BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1531—1533 (1969)

The Reactions of a Mixture of Benzene and *cis*-2-Butene Photosensitized by Cadmium

Shigeru TSUNASHIMA, Shin SATOH and Shin SATO

Department of Applied Physics, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received November 15, 1968)

Using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene, the lifetime of triplet benzene has been estimated to be of the order of 10^{-5} sec for both benzene-d_0 and -d_6. This technique provides a new method for measuring the lifetime of the triplet state of some molecules.

Recently, the efficiencies of hydrocarbons in quenching the triplet cadmium have been measured using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene.[1] In the cases examined previously, the activated quencher molecule formed in quenching triplet cadmium atoms did not cause the isomerization of 2-butene.[1] In the case of benzene, however, the molecule thus activated is thought to cause the isomerization, because the isomerization of 2-butene occurs effectively by means of triplet benzene.[2,3] Namely, a two-step energy-transfer-process such as cadmium→benzene →2-butene may be involved in the reactions of a mixture of benzene and 2-butene photosensitized by triplet cadmium. If this energy-transfer-process is indeed involved, it may be possible to estimate the lifetime of triplet benzene.

The lifetime of triplet benzene has already been estimated in the benzene-photosensitized *cis-trans* isomerization of 2-butene[3] and in the benzene-photosensitized phosphorescence of biacetyl.[4] In these cases, however, such complications arise as the estimation of the rate of the intersystem crossing.

With this prospect in mind, a study of the reactions of a mixture of benzene and *cis*-2-butene photosensitized by triplet cadmium was undertaken.

Experimental

Research-grade *cis*-2-butene supplied by the Takachiho Trading Co. was used after bulb-to-bulb distillation. The gas-chromatographic analysis showed that the impurities were less than 0.5%. Spectorgrade benzene supplied by the Wako Chemical Co. was used after recrystallization and bulb-to-bulb distillation. The mass-spectrometric analysis of benzene-d_6 supplied by the Merck Co. showed that the isotopic impurities were less than 2%.

The light source and the apparatus were similar to those reported on in a previous paper.[5]

A mixture of benzene and *cis*-2-butene was irradiated at 270±1°C in the presence of cadmium vapor with a cadmium lamp through a Toshiba UV-29 filter which cut off all wavelengths below 2700Å. After being separated from benzene with a cold trap at −80°C, the 2-butenes were analysed by gas chromatography using a column packed with dimethylsulforane on celite (30 m long) supplied by the Shimadzu Co.

Immediately after each run, the light intensity of the resonance line at 3261 Å was measured using the cadmium-photosensitized *cis-trans* isomerization of *cis*-2-butene assuming the quantum yield to be 0.5.[5] The initial rate of the isomerization (R) was calculated using Eq. (I):

$$R = (([C]+[T])/2t)\ln(([C]+[T])/([C]-[T])) \qquad (I)$$

Here, t represents the reaction time. [C] and [T] are the amounts of *cis* and *trans*-2-butenes respectively obtained after the irradiation.[1]

Results

The rate of the *cis-trans* isomerization of 2-butene was measured at 270±1°C as a function of the benzene pressure (at constant butene pressures) and also of the butene pressure (at a constant benzene pressure and a constant pressure ratio of benzene to 2-butene).

Figure 1 shows the plots of R/R_0 as a function of the benzene pressure at 5.1 mmHg, 14.7 mmHg, and 22.2 mmHg of *cis*-2-butene. Here, R and R_0 are the rates of the isomerization of *cis*-2-butene in the presence and in the absence of benzene respectively. The rate of the isomerization decreased

---

[1] S. Tsunashima and S. Sato, This Bulletin, **40**, 2987 (1967); S. Tsunashima, S. Satoh and S. Sato, *ibid.*, **42**, 329 (1969).

[2] S. Sato, K. Kikuchi and M. Tanaka, *J. Chem. Phys.*, **39**, 239 (1963); M. Tanaka, T. Terao and S. Sato, This Bulletin, **38**, 1645 (1965); M. Tanaka, M. Kato and S. Sato, *ibid.*, **39**, 1423 (1966).

[3] R. B. Cundall, F. J. Fletcher and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1149 (1964); R. B. Cundall and A. S. Davis, *ibid.*, **62**, 1151 (1966).

[4] C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, **46**, 1423 (1967).

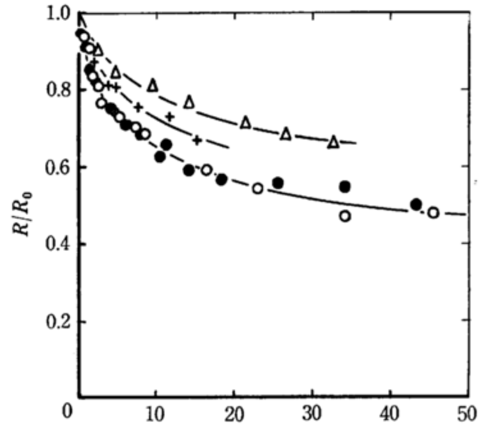

Fig. 1. The ratio of R/R_0 as a function of the benzene pressure at constant 2-butene pressures; 5.1 mmHg (○), 14.7 mmHg (+), and 22.2 mmHg (△) for for benzene-d_0; 5.1 mmHg (●) for benzene-d_6.

