Photolysis of Butene-1 at 1849Å

By Noriho HARUMIYA, Shoji SHIDA and Shigeyoshi ARAI

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The photolysis of gaseous olefins has been studied on ethylene[1,2] and propylene[3], but the study of the photolysis of butene-1 seems not to have been made. The mercury photosensitized decomposition of butene-1, however, has been studied by several workers. Gunning and Steacie[4] showed, from the pressure dependence of the reaction, that in the primary step an excited molecule of butene-1 is produced which either decomposes or is collisionally deactivated. Lossing et al.[5] and recently Cvetanović and Doyle[6] showed that there are two modes of primary dissociation involving the splittings of C–C and C–H bonds, the ratio being estimated to be 1.3—1.6. For the present work we have studied the photolysis of butene-1 with the light of 1849 Å and

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[1] M. C. Sauer and L. M. Dorfman, *J. Chem. Phys.*, **35**, 497 (1961).

[2] H. Okabe and J. R. McNesby, ibid., **36**, 601 (1962).

[3] Work done in this laboratory, to be published.

[4] H. E. Gunning and E. W. R. Steacie, *J. Chem. Phys.*, **14**, 581 (1946).

[5] F. P. Lossing, D. G. H. Mardsen and J. B. Farmer, *Can. J. Chem.*, **34**, 701 (1956).

[6] R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, **37**, 543 (1962).

TABLE I. RELATIVE AMOUNTS OF PRODUCTS FORMED BY PHOTOLYSIS OF BUTENE-1 AT 1849 Å, WITH REFERENCE TO $C_2H_6=10.0$

Time of irradiation: 2 min. Pressure range: 1.7—125 mmHg. The listed values are pressure-independent unless otherwise stated.

H_2	1.7	*iso*-C_5H_{12}	1.8
CH_4	0.4	3-Methylbutene-1	0.8
C_2H_6	(10.0)	2-C_5H_{10}	1.6
C_2H_2	0.5	1-C_5H_{10}	1.1(1.7 mmHg)
C_3H_8	0.6		1.0(125 mmHg)
C_3H_6	3.5(1.7 mmHg)	1,5-Hexadiene	5.8(1.7 mmHg)
	1.1(20—125 mmHg)		6.8(30—125 mmHg)
C_4H_{10}	0.3	4-Methylhexene-1	2.8
trans-C_4H_8-2	0.2	3-Methyl-1,5-hexadiene	3.1
cis-C_4H_8-2	trace	1,5-Heptadiene	
Methylcyclopropane	0.0	C_8	trace
1,3-Butadiene	0.6		

have compared the results with those obtained in the previous works on the mercury-photosensitized reaction. Only the main features of the reaction will be reported on here.

Butene-1 of a pure grade, supplied by the Takachiho-Shoji Co., was purified from mercury using gold foil and was then distilled several times in vacuo. The remaining impurities were 1,3-butadiene (0.09%) and *cis*-butene-2 (<0.05%). A quartz cell, 47 mm. in diameter and 13 mm. thick, was connected to a mercury-free vacuum line. All runs were made statically at room temperature, 22±2°C. An ordinary mercury resonance lamp was used as the light source. The absence of mercury in the system was confirmed by making runs using the light source with a filter which transmitted 2537 Å but not 1849 Å. A 20 m. DMS column was used for the gas chromatographic analysis of light hydrocarbon products (C_2—C_5) and a 10 m. DNP column for heavier ones. Hydrogen and methane were analyzed volumetrically as usual.

Some twenty products, shown in Table I, were analyzed. The amounts of major products were measured with varying irradiation times at a 20 mmHg pressure. Until 4 min. every product increased linearly with time, showing no measurable secondary reaction of the product at this stage of reaction, although the rates of the formation of some products gradually decreased with time after 4 min. The variation in the light intensity by the factor of ten had no effect on the relative amounts of products. The effect of pressure was examined in the range of 1.7 to 125 mmHg. The rates of the formation of all the products except 1,5-hexadiene and propylene were practically constant, irrespective of the pressure (Table I). This is remarkably different from the results in the photosensitized decomposition and suggests that different kinds of excited states are involved. Methylcyclopropane was not found in any appreciable amount,* and C_8 products were found only in a trace; both of these are products in the mercury photosensitization. The polymer formation was not measured, but it may be assumed to be of minor importance on the basis of several pieces of indirect evidence, such as the practical absence of C_8 products (dimer), no visible deposit on the cell wall, and the linearity of the product formation with the irradiation time. The addition of nitric oxide (0—15%) to butene-1 at 20 mm. did not change the amount of propylene, but in the low pressure region below 20 mmHg reduced it to the high pressure value, i. e., 1.1 in Table I. This result seems to indicate that a fraction of propylene is produced molecularly in the primary process.

To explain the above results we may assume the following two primary processes:

$$C_4H_8\text{-}1+h\nu\rightarrow CH_3+C_3H_5 \qquad \text{(A)}$$

$$\searrow H+CH_2=CH-CH-CH_3$$

$$\text{(or } CH_2-CH=CH-CH_3\text{)} \qquad \text{(B)}$$

The hydrogen atoms thus formed are scavenged by butene-1 to give butyl radicals, C_4H_9. Conforming to Cvetanović's procedure, we assume only the recombination reactions of the free radicals thus produced; disproportionations are assumed to be of minor importance. $CH_3+CH_3\rightarrow C_2H_6$, $CH_3+C_3H_5\rightarrow C_4H_8\text{-}1$, $CH_3+C_4H_7\rightarrow$ 2-pentene or 3-methylbutene-1, $CH_3+C_4H_9\rightarrow$ isopentane, $C_3H_5+C_3H_5\rightarrow$1,5-hexadiene, $C_3H_5+C_4H_7\rightarrow$3-methyl-1,5-hexadiene or 1,5-heptadiene, $C_3H_5+C_4H_9\rightarrow$ 4-methylhexene-1. Then,

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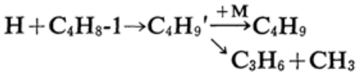
* In an experiment in which butene-1 was photolyzed by mercury photosensitization, methylcyclopropane was actually detected by gas chromatography. In this case the peak of methylcyclopropane was superposed on those of *trans*-butene-2 and isopentane using a DMS column, but it could be separated from the others using a benzylether column.

from the measured yields of products, we obtain the relative yields of radicals as follows: CH_3 39.4, C_3H_5 37.3 (mean value 38.3), C_4H_7 5.5, and C_4H_9 4.6, all with reference to $C_2H_6=$ 10.0. Judging from these results the relative importance of the two primary processes, A and B, are about 7 : 1. Thus, the C–C bond rupture is far more important in the direct photolysis at 1849 Å than in the mercury-photosensitized decomposition. A similar trend has also been found in the photolysis of propylene at 1849 Å.[3]

The formation of propylene can not be explained uniquely in the present stage of study. Possible reactions are $C_4H_8\text{-}1+h\nu\rightarrow C_3H_6+CH_2$ and, in the low pressure region:



$$\begin{array}{l} H+C_4H_8\text{-}1\rightarrow C_4H_9{}'\xrightarrow{+M}C_4H_9 \\ \qquad\qquad\qquad\qquad\quad \searrow C_3H_6+CH_3 \end{array}$$

Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo