Table I. Kinetics of Dissociation and Internal Electron Transfer of $(NH_3)_5Co^{III}N$⟨benzene⟩—⟨benzene⟩$NFe^{II}(CN)_5$^{a}
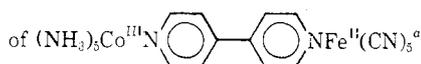
$10^5[Co(NH_3)_5$-$(4,4'$-bipy$)^{3+}]_0$, M	$10^6[Fe(CN)_5$-$OH_2^{3-}]_0$, M	$10^3(k_d + k_{et})$,^{b} sec^{-1}	$10^4 k_{-L}$,^{c} sec^{-1}	$10^3 k_{et}$, sec^{-1}
5.50	14.1	6.9	7.7	2.4
7.28	20.0	6.8	7.7	2.5
7.75	19.5	7.0^d	7.6^d	2.6
8.57	9.3	7.5	7.6	2.5
9.75	9.9	6.9	7.7	2.7
10.0	8.4	7.1	7.6	2.5
10.0	22.9	7.3	8.0	2.7
10.4	9.9	7.1	7.9	2.9
10.4	20.0	7.2	7.8	2.8
11.1	9.6	7.3	8.0	2.8
11.1	11.5	6.7^d	8.0^d	2.8
		7.1^e		7.6
		7.1^e		7.6

^{a} At 25°, pH 8.0 (trizma buffer 5.0×10^{-3} M), $\mu = 0.10$ M (LiClO$_4$), [ascorbic acid] = $(0.51-2.42) \times 10^{-3}$ M, [EDTA^{2-}] = $(0.93-1.86) \times 10^{-4}$ M, [pyridine] = $(4.14-11.0) \times 10^{-2}$ M. ^{b} From measurements at 550 nm. ^{c} From measurements at 450 nm. ^{d} Measurements at 455 nm from time of mixing and fitted simultaneously to a two exponential decay with constants $k_d + k_{et}$ and k_{-L}, respectively. ^{e} This is the concentration of Fe(CN)$_5$(4,4'-bipy)$^{3-}$.

with Fe(CN)$_5$OH$_2^{3-}$, the reaction scheme becomes that shown in Scheme I. Values of $k_{et} + k_d$ were obtained by fitting the observed absorbances A_t at 550 nm to $A_t = A_\infty + (A_0 - A_\infty) \exp[-(k_{et} + k_d)t]$. A_∞ and $k_{et} + k_d$ were taken as adjustable parameters. Values of k_{-L} were obtained by fitting the observed absorbances A_t at 450 nm to $A_t = A_\infty + (A_1 - A_\infty) \exp(-k_{-L}t)$, where values of A_t were taken at sufficiently long times to ensure that less than 2% of I remained, A_1 was the first value of A_t, and A_∞ was measured after ten half-lives. Values of $k_{et} + k_d$ and k_{-L} are listed in columns 3 and 4 of Table I. Additional confirmation for the proposed scheme comes from the ex-

Scheme I

I $\xrightarrow{k_{et}}$ Fe(CN)$_5$(4, 4'-bipy)$^{3-}$

$\searrow k_d$ $\downarrow k_{-L}$

Fe(CN)$_5$py^{3-}
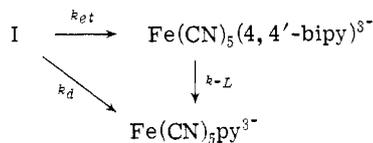
cellent agreement between measurements of the rate of dissociation of Fe(CN)$_5$(4,4'-bipy)$^{3-}$ prepared by reaction of Fe(CN)$_5$OH$_2^{3-}$ with 4,4'-bipyridine (experiments 12 and 13) and measurements in the presence of cobalt.

