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On the Role of Spin Inversion in the Triplet Photochemistry of Benzyl Halides and Benzylammonium Salts

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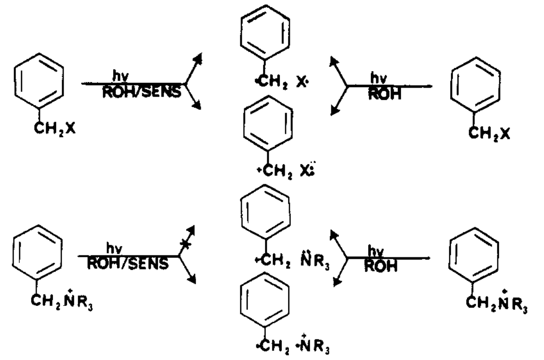
The direct photolysis of benzyl halides and benzylammonium salts yields photoproducts from both diradical and carbonium ion intermediates. The sensitized photolysis yields similar results in the case of the benzyl halides but gives only products derived from a diradical intermediate in the case of the ammonium salt. This selectivity is analyzed qualitatively by using a valence bond approach coupled with ab initio MO–CI calculations. It is shown that the lowest triplet state of a benzyl halide at a point prior to dissociation is the $^3(n_X \rightarrow \sigma^*_{CX})$; in contrast, the $^3(\sigma_{CN} \rightarrow \sigma^*_{CN})$ state is found to be the lowest triplet of the ammonium salt. The former is shown to have an efficient spin-inversion mechanism leading to an ion pair while the latter does not.

Introduction

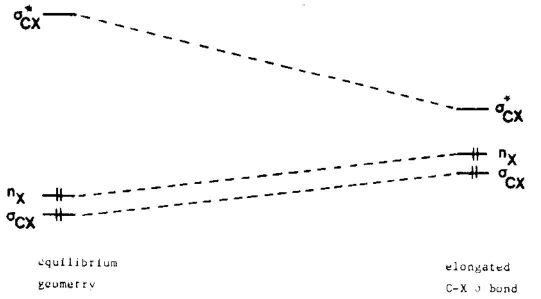
Irradiation of benzyl halides and related molecules in polar nucleophilic solvents often yields photoproducts via a benzyl carbonium ion. After the initial work of Zimmerman et al.,[1] the photosolvolysis of a variety of organic molecules was investigated.[2,3] The results of some of these experiments exhibit a few peculiarities which are noted below.

The direct photolysis of benzyl halides and benzylammonium salts leads to a similar mixture of products obtained from both a benzyl carbonium ion and a benzyl radical.[2d-h] In contrast, the sensitized (acetone) photolysis of these benzyl derivatives is quite dissimilar. The sensitized photoreaction of benzyl halides, like the direct photolysis, results in both homolytic and heterolytic dissociation of the C–X bond.[2f] However, the sensitized irradiation of benzylammonium salts yields photoproducts derived exclusively from a benzyl radical.[2h] This constitutes an interesting case of selectivity and raises the question: Why do the triplet states of benzyl halides and benzylammonium salts behave differently when their excited singlet states react similarily?



In this report the nature of the triplet states of appropriate model compounds is investigated and a rationale for the different photoreactivity of benzylammonium salts and benzyl halides is provided. We suggest that the triplet radical pair $^3(C_6H_5\dot{C}H_2Cl)$ undergoes a facile spin inversion and decays to the ion pair $C_6H_5CH_2^+$:Cl^-, whereas the same process is inefficient for $^3(C_6H_5\dot{C}H_2\dot{N}R_3^+)$. MO calculations at both the ab initio and semiempirical levels are used to support the qualitative arguments.

Nature of the Triplet State. The lowest triplet of a benzyl halide or benzylammonium cation at the equilibrium geometry of the ground state is the $^3(\pi \rightarrow \pi^*)$.[4] However, the energy gap separating the highest filled and lowest vacant σ MO's shrinks during the dissociation process, as shown below for $C_6H_5CH_2X$ (X = halide).



Therefore, at some point along a slice of the potential-energy surface describing the dissociation of $C_6H_5CH_2X$, the MO's, n_X, σ_{CX}, and σ^*_{CX}, will become the frontier orbitals and a crossover from a $^3(\pi \rightarrow \pi^*)$ state to either $^3(n_X \rightarrow \sigma^*_{CX})$ or $^3(\sigma_{CX} \rightarrow \sigma^*_{CX})$ is expected. Similarly, $^3(\sigma_{CN} \rightarrow \sigma^*_{CN})$ is anticipated to be the lowest triplet state of $C_6H_5CH_2NR_3^+$ prior to C–N dissociation. These considerations were tested with the INDO[5a] semiempirical MO

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[1] H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963); H. E. Zimmerman and S. Somasekhara, *ibid.*, **85**, 922 (1963).

[2] (a) A. L. Maycock and G. A. Berchtold, *J. Org. Chem.*, **35**, 2532 (1970); (b) D. A. Jaeger, *J. Am. Chem. Soc.*, **98**, 6401 (1976); (c) D. A. Jaeger, *ibid.*, **97**, 902 (1975); (d) M. A. Ratcliff, Jr., and J. K. Kochi, *J. Org. Chem.*, **36**, 3112 (1971); (e) V. Lillis, J. McKenna, J. M. McKenna, and I. H. Williams, *J. Chem. Soc., Chem. Commun.*, 474 (1974); (f) S. J. Cristol and B. E. Greenwald, *Tetrahedron Lett.*, 2105 (1976); (g) D. C. Appleton, B. Brocklehurst, J. McKenna, J. M. McKenna, M. J. Smith, P. S. Taylor, S. Thackeray, and A. R. Walley, *J. Chem. Soc., Chem. Commun.*, 108 (1977); (h) D. C. Appleton, D. C. Bull, R. S. Givens, V. Lillis, J. McKenna, J. M. McKenna, and A. R. Walley, *ibid.*, 473 (1974).

