Acknowledgment. We thank the Polish Academy of Sciences for support (Research Project MR-I.12).

J. Michalski,* Cz. Radziejewski
Z. Skryzpczyński, W. Dąbkowski
Centre of Molecular and Macromolecular Studies, Polish Academy of Sciences
Boczna 5, 90-362 Lodz, Poland

Received July 21, 1980

Dissociation of the Ethylene Cation: Mechanism of Energy Randomization

Sir:

We wish to discuss the validity of statistical theories of unimolecular dissociation under conditions which correspond to photochemical excitation at very low pressures. We have determined[1] by ab initio calculations the reaction paths of the ethylene cation for its two low-energy dissociations (reactions 1 and 2).

$$C_2H_4^+ \rightarrow C_2H_3^+ + H \qquad (AP = 13.22\ eV)^2 \qquad (1)$$

$$C_2H_4^+ \rightarrow C_2H_2^+ + H_2 \qquad (AP = 13.14\ eV)^2 \qquad (2)$$

Since the threshold energies[2] of these two reactions fall within the second band of the photoelectron spectrum of ethylene, we investigated in detail the dissociation mechanisms of the ground ($\tilde{X}\ ^2B_{3u}$) and first excited ($\tilde{A}\ ^2B_{3g}$) states of $C_2H_4^+$. (Higher electronic states were shown[1] to undergo facile radiationless conversion to the ground state by internal rotation.)

Calculations were done with a simple Dunning (3s2p) GTO basis set either at the open-shell SCF level or with intermediate configuration[3] MOs and a relatively small CI (200–500 CSF). Point calculations were done for the most important structures with and without polarization functions ($3d_c$ and $2p_H$) added to the AO basis set and with larger CI matrices ($\simeq$2500 CSF). Results are given in Figure 1. Details of the calculation will be published elsewhere.[1]

The reaction path of process 2 was found to consist of a sequence of several steps connected by several bottlenecks. Some of these steps are adiabatic and therefore can be studied by conventional statistical theory (RRKM[4,5] or QET[6]). Others involve nonadiabatic interaction and thus require an extension of these theories.

What we wish to point out here is that the presence of all these bottlenecks compels the system to fulfill various requirements and hence compels it to visit a large fraction of phase space. Therefore, the more complicated the reaction path, the more likely it is for a statistical theory to be valid.

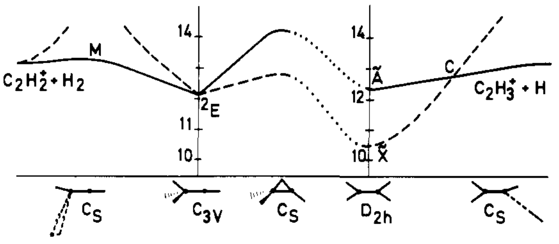


Figure 1. Folding-screen representation of the reaction paths of $C_2H_4^+$. Solid lines, $^2A'$ states; dashed lines, $^2A''$ states; dotted lines, no symmetry at all. Energy scale in eV.

