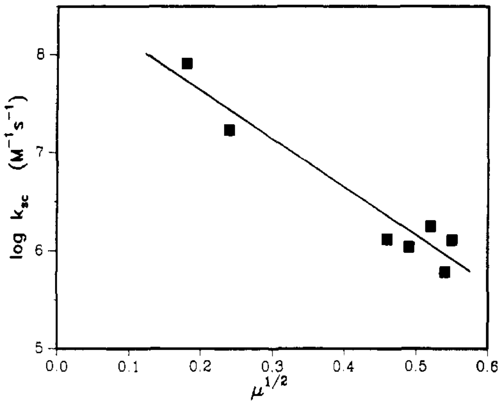

Figure 2. Plot of log k_{sc} vs $\mu^{1/2}$ for pH 4.7.

into k_{sc} by dividing by [EDTA]. This results in values of k_{sc} that range from $\sim 10^8$ to $\sim 10^6$ M^{-1} s^{-1} with increasing μ. A straight line can be forced through the points of a plot of log k_{sc} vs $\mu^{1/2}$ (Figure 2), showing that k_{sc} does, as expected, decrease with increasing ionic strength. Although this treatment is not valid in a quantitative sense at these relatively high ionic strengths, being well beyond the point where the Debye–Hückel limiting law can be applied and a linear plot expected, the slope of the line (−5) is amazingly consistent with the product of the charges of the reacting species. At the same time it must be noted that the value of k_{sc} at μ = 1.0 M is approximately the same as those at $\mu \sim$ 0.3, indicating that k_{sc} ceases to be a function of μ in that range, and/or that the presence of SO_4^{2-} changes the dynamics of the reaction due to a change in the ionic atmosphere surrounding the $Ru(bpy)_3^{3+}$.

The data for pH 8.7 at μ = 0.60 M and pH 11.0 at μ = 1.0 M yield values of k_{sc} of 4.6 × 10^7 and 5.0 × 10^7 M^{-1} s^{-1}, respectively, and demonstrate that they are not a function of [MV^{2+}]. Although the dependence of k_{sc} on μ was not studied at alkaline pH, it is safe to assume that it would show the same general trend as in acidic solution and may have a value $\sim 10^9$ M^{-1} s^{-1} at μ = 0.

Comparison of the values of k_{sc} at high ionic strengths for acidic and basic solutions shows that the rate constant is more than an order of magnitude larger in alkaline medium, consistent with the increasing reducing power of EDTA as it undergoes deprotonation. However, the fact that k_{sc} is $\sim 10^8$ M^{-1} s^{-1} at pH 4.7 and low ionic strengths underscores the necessity of comparing rate constants under the same solution medium conditions.

These factors make it difficult to compare the values of k_{sc} reported here with those in the literature; in fact, they all may be valid for the specific conditions under which they were determined, as long as the reaction was in the domain of strictly first-order kinetics or k_I was extracted from the mixed-order treatment. Nevertheless, there is the strong indication that k_{sc} is a function of the other anions present in the solution.

The important question to address is why k_{sc} is so low, even when account is taken of the effect of ionic strength. Despite the restrictions on the validity of the treatment in Figure 2, extrapolation of the line to μ = 0 yields a lower limit estimate of the value of k_{sc} at pH 4.7; the value of $\sim 4 \times 10^8$ M^{-1} s^{-1} is at least 2 orders of magnitude lower than the diffusion-controlled limit for oppositely and highly charged ions. The result further appears strange if reaction 5 is viewed as being highly exoergic; the reported standard oxidation potentials for EDTA at pH 2 and 9 from polarographic measurements are −0.56 and −0.13 V, respectively.[23]

However, reaction 5 is not highly exoergic; in fact, it may not be exoergic at all. The $E°$ values from polarographic measurements are affected by rapid and irreversible reaction 7, which would make the apparent potential more positive than the reversible one-electron potential. In our recent examination of the reductive quenching of $^*Ru(bpz)_3^{2+}$ (bpz = 2,2′-bipyrazine) by EDTA,[12] we estimated, from the general correlation of k_q with the driving force of adiabatic excited-state electron-transfer reactions,[24] that $E_{ox}°$ for the one-electron oxidation of EDTA in alkaline solution is ~ -1.5 V, making reaction 5 endoergic by ~ 0.2 V. If the rate constant for self-exchange of EDTA were comparable to that of $Ru(bpy)_3^{3+}$ (>10^9 M^{-1} s^{-1}),[25] an application of the free-energy relationships for electron transfer[26] would predict values of k_{sc} that are of the same order of magnitude as reported here.

