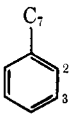
assigned, the chemical-shift assignments of Table I were consistent in that the C_3 chemical shift—the shift expected to be least affected by the substituent—was always closest to that for benzene (except for benzyl chloride, where the chemical shifts for C_2 and C_3 were almost the same).

The most obvious trend from Table I is the correlation between the magnitude of J_{17} and the hybridization of C_7. Increasing the s character of C_7 causes J_{17} to increase from 44.19 Hz in the sp^2–sp^3 system of toluene to 80.40 Hz in the sp^2–sp system of benzonitrile. This trend is quite consistent with previously proposed empirical expressions[3] which have been used to predict bond hybridization in strained systems.[8]

Another trend involving the C-1 carbon atom is the increase in J_{17} as the electronegativity of the C-7 substituent increases, for both the carbonyl and the sp^3 cases. However, this substituent effect is several times larger for the carbonyl series (*e.g.*, as -OH changes to -Cl, J_{17} changes by 0.06 and 2.48 Hz for the sp^3 and sp^2 cases, respectively). This observation is consistent with earlier work, where it was shown that $^1J_{C-C}$ values for acetyl compounds[4] vary to over 50%, whereas this variation for *tert*-butyl compounds[7] is much more modest. Perhaps this large difference between carbonyl and sp^3 systems is due to the polarizability of the carbonyl group.

As expected, the magnitude of the J values in Table I is attenuated dramatically beyond the first bond. For these long-range J_{C-C} values, again hybridization and substituent trends are observed. As the s character of C-7 increases, again the magnitude of J_{C-C} increases for J_{37} and J_{47} (but remains the same, or decreases slightly, for J_{27}). As the substituent becomes more electronegative, again the magnitude of J_{C-C} increases for both the sp^2 and sp^3 cases for all the long-range values J_{27}, J_{37}, and J_{47} (except for the sp^3 J_{47} values, where the trend may be reversed). As in the case of J_{17} values, the substituent effect for the long-range J values is much more pronounced for the sp^2 case than for the sp^3 case.

The observation that the three-bonded coupling constant J_{37} is larger than the two-bonded coupling constant J_{27} is most striking. In view of this remarkable observation, ^{13}C-7 *p*-nitrotoluene was synthesized to verify the coupling pattern. For this molecule, whose chemical-shift assignments have been rigorously established,[16] again J_{37} was larger than J_{27} (3.88 and 3.47 Hz, respectively). The observation that $J_{37} > J_{27}$ in the present system, **1**, is quite analogous to the geometrically identical J_{CH} system in benzene (**2**) where $J_{H_1-C_3} > J_{H_1-C_2}$ (7.4 Hz > 1.0 Hz),[17] but is in contrast to the geometrically identical J_{CF} system in fluorobenzene (**3**)



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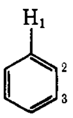

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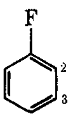

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where $J_{F-C_3} < J_{F-C_2}$ (7.7 Hz < 21.0 Hz).[18]

Acknowledgment. We should like to acknowledge support for this work by the Robert A. Welch Foundation, Grant No. B-325, and by North Texas State University Faculty Research.

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(17) F. J. Weigert and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2967 (1967).

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(19) Robert A. Welch Postdoctoral Fellow, 1970–1972.

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Ligand-to-Metal Intramolecular Electron Transfer in the Reduction of *p*-Nitrobenzoatopentaamminecobalt(III) Ion[1]

Sir:

The hydrated electron, e_{aq}^-, generated in the radiolysis of aqueous solutions, reacts with coordination complexes of cobalt(III) with specific rates very near to the diffusion-controlled limit[2] quantitatively generating Co^{2+}.[3] However, in all the cases reported, no transient species have been detected by pulse radiolysis from the reaction of e_{aq}^- with simple pentaammine complexes.[4–6] These negative results imply either that the electron initially attacks the ligands followed by very rapid intramolecular electron transfer to the metal center or that attack is *via* tunnelling directly into the orbitals of the tripositive metal. We wish to report that the reaction of e_{aq}^- and the reducing radicals $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ with $p\text{-}O_2NC_6H_4CO_2Co^{III}(NH_3)_5^{2+}$ (PNBPA) generates a transient intermediate ($PNBPA^-$) in which the transferred electron is localized on the coordinated *p*-nitrobenzoato ligand; $PNBPA^-$ decays *via* ligand-to-metal intramolecular electron transfer to form Co^{2+}.[7]

