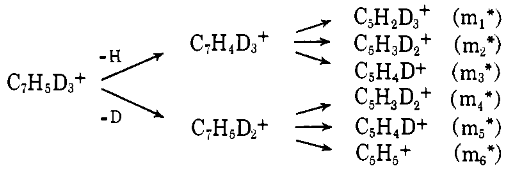

proportions of M^+ ions at about 15.7 eV (the appearance potential of $C_5H_5^+$) which undergo the initial reaction *via* loss of H and D, respectively. Note that each of these metastable decompositions is uniquely determined in the defocused mode.

For the deuterated toluenes it is not possible to determine the decompositions from energy region 5 (*cf.* Table I and Figure 1) because of the overlap of the normal partially deuterated $C_5H_5^+$ ions formed from $C_7H_4D_3^+$ and $C_7H_5D_2^+$. For α-d_3-toluene the (loss of H):(loss of D) ratios for energy segments 1–4[12] are 4.7, 3.9, 1.8, and 1.0, respectively, and for ring-d_5-toluene the ratios are 1.7, 1.5, 1.1, and 1.6. The figures are influenced by (i) a deuterium isotope effect k_H/k_D which decreases with increasing energy[13] and (ii) scrambling *vs.* direct cleavage in the molecular ion. The fact that ratio 4 for ring-d_5-toluene is greater than ratio 3 is an indication of a decrease in the degree of scrambling (favoring H loss) with increasing energy despite a decrease in the isotope effect. In α-d_3-toluene both influencing factors will tend to increase the preference for loss of D with increasing energy. A detailed elucidation of the isotope effects and degree of scrambling in the toluene and cycloheptatriene systems will follow in the full paper.

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[12] Energy segments 1–4 are defined as for benzoic acid in Table I and Figure 1 except that the critical potentials become 11.8 and 15.7 eV instead of 12.7 and 16.0 eV.

[13] M. Vestal and G. Lerner, "Fundamental Studies Relating to the Radiation Chemistry of Small Organic Molecules," Aerospace Research Laboratory Report No. 67-0114, 1967.

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A Simple Molecular Orbital Explanation for the Barrier to Internal Rotation in Ethane and Other Molecules[1]

Sir:

Despite numerous calculations of barriers to internal rotation about single bonds,[2] a simple, qualitative explanation for the source of the barrier has failed to emerge. We here report a very simple explanation which applies to ethane at the independent-electron MO level and which is probably relevant at more sophisticated levels as well.[3]

The independent-electron, minimal basis set LCAO MO's for ethane are highly symmetry determined. The hydrogen 1s functions must enter in combinations characteristic of symmetry groups containing a C_3 axis. These are combined with C–C σ and π bonding and antibonding orbital combinations. The exact energy ordering of the MO's is dependent upon parameter choices, but reasonable choices within the extended Hückel MO (EHMO) method[4] indicate that the lowest seven MO's are C–H bonding, with C–C running through bonding and antibonding, leaving a net C–C σ bond. The highest seven MO's are C–H antibonding with C–C combinations producing a net σ antibond. Three of the seven filled MO's are nondegenerate and therefore contain hydrogen 1s functions in totally symmetric combinations (*i.e.*, all hydrogen 1s coefficients on a methyl group equal). These MO's suffer almost no energy change on going from eclipsed to staggered ethane. The other four filled MO's constitute two doubly degenerate sets, and contain the E-type methyl hydrogen symmetry combinations. These are the forms which are central to hyperconjugation arguments[5] and models,[6] and we shall see that their role in barrier production may be viewed in terms of a hyperconjugative extension to π orbital conformational arguments.[7] The lower energy pair of MO's is describable as C–C pseudo-π bonding, whereas the higher energy pair is C–C pseudo-π antibonding.[8] These MO's are sketched in Figure 1 for staggered and eclipsed ethane.

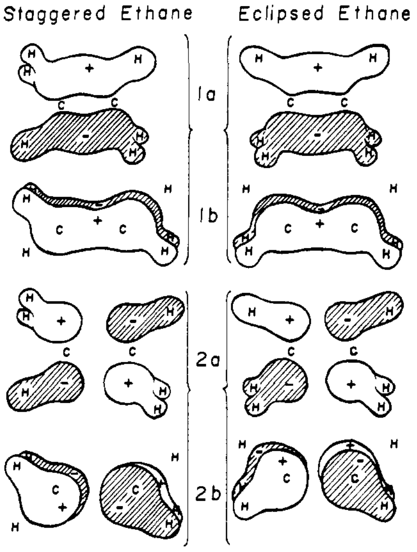

Figure 1. MO's of staggered and eclipsed ethane.

The levels **1** are lower in energy for the eclipsed form than for staggered. This MO stabilizes the eclipsed form by virtue of the bonding interaction between hydrogen 1s functions at opposite ends of the molecule. The levels **2** are lower in energy for the staggered form because the C–C π antibonding combination results in a sign change in the hydrogen coefficients at one end of the molecule. The energy change for levels 2 is the greater, the net effect giving a calculated barrier of

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] J. P. Lowe, *Progr. Phys. Org. Chem.* **6**, 1 (1968).

[3] J. A. Pople and D. P. Santry, *Mol. Phys.*, **7**, 269 (1963); **9**, 301 (1965); J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

[4] R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[5] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, p 43.

[6] A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley, New York, N. Y., 1961, p 131.

[7] R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

[8] The term "pseudo" is used here since we are not dealing with a planar system.

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 systems[7] 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 Olofson[7] 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" shape[7] for a five-membered system, methyl formate must have 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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[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.

[11] R. F. Curl, Jr., *J. Chem. Phys.*, 30, 1529 (1959).

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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, $\lesssim 10^{-6}$ 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 $Ro \equiv Co^{III}(NH_3)_5$ and $L^{3-} \equiv N(CH_2COO)_3{}^{3-}$; and by pH titration, $pK_{a1} = 1.82$ and $pK_{a2} = 7.96$ 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

$$(NH_3)_5Co^{III}LH_n{}^{n+} + Fe^{2+} + (5 - n)H^+ \longrightarrow 5NH_4{}^+ + Co^{2+} + Fe^{III}L \quad (1)$$

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[1] D. Bunn, F. S. Dainton, and S. Duckworth, *Trans. Faraday Soc.*, **57**, 1131 (1961).

[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).

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