To obtain values of k_{et} and k_d, the yields of Fe(CN)$_5$(4,4'-bipy)$^{3-}$ and Fe(CN)$_5$py^{3-} before equilibration must be known. Extrapolating the absorbance at 450 nm to the time of addition of pyridine, yielded the fraction of Fe(CN)$_5$(4,4'-bipy)$^{3-}$,f, produced in the reaction if no equilibration takes place as $(A_{extrap} - A_\infty)/(A_{bipy} - A_{py})$, where A_{bipy} and A_{py} are the absorbances Fe(CN)$_5$(4,4'-bipy)$^{3-}$ and Fe(CN)$_5$py^{3-}, respectively, at a concentration equal to the iron concentration in the run. Values of k_{et}, calculated from $k_{et} = f(k_{et} + k_d - k_{-L})$, are listed in column 5 of Table I.

From the average values of $k_{et} + k_d = 7.1 \times 10^{-3}$ sec^{-1} and $k_{et} = 2.6 \times 10^{-3}$ sec^{-1}, we calculate $k_d = 4.5 \times 10^{-3}$ sec^{-1}. From the latter and $k_f = 5.5 \times 10^3$ M^{-1} sec^{-1}, we obtain 1.2×10^6 M^{-1} for the equilibrium constant of reaction 1. This compares favorably with the range $(0.3-2.0) \times 10^6$ for the equilibrium constants of reactions of Fe(CN)$_5$OH$_2^{3-}$ with nitrogen heterocycles.[11] The value of k_f is somewhat higher than the values $(3-4) \times 10^2$ M^{-1} sec^{-1}

for neutral nitrogen heterocycles, and the increase in rate with increasing positive charge of the entering ligand suggests an ion pair, dissociative mechanism for the substitution reactions of Fe(CN)$_5$OH$_2^{3-}$.[12]

The radicals derived by one-electron reduction of protonated 4,4'-bipyridine[13] or the dimethyl derivative (methyl viologen)[14] are relatively stable, and it is appropriate to inquire if a chemical mechanism is operative in the electron transfer mediated by 4,4'-bipyridine. However, the low reducing power of Fe(CN)$_5$OH$_2^{3-}$ ($E^0 = -0.54$ V)[15] combined with the difficulty in reducing protonated 4,4'-bipyridine or methyl viologen ($E^0 = 0.44$ V)[13] render the chemical mechanism unlikely.[16] We suggest that the resonance exchange mechanism is operative and that the slow rate of intramolecular electron transfer is associated with two factors: a symmetry factor with iron(II) being a π-donor and 4,4'-bipyridine a π-conductor, but cobalt(III) being a σ-acceptor, and a spatial factor, the large distance between the two metal centers preventing the coupling of inner-sphere and solvation shell reorganizations necessary for electron transfer.[17] Additional work using other nitrogen heterocycles as electron mediators is in progress.

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(4) R. D. Cannon and J. Gardiner, Inorg. Chem., 13, 390 (1974).
(5) S. S. Isled and H. Taube, J. Amer. Chem. Soc., 95, 8198 (1973).
(6) H. E. Toma and J. M. Malin, Inorg. Chem., 13, 1772 (1974).
(7) The concentration of I must be kept below 2×10^{-5} M to ensure that it stays in solution.
(8) It was found that I decomposed within a few minutes when exposed to ordinary light. Therefore, mixing of cobalt and iron solutions was carried out in the dark.
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(10) The association constant of Fe(CN)$_5$(4,4'bipy)$^{3-}$ with H$^+$, determined spectrophotometrically in the pH range 4–6, is ~2×10^5. At higher acidity, protonation of the cyanide ligands obtains, and the maximum shifts back toward lower wavelengths.
(11) H. E. Toma and J. M. Malin, Inorg. Chem., 12, 2080 (1973).
(12) The inner sphere portion of the Fe(CN)$_5$OH$_2^{3-}$–Co(NH$_3$)$_5$N$_3^{2+}$ reaction has $k = 1.9 \times 10^3$ M^{-1} sec^{-1} and is controlled by substitution in the iron. The rate is intermediate between that of the tripositive ion and rates for neutral ligands.
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(16) Assuming that the minimum ΔG^* is ΔG^0, we calculate $k_{et} = 1 \times 10^{-4}$ sec^{-1}, a value considerably smaller than the observed value 2.6×10^{-3} sec^{-1}.
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Spin Density Distribution in and Rearrangement of a Naphthobicyclobutane Radical Anion