Consider (Figure 1) the fate of a molecular ion created in the $\tilde{A}\ ^2B_{3g}$ state with an energy higher than 13.22 eV. Initially, the Franck–Condon principle allows the ion to receive energy in three vibrational modes:[7] ν_1 (sym CH stretch), ν_2 (CC stretch), and ν_3 (CH_2 scis). The potential-energy surfaces are such that high barriers exist in every direction except along the stretching motion of a single CH bond. This corresponds to the excitation of a *local* CH stretching mode, i.e., a linear combination of *four* CH normal modes: ν_1, ν_5, ν_9, and ν_{11}. Production of $C_2H_3^+$ fragments is thus accounted for. However, the potential-energy surface of the $\tilde{A}\ ^2A'$ state is crossed (at point C of Figure 1) by that of the ground state ($\tilde{X}\ ^2A''$ for these nuclear configurations) which correlates with a higher asymptote. Thus, at the crossing point C, the system has to decide between heading toward the asymptote of channel 1 or cascading to the ground state $\tilde{X}$. The crossing point C is in fact a conical intersection[8] and the competition is controlled by the amount of internal energy which goes into internal torsion. The larger the angle of twist, the more likely the internal conversion to the ground state, as shown by our calculations of the nonadiabatic coupling matrix element.[1] Hence, energy must flow into the torsional vibration ν_4 for reaction 2 to proceed. We find that energy barriers prevent direct dissociation of ground state $\tilde{X}$ in its usual $CH_2CH_2^+$ conformation according to reaction 2, either by 1,2 or by 1,1 elimination. Its only possibility is to undergo a hydrogen shift (via a hydrogen-bridged structure already considered[9] by Dewar and Rzepa) and to isomerize to the ethylidene structure CH_3CH^+ (^2E state in the C_{3v} point group). This requires excitation of CH bending modes (ν_3, ν_6, ν_{10}, and ν_{12}). In order to proceed further and give rise to reaction 2 by 1,1 hydrogen elimination, the system must leave the $^2A''$ state and switch to the $^2A'$ surface. This is possible if doubly degenerate skeletal vibrations of the CH_3CH^+ structure are excited, because in the degenerate ^2E state the system experiences nonadiabatic interaction (Jahn–Teller effect). Finally, our calculations indicate the presence of a very low ($\simeq$0.13 eV) energy barrier for the last step (at point M of Figure 1), but it was also observed that the more accurate the calculations, the smaller the barrier. Hence, the barrier might very well not exist at all.

In summary, we see that experimentally observed reactions in $C_2H_4^+$ can occur only if energy is redistributed among many molecular normal modes. Something approaching energy randomization comes about naturally, first, as a result of the multistep nature of the reaction path, and secondly as a result of the presence of nonadiabatic processes. The latter factor is particularly interesting and reveals novel aspects on the problem of intramolecular energy transfer. Dissociation of the ethylene cation should be amenable to statistical treatment.

Reactions 1 and 2 have previously been studied by the quasi-equilibrium theory of mass spectra[6] with some success.[10] However, this theory usually assumes fast electronic relaxation to the ground state. This is indeed the case for the upper electronic states $\tilde{B}$ and $\tilde{C}$ as a result of internal rotation[1] but not for state $\tilde{A}$, because the conical intersection between states $\tilde{X}$ and $\tilde{A}$ (point C of Figure 1) acts like a railway switch: electronic relaxation and dissociation take place with comparable rates. Therefore, the success of these calculations must be considered as somewhat fortuitous.

The present discussion of energy randomization raises a number of questions which deserve further consideration.

(1) How general is our explanation? Detailed calculations of

---

(1) C. Sannen, G. Raşeev, C. Galloy, G. Fauville, and J. C. Lorquet, *J. Chem. Phys.*, in press.

(2) R. Stockbauer and M. G. Inghram, *J. Chem. Phys.*, **62**, 4862 (1975).

(3) R. McWeeny, *Mol. Phys.*, **28**, 1273 (1974); L. Salem, C. Leforestier, B. Segal, and R. Westmore, *J. Am. Chem. Soc.*, **97**, 479 (1975); J. Lievin and G. Verhaegen, *Theor. Chim. Acta*, **42**, 42 (1976).

(4) W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, 1973.

(5) S. H. Bauer, *Chem. Rev.*, **78**, 147 (1978); I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.*, **12**, 166 (1979).

(6) H. M. Rosenstock, *Adv. Mass Spectrom.*, **2**, 251 (1963); **4**, 523 (1968); A. L. Wahrhaftig, *MTP Int. Rev. Sci.: Org. Chem., Ser. One.*, 1–24 (1972).

(7) G. Herzberg, "Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, NJ, 1945, p 107.

