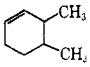
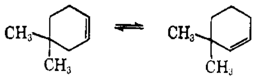
Table IX. Calculated Enthalpy Data (kcal/mol) for Dimethylcyclohexenes

		$\Delta H°$, kcal/mol
	*trans*-Diequatorial	0.00
	trans-Diaxial	0.71
	cis-3-Axial,4-equatorial	0.25
	cis-3-Equatorial,4-axial	0.46
		0.84

experiment might yield either isomer predominantly, depending on the temperature.

With the *gem*-dimethylcyclohexenes, the 4 isomer is predicted to be considerably better than the 3 isomer.

In summary, structures and energies and related data have been calculated for a wide variety of olefinic compounds. As with similar calculations on the alkanes, the bulk of the information obtained is in good agreement with the available experimental data. A few items are not, however, in satisfactory agreement, and these items suggest certain deficiencies in the calculations. In general, the calculations give rather accurate results for compounds which are not highly strained, as was also true with the alkanes. Refinement of the energy functions is now being studied and will be discussed in due course. However, for alkenes or alkanes which are not highly strained, it is believed that the structure–energy calculations described herein and in the previous paper are quite reliable, and insofar as experimental data are available, the calculations appear to give structures and energies within the combined limits of experimental and calculational error in every case.

A Perturbation Molecular Orbital Approach to the Interpretation of Organic Mass Spectra. The Relationship between Mass Spectrometric, Thermolytic, and Photolytic Fragmentation Reactions

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Abstract: Mass spectrometric reactions have been empirically divided into three classes based on metastable observations and the classification of reacting ions as odd- or even-electron ions. Class I reactions are presumed to occur from low-lying electronic states of the parent ion; simplified MO methods may be directly applied to these reactions. First-order perturbation theory (the PMO method)[1] has been expanded to deal with the aromaticity of radical cations. Procedures for applying this simple theory to the major classes of mass spectrometric reactions have been discussed. The electronic relationship between mass spectrometric, thermolytic, and photolytic fragmentation reactions has been reviewed.

Modern approaches to the interpretation of organic mass spectra have been highly successful in explaining the major fragmentation paths of complex molecules.[2] These same theories have also provided the basis for understanding the empirical relationship between mass spectrometric, thermolytic,[3] and photolytic[4] fragmentation reactions. Unfortunately, the present qualitative theory has not generally provided a sound basis for the prediction of relationships between electron impact, thermal, and photoprocesses. The statistical theory of mass spectra[5] (QET) has clearly accounted for the fragmentation of saturated hydrocarbons. The complexity of this theory has prohibited its adoption by organic chemists, and its utility in interpretation of organic mass spectra is very limited. This situation may be contrasted to the recent rapid development of theoretical organic chemistry, wherein simple procedures have been developed for accurately predicting both the course and stereochemistry of a large number of interesting reactions.[1,6]

There are two major factors which have limited the development of a semiquantitative electronic theory of mass spectral fragmentation reactions. (1) The reactive electronic states for ions that are produced by electron impact are not easily defined. The qualitative theory does not explicitly consider the electronic states of reacting ions;[2] however, most reactions are interpreted

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[1] M. J. S. Dewar, *Tetrahedron Suppl.*, **8**, 75 (1966).

[2] (a) F. W. McLafferty, "Interpretation of Mass Spectra," W. A. Benjamin, Inc., New York, N. Y., 1966; (b) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Ions," Holden-Day, Inc., San Francisco, Calif., 1967; (c) K. Biemann, "Mass Spectrometry, Organic Chemical Applications," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[3] (a) D. C. DeJongh, R. Y. VanFossen, and C. F. Bourgeois, *Tetrahedron Lett.*, 271 (1967); (b) E. K. Fields and S. Meyerson, *J. Amer. Chem. Soc.*, **88**, 2836 (1966), and papers cited therein.

[4] (a) A. L. Burlingame, C. Feneslau, W. J. Richter, W. G. Dauben, G. W. Shaffer, and N. D. Vietmeyer, *ibid.*, **89**, 3346 (1967); (b) N. J. Turro, D. S. Weiss, W. F. Haddon, and F. W. McLafferty, *ibid.*, **89**, 3370 (1967), and papers cited therein.

[5] H. M. Rosenstock, M. B. Wallenstein, A. L. Warhaftig, and H. Eyering, *Proc. Nat. Acad. Sci. U. S.*, **38**, 667 (1952).

[6] R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968).

in the qualitative approach, on the basis of consideration of the ground state of the reacting ion. The statistical theory assumes that contributions to reactivity from excited electronic states all cancel. Both of these assumptions conflict with numerous pieces of experimental evidence, and the electronic theories of organic reactivity clearly indicate that the reactive electronic state can determine the course of a reaction.[1,6] (2) The reactivity of molecule ions is not directly analogous to reactivity in even-electron systems. The difference in reactivity between vibrationally excited singlet molecules and the corresponding doublet ions is not at all obvious in resonance theory. Nonetheless, current qualitative interpretations of mass spectra apply resonance theory to doublet ground states of ions by direct analogy with even-electron systems. McLafferty and others have successfully utilized the distinction between cation and radical sites in the interpretation of mass spectral reactions;[2] however, the power of this distinction is diluted in the resonance formalism. Resonance theory does not have a rigorous quantum mechanical basis,[7] and the theory is known to give erroneous predictions of reactivity in many cases, *e.g.*, the distinction between $4n$ and $(4n + 2)$ π-electron systems is not at all clear in the resonance approximation. The extension of the resonance approach to open-shell systems is bound to lead to problems in interpretation.

Neither of the obstacles above are insurmountable, although the first is more difficult than the second. In this paper we will (1) develop a system for empirically defining the reactive electronic state of organic ions, (2) extend Dewar's perturbation method[1,7] to radical cations, and (3) examine the relationship between mass spectrometry, thermochemistry, and photochemistry on this basis.

Reactive Electronic States. Initial States of Ions, State Lifetimes. Organic chemists are primarily interested in the interpretations of spectra which are produced by electron impact with electron energies in the range of 50–100 eV. In order to apply electronic theories of reactivity to the interpretation of these spectra, we must define (at least qualitatively) the reactive states for ions. The quasi-equilibrium theory has provided the basis[5,8] for defining the reactive states of ions. We will examine the initial electronic states of ions, energy redistribution, and the lifetimes of states with respect to reaction times in an attempt to classify qualitatively mass spectral reactions according to types of reactive electronic states.