[3] (a) V. B. Ivanov, V. L. Ivanov, and M. G. Kuz'min, *J. Org. Chem. USSR* (*Engl. Transl.*), **9**, 345 (1973); (b) V. B. Ivanov, V. L. Ivanov, E. M. Kaplan, and M. G. Kuz'min, *Theor. Exp. Chem.* (*Engl. Transl.*), **9**, 193 (1973); (c) V. B. Ivanov, V. L. Ivanov, and M. G. Koz'min, *Mol. Photochem.*, **6**, 125 (1974); (d) V. L. Ivanov, V. B. Ivanov, and M. G. Koz'min, *J. Org. Chem. USSR* (*Engl. Transl.*), **8**, 1263 (1972); (e) V. B. Ivanov, V. L. Ivanov, and M. G. Koz'min, *ibid.*, **8**, 626 (1972); (f) J. Hyomaki and J. Koskikallio, *Acta Chem. Scand., Ser. A*, **31**, 321 (1977); (g) S. Fujita, Y. Ozaki, and H. Nozaki, *Bull. Chem. Soc. Jpn.*, **45**, 2571 (1972).

[4] Here the term $\pi \rightarrow \pi^*$ refers to excitations among MO's mainly localized on the benzene ring. The terms $\sigma_{CX} \rightarrow \sigma^*_{CX}$ and $n_X \rightarrow \sigma^*_{CX}$ refer to excitations among the MO's that are centered mainly on the benzyl carbon and the halogen or ammonium nitrogen.

[5] (a) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970. (b) In an unrestricted MO calculation the electrons of α and β spin are assigned to independent sets of MO's.

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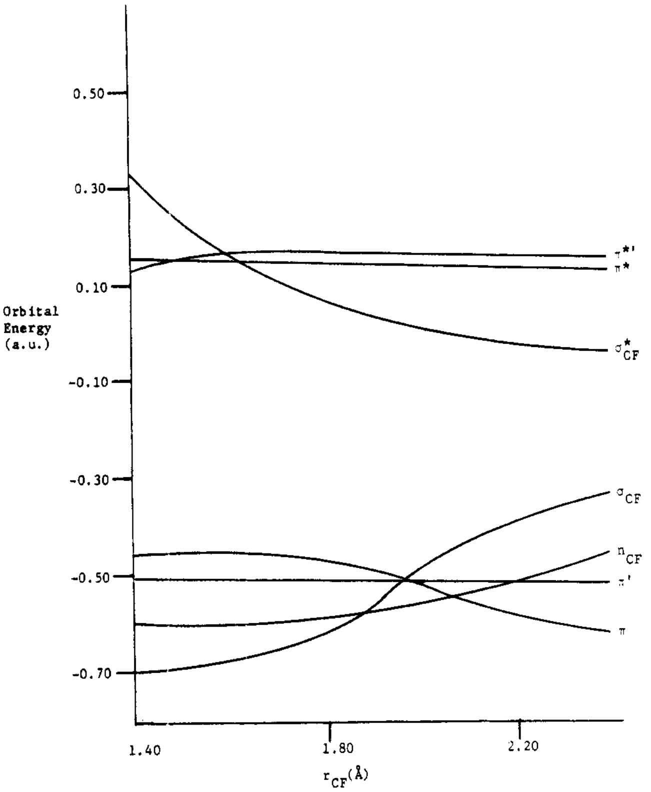


Figure 1. A plot of the relevant INDO orbital energies of benzyl fluoride vs. r_{CF}.

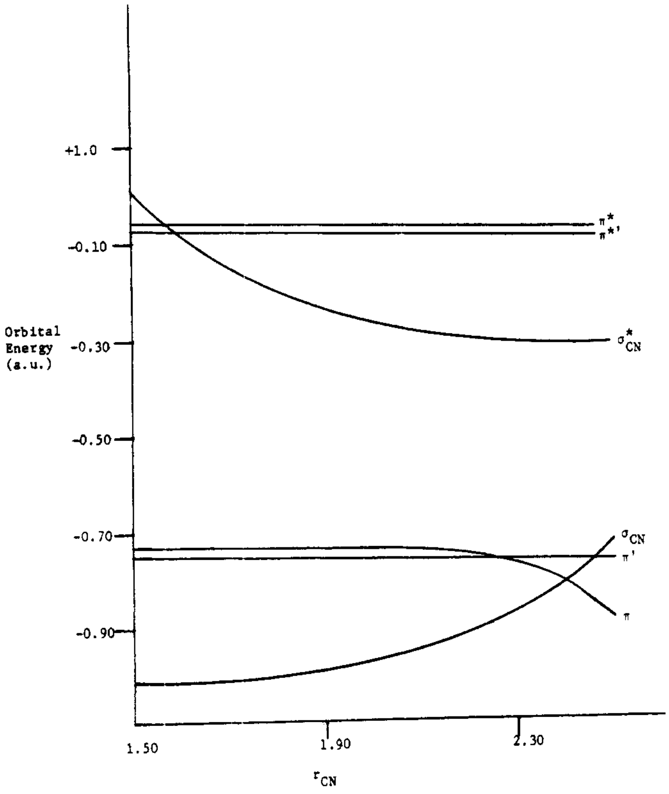


Figure 2. A plot of the relevant INDO orbital energies of benzylammonium cation vs. r_{CN}.

