Energy Partitioning Data as an Ion Structure Probe. Substituted Anisoles

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Abstract: The use of energy partitioning data in determining ionic reaction mechanisms and ion structures is introduced. Metastable peak profiles indicate that ionized anisoles lose formaldehyde upon electron impact by two competitive reaction channels. Energy partitioning studies support the view that these two processes involve four- and five-centered hydrogen transfers, respectively, which is consistent with evidence in the literaturesupporting each of these mechanisms. For the four-centered hydrogen transfer approximately 16% of the reverse activation energy appears as kinetic energy in the reaction of the para-substituted anisoles. This value is independent of the nature of the para substituent. The variation in relative abundance of the two H_2CO elimination processes with substituent provides evidence that hydrogen transfer occurs to a radical site in the formaldehyde elimination reactions. It is suggested that energy partitioning in reactions involving rearrangements to radical sites may in general be nearly independent of the nature of the substituent. Methyl radical loss from the molecular ion of para-substituted anisoles generally occurs by a single reaction channel with a small reverse activation energy (simple cleavage), but *p*-methylanisole reacts by two mechanisms, the energy release data indicating that ring expansion can precede expulsion of $CH_3\cdot$ possibly with formation of protonated tropone as the ionic product.

A complete characterization of the energetics of a unimolecular reaction must include a determination of the reverse activation energy ($\epsilon_0{}^r$) and a measurement of the translational energy (T) of the reaction products. This kinetic energy originates in two sources, the difference between the potential energy of the activated complex and that of the products and the internal energy of the activated complex. We shall therefore write

$$T = T^e + T^{\ddagger} \qquad (1)$$

where T^e and $T^{\ddagger}$ indicate the origin of T from potential and from nonfixed energy of the activated complex, respectively. If the RRKM model is used, the contribution of $T^{\ddagger}$ can be estimated[1] and the relative contributions of the two components to the measured T value can be used to indicate how the reverse activation energy is partitioned between internal and kinetic energy, an important question in molecular dynamics.

Data on energy partitioning is rather difficult to obtain for unimolecular reactions of neutral molecules,[2] but the accuracy with which kinetic energy release (T) values can be measured for metastable ionic reactions[3] confers a decisive advantage to studies on ions.[4] Previously, scattered ionic reactions had been studied in this regard,[5] but our earlier study on the loss of HCN from oxime methyl ethers[6] was the first to consider a series of compounds. It was observed that the kinetic energy released varied with the nature of the substituent and that the reverse activation energy is not statistically partitioned between internal and kinetic energy of the products, nor is it entirely released as translational energy. The relationship between T and the potential energy surface therefore demands further investigation and we have chosen to do this by studying other series of substituted aryl derivatives.

Throughout this paper, as in our previous work, the value of the energy release used is that measured from the metastable peak width at half height. Normally a distribution of energy releases accompanies any fragmentation, and the quantity used here approximates the average release.[7] The distribution of values of the nonfixed energy of the activated complex ($\epsilon^{\ddagger}$) usually does not make the major contribution to the distribution of T values.[8] Rather, this distribution is a direct property of the partitioning of the reverse activation energy, $\epsilon_0{}^r$.

In planning this project it was expected that the results would also provide information on ion structures[10] and ionic reaction mechanisms since the energy partitioning quotient, $T/\epsilon_0{}^r$, embodies information on the potential energy surface for reaction. The process of interest, formaldehyde loss from anisole and sub-

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(1) (a) C. E. Klotz, *J. Chem. Phys.*, **41**, 117 (1964); (b) Y. N. Lin and B. S. Rabinovitch, *J. Phys. Chem.*, **74**, 1769 (1970); (c) M. I. Vestal, "Fundamental Processes in Radiation Chemistry," P. Ausloos, Ed., Interscience, New York, N. Y., 1968; (d) S. A. Safron, W. D. Weinstein, D. R. Herschbach, and J. C. Tully, *Chem. Phys. Lett.*, **12**, 564 (1972); (e) G. H. Kwei, J. A. Norris, and D. R. Herschbach, *J. Phys. Chem.*, **52**, 1317 (1970).

(2) See, for example, (a) M. J. Berry and G. C. Pimentel, *J. Chem. Phys.*, **53**, 3453 (1970); (b) W. G. Clark, K. Dees, and D. W. Setser, *J. Amer. Chem. Soc.*, **93**, 5328 (1971); (c) H. W. Chang, D. W. Setser, and M. J. Perona, *J. Phys. Chem.*, **75**, 2070 (1971); (d) P. N. Clough, J. C. Polanyi, and R. T. Taguchi, *Can. J. Chem.*, **48**, 2919 (1970).

