Photochemistry of Arylmethyl Esters in Nucleophilic Solvents: Radical Pair and Ion Pair Intermediates

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Introduction

The photochemical reactions of arylmethyl compounds with leaving groups (ArCH$_2$−LG) give products from both intermediate arylmethyl radical (ArCH$_2$• •LG) as well as ion pairs (ArCH$_2^+$ $^-$:LG).[1−3] A general mechanism for the formation of both types of products is shown in Scheme 1.[4,5] Typical radical coupling, disproportionation, and hydrogen atom abstraction products are obtained from the radical pair (k_{rad}). In protic, nucleophilic solvents (SOH; water, alcohols, etc.) the ion pair is trapped by the solvent (k_{SOH}) to give substitution products (ArCH$_2$−OS). This latter process is known as photosolvolysis. The competition between the pathways for formation of these critical intermediates is dependent on many factors including the leaving group, the aromatic ring (i.e., benzene versus naphthalene, or benzene versus substituted benzenes), the solvent, and the multiplicity of the excited state involved (singlet versus triplet). These factors are not yet well enough understood to allow reliable predictions of product distribution for any given case because more than one pathway is possible for formation of the radical and ionic intermediates. Four mechanistic extremes have been outlined[5] for fragmentations from a singlet excited state, ^{1}(ArCH$_2$−LG), but only two of these are relevant to the results discussed here: (1) formation of radical pairs (k_{hom}) and ion pairs (k_{het}) competitively;[6] (2) formation first of radical pairs (k_{hom}) followed by electron transfer (k_{etri}) to give ion pairs under suitably polar solvation conditions.[2,7] The possibility of equilibration between radical and ion pairs can be excluded because, for the intermediates formed for most leaving groups, the ion pair in polar solvents is significantly more stable than the radical pair.[8]

Ten years ago, we began exploring the synthetic potential of photochemical arylmethyl cleavage reactions, particularly for the protection of functional groups. This potential can only be realized if the substrate can be designed to make the reaction proceed exclusively to either the radical-derived or the ion-derived products. At

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Scheme 1. General Mechanistic Scheme for the Photodissociations of Benzylic−Leaving Group (ArCH$_2$−LG) Bonds[a]
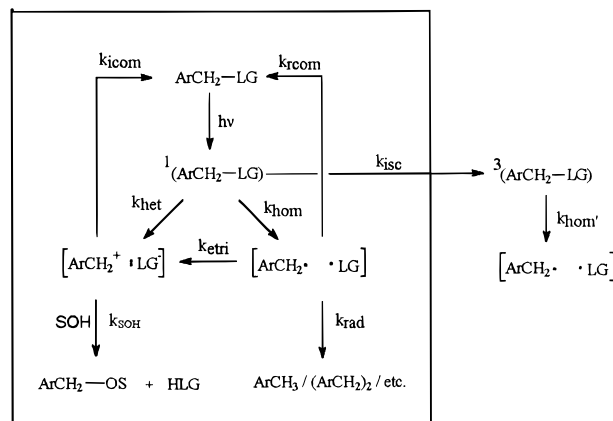
[a] Abbreviations for rate constants: k_{het} = bond heterolysis from the singlet state, k_{hom} = bond homolysis from the singlet state, k_{SOH} = nucleophilic capture of the cation, k_{rad} = reaction(s) of the radical pair, k_{etri} = electron transfer converting the radical pair to an ion pair, k_{isc} = intersystem crossing from the singlet state to the triplet state, $k_{hom'}$ = bond homolysis from the triplet state, k_{icom} = ion pair combination, k_{rcom} = radical pair combination.
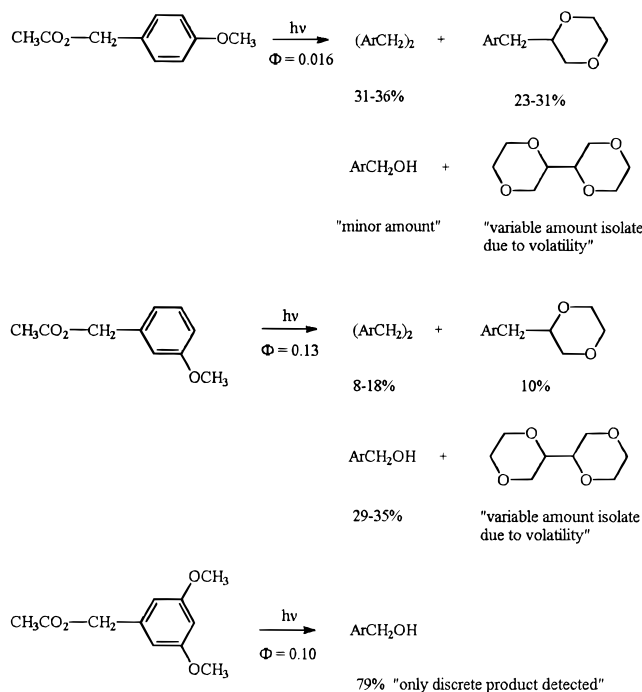
the time we assumed that the the aromatic chromophore, and in particular substituents on the aromatic ring, controlled the competition between k_{hom} and k_{het} and that an understanding of these substituent effects in the excited state would be critical to this design. We began a systematic study of the relationship between rate and substituents (Hammett $\rho\sigma$ correlations) in the excited state for both homolytic and heterolytic excited state bond cleavage reactions. These results would complement the extensive literature on substituent effects in ground state reactions. Our first study identified two leaving groups, carboxylates ($^-$O(CO)R) from esters and amines (NR$_3$) from ammonium salts, that satisfied the criteria necessary to make clear mechanistic conclusions: products from both the radical and ion pairs and excited states with lifetimes in the nanosecond time domain.[9] With more reactive leaving groups (like chloride), the rates are too radid to be easily measured.[10,11] Of the two leaving groups mentioned above, we have found carboxylates more useful because compounds with the varying structural requirements necessary to test mechanistic possibilities are readily synthesized. As well, a major advantage that esters provide as a mechanistic probe is an unreactive triplet state ($k_{hom'}$ = 0)[9,12,13] so that conversion (k_{isc}) of the first formed excited singlet state, ^{1}(ArCH$_2$−LG), to the corresponding triplet state, ^{3}(ArCH$_2$−LG), although decreasing

