

Reaction of Atomic Oxygen with Alkanes. Regioselective Alcohol Formation on γ -Radiolysis of Liquid Carbon Dioxide Solutions of Alkanes

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γ -Radiolysis of liquid carbon dioxide in the presence of cyclohexane, methylcyclohexane, and *cis*- or *trans*-decalin has been studied at 0 °C. The main products were corresponding alcohols and carbonyl compounds. The oxidizing species from carbon dioxide apparently shows selective attack on C-H bonds of alkane in the order tertiary > secondary > primary. The observed tendency could be rationalized in terms of the reaction of ground state triplet oxygen atoms, O(³P), with alkane in liquid carbon dioxide. In the case of *cis*- and *trans*-decalin, highly configurational retention of decalol-9 was observed. The formation of a dimer of alkane was negligibly small. The rapid recombination of radical pairs initially formed by the reaction of O(³P) atoms with alkane in a solvent cage is proposed. In addition, the production of cyclohexanone from cyclohexanol is described.

Reactions of ground state O(³P) atoms, generated by the mercury photosensitized decomposition of nitrous oxide, with organic molecules, such as alkenes,¹ arenes,² alkynes,³ and alcohols,⁴ have been extensively studied by Cvetanović et al., by other workers,^{1f,2c,3} and recently by Havel et al., in gas phase. However, the reactions of O(³P) atoms in condensed phase have drawn little attention, possibly owing to the absence of a convenient method of producing oxygen atoms in condensed phase.⁵

On the other hand, the radiolysis of carbon dioxide has been extensively studied and carbon monoxide is known to be produced from liquid and solid carbon dioxide.⁶ Baulch, Dainton, and Willix reported $G(\text{CO}) = 5.0\text{--}3.5$, $G(\text{O}_2) = 0.2\text{--}0.6$, and $G(\text{O}_3) \leq 0.7$ for ⁶⁰Co γ -irradiation on liquid carbon dioxide.^{6a} The production of O₂ and O₃ suggests that atomic oxygen is an intermediate. We recently investigated the radiolysis of liquid carbon dioxide in the presence of an alkene and observed the formation of the corresponding oxirane and carbonyl compounds.⁷ The similarity of the products to that of the gas-phase reaction of photochemically produced O(³P) atoms with alkene¹ was observed and we suggested that the most appropriate, main oxidizing species from liquid carbon dioxide is a ground state O(³P) atom. Further, formation of a phenylketene on γ -radiolysis of a phenylacetylene in liquid carbon dioxide indicates that the reaction of O(³P) atoms with a phenylacetylene has occurred via a ketocarbene intermediate.^{8,9} Recently, Wojnarovits, Hirokami, and Sato also indicated the formation of O(³P) atoms in γ -radiolysis of a cyclohexene-liquid carbon dioxide mixture.¹⁰ Therefore, it seems that the γ -radiolysis of liquid carbon dioxide is the most convenient method to approach the reactivity of O(³P) atoms with a variety of organic molecules in liquid phase. This paper attempts to obtain the available information on the behavior of the oxidizing species from carbon dioxide, such as O(³P) atoms, in the reaction with an alkane.

The reaction of O(³P) atoms with alkane in liquid phase has been attempted by photolysis of nitrous oxide and ozone. However, competitive reactions of O(³P) and O(¹D) atoms were unavoidable in the case of nitrous oxide¹¹ and the reaction of O(³P) atoms with alkane was hardly observed in the case of ozone,^{12,13} presumably by the effective scavenging of O(³P) atoms by oxygen molecules which is the by-product in the photolysis of ozone.

Results

Cyclohexane. γ -Radiolysis of liquid carbon dioxide (1.4 mol) in the presence of low molar concentrations of cyclohexane (lower than 0.32) was carried out in a stainless steel

autoclave using a ⁶⁰Co (7000 Ci) source at 0 °C for 0.5–2 h. Products were cyclohexanol, cyclohexanone, cyclohexene oxide,¹⁴ and bicyclohexyl, of which *G* values were 2.0–3.1, 0.5–1.3, less than 0.4, and less than 0.3, respectively. The total *G* value of oxygenated product is 2.9–4.7 (molecule/100 eV), which agreed with that of oxygen atoms estimated from *G*(CO) obtained by Baulch et al. in γ -radiolysis of liquid carbon dioxide.^{6a} These data are summarized in Table I. The relative yield of cyclohexanol was about 65% of the products and almost independent of irradiation time and concentration of cyclohexane.

