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The Photolysis of *cis*-2-Butene and Its Implications for Radiation Chemistry

By Yoshihiko HATANO and Shoji SHIDA

Laboratory of Physical Chemistry, Tokyo Institute of Technology, Ookayama, Tokyo

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The direct photolysis at 1849 Å and the mercury-photosensitized reaction at 2537 Å of *cis*-2-butene have been studied in the gas phase at room temperature. It may be considered that the excited singlet state of *cis*-2-butene is formed in the former, and that the excited triplet state of *cis*-2-butene is formed in the latter. *trans*-2-Butene is predominantly produced in the latter, while the decomposition products (e. g., hydrogen, methane, ethane, ethylene, propylene, etc.) predominate in the former. The rates of the formation of all the products are pressure-independent in the former, while in the latter those of all products except *trans*-2-butene decrease rapidly with an increase in the initial pressure. The rate of *trans*-2-butene formation in the latter, however, increases gradually with an increase in the initial pressure until it becomes constant above 100 mmHg. By comparing the pressure-dependence and the product-distribution of these two reactions with the results of the radiolysis of liquid *cis*-2-butene, one may conclude that the excited triplet state of *cis*-2-butene contributes chiefly to the formation of *trans*-2-butene in the radiolysis, while the excited singlet state of *cis*-2-butene contributes chiefly to the decomposition products.

There are two ways in which excited molecules can be formed by ionizing radiation. One is from the neutralization of a positive ion by an electron or by a negative ion; the other is the direct excitation by the high-energy radiation itself. It is generally considered that these excited states consist of high levels of the different state manifolds. However, little attention has been paid to the nature of these states.

In a previous paper(1) on the radiolysis of liquid *cis*-2-butene, it was considered that *trans*-2-butene, which may be produced for the most part through the molecular mechanism, is formed not through the excited singlet state but through the excited triplet state. Moreover, on the basis of this inference, the effects of added aromatic hydrocarbons(1) and nitrous oxide(2),* on the radiolysis could be explained consistently.

The present investigation was undertaken in

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1) Y. Hatano, S. Shida and S. Sato, This Bulletin, **37**, 1854 (1964).

2) Y. Hatano and S. Shida, The 18th Annual Meeting of the Chemical Society of Japan, Osaka, 1965.

* Nitrous oxide has been considered as an effective electron scavenger: $N_2O + e \rightarrow N_2 + O^-$. The addition of nitrous oxide to liquid *cis*-2-butene has the same effect on the formation of *trans*-2-butene as in the case of benzene as an additive.(1)

an attempt to confirm the above inference experimentally. The excited singlet and triplet states of gaseous *cis*-2-butene were formed photochemically. The former was formed by the direct photo-excitation at 1849 Å, while the latter was formed by the mercury-photosensitization at 2537 Å.

Gary and Pickett[3] investigated the ultraviolet absorption of *cis*-2-butene and reported that *cis*-2-butene has a maximum absorption in the region near 1849 Å. The energy level of the first excited singlet state of *cis*-2-butene has been estimated[4,5] to be a little lower than that of $Hg6^1P_1$, 6.7 eV., corresponding to 1849 Å. Therefore, the excited singlet state of *cis*-2-butene may be formed by the direct photo-excitation at 1849 Å. There has been, to the authors' knowledge, no report dealing with the direct photolysis of *cis*-2-butene.

On the other hand, many works have been done on the mercury-photosensitized reaction of olefins.[6] It is generally considered that olefins are excited by the collision between olefin molecules and excited mercury atoms, $Hg6^3P_1$, formed by the irradiation of light at 2537 Å. These excited olefin molecules return to the ground states through decomposition or collisional deactivation. On the basis of the results of the benzene-photosensitized reaction of *cis*-2-butene[7-9] and other evidence,[4,5] the energy level of the first excited triplet state of *cis*-2-butene is estimated to be about 4 eV. which is lower than that of $Hg6^3P_1$, 4.8 eV. Therefore, the excited triplet state of *cis*-2-butene may be formed by the mercury-photosensitization at 2537 Å. The mercury-photosensitized reaction of 2-butenes, especially the cis-trans isomerization, has been reported by Cundall et al.[10] According to them, the overall reaction can be explained in terms of the formation of the vibrationally-excited triplet state of 2-butene.

