**Figure 1.** Absorption spectra and (inset) emission (25 640-cm$^{-1}$ excitation) and excitation (19 230-cm$^{-1}$ emission) spectra of permethylscandocene chloride in a 1:1 (v/v) mixture of isooctane and methylcyclohexane at 298 K.

relative luminescent quantum yield with 366-nm excitation was determined to be 0.01.[5] The excited-state lifetimes based on luminescence decay in solution at 298 K, in an isooctane-methylcyclohexane (1:1 v/v) glass at 77 K, and in the solid state at 298 K were found to be 2.0 μs, 15.0 μs, and 6.5 μs, respectively, when excited at 337 nm by using a nitrogen laser.[6] The relatively long apparent lifetime of luminescence at room temperature suggests that emission occurs from a triplet excited state, a conclusion that is further supported by the absence of any significant change in the emission spectrum at 77 K upon the addition of incremental amounts of ethyl iodide as a heavy-atom intersystem crossing agent, as well as by the forbidden nature of this absorption (absent from the UV–vis spectrum, but observed in the excitation profile).

In an effort to understand the nature of the shoulder peak in the emission spectrum, time-resolved spectroscopy was performed by using a Nd:YAG Q-switched laser and an OMA detector. Two emissions were observed and are preliminarily assigned as fluorescence and phosphorescence. The fluorescent lifetime was determined to be less than 10 ns, while the lifetime of phosphorescence was in close agreement with that observed in the luminescence decay experiment mentioned earlier. Furthermore, the emission maximum at short times following the laser pulse was found to be blue-shifted from the maximum at longer times. This result is consistent with the assignment of the lowest energy emissive state as phosphorescence, with the fluorescence occurring at slightly higher energy. The combination and overlap of the two emissions produce the spectrum observed in Figure 1 (inset).

The effect of the energy of emission as a function of polarity of the solvent was also examined. In general, the emission was blue-shifted in more polar chlorocarbon solvents. Possible assignments for the emissive transition are limited in the d⁰ complex to intraligand, interligand, or ligand-to-metal charge transfer; the latter two would be expected to show solvent dependence. The assignment is further complicated by the emission of Cp* alone in hexane, which shows an absorption and emission spectrum similar to that of the compound of interest. However, the latter emission has a measured room temperature lifetime of only 580 ns under the same conditions employed to study Cp*$_2$ScCl. Furthermore, it is found that the room temperature luminescence in solution of the corresponding aniline derivative, Cp*$_2$ScNHPh, yields an emission maximum centered around 600 nm, conclusively

demonstrating that the observed emission is not simply associated with the Cp* ligand.

Lauher and Hoffmann[7] have reported a theoretical molecular orbital scheme for bent metallocene hydride complexes. They have suggested for this case that the HOMO is the σ-bonding metal hydride orbital (2a$_1$). Since the 2a$_1$ orbital in Cp*$_2$ScCl should be lower in energy than the nonbonding filled p orbitals on the chloride ligand, we suggest that the HOMO is composed of the chloride lone pairs. Optical transitions from this orbital to the 1a$_1$, 1b$_2$, and 2a$_1$* orbitals respectively are then possible. These orbitals are derived from the metal d orbitals admixing with the Cp* π-system. As a preliminary assignment, we hypothesize that the three transitions observed by absorption spectroscopy are associated with transitions from the p-Cl nonbonding HOMO to the orbitals indicated above. Based on this assignment, the forbidden absorption, which is the source of the luminescence, is assigned to the p-Cl → ³(1a$_1$) transition.[8]

Luminescence quenching was observed with a number of aromatic compounds, showing Stern–Volmer correlations with luminescent intensity as a function of quencher concentration. However, the apparent lifetime of the compound was relatively unchanged even at drastically higher concentrations of quencher. This would indicate that in all cases tested[9] the mechanism of quenching is purely a static one, possibly the formation of a π-complex between the aromatic species and the Cp* ring(s) of the organometallic.

