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Meta−Ortho Effect in Organic Photochemistry: Mechanistic and Exploratory Organic Photochemistry[1,2]

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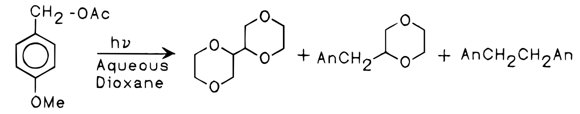
In early research, the meta effect was based on one-electron, Hückel computations and experimental observation, which revealed a selective transmission of electron density to the meta and ortho positions on an aromatic ring in the first excited singlet. However, attention was focused on the meta site. More recent results have confirmed electron density transmission to the ortho site as well. Typical examples involve benzylic cations. Not only are the S_1 cations selectively stabilized by meta-methoxy groups compared with para-methoxy substituents but also the corresponding meta-substituted radicals prove of higher energy than the para-substituted counterparts. Additionally, the $S_0 - S_1$ energy gap is dramatically smaller for the meta-substituted cations and ion pairs compared with the gap for the para-substituted counterparts. Also, the radicals and radical pairs exhibit much larger ground-state − excited-state energy separations. With a closer approach of surfaces, the excited-state ion pairs have an avenue for radiationless decay to ground state not available to the radical pairs. An ab initio computational search for conical intersections was carried out for the 3,5-dimethoxybenzyl cation and radical. This revealed the presence of a degeneracy in the cation at a geometry only slightly perturbed from that of the S_1 minimum. A parallel computation on the 3,5-dimethoxybenzyl radical led to the nearest approach of excited- and ground-state surfaces that was large in comparison and at a very high energy point on the excited-state hypersurface. The geometries of the minimized excited-state species were obtained and the reaction hypersurface found to provide an available route for facile decay of the meta ion pairs to ground state.

Introduction

Perhaps the most fascinating aspect of organic photochemistry is the differing reactivity compared with ground-state behavior. Thus, an excited-state molecule differs from its ground-state counterpart in electron distribution, charges, bond orders, and the various other properties resulting therefrom. The consequence is reactivity, which quite often has no ground-state counterpart.

One example is electron transmission in aromatic molecules. Ingrained in ground-state organic chemistry is the principle of electron tranmission to and from the ortho and para positions by electron donors and withdrawing groups, a phenomenon routinely taught to undergraduates. In contrast, the excited-state counterparts do not follow the ortho−para rule but, rather, exhibit tranmission of electron density to and from the meta and ortho sites. In our early studies, we found both experimental and theoretical support for meta transmissions,[3−5] and the phenomenon was termed the "meta effect". The computations were limited to the Hückel variety available at that time.[6] Also, although the ortho sites exhibited relatively high electron densities, this point was not emphasized.

The meta effect has had an interesting history.[6a] The concept was introduced by the present author in order to understand experimental observations in which electron donors and withdrawing groups positioned meta to the site of reaction enhanced photochemical reactivity.[4,5] More recent studies[7] using CASSCF computations have confirmed the Hückel conclusions, and the point has been made that one might better use the "meta−ortho effect" in describing the phenomenon. One example of the meta-effect, or the meta−ortho effect, is the photochemical solvolysis of the methoxylated benzyl acetates. Here, in the series *p*-methoxybenzyl acetate, *m*-methoxybenzyl acetate, and 3,5-dimethoxybenzyl acetate, there is a sequence of increasing heterolysis versus homolysis. This is outlined in eqs 1, 2, and 3.



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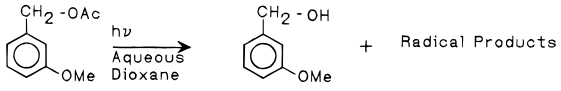

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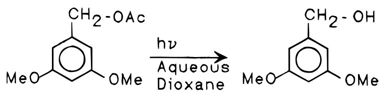

(3)

The photochemical reactivity of the 3,5-dimethoxybenzyl moiety has led to its utility as a protecting group in natural product chemistry.[8] Nevertheless, some of the details of the solvolysis example, as discussed below, have been subject to minor controversy.

