BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (3), 902—907 (1979)

The Relative Rate Constants of Reactions of Oxygen Atoms with Several Olefins in Liquid Carbon Dioxide

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(Received August 19, 1978)

The relative rate constants of reactions of oxygen atoms with several olefins and 2-methylpropane have been determined in liquid carbon dioxide at −18 °C, using the γ-radiolysis of carbon dioxide in the presence of these hydrocarbons. They are : 1-butene, 1.0; *cis*-2-butene, 2.3; *trans*-2-butene, 3.0; 2-methylpropene, 2.9; 2,3-dimethyl-2-butene, 2.0; 2-methylpropane, 0.07. These relative values are very different from those obtained in the gas phase. A possible reason is discussed and a simple theoretical treatment is proposed for the competition between diffusion and reaction on the basis of the idea of a "collision set" in the liquid phase. The reaction of oxygen atoms with paraffin in liquid carbon dioxide seems to be faster than that in the gas phase. The reason is not clear at present.

The γ-radiolysis of liquid carbon dioxide is now believed to be a convenient source of oxygen atoms.[1] When an olefin is present in the γ-irradiated liquid carbon dioxide, the main products are the same compounds as those observed in the reaction of oxygen atoms with the olefin in the gas phase. By measuring the relative yields of products from a γ-irradiated liquid carbon dioxide solution in which two kinds of olefins are present, one can estimate the relative rate constants of reaction of oxygen atoms with olefins. According to Sakurai and his coworkers,[2] the relative rate constants of reaction of oxygen atoms with four olefins in liquid carbon dioxide at room temperature are 1.0 : 1.3 : 1.7 : 1.3 in the order of *cis*-2-butene, 2-methyl-2-butene, 2,3-dimethyl-2-butene, and cyclohexene. These relative values are different from those reported for the reaction of oxygen atoms in the gas phase (1.0 : 3.34 : 4.28 : 1.14).[3] This discrepancy is probably due to the fact that the diffusion process plays a role in determining the rate of reaction in the liquid phase.

The present experiment was attempted to confirm and explain this discrepancy and to gain an insight into the γ-ray-induced oxidation of olefins in liquid carbon dioxide.

Experimental

The carbon dioxide and hydrocarbons used were all purchased from the Takachiho Shoji Co. and were used after thorough degassing and distillation. No detectable impurities were observed by the gas chromatograph equipped with a 5 m dimethyl sulfolane column of 20% w/w on celite.

The sampling tube with a breakable seal attached was made of Pyrex glass, 10 mm in diameter. After a known amount of a hydrocarbon mixture had been condensed in the sampling tube at 77 K, carbon dioxide was introduced. The electron fraction of carbon dioxide in the solution was controlled at 0.98. After having been sealed, the sampling tube was transferred in a Dewar flask containing ice–sodium chloride slush at −18 °C and was shaken so as to homogenize the solute concentration in the solution.

The γ-irradiation was carried out at −18 °C at the dose rate of $1.1\times10^6\ \mathrm{R\,h^{-1}}$, usually for two hours. After irradiation, the sampling tube was immersed into a Dewar flask containing petroleum ether slush at −80 °C and then the seal was broken. It took about one hour for the vaporization of carbon dioxide. The products thus obtained were subjected to gas chromatographic analysis after a known amount of cyclohexane or ethanol was added as the standard. The column used was 2 m polyethylene glycol 1500 of 15% w/w on Uniport B and was operated at room temperature. The products were identified by the retention time of the authentic sample.

Results

In every experiment, 1-butene was used as the competitive reactant, so that the relative rate constants were obtained against the rate constant of reaction of 1-butene with oxygen atoms. Since the gas chromatographic analysis of products was not very reproducible, as can seen from the figures, the following procedure was used for the determination of the relative rate constants and of the formation ratios of products.