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Scheme 2. Photolysis of Methoxy-Substituted Benzyl Acetates in 50% Aqueous Dioxane

$$CH_3CO_2—CH_2 \text{—} OCH_3 \xrightarrow[\Phi = 0.016]{h\nu} (ArCH_2)_2 + ArCH_2\text{—dioxane}$$

31-36%   23-31%

$$ArCH_2OH + \text{bis-dioxane}$$

"minor amount"   "variable amount isolate due to volatility"

$$CH_3CO_2—CH_2 \text{—} OCH_3 \xrightarrow[\Phi = 0.13]{h\nu} (ArCH_2)_2 + ArCH_2\text{—dioxane}$$

8-18%   10%

$$ArCH_2OH + \text{bis-dioxane}$$

29-35%   "variable amount isolate due to volatility"

$$CH_3CO_2—CH_2 \text{—(OCH}_3)_2 \xrightarrow[\Phi = 0.10]{h\nu} ArCH_2OH$$

79% "only discrete product detected"

the efficiency of the reactions, does not affect the product ratios. Therefore, only the possibilities inside the box of Scheme 1 need to be considered. Moreover, the ester leaving group was the one used in the historically important, fundamental report in 1963 by Zimmerman and Sandel[6] describing substituent effects in the photosolvolysis of methoxy-substituted benzyl acetates in aqueous dioxane, Scheme 2.

The observed higher efficiency (Φ) of reaction for the 3-methoxy substrate relative to the 4-methoxy substrate, as well as the increased yield of the ion-derived photosolvolysis product, the benzyl alcohol, for the 3-substituted substrates was clearly contrary to expectations based on ground state reactivity. In the ground state, the methoxy group is electron-donating by its resonance effect from the 4-position (i.e., *para*), resulting in an enhanced rate of cation formation in solvolysis reactions by as much as 4 powers of 10 relative to the unsubstituted case.[14] In contrast, a methoxy group in the 3-position (i.e., *meta*) results in a small rate decrease because of its electron-withdrawing inductive effect. The term "*meta* effect" was introduced to describe the unexpected reactivity for the 3-methoxy-substituted esters in Scheme 2 and for other photochemical reactions with enhanced *meta* reactivity.[15] A theoretical rationalization was provided by simple Hückel MO calculations which predict that, for benzene rings substituted with electron-donating groups, excitation to the singlet state will selectively increase electron density at the *ortho* and *meta* positions. In essence, this *ortho/meta* effect proposes that both the rate-determining photochemical step and the product yields are controlled

by these changes in electron density. Many photochemical reactions involving cation intermediates have shown enhanced reactivity with electron-donating groups in *ortho* or *meta* positions including photoprotonation of alkenes and alkynes,[16] photodehydroxylation of arylmethyl alcohols,[17] and photoprotonation of aromatic rings.[18]

Although time-resolved spectroscopic studies of the radical and ion pairs would be extremely useful in probing the complexities of Scheme 1, no such results have been reported yet for arylmethyl esters. Because these transients have lifetimes in the subnanosecond time domain, they decay faster than they are created by the relatively slower nanosecond bond cleavage process for esters. Therefore, creating measurable concentrations of the transients is difficult. Recent results[19-21] on the picosecond kinetics of the transients in the photolysis of more reactive substrates, diphenylmethyl and ring-substituted diphenylmethyl chlorides, indicate that both radical and ion pairs are formed directly from the excited singlet state. The radical pairs then decay by electron transfer to form ion pairs as well as by diffusional separation.
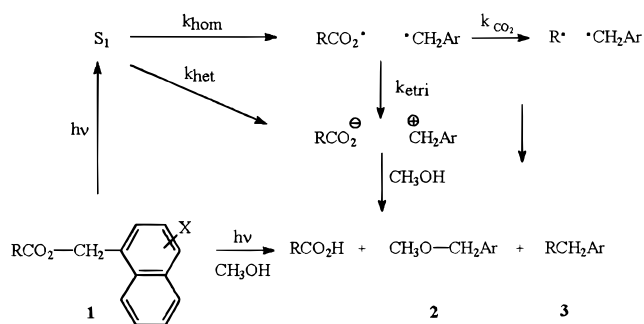
In this Account, both the excited state properties and product yields as a function of structure in the photochemistry of four sets of substituted arylmethyl esters in the solvent methanol will be summarized. A case will be constructed for a mechanism of excited state homolytic cleavage of the arylmethyl–oxygen bond (k_{hom}) followed by electron transfer (k_{etri}) as the dominant pathway for formation of ion pairs. This competition controls product ratios. Direct heterolytic cleavage from the excited singlet state (k_{het}) seems to be, at most, a minor pathway. These results have been briefly reviewed previously.[22,23] Recently, this mechanistic conclusion has been challenged by Zimmerman in favor of his original mechanism, at least for methoxy-substituted benzyl acetates. High-level MO calculations have been used to support the proposal of enhanced heterolytic cleavage from the excited state of *m*-methoxy-substituted benzyl acetates.[15] In part, this Account is a reply to those suggestions.