(8) (a) E. Teller, *J. Phys. Chem.*, **41**, 109 (1937); (b) M. Vaz Pires, C. Galloy, and J. C. Lorquet, *J. Chem. Phys.*, **69**, 3242 (1978); (c) M. Desouter-Decomte, C. Galloy, J. C. Lorquet, and M. Vaz Pires, *ibid.*, 71, 3661 (1979).

(9) M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.*, **99**, 7432 (1977).

(10) M. Vestal and G. Lerner, ARL Report 67-0114, Jan 1967 (available from National Technical Information Service, Springfield, VA 22150); L. W. McKeen and J. W. Taylor, *Int. J. Mass Spectrom. Ion Phys.*, **33**, 167 (1980).

0002-7863/80/1502-7976$01.00/0

reaction mechanisms are not yet very numerous. We note that the dissociation mechanism of the formaldehyde cation was also found[8b] to be controlled by conical intersections. This provides an indication that our discussion might be valid in the case of small polyatomic ions. For large polyatomic ions, electronic relaxation is probably fast, but vibrational randomization is not expected to be complete. Sufficient data are not available for electronically excited neutral molecules although substantial progress has been made in the analysis of the reaction mechanism of excited formaldehyde.[11]

(2) Is energy fully randomized? In spite of a tendency toward energy randomization, the share of energy received by each degree of freedom need not agree with statistical predictions.

(3) Assuming that a statistical treatment is reasonable, are current theories of unimolecular reactions applicable? The conditions of validity of transition-state theory have been discussed by Pechukas et al.[12] in terms of the properties of the potential-energy surfaces. They showed that a proper definition of the transition state requires careful consideration of the shape of the equipotentials. We cannot apply this criterion, since we did not calculate these contour maps in our work (only the reaction path is so far available). Moreover, the extension of this criterion to multidimensional potential-energy surfaces is not obvious. A detailed knowledge of the potential-energy surfaces is also required to carry out the normal mode analysis along the reaction path suggested by Miller et al.[13]

It seems to us, however, that the most urgent task is to incorporate nonadiabatic coupling (which provides novel and interesting features) into conventional transition-state theory. This has been done for spin-orbit interaction by Zahr et al.;[14] RRKM theory is recovered as a limit case. An extension to the case of conical intersections (point C of Figure 1) is in progress in this laboratory.

Acknowledgment. This work has been supported by the Belgian Government (Action de Recherche Concertée), the F.R.F.C. (research grant), and the F.N.R.S. (fellowship to C.S.).

---

(11) R. L. Jaffe and K. Morokuma, *J. Chem. Phys*, **64**, 4881 (1976); J. D. Goddard and H. F. Schaefer, *ibid.*, **70**, 5117 (1979).

(12) P. Pechukas and F. J. McLafferty, *J. Chem. Phys.*, **58**, 1622 (1973); E. Pollack and P. Pechukas, *ibid.*, **69**, 1218 (1978).

(13) W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.*, **72**, 99 (1980).

(14) G. E. Zahr, R. K. Preston, and W. H. Miller, *J. Chem. Phys.*, **62**, 1127 (1975).

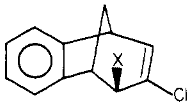
J. C. Lorquet,* C. Sannen, G. Raşeev
Département de Chimie, Université de Liège
Sart-Tilman, B-4000 Liège 1, Belgium

Received July 16, 1980

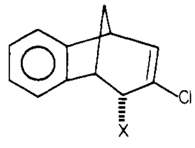
Photochemical Transformations. 29. Stereochemistry of Photorearrangements and Photosolvolyses in Some Dibenzobicyclooctadiene and Benzotricyclooctene Systems[1]

Sir:

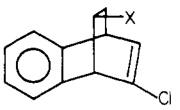
Photosolvolyses and the photochemical Wagner-Meerwein rearrangements accompanying them upon irradiation of certain bridged ring systems containing aromatic rings and good nucleofugal groups have been of interest in this laboratory for some time.[1-4] We have recently[1,4] described our results on the homobenzyl allylic epimeric pairs **1**-Cl/**2**-Cl and **1**-OMs/**2**-OMs, which show remarkably little difference between epimers in photoreactivity or in product formation in their photorearrangements to **3** isomers or in their photosolvolyses to **1** species.