With electron energies of 50–100 eV, EI mass spectra are essentially independent of electron energy. In this region the internal energy distribution for primary ions is approximately equal to the transition probability distribution for initial excitation.[8]

The initial states of a molecule ion can be approximated by a series of doublet states that correspond to removal of a valence electron from any of the levels of the parent molecule. Electron-impact cross sections for removal of a valence electron together with excitation of one or more of the remaining electrons should be intermediate between the cross sections for direct single and double ionization. For the present purposes we will assume that primary ions are formed by simple valence electron removal without additional excitation. Experimental evidence indicates that this is a reasonable approximation in the case of hydrocarbon ions.[9] The state density and the population of states will be determined by the density of energy levels in the molecule and the transition probability for initial excitation.

The derivative of an experimental ionization efficiency curve represents the band envelopes of the relative transition probabilities for formation of the parent ion *vs.* the internal energy of the ion.[10] Extended Hückel calculations[11] for hydrocarbons suggest that only $(2n + 1)$ of the $(3n + 1)$ bonding levels in alkanes contribute to the observed ionization efficiency curves.[9] There are serious objections to the application of the Hückel treatments to alkanes;[12] however, it seems likely that the essential conclusion that there are two major bands of bonding levels in alkanes will be confirmed by refined SCF calculations. It follows that even in hydrocarbons complete energy randomization among the initial states will not be possible as the probability of formation of very highly excited states will be low. This result would have no effect on calculations using the statistical theory[5,8] as long as the contributions of the populated electronic state functions to a given reaction cancel out. The upper level $(2n + 1)$ bonding states of alkanes are equally divided between states that are symmetric and antisymmetric with respect to the plane of the carbon atoms, and it is reasonable to assume that their contributions to a given reaction should cancel. For simple cleavage reactions there will be very little difference between the effects of electronic or vibronic excitation in a given degree of freedom. The substantial success of QET in calculating the mass spectrum of propane[8] has confirmed the validity of the assumption of the unimportance of electronic states in the fragmentation of alkanes. In complex reactions, especially those that proceed *via* electrocyclic pathways, there will be a large difference between electronic and vibronic excitation.[1,6]

There is a substantial amount of evidence which suggests that the assumptions of the statistical theory (complete energy randomization and neglect of electronic state functions) will not be valid for molecules with many π electrons and/or nonbonding valence electrons. In systems with many π electrons, *e.g.*, diacetylene, formation of highly excited ions has been shown to have a low probability by photoelectron spectroscopy.[13] The number of possible states for the initial ion, aside from accidental degeneracy, is given[5a] by

$$\frac{n}{\left(\frac{n+1}{2}\right)!\left(\frac{n-1}{2}\right)!}$$

where n is the number of valence electrons in the ion. Most of these states will be so high in energy that their populations will be insignificant. It is reasonable to assume that the energies of the remaining states will be

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[7] M. J. S. Dewar, *J. Amer. Chem. Soc.*, **74**, 3341, 3345, 3350, 3353, 3355, 3357 (1952).

[8] M. L. Vestal, *J. Chem. Phys.*, **43**, 1356 (1965).

[9] W. A. Chupka and M. Kaminsky, *ibid.*, **35**, 1991 (1961).

[10] (a) J. D. Morrison, *Rev. Pure Appl. Chem.*, **5**, 22 (1955); (b) H. Hurzeler, M. G. Inghram, and J. D. Morrison, *J. Chem. Phys.*, **28**, 76 (1958).

[11] R. Hoffmann, *ibid.*, **39**, 2047 (1963).

[12] M. J. S. Dewar in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 177.

[13] C. Baker and D. W. Turner, *Chem. Commun.*, 797 (1967).

packeted in much the same way as the energies of the initial states. The density of states will increase dramatically with energy, and for states with energies more than 2 eV above threshold there will certainly be the required number of potential surface crossings to ensure randomization of electronic energy within each band. It is not necessarily the case that electronic–vibronic coupling will allow crossings between bands. The two central bands of diacetylene are separated by about 4 eV.[13]

The importance of electronic control of the course of organic reactions has been clearly demonstrated in recent years.[1,6] The neglect of electronic state contributions to reactivity cannot lead to meaningful results if energy randomization is incomplete and/or different states have different reactivities. In this regard, it has been clearly shown that there are two different reactions that lead to loss of a hydrogen atom from the toluene molecule ion,[14] which suggests the existence of "isolated" excited states of this parent ion.

It there are insufficient potential-surface crossings to ensure energy randomization, the relative lifetimes of excited states with respect to the mass spectral time scale are very important. We are primarily concerned with the half-lives of doublet states for the radical cations. The initial states of radical cations will be primarily singly excited doublet states. Doubly excited doublet states for the radical cations will be statistically favored over quartet states by a factor of 2:1 in electron spin inversion. Of the three electrons whose spins may be inverted in a doubly excited doublet state, there is only one which on inversion will give a quartet state. Electronic factors will in general favor doublet states even more. The radiative lifetimes of doublet states generally lie in the range of 10^{-8} to 10^{-7} sec.[15] The oscillator strength and transition probability will in general increase with increasing energy assuming that the matrix elements $\langle n|\Sigma_i r_i|m\rangle$ in the expression for the oscillator strengths[15a] do not change drastically. Thus, the known lifetimes of excited doublet states ($\sim 10^{-8}$ sec) can be considered representative of the probable lifetimes of excited doublet states in a mass spectrometer.

The observation of metastable ions for a given decomposition can provide a qualitative guide to rate constants for the reaction. Comparision of this qualitative rate data with excited doublet state lifetimes should make it possible to roughly classify reactions as those of excited or low-lying doublet molecule ions.

The Importance of Metastable Ions. The mass spectrometric time scale for sector instruments is primarily a function of source design and the magnitude of the ion draw-out fields. The nature of the experiments requires that these factors be roughly constant in general use instruments. The residence time of newly formed ions in the Nier source of the Associated Electrical Industries MS-9 mass spectrometer is the same, within the error of the calculation, as the residence times which Chupka calculated for his instrument,[16] that is, times of the order of 1–5 μsec. The flight times of ions in different general use sector instruments will also be similar, because the required large mass range for organic instruments keeps the accelerating voltage in a defined relationship to instrumental dimensions. The flight times for m/e 200 ions in the MS-9 from the beam-defining slit to the beginning and the end of the field-free region between the electrostatic and magnetic analyzers are of the order of 0.8–1.5 μsec.