(3) (a) J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch. A*, 20, 180 (1965); (b) M. Barber, K. R. Jennings, and R. Rhodes, *ibid.*, 22, 15 (1967); (c) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 661 (1970); (d) J. H. Beynon and R. G. Cooks, *Res./Develop.*, 22 (11), 26 (1971); (e) E. G. Jones, L. E. Bauman, R. G. Cooks, and J. H. Beynon, *Org. Mass Spectrom.*, in press.

(4) Molecular beam studies on long-lived complexes provide another source of such information; see ref 1d.

(5) (a) C. G. Rowland, *Int. J. Mass Spectrom. Ion Phys.*, 7, 79 (1971); (b) M. A. Haney and J. L. Franklin, *J. Chem. Phys.*, **48**, 4093 (1968); (c) K. R. Jennings, *Org. Mass Spectrom.*, **3**, 85 (1970); (d) R. Taubert, *Z. Naturforsch. A*, **19**, 911 (1964).

(6) (a) R. G. Cooks, D. W. Setser, K. Jennings, and S. Jones, *Int. J. Mass Spectrom. Ion Phys.*, **7**, 493 (1971); (b) J. H. Beynon, M. Bertrand, and R. G. Cooks, *Org. Mass Spectrom.*, in press.

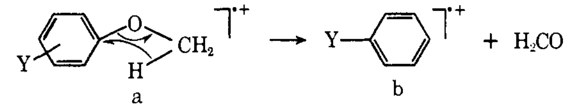
(7) This can be shown by convoluting the calculated peak shapes for a single energy release: J. H. Beynon, A. E. Fontaine, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, **8**, 341 (1972).

(8) The range of energy releases which make up the observed metastable peaks is usually considerably greater than a typical value (~0.1 eV[9]) of $\epsilon^{\ddagger}$.

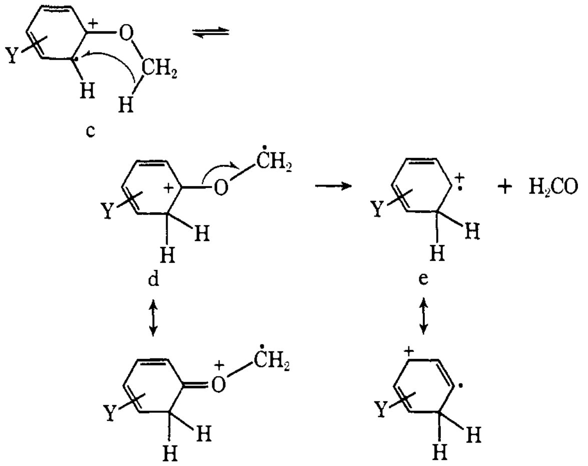
(9) E. G. Jones, J. H. Beynon, and R. G. Cooks, *J. Chem. Phys.*, **57**, 2652 (1972).

(10) Throughout this paper the term "structure" refers to the bonding arrangement, not bond angles and bond distances.

stituted anisoles, has generally been thought[11] to involve a four-centered hydrogen transfer (reaction 2). However, evidence has recently been provided[12] that reaction can occur through the five-centered hydrogen transfer mechanism (reaction 3).[13] The energy partitioning results suggest that both processes occur.



(2)



(3)

Experimental Section

Ionization and appearance potential measurements were obtained using an AEI MS9 mass spectrometer. The instrument was operated at 8 kV, but the electron current (trap current) was reduced to 18 μA and the repeller tied to the ion chamber for these measurements. The electron energy of the MS9 is variable from 5 to about 80 eV using a ten-turn helipot. For this study the instrument was modified so that the potentiometer covered 5 eV and stepping switches were used to allow the full original range to be attained. This modification allowed electron energies to be read directly from the instrument rather than from an external voltmeter.

Ionization and appearance potentials were determined using the semilog plot method.[14] Only the region of the ionization efficiency curve below 1% of the 50-eV ion current was used. Several standards, introduced simultaneously with the sample, were employed for each determination. In general, organic molecular ions were preferred as standards because they tended to give ionization efficiency curves which were more similar in slope to those of the ions of interest than the curves given by the more frequently chosen rare gas ions. The standards were chosen so as not to interfere with the masses of the ions of interest in the unknown and so that their IP's closely bracketed those being determined. Several pairs of standards were used to check the electron energy scale read from the instrument. The error was smaller than the reproducibility of the measurements.

