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 [$R_2\dot{C}\text{-O-}\dot{O}$] 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 [$R_2\dot{C}\text{-O-OH}$]; 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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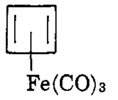
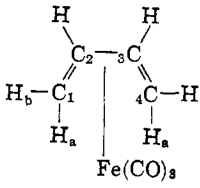
Nuclear Magnetic Resonance Spectra of Cyclobutadiene– and Butadiene–Iron Carbonyl Complexes

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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olefin complexes.[4] The absence of additional splitting in the C^{13} spectrum suggests that the 9-cps splitting of the C^{13} satellites may be the result of a long-range coupling between a ring proton and the single proton directly opposite it on the ring.

The proton resonance spectrum of II has been reported previously.[5] In this investigation proton–proton decoupling experiments and the synthesis of theoretical spectra using the Freqint IV program[6] were used to establish magnitudes of H–H coupling constants. The C^{13} spectrum and proton–proton decoupling experiments were sufficient to determine the following chemical shifts and coupling constants: $\tau_{H_{1a}}$ 9.78 ppm, $\tau_{H_{1b}}$ 8.10 ppm, and $\tau_{H_2} = 4.63$ ppm; $\delta_{C_1} = \delta_{C_4} = +157 \pm 5$ ppm, $\delta_{C_2} = \delta_{C_3} = +112 \pm 5$ ppm, and $\delta_{CO} = -16 \pm 5$ ppm; $J_{H_{1a},H_{1b}} = J_{H_{4a},H_{4b}} = 2.5$ cps, $J_{H_{1a},H_2} = J_{H_{4a},H_3} = 8.2$ cps, $J_{H_{1b},H_2} = J_{H_{4b},H_3} = 6.9$ cps, $J_{H_{1b},H_3} = J_{H_{4b},H_2} = 0.7$ cps, $J_{H_2,H_3} = 4.5$ cps, $J_{C_1,H_{1a}} = J_{C_1,H_{1b}} = J_{C_4,H_{4a}} = J_{C_4,H_{4b}} = 161 \pm 10$ cps, and $J_{C_2,H_2} = J_{C_3,H_3} = 171 \pm 10$ cps.

In II all resonances are shifted to higher fields than in uncomplexed 1,3-butadiene.[7,8] Since these shifts on complex formation are of the same order as for aromatic π-bonding complexes[4,5,7] it seems likely that the bonding in II also involves π-bond interaction with the iron d orbitals rather than direct Fe–C bonding. The large high-field shift of H_{1a} is consistent with the anisotropy associated with the iron carbonyl grouping below the plane of the diene as found by X-ray studies.[9]

The H^1 and C^{13} shifts of I are intermediate between those for H_{1b} and H_2 and C_1 and C_2 in II. The proton resonance is slightly lower than observed for the vinyl hydrogens in norbornadiene–iron tricarbonyl.[5] While C^{13} olefin shifts are relatively insensitive to conjugation, shifts for several molecules have been correlated with π-electron density and free valence parameters.[10–12] In this respect it is interesting that in a plot of C^{13} shift *vs.* H^1 shift, I falls on the same line as do aromatic molecules and ions and their metal carbonyl complexes.[4,10,11] The shifts for II do not.

Experimental measurements and simple theory have shown a dependence of C^{13}–H^1 couplings upon the amount of s character in the C–H bond.[13–15] This coupling in I is much larger than observed for most olefin complexes (155–175 cps) and is intermediate between those of cyclobutene (170 cps)[16] and 1,3,3-trimethylcyclopropene (220 cps).[17] This suggests hybridization of the carbon between sp^2 and sp which is consistent with the strained cyclobutadiene structure. If direct iron–carbon bonding were involved, this strain should approach that in the cyclopropene system and hence the C–H coupling would be larger than observed. However, C–H couplings are strongly sensitive to substituents other than hydrogen and hence a definite conclusion cannot be made. Electronegative substituents have been observed to increase the C–H coupling constant.[14] The apparent absence of a large vicinal H–H coupling and the presence of a longer range interaction in I is uncommon for olefins, but the *cis* vinyl coupling in cyclic olefins is strongly dependent on ring size and decreases to 2.7 cps in cyclobutene and 0.5–1.5 cps in 3,3-dimethylcyclopropane.[16,18–21] Borčić and Roberts[16] suggest that in cyclobutene and cyclopropene this coupling becomes negative. Thus it is possible that in the cyclobutadiene system this coupling is zero or too small to observe. If the cyclobutadiene ring has a true diene structure rather than π-electron delocalization the observed coupling might also be a normal vicinal σ coupling, but this coupling becomes considerably smaller than 9 cps in cyclic dienes as the ring size decreases.[22]

The C–H couplings in II are typical of those in many cyclic olefins, dienes, and their iron carbonyl complexes.[4,7,20] Again, this indicates interaction of the iron d orbitals with the π electrons rather than formation of a carbon–iron bond which would cause large changes in carbon hybridization and hence the C–H couplings. The proton–proton couplings in II cannot all be compared with those in 1,3-butadiene since the latter normally exists in the *trans* rather than the *cis* configuration. The couplings between protons on C_1 and C_2 are all smaller than in 1,3-butadiene but of the same relative magnitudes (*trans* > *cis* > *gem*). Long-range couplings are less in II than in 1,3-butadiene, as would be expected for a *cis* configuration. The couplings J_{H_{1b},H_2}, J_{H_{1b},H_3}, and J_{H_2,H_3} can be compared also with those in cyclopentadiene (5.06, 1.09, and 1.94 cps, respectively) and in cyclohexadiene (9.42, 1.06, and 5.14 cps).[22] As noted earlier, the two vicinal couplings are dependent on ring size. Since both π interaction with iron and delocalization are presumed to occur in the complex II, all of these couplings might be expected to be altered to some extent. No long-range $J_{H_{1b},H_{4b}}$ was observed in II. This interaction is 1.94 cps in cyclopentadiene and 0.91 cps in cyclohexadiene.[22] It is possible that line broadening caused by paramagnetic impurities (*ca.* 1 cps) obscured this coupling.

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