erally necessary to assume isotropic motion. Molecules in the liquid state tumble anisotropically,[14] in most cases, and the dependence of the ^{2}H relaxation times on this anisotropic motion is not the same as that of ^{1}H.[15] The angular dependence of the ^{13}C–^{1}H dipole–dipole relaxation is exactly the same as that of the C–D quadrupole relaxation,[14b] which makes it possible to compare values of T_1 for ^{13}C and ^{2}H under any kind of anisotropic motion. Table I shows the observed quadrupole coupling constants and those calculated from the ^{2}H and ^{13}C relaxation times. The agreement is excellent, within 5–7%, with the exception of phenylacetylene where a substantial contribution to ^{13}C relaxation from chemical shift anisotropy is expected. Thus, for small organic compounds, a comparison of the ^{2}H and ^{13}C spin lattice relaxation times provides a facile determination of the deuterium quadrupole coupling constant and mechanism of carbon relaxation.

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Electron Paramagnetic Resonance Study of Free Radicals in an Adamantane Matrix. VII. Aromatic Hydrogen Addition Radicals

Sir:

In past studies of neutral free radicals in an adamantane matrix, the radicals have been formed by removal of an atom or group of atoms from the precursor molecule,[1-17] although we had noted previously that X-irradiation of isobutylene in adamantane produced some *tert*-butyl radical,[5] thus at least suggesting that hydrogen atom addition to a precursor molecule could occur. We have now prepared hydrogen addition radicals from several aromatic molecules and have shown thereby that this is a general method of radical formation in adamantane. We have found that the details of sample preparation are critically important in determining the nature of the predominant radical produced, that is, a hydrogen abstraction radical ($R\cdot$) or a hydrogen addition radical ($RH_2\cdot$). The factors in the sample preparation which favor $R\cdot$ suggested to us that hydrogen atom scavenging by atmospheric oxygen is occurring. To confirm this hypothesis we prepared degassed samples of adamantane containing molecules such as toluene, which can either lose a hydrogen to form benzyl radical or add a hydrogen to form methylcyclohexadienyl radicals. The X-irradiation of degassed samples produced a large predominance of $RH_2\cdot$ whereas the samples prepared without the exclusion of air produced a predominance of $R\cdot$. Inclusion of I_2, which can act as a hydrogen atom trap, in degassed preparations then dramatically decreased the yield of $RH_2\cdot$ but did not noticeably affect the yield of $R\cdot$. Use of adamantane-d_{16} 96% D as a matrix for preparation of $RH_2\cdot$ resulted in about equal amounts of deuterium and hydrogen atom incorporation, thus demonstrating that some of the hydrogen atoms are produced in the bulk adamantane by the radiolysis and suggesting that a very large negative deuterium isotope effect may be involved.

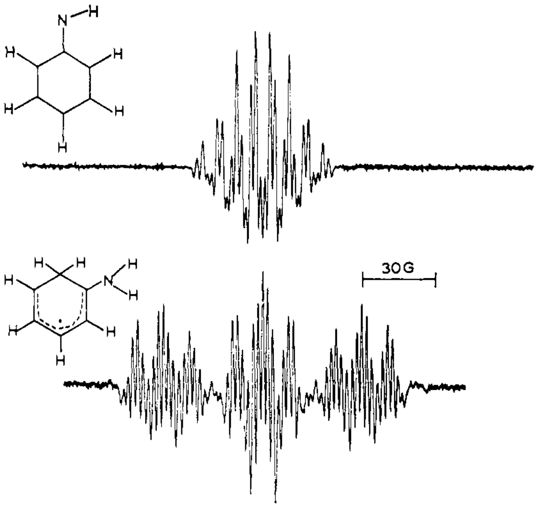

Figure 1. Second derivative epr spectra of anilino radical (top) and 1-aminocyclohexadienyl radical (bottom) in adamantane at room temperature. Both samples were from the same batch, but the upper one was treated for maximum $R\cdot$ radical and the lower one for maximum $RH_2\cdot$ radical as described in the text.

The technique *for preparation of* $R\cdot$ in cases where $RH_2\cdot$ can also be formed involves rapid crystallization of the adamantane by cooling a solution of the desired precursor saturated with prepurified adamantane[6] and with air (or even better with oxygen). The recrystallized adamantane is then vacuum filtered almost to dryness and X-irradiated directly in air. This usually results in >20/1 ratio of $R\cdot/RH_2\cdot$. For hygroscopic

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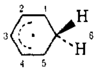
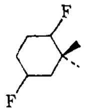
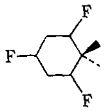
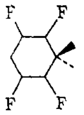
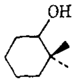
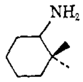
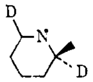
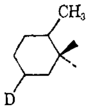
Table I. Hyperfine Splitting Constants (G) for Aromatic Hydrogen Addition Radicals in Adamantane[a]

