3. The idea of isomeric donor–acceptor complexes[15] is supported by our results. Two energy minima are found in the energy surface for pyrene–TCNE, where the TCNE is situated over the center of each one of the two different kinds of rings, respectively. Isomeric complexes are also calculated for anthracene, naphthalene, durene, and *o*-xylene.

Space limitations allow only a short discussion of the first point. In theoretical discussions regarding the interactions between small unsaturated hydrocarbons, Coulson and Davies,[2] and Haugh and Hirschfelder[3] concluded that σ interactions outweigh π interactions. Several authors have implied that the σ electrons may be important in accounting for the stability of so-called π complexes.[16–21] A deficiency in perturbation theory has been invoked to account for the quantitative failure of the π-interaction theory.[7,20,22] The precise relative sizes of the π and σ interactions in molecular complexes are still a moot point. We know that the CNDO/2 method mixes σ and π levels,[23] and in our CNDO/2 calculations several highly energetic filled σ levels are found. However, it should be noted that the larger perturbation energy terms in our calculated results did not arise from near degeneracies of the interacting orbitals. We conclude that the role of the π-electron interactions in determining the stability of a molecular complex has certainly been overestimated in the past.

We will report the details of this work in a full paper. We are also carrying out calculations of a less empirical nature which we hope to present in the near future.

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Metastable Ion Characteristics. VIII. Characterization of Ion Decomposition Mechanisms by Metastable Ion Abundances

Sir:

From a submicrogram sample, the mass spectrometer can provide elemental composition data on a large number of ions produced by unimolecular decomposition of the sample molecules. Many of these ions retain the original arrangement of atoms in the molecule; in fact, Lederberg has proposed computer techniques for the complete elucidation of the structure of any acyclic compound using the *nonrearrangement* product ions of its mass spectrum.[1] Mechanistic studies[2,3] have made it possible to recognize many reactions involving rearrangements, but there is an obvious need for a general test to identify nonrearranged ions in the mass spectrum.[4]

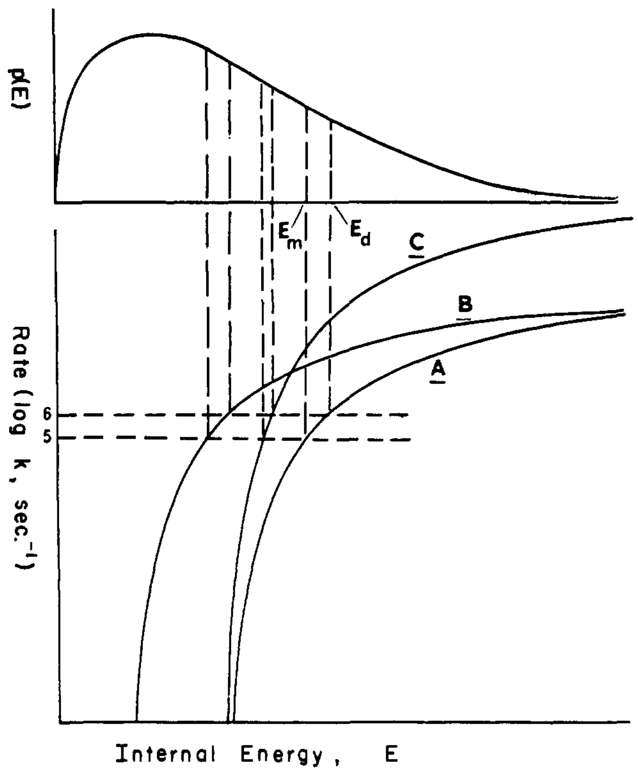

Figure 1. Lower curves: relation of the internal energy of the precursor ions to the corresponding rates of the hypothetical unimolecular reactions A, B, and C; upper curve: proportion of the precursor ions with a particular internal energy content *vs.* energy.

Chupka[5] has pointed out that reactions exhibiting low "frequency factors,"[6] a characteristic of rearrangement reactions, should show abundant metastable ions; surprisingly there apparently has been no attempt to date to utilize Chupka's conclusions in the interpretation of mass spectra.[2,3,8,9]

Referring to Figure 1, curve A describes the effect of the internal energy of the precursor ion (p) on its rate of decomposition. If instrument parameters are such

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Table I. Metastable Ion Abundances *vs.* Reaction Type