Sir:

A few examples of ring cleavage reactions in radical anions are known[1] which, if concerted, are cycloreversion reactions[2] of the type $_\sigma2_s + _\sigma2_s$. In this communication, we wish to report the results of our nmr and esr studies of the NaK alloy reduction of the naphthobicyclobutane (1)[3] (formally [1',8']naphthotricyclo[4.1.0.0^{5,7}]hept-2-ene), which

Table I. HFSC's[a] in Gauss of the Radical Anions of **1** and **2**

Radical Anion of	p	m	o	β	γ
1	(−) 4.59	(−) 1.95	(−) 1.59	(+) 0.18	(−) 0.88
2[4]	4.89	2.11	1.50	0.19	0.64
					0.93

[a] The signs indicated are based upon an INDO calculation on **1** ⋅⁻ (*vide infra*).

Table II. Theoretical HFSC's for **1** ⋅⁻ Calculated[a] by the INDO Method

		Position		
p	m	o	β	γ
−4.34	−0.93	−1.09	+0.08	−0.50

[a] The known bond lengths of naphthalene and bicyclobutane[13] were used in this calculation. Bond lengths of 1.52 Å were assumed for the bonds joining the naphthalene and bicyclobutane moieties in **1** ⋅⁻. The hfsc's are in units of G.

indicate that the strained radical anion of **1** undergoes a facile ring opening reaction; this reaction, if concerted, represents to our knowledge the first report of a $_\sigma 2_a + _\sigma 2_a$ cycloreversion reaction occurring in a radical anion. This study also affords the first report of the spin density distribution in a radical anion containing the bicyclobutane moiety.

Reduction of a dilute solution ($\sim 10^{-4}$ M) of **1** in 2:1 2-methyltetrahydrofuran–1,2-dimethoxyethane with NaK alloy at *ca.* −110° (EtOH slush) afforded a pinkish red radical anion of **1**; analysis of the esr spectrum of **1** ⋅⁻ recorded at −100° afforded the hyperfine splitting constants (hfsc's) shown in Table I. The assignments of the hfsc's of **1** ⋅⁻ were made by comparison with the hfsc's previously reported[4] for the closely related radical anion of **2** (see Table I).

1   2
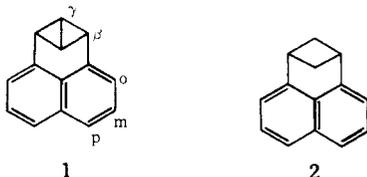
No noticeable changes occurred in the esr spectrum of **1** ⋅⁻ upon warming of the sample to −80°. Upon warming to −60°, however, the esr spectrum of **1** ⋅⁻ began to fade and changed into a rather poorly resolved spectrum that appeared to be due to a mixture of two radical species. Upon continued warming to −20° the observed spectrum was again due to only a single radical species and was analyzed as follows: 6.40 (2 H), 2.70 (2 H), 1.92 (2 H), 0.78 (2 H), and 0.20 G (2 H). This latter spectrum is due to the formation of the radical anion of pleiadiene (**3**), which has previously been reported.[5] Upon recooling of the sample to −100°, the intensity[6] of the esr spectrum of **3** ⋅⁻ was observed to be equal to the intensity of the initial esr spectrum of **1** ⋅⁻ at −100°, which indicates that all of the **1** ⋅⁻ initially present has smoothly rearranged[7,9] to form **3** ⋅⁻ as the only detectable product.