Results

Basic Computation Methodology. Our computations made use of Gaussian94 (Revs D3 and E2), CASSCF with an active space of (8,8) and a 6-31G* basis.[9] Computations were carried

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TABLE 1: CASSCF(8,8)/6-31G* Computations[a]

meta cations		radicals	
dimethoxybenzyl cation S1 geom		dimethoxybenzyl radical D1 geom	
(S1) eigenvalue	−496.681 44	(D1) eigenvalue	−496.850 55
(S0) eigenvalue	−496.683 94	(D0) eigenvalue	−496.932 72
energy gap	0.002 50	energy gap	0.082 17
conical dimethoxybenzyl cation		conical dimethoxybenzyl radical	
(S1) eigenvalue	−496.670 11	(D1) eigenvalue	-496.589 52
(S0) eigenvalue	−496.670 16	(D0) eigenvalue	−496.592 20
energy gap	0.000 05	energy gap	0.002 68
dimethoxybenzyl cation S0 geom		dimethoxybenzyl radical D0 geom	
(S1) eigenvalue	−495.323 95	(D1) eigenvalue	−496.846 50
(S0) eigenvalue	−496.720 58	(D0) eigenvalue	−496.934 29
energy gap	1.396 63	energy gap	0.087 79
conical meta-methoxybenzyl cation		conical meta-methoxybenzyl radical	
(S1) eigenvalue	−382.715 456 3	(D1) eigenvalue	−382.939 44
(S0) eigenvalue	-382.715 163 9	(D0) eigenvalue	−382.847 66
energy gap	0.000 292 4	energy gap	0.091 78

[a] Energies are in hartrees, 627.5 kcal/hartree. [b] For the S1 cation and D1 radical entries, the S0 and D0 energies are those for the corresponding excited-state (S1 and D1) geometries. For the S0 cation and D0 radical entries, the S1 and D1 energies are those for the corresponding ground-state (i.e., S0 and D0).

TABLE 2: Ion and Radical Pair Energies[a]

S_1 dimethoxybenzyl ion pair		D_1 dimethoxybenzyl radical pair	
cation	−496.681 44	radical	−496.850 55
acetate	−227.249 52	acetoxy	−227.181 39
ion pair energy	−0.128 18	total	−724.031 94
SCRF solvation	−0.122 80		
total	−724.181 94		
S_0 dimethoxybenzyl ion pair		D_0 dimethoxybenzyl radical pair	
cation	−496.720 58	radical	−496.921 75
acetate	−227.249 52	acetoxy	−227.181 39
ion pair energy	−0.128 18	total	−724.103 14
SCRF solvation	−0.122 80		
total	−724.221 08		
S_1 para methoxybenzyl ion pair		S_1 para methoxybenzyl radical pair	
cation	−382.745 64	radical	−382.935 65
acetate	−227.249 52	acetoxy	−227.181 39
ion pair energy	−0.128 18	total	−610.117 04
total	−610.12 34		
S_1 meta methoxybenzyl ion pair		S_1 meta methoxybenzyl radical pair	
cation	−382.769 17	radical	−382.932 94
acetate	−227.249 52	acetoxy	−227.181 39
ion pair energy	−0.128 18	total	−610.114 33
total	−610.146 87		

[a] From ref 7. [b] Energies are in hartrees, 627.5 kcal/hartree. Solvation energies for the neutral species are minor and neglected.

out with geometry optimization. For conical intersection computations,[10] in cases it proved advantageous to do a state-average computation with weightings of 0.5, 0.5 for S_0 and S_1 first to provide starting geometry and wave functions. Active space selection was based on the natural orbital populations in the MOs. The conical geometries for both the cation and radical systems give the singlet and doublet energies at the points of nearest approach. Solvation energies were approximated by use of the self-consistent reaction field (SCRF) computation within Gaussian94 using a 6-31G* basis.[9c]

Computational Results. Energies for the 3,5-methoxybenzylic cationic and radical species are listed in Table 1. Here we report the energies of the excited cation (S_1) and radical (D_1) at optimized geometries, the ground-state optimized cation and radical energies, the energies of the ground-state species corresponding to geometries to their excited-state minima, and also the energies at the geometry found for conical intersections/ or avoided crossings. As in our earlier report[7] for comparison of radical pairs with ion pairs, we have included the CASSCF energies of the acetoxyl radical and acetate anion, respectively; however, these species were taken as unexcited. Also, the ion-pairing energy, i.e., the energy of bringing separated ions at infinity to pairing distance, has been included; for details, see ref 7. These values are given in Table 2.