The competition of two olefins A and B for oxygen atoms produced in the radiolysis of carbon dioxide may be described as follows:

$$\mathrm{CO_2} \rightsquigarrow \mathrm{CO} + \mathrm{O} \tag{1}$$

$$\left.\begin{aligned} \mathrm{O} + \mathrm{A} &\xrightarrow{\alpha} \mathrm{P}_{\alpha} \\ &\xrightarrow{1-\alpha} \mathrm{P}_{1-\alpha} \end{aligned}\right\} \tag{2}$$

$$\left.\begin{aligned} \mathrm{O} + \mathrm{B} &\xrightarrow{\beta} \mathrm{Q}_{\beta} \\ &\xrightarrow{1-\beta} \mathrm{Q}_{1-\beta} \end{aligned}\right\} \tag{3}$$

Then the G-value of the P_{α} product can be expressed by this equation:

$$G(\mathrm{P}_{\alpha}) = G_0 \frac{\alpha k_{\mathrm{a}}[\mathrm{A}]}{k_{\mathrm{a}}[\mathrm{A}] + k_{\mathrm{b}}[\mathrm{B}]}. \tag{4}$$

Here, G_0 is the total G-value of products of the reaction of oxygen atoms with two olefins, A and B, and k_{a} and k_{b} are the rate constants of reaction of oxygen atoms with two olefins. If $k_{\mathrm{b}}/k_{\mathrm{a}}>1$, the plots of $G(\mathrm{P}_{\alpha})$ as a function of the mole fraction of [B] give a concave curve, while if $k_{\mathrm{b}}/k_{\mathrm{a}}<1$, a convex curve is found.

Now let us introduce a weighted mole fraction:

$$X = \frac{f[\mathrm{B}]}{[\mathrm{A}] + f[\mathrm{B}]}, \tag{5}$$

where f is a factor to be estimated. If the f factor is equal to the ratio $k_{\mathrm{b}}/k_{\mathrm{a}}$, the plots of $G(\mathrm{P}_{\alpha})$ as a

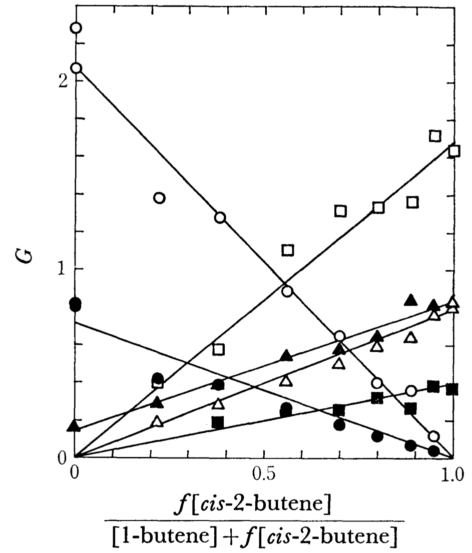

Fig. 1. The *G*-values of products from the mixture of 1-butene and *cis*-2-butene in carbon dioxide solution as a function of the weighted mole fraction of *cis*-2-butene. The value of *f* is taken as 2.3.
○ 1-Butene oxide; ● butanal; □ *cis*-2-butene oxide; △ *trans*-2-butene oxide; ■ 2-methylpropanal; ▲ 2-butanone.

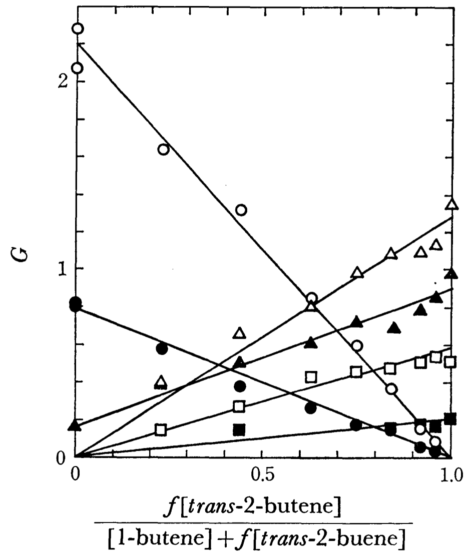

Fig. 2. The *G*-values of products from the mixture of 1-butene and *trans*-2-butene in carbon dioxide solution as a function of the weighted mole fraction of *trans*-2-butene. The value of *f* is taken as 3.0.
○ 1-Butene oxide; ● butanal; □ *cis*-2-butene oxide; △ *trans*-2-butene oxide; ■ 2-methylpropanal; ▲ 2-butanone.