Compound	Transition	[daughter]/ [base peak], %	[metastable]/[daughter], %[a]	
			Rearrangement	Cleavage
2-Hexanone	$M - C_3H_6$	48	0.019	
	$M - CH_3$	5.8		3.2
	$M - C_4H_9$	100		<0.001
2-Octanone	$M - CH_3$	3.9		3.1
	$M - C_5H_{10}$	100	0.014	
3-Hexanone	$M - C_2H_4$	3.0	0.78	
	$M - C_2H_5$	100		0.021
Butyraldehyde	$M - C_2H_4$	100	0.30	
	$M - C_2H_5$	77		0.017
Methyl *n*-butyrate	$M - C_2H_4$	71	0.19	
	$M - C_3H_7$	100		<0.001
n-Propyl acetate	$M - C_3H_5$	27	0.14	
	$M - C_3H_6$	1.4	0.21	
	$M - C_3H_7$	100		<0.003[c]
1-Butanol	$M - OH$	3.3		<0.002
	$M - H_2O$	100	0.29	
	$M - H_3O$	13	0.95	
1-Heptanethiol	$M - SH$	0.4		<0.001
	$M - H_2S$	17	0.76	
1-Chlorohexane	$M - Cl$	1.6		<0.001
	$M - HCl$	8.6	0.052	
	$M - C_2H_5$	100	0.070	
1-Chloroheptane	$M - Cl$	0.15		<0.006
	$M - HCl$	0.80	<0.001	
	$M - C_3H_7$	100	0.016	
1-Bromohexane	$M - C_2H_5$	50	0.81	
	$C_3H_7 \rightarrow C_3H_5$	50	0.27[b]	
Butyrophenone	$M - C_2H_4$	6.6	2.0	
	$M - C_3H_7$	100		<0.01
	$C_7H_5O \rightarrow C_6H_5$	48		0.97
Benzophenone	$M - CO$	1.4	>0.1[b]	
	$M - C_6H_5$	100		0.016
Benzyl methyl ketone	$M - C_2H_2O$	25	3.2	
	$M - C_2H_3O$	86		<0.01
n-Butyl benzoate	$M - C_4H_8$	18	0.31	
	$M - C_4H_7$	57	0.18	
	$M - C_4H_9O$	100		0.003[c]
Phenetole	$M - C_2H_4$	100	0.20	
	$M - C_2H_5$	1.3		<0.02
β-Phenylethanol	$M - CH_2O$	60	0.58	
	$M - CH_3O$	100		<0.01
Benzonitrile	$M - CN$	3.7		0.055
	$M - HCN$	31	1.0	
Nitrobenzene	$M - NO$	10	1.4	
	$M - NO_2$	100		0.015
n-Decylbenzene	$M - C_9H_{18}$	100	0.45	
	$M - C_9H_{19}$	82		<0.001[c]

[a] Abundances measured as peak heights on a Hitachi RMU-6D under identical conditions: electron energy, 75 eV; accelerating potential, 3.6 kV; exit slit, 0.50 mm; oven, 185°; source, 175°. The detection limits were frequently reduced by interference of normal ions. [b] Flat-top metastable. [c] Measured on a Hitachi RMU-7 by the defocusing technique: M. Barber and R. M. Elliott, ASTM E-14 Conference on Mass Spectrometry, Montreal, June 1964.

that rates of 10^5–10^6 sec^{-1} are required for decomposition in the metastable region, then the average energies required for metastable (m_A*) and daughter ion (d_A) formation will be E_m to E_d, and $>E_d$, respectively (ignoring "missing metastables").[7] The resulting abundances [m_A*] and [d_A] are determined by the original distribution of energy values of the precursor ions (see top of Figure 1) and by the corresponding rates leading to m_A* and d_A relative to the rates of any competing decompositions. Lowering the activation energy of the reaction (curve B) would increase [m*] if there are competing reactions but otherwise should not change [m*] substantially if the slope of the corresponding region of the precursor energy distribution curve is relatively flat. However, shifting curve A in the rate axis to curve C, although again increasing [m*] if there are competing reactions, would narrow the range of precursor ion energies leading to metastables, and thus *lower* [m*]. If both reactions A and C are possible, [m_A*] < [m_C*]; however, if reactions B and C are operative, [m_B*] ≫ [m_C*], even though [d_C] > [d_B].

Reactions such as curve C with high upper rate limits (approaching vibrational frequencies) are typically those that involve simple cleavage of a labile bond. For a reaction with a specific steric requirement, such as a rearrangement reaction, this upper limit will be substantially lower, as in curves A and B, because of the high entropy of activation.[10] Other types of reactions may also exhibit a lowered maximum rate; however, this reasoning would predict that *a process producing an abundant ion does not involve rearrangement if the corresponding metastable ion is not abundant.*[11]

(10) The fraction of effective rotor forms is reduced in the transition state, lowering the "frequency factor."[6]

(11) Also, as observed, rearrangement peaks should exhibit lower appearance potentials than direct cleavage peaks of equal intensity.

This is substantiated by data (examples in Table I) on metastable peaks formed in 72 processes producing major fragment ions in a variety of spectra. For the 25 in which $[m^*]/[d] < 0.01\%$, all but 3 involve simple bond cleavages. For one of these a nonrearrangement path is possible; for the others the rearranged product ions exhibit abundances $<5\%$. Values of $[m^*]/[d] > 0.01\%$ are shown by 34 processes apparently involving rearrangement. Large values can also arise from particular cleavages, such as $M - CH_3$, and those involving secondary decompositions. Some types of reactions for particular compound classes show self-consistent $[m^*]/[d]$ values. It appears that with certain modifications, such as a correction for competing reactions, this value may provide a quantitive characteristic of reaction type.