One more energetic contributor, namely solvation, also is included. Literature[11] solvation energies of cations are in the range of 50 to 100 kcal/mol. These may be approximated using Onsager reaction field theory.[12,13] Gaussian94 provides the SCRF computational methodology for estimating the solvation energy involved. The solvation energy was taken as the difference between the S_0 RHF/6-31G* energy of the ion pair and the corresponding S_0 SCRF/6-31G* energy for the ion pair. These values are recorded in Table 2.

Additionally, the results of the ion pair and radical pair computations are shown schematically in Figure 1. It was necessary to select geometry coordinates; each coordinate is a function of structure. One selected was the interatomic distance between the methoxy-substituted carbons (i.e., C_4 and C_6). This choice is used in Figure 2a. Another coordinate is the angle $C_4{-}C_5{-}C_6$ and is utilized in Figure 1b,c (see Figure 2 for atom numbering). It was required that the ordinate for the ion pair be shifted relative to that of the radical pair because of the much higher energy of the radical pair species. In view of the error limit in ion pair solvation energy obtained, it is inappropriate to take the precise energy differences between the ion pair and radical pair as meaningful. But the differences in energies are much larger than this potential uncertainty, and thus a semi-quantitative comparison is possible (vide infra).

Inspection of Figure 1a,b,c reveals several interesting features discussed below. However, for the moment, we recognize that we are dealing with different slices of a multidimensional hypersurface. Thus, Figure 1a shows that there is no barrier between the conical intersection and the S_0 minimum, while Figure 1b with a different route along the hypersurface does present a barrier.

It also was of interest to assess the charge distributions in S_1 of anisole and 3,5-dimethoxybenzene. These are given in Figure 2. The aim here was to assess the tranmission of electron density from the donor methoxyl groups to different sites in the aromatic ring. This, of course, had been done decades ago in our early Hückel computations.

Interpretative Discussion

As noted above, one of our original examples consisted of a comparison of the reactivity of *p*-methoxybenzyl acetate, *m*-methoxybenzyl acetate, and 3,5-dimethoxybenzyl acetate. While the para isomer gave rise solely to free radical type products, the meta isomer led to both free radical and ionic (i.e., solvolysis) products. The 3,5-dimethoxy isomer cleanly afforded only ionic, solvolysis product.

In addition, with increasing meta-methoxyl substitution, the excited-state lifetimes decreased while the excited-state reactivity increased. Similarly, meta-methoxy substitution enhanced the quantum efficiency.

Although the meta−ortho effect has been commonly accepted, there has been some controversy regarding the mode of formation of the solvolysis products in the example of the solvolysis of benzylic acetates. Thus, there has been the question of whether the benzylic cations are formed in the initial

