compounds. The results are shown in Table II. Here I_a/I_0 is the ratio of the absorbed light intensity to the incident light intensity as calculated from the empirical relation quoted in the preceding section. The data are consistent with those of the previous paper.

Figure. 1 shows the time dependence of the *cis-trans* ratio, with olefin and benzene pressures of 3.9 and 39 mmHg respectively. It is evident that butene-2 and pentene-2 behave very similarly, except that the photostationary ratios differ. Table III summarizes the photostationary ratios.

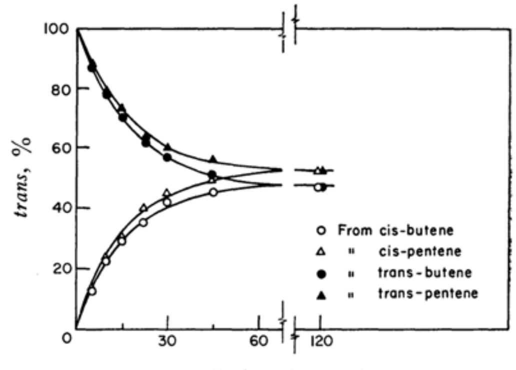

Fig. 1. The time dependence of the *cis-trans* ratio.
Olefin pressure: 3.9 mmHg, Benzene pressure: 39 mmHg.

TABLE III. PHOTOSTATIONARY *cis-trans* RATIOS AT VARIOUS PRESSURES

Benzene pressure mmHg	Olefin pressure mmHg	Stationary ratio (*trans* %)* Butene-2	Pentene-2
39.2	0.20	47	58
39.2	0.39	50	52
39.2	0.78	50	53 (53)
39.2	3.92	48 (48)	52 (53)
39.2	7.83	48	53 (52)
7.8	1.57	(48)	(53)

* The values were obtained with the *cis* isomer as the starting compound, except for the values in parentheses, which were obtained with the *trans* isomer as the starting compound.

thus obtained at various pressures of benzene and olefins. In the case of butene-2, the *cis* compound is favored, while in the case of pentene-2 the reverse is true, although the difference is not very pronounced.

Discussion

As may be seen in Table I, all the isomerization rates are nearly the same, irrespective of the pressure of the olefins, if the benzene pressure is kept constant. In other words, the fractions of the excited benzene molecules which sensitize the isomerization are almost constant over the pressure range investigated. At considerably lower pressures, however, the isomerization rate has been observed to decrease.[5]

As a basis for discussion, we will employ the same reaction mechanism as that assumed in a previous paper.[4]

$$\mathrm{B} + h\nu \rightarrow {}^1\mathrm{B}_n \qquad (1)$$

$${}^1\mathrm{B}_n + \mathrm{M} \rightarrow {}^1\mathrm{B}_0 \qquad (2)$$

$${}^1\mathrm{B}_0 \begin{array}{l} \nearrow \mathrm{B} + h\nu \qquad (3) \\ \searrow {}^3\mathrm{B}_n \qquad (4) \end{array}$$

$${}^1\mathrm{B}_0 + \mathrm{B} \rightarrow \mathrm{B} + \mathrm{B} \qquad (5)$$

$${}^3\mathrm{B}_n + \mathrm{M} \rightarrow {}^3\mathrm{B}_0 + \mathrm{M} \qquad (6)$$

$${}^3\mathrm{B}_0 \rightarrow \mathrm{B} \qquad (7)$$

$${}^3\mathrm{B}_0 + \mathrm{B} \rightarrow \mathrm{B} + \mathrm{B} \qquad (8)$$

$${}^1\mathrm{B}_0 + \mathrm{C} \rightarrow \mathrm{B} + {}^1\mathrm{A} \qquad (9)$$

$${}^3\mathrm{B}_0 + \mathrm{C} \rightarrow \mathrm{B} + {}^3\mathrm{A} \qquad (10)$$

$${}^1\mathrm{A} \begin{array}{l} \overset{1-\alpha}{\nearrow} \mathrm{C} \\ \underset{\alpha}{\searrow} \mathrm{T} \end{array} \qquad (11)$$

$${}^3\mathrm{A} \begin{array}{l} \overset{1-\beta}{\nearrow} \mathrm{C} \\ \underset{\beta}{\searrow} \mathrm{T} \end{array} \qquad (12)$$

where B, C and T refer to benzene, *cis* and *trans*-olefins respectively, and where A refers to the excited olefin.

In this paper, we are concerned only with the *cis-trans* isomerizations. These reactions are believed to occur through the triplet-triplet[2,9] energy transfer, at least in the pressure range investigated.*1 Consequently, we will neglect reactions 9 and 11 in the following discussion.

