Pritchard[3] and Flygare, Narath and Gwinn[4] suggested the possibility of formation of the radical anion. The electron spin resonance spectrum of cyclopropane radical anion now has been observed.[5]

Sodium metal[6] in tetrahydrofuran[7] produced no observable resonance signal from cyclopropane. Sodium in dimethoxyethane[7] produced a weak signal, inadequate to obtain fine structure. Potassium and rubidium metals separately in dimethoxyethane produced signals of higher intensity, and some fine structure could be observed. The use of a sodium–potassium alloy in 2:1 tetrahydrofuran–dimethoxyethane at $-168°$[8] produced a completely resolved spectrum consisting of seven lines of binomial intensity (1:6:15:20:15:6:1) as expected for interaction with six equivalent protons. The separation between lines is 2.33 gauss with a line width of 0.44 gauss.[9] The g-factor is 2.0027. Calibration was by means of peroxylamine disulfonate. The spectrum disappears on warming to $-100°$ but reappears on cooling again.

The work on cyclopropanes is being avidly continued and is being extended to other systems.[10]

(3) N. Muller and D. E. Pritchard, J. Chem. Phys., **31**, 768 (1959).

(4) W. H. Flygare, A. Narath and W. D. Gwinn, ibid., **36**, 200 (1961).

(5) A Varian Associates V-4500 spectrometer with 100 kc. modulation was used for this work.

(6) The metals were distilled directly into the quartz sample tubes on a high vacuum line.

(7) Solvents were purified exhaustively until a blue solution of potassium could be supported for many days at room temperature.

(8) J. R. Bolton, Mol. Phys., **6**, 219 (1963).

(9) Variation in line width (presumably due to electron exchange with free cyclopropane) and in intensity occurs from sample to sample but the separation between lines is constant at 2.33 gauss.

(10) NOTE ADDED IN PROOF.—Since submission, a number of systems have been observed to present hazard. Some sample tubes have burst with considerable violence even though sealed under high vacuum and stored in liquid nitrogen. The lifetimes vary from minutes to days depending on the compound used.

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Mössbauer Resonance Effects in Iron⁰ Organometallic Complexes

Sir:

We wish to report the Fe^{57} Mössbauer resonance[1] absorption results of a series of diene–iron tricarbonyl complexes and dienyl–iron tricarbonyl complex cations. In common with most other iron compounds, the Mössbauer spectra of these materials consist of two absorption lines of equal intensity. The pertinent data are listed in Table I. The center of gravity of the two lines (δ) and the separation (Δ) are given in millimeters per second.[2]

Group I compounds consist of the neutral diene–iron tricarbonyls, group II contains the salts of the dienyl–iron tricarbonyl cations, while $Fe(CO)_5$ and $Fe(CO)_3$-$(PPh_3)_2$ are listed together as group III. The data for $Fe(CO)_5$[3] and for cyclooctatetraene–iron tricarbonyl[4] have been reported. Our data on splittings agree, but a comparison of the absolute chemical shift is clouded by lack of accepted standards.

It is seen from Table I that the diene–iron tricarbonyl complexes show strong quadrupole splitting and possess a chemical shift within the fairly narrow region $\delta = 0.2$

(1) An excellent introduction to the subject is H. Frauenfelder, "The Mössbauer Effect," W. A. Benjamin Co., New York, N. Y., 1962.

(2) Natural abundance Fe^{57} proved adequate for these studies. A copper–cobalt[57] source was utilized at room temperature in a constant velocity servo-controlled loudspeaker drive system. Spectra were all obtained at 78°K. on thin samples (40–80 mg./cm.²). Type 302 stainless steel absorbs, at room temperature, at -0.325 mm./sec. relative to this Cu–Co[57] source.

(3) L. M. Epstein, J. Chem. Phys., **36**, 2731 (1962).

(4) G. K. Wertheim and R. H. Herber, J. Am. Chem. Soc., **84**, 2274 (1962).