Methylcyclohexane. The products in the radiolysis of liquid carbon dioxide (1.4 mol) in the presence of methylcyclohexane (7.1–9.7 mmol) were methylcyclohexanols and cyclohexylcarbinol (their combined *G* value was 2.8–3.2) and three isomers of methylcyclohexanone (*G* = 0.5–1.0). The total *G* value of product was 3.4–4.2 (molecule/100 eV). These data and the distribution of alcohols are shown in Table II. A pronounced selectivity of the attack of O(³P) atoms on three types of C-H bonds of methylcyclohexane was observed.

***cis*- and *trans*-Decalin.** Radiolysis of liquid carbon dioxide (1.4 mol) in the presence of *cis*-decalin (6.6 mmol) produced isomers of decalol (*G* = 2.5) and decalone (*G* = 0.2), and in the presence of *trans*-decalin (9.4 mmol) produced isomers of decalol (*G* = 2.5) and decalone (*G* = 0.7). The total *G* values of product in the case of *cis*- and *trans*-decalin were 2.8 and 3.2, respectively. From the proportion of *cis*- or *trans*-decalol-9 in produced *cis*- and *trans*-decalol-9, retention of configuration at the tertiary position has been calculated. The distribution of alcohols and retention of configuration are summarized in Table II. Formation of decalol-9 occurs with predominant stereoselectivity on the reaction of O(³P) atoms with *trans*-decalin.

Cyclohexanol. By the radiolysis of cyclohexanol (2.2 mmol) in liquid carbon dioxide (1.4 mol), cyclohexanone (*G* = 6.0) was obtained as a sole product (Table IV).

Discussion

Alcohol Formation. As described above, alkanes were easily oxidized to the corresponding alcohols. Our previous reports^{7,8} indicate that the oxidizing species produced from liquid carbon dioxide by γ -irradiation should be ground state O(³P) atoms. The data of Table II shows the distribution of alcohols by the attack of the O(³P) atoms on C-H bonds of alkane. The distribution per C-H bonds for methylcyclohexane and decalin apparently shows greater preferential attack of O(³P) atoms on C-H bonds in the order tertiary > secondary > primary. The relative reactivity among the three

Table I. Products of γ -Radiolysis of Cyclohexane in Liquid Carbon Dioxide at 0 °C

mmol	Irradiation time, h	Product G value, molecule/100 eV ^a			
		Cyclohexanol	Cyclohexanone	Cyclohexene oxide	Bicyclohexyl
8.9	0.5	2.71 (65.9)	0.93 (22.6)	0.32 (7.8)	0.15 (3.6)
8.8	1	3.14 (65.6)	1.18 (24.6)	0.40 (8.4)	0.07 (1.5)
8.7	2	2.19 (63.3)	1.27 (36.7)	<i>b</i>	<i>b</i>
2.0	1	2.01 (66.3)	0.53 (17.5)	0.37 (12.2)	0.12 (4.0)
18.9	1	2.37 (68.1)	0.56 (16.1)	0.30 (8.6)	0.25 (7.2)

^a Relative yields are shown in parentheses. ^b Not detected.

Table II. Products of γ -Radiolysis of Alkanes in Liquid Carbon Dioxide at 0 °C

Registry no.	Alkane	mmol	Irradiation time, h	Product G value		Alcohol distribution, %			Alcohol distribution per C-H bonds			Retention of configuration, %
				Alcohols	Ketones	Prim	Sec	Tert	Prim	Sec	Tert	
108-87-2	Methylcyclohexane	7.1	1	3.22	0.95 ^a	0.6	47.8	51.6	0.05	1	10.8	
			2	2.97	0.48 ^a	2.0	52.2	45.8	0.13	1	8.78	
			3	2.81	0.56 ^a	2.1	55.2	42.7	0.13	1	7.74	
493-01-6	<i>cis</i> -Decalin	6.6	3	2.54	0.21 ^b		28.7	71.3		1	19.8	83
493-02-7	<i>trans</i> -Decalin	9.4	3	2.54	0.65 ^b		39.0	61.0		1	12.5	93

^a Three isomers of methylcyclohexanone. ^b Isomers of decalene.

