3. When propylene-d_6, instead of cyclopropane-d_6, is added to n-C_5H_{12} or i-C_5H_{12}, propane-d_6 appears again as a major product, but from the mass spectrum it was seen that, in agreement with observations made in analogous gas phase systems,[4d] the propane-d_6 has the structure CD_3CDHCD_2H. Mass spectrometric analysis of the propane fraction (C_3D_8, 45%; C_3D_7H, 10%; CD_3CDHCD_2H, 45%) formed in the radiolysis of a n-C_5H_{12}–n-C_5D_{12}–CD_3CDCD_2–CCl_4 (1:1:0.01:0.01) mixture at 193°K indicates that the majority of the propane must also be produced by an H-$_2$transfer reaction. Addition of a free-radical scavenger such as oxygen reduces the yield of C_3D_7H relative to the yields of C_3D_8 and CD_3CDHCD_2H.

4. H_2-transfer reactions to other unsaturates such as C_2D_2, C_2D_4, and $CD_3CD_2CDCD_2$ have also been noted to occur with high efficiency. For instance, CD_2HCD_2H is formed with a G value of 2 when a C_5H_{12}–CCl_4 (1:0.03) mixture is irradiated in the presence of C_2D_4. Furthermore, the isotopic composition of the ethane fraction [G(ethane) = 1.5] produced in the radiolysis of a i-C_5H_{12}–i-C_5D_{12}–C_2D_4–CCl_4 (1:1:0.03:0.03) mixture, in the presence of oxygen at 193°K, is as follows: C_2D_6, 43%; C_2D_5H, 2%; CD_2HCD_2H, 48%; C_2H_6, 7%.

Besides confirming[2] the important role ion–molecule reactions can play in the condensed phase, the experimental observations reported above demonstrate that it is feasible to carry out systematic quantitative studies of specific ion–molecule reactions in the liquid and solid phases. The results reported here also indicate that the reactions of the parent ion which occur in the gas phase may be expected to take place with comparable efficiency in the condensed phase. It is, furthermore, of particular interest to point out that the present observations imply that, in the condensed phase radiolysis of larger pure alkanes, reaction of the parent ion with neighboring molecules must be slow and may actually not occur prior to neutralization. This conclusion is consistent with the gas phase radiolysis data,[4d] as well as with the interpretations put forward in a number of recent liquid phase studies.[7–9]

A detailed report on ion–molecule reactions occurring in the liquid and solid phase is forthcoming.

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Oxidation by Molecular Oxygen. III. Oxidation of Saturated Hydrocarbons by an Intermediate in the Reaction of Some Carbenes with Oxygen[1–3]

Sir:

In a continuation of our studies on oxidations by molecular oxygen, and on possible oxygen atom transfer reactions,[3] we have found that saturated hydrocarbons are oxidized at room temperature when some carbenes are generated in oxygen-saturated hydrocarbon solvents.[4] As shown in Table I, extensive oxidation of the hydrocarbon solvent occurs when the carbene source is diazofluorene or diphenyldiazomethane but not when it is diethyl diazomalonate or diazocyclopentadiene. Under the same conditions fluorenone induced no oxidation of the solvent and benzophenone led to the formation of ketone and alcohol in a much different ratio than that observed when diphenyldiazomethane was used. Thus, the solvent oxidation is not due to a light reaction involving the ketone derived from the diazo compound; it is probably due to the reaction of oxygen with some intermediate in the photodecomposition reaction. Control experiments indicate that cyclohexanone is not formed by further oxidation of cyclohexanol but must be formed directly from some intermediate in the reaction.

Table I. The Oxidized Products Obtained from the Photodecomposition of Various Diazo Compounds in Oxygen-Saturated Cyclohexane Solutions[a]

Diazo compd or catalyst	Irradiation time, min	Cyclohexanol yield,[b] %	Cyclohexanone yield,[b] %	Yield of ketone from diazo compd,[b] %
Diazofluorene	300	29	19	55
	125	29	22	...
None	300	<1	<1	...
Fluorenone	300	<1	<1	...
Diphenyldiazomethane	6.3	5.7	2.0	37
	20	10.5	3.6	...
	47	15	6.8	...
	88	21	13	80
Benzophenone	7	1.2	2.4	101
	28	6.3	10.5	104
	52	11	18	101
	71	18	25	100
$N_2C(CO_2Et)_2$	300	<1	<1	...
Diazocyclopentadiene	300	*ca.* 1	*ca.* 0.7	...

[a] In all experiments oxygen was continuously bubbled through the solutions contained in Pyrex, maintained at 25°, and irradiated with a sun lamp. As shown by infrared spectra diazofluorene, diethyl diazomalonate, and diazocyclopentadiene completely react in 2–4 hr and diphenyldiazomethane in less than 1 hr. [b] Assayed by gas chromatography; yields based on the initial amounts of the diazo compounds or ketone catalysts.

The reactivity of the diazofluorene–oxygen system toward primary, secondary, and tertiary hydrogens was determined from the yield of alcohols obtained following lithium aluminum hydride reduction of the products from the oxidation of 2-methylbutane and adamantane. With 2-methylbutane the relative reactivity per hydrogen is: primary, (1); secondary, 15; tertiary, 140. With adamantane it is: secondary, (1); tertiary, 10. The selectivity is somewhat reminiscent of radical reactions although it is greater than that shown by most radical species.[5] In order to distinguish between a hydrogen abstraction and an insertion mechanism for the oxidation, *cis*- and *trans*-1,2-dimethylcyclohexane were oxidized separately by the diazofluorene–oxygen system. Both hydrocarbons give

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[1] Presented at the 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts of Papers, Division of Organic Chemistry, p 14S.