In this paper, experiments on the direct photolysis and the mercury-photosensitized reaction of *cis*-2-butene were undertaken in order to get some information about the role of lower excited singlet and triplet states in the radiolysis of *cis*-2-butene.

Experimental

Materials.—Matheson research-grade *cis*-2-butene was used after the usual degassing and bulb-to-bulb distillations. It was found by gas chromatography to contain less than 0.4% *trans*-2-butene.

In the experiments on the direct photolysis of gaseous *cis*-2-butene, it was prepared using the mercury-free vacuum line and was purified using gold-foil in a cold trap.

Irradiation.—In the experiments on the direct photolysis at 1849 Å, an ordinary mercury resonance lamp was used as the light source. A cylindrical quartz cell, 50 mm. in diameter and 20 mm. thick, was connected to a mercury-free vacuum line. Moreover, the absence of mercury in the system was confirmed by making sure that the reaction did not take place at all when *cis*-2-butene was irradiated for 30 min. with the light source of 2537 Å.

In the experiments on the mercury-photosensitized reaction at 2537 Å, the light source and the reaction cell were the same as those used in the experiments on the direct photolysis. A droplet of mercury in the reaction cell provided a constant pressure of mercury vapor. The light shorter than 2100 Å was cut off with a filter.

All runs were made statically at room temperature, 25 ± 3°C.

Analysis.—The analytical procedures were almost the same as in the radiolysis.[1]

After irradiation the gases noncondensable at -196°C (hydrogen and methane) were collected and measured by an analysis device composed of a Toepler pump, a McLeod gauge, and a copper oxide furnace. Products condensable at -196°C were analyzed by a home-made reduced-pressure-type gas chromatograph. A benzyl ether column was used mainly at room temperature, for the separation of C_1—C_4 hydrocarbons.

Results and Discussion

Table I shows the amounts of the major products of the direct photolysis of gaseous *cis*-2-butene at 1849 Å, the mercury-photosensitized decomposition of gaseous *cis*-2-butene at 2537 Å, and the γ-radiolysis[1] of liquid *cis*-2-butene. A marked difference between the relative rates of formation for

TABLE I. PRODUCTS FROM THE DIRECT PHOTOLYSIS OF GASEOUS *cis*-2-BUTENE AT 1849 Å AND THE MERCURY-PHOTOSENSITIZED REACTION OF GASEOUS *cis*-2-BUTENE AT 2537 Å AND THE γ-RADIOLYSIS OF LIQUID *cis*-2-BUTENE

	Direct photolysis[a] 10^{-7} mol./min.	Mercury-photosensitized reaction[b] 10^{-7} mol./min.	γ-Radiolysis[c] molec./100 eV.
H_2	1.73	0.00	1.02
CH_4	0.97	0.00	0.21
$C_2H_6+C_2H_4$	1.03	0.00	0.11
C_2H_2	0.33	0.00	0.11
C_3H_6	1.03	0.02	0.13
n-C_4H_{10}	0.40	0.10	0.83
1-C_4H_8	1.47	0.06	0.40
trans-2-C_4H_8	0.50	10.8	2.29

a) The irradiation time: 3 min.
The initial pressure of *cis*-2-butene: 120 mmHg.
b) The irradiation time: 5 min.
The initial pressure of *cis*-2-butene: 100 mmHg.
c) The dose rate: 2.21×10^{19} eV./g. hr.
The total dose: $(0.30-3.59)\times10^{21}$ eV./g.

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3) J. T. Gary and L. W. Pickett, *J. Chem. Phys.*, **22**, 599 (1954).

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

5) J. R. Platt, *J. Chem. Phys.*, **18**, 1168, (1950).

6) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Pub. Co., New York (1954).

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

8) R. B. Cundall, F. J. Fletcher and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).

9) P. Siegel, *J. Chem. Phys.*, **42**, 1953 (1965).

10) R. B. Cundall and T. F. Pamler, *Trans. Faraday. Soc.*, **56**, 1211 (1960).

these reactions may be noted. In the mercury-photosensitized decomposition, *trans*-2-butene is a major product, but not in the direct photolysis. To compare these reactions more precisely, the dependence of the rates of formation on the irradiation time and the pressure was examined.

