

about 3 kcal/mol. Energy level 2 dominates level 1 for a very simple reason. Since MO's 2 have a planar node bisecting the C-C bond, they require a larger normalizing coefficient than do MO's 1. This results in larger coefficients at the hydrogens, and a greater end-to-end interaction. Coulson has emphasized this factor in the MO theory of bonding.⁹ This effect is good reason for expecting the higher occupied MO's to often dominate the others when considering end-to-end orbital interactions in conformational studies.

The reason for the nondegenerate MO's being so unimportant is that their high symmetry at the methyl groups results in very little preference for eclipsed *vis-à-vis* staggered.

Studies of the ethane barrier have been made by other methods. The studies by Pople, *et al.*,³ using a perturbed localized bond model as well as SCF MO calculations led to the conclusion that the barrier was due to end-to-end hydrogen repulsions produced by partial multiple bond character. It thus appears that the above simple analysis based on EHMO results is in some accord with conclusions derived from more accurate (but less transparent) methods.

The above considerations fit quite naturally into the usual π orbital arguments for conjugated systems⁷ if we denote the methyl group as a hyperconjugative extension of the molecule. Then ethane becomes analogous to butadiene, with staggered ethane being preferred for the same reason that *trans*-butadiene is preferred.⁷ The highest occupied (π) MO (HOMO) is end-to-end antibonding. Hoffmann and Olofson⁷ have utilized this device for predicting the most favorable position for the methyl group as a whole. Here we extend it to predict the more favorable conformation.

In propene, the HOMO is π bonding in the vinyl group and π antibonding in the formally single C-C bond. Thus, this MO again corresponds to the highest occupied butadiene π MO and favors a methyl conformation wherein one methyl C-H bond is *cis* coplanar with the vinyl group.¹⁰ This has been observed to be the favored conformer in propene and, indeed, in almost every molecule studied having a double bond adjacent to a methyl rotor.² Removal of electrons from the HOMO should reduce the torsional barrier. Since the lowest empty MO is π antibonding in the vinyl group, the $\pi^* \leftarrow \pi$ excited molecule, or the anion, should also have a reduced barrier.

Molecules in which a double bond is one more bond distant also appear to be properly handled by this approach. Thus, to achieve the preferred "U" shape⁷ for a five-membered system, methyl formate must have

(9) C. A. Coulson, *Mol. Phys.*, **15**, 317 (1968).

(10) There are eight lower MO's, and some of these change in energy more (as much as four times) than does the HOMO. Some of these MO's do not require a node in the C-C-C plane, and in such cases the in-plane methyl and vinyl protons will have nonzero coefficients, in contrast to the HOMO. Since some of these protons approach each other rather closely in the stable rotameric form, these MO's undergo relatively large energy changes upon internal rotation. In our calculations, these MO energy changes cancelled to such an extent that the final energy difference was almost identical with that due to the HOMO alone. However, these lower MO energy changes are understandably sensitive to changes in structural parameters and choice of hydrogen 1s function exponent. Furthermore, the EHMO calculations gave a barrier of roughly one-half that observed. Obviously, we have no grounds for claiming that the hyperconjugative interaction is the sole or even major factor in this case. It does appear, however, to work in the same "direction" as the net barrier.

the methyl group *cis* and staggered with respect to the carbonyl oxygen, as is observed.¹¹

The barrier in methanol (O-H assumed in plane of paper) is produced by MO's related to forms **1a** and **2a**. (These are roughly reproducible by removing the two small hydrogen functions from one end of the forms **1a** and **2a** above.) By symmetry, MO's related to **1b** and **2b** do not change energy at all. Presumably, this reduction from two *pairs* of participating orbitals to two individual orbitals is partly responsible for the observed fact that the barrier in methanol is smaller than that in ethane.

We feel that the results described here provide a partial basis for a much needed, simple approach to barriers. Clearly, it is not a method which will be infallible or quantitative.¹⁰ It should augment, rather than replace, the computational efforts of recent years.

