the (trimethylsilyl)methyl ethers 2 and 3 and thioether 4 (E_1/2(+) < 1.15 V)\(^{26}\) suggest that these donor-acceptor pairs should participate in efficient electron-transfer processes. Indeed, the ethers 2–4 are quenchers of pyrrolium salt 1 fluorescence with quenching rate constants approaching the diffusion-controlled limit (ca. \((1-3) \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}\) in MeCN at 25 °C). As expected, sequential electron transfer–desilylation in these systems is competitive with the quenching mode involving reversible electron transfer and results in generation of photoaddition products. Thus, irradiation\(^{10}\) of MeCN solutions of 1 (0.04 M) in the presence of ethers 2–4 (0.11 M) followed by base workup and purification by chromatographic methods leads to isolation of the photoadducts 5–7 (20–35%) along with the bipyrrolidine 8 (9–39%).\(^{11}\)Assignment of product structures is aided by comparisons of characteristic spectroscopic data\(^{12}\) for these substances with those of closely related materials.\(^{26}\) Careful analysis of the product mixtures in each case failed to reveal the presence of regioisomeric adducts, which could have arisen through isomerization of the initially formed primary radicals 11 to thermodynamically more stable secondary or tertiary counterparts 12\(^{13}\) or of silicon-containing photoadducts arising by deprotonation of the cation radical intermediates 10 (Scheme 1). Finally, the superiority of the regiocontrol offered by the desilylation route for electron-transfer–promoted radical production is exemplified by the comparative results of reactions of the salt 1 with the silylmethyl-substituted ether 3 and methyl isopropyl ether. In the latter case, photoaddition (MeCN) occurs to generate an ca. 2:1 ratio of the adducts 6 and 9 arising by nonselective radical cation deprotonation and resulting in insertion of the pyrrolidinyl unit into the respective primary and tertiary α-CH bonds.\(^{14}\)

Further investigations with the \(([(\text{trimethylsilyl})\text{methoxy}]\text{alkyl})\text{quinolinium perchlorates 13–15}\)\(^{15}\) demonstrate that sequential electron transfer–desilylation serves as a useful route for diradical generation as part of methods for heterocycle ring construction. The salts employed in this study were prepared by either N- or C-alkylation of the corresponding quinolines with the appropriate \(([(\text{trimethylsilyl})\text{methoxy}]\text{alkyl})\text{iodide or mesylate followed by N-methylation (for 14 and 15) and perchlorate ion exchange. The greatly diminished fluorescence quantum yields for 13–15 vs. the methyl analogues 16–18\(^{15}\) suggests that intramolecular electron transfer occurs efficiently in the singlet excited states of the silicon-containing salts. Irradiation of MeCN solutions of 13–15\(^{15}\) followed immediately by hydrogenation (PtO\(_2\)), base workup, and silica gel chromatography leads to isolation of the respective cyclized products 19–21 in yields ranging from 41% to 61%.\(^{16}\) The reduction step is required in the workup procedure in order to convert the initially formed dihydroquinolines into the more stable, isolated tetrahydroquinoline ring containing products.\(^{16}\)

The results presented above show that routes mediated by photoinduced, sequential electron transfer–desilylation serve as unique methods for regiocontrolled production of heteroatom-substituted carbon radicals. Continuing efforts are designed to explore the generality of the process and, in particular, to determine if electron-transfer-sensitized reactions of (trialkylsilyl)methyl ether and amine systems are useful for radical generation in a variety of synthetic applications.\(^{17}\)

Acknowledgment. Support for these studies by NSF (CHE-08240) and NIH (GM-27251) is acknowledged. The Korean Science and Engineering Foundation provided partial funding for a portion of the studies conducted by U.C.Y. The expert technical assistance offered by Susan M. Hanley is appreciated.

(15) The fluorescence quantum yields in MeCN at 25 °C: 13, 0.004; 14, 0.027; 15, 0.021; 16, 0.85; 17, 0.36; 18, 0.60.

**Sonochemical Activation of Transition Metals**

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Received July 12, 1984

The activation of transition metals remains an important goal and continues to engender major efforts in heterogeneous catalysis,\(^{1}\) metal-vapor chemistry,\(^{2}\) and synthetic organometallic efforts.\(^{3}\) We wish to report that the use of high-intensity ultrasound dramatically enhances the reactivity of transition-metal dispersions. Ultrasound ameliorates the condition necessary for the preparation of early-transition-metal carbonyl anions, and we believe that the technique has general ramifications.

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The effects of ultrasound in heterogeneous systems come principally from microstreaming and from acoustic cavitation on the surface. The former creates local turbulent flow and thus can induce significant improvements in mass transport between solution and surface. The latter produces the impingement of a supersonic "microjet" of solvent upon the surface, thus creating surface erosion and pitting. These phenomena are largely responsible for ultrasonic cleaning. In the presence of reactive metals such as Zn, Mg, or Li, this pitting action exposes a reactive site. The former creates local turbulent flow and thus supersonic "microjet" of solvent upon the surface, thus creating a reactive site.

In Table I for the synthesis of early transition-metal carbonyl clusters, we have chosen those systems of VC13(THF)3 in THF, or TaCl5 in diglyme. In all cases the yields are at least comparable to other methods requiring elevated temperatures and pressures of CO.