function of X will give a straight line:

$$G(P_\alpha) = G_0\alpha(1-X). \tag{6}$$

A similar linearity can be obtained for the products of the reaction with B olefin:

$$G(Q_\beta) = G_0\beta X. \tag{7}$$

Consequently, once an appropriate value of *f* is obtained, all of the addition products formed in Reactions 2 and 3 should give straight lines when the *G*-values

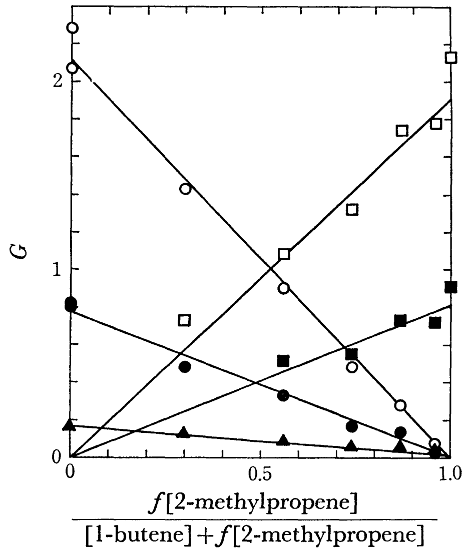

Fig. 3. The *G*-values of products from the mixture of 1-butene and 2-methylpropene in carbon dioxide solution as a function of the weighted mole fraction of 2-methylpropene. The value of *f* is taken as 2.9.
○ 1-Butene oxide; ● butanal; □ 2-methylpropene oxide; ■ 2-methylpropanal; ▲ 2-butanone.

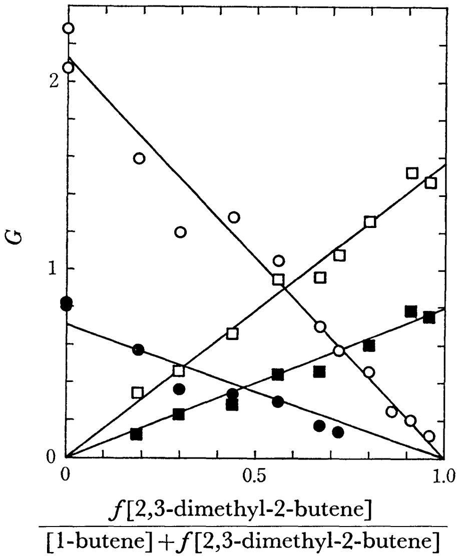

Fig. 4. The *G*-values of products from the mixture of 1-butene and 2,3-dimethyl-2-butene in carbon dioxide solution as a function of the weighted mole fraction of 2,3-dimethyl-2-butene. The value of *f* is taken as 2.0.
○ 1-Butene oxide; ● butanal; □ 2,3-dimethyl-2-butene oxide; ■ 3,3-dimethyl-2-butanone.

are plotted as a function of the weighted mole fraction X.

Figure 1 shows such plots for the competition of 1-butene and *cis*-2-butene. Calculations with trial and error showed that the error introduced in the estimation of *f* was less than 10% in all cases examined except for the mixture of 1-butene and 2-methylpropane.

When more than two addition products are formed in the reaction of oxygen atoms with olefin, the ratio