(7) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

(8) Ligand-to-metal charge-transfer transitions are frequently associated with radical dissociation. It was noted at high N₂ laser intensities that the compound of interest decomposes, effecting changes in the Cp* region of the NMR spectra taken in C₆D₆. However, the nature of the decomposition was not investigated further because the decomposition only occurred at high laser intensities. Nevertheless, one would expect rapid radical recombination for the d⁰ complex because of its high Lewis acidity if radicals are indeed formed.

(9) Quenchers employed were toluene, xylenes, biphenyl, 1,2,4,5-tetrachlorobenzene, p-dibromobenzene, hexachlorobenzene, hexamethylbenzene, phenylacetylene, diphenylacetylene, and fluorene. The usual ketone and amine quenching agents could not be employed due to their thermal reactivity with the complex of interest.

## Control of Product Distribution by Marcus Type Electron-Transfer Rates for the Radical Pair Generated in Benzylic Ester Photochemistry

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The solution photochemistry of benzylic compounds with leaving groups (ArCH$_2$-LG) is well known[1-3] to yield products resulting from both ionic (ArCH$_2$⁺⁻LG) and radical (ArCH$_2$•⁻•LG) intermediates. Moreover, it has been recognized that the final composition of the product mixture need not be a direct measure of the initial excited-state bond cleavage process since electron transfer may allow interconversion between the radical pair and the ion pair. In fact, solution redox potentials suggest that the ion pair should be significantly more stable than the radical pair for most of the common leaving groups.[3] We now report results for a series of 1-naphthylmethyl esters, **1**,[4] that clearly show that

(5) The quantum efficiency was measured relative to that of anthracene in hexane by adjusting the optical densities of the two samples to be equal and then integrating the area under the respective emission curves. The quantum efficiency of anthracene at 366 nm was assumed to be 0.29 (Parker, A. C. *Photoluminescence of Solutions*; Elsevier Publishing Co.: Amsterdam, The Netherlands, 1968; p 266).

(6) The excited-state decay followed simple first-order kinetics.

(1) Cristol, S. J.; Bindel, T. H. *Organic Photochemistry*; Marcel Dekker: New York, 1983; Vol. 6, p 327.

(2) Arnold, B.; Donald, L.; Jurgens, A.; Pincock, J. A. *Can. J. Chem.* **1985**, *63*, 3140.

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Communications to the Editor

*J. Am. Chem. Soc., Vol. 111, No. 24, 1989* 8949

**Table I.** Product Yields for the Photolysis of Esters **1** in Methanol

| substrate | $2^a$ | $3^b$ | $4^a$ | 2/4 | log $k_{ET}^{X\,c}$ | $E^{ox\,d}$ |
|---|---|---|---|---|---|---|
| **1a** (X = H) | 84 | 60 | 16 | 5.3 | 10.41 | 0.47 |
| **1b** (X = 4-CN) | 12 | 12 | 80 | 0.15 | 8.86 | 0.72 |
| **1c** (X = 3-OCH₃) | 31 | 38 | 52 | 0.60 | 9.46 | $0.50^e$ |
| **1d** (X = 4-CH₃) | 93 | 72 | 7 | 13 | 10.79 | 0.35 |
| **1e** (X = 4-OCH₃) | 74 | 59 | 24 | 3.1 | 10.17 | 0.04 |
| **1f** (X = 4-OCH₂CH₃) | 80 | 60 | 22 | 3.6 | 10.23 | $0.04^f$ |
| **1g** (X = 4,8-(OCH₃)₂) | 47 | 33 | 51 | 0.92 | 9.62 | −0.05 |
| **1h** (X = 4,7-(OCH₃)₂) | 35 | 29 | 48 | 0.73 | 9.54 | −0.06 |

$^a$ By calibrated HPLC. $^b$ By weight of isolated product. $^c$ Assuming $k_{CO_2}$ = 4.8 × 10⁹ s⁻¹. $^d$ Oxidation potential in volts in CH₃CN versus SCE.[9a] $^e$ Not measured but estimated from the Hammett relationship with $\rho^+$ = 0.48 mV/$\sigma^+$.[9a] $^f$ Not measured but assumed equal to that for 4-OCH₃.