TABLE I
MÖSSBAUER PARAMETERS FOR VARIOUS IRON ORGANOMETALLIC COMPLEXES

	δ_{Cu}, mm./ sec.	Δ, mm./ sec.
Group I		
2-Methoxy-3,5-hexadiene–Fe(CO)₃	-0.218	1.71
racemic-5,6-Dimethyl-1,3,7,9-tetradecaene–Fe₂(CO)₆	$-.216$	1.69
Alloocimine–Fe(CO)₃	$-.214$	1.75
meso-5,6-Dimethyl-1,3,7,9-tetradecaene–Fe₂(CO)₆	$-.208$	1.58
2-Hydroxy-3,5-hexadiene–Fe(CO)₃	$-.202$	1.56
Butadiene–Fe(CO)₃	$-.198$	1.46
7-Acetoxy-bicycloheptadiene–Fe(CO)₃	$-.191$	2.01
1-Phenylbutadiene–Fe(CO)₃	$-.178$	1.59
2,4-Hexadienoic acid–Fe(CO)₃	$-.178$	1.63
Cyclooctatetraene–Fe(CO)₃	$-.140$	1.26
Group II		
1,5-Dimethylpentadienyl–Fe(CO)₃⁺BF₄⁻	-0.126	1.83
1-Methyl-pentadienyl–Fe(CO)₃⁺SbCl₆⁻	$-.126$	1.69
Cyclohexadienyl–Fe(CO)₃⁺ClO₄⁻	$-.122$	1.66
1-Methyl-pentadienyl–Fe(CO)₃⁺ClO₄⁻	$-.117$	1.70
1-Methyl-pentadienyl–Fe(CO)₃⁺BF₄⁻	$-.117$	1.72
Cycloheptadienyl–Fe(CO)₃⁺BF₄⁻	$-.111$	1.57
1-Methyl-pentadienyl–Fe(CO)₃⁺PF₆⁻	$-.103$	1.67
Bicyclooctadienyl–Fe(CO)₃⁺BF₄⁻	$-.098$	1.79
Group III		
Bistriphenylphosphine–Fe(CO)₃	-0.324	2.76
Iron pentacarbonyl	-0.282	2.60

± 0.025 mm./sec. The range of ligands in complexes listed include non-conjugated dienes and substituted dienes as well as tetraene–diiron hexacarbonyl complexes; this range might therefore be considered characteristic of such complexes. The notable exception in group I is cyclooctatetraene–iron tricarbonyl; both in chemical shift and quadrupole splitting this substance appears to be abnormal. The reasons for these deviations are not yet clear. The shift for cyclooctatetraene–$[Fe(CO)_3]_2$ is 0.05 mm./sec. less,[4] which places it in a "normal" position.

These shifts are small compared to those of inorganic salts which, at 78°K., typically give $\delta = +0.35$ for Fe^{3+}, $\delta = +1.20$ for Fe^{2+},[5] and $\delta = -1.0$ for Fe^{6+},[6] converted to the Cu–Co⁵⁷ source.

The cationic complexes listed in group II clearly form a separate group based upon their chemical shift, though they display roughly the same range of quadrupole splitting as seen in the diene–iron tricarbonyl complexes. In contrast to ferrocinium salts,[3,7] the chemical shift and quadrupole splitting of salts of the 1-methylpentadienyl–iron tricarbonyl cation are relatively insensitive to the nature of the anion.

The cations absorb at higher values than do the diene–$Fe(CO)_3$ complexes; however, the effect is small and certainly would not seem large enough to support the suggestion[8] that these complexes be regarded now as Fe^{2+} systems containing a carbanion as a ligand. Even considered as Fe^0 systems bonded to a carbonium ion ligand, the differences between group II complexes and group I complexes seem small. The mean difference in chemical shift between the two is 0.09 mm./sec. Epstein[9] has shown that a difference of 0.04 mm./sec. exists between tris-5-nitrophenanthroline and tris-

(5) S. DeBenedetti, G. Lang, and R. Ingalls, Phys. Rev. Letters, **6**, 60 (1961).

(6) G. K. Wertheim and R. H. Herber, J. Chem. Phys., **36**, 2497 (1962).

(7) G. K. Wertheim and R. H. Herber, ibid., **38**, 2106 (1963).

(8) E. O. Fischer and R. D. Fischer, Angew. Chem., **72**, 919 (1960).

(9) L. M. Epstein, paper delivered at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April 1, 1963.

5-phenylphenanthroline–Fe^{+2} complexes at liquid nitrogen temperature; this difference presumably involves a fairly long range effect and suggests that a greater separation between group I and group II complexes might have been expected.

The small difference between group I and group II may perhaps be rationalized in terms of the duality of the bonding of ligands attached to transition metals in low oxidation states. The carbonium ion ligand might be expected to result in a decrease in electron density, including 4s, in iron in the "forward coordination" when compared to a neutral diene and therefore give rise to a positive chemical shift. However, the back donation of d electrons into the carbonium ion ligand would be stronger than for the diene; the resulting lowering of 3d electron density about iron would decrease the shielding of the 4s electron density and thereby cause a negative chemical shift. The two effects would therefore tend to nullify each other. The net result is a small decrease in effective s density and a corresponding positive shift.

The dominance of forward coordination over back donation is also illustrated in the chemical shifts of $Fe(CO)_5$ and $Fe(CO)_3(PPh_3)_2$ whose stereochemistry differs from the group I and II complexes. The strong electron donating properties of the triphenylphosphine group result in a net negative shift compared to $Fe(CO)_5$.

In contrast to the small effects of chemical bonding on the shift δ, there exists within each group a considerable variation in splitting Δ. The splitting is observed to be greatest for molecules displaying axial symmetry, such as $Fe(CO)_5$, $Fe(CO)_3(PPh_3)_2$, and 7-acetoxy bicycloheptadiene $Fe(CO)_3$. The large effects on the splitting caused by slight structural changes suggests that further analysis of the origins of electric field gradients in these molecules is desirable and may prove helpful in establishing certain stereochemical relations.