Regarding the relationship of k_{sc} to the quantum yield of formation of $MV^{\bullet +}$ ($\Phi(MV^{\bullet +})$) in the $Ru(bpy)_3^{2+}/MV^{2+}/EDTA$ model photochemical system, $\Phi(MV^{\bullet +}) = \eta_{*}\eta_q\eta_{ce}\eta_{sc}(1 + \eta_{red})$, where η_{*} is the efficiency of formation of $^*Ru(bpy)_3^{2+}$ (~ 1),[27] and η_{red} is the efficiency of reduction of MV^{2+} by $EDTA_{red}^{\bullet}$ ($= k_{red}[MV^{2+}]/(k_{red}[MV^{2+}] + k_{dec})$). Reaction 8 and its overall

$$EDTA_{red}^{\bullet} \xrightarrow{k_{dec}} \text{products} \qquad (8)$$

rate constant (k_{dec}) reflect all the modes of conversion of $EDTA_{red}^{\bullet}$ to unreactive products, especially those that are pH dependent.

In order to optimize the yield of $MV^{\bullet +}$, all the values of η should be maximized. A high concentration of MV^{2+} will maximize η_q and η_{red}; a high concentration of EDTA (but a low ionic strength!) will maximize η_{sc}, but those parameters that enhance reaction 4 (high η_q and I_a) will diminish η_{sc}, especially under laser-flash conditions. Furthermore, η_{ce} is maximized at low [MV^{2+}], [EDTA], and μ.[14] When consideration is given to the prospect that η_{ce} and η_{sc} may be dependent as well on the nature of the solutes used to control μ, one can see that the optimization of the quantum yields of $MV^{\bullet +}$ and the total modeling of the system will require the consideration of the many interlocking relationships that involve the components of the solution medium.

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Synthesis of Tetrakis(trifluoromethyl)lead

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The interesting new compound $Pb(CF_3)_4$ has been prepared by a technique that promises to be a very broadly adaptable route to the synthesis of new σ-bonded metal compounds of relatively low thermal stability. This trifluoromethyl compound is one of the last remaining unsynthesized trifluoromethyl compounds of group IV, and although it is too unstable to be isolated at temperatures required for conventional synthetic methods (>100 °C), it is stable at room temperature when isolated from radiation sources.

We have earlier reported a synthesis of σ-bonded metal compounds based on cocondensation of metal atoms with free radicals[1]

$$M(g) + nR^{\bullet} \xrightarrow{-196\ °C} M(R)_n$$

where R is any conveniently generated free radical. When reactions were tried with lead vapor and plasma-produced trifluoromethyl radicals in the apparatus described,[1] no significant quantity of tetrakis(trifluoromethyl)lead was produced.

Lead trifluoromethyl compounds were unknown until 1978,[2] when the compounds tris(trifluoromethyl)methyllead and bis(trifluoromethyl)dimethyllead were prepared in our laboratory by a series of transfer reactions with bis(trifluoromethyl)mercury.[3] The synthesis of tetrakis(trifluoromethyl)lead, $Pb(CF_3)_4$, has now been accomplished in low yields by cocondensation of lead dichloride with trifluoromethyl radicals generated from a hexafluoroethane plasma source:

$$C_2F_6 \xrightarrow[100\ \mathrm{W},\ 14\ \mathrm{MHz}]{\mathrm{rf}} 2CF_3^{\bullet}$$

$$PbCl_2(g) + 4CF_3^{\bullet} \xrightarrow{-196\ ^{\circ}C} Pb(CF_3)_4 + Cl_2$$

This is the first successful synthesis of tetrakis(trifluoromethyl)lead.

The reactor used in this work has been illustrated elsewhere.[1] In a typical reaction, 1 g of dry lead dichloride was placed in a quartz crucible, which was then placed inside a resistively heated crucible heater. The radio frequency signal was supplied by a 100-W, 1356-MHz radio frequency generator, which was capacitively coupled to the reactor. The hexafluoroethane flow rate was set between 1 and 2 mmol/min, and the total pressure was maintained at less than 2 Torr. After completion of the reaction, the volatile products were vacuum distilled through a −110 °C trap to remove the excess hexafluoroethane and chlorine produced in the reaction. Care must be taken to minimize the exposure of the less volatile products to the chlorine produced or otherwise no trifluoromethyl-substituted lead compounds will be detected. If such care is taken, nearly all of the trifluoromethyllead compound is $Pb(CF_3)_4$, according to fluorine NMR spectra.

If the products are exposed to chlorine, several small NMR and GLC peaks appear of partially chlorinated lead trifluoromethyl compounds. If $PbBr_2$ or PbI_2 is used as a precursor, separation and removal of the halogen is more difficult owing to the more similar volatility of the minor products compared to that of $Pb(CF_3)_4$, and lower yields result.