**Scheme I.** The Mechanism of Photolysis of 1-Naphthylmethyl Esters **1** in Methanol
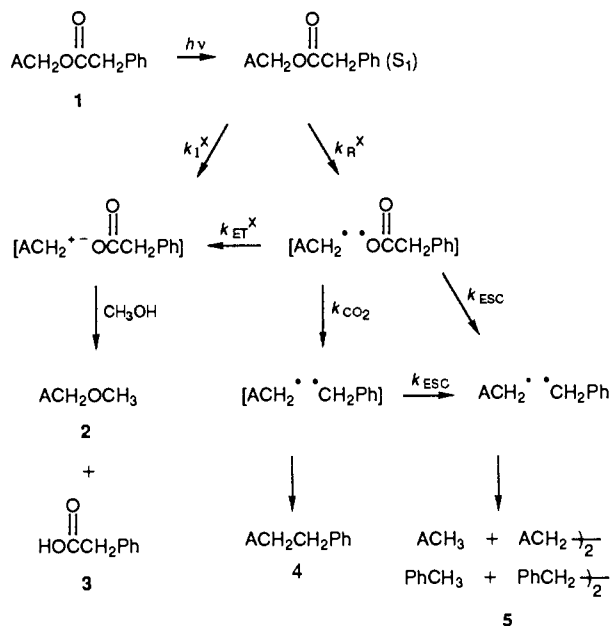


systematic variation of the oxidation potential of the benzylic radical can determine the rate of this electron transfer and hence the product composition in a photochemical benzylic cleavage.

As shown in eq 1 (A = $C_{10}H_{7-n}X_n$), direct irradiation of these esters in methanol results in the formation of three major products.
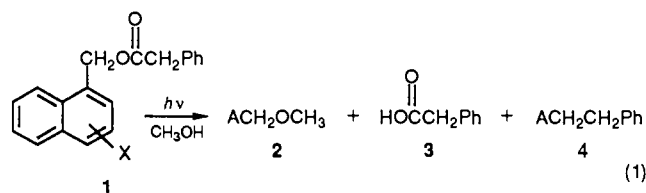


Good mass balance (determined by calibrated HPLC for **2** and **4** and by weight of isolated material for **3**) is obtained (Table I). Minor amounts of out-of-cage coupling and hydrogen-abstraction products of the 1-naphthylmethyl radical were observed by GC/MS particularly for X = 4-CN, 3-OCH₃, and 4,7-(OCH₃)₂ (vide infra). As shown in Scheme I, ether **2** and carboxylic acid **3** are formed by trapping of the 1-naphthylmethyl cation and the (phenylacetyl)oxy anion, respectively, by the solvent methanol. In contrast, **4** results from in-cage coupling of the 1-naphthylmethyl radical with the benzyl radical formed by loss of carbon dioxide from the (phenylacetyl)oxy radical.
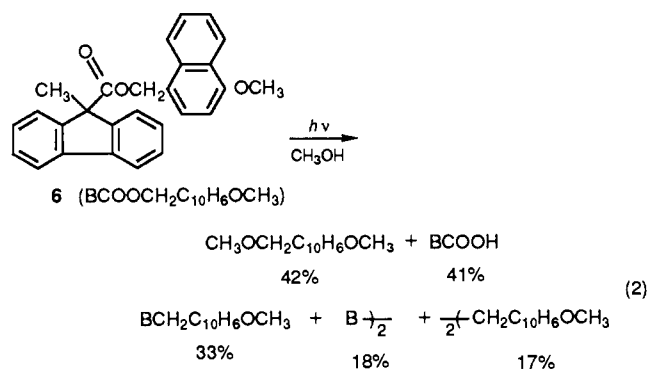
The mechanism for formation of these critical intermediates is shown in Scheme I. The product composition as a function of