The radiolysis of aqueous solutions generates e_{aq}^-, OH, and H radicals with G values (number of molecules produced per 100 eV of energy absorbed) of 2.8, 2.8, and 0.6, respectively.[8] In a N_2O-saturated solution (2.5×10^{-2} M), e_{aq}^- is efficiently scavenged

$$e_{aq}^- + N_2O \longrightarrow OH + N_2 + OH^-$$
$$k = 5.6 \times 10^9\ M^{-1}\ \text{sec}^{-1}$$

The reducing radicals $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ can be generated conveniently

$$OH/H + HCO_2^- \longrightarrow \cdot CO_2^- + H_2O/H_2$$
$$k = 2.5 \times 10^9/2.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$$
$$OH/H + (CH_3)_2CHOH \longrightarrow (CH_3)_2\dot{C}OH + H_2O/H_2$$
$$k = 1.3 \times 10^9/5.0 \times 10^7\ M^{-1}\ \text{sec}^{-1}$$

N_2O-saturated neutral aqueous solutions of PNBPA (as the ClO_4^- salt)[9] in the presence of 0.1 M formate

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(1) Supported in part by NSF Grant GP 11213 and by NIH Grant GM 13557.

(2) E. J. Hart and M. Anbar, "The Hydrated Electron," Wiley-Interscience, New York, N. Y., 1970.

(3) D. Katakis and A. O. Allen, *J. Phys. Chem.*, **68**, 1359 (1964); N. Zevos, *ibid.*, **72**, 1506 (1968).

(4) J. H. Baxendale, E. M. Fielden, and J. P. Keene, *Proc. Roy. Soc., Ser. A*, **286**, 320 (1965).

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(6) The transient observed in the reaction of e_{aq}^- with $Co(bipy)_3^{3+}$ has been attributed to low-spin Co(II): W. L. Waltz and R. G. Pearson, *J. Phys. Chem.*, **73**, 1941 (1969).

(7) $Co(NH_3)_5^{3+}$ is also reduced to Co^{2+} by $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$, as well as by e_{aq}^-: E. P. Vanek and M. Z. Hoffman, manuscript in preparation.

(8) M. Anbar in "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Wiley-Interscience, New York, N. Y., 1968, p 651.

(9) The complex was synthesized using the procedure of E. S. Gould

Table I. Decay of PNBPA$^-$

Reactive species	[PNBPA], *M*	Solute present	Gas purge	pH	Dose/pulse, krads	$10^{-3}k$, sec^{-1}
e_{aq}^-	5.0×10^{-4}	1.0 *M tert*-butyl alcohol	Ar	7.7	2.4	2.9
	5.0×10^{-4}	1.0 *M tert*-butyl alcohol	Ar	7.7	2.4	2.7
	5.0×10^{-4}	1.0 *M tert*-butyl alcohol	Ar	7.7	4.0	3.1
	5.0×10^{-4}	1.0 *M tert*-butyl alcohol	Ar	7.7	4.0	2.9
	8.3×10^{-5}	0.2 *M tert*-butyl alcohol	Ar	7.7	2.4	2.5
	8.3×10^{-5}	0.2 *M tert*-butyl alcohol	Ar	7.7	2.4	2.5
$\cdot CO_2^-$.	5.0×10^{-4}	0.1 *M* HCO_2^-	N_2O	7.1	2.4	2.0
$(CH_3)_2COH$	1.0×10^{-4}	0.1 *M* 2-propanol	N_2O	5.5	0.75	2.4
	1.0×10^{-4}	0.1 *M* 2-propanol	N_2O	5.5	0.75	2.5
					Av	2.6×10^3 sec^{-1}