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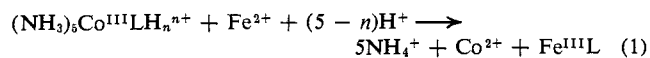
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A Binuclear Intermediate Preceding the Cobalt(III)-Iron(II) Electron Transfer Process

Sir:

Redox reactions between metal ions are commonly thought of as proceeding in two stages: (i) formation of a binuclear precursor complex with original valencies unaltered, and (ii) intramolecular electron transfer. The two processes are not necessarily distinct in all cases, but when they are so, it becomes of interest to evaluate their respective contributions to the overall activation free energy. Evidence of precursor complexes has been found in the azide-catalyzed exchange between ferrous and ferric ions,¹ and more recently in the Co^{III}-Cr^{II} system,^{2,3} but in both cases the intermediate is short-lived (estimated lifetime, $\leq 10^{-6}$ sec in the Co^{III}-Cr^{II} system); and in other systems the same conclusion has been drawn from the expected thermodynamic stability of the precursor complexes.^{4,5} We have studied a Co^{III}-Fe^{II} reaction, and we now report what appears to be the first measurement of the lifetime of a precursor complex.

Nitrilotriacetic acid forms a pentaamminecobalt(III) complex in which the tertiary nitrogen and two carboxyl groups remain free to coordinate a second metal ion. In acid solution the predominant species is RoLH_2^{2+} , where $\text{Ro} \equiv \text{Co}^{\text{III}}(\text{NH}_3)_5$ and $\text{L}^{3-} \equiv \text{N}(\text{CH}_2\text{COO})_3^{3-}$; and by pH titration, $\text{p}K_{a1} = 1.82$ and $\text{p}K_{a2} = 7.96$ at 25°, ionic strength 1.0 (NaClO_4). In a glycine buffer (pH 1.3-3.4), reaction with Fe^{2+} proceeds according to the equation



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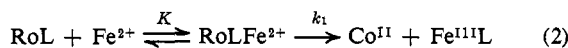
(2) M. P. Liteplo and J. F. Endicott, *J. Amer. Chem. Soc.*, **91**, 3982 (1969).

(3) R. C. Patel, R. E. Bell, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).

(4) R. D. Cannon and J. E. Earley, *J. Amer. Chem. Soc.*, **88**, 1872 (1966).

(5) W. G. Movius and R. G. Linck, *ibid.*, **91**, 5394 (1969).

and the kinetics are consistent with a bridged mechanism involving chelation of Fe^{2+} prior to electron transfer



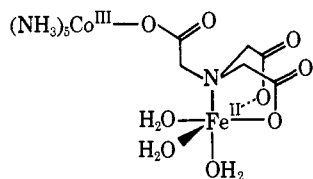
$$-\frac{d}{dt}[\text{Co}^{\text{III}}] = k_1[\text{RoLFe}^{2+}] = \frac{k_2[\text{Fe}^{\text{II}}][\text{Co}^{\text{III}}]}{1 + \{\text{H}^+\}^2/K_{a1}K_{a2} + \{\text{H}^+\}/K_{a2} + K[\text{Fe}^{\text{II}}]} \quad (3)$$

where

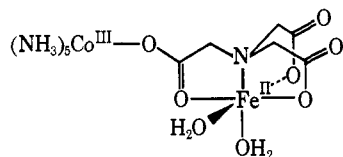
$$k_2 = k_1K \quad (4)$$

The term "1" in the denominator of eq 3 is negligible under all the conditions used. At low pH, with ferrous ion in moderate (*ca.* 20-fold) excess over cobalt(III), the reaction is pseudo-first order in $[\text{Fe}^{\text{II}}]$. We observe $k_2 = 1.0 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° , ionic strength 1.0 M (NaClO_4), confirming that the polydentate ligand greatly facilitates electron transfer (*cf.* $\text{L} = \text{Cl}^-$, $k_2 = 1.35 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$; $\text{L} = \text{C}_2\text{O}_4^{2-}$, $k_2 = 0.43 \text{ M}^{-1} \text{ sec}^{-1}$).^{6,7} At higher ferrous concentrations and at the upper end of the pH range the rate approaches a limit, as required by eq 3; whence $K = 1.1 \times 10^6 \text{ M}^{-1}$ and $k_1 = 9.4 \times 10^{-2} \text{ sec}^{-1}$, corresponding to a lifetime of about 10 sec.