In all but a few cases compounds were introduced through the heated inlet system. The small sample depletion that occurred in the course of obtaining data was compensated for by taking measurements both as the electron energy was lowered and again as it was raised. Only a few points were taken as high energy, but in the low-energy region readings were taken every 0.1 or 0.05 eV. At least four sets of ionization efficiency measurements, representing at least two separate sample introductions, were obtained for each ion. The resulting IP or AP values had an overall spread of less than 0.15 eV and were averaged to give the reported results. The reproducibility of these data is comparable with that found by others using similar methods.[15]

All measurements of kinetic energy release were performed on the Hitachi RMH-2 mass spectrometer[16] modified as previously described.[17] Standard operating conditions were: ionizing electron energy 70 eV, electron current (total emission) 1 mA, ion source temperature 150°, and ion acelerating voltage 8–10 kV. A narrow energy resolving β-slit was used for maximum energy resolution and the accelerating voltage scan method[18] was used to plot metastable peaks. The metastable peak width at half height was used to derive T in the usual way[19] after correction for the energy spread of the main beam. The correction for the energy spread in the main beam is made by subtracting the main beam width from the metastable peak width, both values being extrapolated to zero β-slit widths. Since the reaction of interest gives rise to a composite metastable peak, a Du Pont Model 310 curve resolver was used to separate the two components. Hence, while the width of the composite metastable peak was reproducible to $\pm 3\%$ on separate scans, the deconvolution procedure resulted in larger errors in T values than normally achieved in this laboratory. In order to reduce the error introduced on deconvolution, 4 to 10 scans were made of each peak and these were deconvoluted separately in order to reduce systematic errors. Errors are estimated as $\pm 15\%$ in T and $\pm 7\%$ in the relative abundances of the two processes.

Results

A series of meta- and para-substituted anisoles including both electron-donating and electron-withdrawing groups was chosen for study. In some cases metastable loss of formaldehyde was not observed because competitive processes were favored. In particular, strongly electron-donating groups stabilize the $(M - CH_3)^+$ ion (f) so effectively that metastable elimination of H_2CO could not be detected. The formation of the quininoid ion f is also the reason why *p*-nitroanisole loses NO· rather than H_2CO. The majority of the anisoles studied, however, showed a metastable peak for formaldehyde loss, and this was always composite, as illustrated in Figure 1 by the case of *p*-methylanisole. This indicates that two separate processes contribute to the formaldehyde elimination reaction.

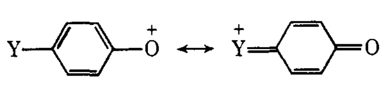


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Table I summarizes the experimental results for H_2CO loss from the para-substituted compounds. It includes two values of the kinetic energy release, corresponding to the narrow and the broad components of the metastable peak and denoted T_s and T_l, respectively. The relative abundances of these two components are also entered (in parentheses). Other columns give the ionization potential of the anisole $IP(A)_{420°K}$, the appearance potential of the $(M - H_2CO)\cdot^+$ fragment ion $AP((M - H_2CO)\cdot^+)_{420°K}$ and the ionization potential of the corresponding monosubstituted ben-

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(11) (a) C. S. Barnes and J. L. Occolowitz, *Aust. J. Chem.*, **16**, 219 (1963); (b) Z. Pelah, J. M. Wilson, M. Ohashi, M. Budzikiewicz, and C. Djerassi, *Tetrahedron*, **19**, 2233 (1963); (c) F. W. McLafferty and M. M. Bursey, *J. Org. Chem.*, **33**, 124 (1968)

(12) M. J. Lacey, C. G. Macdonald, and J. S. Shannon, *Org. Mass Spectrom.*, **5**, 1391 (1971).

(13) This reaction is written as occurring by a stepwise mechanism in order to account for the observed hydrogen scrambling.[12]

(14) F. P. Lossing, A. W. Tickner, and W. A. Boyce, *J. Chem. Phys.*, **19**, 1254 (1951).

(15) (a) P. Brown, *Org. Mass Spectrom.*, **3**, 1175 (1970); (b) H. F. Holtzclaw, R. L. Lintvedt, H. E. Baumgarten, R. G. Parker, M. M. Bursey, and P. F. Rogerson, *J. Amer. Chem. Soc.*, **91**, 3774 (1969); (c) K. Pihlaja and J. Jalonen, *Org. Mass Spectrom.*, **5**, 1363 (1971).

(16) J. H. Beynon, W. E. Baitinger, J. W. Amy, and T. Komatsu, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 47 (1969).

