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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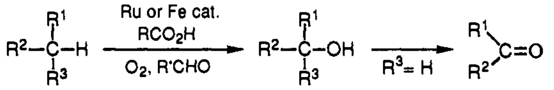
Oxygenation of unactivated C–H bonds with metal complex catalysts is of importance from both synthetic and biological points of view.[2] Catalytic oxidations of alkanes have been explored by using various oxidants,[3] and those with molecular oxygen under mild conditions[4] are especially rewarding goals. 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.



$$R^2\text{–}C(R^1)(R^3)\text{–}H \xrightarrow[O_2,\ R'CHO]{\text{Ru or Fe cat.},\ RCO_2H} R^2\text{–}C(R^1)(R^3)\text{–}OH \xrightarrow[R^3 = H]{} R^1R^2C{=}O \qquad (1)$$

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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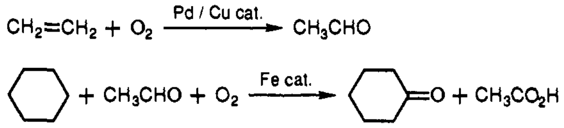
responding ketones and alcohols highly efficiently (entries 1-6). The oxidation of methylcyclohexane shows that the tertiary/secondary C-H bond selectivity on a per bond basis is 11 and that no oxidation occurs at the primary C-H bond. Poorly reactive linear alkanes also can be oxidized readily under the present reaction conditions (entry 7). Alkylated arenes are oxidized at the benzylic position selectively (entry 8). The aldehydes used are converted into the corresponding carboxylic acids.

In order to gain insight into the mechanism of the present oxidation of alkanes, the relative reaction rates of the iron-catalyzed oxidation of four substituted toluenes ($XC_6H_4CH_3$, X = *p*-CH_3, H, *p*-Cl, and *p*-NO_2) with molecular oxygen in the presence of heptanal in CH_2Cl_2 were determined by the GLC analysis of the oxygenated products. The rate data correlate well ($\gamma = 0.999$) with the Hammett linear free energy relationship with use of σ^+ values. The ρ value (-1.69) thus obtained is consistent with that observed for the oxidation of substituted toluenes by oxoiron porphyrin (-1.69).[7] The intramolecular deuterium isotope effect of the iron-catalyzed oxygenation of 1,1-dideuterio-1,3-diphenylpropane was determined to be 5.0 by GC-MS analysis of the product ketones. This value is smaller than that observed with cytochrome P-450 (11).[8] Furthermore, the intermolecular isotope effect of the oxygenation of cyclohexanes was determined to be 5.5 by GLC analysis of the oxygenated products obtained from the competitive reaction of cyclohexane and cyclohexane-d_{12}. The value 5.5 is quite similar to the value of 5.4[31] obtained for the oxidation with non-porphyrin oxoiron species. The observed intra- and intermolecular isotope effects indicate that C-H bond breaking is a crucial step. Intermediacy of alkyl radicals is supported by both these data and detection of cyclohexyl chloride from the oxidation of cyclohexane in CH_2Cl_2. Although it is premature to discuss the precise mechanism at the present stage, the reaction can be rationalized by assuming the following pathways. The reaction of aldehydes with molecular oxygen[9] in the presence of either ruthenium complexes or iron complexes derived from iron powder and acetic acid would give peracids,[10] which subsequently react with the metal complexes to afford oxometal species[5,6,11] along with carboxylic acids. Hydrogen abstraction of alkanes with oxometal species, followed by hydroxy ligand transfer to the resulting radical, would give alcohols. Alcohols can be converted into ketones under the same reaction conditions. Iron- and ruthenium-catalyzed oxidations of alkenes under the same reaction conditions give epoxides selectively,[12] indicating the presence of oxometal species. The oxidation of *cis*-stilbene gives the corresponding epoxides nonstereospecifically (trans/cis = 83/17), indicating that the present epoxidation is not due to the reaction with peracids formed in situ. It is noteworthy that the present catalytic system is quite different from the $\mathrm{Gif^{IV}}$ system ($\mathrm{Fe^{II}}$ catalyst/O_2/$\mathrm{Zn^0}$).[3f,4b,c] That is, tertiary/secondary C-H bond selectivity on a per bond basis for the oxidation of adamantane is 20 for our system and 0.25 for the $\mathrm{Gif^{IV}}$ system, and the ratio of cyclohexene oxide/(2-cyclohexen-1-one + 2-cyclohexen-1-ol) for the oxidation of cyclohexene is 95/5 for our system and 0 for the $\mathrm{Gif^{IV}}$ system.

Oxidative transformation of cyclohexane to cyclohexanone is of importance from an industrial point of view. Cobalt-catalyzed aerobic oxidation of cyclohexane has been used commercially; however, the total yield of cyclohexanone and cyclohexanol is quite low.[13] Our oxidation reaction provides a powerful industrial strategy for the synthesis of cyclohexanone by combination of Wacker oxidation of ethylene with the present iron-catalyzed oxidation of cyclohexane. Practically, the oxidation of cyclohexane can be performed without a solvent under slightly modified reaction conditions. Actually, the oxidation of cyclohexane without a solvent in the presence of iron powder catalyst (0.025 mol %), acetic acid (0.025 mol %), and acetaldehyde (10 mol %) at 70 °C under 8 atm of O_2 gave cyclohexanone (60%) and cyclohexanol (40%) with a high turnover number (146) along with acetic acid. The combined yield of cyclohexanone and cyclohexanol is almost 100%. Cyclohexanol can be converted into cyclohexanone readily under the same reaction conditions.



Work is in progress to provide definitive mechanistic information and to apply the present new method to other systems.

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Novel Ion-Molecule Reactions of C_{60}^{2+} with NH_3

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With the recent discovery of a new class of carbon molecules, named fullerenes,[1-3] a new area of chemical endeavor has been opened. Since Kratschmer and co-workers[4] have shown that C_{60} can be obtained in relatively large amounts by pyrolyzing graphite in a helium environment, an intense study of the physical and chemical properties of this intriguing class of carbon molecules has begun. In addition, a wide range of theoretical[5-8] calculations have been carried out.

The solution-phase chemistry of C_{60} with oxygen[9] and various amines[10] has shown some insight into its unique reactivity. Cox and co-workers[9] have reported the production and isolation of a fullerene monoepoxide, $C_{60}O$, produced by dissolving C_{60} in oxygen-rich benzene. C_{60}, when dissolved in propylamines,[10] undergoes addition of as many as 12 solvent molecules to the C_{60}

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† Alfred P. Sloan Foundation Fellow 1991-1993.

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