method. The energy variation of the relevant MO's of $C_6H_5CH_2F$ and $C_6H_5CH_2NH_3^+$ caused by elongating the C–F and C–N bonds is demonstrated in Figures 1 and 2, respectively. In both cases the σ-type MO's are seen to become the frontier orbitals prior to dissociation. The eigenvalues of the α and the β MO's of the lowest triplet configuration of $C_6H_5CH_2F$ and $C_6H_5CH_2NH_3^+$ computed with the spin-unrestricted[5b] INDO method are presented in Figures 3 and 4. Examination of these figures reveals that the lowest triplet MO configuration of the two benzyl derivatives is produced by electronic excitations within the σ rather than the π manifold.

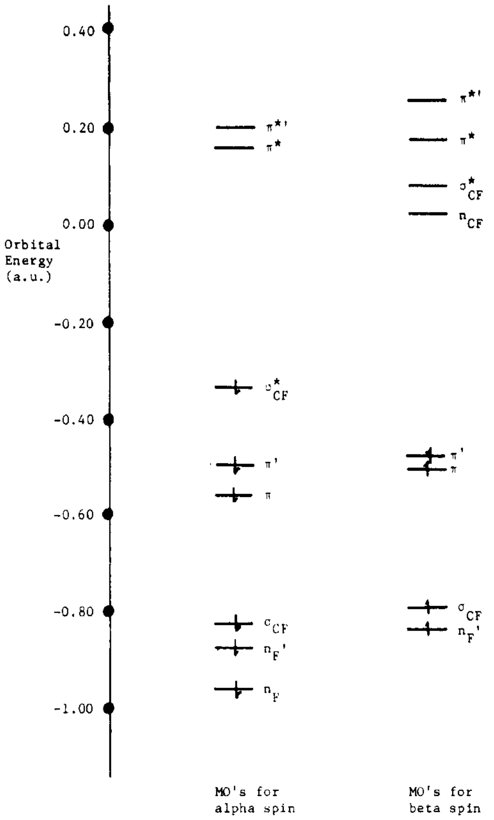


Figure 3. The eigenvalues for the relevant spin unrestricted (INDO) MO's for triplet $C_6H_5CH_2F$ (r_{CF} = 2.0 Å).

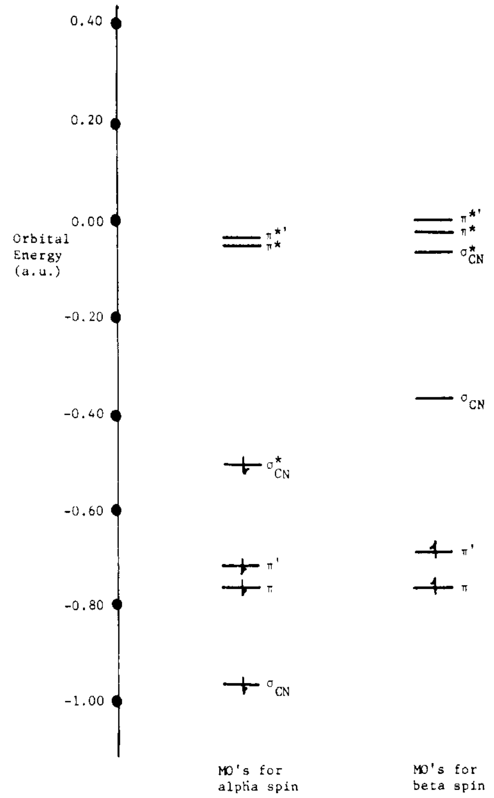
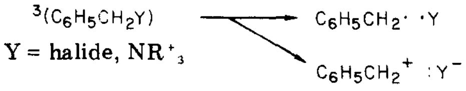


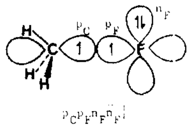
Figure 4. The eigenvalues for the relevant spin-unrestricted (INDO) MO's for triplet $C_6H_5CH_2NH_3^+$ (r_{CN} = 2.2 Å).

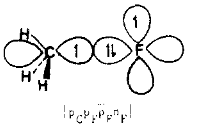
It is evident from the above results that CH_3F and $CH_3NH_3^+$ can serve as adequate model systems for analyzing the decay and/or spin-inversion processes shown below.

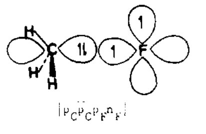


A valence-bond (VB) description of the molecular species involved in the above transformations will be used hereafter, as it provides a particularly simple insight into the problem at hand.

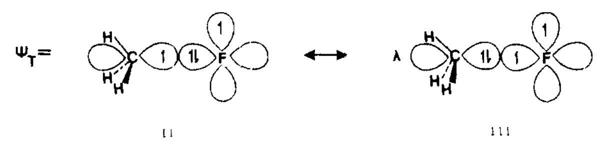
A. A VB Description of Triplet CH_3F. The lowest triplet state of CH_3F can be generated from a minimal set of VB basis configurations. This is shown in Appendix I where the triplet configurations are described in terms of resonance structures I–III.