TABLE 1. FRACTIONAL YIELDS OF THE ADDITION PRODUCTS FORMED IN THE REACTION OF OXYGEN ATOMS WITH FIVE OLEFINS

Olefin	Product	Liquid phase		
		in CO_2 −18 °C (This work)	in N_2[5] 77 K	Gas phase[4]
1-Butene	1-Butene oxide	0.70	0.58	0.53
	Butanal	0.25	0.41	0.43
	2-Butanone	0.05	0.01	0.04
cis-2-Butene	*cis*-2-Butene oxide	0.46		0.25
	trans-2-Butene oxide	0.21		0.26
	2-Methylpropanal	0.10		0.23
	2-Butanone	0.23		0.26
trans-2-Butene	*cis*-2-Butene oxide	0.20		0.15
	trans-2-Butene oxide	0.43		0.33
	2-Methylpropanal	0.07		0.21
	2-Butanone	0.30		0.31
2-Methylpropene	2-Methylpropene oxide	0.70	0.55	0.54
	2-Methylpropanal	0.28	0.45	0.43
	2-Butanone	0.02	0.001	0.03
2,3-Dimethyl-2-butene	2,3-Dimethyl-2-butene oxide	0.66		0.52
	3,3-Dimethyl-2-butanone	0.34		0.48

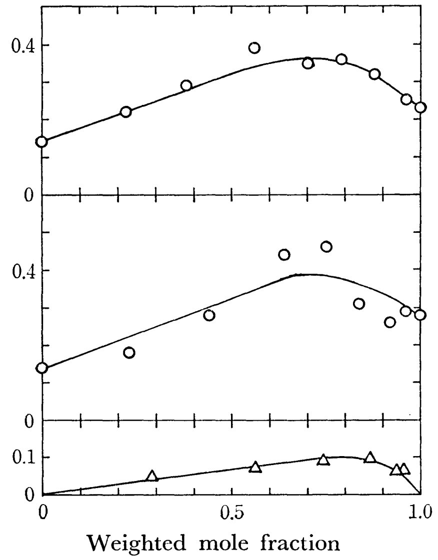

Fig. 5. The G-values of the largest minor products from the mixtures of 1-butene and *cis*-2-butene, 1-butene and *trans*-2-butene, and 1-butene and 2-methylpropene, respectively, from the top to the bottom, as a function of the weighted mole fraction of the competitive reactant for 1-butene. ○ Propanal; △ acetone.

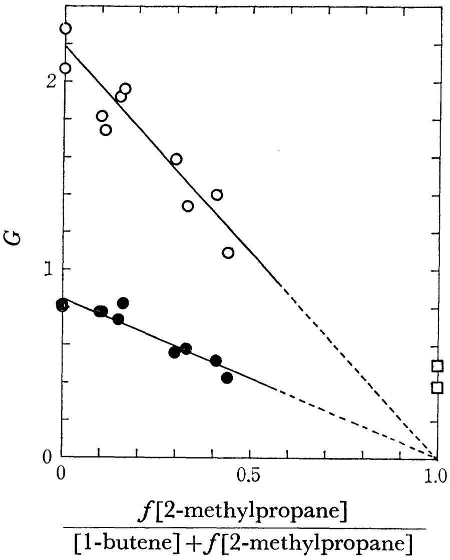

Fig. 6. The G-values of products from the mixture of 1-butene and 2-methylpropane in carbon dioxide solution as a function of the weighted mole fraction of 2-methylpropane. The value of f is taken as 0.07. ○ 1-Butene oxide; ● butanal; □ 2-methylpropene oxide after 2 hour-irradiation, see text for the detail.

of the slopes of the two straight lines obtained from the plots of $G(P_{\alpha 1})$ and $G(P_{\alpha 2})$ corresponds to the formation ratio of the two products, $P_{\alpha 1}$ and $P_{\alpha 2}$. In the case of the mixture of 1-butene and *cis*-2-butene (Fig. 1), 2-butanone is a common product from two olefins. In such a case, the formation ratio was estimated from the intercepts of the linear relations at X=0.0 and 1.0.

Figures 2, 3, and 4 show the results obtained with the mixtures of 1-butene and *trans*-2-butene, 1-butene and 2-methylpropene, and 1-butene and 2,3-dimethyl-2-butene, respectively. In every case, several minor products were observed, the total yield of which was estimated as about 10% of the main addition products by measuring the peak areas in the gas chromatograms. In the case of 2,3-dimethyl-2-butene, the total G-value of the addition products is about 10% smaller than those obtained with other olefins. This fact is consistent with the observation that the fraction of the fragmentation products in the gas phase reaction of oxygen atoms with 2,3-dimethyl-2-butene is larger than those obtained with other olefins.[4] Figure 5 shows the largest amounts of minor products observed

