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The Gas-Phase Radiolysis of Cyclopropane

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Cyclopropane is used as a good positive-ion scavenger in the radiolysis of hydrocarbons[1] and it can undergo an H_2 transfer reaction with a hydrocarbon positive ion.[2] On the radiolysis of cyclopropane itself, however, only a few reports have been published.[3-6] In the present study, the effects of additives, such as SF_6 and C_2H_4, on the formation of hydrogen and various hydrocarbon products in the gas-phase radiolysis of cyclopropane have been examined. The results are rather similar to those in the radiolysis of olefins, although cyclopropane apparently belongs to paraffinic hydrocarbons in chemistry. The olefinic properties of cyclopropane have also been pointed out elsewhere.[7] The effects of some paraffinic hydrocarbons added to cyclopropane have also been examined: a large increase of propane formation has been observed and ascribed to ion-molecule reaction involving H^- and H_2^- transfer processes.

Experimental

All the materials in the experiment were supplied by the Takachiho-Shoji Co. The gas-chromatographic analysis of cyclopropane using a dimethyl sulfolane column showed a purity of 99.96%. The cyclopropane contains 0.024% of propane and 0.016% of propylene. It was used after usual degassing and distillation in a vacuum line. The sulfur hexafluoride and some paraffins used as additives were of a high purity and were used without further purification. The cell for irradiation was a glass ampule with a volume of 50m*l*. The total gas pressure was 760 mmHg. The samples were irradiated by Co^{60} γ-rays at room temperature. The dose rate was 5.0×10^{19} eV/g·hr, and the total dose was 6.0×10^{20} eV/g. The quantitative analysis of hydrogen and methane was carried out by means of a Toepler pump equipped with a gas burette. Hydrocarbon products were analysed by gas chromatography using a dimethyl sulfolane column and by mass spectrometry.

Results and Discussion

Table 1 shows the *G*-values of products in the gas-phase radiolysis of cyclopropane. The relative yields of C_2 and C_3 hydrocarbon products are different from those reported by Ausloos *et al.*[6] This difference may be due to the large difference in the sample pressure in the experiments. The *G*-value of hydrogen is almost equal to that of Yang.[4] It is known in general that the *G*-values of hydrogen from paraffinic hydrocarbons in the gas-phase radiolysis are about 5—8,[8-12] while they are about 1 from olefins.[13] As is evident from Table 1, the yield of hydrogen from cyclopropane is very near to those from olefins. In the gas-phase radiolysis of paraffins, a rapid decrease in $G(H_2)$ is observed upon the addition of a small amount of an electron scavenger.[10] In this experiment, however, $G(H_2)$ from cyclopropane is scarcely suppressed at all by the addition of SF_6 as an electron scavenger, even at high concentrations, ~1 mol%. This hydrogen yield is also unaffected by the addition of C_2H_4 (~1 mol%). The experimental results described above are rather similar to those of olefins. Thus, the primary process of the hydrogen formation in the gas-phase

TABLE 1. *G*-VALUES[a] OF PRODUCTS FROM THE GAS-PHASE RADIOLYSIS OF CYCLOPROPANE

Product	*G*-value
Hydrogen	1.36
Methane	0.38
Ethylene	2.40
Propane	0.52
Propylene	0.27
Isobutane	0.03
n-Butane	0.37
Acetylene	b)
Allene	b)
trans-2-Butene or Isopentane	0.14
Methylcyclopropane	0.18
n-Pentane	0.10
Allylene	0.03
1-Pentene	0.03
2,3-Dimethylbutane or 2-Methyl pentane	0.13
3-Methylpentane	0.06
n-Hexane	0.03
C_6(others)	0.07

a) Initial values. These values were almost independent of total dose up to 1.0×10^{21} eV/g.
b) These products could not be determined quantitatively upon this column in gas chromatography.

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[1] See, for example, K.-D. Asmus, J. M. Warman, and R. H. Schuler, *J. Phys. Chem.*, **74**, 246 (1970).

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[5] H. Umezawa and F. S. Rowland, *J. Amer. Chem. Soc.*, **84**, 3077 (1962).