Table III. Relative Reactivity of C-H Bonds by the Attack of Active Species

Active species	Substrate	Condition	Relative reactivities per C-H bonds			Ref
			Prim	Sec	Tert	
O(³ P)	Methylcyclohexane	Liq CO ₂ , γ ray, at 0 °C	1	9	80	This work
O(³ P)	<i>cis</i> -Decalin	Liq CO ₂ , γ ray, at 0 °C		1	20	
O(³ P)	<i>trans</i> -Decalin	Liq CO ₂ , γ ray, at 0 °C		1	13	
<i>t</i> -BuO·	<i>n</i> -Butane ^a and 2,3-dimethylbutane ^b	<i>t</i> -BuOCl, <i>h</i> ν , at 0 °C in several solvents	1	11-14	69-89	15
O(¹ D)	Propane ^c and isobutane ^d	Ozone, 2537 Å, at 87 K in liq argon	1	0.9	1.0	17
O(¹ D)	Methylcyclohexane	N ₂ O, 1849 Å, at 0 °C	1	1.1	1.4	11
O ⁻	Aliphatic alcohols and monocarboxylic acids	Aqueous solution, at high pH, pulse radiolysis	1	4.8		18

^a Registry no., 106-97-8. ^b Registry no., 79-29-8. ^c Registry no., 74-98-6. ^d Registry no., 75-28-5.

types of C-H bonds of methylcyclohexane can be presented: primary C-H bond:secondary C-H bond:tertiary C-H bond = 1:9:80 (Table III). Similar results were obtained by *cis*- and *trans*-decalin. The relative reactivity of the three types of C-H bonds on hydrogen abstraction by *tert*-butoxy radical in several solvents (*n*-butane and 2,3-dimethylbutane) at the same temperature as our experiment were reported by Walling and Jacknow¹⁵ (see Table III). Our result is in excellent agreement with that obtained by the hydrogen abstraction of *tert*-butoxy radical from alkane. Therefore, the present alcohol formation would be caused by hydrogen abstraction and followed by the recombination of radical pair. In contrast to this, excited singlet state O(¹D) atoms are well known to exhibit little discrimination in their attack on the primary, secondary, and tertiary C-H bonds of alkane in gas phase¹⁶ and condensed phase.^{11,17} Hydrogen abstraction by oxygen radical anion, O⁻, from saturated compounds shows preferential attack on C-H bonds in the same order by the attack of *tert*-butoxy radical, but the relative reactivity of secondary C-H bond against primary C-H bond for hydrogen abstraction with O⁻ anion is about half as high as the relative reactivity with *tert*-butoxy radicals.¹⁸ Further, it seems that alkyl radical and OH⁻ anion thus formed do not take part in alcohol

formation. Thus, these results exclude the possibility of O⁻ anion as well as O(¹D) atoms from the precursor of alcohols.

There are reports of carbon trioxide, CO₃, formation by the reaction of singlet O(¹D) atoms with carbon dioxide in gas phase and condensed phase.¹⁹ Excited carbon trioxide stabilizes either by collisional deactivation forming ground state CO₃ or by decomposition producing carbon dioxide and O(³P) atoms. In liquid phase, excited carbon trioxide may be effectively deactivated by collision. It would be difficult to demonstrate the possibility of the participation of CO₃ in the present reaction without the knowledge of the reactivity of CO₃ with organic compounds, such as alkane.

It seems likely that hydrogen abstraction from an alkane by O(³P) atoms results in the formation of an alkyl radical and OH radical. In the case of cyclohexane, only a trace amount of bicyclohexyl was obtained. Any dimer was not detected even in the case of methylcyclohexane or decalin. Therefore, we assume that the rapid recombination of radical pair in a solvent cage may occur and result in the formation of the corresponding alcohol.

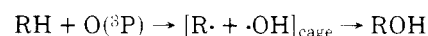
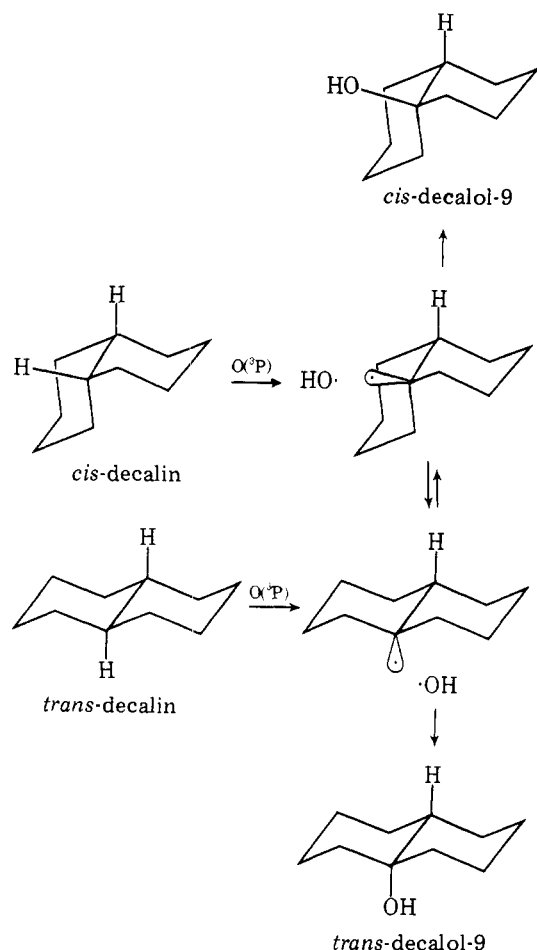