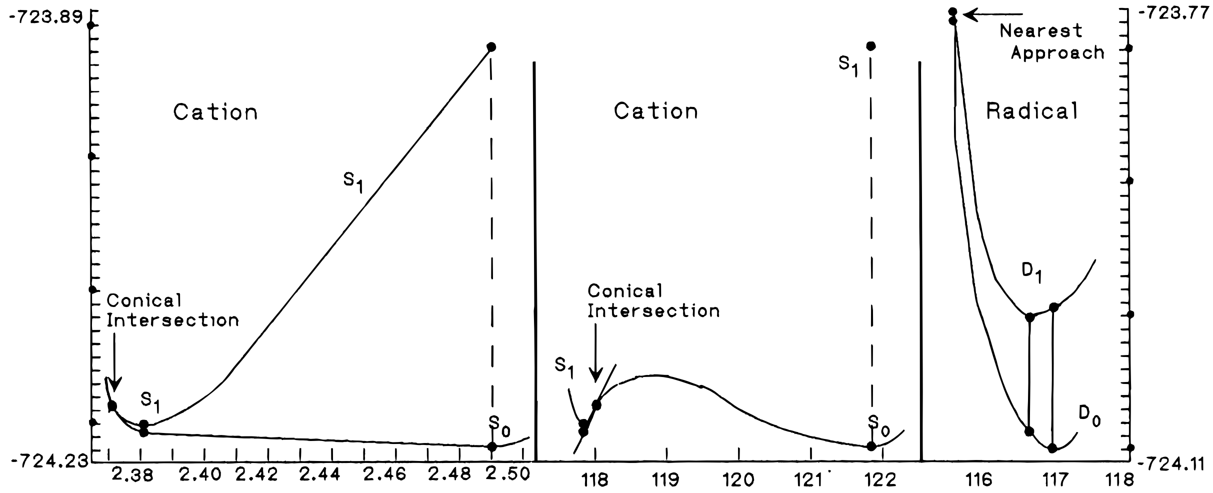


Figure 1. Heterolytic and homolytic dissociation processes with a conical intersection in the heterolysis case. Cross sections: (a) uses distance 4−6 as the horizontal coordinate; (b) and (c) use angle 4, 5, 6. Energies are in hartrees. For this numbering, see Figure 2.

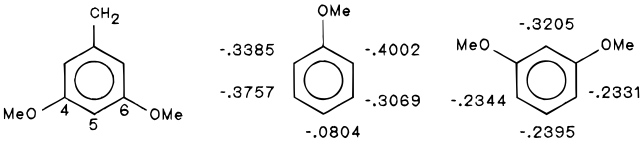
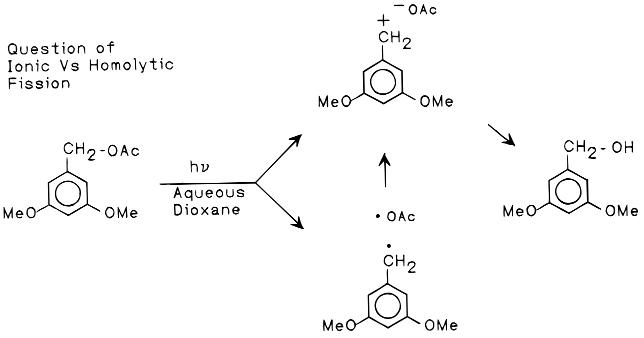


Figure 2. Dimethoxybenzyl numbering and electron distribution in S_1 anisole and S_1 3,5-dimethoxybenzene.

SCHEME 1: Two Alternative Modes of Cation Generation



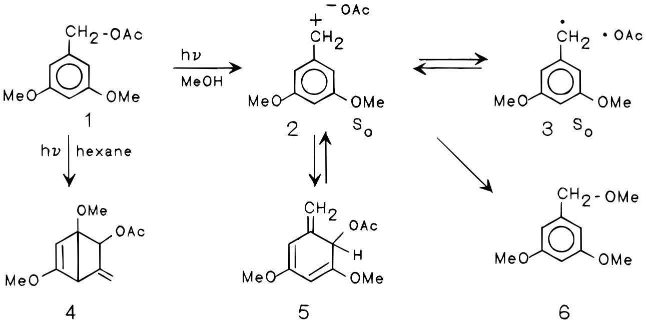
C−O bond fission or, instead, with initial homolysis followed by electron transfer. The two alternatives are shown in Scheme 1.

Our more recent efforts[7] have utilized more modern computational methodology and made use of Gaussian92.[9] This last publication aimed at determining whether C−O bond stretching of the S_1 benzylic acetates was more favorable heterolytically or homolytically. To this end, the energies of the ion and radical pairs were determined. Since any single S_1 reactant is common to both types of fission, one needs to compare only the dissocated pairs, namely the benzyl acetate ion pair with the benzyl acetoxy radical pair.