I

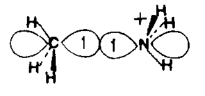

II


III

At infinite C–F separation, the covalent structures I and II are degenerate and are lower in energy than the ionic structure III.[6] As the internuclear distance decreases, both I and II are destabilized owing to the repulsion between the electrons having identical spins centered in the P_C and P_F atomic orbitals (AO's).[7] However, structure II is stabilized relative to I by mixing with structure III (see Appendix I); therefore the lowest triplet state of CH_3F, Ψ_T, is expected to be described by VB structure II mixed with a small amount of III, as shown below.



B. Triplet States of $CH_3NH_3^+$. Since NH_3^+ does not have a lone pair, the lowest triplet state of $CH_3NH_3^+$ can be described by the purely covalent VB structure IV which is analogous to structure I in the case of CH_3F.


IV

Therefore, we conclude that the lowest triplet states of $C_6H_5CH_2F$ and $C_6H_5CH_2NH_3^+$ at some point prior to dissociation are characterized by distinctly different VB structures.

Ab Initio MO–CI Computations. MO–CI computations were used to test the ideas presented in the previous section.[8] The STO-3G[9] basis set was used and a standard molecular geometry[5a,10] was assumed. In the case of CH_3F the CI was performed by using the 838 space-spin configurations derived from all single and double excitations from the six highest occupied MO's of the $^3(\sigma_{CF} \rightarrow \sigma^*_{CF})$ and $^3(n_F \rightarrow \sigma^*_{CF})$ configurations. The 182 space-spin configurations derived from single and double excitations from the four highest occupied MO's of the $^3(\sigma_{CN} \rightarrow \sigma^*_{CN})$ configuration were used in the case of $CH_3NH_3^+$. The lowest triplet state of CH_3F (r_{CF} = 2.0 Å) was found to be 97.7% $^3(n_F \rightarrow \sigma^*_{CF})$. The lowest triplet state of $CH_3NH_3^+$ (r_{CN} = 2.2 Å) was found to be 99.9% $^3(\sigma_{CN} \rightarrow \sigma^*_{CN})$.

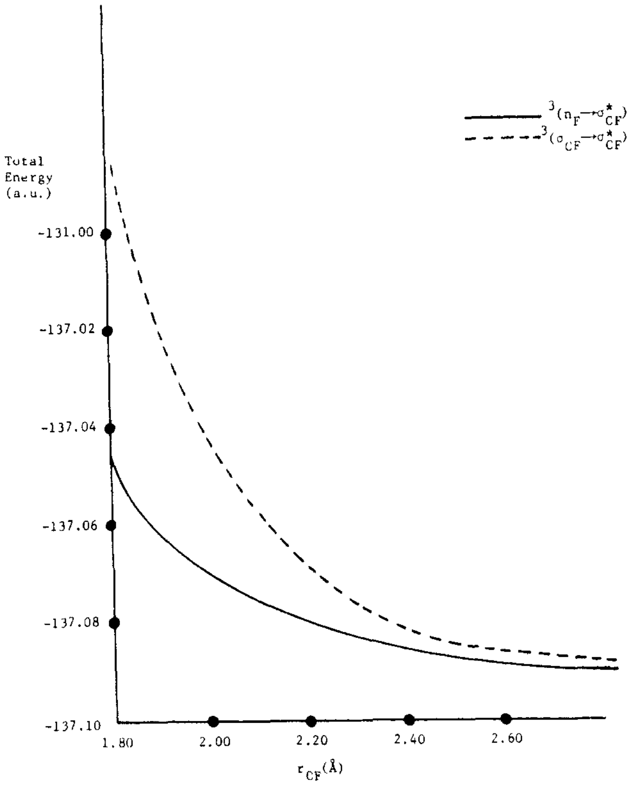


Figure 5. A plot of the STO-3G + CI total energy of the $^3(n_F \rightarrow \sigma^*_{CF})$ and $^3(\sigma_{CF} \rightarrow \sigma^*_{CF})$ states of CH_3F vs. r_{CF}.

The above results suggest that the lowest triplet states of CH_3F and $CH_3NH_3^+$ are described by single MO configurations. In order to compare these MO wavefunctions with the previously described VB states, the MO configurations must be mapped into the VB wave functions. This is done in Appendix II and the results are summarized below. It is concluded from this exercise that the ab initio calculations agree with our suggestion that the lowest triplet state of CH_3F is described by structure II mixed with III and that the lowest triplet state of $CH_3NH_3^+$ is described by structure IV. The energy difference between the $^3(n_F \rightarrow \sigma^*_{CF})$ and $^3(\sigma_{CF} \rightarrow \sigma^*_{CF})$ states of CH_3F is found to increase as the C–F internuclear separation decreases (Figure 5). This is expected as the interaction of structures II and III should increase as the $\langle p_C | p_F \rangle$ overlap integral increases.

Photochemical Pathways of the Triplet States. A. Dissociation to a Diradical. The dissociation of the triplet species characterized by structures II and IV will give rise to photoproducts derived from diradical intermediates, as shown below, because the VB wave function of these structures correlates smoothly with the wave function of a diradical. *This will occur unless there is an alternate decay mechanism.*

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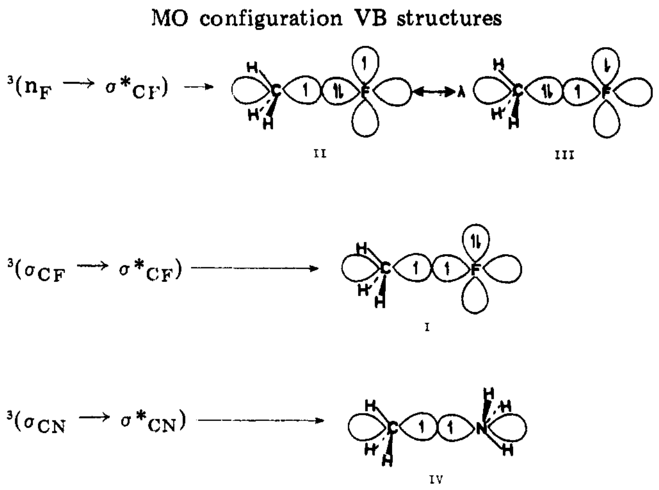
[6] From a consideration of the pertinent ionization potentials and electron affinities, it is seen that the ionic structure III will be destabilized relative to the covalent structures by a factor of about 16 eV at $r_{CF} = \infty$.