Metastable ions are collected in double-focusing instruments for unimolecular ionic decompositions that occur in the field-free region between the electrostatic and magnetic analyzers. If a normal metastable ion is observed, the rate constant for formation of the daughter ion may be bracketed between 10^4 and 10^6 sec^{-1} because of the limitations imposed by the mass spectral time scale.[16] These rate constants are considerably larger than the reciprocal of the half-lives of highly excited doublet states. Observation of a normal metastable for reaction of an odd-electron ion can be taken as evidence that the reaction (or reactions) in question occurred from a low-lying doublet state of the radical cation. If a molecule has an extensive π-electron system and several heteroatoms such as fluorine and nitrogen, removal of a nonbonding electron or a high-energy π electron would produce several states with energies that differed by as much as 2 eV; however, the wave functions for all of these states would directly correspond to the bonding and nonbonding wave functions of the un-ionized ground state. If intersystem crossing to states in which the unpaired electron is in an antibonding orbital can be neglected, we can directly deal with these reactions using approximate MO methods. Experimental evidence, particularly the results of linear free energy relationships and selectivity in 70-eV mass spectra, suggest that these assumptions are justified.

There are two classes of even-electron ions that are very important in the interpretation of organic mass spectra, namely fragments formed by a loss of a radical and doubly charged molecule ions. Even-electron fragment ions that are formed in reactions which produce intense metastable ions should be formed in low-lying electronic states. If the unpaired electron in the parent ion participates in the bond-breaking process, which is very likely the case in the simple cleavage of ketones, etc., the daughter ion should be formed in a low-lying singlet state. In all other cases the triplet states of the daughter ion should be as probable as singlet states. The initial states of doubly ionized molecules will be divided between singlet and triplet states, with a probable excess abundance of triplet states. Intersystem crossing will increase the population of triplet states because of their longer radiative lifetimes. The half-lives for triplet–singlet emissions are generally longer than the time scale for metastable observation in a mass spectrometer. Thus, it is probable that most of the decompositions of doubly charged ions occur from electronically excited states of the ion.

Quantitative correlations of a large number of mass spectrometric fragmentation reactions with substituent constants obtained from solution data have been described in recent reports.[17] Metastable ion data have

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(14) F. Meyer and A. G. Harrison, *J. Chem. Phys*, **43**, 1778 (1965).

(15) (a) G. A. Robinson in "Molecular Physics," Vol. 3, D. H. Williams, Ed., Academic Press Inc., New York, N. Y., 1962; (b) J. E Hessar and K. Dressler, *J. Chem. Phys*., **45**, 3149 (1966).

(16) W. A. Chupka, *ibid*., **30**, 191 (1959).

(17) (a) M. L. Gross and F. W. McLafferty, *Chem. Commun*., 254 (1968); (b) M. M. Bursey, *Org. Mass Spectrom*., 1, 31 (1968); (c) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc*., **89**, 1 (1967); (d) M. M. Bursey and F. W. McLafferty, *ibid*., **88**, 5023 (1966), and papers cited therein.

been published for the decomposition of monosubstituted benzophenones;[17a] allof the compounds in the series gave significant metastables for loss of the substituted benzoyl radical. In this series a very good correlation was obtained between the 70-eV ion intensities and Hammett σ values.[17b] The Hammett correlations are linear free energy relationships which correlate the rate of a reaction with the small electronic perturbations introduced by different substituents located at positions remote from the reaction site. These correlations would not have been possible if the reactive electronic states of the parent ions included states in which the unpaired electron was in an antibonding orbital. The reaction parameters (ρ constants) for reactions from electronic states in which the unpaired electron is in a bonding or an antibonding orbital must be different. Either the population of states must have been the same for a wide variety of substituents, which seems unlikely, or contributions from states in which the unpaired electron is in an antibonding orbital were sufficiently small that they can be safely ignored.

There are several cases in which the Hammett correlation fails for mass spectral reactions, *e.g.*, loss of NO from substituted nitrobenzenes. As the original authors indicated[17d] it is likely that different electronic states are involved in the reactions depending on the nature of the substituent. Information about metastable ions in this series would allow one to qualitatively decide if the electronic differences controlled the rate of initial rearrangement to a spiro structure, or subsequent loss of NO. If metastable ions were observed for loss of NO throughout the series it would suggest that the rates of initial rearrangement were highly dependent on the electronic state of the reacting ion.

Discrimination between primary and secondary hydrogen abstraction reactions can also provide a substantial amount of information about the internal energies and reactive states of ions. Djerassi and coworkers have reported several studies of primary–secondary discrimination in mass spectra.[18,19] The clearest test of primary–secondary discrimination is given by the mass spectra of specifically deuterated derivatives of *n*-butyl isobutyl ketone.[18] In this compound primary or secondary abstraction leads to elimination of propylene as a neutral, and secondary hydrogen abstraction is favored by at least 10:1. When these values are compared with data obtained for the Norrish type II process in ketones[20,21] and its radiolysis analog,[21] it is clear that the "effective temperature" for the mass spectral process (assuming an exponential rate law) is not more than 150°. This suggests that the McLafferty rearrangement occurs only in those ions that have reached their electronic ground state by emission of a photon and not by vibrational relaxation. If the highly excited ions (internal energies more than 2 eV above threshold) that are produced in 70-eV mass spectra reacted from electronically excited states or their vibrationally excited ground states, the primary–secondary discrimination should have been much smaller than observed.

In this regard the low-voltage mass spectra of aliphatic ketones[22] is very interesting. At low voltages hydrogen scrambling occurs as well as δ-hydrogen rearrangements. Both of these processes are unimportant in 70-eV mass spectra. It is plausible that these processes occur from metastable excited states of the molecule ion. For small excitation energies the density of states will be relatively low and the transition probability for the most favorable transition will be lower than for highly excited-states. These two factors could increase the excited state lifetime enough to make excited states important in complex reactions such as the δ-hydrogen rearrangement. At high electron energies the proportion of ions formed with small internal energies will be small, which accounts for the unimportance of the specific low-voltage processes in 70-eV mass spectra.