Perhaps the philosophy was not made clear enough in that publication, and there is some advantage now to restating the problem, the questions, and then how the results deal with both of these.[14]

First, by comparing the energies of the fully dissociated species, one learns which C−O bond stretching process is lower in energy. Second, initial bond stretching is an excited-state phenomenon occurring from the S_1 hypersurface via the conical intersection. But photoproduct must arise from a ground state (i.e., S_0) species. Bond stretching is not necessarily complete at the point where a ground-state species is engendered. Precisely where internal conversion to S_0 occurs is a matter of considerable interest and consequence. In addition, there is no reason to presume that the two different modes of bond stretching and fission lead to equal probabilities of radiationless decay to ground state. Third, one needs to recognize that one is dealing with an excited-state phenomenon in the initial bond stretching but with ground-state behavior once the bond is fully broken with internal conversion to give a ground-state ion pair or radical pair.

SCHEME 2: Rationale for Formation of an Isomeric Acetate



Very recently a relevant Communication has appeared[15] with evidence for formation of an acetate isomer **5** of the reactant 3,5-dimethoxybenzyl acetate (**1**). While the extent of formation of this strongly absorbing transient is uncertain, the chemistry can be understood as further behavior of the ion pair **2** whose formation is preferred on the excited-state surface. Thus the formation of **2** differs from the normal solvolysis product only in ortho rather than benzylic bonding with its ion pair partner. Note Scheme 2. This mode of formation of **2** is one of three possibilities entertained by Pincock.[15] Since the partition among photoproducts is a ground-state matter, occurring after the conical intersection has been utilized, this is not relevant to the meta−ortho effect and really does not "complicate" the matter of the phenomenon. Still, the dramatic effect of solvent methanol versus hexane in diverting the reaction to solvolsis is in accord with the preference for S_1 heterolysis.

Thus, most of the controversy in interpreting the meta effect (the meta−ortho effect) has arisen from not distinguishing the portion of the reaction that occurs on the excited-state surface from that portion that takes place after radiationless decay. For

TABLE 3: Excited-State Characteristics of Anisole and Benzyl Acetates

	anisole	*p*-methoxybenzyl	*m*-methoxybenzyl	3,5-dimethoxybenzyl
ϕ_f	0.29[c]	0.17[a]	<0.01[a]	<0.01[a]
τ_s	8 ns[c]	6 ns[a]	<1 ns[a]	<1 ns[a]
k_{dtot}	0.13×10^8 s^{-1}	1.67×10^8 s^{-1}	$>10^9$ s^{-1}	10^9 s^{-1}
ϕ_r		0.016[b]	0.13[b]	0.10[b]
k_r		2.67×10^6 s^{-1} [b]	$>1.3 \times 10^8$ s^{-1} [b]	$>1.0 \times 10^8$ s^{-1} [b]

[a] From ref 18a. [b] From ref 4. [c] From ref 19.

example, it has been suggested that the present author believes the reactions to be adiabatic;[15] this is not the case.[17]

Dealing first with the relation between meta and ortho electron transmission and chemical reactivity, we see in Figure 2 that the electron density and negative charge in anisole and in 3,5-dimethoxybenzene are greatest in the ortho and meta positions. These same results, but more approximately, were reported in our original 1963 publication[4] using simple Hückel computations. Correlating with this theory is the greater reactivity in terms of quantum yield. The quantum efficiency (cf. Table 3) for the meta and 3,5-dimethoxybenzyl acetate solvolysis in aqueous dioxane was found to be 0.13 for the meta isomer and 0.10 for the 3,5-dimethoxy one in contrast with the low efficiency of 0.016 in the case of the para isomer.

