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The Reaction of O(^{3}P) Atoms with Indene and Phenanthrene Induced by the γ-Radiolysis of Liquid Carbon Dioxide

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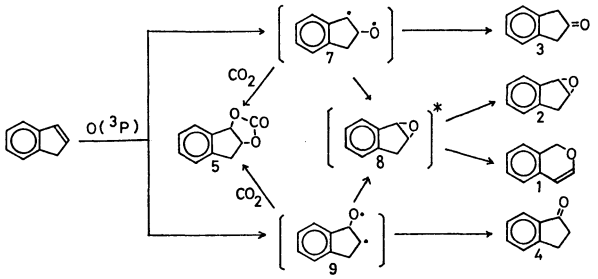
Synopsis. The γ-radiolysis of liquid CO_2 with indene and phenanthrene gives the corresponding oxirane and carbonyl compounds, together with some products which are unexpected on the basis of the reaction of (^{3}P) with aliphatic olefins: (i) the corresponding cyclic carbonate; (ii) 1*H*-2-benzopyran and a dimer for indene, and (iii) dibenz[*b*,*d*]oxepin and 2,2′-biphenyldicarbaldehyde for phenanthrene. The mechanisms of the formation of these products are discussed.

It has been shown that the γ-radiolysis of CO_2 in the liquid phase produces oxygen atoms.[1] We have recently studied the radiolysis of liquid CO_2 with various organic compounds, such as olefins,[2] saturated hydrocarbons,[3] and phenylacetylenes,[4] and have observed the formation of the corresponding oxidation products. On the basis of the reaction mechanism, it has been concluded that the most reasonable oxidizing species must be a ground-state oxygen atom. Recently, Wojnarovits *et al.*[5] also indicated the formation of O(^{3}P) atoms in the γ-radiolysis of a cyclohexene-liquid CO_2 mixture. Therefore, one may expect the radiolysis of liquid CO_2 to be useful for the generation of O(^{3}P) atoms in the liquid phase. The purpose of this work is to clarify the reactivity of O(^{3}P) atoms with condensed-ring compounds, such as indene and phenanthrene, the reactions of which with oxygen atoms are not known, and to explore the possibility of capturing CO_2 by intermediates of the reactions of O(^{3}P) atoms with the above compounds.

The irradiation of an indene-liquid CO_2 mixture was carried out using a ^{60}Co source at 0 °C; the results are summarized in Table 1. The following features were observed; (i) the products were 1H-2-benzopyran (**1**), 1,2-epoxyindan (**2**), 2-indanone (**3**), 1-indanone (**4**), 1,2-indandiyl carbonate (**5**), and an indene dimer (**6**),[6] among which **2** and **3** were the main products; (ii) the total G values of the oxygen-containing products were *ca.* 5.3 and 3.8 for 2 and 17 hrs irradiation respectively, which are consistent with the $G(CO)=3.5$—5.0 obtained by the γ-radiolysis of liquid CO_2 at −48 °C,[1] and hence the G values suggested that the oxygen atoms generated on the radiolysis of liquid CO_2 are trapped effectively by indene; (iii) on the basis of the γ-irradiation to **2** or **3** in liquid CO_2,[7] it was found that the further reactions of the main products to form their isomers and **5** are negligibly small, except for a slight isomerization of **2** to **3**, and (iv) 1*H*-2-benzopyran (**1**) was formed by the pyrolysis of **2** at 300 °C.

On the basis of these observations, we propose the following scheme for the formation of the oxygen-containing products of indene:



In the first step, the oxygen atom adds to the double bond of indene, preferentially at the C-2 carbon atom. The biradical (**7** or **9**) thus formed undergoes ring closure to an epoxide or undergoes a rearrangement to the carbonyl compounds (**3** or **4**); 2-indanone(**3**) is also produced, partly by the further isomerization of the **2** primarily produced. The epoxide (**8**) initially formed may possess a vibrationally excess energy and may be rearranged partly to **1**. Furthermore,

Table 1. Radiolysis of the indene-liquid CO_2 system

Irrad. time (h)	Conv. (%)	Product yield (%)[a] (G value)					
		1	**2**	**3**	**4**	**5**	**6**
2	4.2	2.8 (0.17)	29 (1.7)	51 (3.1)	3.3 (0.19)	1.7 (0.10)	7.8 (0.47)
17	42	1.5 (0.11)	24 (1.7)	23 (1.7)	2.7 (0.20)	1.4 (0.10)	1.0 (0.07)

a) All the products were analyzed with a 3-m PEG 20 M column at 150 °C. The product yields are based on the amount of indene consumed.