Using the reasoning outlined above, 50–70-eV induced mass spectrometric fragmentation reactions may be qualitatively divided into three classes. Class I reactions are those which occur from low-lying doublet or singlet states. This class includes all reactions of molecule ions which give rise to significant metastable peaks, and decomposition reactions of even-electron ions that were initially formed in low-lying singlet states. Class II reactions are those which occur from excited electronic states including states with electrons in antibonding orbitals. This class includes most of the decompositions of doubly ionized molecules, and reactions of molecule ions for which metastable peaks cannot be detected. Class III reactions are those reactions for which the reactive electronic states are indeterminant. This class must include many of the reactions of even-electron fragment ions and reactions of molecule ions for which only very low intensity metastable ions can be detected.

Reactions of class I should follow the PMO treatment and orbital symmetry selection rules for thermal reactions.[1,6] Reactions of class II should be interpretable on the basis of MO treatments of excited-state reactivity.[1,6] Using this approach it should be possible to produce an accurate account of the relationship between mass spectrometric reactions and thermal and photochemistry. In the following section we will develop the PMO treatment of radical cations. The following paper will apply the approach to a selected number of examples of electrocyclic mass spectral reactions.

Application of the PMO Method. Mass spectrometric reactions can generally be divided into three groups, namely, simple cleavage, internal displacement reactions, and electrocyclic reactions. The third class is the most interesting and we will deal with it first.

Mass Spectrometric Electrocyclic Reactions. Aromaticity of Doublet Ions. We know of no exceptions to Dewar's rules[1] for electrocyclic reactions in uncharged systems; the extensions of the application of these rules to mass spectrometric reactions is straightforward.

The rules are (1) *thermal electrocyclic reactions take place via aromatic states*, and (2) *electrocyclic reactions of excited states of closed-shell molecules take place via antiaromatic transition states.* Analogous reactions of radicals take place more readily than those of cor-

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(18) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *Tetrahedron*, 22, 1391 (1966).

(19) C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, 87, 5747 (1965).

(20) C. H. Nicol and J. G. Calvert, *ibid.*, 89, 1790 (1967).

(21) P. Ausloos, *J. Chem. Phys.*, 65, 1616 (1961).

(22) W. Carpenter, A. M. Duffield, and C. Djerassi, *J. Amer. Chem. Soc.*, 90, 160 (1968).

responding (even-electron) ions, but without electronic stereospecificity.

The extension of Dewar's first rule to reactions of radical cations, which occur from states in which the unpaired electron is in a bonding or nonbonding orbital (class I reactions), only requires determination of the aromaticity of systems that are isoelectronic with the proposed transition state.

The original definition of "aromaticity" should be adequate for our purposes; *i.e.*, a cyclic conjugated system is aromatic if its π-bond energy is significantly higher than that of an open-chain conjugated analog. The aromaticity of molecule ions can be deduced in direct analogy to the highly successful PMO treatment of closed-shell systems;[1] however, some of the PMO expressions[7] must be modified to deal with radical cations.

The aromaticity of a given system can often be deduced by determination of the first-order perturbation introduced by union of two atoms in a conjugated chain to form a cyclic conjugated system. The expression for the first-order change in π-bond energy for intramolecular union between two different atoms r, s in the same conjugated system is given[23] by

$$\Delta E_{\pi\text{-RS}} = 2\beta P_{rs} \tag{1}$$

where P_{rs} is the Hückel π-bond order between atoms r and s in the original system. This expression can be applied directly to systems that are of interest in mass spectroscopy; however, the difficulty of obtaining the mobile bond orders in the open-chain systems limits the general utility of eq 1.

We can also obtain the π-bond energy of radical cations by examination of the first- and second-order changes in π energy on union of an odd AH radical R with an odd AH cation S.

The change in π energy that accompanies union of two odd AH radicals, both of which have a singly occupied NBMO, has been given (eq 42 of ref 7) by

$$\Delta E_{\pi\text{-RS}} = 2a_{or}b_{os}\beta_{rs} - 2\left\{\sum_{m\neq 0}^{\text{occ}}\sum_{n}^{\text{all}} - \sum_{m}^{\text{all}}\sum_{n\neq 0}^{\text{occ}}\right\}\frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} + \sum_{m\neq 0}^{\text{all}}\frac{a_{mr}^2 b_{os}^2 \beta_{rs}^2}{E_m} + \sum_{n\neq 0}^{\text{all}}\frac{a_{or}^2 b_{ns}^2 \beta_{rs}^2}{F_n} \tag{2}$$

where a_{mr} and b_{ns} are MO coefficients in R and S. If two NBMO's contain but one electron, the development following Dewar's method[7] gives the change in π energy on union as

$$\Delta E_{\pi\cdot\text{RS}^+} = a_{or}b_{os}\beta_{rs} - 2\left\{\sum_{m\neq 0}^{\text{occ}}\sum_{n}^{\text{all}} - \sum_{m}^{\text{all}}\sum_{n\neq 0}^{\text{occ}}\right\}\frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} + {}^1/_2\left\{\sum_{m\neq 0}^{\text{occ}}\frac{a_{mr}^2 b_{os}^2 \beta_{rs}^2}{E_m} + \sum_{n\neq 0}^{\text{all}}\frac{a_{or}^2 b_{ns}^2 \beta_{rs}^2}{F_n}\right\} \tag{3}$$

If both R· and S$^+$ are alternate HC systems, the last term in eq 3 vanishes. However, the magnitude of the second term with respect to the first is no longer such that the second term can be safely neglected as in the case of the union of two radicals. If R and S are alternate HC systems, the orbital energies E_m of R and F_n of S must be symmetric about the energy of the NBMO's E_0 and F_0 in both systems. E_0 and F_0 are assumed to be zero in the PMO treatment. Using this we can rewrite the second term in eq 3

$$\text{term II} = -2\left\{\sum_{m\neq 0}^{\text{occ}}\sum_{n}^{\text{all}} - \sum_{m}^{\text{all}}\sum_{n\neq 0}^{\text{occ}}\right\}\frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m - F_n} = -4\sum_{m\neq 0}^{\text{occ}}\sum_{n\neq 0}^{\text{occ}}\frac{a_{mr}^2 b_{ns}^2 \beta_{rs}^2}{E_m + F_n} - 2b_{os}^2\sum_{m\neq 0}^{\text{occ}}\frac{a_{mr}^2 \beta_{rs}^2}{E_m} - 2a_{or}^2\sum_{n\neq 0}^{\text{occ}}\frac{b_{ns}^2 \beta_{rs}^2}{F_n}$$