An even more telling point is that the fluorescence lifetimes of the meta-methoxybenzyl acetate and the 3,5-dimethoxybenzyl acetate are very short (again refer to Table 3) compared with that of the para-methoxybenzyl acetate. Thus, the meta-methoxy substituted benzylic acetates disappear from the excited-state hypersurface rapidly relative to their para counterpart. Part of this rapid departure from the excited-state surface is due to radiationless decay, and part is due to a rate of reaction that is minimally ca. 50 times more rapid than the para isomer. Only lower limits on the rates of reaction and radiationless decay are known owing to experimental limitations in obtaining the very rapid overall rate of decay of the meta isomers. From these observations we see that the meta effect is an excited-state phenomenon.

We now turn to theory and the reasons for the effect. First, reference to Table 2 reveals for the substituted benzyl acetate ion pairs the energy is lowered by meta-methoxyl substitution compared with para. Again, it is stressed that the use of complete dissociation of the C−O bond is a device to determine which stretching process is favored. This does not signify that we are assuming the mechanism to be adiabatic with the fully dissociated S_1 pairs a reality.

A second conclusion also derives from Table 2. We see that selective meta energy lowering is not predicted by homolytic fission. Rather, if homolytic bond stretching were involved, it would be the para-methoxyl isomer that would be preferred.

Finally, the energetic effect favoring heterolysis increases in the series *p*-methoxyl < *m*-methoxyl < 3,5-dimethoxyl[20] in accord with experiment. Of course, there is the possibility for equilibration of ion pairs and radical pairs, by electron transfer. However, in the present case of the 3,5-dimethoxybenzyl acetate this seems, for energetic reasons, to be likely mainly for the monomethoxybenzylic acetates.

Thus far we have dealt only with the preference for alternative bond stretching processes on the excited-state hypersurface. In a variety of our publications we have noted that there are two different factors that control photochemical reactivity. (A) One is the nature of the excited-state hypersurface with molecules preferring low-energy pathways that avoid large barriers.[2,3a,21] (B) The second is the probability of radiationless decay to a given photoproduct via an efficient conical intersection (or avoided crossing) in the case of a singlet, or via efficient intersystem crossing in the case of a triplet.[2b,22−24] As has been made clear in these discussions,[21] in complex rearrangements one most often encounters control by low-energy pathways, and such pathways do find a late conical intersection to use.[25] It is for this reason that "organic mechanistic intuition" has been so successful in dealing with photochemical reactions, since the low-energy pathways are those predicted by the organic chemist. Still, for reactions where little geometric reorganization is involved, such as the present benzylic acetate reactions, efficient conical intersections play a more important role.

Thus, the search for conical intersections in the benzyl acetate photochemistry was important. At the outset, inspection of the $S_0 - S_1$ energy gaps revealed a fascinating generality. Meta substitution brought the $S_0 - S_1$ curves closer and diminished the gap between the S_1 minimum (i.e., geometry optimized) and its S_0 counterpart with the same geometry. (The same is not true for geometries with a minimum S_0 energy. Note Table 1 and Figure 1.)

In order to explore further the mode of internal conversion in the photochemical solvolysis of the methoxybenzyl acetates, we used the elegant technique of Prof. Michael Robb of King's College London for locating and identifying conical intersections. This is available within Gaussian94.[9b]

The results are given in Table 1 and also depicted in Figure 1 in the case of the dimethoxybenzyl cation and radical fission. One sees that there is a nearest approach of S_1 and S_0 surfaces within 0.31 kcal/mol (0.000 05 hartrees), and that this effective intersection is only 7.19 kcal/mol (0.011 hartree) above the S_1 minimum. Contrasted with this, the ground-state − excited-state radical surfaces are drastically separated with a nearest approach of 16.8 kcal/mol (0.002 68 hartrees) at a point 164 kcal/mol (0.261 hartrees) above the radical, D1, minimum. For the meta-methoxyl cation and radical, a similar situation is seen in Table 1 with a small ground-to-excited-state separation for the cation and a large one for the radical.