The products of five reactions were collected at −110 °C, combined, and vacuum distilled. The fraction containing virtually all of the trifluoromethyllead compound very slowly passed a −78 °C trap. This fraction was then separated on a gas chromatograph (10% SE-30 on Chromosorb P) from the fluorocarbon catenation products also produced in the plasma. All of the product was placed in a preweighed capillary, sealed under vacuum, and weighed [21.4 mg of $Pb(CF_3)_4$]. A gas-phase weight determination gave 480 g/mol. (The calculated value is 483 g/mol.) The yield of tetrakis(trifluoromethyl)lead was between 1 and 2 mg/h.

Tetrakis(trifluoromethyl)lead is a colorless liquid that hydrolyzes in water to form fluoroform. With the mass spectrometer cooled to room temperature, the mass spectrum consisted of $Pb(CF_3)_n^+$ species and fluorocarbon fragments. The following lead species were observed (each envelope had the isotopically correct pattern but is given here in terms of ^{208}Pb isotopes only): *m/e* 208, Pb^+ (82%); *m/e* 227, PbF^+ (61%); *m/e* 277, $Pb(CF_3)^+$ (75%); *m/e* 346, $Pb(CF_3)_2^+$ (18%); *m/e* 415, $Pb(CF_3)_3^+$ (100%); *m/e* 465, $Pb(CF_3)_3CF_2^+$ (less than 1%). The fluorine NMR spectrum, taken on a neat liquid in a capillary, gave a singlet at −41 ppm from $CFCl_3$; $J(^{207}Pb\text{–}F)$ = 808 Hz. The gas-phase infrared spectrum contains absorptions at 1240 (m), 1150 (vs), 1105 (w), 1065 (s), 1030 (w), and 720 cm^{-1} (m).

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Registry No. $Pb(CF_3)_4$, 4556-29-0; $PbCl_2$, 7758-95-4; C_2F_6, 76-16-4.

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Time-Dependent Photoselection Results for Ruthenium(II) Diimine Complexes

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Krausz[1] has reported that our time-dependent excitation polarization results[2] for $Ru(bpy)_3^{2+}$ in glassy solution at 77 K could not be verified in his laboratory. While, in general, a negative result as he has reported must be viewed with caution, the confusion created by his report and the importance of this time-dependent result to establishing the correct mechanism for localization of the emitting triplet of the $Ru(bpy)^{2+}$ species necessitates a response.

In our work,[2] we pointed out that the decrease of the maximum excitation polarization from a value as high as $P_{max} \sim 0.4$ at short times (5–10 ns) to the steady-state $P_{max} \sim 0.23$ for those glassy solvents meant that the mechanism of localization necessarily was *intrinsic*, not *environmental* (solvent driven) as suggested by Krausz on the basis of excited-state resonance Raman[3] and emission measurements at the melting point of the glassy solvent.[4] This conclusion of intrinsic localization necessarily derived from the earlier excitation polarization result of Carlin and De Armond,[5] which was obtained in glassy solution at *77 K*, where solvent motion is not expected. Recent excited-state resonance Raman results by Brus and Carroll[6] concur with our conclusion that the localization is intrinsic.

Most recently, we have, in a detailed paper,[7] presented a model for the rationale of the magnitude of the steady-state excitation *P* in a variety of Ru(II) diimine complexes. The model describes the potential surfaces of the excited MLCT singlet and the emitting triplet states, noting that the singlet state consists of localized and delocalized regions and it is for this reason that the anomalous P_{max} magnitude is observed for Ru(II) tris- and bis(diimine) complexes.

Concurrently, we did report time-resolved P_{max} data for a number of tris(diimine) complexes, including the mixed-ligand complexes $[Ru(bpy)_2(phen)]^{2+}$ and $[Ru(phen)_2(bpy)]^{2+}$, for which P_{max} at 0–5 ns was found to be 0.43 in pure ethanol glass. Other complexes, including $[Ru(phen)_3]^{2+}$, $[Ru(bpz)_3]^{2+}$, and $[Ru(pq)_3]^{2+}$ (bpz = 2,2′-bipyrazine and pq = 2,2′-pyridylquinoline) as the original $[Ru(bpy)_3]^{2+}$, evidence solvent dependence in the decay of the polarization value (*P*).

We have pointed out that the original interpretation[2] of the time-dependent P_{max} as resulting from exciton hopping between the chelate rings is incorrect and that this fast decrease of *P* results from the spin–lattice relaxation (SLR) between the closely spaced spin states of this emitting triplet. While the details of the phonon spectrum for glassy solution are not well-known, the data for crystalline systems would suggest that at 77 K in glassy solution saturation of the lattice phonon modes would not be likely, since a large number of phonon modes would exist at this temperature. Thus, the suggestion by Krausz that our experimental laser intensity affects the equilibration of the spin state and could give rise to artifactually high *P* values seems unlikely. Further, in our measurement technique using a Molectron dye laser system as the excitation source, the laser beam was focused to a tight spot and also defocused to give low signal intensity. No difference in

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