Set 1: Photolysis of Substituted 1-Naphthylmethyl Phenylacetates 1[24,25]

The photolysis in methanol of these substrates resulted in particularly simple product mixtures, Scheme 3. The ether **2** and phenylacetic acid were obtained from the ion pair, and the hydrocarbon **3**, resulting from loss of CO_2, was the major product from the radical pair (for com-

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Scheme 3. Product Distribution and Mechanistic Scheme for the Photolysis of the Esters 1 in Methanol

$$S_1 \xrightarrow{k_{hom}} RCO_2{}^{\bullet} \quad {}^{\bullet}CH_2Ar \xrightarrow{k_{CO_2}} R^{\bullet} \quad {}^{\bullet}CH_2Ar$$

with k_{het}, $h\nu$, k_{etri}

$$RCO_2{}^{\ominus} \quad {}^{\oplus}CH_2Ar$$

$$CH_3OH$$

$$RCO_2{-}CH_2\text{-}(naphthyl\text{-}X) \xrightarrow[CH_3OH]{h\nu} RCO_2H \;+\; CH_3O{-}CH_2Ar \;+\; RCH_2Ar$$

1   2   3

Entry	X	R	%2	%3
1	4-OCH₃	PhCH₂	74	24
2	3-OCH₃	PhCH₂	31	52
3	H	PhCH₂	84	16
4	4-OCH₃	9-CH₃ Fluorenyl	42	33
5	4-CH₃	9-CH₃ Fluorenyl	63	12
6	H	CH₃	98	-
7	H	CH₃CH₂	93	6
8	H	(CH₃)₂CH	80	6
9	H	(CH₃)₃C	71	9
10	H	PhCH₂CH₂	92	7

parison with Scheme 2, entries 1−3 have been selected from the 11 compounds studied). In contrast to benzyl acetates, Scheme 2, the 3-methoxy compound gave a lower yield of the ion-derived product (31%) than the 4-methoxy isomer (74%). Moreover, the highest yield (84%) is for the unsubstituted compound. The clue to understanding these results was provided by Dayal De-Costa, a doctoral student at the time, whose plot of the percent yield of **2** versus σ^+ was parabolic with low yields for both strong electron-donating and -withdrawing substituents. This observation of a parabolic free energy relationship reminded us of Marcus's theory,[26] and we therefore began to consider the process of electron transfer converting the radical pair to the ion pair, k_{etri} in Scheme 1. Very quickly, our working hypothesis became that homolytic cleavage from the excited singlet state, rather than heterolytic cleavage, was the dominant process for all substrates, i.e., $k_{hom} \gg k_{het}$. As a consequence, product yields will be controlled by two competing rate constants, k_{etri} and k_{CO_2}, where the latter is the rate of decarboxylation of the (phenylacetyl)oxy radical (R = PhCH₂), Scheme 3. This is a classic "radical clock" mechanism[27] although at the time the rate constant of decarboxylation was unknown. Picosecond laser flash photolysis (LFP) studies had provided a value of $k_{CO_2} = 1.8 \times 10^{10}$ s^{-1} for the (9-methylfluorenyl)carboxyl radical,[28] and this was used as the calibrating reaction for our results (entries 4 and 5, Scheme 3).

The assumption was made that structural changes in the ester are acting in an orthogonal way: the R group only has an effect on k_{CO_2} while the aromatic ring, and its substituents, only has an effect on k_{etri}. The mechanistic
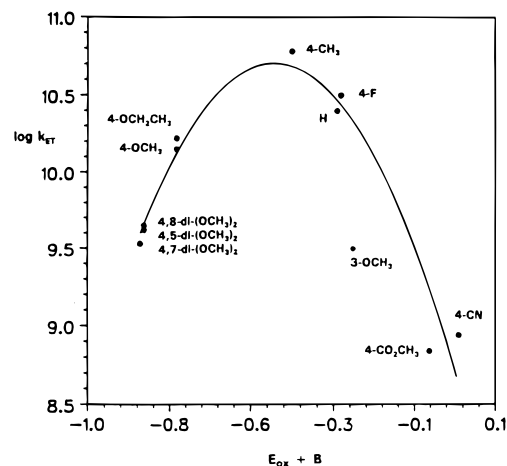

