energies, and its structure will be distorted due to the Jahn–Teller effect. On the other hand, the a_1'' level is lower than e'' in I and III, yielding a nondegenerate HOMO. These results are consistent with previous extended Hückel calculations as mentioned above.[7a,8]

The order of the a_1'' and e'' levels seems to be determined mainly by the antibonding π-interaction between the molybdenum 4d orbitals and the filled 3p orbitals of the bridging ligand atoms. These orbitals are derived from the same type of molybdenum 4d orbitals as shown in Figure 3. The interaction destabilizes only the e'' orbital because the a_1'' does not interact with the p orbitals due to the mismatch in symmetry. Since sulfur is less electronegative than chlorine, the energies of its 3p orbitals are closer to those of the molybdenum 4d orbitals. Therefore, the sulfur ligands in I′ and III′ are expected to have stronger π-interactions with metal d orbitals, and to destabilize the e'' orbital more than the chlorine ligands in II′.

As shown in Figure 2, I′ and III′ have very similar energy level diagrams in the HOMO–LUMO region except that the three highest occupied orbitals have more metallic character in III′ than in I′. Our preliminary calculation has also shown that the electronic levels of I′ change similarly to those of III′ when the structures are distorted in the C_{2v} symmetry in such a way as observed in III. Especially, the HOMO a_1'' orbital is influenced very little by the distortion in both compounds. Therefore, the electronic structures of I and III should be very similar though only III exhibits distortion of the metal triangle in the X-ray structure analysis. The interplay of electronic and steric influences that distorts III may be very delicate and/or complex. However, the lack of distortion in I can be explained straightforwardly by the nondegeneracy of the HOMO.

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Supplementary Material Available: Tables SI–SIV containing listings of crystallographic data, atomic parameters, anisotropic thermal parameters, and bond distances and angles for compound I (5 pages); listing of observed and calculated structure factors for compound I (10 pages). Ordering information is given on any current masthead page.

Use of Nuclear Potential To Investigate the "Atomic Size" Dependency of Populations Defined within the Theory of Atoms in Molecules

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A recent publication[1] has criticized results obtained using the theory of atoms in molecules[2] by claiming that the "atomic size" dependency of the form of the charge distribution leads to erroneous and unaccountable errors in the predictions of the theory. The interpretation of the behavior of simple model systems is used to claim that the location of the zero-flux surface depends upon atomic orbital size. These models are the foundations of the critical arguments that follow regarding the exaggeration of the atomic populations predicted by the theory of atoms in molecules and consequently their unreliability as a basis for the investigation of physical phenomena.

The second model presents a "1:1 LCAO-MO" model which "localizes a known, and preferably equal, electron population on each atom".[1] A system with carbon and oxygen separated by 2.70 bohr is presented with each nucleus having a Slater sp hybrid atomic orbital. One electron is put into this system, and the resulting distribution produces a critical point (the point at which the charge density reaches a minimum along the interatomic axis) closer to the carbon nucleus than to the oxygen along the interatomic axis. An integration is performed within the regions bounded by the zero-flux surface in the gradient vector field, and the atomic populations are determined, with the carbon atom having 0.30 and the oxygen 0.70 of the electronic charge. The author claims that the failure to distribute the population equally between the two atoms demonstrates the "atomic size" dependency and hence the weakness of the theory of atoms in molecules.

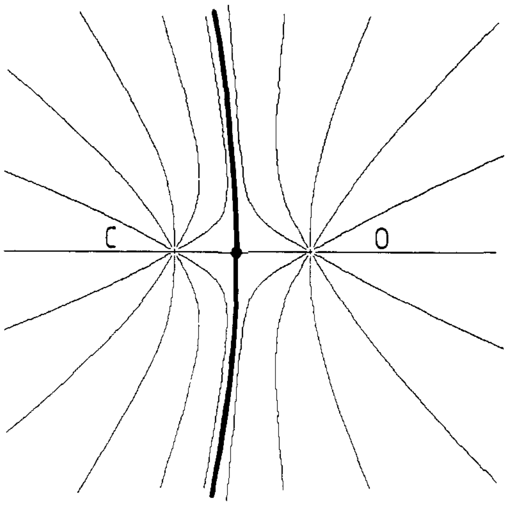

Figure 1. Gradient vector field of the nuclear potential of the system as defined in eq 1. The surface of balanced forces between the two nuclei has been darkened for emphasis, the intersection of this surface with the internuclear axis is represented by a black dot, and the position of each nucleus is represented by a cross.

The implicit assumption used above is that the amount of charge should be evenly divided between the two atoms of this system. We propose a simple consideration of the nuclear potential[3] between these two atoms to demonstrate that this cannot be so. The nuclear potential generates the nuclear–electron attraction, the dominant force within a molecular system, and is responsible for the form of the molecular distribution.[3] The nuclear potential, for a given nuclear configuration, X, with nuclear charges, Z_α, is defined as

$$V(r;X) = \sum_\alpha Z_\alpha(|r - X_\alpha|)^{-1} \qquad (1)$$

Given the model system described above, one finds the nuclear potential, as displayed by its gradient vector field, has the form found in Figure 1. The lines shown in the figure are those of force (the gradient of the potential), i.e., lines along which a negative test charge moves under the influence of the nuclear potential. The system is divided into two regions of space in which the lines of force lead to one nucleus or the other, i.e., regions of space in which a test charge is dominated by the potential of that nucleus. Figure 1 shows that the region of space in which the test charge is dominated by oxygen is larger than that for carbon. The form of the distribution of one electron under the influence of this potential will not have an equal amount of charge on each atom, and integration of the atomic populations of such a distribution should yield a larger population for oxygen.