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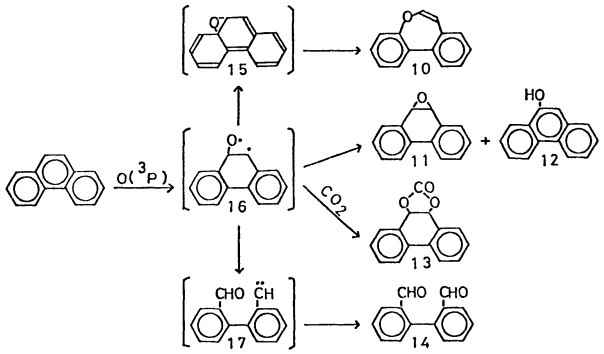
Table 2. Radiolysis of the phenanthrene-liquid CO_2 system

Irrad. time (h)	Conv. (%)	Product yield (%)[a] (G value)				
		10	**11**	**12**[b]	**13**	**14**
3	5	1.3 (0.04)	35 (1.1)	46 (1.4)	2.9 (0.09)	0.9 (0.03)
17	15	1.2 (0.02)	6.1 (0.10)	15 (0.24)	2.6 (0.04)	4.4[c] (0.07)

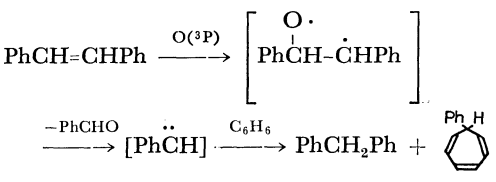
a) All the products were analyzed with a 1-m Silicone OV-17 column at 180 °C. b) This product was determined to be 9-methoxyphenanthrene. c) The addition of isopropyl alcohol (13 mmol) decreased the yield of **14** to trace amounts.

the biradical (**7** or **9**) captures CO_2 to form **5**, probably because of its dipolar character.

In the case of phenanthrene (Table 2), the products were dibenz[*b*,*d*]oxepin (**10**), 9,10-dihydro-9,10-epoxyphenanthrene (**11**), 9-phenanthrol (**12**), 9,10-dihydro-9,10-phenanthrylene carbonate (**13**), and 2,2′-biphenyldicarbaldehyde (**14**). The main products were **11** and **12**. The further reactions of the main products to form their isomers, **13** and **14**, are negligibly small, because the γ-radiolysis of liquid CO_2 in the presence of **11** or **12** gave such products in very low yields (the *G* values were all less than 0.03). Consequently, the initial reaction of the oxygen atom is the addition to the 9,10-bond of phenanthrene, the so-called K-region, to form a biradical:



The biradical (**16**) may be transformed into the products by the following possible modes: (i) the ring closure or rearrangement of **16** to give **11** or **12** respectively; (ii) the ring closure to **15**, which then undergoes thermal valence isomerization to **10**; (iii) capturing CO_2 to form **13**, or (iv) the fission of a carbon-carbon bond of **16** to form a carbene (**17**), which is then oxidized to **14**. The (ii) mode is also observed in the photorearrangement of **11** to **10**.[8] Although there is no direct evidence for the (iv) mode, it may be supported by the following facts: (a) the addition of isopropyl alcohol, which is known to react with a carbene,[9] to this reaction system resulted in a pronounced decrease in the **14**, despite the fact that the yields of the other products remained unaltered, and (b) the radiolysis of the *trans*-stilbene-benzene-liquid CO_2 system gave benzaldehyde, diphenylmethane, and 7-phenylcycloheptatriene, besides oxirane and carbonyl compounds, whose formation can be explained by the following scheme:[10]



Experimental

Procedure. The experimental procedures were essentially the same as those reported previously in the reaction of atomic oxygen with alkanes.[3] A mixture of liquid CO_2 (1.4 mol) and indene (4.3 mmol) or phenanthrene (2.8 mmol) in a stainless-steel autoclave was irradiated by means of a ^{60}Co source at 0 °C. The dose rate, as measured by ferrous sulfate dosimetry, was 1.7×10^{19} eV/g h. The products were identified by a comparison of the retention times of the GLPC and the mass spectra with those of authentic samples.

Materials. Commercial indene and phenanthrene were purified by distillation and by recrystallization from methanol respectively before use. The carbon dioxide (99.99%, Fuji Koatsu Gas Co., Ltd.) was used without further purification. Authentic samples of the products, **1**,[11] **2**,[12] **3**,[13] **4**,[14] **10**,[8] **11**,[15] **12**,[16] and **14**,[17] were prepared by the literature procedures. 1,2-Indandiyl carbonate (**5**) and **13** were prepared by reactions of *cis*-1,2-indandiol and *cis*-9,10-dihydroxy-9,10-dihydrophenanthrene with diethyl carbonate respectively, according to the method of Overberger and Drucker.[18] All the products synthesized were identified by means of their melting points and NMR spectra or by means of their mass spectra.

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6) The mechanism of the formation of **6** will be reported and discussed elsewhere.

7) The γ-radiolysis of liquid CO_2 in the presence of **2** (2.3 mmol) or **3**(2.3 mmol) was carried out under conditions similar to those used for indene-liquid CO_2 system. Only small amounts of the products, **1**, **3**, **4**, and **5**, were formed for **2**, and the *G* values were as follows: **1** ($G=0.02$); **3** (0.79); **4** (0.01); **5** (0.02). In the case of **3**, no such products could be detected.

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