FIGURE 1. log of the rate of electron transfer for converting the radical pair to the ion pair as a function of the oxidation potential of the 1-naphthylmethyl radical. The fit to the Marcus equation gives the reorganization energy, $\lambda_S = 0.5$ eV. A detailed discussion of the fitting procedure and of the value of B is in the original publication.[25] Reprinted with permission from ref 25. Copyright 1993 American Chemical Society.

analysis then becomes cyclic; one known k_{CO_2} value, along with product ratios for a set of substrates, allows the determination of k_{etri} values for the corresponding radical pairs. These k_{etri} can then be used to determine other k_{CO_2} values. In this way, a value of 4.6×10^9 s^{-1} was obtained for k_{CO_2} for R = PhCH₂. The resulting values of $\log(k_{etri})$ for conversion of the radical to ion pairs for the substrates **1** were then plotted versus the oxidation potentials of the 1-naphthylmethyl radicals[8] as in Figure 1. We were gratified to observe that "...a *charge separation* reaction was also found to exhibit the full range of behaviour predicted by Marcus' theory." [29]

Set 2: Photolysis of 1-Naphthylmethyl-Substituted Acetates[30]

The rationalization of product yields by the radical clock assumption discussed above leads to the possibility of switching the clock, i.e., using product yields and k_{etri} as the clock reaction to determine k_{CO_2} as a function of R.

For this set of esters, RCO₂−CH₂Ar (Ar = 1-naphthyl), the yield of the ether **2** changes predictably as a function of R (entries 6−10, Scheme 3), leading to rate constants ($k/10^9$ s^{-1}) of RCO₂$^{\bullet}$ decarboxylation: <1.3 (R = CH₃); 2.0 (R = CH₃CH₂); 2.3 (R = PhCH₂CH₂); 6.5 (R = (CH₃)₂CH); 11 (R = (CH₃)₃C). These values gave us added confidence that our mechanistic proposal was correct both because the order makes chemical sense and because the values fit expectations grounded on the measured value for R = 9-methyl-9-fluorenyl (18×10^9 s^{-1})[28] and estimated values around 1×10^9 s^{-1} for R = CH₃.[31,32] On the basis of radical stability arguments, these two acyloxy radicals should be the fast and slow extremes, respectively, for the decarboxylation rate constants for the cases examined.

The suggestion that the lifetime of the acyloxy radical can be used as a probe for the reactivity of the radical

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pair generated in arylmethyl ester photochemistry has been one of the targets of a recent criticism[15] of the mechanism proposed in Scheme 3:

A main argument used by Pincock as supporting initial homolytic fission of the benzylic esters was that the benzyl pivalates[33] afforded considerably more free radical final products than did the acetates. The idea here is that a pivaloxy free radical once formed will rapidly decarboxylate with formation of the *tert*-butyl radical and thus serve to trap an initial homolysis product...

The diversion of the reaction by use of pivalate esters seemed inconclusive. It has been long known that the rate of homolysis in the parallel case of peroxides is enhanced by the presence of potentially stable free radicals such as *tert*-butyl. This rate enhancement results from concerted loss of the CO_2 moiety and formation of the *tert*-butyl radical as homolysis proceeds. Thus pivaloyl peroxides decompose at a greatly enhanced rate relative to acetyl and benzoyl peroxides.

In analogy, the use of the pivalate ester in place of acetate could enhance the rate of homolysis by virtue of concerted fragmentation of the incipient radical pair to give carbon dioxide and *tert*-butyl radical.

Although the focus of these comments by Zimmerman is on benzyl pivalates rather than 1-naphthylmethyl esters, their essence is that acyloxy radicals ($R-CO_2^{\bullet}$) do not exist as discrete intermediates if the radical R is as stable as, for example, *tert*-butyl and benzyl. In support of this argument, the half-lives (in minutes at 60 °C by extrapolation from higher temperatures) for the thermal decomposition of the peresters, $RCO_2-OC(CH_3)_3$, in chlorobenzene as a function of R are 50 000 (R = CH_3), 1700 (R = $PhCH_2$), and 300 (R = $C(CH_3)_3$).[34] The mechanism proposed for these reactions was fragmentation by a concerted two-bond transition state. Because this order follows the decrease in yield (98%, 84%, 71%) of the ion-derived product in the photolysis reactions of **1** (Scheme 3, entries 6 (R = CH_3), 3 (R = $PhCH_2$), and 9 (R = $(CH_3)_3C$, respectively), the comments in the quote are certainly justified and deserve a response.

Several features of the photochemical reactions, which generate acyloxy radicals at 20 °C, suggest that these radicals do have discrete lifetimes that can be used as "clocks" for probing their reactivity.

