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- (15) All of the thermochemical measurements were made at the University of Manchester and they will be reported fully in forthcoming papers. Briefly, the following methods were used to measure enthalpies from which enthalpies of formation could then be calculated. For  $W(NMe_2)_6$  the heat of hydrolysis in 0.1 M aqueous HCl was measured; the products were  $[NMe_2H_2]Cl$  and  $H_2WO_4$ . For  $W_2(NMe_2)_6$  both combustion bomb calorimetry and an oxidative hydrolysis reaction employing acidic dichromate were used. The same type of oxidative hydrolysis reaction was also used for  $Mo(NMe_2)_4$  and  $Mo_2(NMe_2)_6$ . The enthalpies of sublimation of all compounds were measured using the vacuum-sublimation, drop-microcalorimeter technique previously described by F. A. Adediji et al., *J. Organomet. Chem.*, **97**, 221 (1975).
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J. A. Connor, G. Pilcher, H. A. Skinner

Chemistry Department, University of Manchester  
Manchester M13 9PL, United Kingdom

M. H. Chisholm

Department of Chemistry, Princeton University  
Princeton, New Jersey 08540

F. A. Cotton\*

Department of Chemistry, Texas A&M University  
College Station, Texas 77843

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### Perturbation Molecular Orbital Treatment of Free-Radical Hydrogen-Abstraction Reactions

Sir:

The successful PMO treatment<sup>1</sup> of the reactivity and regioselectivity in dicyanomethyl radical additions to alkenes and of the reactivity in  $CF_3\cdot$  radical additions to alkenes using MINDO/3 data<sup>2-4</sup> prompted us to extend this approach to hydrogen-abstraction reactions for which kinetic data are available,<sup>5</sup> e.g., the reactions of  $CF_3\cdot$  and  $CH_3\cdot$  radicals with alkanes.<sup>6</sup>

For the reaction of each radical we calculated Fukui's delocalizabilities  $D_r^{(R)}$ ,<sup>7,8</sup> according to

$$D_r^{(R)} = \sum_i \frac{c_{ri}^2}{\alpha - \epsilon_i} (-\beta) + \sum_i^{unocc} \frac{c_{ri}^2}{\epsilon_i - \alpha} (-\beta)$$

This treatment implies that only the mutual interactions of the radical SOMO and the AO of the hydrogen to be abstracted in all occupied and unoccupied MO's of the alkane are considered. The resonance integral  $\beta$  for each series of abstractions

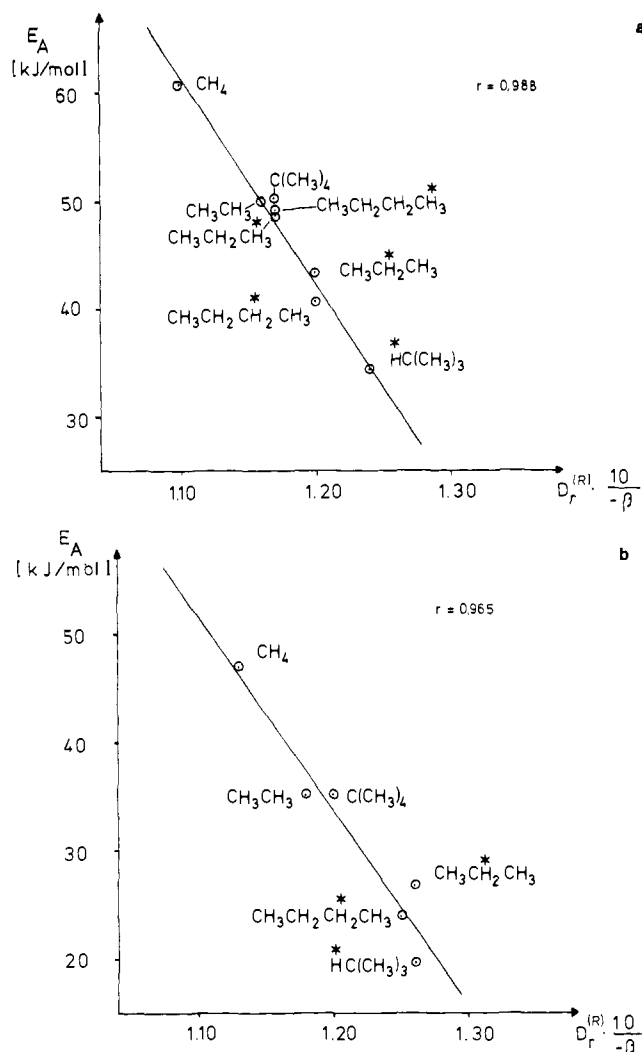


Figure 1. Activation energy ( $E_A$ ) for hydrogen abstraction from various alkanes at the marked positions (a) by  $CH_3\cdot$ <sup>10</sup> and (b) by  $CF_3\cdot$ <sup>11</sup> radicals vs. delocalizabilities  $D_r^{(R)}$  (in units of  $\beta$ ).