Table 2. The relative rate constants of reaction of oxygen atoms with several hydrocarbons in liquid carbon dioxide and in the gas phase[3]

Hydrocarbon	Relative rate	
	In CO_2 at $-18\ ^\circ C$ (This work)	In the gas phase at room temp[a]
1-Butene	1.0	1.00
cis-2-Butene	2.3	4.13
trans-2-Butene	3.0	4.91
2-Methylpropene	2.9	4.35
2,3-Dimethyl-2-butene	2.0[b]	13.8
2-Methylpropane	0.07	0.015[c]

a) Because of the low activation energies, the relative rates shown in this Table are almost the same as those at the temperature of $-18\ ^\circ C$. b) This value is somewhat smaller than that expected from the previous work.[2] The explanation of the discrepancy is not yet clear. c) Calculated on the basis of $k_{\mathrm{butane}}/k_{\mathrm{2\text{-}methylpropene}}=0.0018$[3] and $k_{\mathrm{2\text{-}methylpropane}}/k_{\mathrm{butane}}\simeq 2$.[6]

with three different mixtures which did not show the linear relationship with X. This is probably due to the fact that these minor products are formed in the reaction of radicals produced in fragmentation processes with hydrocarbons.

Figure 6 shows the competition between 1-butene and 2-methylpropane. Since the value of f was very small, the error introduced in its estimation was probably about 20%.

The formation ratios and the relative rate constants thus obtained are summarized in Tables 1 and 2, together with those obtained in the gas phase and in liquid nitrogen.[4-6]

Discussion

Reaction Mechanism. As Table 1 shows, the main addition products obtained in the present experiment are the same as those obtained by Cvetanović for the gas phase reaction of oxygen atoms.[4] The difference in their formation ratios may be explained in terms of the solvent effect.

According to the Cvetanović mechanism, oxygen atoms in the ^3P state mainly add to the less substituted of the two doubly bonded carbon atoms and the initial adduct rearranges to the final products by ring closure (to form epoxide) and by migration of an H atom or alkyl group, from the C atom to which the oxygen atom becomes attached to the other C atoms of the original bond (to form carbonyl compounds). In the present reaction system, the migration of an H atom or an alkyl group may be somewhat restricted by the solvent, carbon dioxide. This effect seems to correspond with the observation that the fraction of epoxide is larger than that of carbonyl compounds, compared with that in the gas phase, in every olefin. Exactly the same effect can interpret the difference in the *cis-trans* ratio of the two 2-butene oxides produced in the reaction of 2-butene ; *i.e.*, the rotation around the C–C axis in the initial adduct is more restricted in liquid carbon dioxide than in the gas phase. In the liquid nitrogen solution, however, Hirokami and Cvetanović found that the formation ratios of epoxide/carbonyl compounds obtained with propylene, 1-butene, and 2-methylpropene are consistent with those obtained in the gas phase at room temperature.[5] This discrepancy seems to suggest that there is a small but definite interaction between the initial adduct and carbon dioxide.

Moreover, the comparison of the formation ratios listed in Table 1 suggests that the ratio between the addition of oxygen atoms to the less substituted and that to the more substituted of the two doubly bonded carbon atoms is not dependent upon the phase but on the temperature at which the reaction occurs ; *i.e.*, the yields of 2-butanone, which is the product formed through the addition reaction of oxygen atom to the more substituted carbon atom in the reactions of 1-butene and of 2-methylpropene, are very small in liquid nitrogen compared with those obtained in the gas phase and in the carbon dioxide solution $-18\ ^\circ C$.

The quantitative analysis of the fragmentation products could not be carried out because of the experimental difficulty of the measurement of the small peaks appearing in the gas chromatogram. Only the largest minor products obtained with three systems are shown in Fig. 5. The formation of propanal from the solution containing 2-butene and of acetone from the solution containing 2-methylpropene may be explained by the decomposition of the initial adduct followed by the radical-radical reactions.