The approximation[1] that E_m and F_n may be replaced by an average orbital energy $\tilde{E}$ in these second-order perturbation expressions allows us to simplify further

$$\text{term II} \approx \frac{-\beta^2}{2\tilde{E}}\left\{\sum_{m\neq 0}^{\text{occ}} 2a_{mr}^2 \sum_{n\neq 0}^{\text{occ}} 2b_{ns}^2 + 2b_{os}^2\sum_{m\neq 0}^{\text{occ}} 2a_{mr}^2 + 2a_{or}^2\sum_{n\neq 0}^{\text{occ}} 2b_{ns}^2\right\} \tag{4}$$

On rearrangement

$$\text{term II} \approx \frac{-\beta^2}{2\tilde{E}}\left\{\left(\sum_{m\neq 0}^{\text{occ}} 2a_{mr}^2 + a_{or}^2\right)\times\left(\sum_{n\neq 0}^{\text{occ}} 2b_{ns}^2 + b_{os}^2\right) + b_{os}^2\sum_{m\neq 0}^{\text{occ}} 2a_{mr}^2 + a_{or}^2\sum_{n\neq 0}^{\text{occ}} 2b_{ns}^2 - a_{or}^2 b_{os}^2\right\}$$

The π-electron charge density in AH radicals is unity and is given by the expression[24]

$$\sum_{m\neq 0}^{\text{occ}} 2a_{mr}^2 + a_{or}^2 = 1$$

Application of this expression and rearrangement of terms leads to a simplification of expression 4.

$$\text{term II} \approx \frac{-\beta^2}{2\tilde{E}}\{1 + a_{or}^2 + b_{os}^2 - 3a_{or}^2 b_{os}^2\}$$

The average orbital energy in an AH system should be close to the value of the resonance integral. If $\tilde{E}$ is related to β by a factor of $^{10}/_8$ as suggested by Dewar,[1] we can rewrite eq 3 with inclusion of approximate values for the second-order correction to the first-order energy as

$$\Delta E_{\pi\text{-RS}\cdot+} = \{a_{or}b_{os} - {}^2/_5(1 + a_{or}^2 + b_{os}^2 - 3a_{or}^2 b_{os}^2)\}\beta \tag{5}$$

The equation contains only terms in the NBMO coefficients of R and S. These coefficients can be obtained by the following simple procedures.[1,25] If alternate atoms in an odd-alternate hydrocarbon are starred in such a way that the starred set is more numerous, the NBMO coefficients of the unstarred atoms are zero, and the sum of the NBMO coefficients on the starred atoms attached to a given unstarred atom will be zero. Thus, for a linear odd AH, such as pentadienyl, the coefficients will be

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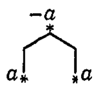
[23] M. J. S. Dewar, *Rev. Mod. Phys.*, **35**, 586 (1963).

[24] C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.*, **36**, 193 (1940).

[25] H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 275 (1950).



where a is a normalization factor, since the sum of the squares of the NBMO coefficients must be equal to 1, for pentadienyl

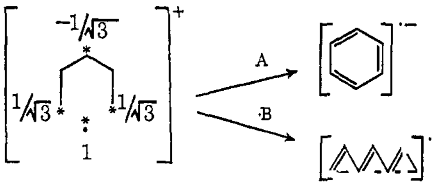
$$a^2 + a^2 + a^2 = 1$$

or

$$a = 1/\sqrt{3}$$

This procedure can be easily extended to complex systems which contain even-numbered rings and/or branched chains.

In order to illustrate this method we will examine the aromaticity of the benzene radical cation using both eq 1 and eq 5. The 1,6 bond order in the hexatriene radical cation is given by Hückel calculations[26] as 0.03. Using these data and eq 1, the resonance energy of the benzene radical cation should be approximately 0.06β. The aromaticity of the benzene radical cation may also be determined by examining the ΔE_π of union for pentadienyl and methyl to give, respectively, the benzene and the hexatriene ions (since the definition of aromaticity does not involve the σ skeleton, the π energies of these two systems must be compared when we discuss the aromaticity of the benzene molecule ion).



The coefficients of the NBMO's for the two AH systems are indicated in the figure. The resonance energy ($\Delta E_{\pi R}$) benzene $\cdot^+$ will be given by

$$\Delta E_{\pi R} = \Delta E_{\pi A} - \Delta E_{\pi B}$$

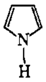
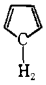
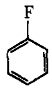
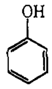
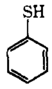
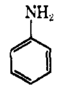
or

$$\Delta E_{\pi R} = \{1/\sqrt{3} - {}^2/_5(1 + {}^1/_3 + 1 - 1)\}\beta$$
$$= 0.04\beta$$

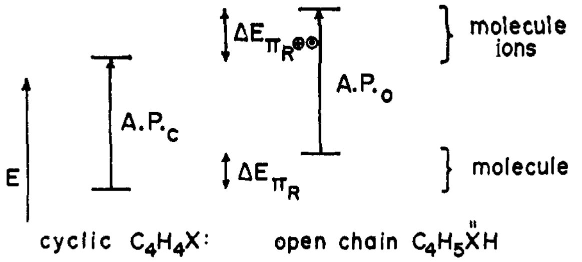
Both of the results suggest that the benzene radical cation should be at least an order of magnitude less aromatic than benzene itself. (The PMO treatment gives values of 0.60β and 1.15β for the resonance energy of neutral benzene using the same approaches as indicated above.) This is in complete accord with the evidence which indicates that the benzene molecule ion exists in an open-chain form at emission voltages well above threshold.[27] The fact that the toluene molecule ion rearranges to a cycloheptatriene ion[28] and the aniline molecule does not appreciably rearrange to the azepine molecule ion can also be clearly explained on this basis. The cycloheptatriene molecule ion is electronically analogous to the open-chain form of the benzene radical cation.[29] The corresponding azepine molecule should also be nonaromatic; however, the aniline molecule ion in its low-lying electronic states should be an aromatic system (see below) and would not be expected to rearrange prior to loss of a hydrogen atom.