were subjected to a 30-nsec pulse of 2.3-MeV electrons and the resulting transient optical absorption spectrum was recorded.[10] Figure 1 shows the transient spectrum from $\cdot CO_2^-$ + PNBPA; for comparison, the transient spectrum from $\cdot CO_2^-$ + *p*-nitrobenzoate (free ligand; PNB) is also shown. It is obvious that the spectra of the transient species from the reduction of PNBPA and PNB by $\cdot CO_2^-$ are identical. Furthermore, the identical absorption spectrum was obtained from the reaction of $(CH_3)_2\dot{C}OH$ + PNBPA and e_{aq}^- + PNBPA (in the presence of *tert*-butyl alcohol as an OH radical scavenger). All the evidence indicates that both external electron transfer from $\cdot CO_2^-$ and $(CH_3)_2\dot{C}OH$ and direct e_{aq}^- attack generate the reduced form of the complex, PNBPA$^-$, in which the added electron is localized on the *p*-nitrobenzoato ligand, $O_2\dot{N}C_6H_4CO_2Co^{III}(NH_3)_5^+$. By following the formation of the transient spectrum, the rate constants for these one-electron transfer reactions were determined

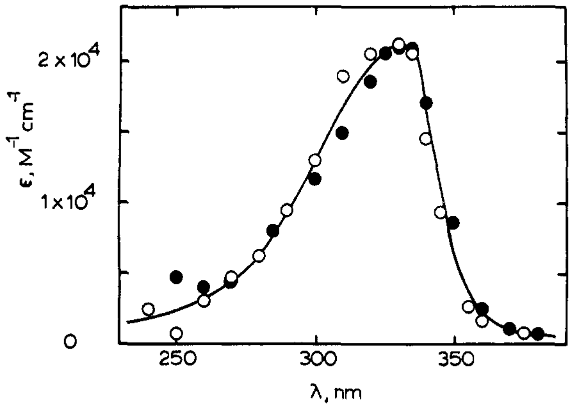

Figure 1. Transient absorption spectrum generated from the reaction of $\cdot CO_2^-$ with (a) 2×10^{-4} *M* *p*-$O_2NC_6H_4CO_2Co^{III}(NH_3)_5^{2+}$, pH 5.6, 0.1 *M* HCO_2^- (●); (b) 2×10^{-4} *M* *p*-$O_2NC_6H_4CO_2^-$, pH 7.0, 0.1 *M* HCO_2^- (○). Dose/pulse = 1 krad. ε values are corrected for the consumption of the substrate.

$$\cdot CO_2^- + PNBPA \longrightarrow PNBPA^- + CO_2$$
$$k = 1.9 \times 10^9\ M^{-1}\,sec^{-1}$$
$$(CH_3)_2\dot{C}OH + PNBPA \longrightarrow PNBPA^- + (CH_3)_2CO + H^+$$
$$k = 2.6 \times 10^9\ M^{-1}\,sec^{-1}$$

In comparison, $k(e_{aq}^- + PNBPA) = 8.0 \times 10^{10}\ M^{-1}\,sec^{-1}$.

The disappearance of the absorption spectrum of PNBPA$^-$, monitored at 350 nm, is *via* first-order kinetics independent of [complex], radiation dose, or method of generation (Table I) with an average value of $k = 2.6 \times 10^3$ sec^{-1} (±20%). The decay of the transient does not generate any permanent product absorbing at $\lambda > 300$ nm. In comparison, the electron adduct to the free ligand, PNB$^-$, decays *via* second-order kinetics and generates a strongly absorbing permanent product, presumably *via* disproportionation–combination processes.