First, evidence for the existence of unstable acyloxy radicals as transient intermediates has been provided by LFP experiments. For instance, very recently "Direct Observation of Carbon–Carbon Bond Cleavage in Ultrafast Decarboxylations" has been reported for $(Ar)_2C$-$(OH)CO_2$ radicals in water.[35] When Ar is unsubstituted phenyl, $k_{CO_2} = 8 \times 10^{11}$ s^{-1}, i.e., a lifetime of 1.2 ps. Previously, the rate of decarboxylation of the acyloxy radical **4** generated by excitation of the peroxide had been measured in acetonitrile at room temperature, eq 1.[28] The radical **5** grew by first-order kinetics with a rise time of 55 ± 15 ps ($k = 1.8 \times 10^{10}$ s^{-1}). As described above, we have used this value as our radical clock standard.

Second, many acyloxy radicals have now been trapped before decarboxylation. For instance, primary alkyl acy-

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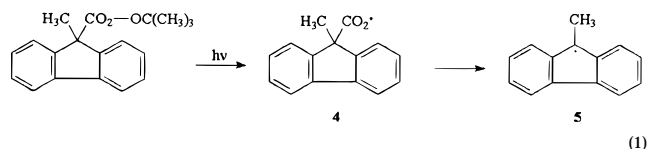
loxy radicals ($RCO_2^{\bullet}$) have been trapped by in-cage disproportionation in the pyrolysis of diacyl peroxides at temperatures ranging from 80 to 105 °C.[36] As well, the radical **6** was trapped at room temperature in a bimo-

6
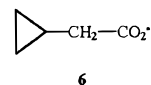
lecular step with the very reactive H atom donor PhSeH in yields ranging from 0% at 53 °C to 50% at −45 °C.[37] Recently reported[38] bond dissociation energies (kcal/mol) for R–H as a function of R (104 (R = CH_3); 100 (R = CH_3-CH_2); 96 (R = $(CH_3)_2CH$); 94 (R = $(CH_3)_3C$; compared with a value[39] of 97 (R = cyclopropylCH_2)) suggest that the rate constant for decarboxylation of **6** should be comparable to that for a secondary radical. Nevertheless, it is still a discrete intermediate. Acyloxy radicals that would give tertiary radicals after loss of CO_2, such as pivaloyloxy, have not yet been trapped.

Third, ^{18}O exchange studies in ester photochemistry have clearly demonstrated that there is an internal return pathway for the scrambling of the acyl and carbonyl oxygens.[40–43] The suggestion has been made that this exchange could be a concerted 1,3-migration.[41] However, in some cases,[42,43] simultaneous racemization at the alkyl oxygen carbon of the ester demonstrates that discrete intermediates (radical or ion pairs) must be formed, followed by collapse back to starting material (k_{rcom} and k_{icom} in Scheme 1). There is good evidence from a comparison between ground state solvolysis reactions in methanol, i.e., only ion pair intemediates, that some of this return must occur from the radical pair (k_{rcom} for $RCO_2^{\bullet}$ $^{\bullet}CH_2Ar$).[43] In these latter cases, R = $PhCH_2$, but the acyloxy radical is still trapped by internal return, i.e., has a discrete lifetime.

Fourth, there is a systematic change in the rates of decarboxylation as determined by the photochemical radical clock method. The sequence through CH_3, primary, secondary, and tertiary makes chemical sense. We place no special emphasis on the $(CH_3)_3CCO_2$ radical although the larger decrease in the yield of the ion-derived product on going from acetates to pivalates provides a stronger contrast than any other possible pair. Moreover, the excited singlet state properties ($\tau_S = 40$ ns, $\phi_F = 0.14$) of this set of esters (Scheme 3, entries 3 and 6–10) is independent of R.[30] There is no indication in the photo-

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chemical reactions of the 1-naphthyl derivatives of "...enhanced rate of homolysis by concerted fragmentation of the incipient radical pair..." [15] which would require a decreased τ_S.

There are two very obvious explanations for the difference between the thermal and photochemical behavior of substrates fragmenting to acyloxy radicals. The first is the high temperatures required for the former. In the pyrolysis of an acyl peroxide, such as $PhCH_2CO_2-OC(CH_3)_3$, the temperatures used to obtain activation parameters ranged from 80 to 100 °C.[44] Clearly this will have an effect on the reactivity of any short-lived transients. The second observation is that, in the pyrolysis reactions, there is considerable ionic character in the transition state, as indicated by the correlation with σ^+ ($\rho^+ = -1.04$ at 100 °C) for $ArCH_2CO_2-OC(CH_3)_3$ decomposition kinetics.[44] Moreover, the ρ^+ has increased to -1.20 by 56 °C, indicating that an even larger value would be expected at room temperature. A very similar $\rho^+ = -1.1$ has been observed for H atom abstraction by bromine atoms from substituted toluenes, reflecting a similar polar transition state.[45,46] The ionic character in the thermal reactions is attributed to polar resonance forms, e.g., **7**, for the


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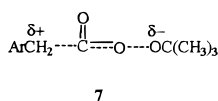
transition state in the pyrolysis of peresters.[47] A similar polarity effect would be expected in the pyrolysis reactions of peresters on changing from acetate to pivalate. The ionic character in the transition state lowers the barrier for the concerted two-bond process for the pivalate. In contrast, $\rho = 0$, as determined by our photochemical radical clock method, for the rate constants for decarboxylation of the $ArCH_2CO_2$ radicals generated in the photolysis of nine substituted $ArCH_2CO_2-CH_2-(1-naphthyl)$ esters at room temperature in methanol.[48] In the absence of the departing electronegative alkoxy radical and in the polar solvent, methanol, the rates of decarboxylation are apparently not influenced by the electron-donating ability of the aromatic ring.