[7] Expansion of the Heitler–London wave function for a triplet configuration consisting of two orbitals, ϕ_A and ϕ_B, and two electrons yields the following expression for the energy: $E_A + E_B + J_{AB} + (-2\beta_S - K)$. Expansion of the wave function for a two-orbital–three-electron system yields the following: $2E_A + E_B + E_AS^2 + J_{AA} + J_{AB} + 2\langle\phi_A\phi_A|1/r|\phi_A\phi_B\rangle + (-2\beta_S - K)$. The term $(-2\beta_S - K)$ appears in both these expressions and is known as exchange repulsion. This term becomes increasingly destabilizing as the overlap of ϕ_A and ϕ_B, S, increases.

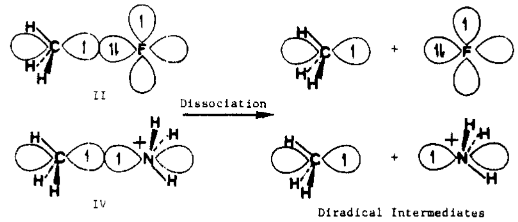
[8] The equivalence of the VB and MO–CI wave functions for the case of H_2 is shown in J. C. Slater, "Quantum Theory of Molecules and Solids", Vol. I, McGraw-Hill, New York, 1963.

[9] W. J. Hehre, R. F. Stewert, and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969).

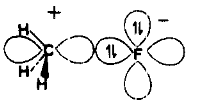
[10] The geometric perturbations accompanying the relaxation of the first triplet are not expected to alter the properties of the triplet state which are pertinent to this work.



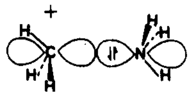
alternate decay mechanism.



B. Formation of an Ion Pair. In polar solvents the ground state of the benzyl derivatives prior to dissociation is a carbonium ion pair analogous to structures V and VI.[11]

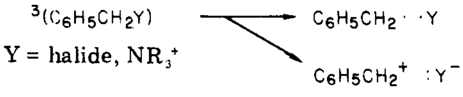


V



VI

The triplet complexes must invert a spin in order to decay to these ionic structures, so an efficient spin-inversion mechanism is required for such a process. In order to determine the relative efficiencies of diradical dissociation vs. spin inversion and ion formation (see below), the conditions which promote spin inversion must be investigated.



$$^3(C_6H_5CH_2Y) \rightarrow C_6H_5CH_2\cdot\ \cdot Y \qquad ^3(C_6H_5CH_2Y) \rightarrow C_6H_5CH_2^+\ :Y^-$$

Y = halide, NR_3^+

Mechanism of Spin Inversion. The probability of a transition from a triplet state, Θ_T, to a singlet state, Θ_S, is proportional to the spin–orbit (SO) coupling matrix element between the singlet state and the three Cartesian micro levels, T_k ($k = x, y, z$) of the triplet state.[12,13]

The one-electronic part of the SO coupling operator, $\hat{H}_{SO}$, is written as a sum of the pairwise interactions between electron i, having angular momentum $\hat{l}$ and spin $\hat{S}$, and all the nuclei, N, having charge Z_N (eq 1).[14]

$$\hat{H}_{SO} = \sum_i \sum_N \frac{Z_N e^2}{2m^2c^2} \frac{\hat{l}(i)\cdot\hat{S}(i)}{r_{iN}^3} \qquad (1)$$

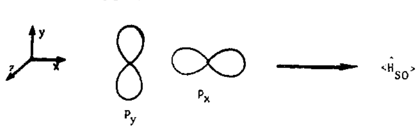
In a Cartesian space, the $\hat{l}\cdot\hat{S}$ operator is expanded as

$$\hat{l}\cdot\hat{S} = \hat{l}_x\cdot\hat{S}_x + \hat{l}_y\cdot\hat{S}_y + \hat{l}_z\cdot\hat{S}_z \qquad (2)$$

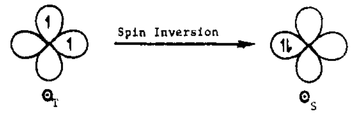
By using this equation the Cartesian components of $\hat{H}_{SO}$ can be expressed proportionally to the angular momenta ($\hat{l}_k$) matrix elements shown in eq 3. C is the constant, $e^2\hbar^2/2m^2c^2$, A_S and A_T are the normalization constants for the singlet and triplet wave functions, and ϕ_a and ϕ_b are the AO's that contain the unpaired electrons with identical spins in the leading VB structure of the triplet wave function.