The PMO method indicates that homonuclear five-electron, five-orbital π systems should be nonaromatic.[1] The introduction of a heteroatom into the five-electron system could result in an increase in aromaticity by alteration of the bond orders in the open-chain analog (eq 1). We can directly approach the problem of the aromaticity of five-electron, five-orbital systems by examining the appearance potentials of five-membered-ring heterocycles and the corresponding monosubstituted benzenes, which should be a reasonable model for the open-chain analogs of the heterocycles. Table I lists the appearance potentials[30] of a series of five-membered heterocycles and monosubstituted benzene derivatives.

Table I. Appearance Potentials (AP) for Five-Membered Heterocycles and Monosubstituted Benzenes

					
AP, eV	8.89	8.86	9.03	8.9	
					
AP, eV	9.75	9.20	8.50	8.33	7.70

The ground states of the cyclic $C_4H_4\ddot{X}$ systems are definitely aromatic,[1] and the appearance potentials for the molecule ions in this series are relatively constant as required by the node at X in the highest occupied MO in these systems.[31] The appearance potentials of the molecule ions of the open-chain analogs of the five-membered heterocycles will depend strongly on the electronegativity of the heteroatom (see Table I). This situation may be represented by a hypothetical energy diagram.



The resonance energy $\Delta E_{\pi R}$ for the un-ionized systems will decrease slightly with an increase in the electronegativity of $\ddot{X}$. The appearance potential of the cyclic molecule ion, AP_c, will be virtually independent of $\ddot{X}$. This means that the resonance energy of the cyclic molecule ion with respect to its open-chain analog,

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(26) C. A. Coulson and A. Streitwieser, Jr., "Dictionary of π-Electron Calculations," W. H. Freeman and Co., San Francisco, Calif., 1965.

(27) J. Momigny, L. Brakier, and L. D'or, *Bull. Classe Sci. Acad. Roy. Belg.*, **48**, 1002 (1962).

(28) H. M. Grubb and S. Meyerson, "Mass Spectrometry of Organic Ions," F. W. McLafferty, Ed., Academic Press Inc., New York, N. Y., 1963, p 453.

(29) (a) K. L. Reinhart, Jr., A. C. Bachholz, and G. E. Van Lear, *J. Amer. Chem. Soc.*, **90**, 1073 (1968); (b) A. V. Robertson, M. Marx, and C. Djerassi, *Chem. Commun.*, 414 (1968).

(30) R. W. Kiser, "Introduction to Mass Spectrometry," Prentic-Hall, Inc., Englewood Cliffs, N. J., 1965, p 308.

(31) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 195.

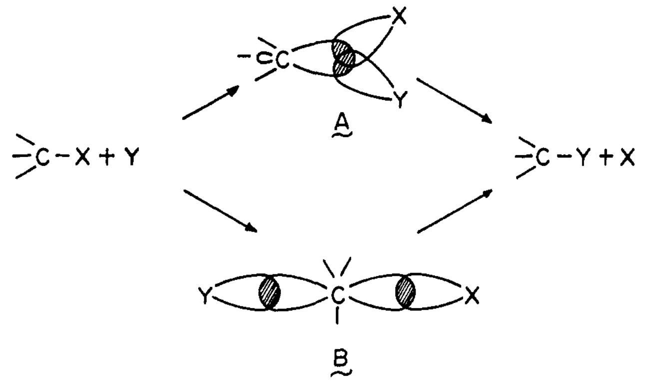


Figure 1.

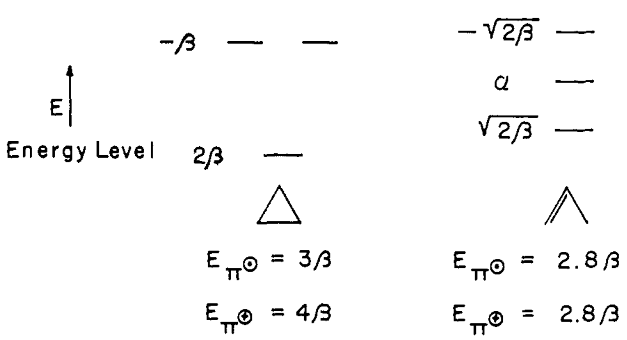


Figure 2.

$\Delta E_{\pi R\cdot +}$, should increase with the increasing electronegativity of $\ddot{X}$.

The analysis above has two clear consequences for the interpretation of electrocyclic reactions that belong to class I, *i.e.*, that give prominent metastables. These are (1) mass spectrometric electrocyclic class I reactions in even-orbital systems should follow the patterns established for neutral analogs, though stereochemical control should not be as pronounced; (2) five-orbital transition states will be preferred for electrocyclic class I reactions especially if the system contains an oxygen heteroatom.

Class I Internal Displacement Reactions. Displacement reactions may be treated in the PMO formalism[32] by constructing analogies to the two relevant transition states for displacement with and without inversion at carbon.

The two transition states A and B (Figure 1) may be respectively approximated by the cyclopropenyl and allyl MO systems. The analogy between A and cyclopropenyl is graphically obvious; this is not necessarily the case for the relationship of B to the allyl system. The only difference between B and the allyl system is in the phase inversion at the central carbon. The 1,3-β in B would be negative and in allyl the 1,3-β should be positive. This difference is trivial since the Hückel approximation sets these β's to zero. When the reactive site, Y, is a radical we must deal with a three-orbital, three-electron system, and when Y reacts through a cation center, we will deal with three-orbital, two-electron systems. Figure 2 shows the HMO energy levels[31] for cyclopropenyl and allyl, and the π energies for three- and two-electron cases. Radical displacement *without inversion* of configuration should be slightly favored in class I mass spectrometric reactions, and internal displacement by cation centers *without inversion* of configuration should be definitely dominant in class I reactions. The relative rates for internal displacement reactions will depend on the geometry of the system, and also on the nature of the reacting centers $\gt C$ and X and Y (Figure 1). The effect of structural changes in $\gt C$ and X on the relative rates of displacement reactions will be analogus to these effects on the rate of simple cleavage.