[2] This research was supported by Research Grant GM-09585 from the Division of General Medical Sciences, Public Health Service.

[3] Part II: G. A. Hamilton, *J. Am. Chem. Soc.*, **86**, 3391 (1964).

[4] Under the same conditions aromatic solvents give low yields of phenols (1–3%), and olefinic solvents give a large number of products which have not been investigated further.

[5] R. F. Bridger and G. A. Russell, *J. Am. Chem. Soc.*, **85**, 3754 (1963).

the same mixture of tertiary alcohols. Thus, presumably the oxidation occurs by a hydrogen abstraction mechanism. As determined from competition experiments the isotope effect (k_H/k_D) for the abstraction of hydrogen from cyclohexane is 4.6, and for the formation of ketone from some intermediate is low (probably $k_H'/k_D' = 1.4–1.8$). The value, 4.6, is similar to isotope effects often observed[6] for the abstraction of hydrogen atoms by radical reagents, and 1.4 to 1.8 is similar to the isotope effect observed for the formation of alcohol and ketone from *sec*-alkylperoxy radicals.[6] Stress relaxation measurements during the light-catalyzed autoxidation of a diazofluorene-containing sample of ethylene–propylene rubber indicated that at temperatures above 50° scission of the polymer occurs. The reaction is similar to that observed with samples containing benzoyl peroxide[7] and strongly suggests that radicals are involved in the carbene–oxygen oxidation. Although hydroperoxides are often formed in radical oxidations, none was detected (by titration) following the oxidation of cyclohexane.

The benzophenone-catalyzed oxidation (Table I) is probably due to hydrogen atom abstraction from cyclohexane by the triplet state of benzophenone[8] followed by reaction of the cyclohexyl radical with oxygen and subsequent reactions of the cyclohexylperoxy radical.[9,10] The oxidation caused by the diazo compounds cannot be due to hydrogen abstraction by the carbene because a different ratio of products is formed, and fluorenylidene does not give rise to sufficient abstraction of hydrogen atoms from cyclohexane[11,12] to account for the high yields of oxidized products observed in the present work.[13] Thus, presumably the oxidation is caused by a carbene–oxygen adduct.

It is surprising that our results indicate that the carbene–oxygen adduct acts as a radical species. Carbonyl oxides are intermediates in the ozonolysis of olefins,[15] and there is strong evidence that such intermediates are best represented by a dipolar resonance hybrid I $[R_2C{=}O^+{-}O^- \leftrightarrow R_2C^+{-}O{-}O^-]$.[15] Also, Bartlett and Traylor[16] concluded that the reaction of diphenylcarbene with oxygen leads to a strongly dipolar species. However, their results could be explained if the diradical II $[R_2\dot{C}{-}O{-}\dot{O}]$ reacts much more slowly with another molecule of II, to produce isotopically mixed oxygen, than with other components in the system. The results reported here imply that the carbene–oxygen adduct is II but they could be explained if I reacted with hydrocarbons in such a way that radicals are eventually generated. We suggest that II abstracts a hydrogen atom from the alkane to give an alkyl radical and III $[R_2\dot{C}{-}O{-}OH]$; the alkyl radical may react with II, III, or oxygen to lead eventually to alcohols and carbonyl compounds by steps similar to those involved in other autoxidations of hydrocarbons.[9,10] The reaction of the alkyl radical with II or III could explain the relatively high ratios of alcohol to ketone which are observed.

The carbenes which lead to the largest amount of hydrocarbon oxidation are those which readily become triplets.[17,18] Such carbenes are known to react with oxygen more readily than singlet carbenes.[17,18] It is interesting that the triplet carbene apparently reacts with oxygen (which is a triplet) to give a triplet carbene–oxygen adduct.[19]

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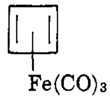
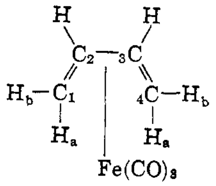
Nuclear Magnetic Resonance Spectra of Cyclobutadiene– and Butadiene–Iron Carbonyl Complexes

Sir:

We wish to report analysis of the H^1 and C^{13} nuclear magnetic resonance spectra of cyclobutadiene–iron tricarbonyl (I) and *cis*-1,3-butadiene–iron tricarbonyl (II).



I



II

The proton resonance spectrum of I consists of a single peak, τ 6.09 ppm, as reported previously,[1] indicating magnetic equivalence of all four protons. From the C^{13} satellites, $J_{C,H} = 191 \pm 1$ cps. Each satellite is a doublet with a splitting of 9 cps.

The C^{13} spectrum of I consists of a single line at -16.2 ± 1.0 ppm ($CS_2 = 0$) and a doublet centered about $+131.8 \pm 1.0$ ppm with a splitting of 191 ± 1 cps. The lower field resonance is in the region characteristic of metal carbonyls[2–4] and the high-field doublet is in the region of other metal carbonyl–

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