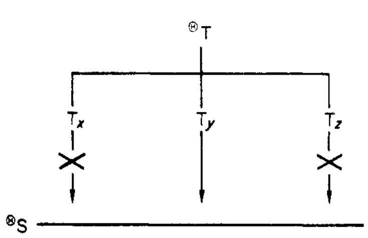
$$\langle \hat{H}_{SO} \rangle_k = \pm \frac{CA_SA_T}{2^{1/2}\hbar} \left\langle \phi_a \left| \frac{\hat{l}_K Z_N}{r^3} \right| \phi_b \right\rangle \qquad (3)$$

The only significant contributions arise from integrals over mutually perpendicular AO's. This gives rise to a component k of $\langle \hat{H}_{SO} \rangle$ which is perpendicular to the plane of the two AO's; for example, an integral over the AO's p_x and p_y creates $\langle \hat{H}_{SO} \rangle_z$.



Thus, spin inversion can be effectively induced if an electron is allowed to circulate between two perpendicular AO's.[15] Generation of a component k of $\langle \hat{H}_{SO} \rangle$ amounts to coupling of the kth micro level of the triplet state to the singlet state. For example, if only $\langle \hat{H}_{SO} \rangle_y$ is nonzero, then spin inversion in T_y will be faster than in T_x or in T_z.





Inspection of structures II and IV reveals that only the former triplet species will decay efficiently to an ion pair, as structure IV does not meet the requirement of having the unpaired electrons in perpendicular orbitals. In the designated coordinate system, the perpendicular AO's are in an xy plane so that the only nonvanishing component of the SO coupling is $\langle \hat{H}_{SO} \rangle_z$. This means that of the three

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[11] The ion-pair intermediate observed during photolysis has been shown to be identical with the ionic intermediate observed during thermal solvolysis.

[12] The effects of density of vibronic levels and the Franck–Condon overlap are discussed in G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, **37**, 1962 (1962); G. W. Robinson and R. P. Frosch, *ibid.*, **38**, 1187 (1963); J. Jortner, S. A. Rice, and R. M. Hochstrasser, *Adv. Photochem.*, 7, 149 (1969); J. Jortner, *Pure Appl. Chem.*, **27**, 389 (1971).

[13] The three micro levels of the triplet state defined over the Cartesian axis differ in their spin wave functions and are shown below for a triplet state having two singly occupied orbitals ϕ_1 and ϕ_2:

$$T_k \equiv (\phi_1\phi_2 - \phi_2\phi_1) \begin{cases} (1/\sqrt{2})(\alpha\beta - \beta\alpha) = T_x \\ (1/\sqrt{2})(\alpha\alpha + \beta\beta) = T_y \\ (1/\sqrt{2})(\alpha\alpha - \beta\beta) = T_z \end{cases}$$

See E. P. Wigner, "Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra", Academic Press, New York, 1959.

[14] S. P. McGlynn, T. Azumi, and M. Kinoshita, "The Triplet State", Prentice-Hall, Englewood Cliffs, NJ, 1969.

[15] Spin inversion is brought about by the torque which is associated with the change in angular momentum induced by the circulation of the electron between the perpendicular AO's; see L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, 11, 92 (1972); L. Salem, *Pure Appl. Chem.*, **33**, 317 (1973); S. Shaik and N. D. Epiotis, *J. Am. Chem. Soc.*, **100**, 18 (1978); S. Shaik, *ibid.*, *101*, 3184 (1979).

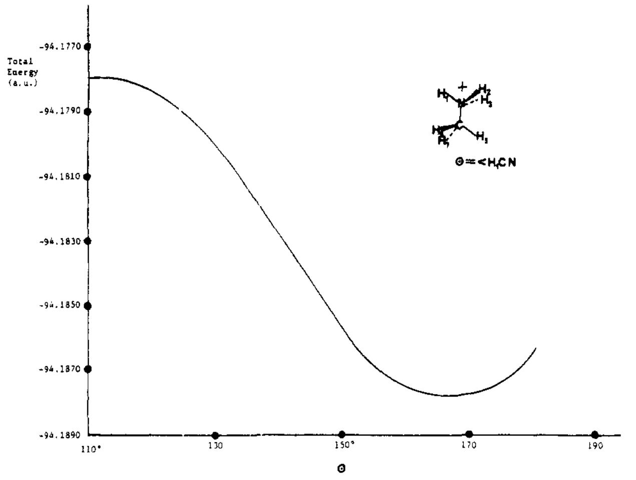
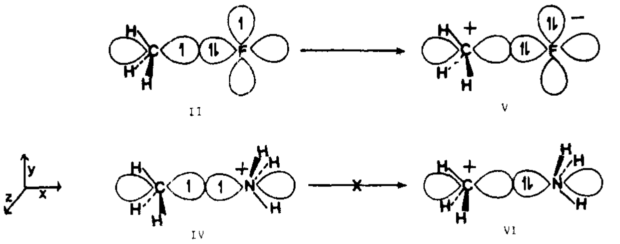


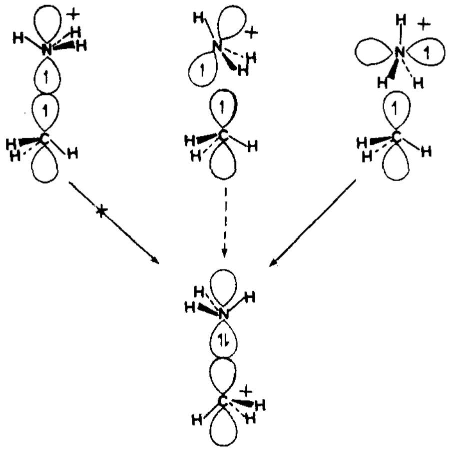
Figure 6. A plot of the energy, computed with an STO-3G basis, of the lowest triplet configuration of $CH_3NH_3^+$ vs. the angle $\Theta = <H_1NC$.

micro levels of the triplet state of CH_3F, only T_z will give rise to ions efficiently.