Table IV. γ -Radiolysis of Cyclohexane and Cyclohexanol in Liquid Carbon Dioxide^a

Cyclohexane, mmol	Cyclohexanol, mmol	Product <i>G</i> value			
		Cyclohexanol	Cyclohexanone	Cyclohexene oxide	Bicyclohexyl
2		2.7	0.9	0.3	0.2
2	0.2		2.5	<i>b</i>	<i>b</i>
	2		6.0	<i>b</i>	<i>b</i>

^a Irradiation; 0.5 h, in liquid carbon dioxide (1.4 mol) at 0 °C. ^b Not detected.

With regard to further details of the alcohol formation, it would be interesting to know the recombination process of the radical pair in liquid carbon dioxide. It was observed in the radiolysis of liquid carbon dioxide with decalin that the distribution of tertiary alcohols shows excellent retention of configuration at the tertiary positions of *cis*- and *trans*-decalin. On the hydrogen abstraction of O(³P) atoms from the tertiary position of *cis*-decalin, *cis*-9-decalyl radical must be formed initially. 9-Decalyl radicals were examined by various methods, and conformational conversion from *cis*-9-decalyl radical to the more stable *trans*-9-decalyl radical has been known to occur easily.²⁰ It seems likely that *cis*-9-decalyl radical which formed initially from *cis*-decalin may recombine with OH radical in a solvent cage to give *cis*-decalol-9. The recombination of *cis*-9-decalyl radical with OH radical may compete with the conversion of *cis*-9-decalyl radical to *trans*-9-decalyl radical to some extent. In the case of *trans*-decalin, 9-decalol was obtained with higher retention of configuration as the equilibrium between the two 9-decalyl radicals lies to *trans*-9-decalyl radical.



Ketone Formation. In all runs, small amounts of ketones were formed as a by-product. The *G* values of the formation of cyclohexanone from cyclohexane are approximately con-

stant regardless of dose (Table I). It seems likely that ketones were formed as a primary product from alkanes. Nevertheless, a slight increase in *G* value of cyclohexanone as dose was observed. We would like to suggest that a secondary reaction of cyclohexanol with O(³P) atoms might be involved. Actually, radiolysis of a cyclohexane–cyclohexanol mixture (10:1) in liquid carbon dioxide resulted in a remarkable increase in *G* value of cyclohexanone formation (Table IV). Further, radiolysis of cyclohexanol in liquid carbon dioxide gave cyclohexanol as a sole oxidized product in high yield (*G* = 6.0). The oxidation process of cyclohexanol can be accounted for by an initial α -hydrogen abstraction by O(³P) atoms, followed by the fast recombination of geminate radical pairs in a solvent cage to form unstable *gem*-diol which was easily dehydrated, or followed by disproportionation of the radical pairs in a solvent cage producing cyclohexanone and water.

Experimental Section

General Procedure. γ -Radiolysis of liquid carbon dioxide (1.4 mol) in the presence of 0.03–0.3 M concentrations of an alkane was carried out in a stainless steel autoclave (65 mL) using a ⁶⁰Co (7000 Ci) source at 0 °C for 0.5–3 h. Reactions were run to less than ca. 10% completion to avoid secondary oxidation. The dose rate, measured with the Fricke dosimeter solution, was 1.7×10^{19} eV/g·h. The products were identified by comparison of retention times of GLC and mass spectra (Hitachi RMS-4 GC/MS, Carbowax 20M, 6 m) with those of authentic samples.

Air in an autoclave was replaced with about 20 g of carbon dioxide three times in every experiment before the autoclave was filled out with liquid carbon dioxide. The loss of alkane after this procedure was negligible. The solubilities were checked by quartz autoclave (12 mL).