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The Nature of the So-Called Coordination Compound $(Azobenzene)_2PtCl_4$

Sir:

The compound $(AB)_2PtCl_4$ (AB = azobenzene) reported by Kharasch and Ashford[1] has often been cited as an example of the coordinating ability of the azo group,[2-4] and olefinic type bonding has been suggested.[1,5] Since we have observed that the bonding of *cis*-aliphatic azo compounds to platinum(II)[6] occurs through the lone pairs on the nitrogen atoms, it was of interest to us to further characterize this compound.

Following Kharasch and Ashford's procedure, 1 g of *trans*-azobenzene was added to 0.5 g of $PtCl_4$ in 10 ml of glacial acetic acid, and the mixture was warmed on the steam bath for 1 hr. A brick red solid is precipitated after the platinic chloride dissolves. (If hydrated platinic chloride is used, the same compound precipitates almost immediately.) The precipitate appears soluble in organic solvents as reported by Kharasch and Ashford, and as such supports their formulation. However, if the solvents are dried over a molecular sieve, the solid is totally insoluble. Elemental analysis revealed that the compound has the empirical formula $[AB\text{-}H^+]_2PtCl_6{}^{2-}$. Elemental analysis of the solid after washing with wet solvents gives values for C and N which decrease as washing progresses, although their ratio remains constant. Simultaneously the percentage of platinum increases from 25.0 to 30.7% depending on the amount of washing. This indicates that trace amounts of water partially hydrolyze the conjugate acid to free azobenzene which colors the wash liquid. There is no true solubility of the compound. Since the earlier workers analyzed only for platinum, the platinum content appropriate to their suggested complex $(AB)_2PtCl_4$, 27.84%, can be reached in the course of washing.

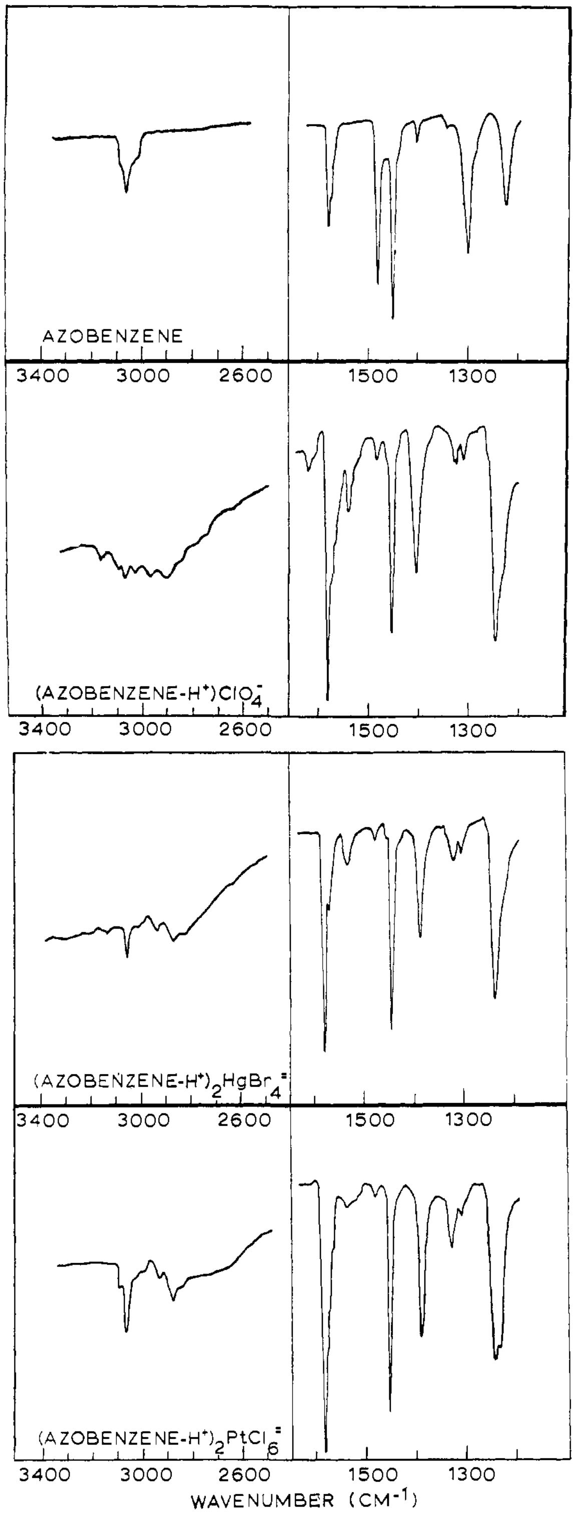

Figure 1. Infrared spectra.

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