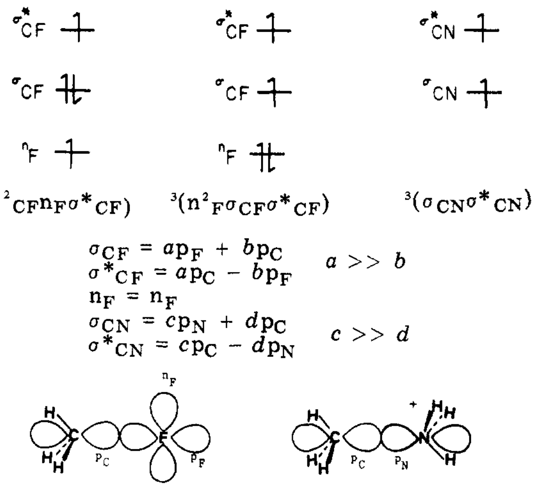
Therefore, benzyl halides (or any other benzyl derivatives where the leaving group has a lone pair) can achieve an ionic intermediate via their $^3(n_X \rightarrow \sigma^*_{CX})$ state, while benzylammonium salts and related compounds cannot decay to an ionic intermediate as the $^3(\sigma_{CN} \rightarrow \sigma^*_{CN})$ state does not have the requisite perpendicular AO relationship.

The ammonium compounds could significantly increase the probability of transition from their lowest triplet state to the carbonium ion pair by twisting the ammonium moiety in a manner illustrated below.



These motions should be electronically stabilizing, as they reduce the repulsion of the two unpaired electrons with identical spins.[7] This expectation is verified for the lowest triplet configuration of $CH_3NH_3^+$ by ab initio MO calculations. The results are presented in Figure 6, where it is seen that the energy minimum is reached at a twist angle of about 50°. Such motions may be too slow (in comparison with the diffusion of the radicals away from each other) owing to the steric bulk of the substituents in the case of $C_6H_5CH_2N(CH_3)_3^+$. These effects could be tested by photosensitizing a system with smaller substituents ($C_6H_5CH_2NH_3^+$, for instance) or by varying the viscosity of the solvent in order to change the rate of diradical decomposition relative to the twisting motion. A different way of testing these ideas is to carry out the sensitized photolysis of benzylphosphonium salts. This might lead to an ionic intermediate as (1) the C–P bond is long enough that the steric inhibition to twisting might be decreased; (2) since $\langle \hat{H}_{SO} \rangle$ is proportional to the nuclear charge Z_N (see eq 1–3), the "heavy-atom effect" will induce strong SO coupling at smaller twist angles in comparison to an ammonium salt.

Scheme I



$^3(\sigma^2{}_{CF}n_F\sigma^*{}_{CF})$ $^3(n^2{}_F\sigma_{CF}\sigma^*{}_{CF})$ $^3(\sigma_{CN}\sigma^*{}_{CN})$

$$\sigma_{CF} = ap_F + bp_C \qquad a >> b$$
$$\sigma^*_{CF} = ap_C - bp_F$$
$$n_F = n_F$$
$$\sigma_{CN} = cp_N + dp_C \qquad c >> d$$
$$\sigma^*_{CN} = cp_C - dp_N$$

McKenna et al. suggested that the absence of solvolysis products in the sensitized photolysis of benzylammonium salts is due to the fact that the ion pair and the radical pair will benefit equally from solvation so that there is nothing to be gained from electron transfer. This point could be tested by conducting the sensitized photolysis of benzylsulfonium salts. The direct photolysis of these salts leads to a mixture of products from both ionic and diradical pathways.[2a] The sulfonium salts are differentiated from their ammonium counterparts because the former have a lone pair. Therefore, we expect that the lowest triplet of the benzylsulfonium cation, at some moderate C–S separation, is the $^3(n_S \rightarrow \sigma^*_{CS})$ and that this triplet species could decay to an intermediate carbonium ion pair via a spin–orbit coupling mechanism.

In summary we conclude the following: (a) The lowest triplet state of $C_6H_5CH_2X$ (X = F, Cl, Br, I, OAC, SR_2^+, etc.) prior to C–X dissociation is described as a VB structure having two singly occupied perpendicular AO's centered on C and X. This allows for efficient spin inversion to a singlet ion pair, $C_6H_5CH_2^+{:}X^-$, by a spin–orbit coupling mechanism. (b) Only one of the three triplet micro levels will produce ions efficiently. Further insight into the role of spin inversion in these reactions can be gained by selective excitation of the three triplet sublevels which should decay to the ion pair with varying efficiencies. Recent developments in this area[16,17] can hopefully be extended to such studies. (c) The lowest triplet state of $C_6H_5CH_2NR_3^+$ prior to the C–N dissociation is described by a VB structure which has the two unpaired electrons in collinear AO's. This does not allow for efficient spin inversion and generation of $C_6H_5CH_2^+{:}NR_3^-$, unless a

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(16) Selective population of triplet sublevels is reviewed in, M. A. El-Sayed, *Annu. Rev. Phys. Chem.*, **26**, 235 (1975).