The amount of the major products were measured at various irradiation times in the direct photolysis. The initial pressure of *cis*-2-butene was 40 mmHg. Until 3 min. of irradiation every product increased linearly with the time, showing no measurable secondary reaction of the product at this stage of reaction, although it decreased with time after 3 min. Figure 1 shows the rates of the formation of major products at various initial pressures for the irradiation time of 3 min. It may clearly be seen that the rates of the formation of all products are practically constant at pressures between 20 and 120 mmHg. These features agree with the results of the direct photolysis of propylene,11) 1-butene12) and cyclopentene13) at 1849 Å.

The amounts of the major products were also measured at various irradiation times in the mercury-photosensitized reaction. The initial pressure of *cis*-2-butene was again 40 mmHg. Until 5 min. of irradiation every product increased linearly with the time; then it decreased with time after 5 min. Figure 2 shows the rates of the formation of major products at various initial pressures for the irradiation time of 5 min. It may clearly be seen that the rates of the formation of all products except *trans*-2-butene are strongly pressure-dependent. This is remarkably different from the results of the direct photolysis. The rates of the formation of all products except *trans*-2-butene rapidly decrease with an increase in the initial pressure. The rate of *trans*-2-butene formation, however, increases gradually with an increase in the initial pressure until it becomes constant above 100 mmHg.

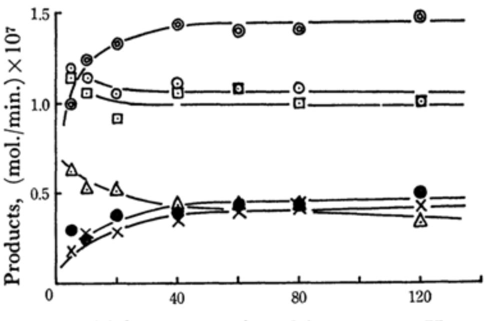

Fig. 1. Pressure-dependence of the formation of major products in the direct photolysis of *cis*-2-butene at 1849 Å

—◎— 1-C_4H_8 —⊙— $C_2H_4+C_2H_6$
—⊡— C_3H_6 —●— *trans*-2-C_4H_8
—×— *n*-C_4H_{10} —△— C_2H_2

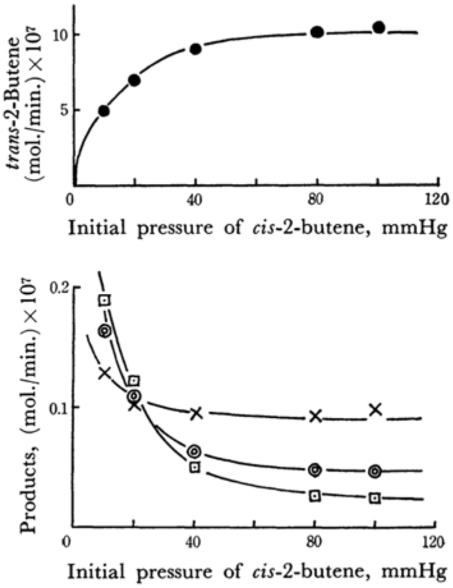

Fig. 2. Pressure-dependence of the formation of *trans*-2-butene and other products in the mercury-photosensitized reaction of *cis*-2-butene at 2537 Å.

—×— *n*-C_4H_{10} —◎— 1-C_4H_8
—⊡— C_3H_6 —●— *trans*-2-C_4H_8

On the basis of these data, it seems reasonable to assume that the excited triplet state of *cis*-2-butene is more readily deactivated than the excited singlet state of *cis*-2-butene. In other words, the life-time of the latter is shorter than that of the former, and the latter decomposes with a larger probability before the collisional deactivation. The ratio of the cis-trans isomerization to the decomposition is 60 at the pressure of 100 mmHg in the mercury-photosensitized reaction, while it is 0.07 at the pressure of 120 mmHg in the direct photolysis. Thus, the excited triplet state may contribute much more effectively to the formation of *trans*-2-butene than does the excited singlet state.

These results may reasonably be explained by the following mechanisms.

In the direct photolysis of gaseous *cis*-2-butene at 1849 Å, the excited singlet state of *cis*-2-butene is formed, giving chiefly such decomposition products as C_1, C_2 and C_3 hydrocarbons:

$$\text{Cis} + h\nu \rightarrow \text{Cis}^* \text{ (singlet)} \tag{1}$$

$$\text{Cis}^* \text{ (singlet)} \rightarrow \text{Decomp. products} \tag{2}$$

where Cis and Cis*(singlet) indicate the ground state and the first excited singlet state of *cis*-2-butene respectively.