Set 3: Photolysis of Substituted Benzyl Acetates 8 (R = CH₃) and Pivalates 8 (R = C(CH₃)₃)[13]

Because of the contrast between the mechanistic proposals for the substituted benzyl esters, Scheme 2,[6,15] and the 1-naphthylmethyl esters **1**, Scheme 3,[24,25,30] a more detailed examination of the former seemed essential. The original study[6] was limited to three substituted benzyl acetates: 3-methoxy, 4-methoxy, and 3,5-dimethoxy. Only examination of a wider range of substituents revealed the importance of the electron transfer step in the photochemistry of the 1-naphthylmethyl esters. The photolysis in methanol of 12 substituted benzyl esters (six acetates

Scheme 4. Product Distribution and Mechanistic Scheme for the Photolysis of the Esters 8 in Methanol
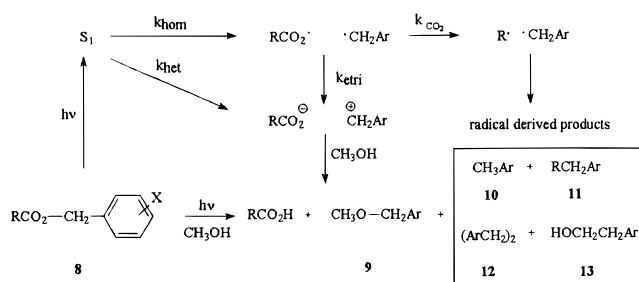
Entry	X	R	%9	%10,11,12,13
1	H	CH₃	26	68
2	4-OCH₃	CH₃	1.7	87
3	3-OCH₃	CH₃	32	64
4	3-OCH₃	C(CH₃)₃	10	83

and six pivalates) gave more complicated mixtures, Scheme 4 (only four of twelve examples are shown), than the previously studied 1-naphthylmethyl esters, Scheme 3. The main differences were the higher yields of the out-of-cage dimers **12** and the formation of the disproportionation product **10** when R = C(CH₃)₃.

However, a mechanistic comparison of sets 1 and 2 with set 3 leads to a self-consistent conclusion for all three. In all comparisons of acetates and pivalates, the yield of the ion-derived product is lower for the pivalate (entries 3 and 4, Scheme 4). Moreover, the *meta* effect seems important only when comparing 3-methoxy with 4-methoxybenzyl acetate, as in Scheme 2. With results available from more substituents, the 3-methoxy compound is revealed to have a product distribution very similar to that of the unsubstituted compound (entries 1 and 3, Scheme 4); by comparison, the 4-methoxy compound has a quite different product distribution. Finally, application of the radical clock mechanism again allows the estimation of k_{etri} values for converting the radical pair to the ion pair. When the $\log(k_{etri})$ values are plotted against E_{ox} values for the substituted benzyl radicals,[49] the Marcus correlation,[50,51] Figure 2, again shows both the normal and inverted regions as for the 1-naphthylmethyl esters, Figure 1.

The photolysis of these three sets of esters is therefore best rationalized by a mechanism that is dominated by homolytic cleavage from the excited singlet state (k_{hom}) to give an in-cage radical pair. The ion pair is formed principally by electron transfer (k_{etri}); direct heterolytic cleavage (k_{het}) from the excited state is, at most, a minor pathway.

This conclusion leads to an important observation. Because the above mechanism predicts a small reorganization energy for the electron transfer step (k_{etri}) for both sets of radical pairs (Figures 1 and 2), the parabola of the Marcus plots is narrow on the ΔG scale. This means that both the normal and inverted regions can only be ob-

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(50) A cautionary note is required here. Our results for multiple methoxy-substituted benzyl esters, ref 52, do not fit into this mechanistic scheme. The reasons for this are currently under investigation.

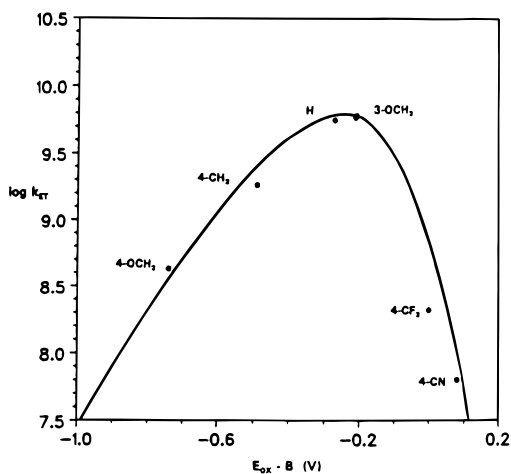(51) Pincock, J. A.; Wedge, P. J. *J. Am. Chem. Soc.* **1994**, *59*, 5587−5595.

