The Photolysis of Propylene at 1849Å

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A number of studies have been made on the mercury-photosensitized reaction of olefins, but only a few on the direct photolysis.[1-4] In a previous paper[3] we reported a study on the photolysis of butene-1 by the light of 1849 Å, and compared the results with those which had been obtained in the mercury-photosensitized reaction.

The present note concerns a similar study on the photolysis of propylene at 1849 Å. As for the mercury-photosensitized reaction of propylene, it has been known that the primary step is the formation of an excited molecule, which either decomposes or collisionally deactivates,[5] and that the splitting of the C–H bond is the predominant process.[5-8]

The purest propylene commercially available (99.9%) was used after distillation; gas chromatographic analysis did not show any impurity. The absence of mercury vapor in the reacting system was confirmed experimentally.[3] The light source and the method of product analysis are similar to those in the previous work.[3] Dimethylsulfolane and squalane columns were used in gas chromatography. Some experiments were also made on the mercury-photosensitized reaction.

On irradiation the amounts of most products linearly increase initially, but gradually curve off after a few minutes. The latter fact may be ascribed to the decrease in the transparency of the quartz window due to the possible deposit of polymers. The light intensity has no appreciable effect on the relative yields of products. The rates of formation of all the products measured are practically independent of the propylene pressure over the 10—70 mmHg range, although slight, linear increases with the pressure were detected. This pressure dependence is quite different from that observed in the mercury-photosensitized reaction,

TABLE I. RELATIVE YIELDS OF THE PRODUCTS IN THE PHOTOLYSIS OF PROPYLENE AT 1849Å NORMALIZED TO $C_2H_6=1.00$

Time of irradiation, 1 min.
Pressure of propylene, 20 mmHg
Room temperature

Product	Relative yield
Hydrogen	0.76
Methane	0.67
Acetylene	1.00
Ethylene	0.93
Ethane	0.58
Propane	1.00
Allene	0.20
Methylacetylene	0.40
n-Butane	∼0
i-Butane	0.74
Butene-1	1.3
2-Methylpentane	0.73
4-Methylpentene-1	1.8
2,3-Dimethylbutane	∼0
n-Hexane	∼0

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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] N. Harumiya, S. Shida and S. Arai, This Bulletin, **38**, 142 (1965).

[4] H. Okabe, H. D. Beckey and W. Groth, private communication.

[5] A. B. Callear and R. J. Cvetanovic, *J. Chem. Phys.*, **24**, 873 (1950).

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

[7] M. Avrahmi and P. Kebarle, *J. Phys. Chem.*, **67**, 354 (1963).

[8] C. A. Heller and A. S. Gordon, *J. Chem. Phys.*, **42**, 1262 (1965).

where all the products showed marked maxima in the pressure region of 10—30 mmHg. This indicates that the life-time before the decomposition of the excited state is very short, less than 10^{-9} sec. This behavior is similar to that found in the photolysis of butene-1. Table I shows the relative yields of products, normalized to $C_2H_6=1.00$.

For simplicity the following three primary processes are assumed, although others could occur.

$$C_3H_6+h\nu \rightarrow H+C_3H_5(\text{allyl}) \tag{1}$$

$$C_3H_6+h\nu \rightarrow CH_3+C_2H_3(\text{vinyl}) \tag{2}$$

$$C_3H_6+h\nu \rightarrow CH_2+C_2H_4 \tag{3}$$

The first two have generally been used for the mercury-photosensitized reaction,[5-8] and the last one has recently been found by Okabe et al. by the field ion mass spectrometer in the photolysis at 1849 Å. All the products found can be qualitatively explained with these primary processes and the subsequent radical reactions. It is to be noted, however, that butene-1 may be formed by the following two reactions.

$$CH_3 + C_3H_5 \rightarrow C_4H_8 \tag{4}$$

$$CH_2 + C_3H_6 \rightarrow C_4H_8 \tag{5}$$

The yield of C–C bond split, 2 and 3, producing methyl and methylene may be given by $CH_4+2C_2H_6+i\text{-}C_4H_{10}+C_4H_8=3.15$. On the other hand, the yield of C–H bond split, 1, producing allyl radicals may be give by the summed yield, 4-methylpentene-1 + allene + methylacetylene + xC_4H_8 = 2.40 + xC_4H_8, where x means the unknown fraction of butene-1 formed by 4.

Apart from the details of the formation of each products, it may be seen from Table I that the C–C bond split occurs to a comparable extent as the C–H bond split. This conclusion is in contrast with the results in the mercury-photosensitized reaction. Further, the result that the C–C bond split is more favored in the direct photolysis at 1849 Å than in the sensitized reaction is in accord with that obtained in the photolysis of butene-1 in the previous work.[3]