In the mercury-photosensitized reaction, on the other hand, the overall reaction is explained by

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11) T. Nishikawa, S. Arai and S. Shida, to be published.
12) N. Harumiya and S. Shida, This Bulettin, **38**, 142 (1965).
13) N. Sakai and S. Shida, to be published.

the formation of a vibrationally-excited triplet state of *cis*-2-butene in a fashion similar to that described by Cundall:[10)]

$$\mathrm{Hg^1S_0 + h\nu \rightarrow Hg^3P_1} \qquad (3)$$

$$\mathrm{Hg^3P_1 \rightarrow Hg^1S_0 + h\nu} \qquad (4)$$

$$\mathrm{Hg^3P_1 + Cis \rightarrow Cis^{**}\ (triplet) + Hg^1S_0} \qquad (5)$$

$$\mathrm{Cis^{**}\ (triplet) + Cis \rightarrow Cis^{*}\ (triplet) + Cis} \qquad (6)$$

$$\begin{tikzcd} \mathrm{Cis^{*}\ (triplet)} \arrow[r] \arrow[dr] & \mathrm{Trans} & (7) \\ & \mathrm{Cis} & (8) \end{tikzcd}$$

$$\mathrm{Cis^{**}\ (triplet) \rightarrow Decomp.\ products} \qquad (9)$$

where Cis*(triplet) and Cis**(triplet) indicate the first excited triplet state and the vibrationally-excited triplet state of *cis*-2-butene respectively. The steady-state treatment leads to Eqs. I and II:

$$R_i \simeq \frac{k_7 I}{k_7 + k_8} \quad \text{at a higher pressure} \qquad \text{(I)}$$

$$R_d = \frac{k_5 k_9 I P}{(k_4 + k_5 P)(k_9 + k_6 P)} \qquad \text{(II)}$$

(P=the initial pressure of *cis*-2-butene)

where R_i and R_d indicate the rate of the formation of *trans*-2-butene and that of the decomposition products respectively. From Eq. I, it seems that the rate of the formation of *trans*-2-butene should be pressure-independent at a higher pressure. From Eq. II, it seems that the rate of the formation of decomposition products should become zero at higher pressures.

In view of the fact that the radiolysis of *cis*-2-butene mentioned above[1)] is the reaction in the liquid phase, the most reasonable conclusion to be drawn from the above discussion is that the excited triplet state of *cis*-2-butene may contribute chiefly to the formation of *trans*-2-butene in the radiolysis, while the excited singlet state of *cis*-2-butene may contribute chiefly to the decomposition products. Comparing the patterns of the distribution of decomposition products in the three reactions, one may find that the pattern of the distribution in the radiolysis is similar to that in the direct photolysis. Thus, the following mechanism may be proposed for the radiolysis of liquid *cis*-2-butene:

$$\begin{tikzcd} & \mathrm{Cis} \arrow[r] \arrow[dr] & \mathrm{Cis^+ + e} & & \\ \mathrm{Cis^+ + e} \arrow[rr] & & \mathrm{Cis'} \arrow[r] \arrow[dr] & \mathrm{Cis^*\ (singlet)} \arrow[r] & \mathrm{Decomp.\ products} \\ & & & \mathrm{Cis^*\ (triplet)} \arrow[r] \arrow[dr] & \mathrm{Trans} \\ & & & & \mathrm{Cis} \end{tikzcd}$$

where Cis′ indicates the highly-excited states of the different state manifolds. This mechanism consistently explains the results reported in the previous paper[1)] on the radiolysis of liquid *cis*-2-butene.

As was pointed out at the beginning of this paper, the excited states formed by ionizing radiation consist of high levels of the different state manifolds. From a spectrometric investigation, however, it may be considered that the excited molecules in these higher levels go down rapidly to the lower states, passing through the complex crossing of potential energy surfaces. Moreover, it may not be necessary to consider vibrationally-excited states for a reaction in the liquid phase. After all, the lowest excited states may be the most important for the chemical reaction in this system. Therefore, it seems permissible to consider the excited states formed by ionizing radiation on the basis of data about the lowest excited states formed photochemically.

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