(17) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *ibid.*, **3**, 313 (1969); (b) J. H. Beynon, R. M. Caprioli, and T. Ast, *ibid.*, **7**, 88 (1971); (c) T. Ast, J. H. Beynon, and R. G. Cooks, *J. Amer. Chem. Soc.*, **94**, 6611 (1972).

(18) (a) M. Barber and R. M. Elliot, paper presented at the 12th Annual Conference on Mass Spectrometry and Allied Topics, Montreal, 1964, ASTM Committee E-14; (b) K. R. Jennings, *J. Chem. Phys.*, **43**, 4176 (1965).

(19) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, **3**, 661 (1970); (b) J. H. Beynon, R. M. Caprioli, and T. Ast, *ibid.*, **5**, 229 (1971).

Table I. Energetics for Para-Substituted Anisoles (H_2CO Loss)[a]

Y	T_l	T_s	IP(A)	AP((M − $H_2CO)\cdot^+$)	IP(B)	$\Delta H_f°(A)$[b]	$\Delta H_f°(B)$[b]	ϵ_{excess}	T/ϵ_{excess}
H	0.32 (60%)	0.02_3 (40%)	8.2_0	11.5_0	9.2_1	−0.69	+0.86	1.9_6	0.17
CH_3	0.36 (70%)	0.02_1 (30%)	7.8_5	11.2_3	8.6_7	−1.00	+0.52	2.2_6	0.16
Cl	0.35 (>95%)	*c* (<5%)	8.1_8	11.4_2	8.9_9	−1.05	+0.55	2.0_6	0.17
Br	0.28 (85%)	0.01_8 (15%)	8.39[e]	11.52[f]	8.98[e]	−0.53	+1.04	2.1_2	0.14
CN	0.36 (40%)	0.044 (60%)	8.7_4	12.3_9	9.7_7	+0.66	+2.31	2.1_8	0.17
NH_2	*d*	*d*	6.9_2	9.5_8	7.6_3	−0.50	+1.08		
OH	*d*	*d*	7.5_0	10.3_0	8.5_0	−2.65	−1.00		
OCH_3	*d*	*d*	7.4_5	11.0_0	8.2_0	−2.24	−0.69		

[a] All values are in electron volts. Ionization potentials, appearance potentials, and kinetic energy data refer to ~420°K. [b] Derived as explained in text. Refer to 298°K. [c] Abundance too low to allow determination. [d] Not observed. [e] Value from ref 22. [f] Value from ref 20.

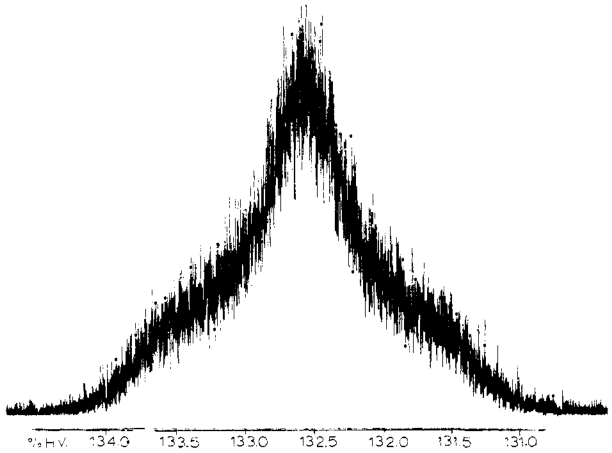

Figure 1. Metastable peak for H_2CO loss from the *p*-methylanisole molecular ion. HV represents the ion accelerating voltage required to transmit the main beam of stable ions.

