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γ-RADIOLYSIS OF AN OLEFIN-LIQUID CARBON DIOXIDE MIXTURE

Hiroshi SAKURAI, Koichi AKIMOTO, Susumu TOKI, and Setsuo TAKAMUKU
The Institute of Scientific and Industrial Research,
Osaka University, Suita, Osaka 565

Radiolysis of an aliphatic olefin(0.01 mol)-liq. CO_2(1 mol) mixture has been investigated at room temperature. The main products were the corresponding epoxide and carbonyl compounds. A biradical intermediate which is formed by addition of oxygen atom to olefinic double bond is proposed. The nature of the oxidizing species is discussed.

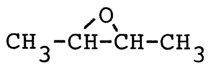
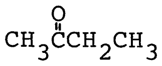
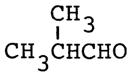
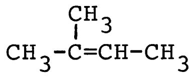
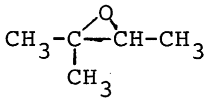
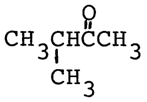
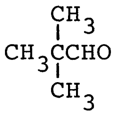
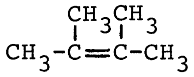
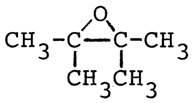
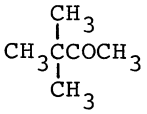
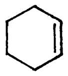
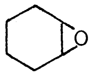
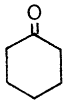
The radiolysis of carbon dioxide has been extensively investigated.[1] In liquid[2] and high-density gases[3] of carbon dioxide, a geminate recombination is an important process and leads to the formation of the excited CO_2*, CO, and O atoms as primary species. The last, forming O_2 and O_3, is shown to be trapped by the addition of olefin and also by other O atom scavengers.

Recently, on the other hand, Ishizaki and Sato have shown that toluene is oxidized to cresols in the radiolysis of liquid carbon dioxide at 0°C, and O^- and/or CO_3^- are suggested for the oxidizing species.[4] The formation process and the reactivity of these active species from liquid carbon dioxide seem to be of interest. The present investigation provides further information on the reactivity of the active species with olefins.

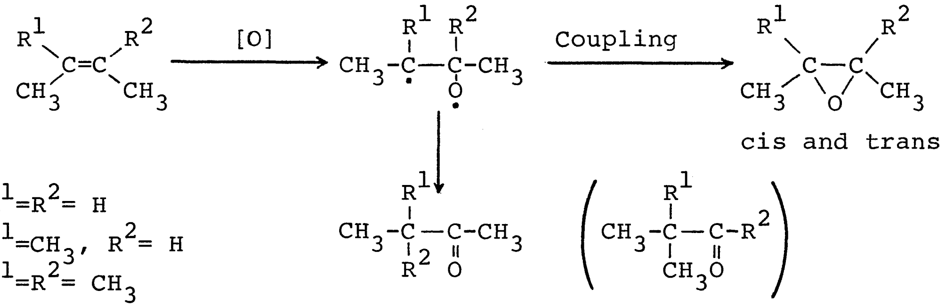
Irradiation of an olefin-liq. CO_2 mixture(0.01:1 mol) was carried out in a stainless steel autoclave(50 ml) using a ^{60}Co, 7000 Ci source at room temperature for ca. 20 hr. The products were identified by comparison of glc and mass spectra with those of authentic samples obtained commercially or synthesized. The relative reactivity ratio was obtained by the radiolysis of 1:1 mixture of two olefins. The results are shown in Table I.

The following trends were observed; (i) the relative reactivity suggests that the oxidizing species is slightly electrophilic, (ii) an epoxidation is preferential but the path is not stereospecific as observed in the formation of cis- and trans-2,3-epoxybutane from cis-2-butene, (iii) rearranged carbonyl products are always formed. On the basis of these observations, a ground state oxygen atom, O(^{3}P), is most reasonable as the oxidizing species and the following scheme may explain the present products.

Table I. Radiolysis of Olefin-Liquid Carbon Dioxide Mixture at Room Temperature.

Olefin	Relative Rate k/k(cis-2-Butene)	Products (%)		
CH_3-CH=CH-CH_3 cis	1.0	 cis 54, trans 23	 $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$ 17	 $CH_3\overset{CH_3}{\overset{\mid}{C}}HCHO$ 6
 $CH_3\text{-}\overset{CH_3}{\overset{\mid}{C}}\text{=CH-}CH_3$	1.3	 74	 $CH_3\underset{CH_3}{\underset{\mid}{C}}H\overset{O}{\overset{\|}{C}}CH_3$ 15	 $CH_3\underset{CH_3}{\underset{\mid}{\overset{CH_3}{\overset{\mid}{C}}}}CHO$ 11
 $CH_3\text{-}\overset{CH_3}{\overset{\mid}{C}}\text{=}\overset{CH_3}{\overset{\mid}{C}}\text{-}CH_3$	1.7	 72	 $CH_3\underset{CH_3}{\underset{\mid}{\overset{CH_3}{\overset{\mid}{C}}}}COCH_3$ 28	
	1.3	 83	 17	

Scheme I



The reactivity of O(^{3}P) atom with olefin in gas phase has been investigated photochemically by Cvetanović and Sato.[5] The present results are also consistent with those previous observations, though the electrophilicity of the active species was not so remarkable as in gas phase [the relative rate in the gas-phase reaction of O(^{3}P) atom; cis-2-butene, 1.0; 2-methyl-2-butene, 3.3; 2,3-dimethyl-2-butene, 4.3; cyclohexene, 1.1].[5] The different reaction conditions such as phase and solvent may affect on the nature of the active species. The present results, however, do not exclude the contribution of other active species such as CO_3 which was postulated as an intermediate in the reaction of O atom with CO_2.[6]

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