the substituent, X, is determined by the changes in the rate constants $k_I^X$, $k_R^X$, and $k_{ET}^X$. The competition could occur in the primary excited-state process, i.e. $k_I^X$ versus $k_R^X$.[5] The "meta effect",[7] initially postulated to rationalize the effect of substituents on the preference for products derived from ionic intermediates for benzylic acetate photochemistry is based on this assumption. However, this explanation is unsatisfactory for the results in Table I, since both the unsubstituted (X = H) and the 4-methoxy compounds give higher yields of ether **2** than does the 3-methoxy substrate. We propose that the results for these esters can be explained by assuming that $k_R^X \gg k_I^X$ for all X and that the competition occurs between electron transfer $(k_{ET}^X)$ and decarboxylation $(k_{CO_2})$.[8,11] A referee of a previous version of this paper informed us that there is precedence for this idea. CIDNP results demonstrate that products derived from ion pairs can be formed by electron transfer in a R· ·O₂CR radical pair.[12]

If this is true, $k_{CO_2}$, the rate of decarboxylation of the (phenylacetyl)oxy radical, is serving as a "radical clock"[13] for the rate of electron transfer, and the product ratio $2/4 = k_{ET}^X/k_{CO_2}$. Although the rate of this particular clock is unknown, a very good estimate of it can be made as follows.

Photolysis of ester **6** ($BCO_2CH_2C_{10}H_6OCH_3$) gives the products shown in eq 2. Therefore, if the same mechanism applies, $k_{ET}/k_{CO_2}$ = 0.84. The known[14] rate (1.8 × 10¹⁰ s⁻¹) of decarboxylation



$$CH_3OCH_2C_{10}H_6OCH_3 + BCOOH$$
$$42\% \qquad\qquad 41\%$$

$$BCH_2C_{10}H_6OCH_3 + B\text{-}\tfrac{1}{2} + \tfrac{1}{2}\text{-}CH_2C_{10}H_6OCH_3$$
$$33\% \qquad\qquad 18\% \qquad\qquad 17\%$$

(2)

of the (9-methyl-9-fluorenoyl)oxy radical allows calculation of $k_{ET}$ = 1.5 × 10¹⁰ s⁻¹. If the reasonable assumption is made that the rate of electron transfer in the radical pair is dependent on the structure of the carbon radical but independent of the structure of the carboxyl radical, then, for the substrate **1e** (X = 4-CH₃O), the product ratio of $2/4$ = 3.1 = $k_{ET}^X/k_{CO_2}$ = 1.5 × 10¹⁰ s⁻¹/$k_{CO_2}$. Therefore, the rate constant for the clock process, the decarboxylation of the (phenylacetyl)oxy radical, equals 4.8 × 10⁹ s⁻¹.[15]

(4) All new compounds gave satisfactory spectral and elemental analysis.

(5) The radical pair formed will be a singlet pair since the excited triplet of naphthylmethyl esters is unreactive.[2,6]

(6) Matuszewski, B.; Givens, R. S.; Neywick, C. V. *J. Am. Chem. Soc.* **1973**, *95*, 1973. Givens, R. S.; Matuszewski, B.; Neywick, C. V. *J. Am. Chem. Soc.* **1974**, *96*, 5547.

(7) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915.

(8) The alternate pathway, $k_I^X \gg k_R^X$, would make the formation of products derived from the radical pair unlikely. This is true because estimation of the oxidation potentials of the naphthylmethyl radical (0.47 V versus SCE in CH₃CN)[9] and an acyloxy anion (1.8 V versus NHE in CH₃CN)[10] suggests that conversion of the ion pair to the radical pair would be endothermic by about 1 eV in acetonitrile.