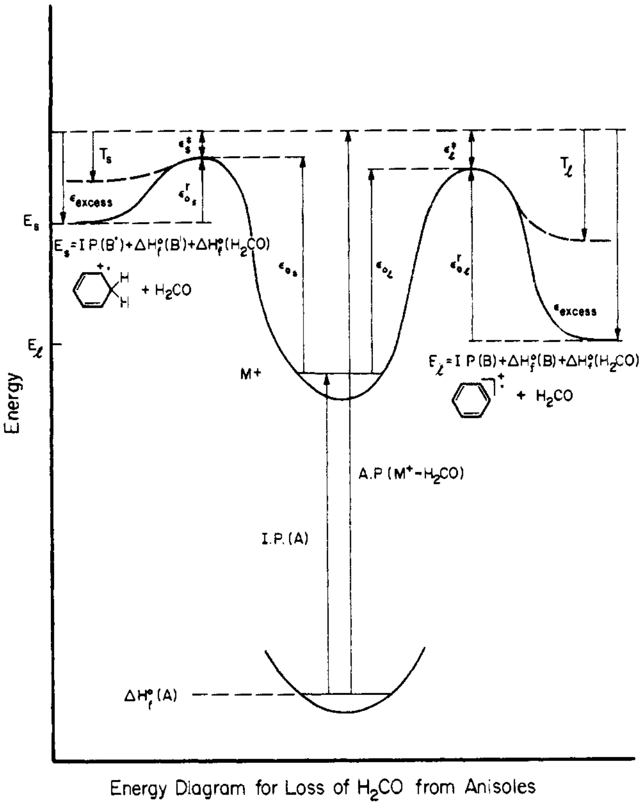

Figure 2. Loss of H_2CO from the anisole molecular ion *via* two competitive reaction channels. Subscripts s and l refer to the processes which are accompanied by release of smaller and larger amounts of kinetic energy (T), respectively. The symbol A refers to the substituted anisole, B to the corresponding substituted benzene, and B′ to the isomeric cyclohexadiene. ϵ_0 and ϵ_0^r are forward and reverse activation energies, $\epsilon^{\ddagger}$ is the nonfixed energy of the activated complex, and ϵ_{excess} is the sum of ϵ_0^r and $\epsilon^{\ddagger}$. E_s and E_l refer to the ground-state energies of the products of the two reactions. For simplicity all energy distributions are replaced by discrete values. T_l and T_s include contributions from $\epsilon^{\ddagger}$ and ϵ_0^r.

zene $IP(B)_{420°K}$. Standard heats of formation of the anisole and the substituted benzene at 298°K are also given in each case. Many of these latter values are taken from the literature;[20] the others interpolated from literature data. The final entries in Table I refer only to the process giving rise to the larger T value; the quantity ϵ_{excess} is defined by the relationship

$$\begin{aligned}\epsilon_{excess} &= \Delta H_f(A)_{0°K} + AP((M - H_2CO)\cdot^+)_{0°K} - \\ &\quad [\Delta H_f(B)_{0°K} + \Delta H_f(H_2CO)_{0°K} + IP(B)_{0°K}] \\ &= AP((M - H_2CO)\cdot^+)_{0°K} - IP(B)_{0°K} + \\ &\quad \Delta H_f(A)_{0°K} - \Delta H_f(B)_{0°K} - \Delta H_f(H_2CO)_{0°K} \quad (4)\end{aligned}$$

Figure 2 illustrates the energetics of H_2CO loss from the unsubstituted anisole molecular ion and shows the interrelationships between the various thermochemical quantities appearing in Table I and eq 4. The energy ϵ_{excess} is the sum of the reverse activation energy and the nonfixed energy ($\epsilon^{\ddagger}$) of the activated complex at threshold. Thus $\epsilon^{\ddagger}$ refers to an activated complex which fragments at the minimum rate permitted by the ion source residence time. Under the zero repeller conditions used for appearance potential determinations, the average source residence time of the MS 9 is several microseconds.[21] Ions also traverse the first field-free region of the RMH-2, operated at 2–4 V repeller settings, several microseconds after formation.[21] Hence, to a good approximation, the ions for which ϵ_{excess} is calculated from eq 4 have the same lifetimes and, hence, internal energies as those whose kinetic energies (T) are measured. It must be emphasized that any differences between $\epsilon^{\ddagger}$ (metastable ions) and $\epsilon^{\ddagger}$ (threshold, ion source) will have a negligible effect on ϵ_{excess} in reactions such as those studied here where ϵ_0^r makes the overwhelming contribution to ϵ_{excess} (see Discussion).

In order to evaluate ϵ_{excess}, enthalpies at 298°K rather

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(20) J. L. Franklin, J. F. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS 26, National Bureau of Standards, Washington, D. C., 1969.

(21) For data on the MS9 source residence time, see J. H. Beynon, J. A. Hopkinson, and G. R. Lester, *Int. J. Mass Spectrom. Ion Phys.*, 1, 343 (1968); for data on the RMH-2, see ref 16.