The steady-state radiolysis[11] of an O_2-free solution of 1×10^{-3} *M* PNBPA in 0.2 *M* formate at pH 3.8 (acetic acid buffer) generates Co^{2+} [12] with a value of $G(Co^{2+}) = 6.3 \pm 0.3 = [G(e_{aq}^-) + G(\cdot CO_2^-)] = [G(e_{aq}^-) + G(OH) + G(H)]$. There can be absolutely no question that PNBPA$^-$ decays *via* ligand-to-metal intramolecular electron transfer with the concomitant release of the ligands into solution.

$$O_2\dot{N}C_6H_4CO_2Co^{III}(NH_3)_5^+ \longrightarrow Co^{2+} + O_2NC_6H_4CO_2^- + 5NH_3$$
$$k = 2.6 \times 10^3\ sec^{-1}$$

This appears to be the first reported observation of the intermediate produced when an electron is initially transferred to a ligand of a metal complex and the measurement of the rate of transmission of that electron through the ligand into the metal center. In our previous communication on e_{aq}^- + $C_6H_5CO_2Co^{III}(NH_3)_5^{2+}$ (BPA), we pointed out[5] that no transient was observed within the time resolution of the pulse instrumentation (~0.5 μsec).[13] Inasmuch as the electron adduct to $C_6H_5CO_2^-$ shows a very intense absorption maximum at 310 nm (ϵ_{310} $2.5 \times 10^4\ M^{-1}\,cm^{-1}$),[14] it is certain that if the electron were localized on the benzoato ligand for a period of time in excess of the instrumental time limitation, the transient would be observed. Thus, *if* initial electron attack on BPA occurs at the benzoato ligand, the specific rate of intramolecular electron transfer must be $>10^7$ sec^{-1}. If the nature of electron attack on BPA were similar to that on $C_6H_5CO_2^-$, then the incoming electron would add to a π orbital conjugated throughout the ligand.[14] The overlap of the metal orbitals with those of the carboxylate ligand would provide an extremely

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and H. Taube, *J. Amer. Chem. Soc.*, **86**, 1318 (1964); elemental and spectral analysis established its purity.

(10) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 73, 3794 (1969).

(11) Total dose up to 7×10^{17} eV; maximum decomposition of the complex <10%.

(12) Analyses for Co^{2+} were performed as described by E. R. Kantrowitz, M. Z. Hoffman, and J. F. Endicott, *J. Phys. Chem.*, 75, 1914 (1971).

(13) An attempt to observe this transient with the pulse apparatus at the Christie Hospital, Manchester, England, with a time resolution of 0.1 μsec was also unsuccessful. Assistance of Dr. J. H. Baxendale is gratefully acknowledged.

(14) M. Simic and M. Z. Hoffman, *J. Phys. Chem.*, in press.

facile pathway for electron transmission consistent with the lower limit of the rate constant. In PNBPA, on the other hand, the strongly electrophilic nitro group serves as a trap for the attacking or transferred electron so that electron transmission into the metal center is considerably slower. The reaction of e_{aq}^- with aromatic nitro compounds shows the effect of electron localization of the NO_2 group[15] with the pK_a for the protonation–deprotonation of these radicals having values of 2.2–3.9.[16]

These results are of relevance to electron-transfer processes involving external reducing agents.[17] However, it is premature at this time to attempt to account for the behavior of PNBPA when reduced by Cr(II)[18] on the basis of the observations reported here involving much simpler one-electron reducing agents.

Acknowledgment. We thank Dr. E. Hayon for his interest in this work and for making the pulse radiolysis apparatus available to us.

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(19) (a) Boston University; (b) University of Texas; the encouragement of Professor E. L. Powers is appreciated.