(9) (a) Wayner, D. D. M. Personal communication. (b) Wayner, D. D. M.; Griller, D. J. *J. Am. Chem. Soc.* **1985**, *107*, 7764.

(10) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer-Verlag: New York, 1987; pp 45 and 62.

(11) Although product distribution could be controlled by the values of all four of the rate constants, i.e. $k_I^X \simeq k_R^X$, this possibility is unnecessarily complicated for the substrates studied here.

(12) Lawler, R. G.; Barbara, P. F.; Jacobs, D. *J. Am. Chem. Soc.* **1978**, *100*, 4912.

(13) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317.

(14) Falvey, D. E.; Schuster, G. B. *J. Am. Chem. Soc.* **1986**, *108*, 7419.

(15) This value cannot be wrong by very much since it must be within the relatively small range between 10⁹ s⁻¹ estimated for the (methylacetyl)oxy radical[16] and 1.8 × 10¹⁰ s⁻¹ estimated for the fluorenoyloxy radical.[14]

(16) Braun, W.; Rajbenbach, L.; Eirich, R. F. *J. Phys. Chem.* **1962**, *66*, 1591. Kaptein, R.; Brokken-Zijp, J.; de Kanter, J. J. *J. Am. Chem. Soc.* **1972**, *94*, 6280.
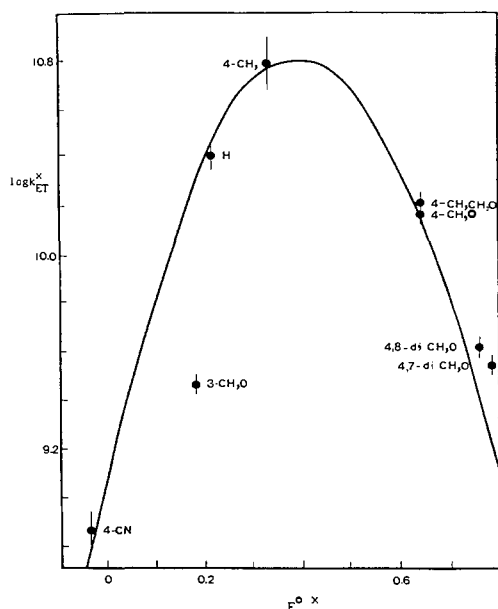
**Figure 1.** Plot of log $k_{ET}^X$ versus $E^{\circ\ X}$ of electron transfer for the conversion of the radical pair to the ion pair. The curve is a fit to eq 3 assuming log $A$ = 10.8 and $\lambda$ = 0.39 eV. The error bars assume a ±2% error in determination of product yields.

Using this value, the $k_{ET}^X$ values for the substrates **1a–1h** can be estimated (Table I).[17]

There has been considerable recent interest in electron transfer and, in particular, the relationship between the rate ($k_{ET}^X$) and the free energy change ($\Delta G^{\circ}{}_{ET}^X$) for the process. Marcus theory, shown in a simple form[18] in eq 3 where $\lambda$ is the reorganization

$$k_{ET}^X = A \exp\{-[\lambda(1 + \Delta G^{\circ}{}_{ET}^X/\lambda)^2/4]/RT\} \qquad (3)$$

energy, has been particularly successful in correlations of this data. To apply eq 3 to the rates of electron transfer determined here, values of $\Delta G^{\circ}{}_{ET}^X$ as a function of X are necessary. These can be evaluated from oxidation potential measurements according to eq 4 where the last term is the electrostatic free energy. The $\Delta G^{\circ}{}_{ET}^X =$

$$E^{\circ\ X}(ACH_2{}^{\bullet},CH_3OH) - E^{\circ}(PhCH_2CO_2{}^{-},CH_3OH) - e^2/Dr_{12} \qquad (4)$$