Table II. Energetics for Meta-Substituted Anisoles (H_2CO Loss)[a]

Y	T_1	T_s	IP(A)[b]	AP(($M - H_2CO)\cdot^+$)[b]	IP(B)	ϵ_{excess}	T/ϵ_{excess}
CH_3	0.27 (55%)	0.02_0 (45%)	8.35	11.22	8.6_7	2.2_6	0.12
Cl	0.19 (30%)	0.03_1 (70%)	8.72	11.68	8.9_9	2.2_9	0.08
Br	0.23 (40%)	0.01_9 (60%)	8.69	11.59	9.98[c]	2.2_4	0.10
CN	0.19 (40%)	0.03_7 (60%)	9.11	12.23	9.7_7	2.0_2	0.10
OH	0.13 (25%)	0.02_6 (75%)			8.5_0		

[a] All values are in electron volts. All data taken at ~420°K. [b] Values from ref 22. [c] Value from ref 20.

than 0°K have been used while ionization and appearance potentials at 420°K have been employed. The enthalpy difference $\Delta H_f°(A) - \Delta H_f°(B) - \Delta H_f°(H_2CO)$ appears in eq 4 as does the difference AP(($M - H_2CO)\cdot^+$) − IP(B). The latter term causes the major source of error in using the higher temperatures since the difference in the thermal energies of the anisole and the benzene could be 0.1 to 0.2 eV. AP(($M - H_2CO)\cdot^+$) would therefore be too small and this means that ϵ_{excess} calculated using the high temperature is too small by this amount. It must be emphasized that this error must be similar for each compound in the series and that it represents <10% of ϵ_{excess} for reaction 2.

The use of eq 4 to calculate ϵ_{excess} requires that one further criterion be fulfilled. This is that the (($M - H_2CO)\cdot^+$) ions have the same structures as those resulting from the direct ionization of the substituted benzenes (B). Since there is independent evidence[3e,11] that anisoles do fragment to give the substituted benzene molecular ions, this can be assumed and the energy partitioning data used to test the validity of the assumption. The larger kinetic energy release (T_1) must be associated with formation of the substituted benzene since all alternative ionic products probably would be less stable and, therefore, can be associated with the much smaller release T_s. Equation 4 assumes that ionization of the substituted benzenes gives unexcited ground-state molecular ions. The agreement achieved between our IP(B) values and literature photoionization data (see below) indicates that this condition is fulfilled.

Literature ionization and appearance potential values are available for comparison with some of the data in Table I. All the values of IP(B), except that for toluene which is 0.15 eV low, are within 0.08 eV of the best photoionization values given in a standard compilation.[20] The AP(($M - H_2CO)\cdot^+$) values fall within 0.2 eV of those reported by Brown using a method of determination similar to that used here.[22] The anisole ionization potentials, which are included in Table I but not actually used in the energy partitioning calculations, are in poorer agreement with Brown's data being some 0.2 to 0.7 eV lower.

Table II summarizes the available data on the meta-substituted anisoles. In this case the AP(($M - H_2CO)\cdot^+$) values are those of Brown.[22] The $\Delta H_f°(A)$ values are taken as identical with those of the para-substituted anisoles and are therefore not listed. The $\Delta H_f°(B)$ values given in Table I of course apply to both series of anisoles. Once again ϵ_{excess} and the energy partitioning quotient T/ϵ_{excess} refer only to the reaction associated with the larger release T_1. The marked effect of substituents upon the relative contributions of the two H_2CO elimination processes is illustrated in Figures 3–6 which juxtaposes the metastable peak shapes observed in the *m*- and *p*-chloro and *m*- and *p*-cyano cases. Comparisons of the shapes of these metastable peaks provides substantial evidence against loss of substituent identity in these reactions.

In order to interpret the mechanism of composite metastable peak formation several experiments were done using *p*-methylanisole, chosen because the two processes are of comparable abundance. First, the pressure in the first field-free region of the mass spectrometer was raised from 1×10^{-6} to 2×10^{-5} Torr by admitting air. The signal was unchanged in shape, neither contributing process being pressure enhanced. Second, the effect of source temperature upon the composite metastable peak was studied by taking measurements over the range 110–260°. No detectable change in peak shape and, hence, in T values occurred. Third, the effect of lowering the ionizing electron energy was investigated. At a nominal 19 eV the metastable ion signal was $\sim 10^{-2}$ of its value at 70 eV, but both components were still present and no change in their relative abundance could be detected. Finally, and most significantly, the anisole molecular ion was generated by fragmentation of the corresponding *O*-methyl oxime ether; it behaved identically to the ion generated by direct ionization.[23] Analogous results were obtained for the anisole molecular ion generated by direct ionization and by fragmentation of dimethoxybenzene.

The energy release accompanying the loss of $CH_3\cdot$ from the molecular ions of the para-substituted anisoles was also measured (Table III). This reaction, which is apparently competitive with H_2CO elimination,[22] gave a composite metastable peak only for the *p*-methyl compound.