Class I Cleavage Reactions. The PMO method is uniquely capable of providing semiquantitative predictions of the relative rates of homolytic cleavage reactions in radical cations. Most of the interesting homolytic cleavages involve new π-bond formation (*e.g.*, β cleavage in aromatic and vinyl systems and α cleavages in ketones and ethers), and these can be dealt with directly by PMO methods. If no new bonds are formed in the cleavage process, the relative rate should be a direct function of the bond strength and the ionization potentials of the resulting radicals.

We can consider a cycle for ionization and β cleavages in the system Ar–CH$_2$–R.

$$\begin{tikzcd}
\mathrm{ArCH_2R} \arrow[r, "\Delta E_2"] \arrow[d, "\Delta E_1"', "(-e)"] & \mathrm{ArCH_2\cdot} + \mathrm{R\cdot} \arrow[d, "\Delta E_3"', "(-e)"] \\
\mathrm{ArCH_2R\cdot^+} \arrow[r, "\Delta E_4"] & \mathrm{ArCH_2^+} + \mathrm{R\cdot}
\end{tikzcd}$$

a_{or}

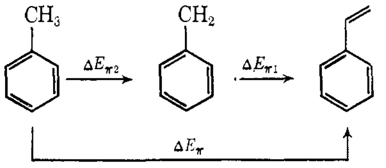
In this cycle

$$\Delta E_2 = \Delta E_{\sigma_2} + \Delta E_{\pi_2}$$

The value of ΔE_{σ_2} should be independent of the nature of the π system Ar, to a first approximation, and can be treated as a constant when one considers cleavage of the same R group. A satisfactory approximation of ΔE_{π_2} has been given[33] as

$$\Delta E_{\pi_2} = 2\beta(1 - a_{or}) \qquad (6)$$

where a_{or} is the NBMO coefficient at the cleavage site. This result was obtained from the following analysis. Consider the π-energy changes for the reactions



The following relationships define these energies

$$\Delta E_{\pi_1} = 2a_{or}b_{os}\beta$$

$$\Delta E_{\pi} \approx E_{\pi}(\mathrm{CH_2{=}CH_2}) = 2\beta$$

The latter relationship holds because there is no first-order change in π energy upon union of two alternate HC's;[1] the NBMO coefficient for methyl (b_{os}) is 1. Combination of these equations gives eq 6.

ΔE_1 and ΔE_3 are the respective ionization potentials for ArCH$_2$–R and ArCH$_2\cdot$, so that ΔE_4 is given by

$$\Delta E_4 = 2(1 - a_{or})\beta + \Delta E_{\sigma 2} + W_{\mathrm{ArCH_2\cdot}} - W_{\mathrm{ArCH_2-R}} \qquad (7)$$

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(32) M. J. S. Dewar, personal communication.

(33) M. J. S. Dewar and R. J. Sampson, *J. Chem. Soc.*, 2789 (1956); 2945, 2952 (1957).

The success of Smith's approach to the appearance potentials of aromatic hydrocarbons[34] suggests that the difference between the appearance potentials of $\mathrm{ArCH_2^+}$ and $\mathrm{ArCH_2R\cdot^+}$ from the corresponding neutrals should be small, and approximately constant. Smith's approximation to the first ionization potential of a hydrocarbon is

$$W_{\mathrm{Ar}} = v + e^2/2C$$

where v is the work function of graphite and C is the coulombic capacitive energy for a charged particle the same size as the aromatic system. The value of C will change only slightly on addition of a methylene to a π-electron system, and the other parameters will not change. Using the approximation that $W_{\mathrm{ArCH_2^-}} - W_{\mathrm{ArCH_2R}}$ is constant, eq 7 may be reduced to

$$\Delta E_4 = -2a_{or}\beta + C \tag{8}$$

when we are considering reaction in which the same R group is eliminated.

The clear success of substituent effect correlations for class I mass spectrometric cleavage reactions[17] strongly suggests that mass spectrometric reaction rates can be empirically treated by equations of the type

$$K = A \exp \frac{(-E^{\mp})}{(E^0)} \tag{9}$$

where A would be an energy-dependent frequency factor and E^0 should depend on the emission voltage, the source temperature, and the reactive state of the ion (if radiative decay occurs prior to reaction, E^0 will be appropriately diminished). The substituent correlations relate the logs of rates to substituent parameters that are linearly related to $E^{\mp}$, the effective activation energy (for mass spectral reactions this is primarily an internal entropy term). In the case of β cleavage the relationships given in eq 10 should hold

$$\log K = C(-2a_{or}\beta) - C' \tag{10}$$

where C and C' are constants.

It is clear from this analysis that β cleavage should be substantially more important than cleavage at sites remote from a π-electron system in accord with numerous observations.[2b]

The results obtained above for β-cleavage reactions can be directly applied to the problem of the aromaticity of the aniline molecule ion, which we have mentioned earlier. The isoconjugate HC system for the aniline molecule ion is the benzyl radical. The open-chain reference for consideration of aromaticity should be the heptatrienyl radical. The π-electron energies of the toluene and heptatrienyl molecule ions should be very similar; however, the change in π energy on cleavage of a β proton is, respectively, 1.24β and β. The difference in π energy for the two systems should be approximately 0.24β, which is substantial when compared to the values for the benzene radical cation. Toluene rearranges[28] before cleavage because of the lack of stability of the benzene$\cdot^+$ π system; however, aniline does not appreciably rearrange[29] until after the β cleavage which forms a protonated nitrene cation.

The relative rates of α-cleavage reactions can be handled directly with the PMO method. The energy changes on α cleavage

$$[\mathrm{RR'{-}CH{-}\dot{X}{-}R''}]^+ \xrightarrow{\Delta \mathrm{E}} [\mathrm{R{-}CH{=}X{-}R''}]^+ + \mathrm{R}\cdot$$

will be given by

$$\Delta E = \Delta E_\pi + \Delta E_\sigma$$

The value of E_π can be obtained directly, and is identical with change in π energy for union of two AH radicals[5a]

$$\Delta E_\pi = 2a_{or}b_{os}\beta_{rs} \tag{11}$$

when a_{or} and b_{os} are the NBMO coefficients at atoms r and s in the AH radicals. If R and R′ above are alkyl residues or hydrogen atoms, the value of ΔE_π is simply $2\beta_{rs}$. The value of ΔE_σ will depend on the stability of R·′, but should be constant when one considers reactions involving cleavage of the same group.