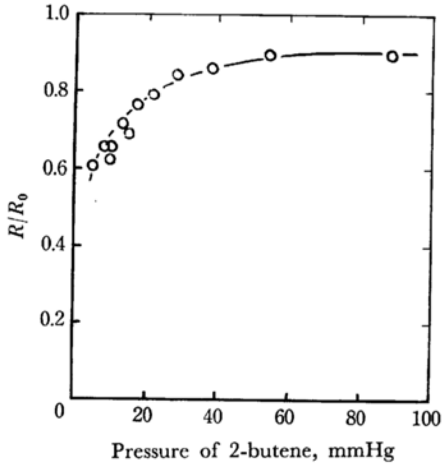

Fig. 2. The ratio of R/R_0 as a function of the 2-butene pressure at 10.9 mmHg of benzene-d_0.

with an increase in the benzene pressure. The effect of benzene-d_6 on the rate of the isomerization was almost the same as that of benzene-d_0; *i. e.*, there was no hydrogen-deuterium isotope effect on the rate of isomerization.

Figure 2 shows the plots of R/R_0 as a function of the 2-butene pressure at 10.9 mmHg of benzene. The rate of the isomerization increased with an increase in the butene pressure.

As is shown in Fig. 3, the R/R_0 values obtained with equal pressures of benzene and 2-butene increased with an increase in the total pressure. This clearly indicates that an energy transfer process such as cadmium→benzene→2-butene is involved in the mechanism.

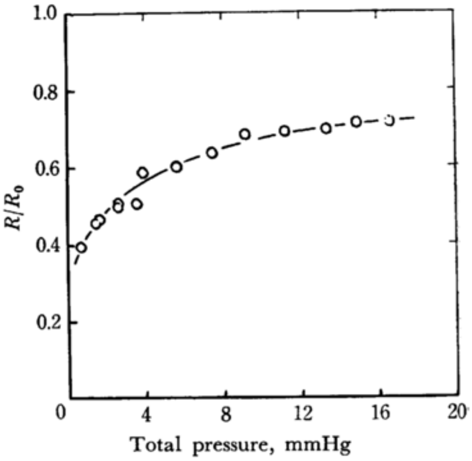

Fig. 3. The ratio of R/R_0 as a function of the total pressure at equal pressures of benzene-d_0 and 2-butene.

Discussion

If a benzene molecule quenches only the triplet cadmium atom and does not cause the *cis-trans* isomerization of 2-butene, a linear relationship should be obtained between R/R_0 and the pressure ratio, [benzene]/[2-butene].[1] As is shown in Fig. 4, this is not the case with benzene-2-butene mixtures. If an activated benzene molecule formed in quenching triplet cadmium can always cause the *cis-trans* isomerization without following the other reaction paths, the rate of the isomerization should not be affected by the pressure of benzene or 2-butene. However, the ratio R/R_0 is affected by the pressure change in both benzene and 2-butene. These facts indicate that only a part of the activated benzene formed in quenching triplet cadmium

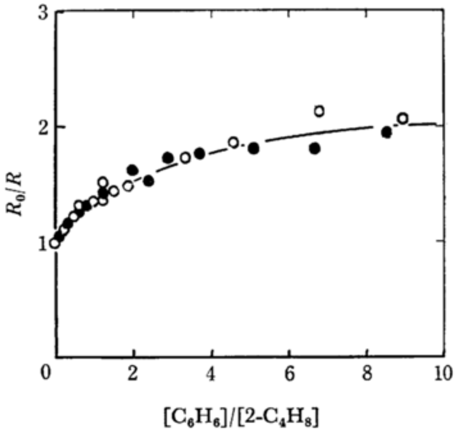

Fig. 4. The ratio of R_0/R as a function of the ratio of the pressure of benzene to that of 2-butene. ○: benzene-d_0; ●: benzene-d_6.

---

5) S. Tsunashima and S. Sato, This Bulletin, **41**, 284 (1968).

gives rise to the isomerization of 2-butene.

To explain these results, the following mechanism may be suggested:

$$\mathrm{Cd} + h\nu \rightarrow \mathrm{Cd}^*$$

$$\mathrm{Cd}^* + 2\text{-}\mathrm{C_4H_8} \rightarrow \mathrm{Cd} + 2\text{-}\mathrm{C_4H_8}^* \tag{1}$$

$$2\text{-}\mathrm{C_4H_8}^* + \mathrm{M} \rightarrow \tfrac{1}{2}cis + \tfrac{1}{2}trans + \mathrm{M} \tag{2}$$

$$\mathrm{Cd}^* + \mathrm{C_6H_6} \rightarrow \mathrm{Cd} + \alpha\mathrm{C_6H_6}^* + (1-\alpha)\mathrm{C_6H_6}' \tag{3}$$

