REEVALUATION OF ORBITAL INTERACTIONS IN SUBSTITUTED RADICALS.
TRANSFER OF RADICAL PROPERTIES TO THE SUBSTITUENT ATOM

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Abstract: Theoretical calculations have shown that a nonbonded pair orbital on an
atom attached to a radical center can be higher in energy than the SOMO of the
unsubstituted radical. The mixing of the orbitals produces a SOMO which contains
the major contribution from the nonbonded pair orbital, thus transferring radical
character to the substituent atom.

Recent studies in several laboratories have focused on the effects of various substi-
tuents on the rates of radical reactions[1-4] and on the delocalization of spin density.[5] The
interactions of a radical center with adjacent bonding and nonbonding pairs of electrons have
been qualitatively analyzed using PMO theory, the interactions being illustrated in the
energy diagrams in Fig. 1.[6] From a quantitative viewpoint there are serious errors in
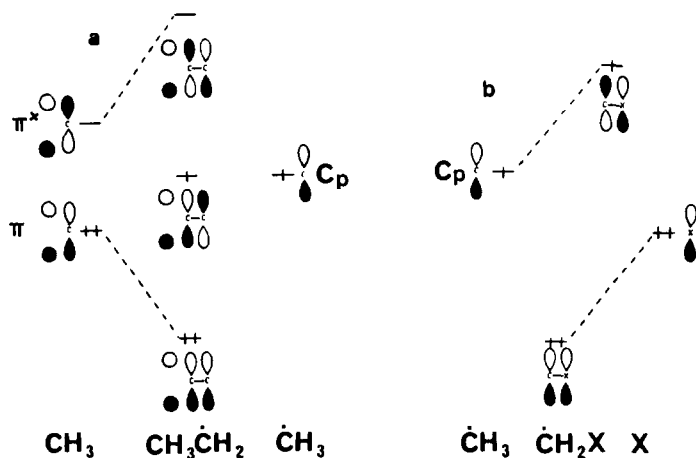

Fig. 1. Orbital interactions between a radical center and adjacent bonding and
nonbonding pairs of electrons.[6]

the assignment of the relative energy levels in both of the diagrams in Fig. 1 which have
resulted in the failure to recognize potentially unique properties of certain substituted
radical systems. Recent calculations in our laboratories have resulted in the recognition of

these errors.

In the energy diagram for the ethyl radical the SOMO of CH_3 is placed symmetrically between the π and and π^*- type methyl group orbitals. In such a situation the mixing of the MO's will result in little, or no, change in the energy of the SOMO on going from CH_3 to CH_3CH_2. This, however, is not the case. The SOMO of CH_3 (-12.7 eV, 4-31G level) lies fairly close in energy to the π-type methyl group orbital ($\sim$ -14.5 - -15.0 eV). Therefore the SOMO-π interaction will be dominant resulting in an elevation in energy of the SOMO in CH_3CH_2 (-9.5 eV) (see Fig. 2a).
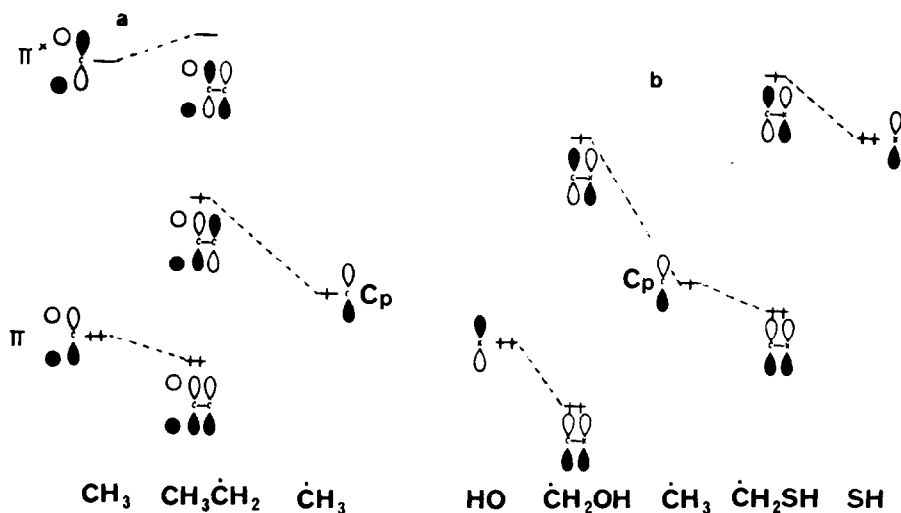
Fig. 2. Corrected orbital interactions between CH_3 and adjacent bonding and nonbonding pairs of electrons.

The orbital interactions of $HOCH_2$ and $HSCH_2$ were discussed in terms of the interactions shown in Fig. 1b.[6] The assumption appears to have been made that the SOMO energy level will always reside <u>above</u> the nonbonded pair energy level. Our calculations show that this is not always the case. For example, the energy of the π-type, nonbonded pair orbital of H_2O is -13.6 eV, which is lower in energy than the SOMO of CH_3. The mixing of the SOMO of CH_3 with the nonbonded pair orbital produces the SOMO of $HOCH_2$ with an energy of -9.4 eV with the wave function shown below with the dominant contribution from the C 2p AO. In contrast, the

energy of the nonbonded pair orbital of H_2S is -10.4 eV, <u>higher</u> in energy than the SOMO of CH_3. In this case the orbital mixing produces a SOMO (-8.3 eV) with dominant contribution from the S 3p AO. <u>Most of the spin density resides on sulfur.</u> This is represented in **2**.

The results of ESR studies have indicated considerable delocalization of spin density onto an adjacent sulfur atom.[7] The hyperfine coupling constant <u>a</u> in $^-O_2CCH_2CHCO_2^-$ of 20.4 G (for CH_3 <u>a</u> = 23 G) is lowered to 15.17 G in $^-O_2CCH_2SCHCO_2^-$ and ~ 11G in $^-O_2CCH_2SSCHCO_2^-$, while in $CH_2CO_2^-$ (<u>a</u> = 21.2 G) it is lowered to 13.4 G in $^-SCHCO_2^-$.[7]

The extensive delocalization of spin density onto an adjacent sulfur atom should give rise to unique chemical reactivity, an example of which appears to be present in the thermolysis of the azocompounds **3** (R = CH_3, C_6H_5) which produces the unusual distribution of products shown (R = CH_3), particularly CH_3S-S-CH_3.[2] The corresponding methoxy-substituted

azopropane produces only the normal coupling and disproportionation products, with typical activation parameters ($\Delta H^{\ddagger}$ = 34.4 kcal/mole, $\Delta S^{\ddagger}$ = +16.5 e.u.).[2] The activation parameters for the thermolysis of **3** are highly unusual (R = CH_3: $\Delta H^{\ddagger}$ = 28.7, $\Delta S^{\ddagger}$ = -16.0; R - C_6H_5: $\Delta H^{\ddagger}$ = 29.6, $\Delta S^{\ddagger}$ = -12.6),[2] more typical of a constrained cyclic transition state such as **4** in which the development of odd electron density on sulfur results in a bonding interaction.

Similar dominant delocalization of spin density onto an adjacent atom is expected when the nonbonded AO lies above the SOMO of the parent radical. Our calculations show that the nonbonded AO's on F, O, N and Cl lie below the SOMO of CH_3, while those on S and P (as well as other atoms lower in the periodic table) lie <u>above</u> the SOMO of CH_3. It appears that little attention has been paid to the physical and chemical properties of such systems.

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