Discussion

Composite metastable peaks, other than those due to accidental overlap of peaks, may arise when two forms (either structural isomers or isolated electronic states) of either the reactant ion, the product ion, or the neutral product are involved in a particular reaction. The reaction $H_2\cdot^+ \rightarrow H^+ + H\cdot$, for example, gives a composite metastable peak since two electronic states of $H_2\cdot^+$ undergo the process (which is always collision-induced), but do so with release of different kinetic energies and so give metastable peaks of different

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(22) P. Brown, *Org. Mass Spectrom.*, 4, 519 (1970).

(23) This result was found to be generally true of the ($M - HCN)\cdot^+$ ion in substituted oxime ethers and the corresponding anisole molecular ions once it was recognized that the para-substituted oxime ethers give ($M - HCN)\cdot^+$ ions which, in their metastable fragmentation by H_2CO loss, behave identically with the metastable ions generated by direct ionization of the meta substituted anisoles. Hence, oxime ether ions with sufficient energy to fragment in the ion source lose HCN by a five-membered rearrangement mechanism.[6b] Metastable oxime ether molecular ions fragment by either a four- or a five-membered rearrangement depending upon the substituent.[6b]

Table III. Kinetic Energy Release for $CH_3\cdot$ Loss from Substituted Anisoles

	Substituent						
	H	p-NH_2	p-OH	p-CN	p-Cl	p-CH_3[a]	o-CH_3[a]
T, eV	0.044	0.144	0.078	0.060	0.077	0.046 and 0.39	0.048 and 0.45
ϵ_{excess}[b]	0.58	0.87	1.26	0.43	0.81	0.56	

[a] These two compounds gave composite metastable peaks and the values given refer to the components obtained by deconvolution. [b] Approximate values (see Discussion).

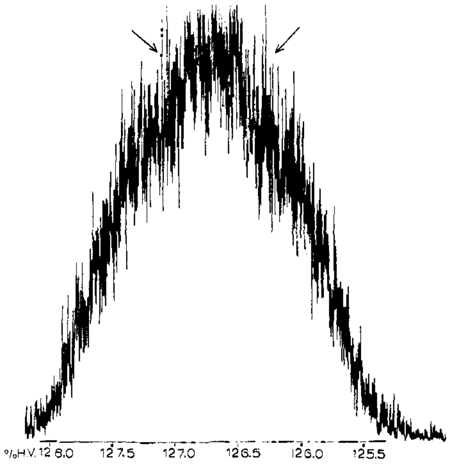

Figure 3. Metastable peak for H_2CO loss from p-chloroanisole.

Figure 5. Metastable peak for H_2CO loss from m-chloroanisole.

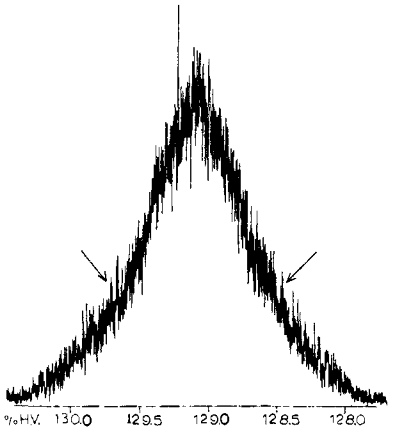

Figure 4. Metastable peak for H_2CO loss from p-cyanoanisole.

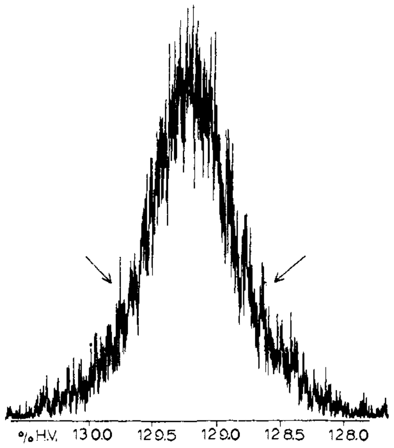

Figure 6. Metastable peak for H_2CO loss from m-cyanoanisole.

widths.[24] Composite metastable peaks also result when the same reaction occurs both unimolecularly and by a collision-induced process. The composite metastable peak for $CH_3OCH_3^+ \rightarrow CH_2{=}O^+CH_3 + H\cdot$ is an example of this type.[25] A composite metastable peak can also be associated with two competing unimolecular fragmentations from the same parent ion as exemplified by the loss of H· from the triphenylphosphine oxide molecular ion.[26] In this case H· loss occurs from two distinct sites in the same ion by two different reaction channels.