$$\mathrm{C_6H_6}^* \rightarrow \mathrm{C_6H_6} \tag{4}$$

$$\mathrm{C_6H_6}^* + \mathrm{C_6H_6} \rightarrow 2\mathrm{C_6H_6} \tag{5}$$

$$\mathrm{C_6H_6}^* + 2\text{-}\mathrm{C_4H_8} \rightarrow \mathrm{C_6H_6} + 2\text{-}\mathrm{C_4H_8}^* \tag{6}$$

$$\mathrm{C_6H_6}' + \mathrm{M} \rightarrow \mathrm{C_6H_6} + \mathrm{M} \tag{7}$$

where Cd* and 2-C_4H_8* are, respectively, a triplet cadmium atom and a triplet 2-butene molecule which isomerizes to *cis*- or *trans*-2-butene with an equal probability by collisional deactivation.5) C_6H_6* may be a triplet benzene molecule in the state of $^3B_{1u}$, because its excitation energy is close to that of triplet cadmium. C_6H_6' denotes an activated quencher molecule which can not cause the isomerization of 2-butene and which is probably the vibrationally-excited ground state of benzene. α is the fraction of C_6H_6* formed by the reaction (3).

The steady-state treatment of the above mechanism gives the following equation:

$$(1-\beta)/(R/R_0-\beta) = 1/\alpha(1+k_4/k_6[\mathrm{C_4H_8}] + (k_5/k_6)([\mathrm{C_6H_6}]/[\mathrm{C_4H_8}])) \tag{II}$$

where

$$1/\beta = 1 + (k_3/k_1)([\mathrm{C_6H_6}]/[\mathrm{C_4H_8}])$$

The left-hand side of Eq. (II) involves k_3/k_1, which is the relative efficiency of benzene against 2-butene in quenching triplet cadmium.

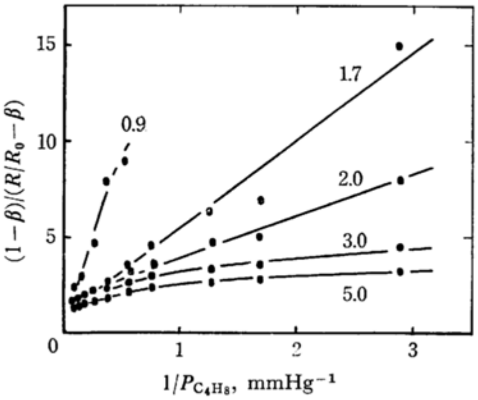

Fig. 5. The plots of Eq. (II) at various values of k_3/k_1 as a function of the reciprocal of the 2-butene pressure.

Using the data obtained with a constant pressure ratio, the left-hand side of Eq. (II) is in Fig. 5 plotted against the reciprocal of the 2-butene pressure, assuming various values for k_3/k_1. As the figure shows, the relation in Eq. (II) holds when the value of k_3/k_1 is assumed to be in the range of 2.5—1.5. This value is slightly larger than that calculated from the quenching cross-section of benzene obtained by Steacie and LeRoy by a physical method.6) The value also is a little larger than those of olefins.1) This is not unreasonable because benzene has six π-electrons and the excitation energy of triplet benzene is close to that of triplet cadmium.

Using the data obtained at a constant benzene pressure (Fig. 2), the α ratios are estimated to be 0.77 ± 0.18 (2.5), 0.71 ± 0.20 (2.0), and 0.66 ± 0.23 (1.67), where the values in parentheses indicate the assumed values of k_3/k_1. That is, triplet benzene is about 70% formed through the reaction (3), although the ratio depends slightly on the estimation of k_3/k_1.

The rate constant ratios of k_5/k_6 and k_4/k_6 are estimated to be 0.05 and in the order of 10^{-4} mol/*l* using Eq. (II). k_5/k_6, which is the ratio of the rate constant of the self-quenching of triplet benzene against that of the energy-transfer process to 2-butene, is very small. This is consistent with the results obtained in the benzene-photosensitization of 2-butene.2)

The lifetime of triplet benzene ($1/k_4$) is estimated to be in the order of 10^{-5} sec assuming the value of k_6 to be 10^9 *l*/mol sec (*cf.* 0.96×10^9 *l*/mol sec4) and 2.0×10^9 *l*/mol sec3,7)). The value of the lifetime is correct, however, in terms of the order because of a large experimental error and because of the uncertainty of the values used for the calculations, such as k_3/k_1, α, and k_6. In the benzene-photosensitization, the lifetime of triplet benzene has been estimated to be 12 μsec3) and 26 μsec4) at room temperature. In spite of a higher temperature and a different source of triplet benzene, the lifetime estimated here agrees well with the literature values.3,4)

In conclusion, it may be said that the lifetime of the triplet state of some molecules can be estimated using the cadmium-photosensitized *cis-trans* isomerization of 2-butene, although this method contains a few parameters.

---

6) E. W. R. Steacie and D. J. LeRoy, *J. Chem. Phys.*, **11**, 164 (1943).

7) A. Morikawa and R. J. Cvetanović, *Can. J. Chem.*, **46**, 1813 (1968).