Radical	Temp, K°	a_1	a_2	a_3	a_4	a_5	a_6	g
	244	9.04	2.77	13.25	2.77	9.04	47.85	2.0028
	265	16.44 (F)	2.60	13.80	7.75 (F)	9.00 (F)	45.66	2.0030
	255	18.00 (F)	2.70	33.30 (F)	2.70	18.00 (F)	45.60	2.0040
	263	19.35 (F)	7.28 (F)	13.32	7.28 (F)	19.35 (F)	45.60	2.0032
	Room temp	<1.0 (H)	2.53	13.13	2.53	9.65	44.65	2.0033
	Room temp	1.96 (N) 1.85 (H)	2.10	13.10	2.10	8.90	41.85	2.0033
	Room temp	5.10 (N)	0.43 (D)	13.50	2.80	10.00	48.81 (H) 7.15 (D)	2.0030
	Room temp	8.65 (CH_3)	2.73	12.88	0.42 (D)	7.15	45.29	2.0032

[a] The hfs quoted are those which give a good fit in computer simulations to the experimental spectra but are thought to be good only to ±0.1 G in most cases.

and/or solid substances such as phenol, a vacuum cosublimation at ~150° followed by crushing in air was found to produce results nearly as good as the above method.

The easiest method for *preparation of* $RH_2\cdot$ in cases where $R\cdot$ can also be formed is to place the recrystallized or sublimed adamantane powder, prepared as above, in an evacuated die (~0.1 mm) for ~1 min and press to ~50,000 psi. The resulting pellet is apparently impervious to rediffusion of atmospheric oxygen and can be handled and irradiated in air. This technique usually results in $>10/1$ ratio of $RH_2\cdot/R\cdot$. Figure 1 shows the room temperature epr spectra of X-irradiated adamantane recrystallized from aniline; the upper trace belongs to a sample treated for maximum $R\cdot$ and the lower trace to a sample treated for maximum $RH_2\cdot$ as described above. The epr spectrum of the anilino radical in the upper trace exhibits a vanishingly small amount of $RH_2\cdot$ as evidenced by the lack of lines in the wings, whereas the lower epr spectrum is primarily of the radical formed by hydrogen addition ortho to the amino group, with lesser amounts of para addition radical causing the small outer lines. It is clear from an examination of this figure that the relative yield of $R\cdot$ and $RH_2\cdot$ can be changed sufficiently to enable separate study of each.

Benzene, toluene, aniline, phenol, and pyridine can all add a hydrogen atom under appropriate conditions to form cyclohexadienyl and substituted cyclohexadienyl radicals. The hydrogen attaches preferentially ortho to the substituent with smaller amounts of para addition. The ortho/para ratio is apparently independent of the amount of hydrogen atom scavenger present but is affected considerably by the presence of deuterium on the ring. For example, 2,6-dideuteriopyridine yields more para addition than normal pyridine and toluene-*4-d* shows less para addition than normal toluene.

Fluorinated benzenes also add hydrogen to form fluorinated cyclohexadienyl radicals. These are ordinary π-type radicals (the fluorine hfs is about twice the proton hfs that it replaces) in contrast to the anion radicals of some of the precursors which have recently been reported to be σ-radicals with extremely large fluorine hfs.[18] The hydrogen is not observed to add to a position occupied by fluorine except in the case of hexafluorobenzene.

Table I summarizes the hfs of several of the $RH_2\cdot$ radicals that we have studied. The cyclohexadienyl radical in adamantane-d_{16} has the same hfs, within experimental error, as those found by Fessenden and Schuler[19] in liquid 1,4-cyclohexadiene during continuous electron irradiation. The hfs of the other radicals in the table, reported here for the first time, show remarkable similarity to the unsubstituted cyclohexadienyl radical. A detailed analysis of the rather complicated overlapping epr spectra obtained for many of these radicals will be published later.

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Mixed Valence Spectrum and Cyclic Voltammetry of Binuclear Iron Cyano Complexes

Sir:

The vast majority of mixed valence compounds is represented by polynuclear crystalline compounds.[1] Complexes with only two metallic centers exhibiting intervalence electron transfer spectra have been recently studied by Taube and by Cowan.[2] In our search for simple systems showing intervalence electronic transitions, we investigated the reaction of $Fe^{III}(CN)_5NH_3{}^{2-}$ with $Fe^{II}(CN)_6{}^{4-}$. Job's method[3] has been applied to solutions containing the two mononuclear complexes showing that a binuclear species is formed. Since the hexacyano complex of low-spin iron(II) is extremely unlikely to undergo ligand substitution, it is assumed that the ammonia molecule of the prusside species is replaced by one nitrogen end of the hexacyanoferrate(II). Thus the binuclear ion $[(CN)_5Fe^{III}NC)Fe^{II}(CN)_5]^{6-}$ is formed, abbreviated as [III-II]. For preparative purposes equivalent solutions of the two mononuclear constituents (1 mmol) were passed over an ion-exchange column (Dowex 50) in the acid form. The resulting solution was titrated with an appropriate base to pH 7 and evaporated to dryness under reduced pressure. *Anal.* Calcd for $Na_6[Fe_2(CN)_{11}]\cdot 2H_2O$: Fe, 19.5; C, 23.1; H, 0.7; N, 27. Found: Fe, 19.4; C, 23.1; H, 1.4; N, 29.1. Identical results were obtained by the combination of $Fe^{II}(CN)_5NH_3{}^{3-}$ and $Fe^{III}(CN)_6{}^{3-}$.