What this signifies is that along the route from S_1 reactant to ion pair or radical pair, the excited state has a much more facile route for radiationless decay by selecting the ion pair choice. The conical intersection for the meta isomers not only is one with a negligible energy gap but also occurs at a low-energy point on the hypersurface. In contrast, the $D_1 - D_0$ nearest approach occurs at a very high energy site on the hypersurface with a larger $D_1 - D_0$ energy gap. Since the geometric parameter selected as a reaction coordinate is arbitrary, we cannot be certain just how far along the reaction route the conical intersection is encountered. Nevertheless, with the one coordinate of six-ring bond angle selected, it is interesting that the intersection for the ion pair occurs rather close to the geometry of the equilibrated excited singlet (i.e., the S_1 minimum). Inherent in this discussion is the assumption made earlier that the excitation is mainly located in the benzylic portion of the ion pair rather than the acetate moiety.

At this juncture we have several conclusions: (1) heterolytic bond stretching of the meta-benzylic acetates is preferred energetically over homolytic bond stretching; (2) the meta isomers have a low-energy conical intersection available permitting internal conversion to ground state as heterolysis occurs while such conical intersections or avoided crossings are not to be found on homolysis. A third conclusion comes from our earlier study[7] where *p*-methoxybenzyl acetate was found to undergo homolytic bond stretching with lower energy than the meta isomer. If homolysis were the mode of bond scission, one would then predict the para isomer to be more reactive than the meta, in contrast with experiment.

More general than the problem of the benzylic acetate problem and of real importance is that conical interaction computations lead to the nearest approach of two states. Thus a second and equally important consideration is the energy required to reach this point on the reaction hypersurface. State intersections at energies much higher than the upper state minimum are really not funnels, or bifunnels, leading to internal conversion as described earlier by the present author and Michl.[21,22]

With the above discussion of the excited-state process, we are still left with consideration of what happens to the ground-state species arising from internal conversion. Table 2 confirms expectation that the ground-state ion pair is of lower energy than the radical pair for the 3,5-dimethoxybenzyl case. This is in agreement with the literature conclusion.[16] In the case of the 3,5-dimethoxybenzyl acetate ion and radical pair, both the computations and experiment suggest that there is little electron exchange by the initially formed ion pair to afford a radical pair. One can envision a potentially reversible ground-state electron exchange to interconvert the ground-state ion pair with its radical pair counterpart. The endothermicity of ca. 75 kcal/mol (0.12 hartrees) seems formidable. But this value includes the estimated ion pairing and also solvation energies, both of which are known with less certainty than the gas-phase cation and radical energies. Also, our original studies were in 50% aqueous dioxane and 50% aqueous ethanol. The solvation energy in pure methanol should be markedly lower and thus facilitate radical pair formation by ground-state electron transfer within ion pairs. In the present discussion we have assumed the more ionic solvent used earlier.

Nevertheless, in principle, such an exchange is potentially possible. This raises an important point. The meta effect is indeed an excited-state phenomenon as was initially proposed decades ago by the present author. One needs to differentiate between those observables resulting from the excited-state structure and those which derive from the ground state subsequently formed. The high quantum yields and rates characteristic of meta isomers result from the excited state. The partition between ionic and radical type products, in contrast, is seen to be a ground-state phenomenon, at least in the present case. To the extent that the rate of electron exchange is competitive with nucleophilic capture by an ion pair and with free-radical reactions by the radical pair, the product ratio might well be perturbed by processes consuming the radical pair. In any case, the observation of such ground-state processes, while interesting,[18] is not relevant to the meta (ortho−meta) effect. For example, the diversion of the reacting system to give increased radical type products by use of the pivalate anion occurs after radiationless decay via the conical intersection and is not relevant to the excited-state meta effect.