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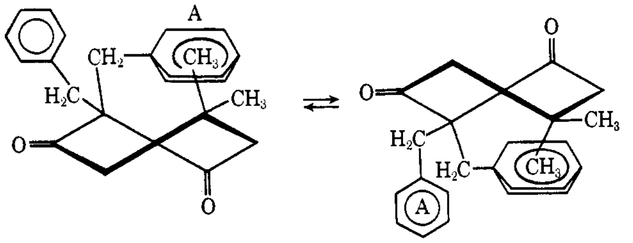
Experimental Demonstration of the Relative Flexibility of Boat and Chair Forms of the Cyclohexane Ring

Sir:

It is generally recognized that eclipsing interactions are diminished in the boat forms of cyclohexanones, and, as a result, a number of cases of monocyclic alkyl-substituted cyclohexanones existing nearly exclusively in a twist-boat conformation have been identified.[1] The latter is often called the flexible form, a reference to the mechanical mobility of ball and stick models which can be easily distorted and interconverted among the variety of possible conformations. In contrast, the chair cyclohexane is designated as the rigid form because of the mechanical resistance experienced in conformational transformations of the models.[2,3] However, actual differences in mobility of the boat and chair forms have never been demonstrated[4] experimentally, *i.e.*, by any direct measurement of *molecular* rather than model energy parameters. Thus, it has always been a matter of interest as to whether the mechanical properties of the model in any way reflect factors inherent in the molecular structure to which analogy is presumed.

We now present direct evidence of the greater mobility of the boat as compared to the chair form gathered in studies of the pmr spectra of 1,1-dimethyl-4,4-dibenzylcyclohexane (**1**) and its derivatives. In view of earlier observations[1] and generalizations[2] (cited above) we can confidently anticipate that the 3,5-diketone **2** would manifest all the features of the boat form. Thus, its pmr shows only three sharp singlets, aside from the phenyl multiplet grouping centered on *ca.* 430.2 Hz. These singlets are structurally correlated in Table I. Precisely the same spectrum is seen at temperatures below $-80°$. This suggests that low temperatures do not freeze out any important modes or seriously interfere with the flexibility, hence interconvertibility, of the boat conformations.

In support of this conclusion is the unusually high field of the methyl singlet, 19.5 Hz, which is to be identified with conformations of **2** bringing the respective methyl groups within the shielding cones of the transannular benzene rings in rapid alteration. Only an extremely flexible motion sweeping the groups attached at the bowsprit (1,4) positions back and forth could accommodate these pmr characteristics of the twist-boat conformation of **2**. Furthermore, this mobility of boat–boat interconversions persists at temperatures far below that required to observe slowing (half-peak separation, $-66.7°$)[3] of the rate of chair–chair interconversions.



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On the other hand, the parent molecule **1**, which in the boat form is characterized by serious eclipsing interactions among the substituents of the cyclohexane ring, would be expected to prefer the chair conformation. The pmr of **1** clearly reveals it to be in an exceedingly rigid chair even at ambient temperatures (see Table I). It exhibits two widely separated, sharp, methyl singlets corresponding to very different environments of these groups, which, apparently, are very resistant to interconversion. Furthermore, neither of these methyl singlets is unusually shielded, in keeping with chair conformations in which the shielding cones of the transannular benzene rings are far removed from influencing the methyl resonances. Moreever, there are also to be noted two distinct benzylic methylene absorptions, which are indicative of a lack of mobility in conformational interconversions, and quite different than was demonstrated (above) for the twist-boat **2**. Finally, we note in the spectrum of **1** the broad band of unresolved multiplets ranging from 92 to 44 Hz. These comprise the absorptions of the

(1) See, for examples, N. L. Allinger and H. M. Blatter, *J. Amer. Chem. Soc.*, 83, 994 (1961), and C. Djerassi, E. J. Warawa, J. M. Berdahl, and E. J. Eisenbraun, *ibid.*, 83, 3334 (1961).

(2) For a discussion of these terms, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 204 *et seq.*, and P. Hazebroek and L. J. Oosterhoff, *Discuss. Faraday Soc.*, 10, 87 (1951).

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(4) Possible indirect demonstrations of the flexibility of the twist-boat conformation could be deduced from various data reported by: (a) N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, 82, 2393 (1960); (b) E. W. Garbisch and D. B. Patterson, *ibid.*, 85, 3228 (1963); and (c) H. Booth and G. C. Gidley, *Tetrahedron Lett.*, 1449 (1964).