When 2-methylpropane was used as the solute, the main products observed were alcohols: 2-methyl-1-propanol and 2-methyl-2-propanol. With the increase in irradiation time, 2-methylpropene oxide and 2-methylpropanal became important products. These compounds must be formed through a secondary reaction: *i.e.*, the reaction of oxygen atoms with 2-methylpropene eventually produced in the system. A similar observation can always be made when paraffin molecules are used as the solute.[7]

Relative Rate Constants. As Table 2 shows, the differences in relative rate constants obtained with six hydrocarbons in liquid carbon dioxide are much smaller than those obtained in the gas phase, which suggests that the diffusion process plays a role. However, the difference between 1-butene and other butenes in the relative rate constants cannot simply be explained by the assumption that all of the reactions of oxygen atoms with olefins in the liquid phase are diffusion-controlled.

It is well known that collisions between two species A and B in a solvent occur in sets. Therefore, the total collision frequency, Z_{AB}, may be expressed as the product of the average collision number, n, in a collision set and the diffusion-controlled collision frequency, k_D.

$$Z_{AB} = n\,k_D \tag{8}$$

$$k_D = 4\pi(D_A+D_B)(r_A+r_B) \qquad (9)^{8)}$$

Here D is the diffusion coefficient and r is the collision radius.

Now let us assume that the p fraction of the collision is effective ; then the rate constant of the reaction

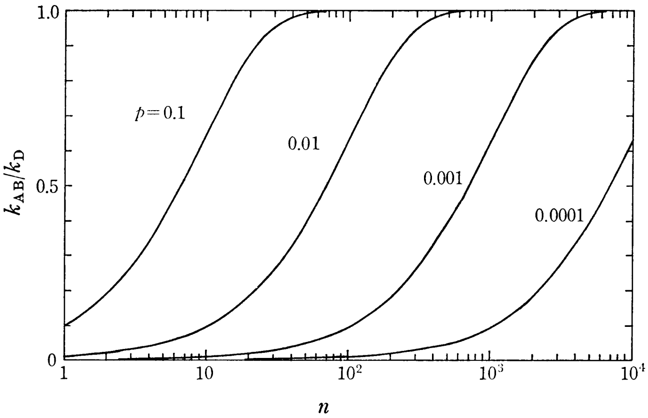

Fig. 7. The ratio of k_{AB}/k_D as a function of the average collision number n in a collision set at different values of effective collision fractions.

between A and B may be expressed as follows:

$$k_{AB} = k_D[1-(1-p)^n]. \tag{10}$$

Here, $(1-p)^n$ corresponds to the fraction of collisions which do not lead to the reaction. At the two extreme cases, $p \ll 1$ and $p \approx 1$, Eq. 10 is converted into Eqs. 11 and 12, respectively.

$$k_{AB} = npk_D = pZ_{AB} \tag{11}$$

$$k_{AB} = k_D \tag{12}$$

The former is the usual expression for the reaction-controlled reaction and the latter for the diffusion-controlled reaction. Figure 7 shows the k_{AB}/k_D ratio as a function of the average collision number in a collision set at several p values.

Recent measurements of the absolute rate constants and of the activation energies for the reaction of oxygen atoms with olefins in the gas phase[9,10] allowed us to estimate the p values. By taking 2.0×10^{11} l mol^{-1} s^{-1} as the collision frequency between oxygen atoms and olefins in the gas phase at −18 °C (the collision diameter was assumed to be 4.0 Å), we estimated the following p values : 0.01 for 1-butene, 0.05 for other butenes, and 0.3 for 2,3-dimethyl-2-butene.

On the other hand, the estimation of n is a very difficult problem. Several theoretical treatments have been proposed[11,12] and have suggested n=10—100 in the solutions which are not too viscous. We calculated the n values so as to satisfy the following equation:

$$\frac{k}{k_{1\text{-butene}}} = \frac{1-(1-p)^n}{1-(1-p_{1\text{-butene}})^n}. \tag{13}$$

The values obtained were 30—50 for butenes and 70 for 2,3-dimethyl-2-butene. The fact that a somewhat larger n value was obtained for 2,3-dimethyl-2-butene may be due to the fact that the value of k_D for this compound is smaller than that for butenes because of the large molecular dimension. If k_D for 2,3-dimethyl-2-butene is assumed to be 10% smaller than that for butenes, the number of 50 can be obtained for n. As the conclusion of this calculation, we may state that the reactions of oxygen atoms with *cis*-, *trans*-2-butenes, 2-methylpropene, and 2,3-dimethyl-2-butene in liquid carbon dioxide are almost diffusion-controlled.