Relevantly, the 3,5-dimethoxybenzyl carboxylate system was found to be an anomaly in a 1994 study by Pincock,[17b,26] and this may result from the large S_0 cation-to-radical endothermicity. The 3,5-dimethoxybenzyl system is, indeed, unique in affording clean ionic heterolysis, which has proven to be of use in providing a photochemically sensitive protecting group.[8]

Conclusion

The meta effect (or meta−ortho[29] effect) results from selective electron transmission to the meta and ortho sites in S_1 and contrasts with ground-state ortho−para tranmission. In the solvolysis of methoxy-substituted benzyl acetates, this effect results in a rapid rate of acetate expulsion when the electron-donating methoxyl groups are meta. The rapid excited-state reaction and radiationless decay rates for the meta-substituted benzylic acetates provide experimental evidence, while ab initio computations provide theoretical support. The Gaussian CASSCF computations reveal that heterolytic bond stretching in the excited state is favored for the meta compounds in accord with observation while homolytic bond stretching would slightly be favored by para substitution in contrast with experiment. Conical intersection computations reveal that the meta compounds have an efficient pathway to ground state as the C−O bond stretches while the para isomers do not. It is noted that electron transfer between ground-state ion and radical pairs subsequent to ground-state formation is unrelated by definition to the meta effect and that literature correlations using ground-state observations and parameters deal only with these final, S_0 processes.[30] Hence it appears that the present author and Prof. Pincock have been discussing different aspects of the benzylic acetate reaction, and the controversy is less than real.

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged with special appreciation for its support of basic research.

References and Notes

(1) This is Paper 185 of our photochemical series and Publication 249 of our General Sequence.

(2) For our previous three publications, note: (a) Zimmerman, H. E.; Sebek, P. *J. Am. Chem. Soc.* **1997**, *119*, 3677−3690. (b) Zimmerman, H. E. An Overview of Phenomena and Generalizations Introduced by the Zimmerman Group. *Inter-Am. Photochem. Soc. Bull.* **1997**, *20*, May issue (1), 74−98. (c) Zimmerman, H. E. Some Theoretical Applications to Organic Chemistry. In *Modern Electronic Structure Theory and Applications in Organic Chemistry*; Davidson, E., Ed.; World Scientific Publishing Co.: River Edge, NJ, 1998.

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(6) (a) It needs to be noted that our studies were prompted by the experimental observation of Egbert Havinga, who noted a photochemical hydrolysis of meta-nitrophenylphosphates lacking a parallel acceleration for the para isomer. At the time, Havinga[8b] commented that the phenomenon had no mechanistic rationale. (b) Havinga, E.; De Jong, R. O.; Dorst, W. *Recl. Trav. Chim.* **1956**, *75*, 378. (c) Subsequent studies by Havinga provided further examples.[6d−f] (d) Havinga, E.; Kronenberg, M. E. *Pure Appl. Chem.* **1968**, *16*, 137. (e) De-Jong, R. O.; Havinga, E. *Recl. Trav. Chim.* **1968**, 1318. (f) Havinga, E.; Cornelisse, J. *Chem. Rev.* **1975**, *75*, 353.

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(25) This statement is not to be interpreted that such reactions will be adiabatic, but rather an initial complex rearrangement on the excited surface may lead to a low-energy conical intersection and then onward to photoproduct via S_0.

(26) In the most recent publication[15] on the subject the same Marcus plot lacks this point.

(27) (a) Our early mechanisms have involved radiationless decay after an initial excited state rebonding (e.g., note ref 26). (b) Our work on funnels (bifunnels) in ref 21 dealt with routes from excited- to ground-state surfaces. (c) Note also more recent discussions in refs 2b and 26d. (d) Zimmerman, H. E.; Kutateladze, A. G.; Maekawa, Y.; Mangette, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 9795−9796.

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(30) Finally, several views attributed to the present author have not been held. The benzyl carboxylate reaction has not been thought to be an adiabatic process; we have repetitively noted[27] that few photochemical reactions proceed adiabatically. Additionally, we have not commented that acyloxy free radicals of the type $PhCH_2{-}COO^{\bullet}$ do not exist; we have stated that there is evidence[28] that in the case of pivaloxy, fragmentation to acetone and *tert*-butyl radical *may* occur as the radical is engendered. Evidence for the existence of other, less stabilized acyloxy free radicals is really unrelated to what we have published. Similarly, our mechanism was proposed for the case of the para- and meta-substituted benzyl acetates and may or may not apply to substantially different systems such as naphthylmethyl carboxylates.