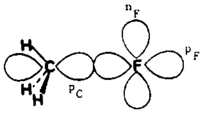
(17) Different rates of decomposition were observed for the sublevels of the first triplet state of dimethyl-*s*-tetrazine. See B. Dellinger, R. M. Hochstrasser, and A. B. Smith, III, *J. Am. Chem. Soc.*, **99**, 5834 (1977).

twisting motion of the ammonium moiety becomes feasible.

Appendix I

The basis wave functions (with $M_S = 1$) describing structures I–III are (overlap is neglected):

$$\phi_1 = |p_C p_F n_F \bar{n}_F|$$
$$\phi_2 = |p_C p_F \bar{p}_F n_F|$$
$$\phi_3 = |p_C \bar{p}_C p_F n_F|$$



The triplet states are written as linear combinations of the basis wave functions:

$$\Psi_j = \sum_i C_{ij}\phi_i \qquad i = 1, 2, 3$$

The secular determinant is as follows:

$$\begin{vmatrix} H_{11} - \epsilon & H_{12} & H_{13} \\ H_{21} & H_{22} - \epsilon & H_{23} \\ H_{31} & H_{32} & H_{33} - \epsilon \end{vmatrix} = 0$$

The off-diagonal matrix elements are

$$H_{12} = H_{21} = \langle\phi_1|\hat{H}|\phi_2\rangle = -\left\langle n_F p_F \left| \frac{1}{r_{12}} \right| p_F p_F \right\rangle - \left\langle n_F p_F \left| \frac{1}{r_{12}} \right| n_F n_F \right\rangle - \left\langle n_F p_F \left| \frac{1}{r_{12}} \right| p_C p_C \right\rangle \simeq 0$$

$$H_{13} = H_{31} = \langle\phi_1|\hat{H}|\phi_3\rangle = \left\langle n_F p_C \left| \frac{1}{r_{12}} \right| p_C p_C \right\rangle + \left\langle n_F p_C \left| \frac{1}{r_{12}} \right| n_F n_F \right\rangle + \left\langle n_F p_C \left| \frac{1}{r_{12}} \right| p_F p_F \right\rangle \simeq 0$$

$$H_{23} = H_{32} = \langle\phi_2|\hat{H}|\phi_3\rangle = -\beta_{p_C p_F} - \left\langle p_F p_C \left| \frac{1}{r_{12}} \right| p_F p_F \right\rangle - \left\langle p_F p_C \left| \frac{1}{r_{12}} \right| n_F n_F \right\rangle - \left\langle p_F p_C \left| \frac{1}{r_{12}} \right| p_C p_C \right\rangle > 0$$

H_{12} and H_{13} are sums of bielectronic terms which include a product of perpendicular AO's and are very small in magnitude. A typical value of these integrals is on the order of 10^{-4} au. On the other hand, H_{23} and H_{32} include the "resonance" integral $\beta_{p_C p_F}$ and are significantly greater in magnitude.

This allows us to reduce the 3 × 3 determinant into a 2 × 2 and a 1 × 1 determinant by setting $H_{12} = H_{21} = H_{13} = H_{31} = 0$.

$$\left|\begin{array}{c:cc} H_{11} - \epsilon & 0 & 0 \\ \hdashline 0 & H_{22} - \epsilon & H_{23} \\ 0 & H_{32} & H_{33} - \epsilon \end{array}\right| = 0$$

Three first-order solutions are obtained.

$$\Psi_T = \frac{1}{(1 + \lambda^2)^{1/2}}[\phi_2 + \lambda\phi_3]$$

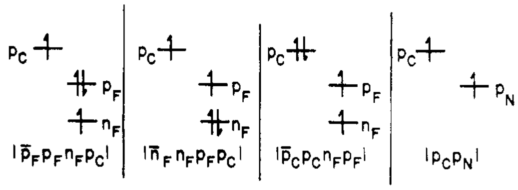
$$\Psi_T' = \frac{1}{(1 + \lambda^2)^{1/2}}[\phi_3 - \lambda\phi_2]$$

$$\Psi_T'' = \phi_2$$

$$\lambda = \frac{H_{23}}{H_{22} - H_{33}}$$

Scheme II

$$^3(\bar{\sigma}_{CF}\sigma_{CF}n_F\sigma^*_{CF}) = |(a\bar{p}_F + b\bar{p}_C)(ap_F = bp_C)(n_F) \times (ap_C - bp_F)|$$
$$= (a^3 + ab^2)|\bar{p}_F p_F n_F p_C| + (b^3 + ba^2)|\bar{p}_C p_C n_F p_F|$$
$$^3(\bar{n}_X n_X \sigma_{CX}\sigma^*_{CX}) = |(\bar{n}_F)(n_F)(ap_F + bp_C)(ap_C - bp_F)|$$
$$= |(\bar{n}_F n_F p_F p_C)|$$
$$^3(\sigma_{CN}\sigma^*_{CN}) = |(cp_N + dp_C)(cp_C - dp_N)|$$
$$= |p_C p_N|$$



Appendix II

The three MO configurations, $^3(\sigma^2{}_{CF}n_F\sigma^*{}_{CF})$, $^3(n^2{}_F\sigma_{CF}\sigma^*{}_{CF})$, and $^3(\sigma_{CN}\sigma^*{}_{CN})$, are depicted in Scheme I. Expansion of the Slater determinants for the MO configurations in terms of the constituent AO's allows them to be expressed in terms of the VB configurations depicted in Scheme II.

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Registry No. CH_3F, 593-53-3; $CH_3NH_3^+$, 17000-00-9; $C_6H_5CH_2F$, 350-50-5; $C_6H_5CH_2NH_3^+$, 28184-70-5.