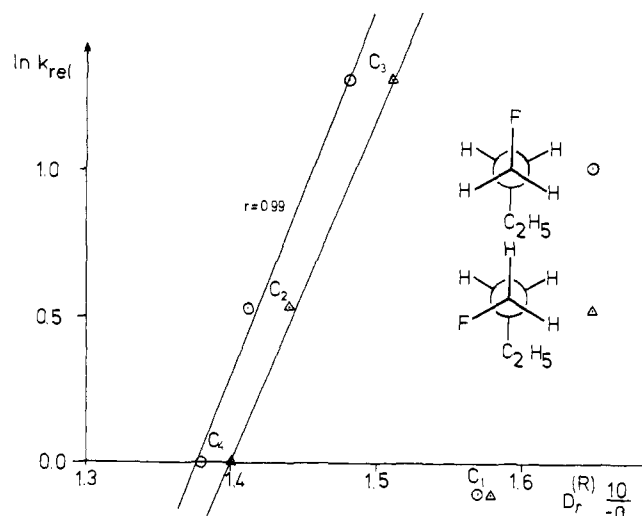


Figure 2. Logarithm of relative rates of hydrogen abstraction<sup>13</sup> ( $\ln k_{rel}$ ) from 1-fluorobutane by chlorine atoms vs. delocalizability ( $D_r^{(R)}$ ) (in units of  $\beta$ ) as calculated for the shown conformations.

was taken as constant. This approximation may be justified on employing the same reagent (radical) and similar substrates.<sup>9</sup> The results of the calculations are listed in Table I.

As can be seen from Figures 1a and 1b there is a fairly good

**Table I.** Arrhenius Activation Energies ( $E_A$ ) and Delocalizabilities ( $D_r^{(R)}$ ) for H abstractions from alkanes by  $\text{CH}_3\cdot$  and  $\text{CF}_3\cdot$  Radicals

alkane <sup>a</sup>	$E_A^-$ ( $\text{CH}_3\cdot$ ) <sup>b</sup>	$D_r^{(R)}$ ( $\text{CH}_3\cdot$ ), <sup>c</sup> $\beta$	$E_A^-$ ( $\text{CF}_3\cdot$ ) <sup>d</sup>	$D_r^{(R)}$ ( $\text{CF}_3\cdot$ ), <sup>e</sup> $\beta$
$\text{CH}_4$	60.9	$-1.10 \times 10^{-1}$	46.9	$-1.13 \times 10^{-1}$
$\text{CH}_3\text{CH}_3$	50.0	$-1.16 \times 10^{-1}$	35.2	$-1.18 \times 10^{-1}$
$\text{CH}_3\text{CH}_2\text{-}$ $\text{C}^*\text{H}_3$	48.7	$-1.17 \times 10^{-1}$		
$\text{CH}_3\text{C}^*\text{H}_2\text{-}$ $\text{CH}_3$	43.3	$-1.20 \times 10^{-1}$	26.8	$-1.26 \times 10^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{-}$ $\text{C}^*\text{H}_3$	49.1	$-1.17 \times 10^{-1}$		
$\text{CH}_3\text{CH}_2\text{C}^*\text{-}$ $\text{H}_2\text{CH}_3$	40.7	$-1.20 \times 10^{-1}$	23.9	$-1.25 \times 10^{-1}$
$(\text{CH}_3)_3\text{C}^*\text{H}$	34.4	$-1.24 \times 10^{-1}$	19.7	$-1.26 \times 10^{-1}$
$\text{C}(\text{CH}_3)_4$	50.4	$-1.17 \times 10^{-1}$	35.2	$-1.20 \times 10^{-1}$

<sup>a</sup> \* indicates the hydrogen abstracted. <sup>b</sup> For gas-phase reactions in  $\text{kJ mol}^{-1}$ .<sup>10</sup> <sup>c</sup> With  $E_{\text{SOMO}}(\text{CH}_3\cdot) = -4.23 \text{ eV}$ .<sup>2-4</sup> <sup>d</sup> Gas-phase results in  $\text{kJ mol}^{-1}$  as cited in ref 11. <sup>e</sup> With  $E_{\text{SOMO}}(\text{CF}_3\cdot) = -6.25 \text{ eV}$ .<sup>2-4</sup>

**Table II.** Hydrogen Abstractions from 1-Fluorobutane by Chlorine Atoms. Logarithm of the Relative Rate Constants ( $\ln k_{\text{rel}}$ ) and Delocalizability ( $D_r^{(R)}$ )<sup>6</sup> for Two Conformations

	$\text{C}_1$	$\text{C}_2$	$\text{C}_3$	$\text{C}_4$
$\ln k_{\text{rel}}^a$	-0.105	0.531	1.308	0
$D_r^{(R)}, \beta 180^\circ b,c$	$-1.57 \times 10^{-1}$	$-1.41 \times 10^{-1}$	$-1.48 \times 10^{-1}$	$-1.38 \times 10^{-1}$
$D_r^{(R)}, \beta 60^\circ b,c$	$-1.58 \times 10^{-1}$	$-1.43 \times 10^{-1}$	$-1.51 \times 10^{-1}$	$-1.40 \times 10^{-1}$