FIGURE 2. log of the rate of electron transfer for converting the radical pair to the ion pair as a function of the oxidation potential of the benzyl radical. The fit to the Marcus equation gives the reorganization energies, $\lambda_V = 0.1$ eV and $\lambda_S = 0.2$ eV. A detailed discussion of the fitting procedure and of the value of B is in the original publication.[13] Reprinted with permission from ref 13. Copyright 1994 American Chemical Society.

served if the set of compounds studied generates radical pairs with redox potentials that are near the maximum on the log k_{etri} versus ΔG plot and, as well, span both sides of this maximum. One has to be lucky, as we were! All compounds could have radical pairs with redox potentials that put them in the normal region; a σ^+ correlation with positive slope will be observed. Conversely, all compounds could form radical pairs with redox potentials that put them in the inverted region; a σ^+ correlation with negative slope will result. For the benzyl acetates, an unusually high yield of the ion-derived product is observed for the *m*-methoxy compound, when compared to the *para* isomer. This results because redox potentials for the corresponding radical pair place it near the maximum on the plot, Figure 2.

Set 4: Photolysis of Substituted 1-Indanyl Acetates 14 (R = CH$_3$) and Pivalates (R = C(CH$_3$)$_3$)[52]

An unresolved question remained regarding the relative reactivity of *m*- and *p*-methoxybenzyl acetate because the quantum yield of reaction is higher for the *meta* (0.13) than for the *para* (0.016) compound, Scheme 2.[6] Moreover, our measurements of singlet lifetimes for the *meta* (<1 ns) and *para* (7 ns) compounds, and the lack of fluorescence for the *meta* compound, suggested that the *meta* compound is extremely reactive.[13] The six indanyl compounds 14, Scheme 5, were chosen for study to avoid any complications due to conformational motion about the reactive C−O bond.[52] The trend in product yields is consistent with the results from the previous three sets of compounds: high yields of the ether 15, the ion-derived product, from the unsubstituted and *m*-methoxy acetates (entries 1 and 3 in Scheme 5) and a much lower yield for the *p*-methoxy compound (entry 5). The change from acetate to pivalate again decreases the yield of 15 significantly, reflecting the increased rate of decarboxylation of $(CH_3)_3CCO_2^\bullet$. Finally, the rate constants ($k_R/10^9$ s^{-1},

(52) Pincock, J. A.; Wedge, P. J. *J. Org. Chem.* **1995**, *60*, 4067−4076.

Scheme 5. Product Distribution for the Photolysis of the Esters 14 in Methanol
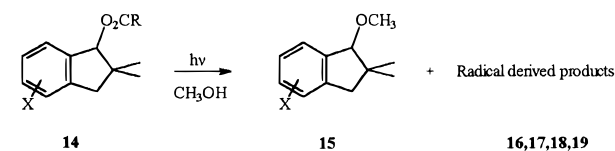
Entry	X	R	15	16,17, 18,19	k_R / 10^9 (s^{-1})
1	H	CH$_3$	52	37	2.8
2	H	C(CH$_3$)$_3$	14	68	3.2
3	6-OCH$_3$ (*meta*)	CH$_3$	60	26	-
4	6-OCH$_3$ (*meta*)	C(CH$_3$)$_3$	13	51	>19
5	5-OCH$_3$ (*para*)	CH$_3$	9	89	1
6	5-OCH$_3$ (*para*)	C(CH$_3$)$_3$	-	100	1

Scheme 5) of excited state reactivity were determined from quantum yield and singlet lifetime measurements. A comparison of the acetate and pivalate esters for X = H and X = 4-OCH$_3$ shows no enhanced reactivity for the pivalates as would be expected for a concerted two-bond decomposition. On the other hand, the *meta* compound 14 (entry 4, Scheme 5) reacts more than 19 times faster than the *para* compound 14 (entry 6, Scheme 5). Only a lower limit can be put on this factor because the singlet lifetime of the *m*-methoxy compound is less than 1 ns. Its very weak fluorescence (ϕ_F < 0.005) also means that a reliable determination of the lifetime will be very difficult. Therefore, the *meta* effect does contribute to reactivity in arylmethyl ester photochemistry, but only because the activation energy to reach the transition state in this polar *homolytic* bond cleavage process is lowered by the enhanced electron-donating ability, in the excited state, of the *m*-methoxy group. An interesting contrast exists in the photochemistry of substituted (2-arylcyclopropyl)-methyl esters 20, where the products, in methanol, are
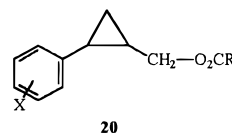

again derived from ion pairs.[53] Now, however, acetates and pivalates behave identically. On the other hand, the transition state is apparently of opposite electron demand when compared to esters, since electron-withdrawing groups enhance the rate. Moreover, the *m*-cyano to H rate ratio is 75:1!

Are These Reactions Adiabatic?