In between these regions there is a surface in three dimensions on which the force on a test charge is equally balanced between the two nuclei. This surface of balanced force is not midway along

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the axis between the two nuclei, but closer to the carbon atom by 0.194 bohr. The larger nuclear charge of the oxygen nucleus results in an unbalanced competition between attractive forces, and the surface at which the force between the two nuclei is balanced is thus pushed toward carbon. One would expect to find the critical point in the distribution of one (or many) electron(s), in the ground state, within this system to be nearer to carbon nucleus. In general, there is a homeomorphism between the form of $V(r)$ and $\rho(r)$, a one-to-one correspondence between the topology of the two scalar fields.[3] However, as a result of the balancing of the quantal and classical forces within a system, the locations of the critical points in $V(r)$ and $\rho(r)$ do not generally coincide, even in a one-electron case, unless demanded by symmetry.[3]

In the present case, the nuclear potential of the oxygen atom controls the system, resulting in a larger region of space being dominated by its attraction. Irrespective of the orbitals used, the electronic distribution of one or many electrons within this system will be unequally distributed between the atoms because of the nature of the nuclear–electronic attraction force resulting from the form of the nuclear potential.

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Iron- and Ruthenium-Catalyzed Oxidations of Alkanes with Molecular Oxygen in the Presence of Aldehydes and Acids

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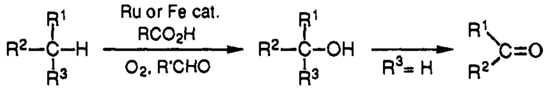
Oxygenation of unactivated C–H bonds with metal complex catalysts is of importance from both synthetic and biological points of view.[2] Catalytic oxidations of alkanes have been explored by using various oxidants,[3] and those with molecular oxygen under mild conditions[4] are especially rewarding goals. During the course of our systematic study on the cytochrome P-450 type oxidations with ruthenium catalysts,[5,6] we have found a novel catalytic aerobic oxidation of alkanes. Ruthenium- and iron-catalyzed oxidations of alkanes with molecular oxygen (1 atm) in the presence of an aldehyde and a catalytic amount of an acid at room temperature give the corresponding ketones and alcohols highly efficiently (eq 1).

Table I. Iron- and Ruthenium-Catalyzed Aerobic Oxidations of Alkanes and Alkylated Arenes in the Presence of an Aldehyde[a]

entry	substrate	conversn,[b] %	product[c]	yield,[d] %
1	cyclohexane	11	cyclohexanone	66
			cyclohexanol	29
2, 3	cyclooctane	15 (8.4)[e]	cyclooctanone	76 (63)[e]
			cyclooctanol	12 (21)[e]
4	methylcyclohexane	16	methylcyclohexanones	20[f]
			methylcyclohexanols	64[g]
5, 6	adamantane	36 (28)[e]	1-adamantanol	75 (71)[e]
			2-adamantanol	6 (3)[e]
			2-adamantanone	5 (4)[e]
7	*n*-decane	4.8	decanones	63[h]
			decanols	24[i]
8	ethylbenzene	20	acetophenone	79
			1-phenylethanol	16

[a] To a stirred mixture of alkane (2.00 mmol), iron powder (0.02 mmol), and acetic acid (0.02 mmol) in dry CH_2Cl_2 (10 mL) was added a solution of heptanal (8.00 mmol) in dry CH_2Cl_2 dropwise at room temperature over a period of 2 h under 1 atm of O_2, and the mixture was stirred for a further 15 h. [b] Determined by GLC analysis based on the starting alkane using an internal standard. [c] Very small amounts of alkyl chlorides could be detected among the products. [d] Determined by GLC analysis based on the converted alkane using internal standard. [e] $RuCl_3{\cdot}nH_2O$ was used instead of iron powder. [f] 2-One:3-one:4-one = 20:57:23. [g] 1-Ol:2-ol:3-ol:4-ol = 69:6:18:7. [h] 2-One:3-one:(4+5)-ones = 24:24:52. [i] 2-Ol:3-ol:(4+5)-ols = 28:22:50.



$$\mathrm{R^2{-}\overset{R^1}{\underset{R^3}{C}}{-}H \xrightarrow[O_2,\ R'CHO]{Ru\ or\ Fe\ cat.\ \ RCO_2H} R^2{-}\overset{R^1}{\underset{R^3}{C}}{-}OH \xrightarrow[R^3=H]{} \begin{matrix}R^1\\ R^2\end{matrix}\!\!>C{=}O} \qquad (1)$$

The catalytic activity of various metal complexes has been examined for the oxidation of adamantane with molecular oxygen (1 atm) in the presence of heptanal and a catalytic amount of acetic acid. Iron powder has proved to be the most effective catalyst among the catalysts examined, although $Fe(OAc)_3$, $FeCl_3{\cdot}6H_2O$, $RuCl_3{\cdot}nH_2O$, and $RuCl_2(PPh_3)_3$ can be used. The effect of aldehydes was examined for the iron-catalyzed oxidation of adamantane. Excellent results were obtained with heptanal and 2-methylpropanal, and acetaldehyde can be used also. A weaker acid is suitable for the present iron-catalyzed oxidation. Acetic acid gives the best result among the acids examined, and the effects of acetic acid and its chloro and trifluoro derivatives are in the order acetic acid > chloroacetic acid > trifluoroacetic acid.

The representative results of the iron- and ruthenium-catalyzed oxidations of various alkanes and alkylated arenes with molecular oxygen (1 atm) in CH_2Cl_2 in the presence of heptanal and a catalytic amount of acetic acid at room temperature are listed in Table I. Cyclic alkanes are readily oxidized to give the cor-

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