Aqueous solutions of [III-II] show a moderately intense (log $\epsilon \approx 3$) band at 1300 nm (7.7 kK). This band obeys Beer's law at concentrations higher than 10^{-2} *M*. Small deviations at lower concentrations are attributed to partial dissociation of the [III-II] dimer. We assign this low energy band to an intervalence charge transfer [III-II] → [II-III]*. This band is observed at the same wavelength in solution as well as in KBr pellets of the solid binuclear compound. The assignment as charge transfer band is supported by the fact that there is no loss of intensity observed upon cooling a KBr pellet of [III-II] to liquid nitrogen temperature. Evidence for a bridge assisted charge-transfer mechanism is furnished by comparing the spectrum of [III-II] with the one of a solution containing a 1:1 mixture of $Fe(CN)_6{}^{3-}$ and $Fe(CN)_6{}^{4-}$. The extension of earlier work[4] into the near-infrared part of the spectrum did not reveal any band in the 700–1500 nm range.

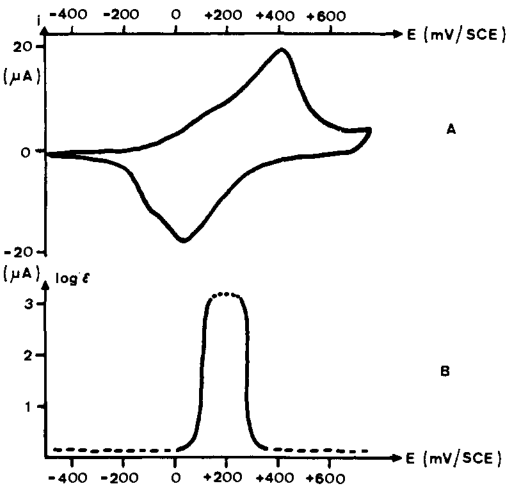

Figure 1. (A) Cyclic voltammogram of 4.5×10^{-4} *M* $Na_6[Fe_2(CN)_{11}]$ in 1 *M* $NaClO_4$, scan rate 0.1 V/min. (B) Extinction coefficient of the 1300-nm intervalence band of $Na_6[Fe_2(CN)_{11}]$ (4.5×10^{-4} *M* in 1 *M* $NaClO_4$) as function of the minigrid potential.

When the asymmetry of the bridging cyanide is neglected the results derived by Hush[5] for symmetrical binuclear mixed valence complexes can be applied. The parameters of the intervalence band (ν, 7.7 kK; ϵ, 3180 M^{-1} cm^{-1}, half-width, 5.1 kK) lead to a delocalization of the optical electron of only about 3%. In fair agreement with the observed value the calculated half-width of the band is 4.2 kK. The small degree of delocalization shows class II behavior[1] of [III-II]. Evidence for trapped valences is also furnished by the infrared spectrum. Two distinct frequencies are observed for the CN stretching vibration at 2060 and 2130 cm^{-1} (KBr pellet of $Na_6Fe_2(CN)_{11}$). These values are to be considered as characteristic for cyano complexes of a two- and three-valent metal.[6]

The electronic spectrum of [III-II] is very similar to that reported for the oxidized form of the dimer of $Fe(CN)_5H_2O^{3-}$.[7] The resulting binuclear species, however, was formulated with two bridging cyanide ligands.

In order to elucidate the optical and electrochemical properties of [III-II], a controlled potential experiment was performed by means of a transparent thin-layer cell.[8] A 0.2-mm flow cell was equipped with a gold minigrid[9] having an optical transparency of 60% (500 lines per in.). The minigrid operates as the working electrode in a potentiostatic circuit used for cyclic voltammetry within the sample compartment (thermostated to 25 ± 0.1°) of a Cary 17 spectrophotometer.

Repeated potential cycling from −400 to +700 mV (*vs.* sce) showed the binuclear species to be readily oxidized and reduced. The overall charge stoichiometry corresponds to

$$2Fe^{3+} + 2e^- \rightleftharpoons 2Fe^{2+}$$

the complex [III-II] being formed as an intermediate at potentials near +200 mV/sce (Figure 1). This re-

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