Reductions under ultrasonic irradiation of the halide salts of Mn, Fe, and Ni were also carried out. The species Mn(CO)5-, Fe(CO)6-, Fe(CO)5-, and Ni(CO)4- were observed as products of their respective systems through infrared spectroscopy. The manganese and iron reactions are quite efficient, while the nickel cluster is formed in small yield. Owing to the increased sensitivity of the manganese and iron compounds, the quantification of these reactions is difficult.

The use of ultrasound has dramatically reduced the temperature and pressure requirements for these reactions. For example, our preparation of V(CO)6- requires pressures of 4.4 atm and 10°C as opposed to the usual conditions of 200 atm and 160°C. It might also be noted that our reported yields, comparable to those using the standard method, were obtained without the use of the Fe(CO)5 catalyst called for in the earlier preparation. Even at 1 atm of CO, yields of the carbonyl anions remain significant using the typical reaction 1 mmol of transition-metal halide was dissolved in 30 ml of THF (tetrahydrofuran) and an excess of sodium sand was added. The mixture was flushed with CO and then maintained under CO during sonication. The system was thermostated so that the maximum temperature reached during ultrasonic irradiation was 10°C; sonication was carried out for 1000 min. This procedure works for a wide range of soluble metal halides. Most noteworthy, however, are the results shown in Table I for the synthesis of early transition-metal carbonyl anions, which are notoriously difficult to prepare. Solubility of the metal halide is important: low yields are observed for the sparingly soluble VCl3 or TaCl5 in THF compared to the soluble systems of VCl3(THF)3 in THF or TaCl5 in diglyme. In all cases the yields are at least comparable to other methods requiring elevated temperatures and pressures of CO.

The transition-metal carbonyl complexes continue to play a major role in organometallic chemistry because of their diverse chemistry and their importance as stoichiometric and catalytic synthetic reagents. Nonetheless, their preparation from the bulk metal remains difficult, and high pressures of CO and high temperatures traditionally have been required to achieve adequate yields. While some recent developments have reduced the pressure and temperature requirements, these synthses involve case-by-case reactions which have not proved to be transferable to other transition metals. The preparation of "activated" transition-metal dispersions, as investigated by Rieke, might appear to be one general method for carbonyl or carbonyl anion syntheses. These activated metals nevertheless require "bomb" conditions (100–300 atm of CO, 100–300°C) to synthesize transition-metal carbonyls. We have found that the use of ultrasonic irradiation facilitates the reduction of a variety of transition-metal salts to an active form that will react with low pressures of CO to form the simple carbonyl anions.

In a typical reaction 1 mmol of transition-metal halide was dissolved in 30 ml of THF (tetrahydrofuran) and an excess of sodium sand was added. The mixture was flushed with CO and then maintained under CO during sonication. The system was thermostated so that the maximum temperature reached during ultrasonic irradiation was 10°C; sonication was carried out for 1000 min. This procedure works for a wide range of soluble metal halides. Most noteworthy, however, are the results shown in Table I for the synthesis of early transition-metal carbonyl anions, which are notoriously difficult to prepare. Solubility of the metal halide is important: low yields are observed for the sparingly soluble VCl3 or TaCl5 in THF compared to the soluble systems of VCl3(THF)3 in THF or TaCl5 in diglyme. In all cases the yields are at least comparable to other methods requiring elevated temperatures and pressures of CO.

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Distance Dependence of Electron-Transfer Reactions: Rate Maxima and Rapid Rates at Large Reactant Separations

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Received August 16, 1984

Early in the history of electron-transfer studies it was pointed out that bimolecular electron transfer can occur over a range of reactant separations.1 However, the values of certain parameters needed for rate calculations have only recently been determined. Specifically, an increasing amount of experimental data on the distance dependence of the electronic coupling element2s3 and on the solvent reorganization energy on distance have important implications for intramolecular electron transfers and for the nuclear configuration changes accompanying electron transfer.

Figure 1. Distance dependence of the first-order rate constant $k(r)$ in the normal and inverted regions, calculated from eq 2-4 using $\beta = 1.2$ A$^2$; $H_{AB}^{0} = 200$ cal, $\lambda_{s} = 1.92$ kcal mol$^{-1}$ and $\sigma = 10$ A. Upper figure: normal region, $\Delta G^{0} = +0.25$ eV; inverted region, $\Delta G^{0} = -2.00$ eV; solid line, classical calculation; dashed line, quantum-mechanical calculation$^4$ with $\eta_{0} = 450$ cm$^{-1}$. Lower figure: the distance dependence of the components of $k(r)$: $(\Delta G^{0})^{2} = (1/\lambda^{1/2}) \exp[-(\lambda + \Delta G^{0})^2/(4\lambda R^2)]$.

the nuclear configuration changes accompanying electron transfer have become available.$^5$ Important advances in the formulation of the electron-transfer problem have also been made.$^2,5$ Recently we have undertaken detailed calculations of the distance dependence of the rates of electron-transfer reactions in solution. We find that the dependences of the electronic coupling element and of the solvent reorganization energy on distance have important implications for intramolecular electron transfers and for the forward and back reaction rates and cage-escape yields in light-induced electron-transfer processes.

Since bimolecular electron transfer can occur over a range of separation distances, each with a unique first-order rate constant $k(r)$, the net second-order rate constant for the reaction is given by:

$$k_{obs} = \frac{4\pi N}{1000} \int_{0}^{\infty} g(r)k(r)r^2 \, dr \, M^{-1} s^{-1} \tag{1}$$

where $r$ is the distance between the two redox sites, and $g(r)$ is the pair distribution function. For spherical reactants $r$ is the center-to-center distance and it is generally assumed that $g(r) =$

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