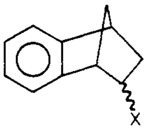
1



2



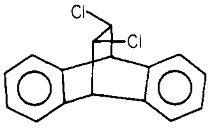
3



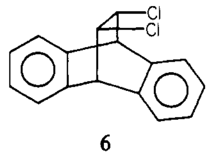
4

In contrast, we now report data on homobenzyl, but nonallylic systems, which do have stereochemical requirements for photoreactivity and preferences for reactions in that (a) the excited chromophore must be anti to the nucleofuge and (b) the major migrating ring is that syn to the nucleofuge. Although these results were not anticipated, a recent report[5] on the 2-benzonorbornenyl system **4** describes a similar large anti preference for photoreactivity.

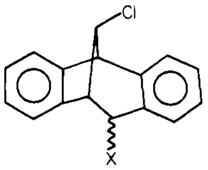
Irradiation at 254 nm of the trans dichloride **5** in acetic acid gave, as major products, the rearranged dichlorides **7**-Cl and the corresponding chloroacetates **7**-OAc in about 75% yield, while compounds **8**-Cl and **8**-OAc were produced in about 25% yield. **7**-Cl and **8**-Cl photosolvolyze more slowly than they are formed. Irradiation of the cis dichloride **6** gave the same products, but in a reverse ratio. Thus the major products of photorearrangement and photosolvolysis are the result of syn migration, rather than those of the clean anti migration seen[6] in ground-state solvolyses.



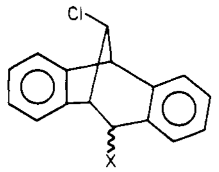
5



6



7



8

That the photorearrangements are not radical processes may be inferred from the accompanying photosolvolyses and from experiments in which the radical chain[7] reductions of **5** and **6** with tri-*n*-butyltin hydride gave identical (approximately equal) amounts of **7**-H and **8**-H.

The stereochemical requirements of the photoreactions are revealed to a greater extent with compound **9**. Irradiation in acetic acid at 300 nm (**5** is transparent at this wavelength) led to **10** epimers as the major products. Thus the chlorine anti to the excited dimethoxybenzo chromophore leaves, while the (unsubstituted) ring syn to the nucleofuge migrates, opposite to the ground-state solvolysis which gave **11** acetates as the sole observed products.

Stereochemical requirements were also seen in the photoreactions of **12** and **13** chlorides and methanesulfonates. Irradiation of **12** at 254 nm in aqueous acetonitrile gave efficient photorearrangements to the benzylic isomers **14** and photosolvolyses to **14**-NHCOCH$_3$ and **14**-OH. Despite irradiation times 20-50 times longer, the epimeric compounds **13**-Cl and **13**-OMs were photoinert (except for the formation of small amounts of

---

(1) Paper 28: Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.*, in press.

(2) Cristol, S. J.; Mayo, G. O.; Lee, G. A. *J. Am. Chem. Soc.* **1969**, *91*, 214.

(3) Cristol, S. J.; Stull, D. P.; Daussin, R. D. *J. Am. Chem. Soc.* **1978**, *100*, 6674 and references therein.

(4) Cristol, S. J.; Strom, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 5707.

(5) Morrison, H.; Miller, A. *J. Am. Chem. Soc.* **1980**, *102*, 372.

(6) Cristol, S. J.; Parungo, F. P.; Plorde, D. E. *J. Am. Chem. Soc.* **1965**, *87*, 2870.

(7) Kuivila, H. J. *J. Org. Chem.* **1960**, *25*, 284. *J. Am. Chem. Soc.* **1966**, *88*, 571.

0002-7863/80/1502-7977$01.00/0 © 1980 American Chemical Society