<sup>a</sup> From the relative selectivities of chlorination in the gas phase at  $78^\circ\text{C}$ .<sup>13</sup> <sup>b</sup> Values for the  $180^\circ$  and  $60^\circ$  conformations at the  $\text{C}_1\text{-C}_2$  bond. All other C-C bonds with  $180^\circ$  conformation. <sup>c</sup> With  $E_{\text{SOMO}}(\text{Cl}\cdot) = -8.34 \text{ eV}$ .<sup>2-4</sup>

linear correlation between the activation energies for H abstraction by  $\text{CH}_3\cdot$  and  $\text{CF}_3\cdot$  radicals and the delocalizabilities.

Thus the principle of maximum overlap<sup>7</sup> using MINDO/3 data<sup>2-4</sup> may serve well in predicting the relative activation energies and (in consideration of the similar  $A$  factors<sup>10,11</sup>) the relative rates of free-radical hydrogen-abstraction reactions. Obviously steric influences<sup>12</sup> can be neglected.

As shown with 1-fluorobutane as an example (Table II, Figure 2), a polar factor only seems to be important for abstraction reactions at the halogen-bearing C atom ( $\text{C}_1$ ).

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**H. Bartels, W. Eichel, K. Riemenschneider, P. Boldt\***  
*Lehrstuhl B für Organische Chemie  
der Technischen Universität  
Braunschweig, Postfach 33 29  
D-3300 Braunschweig, West Germany*  
Received June 26, 1978

## Theoretical ab Initio Calculations of Deformation Densities in Some Binuclear Metal Complexes

Sir:

The ab initio Hartree-Fock method has been applied recently to the calculation of electronic deformation density distributions<sup>1</sup> in the vicinity of transition metal atoms.<sup>3,4</sup> We report here the first theoretical calculations of deformation densities for binuclear metal complexes immediately comparable with experimental works. Deformation density maps were obtained for  $t\text{-}[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (I) and  $(\eta^5\text{-C}_5\text{H}_5\text{Ni})_2\text{-CH}\equiv\text{CH}$  (II). The molecular density is issued from ab initio calculations<sup>5</sup> at the SCF level with double- $\zeta$  basis sets for the valence shells. The atomic density distributions were calculated for each atom with the same basis set as that used in the molecular calculation. The atoms were taken to be neutral and in their ground states. The contours are based upon a grid having an increment of 0.2 au. Positive and negative contours were drawn with an interval of  $0.03 \text{ e}(\text{au})^{-3}$  from 0 to  $\pm 0.18 \text{ e}(\text{au})^{-3}$ .

**Bis(dicarbonyl- $\pi$ -cyclopentadienyliron) (I).** Figure 1 shows the deformation density distribution for I in the plane containing the iron atoms and the terminal carbonyls. A comparison with an experimental deformation density map drawn for the same plane<sup>8</sup> shows that all significant features of the experimental map are correctly reproduced,<sup>19</sup> especially the four density peaks around each metal separated by a negative zone colinear to the Fe-CO bond. The lack of significant features in the region located around the Fe-Fe line, noticed about the experimental deformation density map,<sup>8</sup> is also confirmed. The absence of residues in the metal-metal direction seems to be consistent with the fact that our molecular SCF wave function does not display any significant direct metal-metal bond. This conclusion is based upon the small negative value of the Mulliken overlap population between iron atoms<sup>10</sup> and upon an analysis of the valence shell molecular orbitals, especially of the HOMO which exhibits a strong back-bonding character from the  $d_{yz}$  orbital of iron toward the bridging carbonyls.<sup>12</sup> This analysis illustrates the concept of delocalized multicentered linkages of bridging carbonyl ligands to two or three metals proposed by Chini<sup>13</sup> and Braterman<sup>14</sup> and already corroborated by SCF calculations on  $\text{Co}_2(\text{CO})_8$ <sup>15</sup> and  $\text{Fe}_3(\text{CO})_{12}$ .<sup>11</sup>

**$\pi$ -Acetylenebis(cyclopentadienylnickel) (II).** This complex is supposed to present a direct metal-metal bond because of electron counting and of the very short metal-metal distance (2.345 Å).<sup>7</sup> However, the nature of this bond "straight" or "bent" away from the acetylene<sup>18</sup> is still controversial. The "bent" metal-metal bond model was found by Teo and co-workers to correspond to the character of the HOMO in several  $\text{Fe}_2(\text{CO})_6\text{X}_2$ -type dimers.<sup>16</sup> However, experimental density deformation maps obtained by Wang and Coppens for II exhibit density accumulation with two maxima along the Ni-Ni line, thus favoring the "straight" bond model.<sup>7</sup> We depict in Figure 2 the electron density contour map obtained for the