The relative rate constant of reaction of oxygen atoms with 2-methylpropane obtained in liquid carbon dioxide was five times that obtained in the gas phase when the rate constant of 1-butene was taken as unity in both phases, as is shown in Table 2. We have recently measured the competition of cyclohexane and cyclohexene for oxygen atoms, by using a method similar to that described in the present paper, and found that k(O+cyclohexane)/k(O+cyclohexene)= 0.03.[7] This value conforms to the present result, k(O+2-methylpropane)/k(O+1-butene)=0.07, because the ratio of k(O+2-methylpropane)/k(O+cyclohexane) can be estimated as about unity in the gas phase,[6] and k(O+cyclohexene) in liquid carbon dioxide is 1.3 times k(O+*cis*-2-butene).[2]

In order to apply Eq. 13 to the competition between 2-methylpropane and 1-butene, however, we have to assume that $n \approx 700$. If n=700 is correct, the difference between 1-butene and other olefins in relative rate constant cannot be explained. We have no proper interpretation for this discrepancy at present.

Reacting Species. In the foregoing discussion, all of the addition products are treated as the products of the reaction of oxygen atoms in the ^{3}P state with olefins. In the radiolysis of carbon dioxide, however, active species other than oxygen atoms in the ^{3}P state can be expected to be formed, such as oxygen atoms in the ^{1}D state, CO_3, and ionic species.

The present analysis is based on the experimental fact that the observed addition products are very similar to those obtained in the gas phase reaction of oxygen atoms with olefins. Consequently, if active species other than oxygen atoms in the ^{3}P state should react with olefins exactly in the same manner as do oxygen atoms, we cannot discriminate these species from the ^{3}P oxygen atoms. The species CO_3 might be a candidate.

The participation of ^{1}D oxygen atoms may be ignored because of the high quenching efficiency of carbon dioxide.[13] In the present experiment, we often observed the formation of various alcohols, the formations of which were not reported in the gas phase reaction of oxygen atoms with olefins. This fact suggests that ionic species such as O^- ions are produced in the present system, although they cannot be major reacting species.[14]

References

1) L. Wojnarovits, S. Hirokami, and S. Sato, *Bull. Chem. Soc. Jpn.*, **49**, 2956 (1976).

2) H. Sakurai, K. Akimoto, S. Toki, and S. Takamuku, *Chem. Lett.*, **1975**, 469.

3) R. J. Cvetanović, *Adv. Photochem.*, **1**, 115 (1963).

4) R. J. Cvetanović, *Can. J. Chem.*, **36**, 623 (1958).

5) S. Hirokami and R. J. Cvetanović, *J. Am. Chem. Soc.*, **96**, 3738 (1974).

6) J. T. Herron and R. E. Huie, *J. Phys. Chem.*, **73**, 3327 (1969).

7) R. Yugeta, A. Matsumoto. H. Karasawa. and S, Sato, unpublished data.

8) M. V. Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917).

9) D. L. Singleton and R. J. Cvetanović, *J. Am. Chem. Soc.*, **98**, 6812 (1976).

10) R. Atkinson and J. N. Pitts, Jr., *J. Chem. Phys.*, **67**, 38 (1977).

11) E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

12) G. M. Barrow, "Physical Chemistry for Life Sciences," McGraw-Hill Kogakusha Ltd., Tokyo (1974), p. 336.

13) P. Warneck and J. O. Sullivan, International Conference on Photochemistry, München, 1967, part 1, p. 94.

14) S. Hirokami, L. Wojnarovits, and S. Sato, *Bull. Chem. Soc. Jpn.*, **52**, 299 (1979).