This result provides an immediate rationalization for the fact that α cleavage is very important in the fragmentation of aliphatic ethers and not so important in the fragmentation of aryl alkyl ethers.[2b] In the latter case, ΔE_π would be substantially less than 2β. On the other hand α cleavage of aryl and alkyl ketones show similar patterns;[2b] ΔE_π for the cleavage should be the same in both of these cases.

Correlation of Mass Spectrometric Fragmentation with Thermal and Photochemical Processes. Class I reactions in a mass spectrometer can be directly related to thermal and photochemical processes through the PMO formalism. This relationship should provide a basis for the future prediction of thermal and photochemical reactions based on mass spectral observations. The three types of reactions discussed above should be treated separately.

Mass spectrometric class I electrocyclic reactions should be directly analogous to thermal processes.[1,6] The thermal reactions should have a higher stereoselectivity because of the greater aromaticity of the transition states in even-electron systems. The well-known relationship between the thermal and mass spectrometric retro-Diels–Alder reaction[35] illustrates this point. Electrocyclic reactions of mass spectrometric class II should correlate with photochemical electrocyclic processes[1,6] in which the transition states are preferably antiaromatic.[1] Photochemical electrocyclic processes that involve n → π* states, and which proceed through five-orbital, five-electron (aromatic) transition states, *e.g.*, the Norrish type II cleavage of ketones, should be directly correlated with corresponding class I reactions in the mass spectrometer. The correlation of the McLafferty rearrangement with Norrish type II cleavage has been illustrated many times.[3,36]

The relationship between mass spectral, internal displacement reactions and reactivity under thermal and photochemical excitation will be highly dependent on the respective occupation numbers of the orbitals illustrated in Figures 1 and 2, in addition to the electronic state of the reacting ion in the mass spectrometer. Class I internal displacement reactions, in which the reactive site (Y in Figure 2) is a heteroatom which has nonbonding electrons, would have direct analogs in n → π* or n → σ* photochemical systems. Thermal rearrangements of this type would require more energy,

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(34) F. T. Smith, *J. Chem. Phys.*, **34**, 793 (1961).

(35) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965).

(36) F. W. McLafferty, *Chem. Commun.*, 78 (1966).

and would preferably proceed with stereochemical inversion at the displacement site. All three reaction systems (mass spectrometric, thermolytic, and photolytic) should exhibit similar reactivity for internal radical displacement reactions when the radical site[36] is generated by an initial homolytic cleavage.

Reaction probabilities for β cleavage in thermal and photochemical reactions should be directly related to probability of class I β cleavage in the mass spectrometer (eq 8 will apply in all three cases). Photochemical α-cleavage reactions from $n \rightarrow \pi^*$ states should be directly related to the similar class I reactions in a mass spectrometer (eq 11 should apply in both cases). The related thermal reactions will be highly dependent on the $n \rightarrow \pi^*$ excitation energy of the initial system, and should not be directly related to the mass spectral reactivity.

The relationship between mass spectra and thermal and photochemical fragmentation of molecules is obviously complex. The PMO method together with an analysis of the reactive states of ions offers a simple semiquantitative procedure for interpreting mass spectra and predicting relationships between mass spectral, thermal, and photochemical reactions. Two additional factors should be considered prior to application of these procedures to specific cases. (1) The internal excitation energy for ions that give rise to class I reactions will generally be larger than the excitation energies accessible in thermal and photochemical experiments. This means that highly selective thermal and photoprocesses will very often not have analogs in mass spectra, and many of the high-energy (low probability) processes in mass spectra will not have analogs in thermal and photochemical reactions. In this regard field ionization mass spectra[37] should offer a direct basis for correlation of mass spectra with thermal and photochemical processes. Ion energy distribution on field ionization is much narrower than in electron-impact studies, and the field ionization time scale is substantially different than that for electron-impact mass spectra.[38] Because of the high potentials in the FI source, ion drawout is much faster than for EI sources and the majority of the normal fragment ions in FI mass spectra are formed in less than 10^{-9} sec after ionization. Most of these "field-induced" dissociations are simple cleavage reactions and should be considered as class III reactions. The numerous and often very intense metastable transitions in FI mass spectra represent reactions that very probably occur from the electronic ground state of the reacting ion. (2) It is always possible, and in many cases likely, that a given class I reaction in the mass spectrometer occurs from a rearranged molecule ion that is not accessible at modestly high thermal or photochemical energies. For these reactions the analogy will also break down.

The following paper[39] illustrates the application of these procedures to several selected electrocyclic reactions.

Acknowledgments. The National Institutes of Health has generously supported our work.

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[37] H. D. Becky and H. Hey, *Org. Mass Spectrom.*, 1, 47 (1968).

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[39] R. C. Dougherty, *J. Amer. Chem. Soc.*, 90, 5788 (1968).

Application of the Perturbation Molecular Orbital Method to the Interpretation of Organic Mass Spectra. The Hexahelicine Rearrangement and Other Electrocyclic Mass Spectrometric Reactions

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Abstract: This paper will explore the application of first-order perturbation theory (the PMO method)[1] to the interpretation of several mass spectrometric reactions using the analysis of reactive states of ions previously developed.[1] Our purpose is to illustrate the broad utility of the PMO approach in dealing with electrocyclic reactions. In the previous paper we developed the basis for classification of mass spectral reactions according to the electronic state of the reacting ion. Class I reactions predominantly occur from low-lying (fully bonding) electronic states of the parent. Class II reactions occur from excited electronic states. Observation of a prominent metastable ion for a reaction of an odd-electron parent indicates that the half-life of the parent is sufficiently long to place the reaction in class I. Class II reactions include those reactions of odd-electron parents for which metastable ions are not observed, and most of the reactions of doubly charged ions. The hexahelicene rearrangement, the retro-Diels–Alder reaction, and the McLafferty rearrangement are considered in these terms.

Once we have classified mass spectral reactions according to their electronic type,[1] application of modern theories of reactivity[2] to these reactions is a straightforward problem. Frontier orbital arguments and orbital symmetry selection rules[2b] can be applied

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[1] R. C. Dougherty, *J. Amer. Chem. Soc.*, 90, 5780 (1968).

[2] (a) M. J. S. Dewar, *Tetrahedron Suppl.*, 8, 75 (1966); (b) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, 1, 17 (1968).