Materials. Carbon dioxide (99.99%, Fuji Koatsu Gasu Co. Ltd.) from the tank was used without further purification. Cyclohexane and methylcyclohexane used were of spectral grade and were purified by distillation in a spinning band column (60 cm). Analysis by GLC indicates less than 0.01% impurities. *cis*- and *trans*-decalin were obtained commercially and were distilled. The purity of *cis*- and *trans*-decalin, as determined by GLC, was 96 and 99%, respectively. Cyclohexanol was obtained commercially, and was purified by distillation in a spinning band column followed by further purification by preparative GLC. Analysis by GLC indicates about 0.05% cyclohexanone.

Authentic Samples. Cyclohexanone, cyclohexene oxide, 2-, 3-, and 4-methylcyclohexanol, and 2-, 3-, and 4-methylcyclohexanone were obtained commercially (Tokyo Kasei Kogyo Co. Ltd.). Bicyclohexyl was prepared by hydrogenation of biphenyl over Raney nickel W-6 at 160 °C under 150 atm of hydrogen.²¹ Cyclohexylcarbinol was prepared by the reaction of cyclohexylmagnesium chloride with formaldehyde.²² 1-Methylcyclohexanol was prepared by the reaction of cyclohexanone with methyl magnesium iodide in ether.²³ *cis*- and *trans*-decalol-9 were prepared by oxidation of *cis*- and *trans*-decalin with ozone.²⁴ *cis*- and *trans*-decalol-1- and -2 were prepared by hydrogenation of 1- and 2-naphthol over Raney nickel W-7 at 170 °C under 180 atm of hydrogen.²⁵ 1- and 2-decalone were prepared by oxidation of 1- and 2-decalol with potassium dichromate and concentrated sulfuric acid.²⁶ All the products were identified by their boiling points and NMR and IR spectra or by elemental analysis.

Registry No.—Cyclohexane, 110-82-7; carbon dioxide, 124-38-9.

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Notes

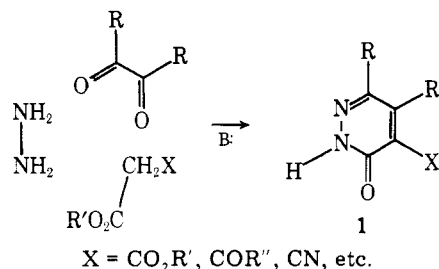
A Facile and General Pyridazine Synthesis from α -Diketone Monohydrazones and β -Keto Esters or β -Diketones

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The Schmidt pyridazine synthesis² formally involves the base-catalyzed condensation of hydrazine, an α -diketone, and an ester activated methylene compound yielding substituted pyridazinones (1). In conjunction with this work, Schmidt and



Druey² reported that, in the absence of a basic catalyst, reaction of benzil monohydrazone (7) with ethyl acetoacetate (8a) yields the "azine" 9a which could not be converted into a ring-closed product (i.e., 10a) although no details were given. There are, however, examples in the literature of similar cyclizations. Reaction of α -diketone monohydrazones (2) with

dimethyl acetylenedicarboxylate (DMAD) yields³ dicarbomethoxy pyridazines 3, presumably via the azines 4 which are also isolated along with several other products (reaction 1). In addition, we have shown⁴ that the stabilized phosphorane 5 yields the pyridazinylmethyltriphenylphosphonium salt 6 on heating (reaction 2).

In the course of another investigation we had occasion to synthesize "azine" 9a. Azine is actually a misnomer since the molecule exists completely (as determined by NMR and IR spectroscopy) in the enamine tautomer, presumably stabilized by intramolecular hydrogen bonding to the benzoyl carbonyl oxygen. To our knowledge, this represents the first example of preference for the enamine tautomer in an azine, although the intermediacy of the enamine form has been postulated⁵ in the α -alkylation of aliphatic ketazines by electron-deficient dienophiles (e.g., maleic anhydride). Throughout this discussion, we will refer to these molecules as azines, although their tautomeric structure should be kept in mind.

Our original intention was to carry out a series of transformations involving the carboethoxy moiety of 9a beginning with saponification. When 9a is heated in aqueous ethanol containing potassium hydroxide a deep red color develops which fades to a very pale yellow after 10 min. The single, colorless product formed retains the carboethoxy group and spectral (IR, NMR, mass spectrum) and elemental analyses indicate that the product is the pyridazine carboxylic ester 10a. The rapidity and efficiency (>90% isolated yield of 10a) of this reaction stands in marked contrast to the earlier reports of the inertness of 9a toward ring closure.²

It is not necessary to isolate 9a and, in fact, considerable