The ring opening of **1** upon reduction with NaK was also confirmed using nmr spectroscopy. Reduction of a 0.3 M solution of **1** in THF-d_8 with NaK at 25° afforded a purplish solution in which the nmr multiplets of **1** were absent and, after extensive contact with the alloy, four new nmr multiplets appeared which were centered at δ 3.26, 3.79, 6.05, and 6.79. A similar reduction of authentic **3** with NaK afforded a purple solution which also exhibited the same four nmr multiplets; we thus assign these nmr multiplets[11] to the pleiadiene dianion. The sample upon quenching with benzoquinone followed by excess water and extraction with ether afforded a residue which contained pleiadiene as determined by nmr analysis.

An INDO calculation[12] on **1** ⋅⁻ afforded theoretical hfsc's for this species (Table II) whose magnitudes were in fairly good agreement with the corresponding experimental hfsc's. This good correlation of the theoretical and experimental splittings of **1** ⋅⁻ together with the close similarity of the

splittings in **1** ⋅⁻ and **2** ⋅⁻ suggests there is probably not a strong interaction of the Walsh π-like orbitals[14] of the bicyclobutane moiety with the homo (Ψ_6) of the naphthalene moiety in **1** ⋅⁻. If present to an appreciable extent, such an interaction[15] might be expected to perturb at least some of the spin densities of **1** ⋅⁻ from the corresponding values observed for **2** ⋅⁻.

Evidence that the geometry of the bicyclobutane portion of **1** (and presumably **1** ⋅⁻ also) is very similar to the geometry of bicyclobutane itself is provided by the ^{13}C nmr data[16] for **1**. The β- and γ-carbon atoms in **1** exhibited ^{13}C–H coupling constants of 162 and 205 Hz, respectively, which are in excellent agreement with the corresponding values of 153 and 205 Hz previously reported[17] for bicyclobutane.

The "driving force" for the transformation of **1** ⋅⁻ into **3** ⋅⁻ almost certainly involves the relief of strain upon ring opening of **1** ⋅⁻; approximately 63 kcal/mol[18] of strain energy is released upon opening of the bicyclobutane ring of **1** ⋅⁻. A second factor which may contribute to the "driving force" is the lowering of the energy of the lowest antibonding MO, which the unpaired electron occupies, upon transformation of **1** ⋅⁻ into **3** ⋅⁻. In **1** ⋅⁻, the unpaired electron occupies Ψ_6 of the naphthalene moiety which has an HMO energy of 0.62$|\beta|$. After ring opening to **3** ⋅⁻, however, the unpaired electron occupies Ψ_8 of the pleiadiene π system which has a lower HMO energy of 0.46$|\beta|$. The potential importance of this latter factor in the ring opening of strained radical anions has previously been emphasized.[19]

The thermal transformation of **1** ⋅⁻ into **3** ⋅⁻ is in sharp contrast to the thermal reaction of neutral **1**, which affords[3] only the naphthocyclobutene **4** upon thermolysis, *via* a

3   4
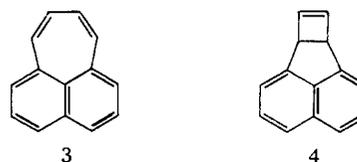
pathway which, if concerted, appears to involve an initial thermally allowed $_\sigma 2_a + _\sigma 2_s$ cycloreversion. Ring opening of **1** to give **3** is also the mode of reaction of the (presumed first) excited state of **1** as previously reported,[3] and a concerted ring opening in this case is a "photochemically allowed" process. Although it is, of course, not possible to demonstrate conclusively that the transformation of **1** ⋅⁻ into **3** ⋅⁻ involves a concerted reaction pathway, a (concerted) cycloreversion of the type $_\sigma 2_a + _\sigma 2_a$ (eq 1) is consistent

$\longrightarrow$ **3** ⋅⁻   (1)
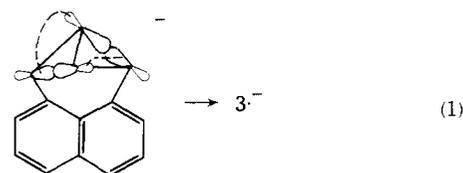
with our experimental findings and is an attractive hypothesis as the mechanism for this transformation.