A steady-state treatment gives the following relation:[4]

$$\frac{\beta I_a}{R_{\mathrm{isom}}} = \frac{k_3+k_4+k_5[\mathrm{B}]}{k_4}\,\frac{k_7+k_8[\mathrm{B}]+k_{10}[\mathrm{C}]}{k_{10}[\mathrm{C}]} \qquad \mathrm{(I)}$$

Equation I indicates that a plot of the reciprocal of the isomerization rate, R_{isom}, against that of the olefin pressure should give a straight line when the pressure of benzene is kept constant. These plots are shown in Fig. 2. The ratio of slope to intercept in Fig. 2 should give $(k_7+k_8[\mathrm{B}])/k_{10}$, which is calculated to be 0.3±0.1 mmHg^{-1} irrespective of the olefin used.*2 Therefore, with more than 3 mmHg of the olefin and at benzene pressures below 50 mmHg, more than 90% of the triplet-excited benzene is utilized for the *cis-trans* isomerization.

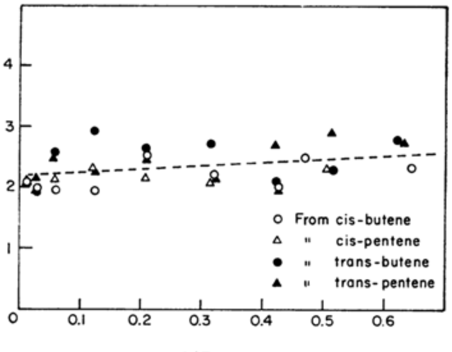

Fig. 2. The relationship between the reciprocals of the isomerization rate and of olefin pressure.

The quantum yields of isomerization are also shown in Table II. The values range from 0.25 to 0.30, again irrespective of the olefin used. Cundall et al. give 0.36±0.02 for this value with butene-2.[2]

In order to discuss the photostationary ratio, it is necessary to consider also the reverse reactions:

$${}^1\mathrm{B}_0 + \mathrm{T} \rightarrow \mathrm{B} + {}^1\mathrm{A} \qquad (13)$$

$${}^3\mathrm{B}_0 + \mathrm{T} \rightarrow \mathrm{B} + {}^3\mathrm{A} \qquad (14)$$

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

*1 The absence of products of decomposition and the pressure independence of the isomerization rates shown in Table I also support this assumption.

*2 If $k_7 \ll k_8[\mathrm{B}]$, the value of k_{10}/k_8 can be calculated for the two olefins. The value thus calculated, $(1.5\pm 0.2)\times 10^2$, is about 10 times larger than that obtained in a previous paper.[4] The reason for this discrepancy is not certain, but it could be due to the very small magnitude of the slope of the plot in Fig. 2.

Here, however, reaction 13 can be disregarded for the same reason for which reactions 9 and 11 were previously neglected. From the proposed mechanism, the following relation is, then, readily obtained:

$$\frac{[\mathrm{C}]_\infty}{[\mathrm{T}]_\infty} = \frac{(1-\beta)k_{14}}{\beta k_{10}} \tag{II}$$

where $[\mathrm{C}]_\infty/[\mathrm{T}]_\infty$ is the photostationary ratio of *cis* to *trans*. The observed values are $1.0_5 \pm 0.1$ for butene-2 and $0.9_5 \pm 0.1$ for pentene-2. On the other hand, in view of Eq. I, the ratio of the initial rates of isomerization at identical benzene pressures is:

$$\frac{R(trans \rightarrow cis)}{R(cis \rightarrow trans)} = \frac{(k_7+k_8[\mathrm{B}])/k_{10}[\mathrm{C}]+1}{(k_7+k_8[\mathrm{B}])/k_{14}[\mathrm{T}]+1}\,\frac{1-\beta}{\beta} \simeq \frac{1-\beta}{\beta} \tag{III}$$

The experimental values are $1.1_5 \pm 0.1_5$, irrespective of the olefin used. Cundall et al. reported 1.37 ± 0.01 for both the photostationary ratio and the ratio of the initial rates of isomerization with butene-2. This would require that k_{10} be exactly equal to k_{14}. In the mercury photosensitization, quenching cross-sections of *cis*- and *trans*-butene-2 have indeed been found to be the same within the limits of experimental error.[10] Although the reason for the discrepancy in the value of the photostationary ratios as found by Cundall et al. and by us remains unknown, it seems worth mentioning that the photostationary ratio is not necessarily equal to the ratio of the initial rates of isomerization, since k_{10} need not necessarily be equal to k_{14}.

Recently, Noyes has pointed out[11] that the quantum yields of fluorescence and intersystem crossing from $^1\mathrm{B}_{1u}$ to $^3\mathrm{B}_{1u}$ in benzene strongly depend on the wavelength of the irradiating light in the region from 2400 to 2600 Å. This presents another potential complication in the investigated reaction.

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[10] S. Tsunashima and S. Sato, to be published.

[11] W. A. Noyes, Jr., W. A. Mulac and D. A. Harter, *J. Chem. Phys.*, **44**, 2100 (1966).