$$\Delta G^{\circ}{}_{ET}^X = E^{\circ\ X}(ACH_2{}^{\bullet},CH_3CN) + A^X - \qquad\qquad\qquad E^{\circ}(PhCH_2CO_2{}^{-},CH_3OH) - e^2/Dr_{12} \qquad (5)$$

$$\Delta G^{\circ}{}_{ET}^X = E^{\circ\ X}(ACH_2{}^{\bullet},CH_3CN) + B \qquad (6)$$

known[9a] values for the oxidation potentials of the naphthylmethyl radicals in acetonitrile can be used, eq 5, where $A^X$ is an unknown solvent correction factor. Making the reasonable assumption that $A^X$ is independent of the substituent X, eq 5 simplifies to eq 6 since the last three terms are all constants. A plot[19] of log $k_{ET}^X$ versus $E^{\circ\ X}$ (Figure 1) shows the shape for Marcus type electron-transfer rates, including the inverted region as the process becomes prohibitively exothermic for the more easily oxidized radicals. The data apparently provide another example of this seldom, and only recently, observed phenomenon.[20,21] A value of $\lambda$ = 0.39 eV gives a good fit ($s$ = 0.15) to eq 3 for all the data but a much better fit ($s$ = 0.09) if the point for 3-OCH$_3$ is not

included.[22] Although it is possible that the 3-methoxy compound is behaving anomalously, we have no good reason for omitting it. This value of $\lambda$ is small, but there is precedent for low values for electron transfer at short distances. A value of 0.48 eV has been reported for intramolecular electron transfer over 5 Å in a radical ion.[21]

(22) The value of $\lambda$ determines the width of the parabola, which is controlled by the magnitude of the change in $k_{ET}^X$ as a function of the change in $\Delta G^{\circ}{}_{ET}^X$. For these substrates, $k_{ET}$ changes by two powers of 10 as $E^{\circ}$ changes from 0.72 V (X = 4-CN) to 0.35 V (X = 4-CH$_3$). The value of $\lambda$ also determines, by definition, $-\Delta G^{\circ}{}_{ET}$ at the maximum in Figure 1 and hence the constant $B$, eq 6, since $\lambda = E^{\circ}{}_{max} + B$. We do not feel confident about reliably evaluating any of the three unknowns that make up $B$, eq 5.

## Corner Flapping: A Simple and Fast Algorithm for Exhaustive Generation of Ring Conformations

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The problem of finding significantly populating conformers has been one of the major obstacles in studying conformationally flexible molecules. A number of algorithms for locating energy minima on a high-dimensional energy hypersurface have been proposed. They can be classified into two categories, random[1] and systematic.[2]

While random generation is the method of choice for macromolecules, the application of a systematic method to a chain molecule ($n$ rotatable bonds) is severely limited due to the fact that the number of trial conformations increases at the rate of $3^n$.[2a,b] However, conformational freedom is greatly reduced in *cyclic structures*, and this is where the possibility exists for developing fast methods of exhaustive conformer generation. Our new algorithm starts from any one of the known conformers and thus avoids the inherent drawback of the conventional ring-closure methods[2c,d] where the nonclosing paths must be covered at least to some depth.

The conformation of a cyclic molecule can be viewed as the up-and-down pattern of ring atoms relative to the average ring plane, ring atoms occupying "corners" of the bonds.[3] Suppose one of the ring atoms is located above the average plane. Simply

(17) (a) Note that when $k_{ET}^X$ exceeds $10^{10}$ s$^{-1}$, cage-escape products are not observed. The diffusional escape rate in methanol is estimated at 3.5 × 10$^9$ s$^{-1}$ assuming two spherical fragments of radius 7 Å.[17b] (b) Gardiner, W. C. *Rates and Mechanisms of Chemical Reactions*; Benjamin: New York, 1969; p 168.
(18) Reference 10, p 32.
(19) The preexponential $A$ value, eq 3, has been set at 6 × 10$^{10}$ s$^{-1}$.
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(3) This idea is independently realized and developed into a different algorithm by Gerber et al.[2e]