The species **1**, excited **1**, and **1** ⋅⁻ thus provide a good example of a molecular system in which the chemistry of the

radical anion is the same as that of the excited state of the corresponding neutral molecule and in which the chemistry of the ground state of the neutral molecule is distinctly different from either of the former. That the mode of reaction of a radical anion might parallel the mode of reaction of the lowest excited state of the corresponding neutral molecule can be anticipated.[20] The only difference between the two species in simple theory is that the radical anion contains an additional electron in a lower orbital; both, however, contain one electron in the same frontier orbital, which so often plays a deciding role in determining the extent and direction of chemical reactivity.[2,21]

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(6) The line widths of the esr spectra of $1\cdot^-$ and $3\cdot^-$ were identical; thus the relative heights of comparable lines in the two spectra could be taken as a measure of the relative amounts of $1\cdot^-$ and $3\cdot^-$.

(7) We believe these results indicate that $1\cdot^-$ rearranges to $3\cdot^-$, although the possibility that the dianion of **1** may be the species that undergoes ring opening cannot be rigorously excluded. A mechanism involving disproportionation of $1\cdot^-$ to form **1** and 1^{2-} followed by ring opening of 1^{2-} to 3^{2-} and then electron transfer is also a conceivable pathway for the formation of the observed $3\cdot^-$. In view of the fact that the naphthalene dianion is known[8] to slowly form only in the presence of an excess of a very electropositive metal (*e.g.*, Li), however, such a disproportionation mechanism would seem to be very unlikely in the present case in which the solution was not in contact with the metal alloy at the time the ring opening was observed by esr. In addition, one would expect the dianion of a dialkyl-substituted naphthalene, such as **1**, to form with even more difficulty than that of naphthalene or perhaps not even at all. Thus we strongly favor the viewpoint that $1\cdot^-$ is the species that undergoes ring opening.

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(9) A particularly interesting contrast to the transformation of $1\cdot^-$ into $3\cdot^-$ is the ring opening of $4\cdot^-$ which yields[10] reduction products of $3\cdot^-$ rather than $3\cdot^-$ itself. Different species apparently result from these two reactions. One interesting possibility, which is suggested on the basis of simple correlation diagrams,[10] is that $4\cdot^-$ may undergo ring opening to give excited $3\cdot^-$, which may then be further transformed into the observed[10] initial reduction product of $3\cdot^-$.

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(11) Full details concerning the nmr spectrum of 3^{2-} will be published separately.

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(15) The apparent absence of such a strong interaction in the case of $1\cdot^-$ is perhaps not surprising since only one of the scf MO's of bicyclobutane derived from an *ab initio* scf calculation[14b] has the proper symmetry (A_2) to mix with the Ψ_6 MO of the naphthalene moiety in this species ($1\cdot^-$) having C_{2v} symmetry.

(16) DMSO-d_6 was used as the solvent for the nmr sample with TMS as the internal reference. The β and γ ^{13}C resonances were at δ 45.5 and 14.5, respectively, and the aromatic ^{13}C resonances were at δ 126.4, 130.1, 131.0, and 139.4. Some of the aromatic ^{13}C resonances were superimposed, resulting in only four distinct aromatic ^{13}C resonance lines.

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(20) Even though a sufficiently strong interaction between the bicyclobutane and naphthalene moieties in $1\cdot^-$ is not present to noticeably perturb the spin densities in $1\cdot^-$, conceptually, for a concerted ring opening of $1\cdot^-$, one must postulate that there is at least some interaction between these two moieties with consequent spin delocalization into the bicyclobutane moiety such that the $_\sigma 2_a + _\sigma 2_a$ cycloreversion, which is forbidden and not observed in the case of **1**, becomes a favorable "allowed" process in the case of $1\cdot^-$. Such an interaction presumably would involve the bicyclobutane MO which has A_2 symmetry.[14b]

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