For arylmethyl ester photochemistry, the *meta* effect, Scheme 1, was originally rationalized by simple Hückel MO calculations. The argument developed was that electron density changes caused by photochemical excitation to the singlet state lead to an enhanced rate for formation of ion pairs.[6] In a more recent study, Zimmerman used *ab initio* calculations at the much higher

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Scheme 6. Energy Cycle for the Conversion of S_1 of Substrates to Both S_0 and S_1 of the Ion and Radical Pairs
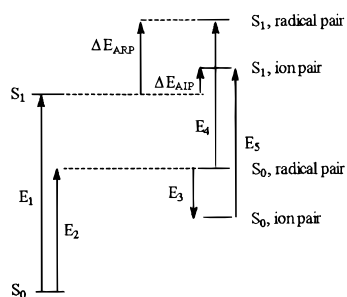
CASSCF(8.8)/6-31G* level.[15] The energies for the 4-methoxybenzyl, 3-methoxybenzyl, and 3,5-dimethoxybenzyl acetate ion and radical pairs were calculated but, in all cases, with the benzyl fragment in S_1, its first excited state. Therefore, the reactions were assumed to proceed from the S_1 excited state of the ester to the S_1 state of the ion and/or radical pair, i.e., adiabatically.

Few organic photochemical reactions are adiabatic, and only one case has been claimed for arylmethyl substrates.[54] In the photodehydroxylation of 9-phenylxanthen-9-ol, **21**, emission is observed from the excited state
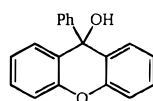
21

of the product cation. The possibility that this could be true for other cases can be tested by the cycle shown in Scheme 6. The question to be answered is whether ΔE_{ARP} and/or ΔE_{AIP}, the change in energy for adiabatic conversion of S_1 of the starting material to S_1 of the radical pair or the ion pair intermediate, respectively, are positive (endergonic) or negative (exergonic). An adiabatic process would be thermodynamically impossible for the endergonic case. Fortunately, experimental values (Table 1) are available for many of the energy terms in the cycle.

Conversion of S_1 for **21** to S_1 of the ion pair is exergonic; this is the only case where experimental evidence indicates an adiabatic benzylic cleavage reaction. For conversion of S_1 of the esters to S_1 of the corresponding radical pair, ΔE_{ARP} is highly endergonic in all cases. As for adiabatic formation of S_1 of the ion pair, in only two cases are the required experimental values available. For both of these, benzyl acetate and 4-methoxybenzyl acetate, the process is slightly endergonic; an adiabatic conversion for compounds with nanosecond lifetimes for their singlet excited

Table 1. Estimated Energies (kcal/mol) for the Species E_1-E_5 in Scheme 6 and for the Adiabatic Conversion of S_1 of the Substrate to S_1 of the Radical Pair (ΔE_{ARP}) and Ion Pair (ΔE_{AIP})

substrate	$E_1{}^a$	$E_2{}^b$	$E_3{}^c$	$E_4{}^d$	$E_5{}^e$	ΔE_{ARP}	ΔE_{AIP}
9-phenylxanthen-9-ol, **21**	100		0 ^{f}	61			−39
1-naphthylmethyl acetate **1** (X = H, R = PhCH$_2$)	89	64	39	116		27	
benzyl acetate **8** (X = H, R = CH$_3$)	106	67	48	129	112	23	6
4-methoxybenzyl acetate **8** (X = 4-OCH$_3$, R = CH$_3$)	100	66	37	126	101	26	1
3-methoxybenzyl acetate **8** (X = 3-OCH$_3$, R = CH$_3$)	101	67	48	129		28	

^{a} Based on absorption and fluorescence spectra or estimates from the absorption spectrum if no emission was observed.[13,25] ^{b} Based on bond dissociation energies[39] and the effect of substituents on these values.[55] ^{c} Based on oxidation potentials of arylmethyl radicals in acetonitrile.[8,49] ^{d} Based on absorption spectra of arylmethyl cations in HFIP, measured for the 4-methoxybenzyl cation and estimated for the benzyl cation,[56] and on pulse radiolysis results for the benzyl cation formed from benzyl chloride.[57] ^{e} Based on absorption spectra of benzyl radicals in hexane.[58] ^{f} Based on pK_R = 1 for the alcohol/cation equilibrium.[54]

states is highly unlikely. For the critical compound, 3-methoxybenzyl acetate, an experimental value for the energy of S_1 of the excited cation is not known. The high-level *ab initio* calculations[15] place S_1 of this ion pair 20 kcal/mol lower in energy than S_1 of the radical pair, i.e., at 109 kcal/mol, predicting that the adiabatic process would be endergonic by 8 kcal/mol.

The conclusion, from this section, is that 3-methoxybenzyl acetate may possibly undergo excited state adiabatic bond cleavage but that the probability is rather low. This question can be answered by the experimental determination of the S_0 to S_1 absorption transition for the 3-methoxybenzyl cation. For the other benzyl ester substrates, the suggestion of adiabatic cleavage is incorrect.

Conclusion

The mechanism proposed by this comprehensive experimental study of arylmethyl esters in the nucleophilic solvent, methanol, is that the dominant photochemical step is homolytic cleavage from the excited singlet state to form a radical pair. As in most organic photochemical reactions, the rate-determining step results in an intermediate that proceeds to products by ground state chemistry. The *meta* effect is an excited state phenomenon that operates on the rate-determining step but, at least for esters, not on the product-determining steps. The implications that these conclusions have on other examples of ArCH$_2$−LG photochemistry in methanol and other solvents have yet to be explored in detail.

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