The formation constant, K , of the binuclear complex is comparable with that of the N-methyliminodiacetato-iron(II) complex ($4.5 \times 10^6 \text{ M}^{-1}$ at 20° in 0.1 M KCl^8), suggesting the presence of two chelate rings; and the spectrum from 300 to 760 nm shows only the characteristic bands of the pentaamminecobalt(III) and iron(II) chromophores, so that there is little doubt that the oxidation states are as shown. Hence we favor structure I for the predominant form of the intermediate, which could be described as an outer-sphere association complex of cobalt(III) and iron(II), in which the two metal ions also happen to be linked by a "nonconducting" carbon-nitrogen chain. It does not follow, however, that the electron is transferred directly across the intervening space; a carboxyl-bridged transition state (II), formed by rapid elimination of H_2O , is equally consistent with the data.



I



II

Further work on reactions with other divalent metals is in progress.

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(7) C. Andrade and H. Taube, *ibid.*, **5**, 1087 (1966).

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Rapid Interchange of Monohapto- and Pentahaptocyclopentadienyl Rings in Tetracyclopentadienyltitanium

Sir:

The first molecule containing both an ($h^1\text{-C}_5\text{H}_5$) and an ($h^5\text{-C}_5\text{H}_5$) group attached to the same metal atom to be studied as a function of temperature by nmr spectroscopy was ($h^5\text{-C}_5\text{H}_5$) $\text{Fe}(\text{CO})_2(h^1\text{-C}_5\text{H}_5)$.¹ It was shown that the ($h^1\text{-C}_5\text{H}_5$) ring is fluxional and all available evidence² strongly favors 1,2 shifts as the predominant rearrangement pathway. However, no indication of interchange of the two rings has been seen, even up to temperatures of $\sim 125^\circ$, where decomposition becomes rapid.³ This may be attributed to the fact that no suitable transition state involving two equivalent rings, each having a relationship to the metal atom intermediate between ($h^1\text{-C}_5\text{H}_5$) and ($h^5\text{-C}_5\text{H}_5$), can be achieved at low activation energy, owing to the lack of available empty orbitals on the iron atom, which has the formal 18-electron configuration. Nor is there any other case in which a genuine ($h^1\text{-C}_5\text{H}_5$)-($h^5\text{-C}_5\text{H}_5$) interchange has been observed.⁴

We now wish to report the first such observation with full, though preliminary, documentation.

The three compounds (C_5H_5)₄M, M = Ti,⁶ Zr,⁷ and Hf,⁸ have all previously been reported. The Zr and Hf compounds exhibit a single, sharp pmr signal at room temperature and no broadening has been observed at the lowest accessible temperatures⁹ ($\sim -150^\circ$), nor have we succeeded in obtaining suitable crystals for X-ray study. Hence the structural and dynamical properties of these molecules remain undefined though there is a strong probability that very rapid interchange of different ring types occurs.

Tetracyclopentadienyltitanium has now been well characterized structurally and dynamically. The compound crystallizes in the hexagonal system, and systematic absences indicate one of the enantiomorphous space groups P6_122 or P6_522 . The unit cell dimensions are: $a = b = 9.214$ and $c = 31.895 \text{ \AA}$. A unit cell

(1) M. J. Bennett, F. A. Cotton, A. Davidson, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Amer. Chem. Soc.*, **88**, 4371 (1966).

(2) F. A. Cotton and T. J. Marks, *ibid.*, **91**, 7523 (1969).

(3) F. A. Cotton and T. J. Marks, unpublished observations.

(4) The ring interchange in (C_5H_5)₃MoNO is a special case, since two of the rings have a very unusual relationship to the metal⁵ quite different from the regular ($h^5\text{-C}_5\text{H}_5$)M geometry, and it is easy to believe that this predisposes them toward facile interchange with the $h^1\text{-C}_5\text{H}_5$ ring.

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