[6] A. A. Scala and P. Ausloos, *J. Chem. Phys.*, **49**, 2282 (1968).

[7] See, for example, L. Joris, P. von R. Schleyer, and R. Gleiter, *J. Amer. Chem. Soc.*, **90**, 327 (1968) and references cited in.

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[12] T. J. Hardwick, *J. Phys. Chem.*, **66**, 1611 (1962).

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radiolysis of cyclopropane may be interpreted, similarly to the case of olefins,[14] in terms of the following two processes: the molecular detachment of the hydrogen molecule and the hydrogen-atom abstraction of hot hydrogen atoms formed by the direct excitation which may involve superexcitation.

TABLE 2. EFFECT OF ADDITION OF HYDROCARBONS ON THE YIELDS OF PROPANE AND PROPYLENE IN THE GAS-PHASE RADIOLYSIS OF CYCLOPROPANE

n-C_6H_{14}			c-C_6H_{12}		
mol%	$G(C_3H_8)$	$G(C_3H_6)$	mol%	$G(C_3H_8)$	$G(C_3H_6)$
0	0.52	0.27	0	0.52	0.27
0.4	1.1	0.50	0.7	0.94	0.42
1.0	0.92	0.49	2.1	1.1	0.46
1.5	1.0	0.50	3.0	1.1	0.46
2.1	1.1	0.50			

The addition of small amounts of some paraffinic hydrocarbons, C_2H_6, n-C_4H_{10}, n-C_5H_{12}, n-C_6H_{14}, and c-C_6H_{12}, caused a definite increase in the propane formation; *e.g.*, in the case of n-C_6H_{14} or c-C_6H_{12}, as is shown in Table 2, the yield of propane increases by as much as that from pure cyclopropane. This increase may be interpreted neither in terms of the direct radiolysis of the additive hydrocarbons nor in terms of simple charge-transfer processes from cyclopropane to the additives. Since, as is also shown in Table 2, the increase in propylene formation due to the addition of c-C_6H_{12} is not very large, the large increase of propane can not be interpreted only by the simple free-radical mechanism, the disproportionation of propyl radicals.

The isotopic distribution of the propane produced in the radiolysis of the following two mixtures was examined; c-C_3H_6- 3 mol% c-C_6D_{12} and c-C_3H_6- 3 mol% c-C_6D_{12}- 5 mol% O_2. In each case, the formation of $C_3H_6D_2$ and C_3H_7D was observed and the quantity of C_3H_7D was more than that of $C_3H_6D_2$. The ratio of these two quantities, about 2.0, is not affected by the presence of O_2. The above results have led us to conclude that the increase in the propane formation may be interpreted in terms of the following ion-molecule reactions:

$$c\text{-}C_3H_6^+ + RH_2 \longrightarrow C_3H_8 + R^+ \tag{1}$$

$$c\text{-}C_3H_6^+ + c\text{-}C_3H_6 \longrightarrow C_3H_7^+ + C_3H_5 \tag{2}$$

$$C_3H_7^+ + RH_2 \longrightarrow C_3H_8 + RH^+ \tag{3}$$

where RH_2 is an additive hydrocarbon. Judging from the results of the isotopic experiments, the H^--transfer reaction (3) is more important for the increase of the propane formation than the H_2^--transfer reaction (1). The occurrence of reaction (2), *i.e.*, the presence of $C_3H_7^+$, was observed in the mass-spectrometric experiment on cyclopropane.[15] The H_2^--transfer to the $C_3H_6^+$ ion produced by the photoionization of propylene[16,17] or by the gas-phase radiolysis of c-C_5H_{10}[18] has already been investigated. In the case of the cyclopropane parent ion, c-$C_3H_6^+$, however, the H_2^--transfer reaction in radiolysis has not been reported in detail, although this process was suggested by Ausloos *et al.*[19] in connection with the gas-phase radiolysis of c-C_6H_{12} with c-C_3D_6 as an additive. The H_2^--transfer reaction of c-$C_3H_6^+$ in a mass spectrometer was reported by Futrell *et al.*[15]

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