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Effect of Solvents on Transition States in the Reactions of *t*-Butoxy Radicals[1]

Sir:

The major products of reaction of *t*-butoxy radicals in the presence of two potential hydrogen donors are determined by the competition

$$(CH_3)_3C\!-\!O\cdot \xrightarrow{k_d} CH_3COCH_3 + CH_3\cdot \qquad (1)$$

$$(CH_3)_3C\!-\!O\cdot + R_1H \xrightarrow{k_{a_1}} (CH_3)_3COH + R_1\cdot \qquad (2)$$

$$(CH_3)_3C\!-\!O\cdot + R_2H \xrightarrow{k_{a_2}} (CH_3)_3COH + R_2\cdot \qquad (3)$$

The rate constant k_{a_1}/k_{a_2} may be measured directly from the relative rates of disappearance of R_1H and R_2H or indirectly by determining k_{a_1}/k_d and k_{a_2}/k_d from *t*-butyl alcohol/acetone ratios obtained in separate experiments in the presence or R_1H and R_2H alone. We wish to report a study of the effect of solvents on these competitions indicating much more significant phenomena than the small solvent effects which have been noted previously in *t*-butoxy radical reactions.[2-4]

TABLE I

DETERMINATION OF k_a/k_d IN REACTION OF *t*-BUTOXY RADICALS WITH CYCLOHEXANE

Solvent	k_a/k_d 100°	k_a/k_d 40°	k_a/k_d 0°	$E_d - E_a{}^a$	log $(PZ)_a/(PZ)_d$
Gas phase	$(203)^b$	$(625)^b$	$(1040)^b$	10.80	-4.77
$C_2Cl_3F_3$	4.29	52.8	487	9.65	-5.04
CH_3CN	$(0.68)^c$	8.12	81.9	9.54	-5.73
C_6H_6	2.82	24.7	207	8.66	-4.63
C_6H_5CN	1.90	16.9	109	8.28	-4.58
C_6H_5Cl	2.65	16.4	91.7	7.21	-3.82
C_2Cl_4	4.14	39.0	293	8.72	-4.49
$C_2H_2Cl_2$ (*trans*)	2.26	14.2	98.9	7.69	-4.16
$C_2H_2Cl_2$ (*cis*)	1.57	9.12	52.2	7.04	-3.92
CH_3COOH	$(0.65)^c$	2.84	12.4	5.80	-3.64

^{a} Difference in activation energies, kcal./mole. ^{b} At 60, 40, and 30° respectively. ^{c} Extrapolated values.

Our technique involves *t*-butyl hypochlorite chlorinations in which reactions 1–3 are steps in a chain sequence, followed by reaction of the radicals produced with *t*-butyl hypochlorite to yield CH_3Cl, R_1Cl, and R_2Cl, respectively, and regenerate $(CH_3)_3C\!-\!O\cdot$.[3] The hypochlorite was decomposed photochemically in excess (5:1) cyclohexane of varying concentrations (0.01–0.5 M) in each of several solvents at 0, 25, 40, 70, and 100° and *t*-butyl alcohol/acetone ratios determined by gas chromatography. Ratios of k_a/k_d then were obtained from plots of alcohol/acetone ratios *vs.* cyclohexane concentration. Plots of log k_a/k_d *vs.* $1/T$ gave excellent straight lines, and some of our ratios, activation energy differences, and ratios of PZ factors are listed in Table I, which also includes gas phase measurements obtained by a slight modification of the same technique.

We see that k_a/k_d ratios vary by over a factor of 100 at the lower temperatures, chiefly as a consequence of changes in the difference in activation energy for the hydrogen abstraction and β-scission processes. As we have pointed out elsewhere[5] solvent effects on competitive radical reactions must reflect different degrees of solvent interaction with the *transition states* rather than with the *radicals* involved (assuming any such "complexing" to be a rapid process) and solvation of the transition state for a β-scission (or other unimolecular radical reaction) is sterically more feasible than solvation of the transition state for hydrogen abstraction. Our results are consistent with this view. Aromatic solvents and the chloroethylenes[6] apparently stabilize the transition state for β-scission by 3–4 kcal. over that for attack on cyclohexane, presumably through the contribution of charge-transfer type structures.

There evidently is no major effect of simple solvent polarity, since energetics in acetonitrile are similar to those in a haloalkane, but the very large facilitation of β-scission in acetic acid suggests that hydrogen bonding is an alternative means of transition state stabilization.[7]

(2) G. A. Russell, *J. Org. Chem.*, **24**, 300 (1959).

(3) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

(4) E. L. Patmore and R. J. Gritter, *J. Org. Chem.*, **27**, 4196 (1962).

(5) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **84**, 1593 (1963).

(6) The chloroethylenes were chosen since they show no significant reaction with *t*-butoxy radicals. We previously have reported a large effect of olefinic solvents on the reactions of the 2-benzyl-2-propyloxy radical.[5]

(7) Evidence for hydrogen bonding of peroxy radicals has been given by F. F. Rust and E. A. Youngman, *J. Org. Chem.*, **27**, 3778 (1962).