The pressure dependence experiments show that, in the case of the anisoles, neither of the two formaldehyde elimination reactions contributing to the composite peak are collision induced. It must, therefore, be established whether two forms of the reactant, of the ionic product, or of the neutral product are responsible for the composite peak in this case.

The first excited state of formaldehyde, the neutral product in the reaction under consideration, has an energy of 76 kcal mol^{-1} (3.3 eV)[27] which is too high to allow the possibility that formation of the ground and first excited states of the neutral are responsible for the composite peak. For the reasons which follow, formation of either the neutral or the ionic product in different vibrational states is not believed to be responsible for the observed composite metastable peaks. First, the fact that the difference $T_1 - T_s$ is not constant for the different substituted anisoles means that two

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(24) J. H. Beynon, R. G. Cooks, and R. M. Caprioli, *Proc. Roy. Soc., Ser. A*, 327, 1 (1972).

(25) J. H. Beynon, M. Bertrand, E. G. Jones, and R. G. Cooks, *Chem. Commun.*, 341 (1972).

(26) M. Bertrand, J. H. Beynon, and R. G. Cooks, *Org. Mass Spectrom.*, in press.

(27) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Shore, *Accounts Chem. Res.*, 5, 92 (1972).

vibrational states of formaldehyde cannot be involved. The formation of the ionic product in two vibrational states is also ruled out on this basis since otherwise the vibrational spacing ($T_l - T_s$) in the ionic product would have to vary from, for example, 0.32 eV for *p*-cyanoanisole to 0.15 eV for *m*-cyanoanisole. Several other qualitative arguments against the idea of two vibrational levels of the ionic product can also be noted. First, the thermochemistry of H_2CO elimination indicates that the products are formed with considerable internal energy. Under these circumstances the fact that only two vibronic states are populated seems unlikely, especially in view of literature data in other ionic fragmentations leading to products in more than one vibrational state.[28] Second, the vibrational spacings in the ionic product are not known but are not expected to be as large as 0.3 eV especially since the spacing does not involve the lower energy levels of the ground electronic state.

The foregoing considerations suggest that the composite nature of the $M\cdot^+ \rightarrow (M - H_2CO)\cdot^+$ transition must be due to either one of two situations: (i) the generation of the ionic product in two different electronic states, from a single reactant ion; or (ii) reaction of two isolated electronic states of the reactant ion. Logically, there exists a third possibility, a single reactant ion and the same products but two completely different reaction channels. This is not considered to be likely. In distinguishing between i and ii, it must be emphasized that i does not exclude the possibility that one or both of the reaction channels will involve intermediates, but it does require that they be in equilibrium with the reactant.

The fact that the relative contributions of the two peaks do not change detectably with electron energy indicates that if two different electronic states of the reactant ion are involved, their energies are similar. In addition, the ionization efficiency curves for the $(M - H_2CO)\cdot^+$ ion showed no breaks or other evidence for two processes with measurably different activation energies. Both these lines of argument involve inferences based on a failure to observe given experimental features. A stronger argument comes from the results of the experiments using different sources of the reactant ion (ionization *vs.* fragmentation). If reaction were occurring from two isolated electronic states, then it could only be fortuitous that two independent methods of generating the reactant ion would yield both states in the same relative proportions. It is therefore unlikely that H_2CO loss occurs from two reactants in isolated electronic states. The results on the competitive reaction, methyl loss, also make the suggestion that there exist isomeric forms of the reactant which are not in equilibrium with each other unattractive. Finally, if isolated electronic states were involved, composite metastable peaks would be likely for $CH_3\cdot$ loss in at least some of the para-substituted anisoles. (As discussed herein, the one methyl elimination for which a composite peak was observed was for *p*-methylanisole; this is a special case in which the composite peak has an entirely different origin.)

Hence, anisoles apparently undergo metastable H_2CO elimination by two reaction channels from the same reactant with formation of different isomers of the product ion. If it is assumed that these are the four-membered and five-membered hydrogen transfer reactions 2 and 3, for which independent evidence is available,[11,12] then the validity of this postulate can be tested using the thermochemical and substituent effect data accrued in this study. It should be noted that the measured appearance potential for the $(M - H_2CO)\cdot^+$ ion can be used in deriving energy partitioning data in spite of the fact that two reactions are involved. This is justified in the light of the evidence already presented which shows that the two reactions have similar activation energies.

The above mechanistic considerations allow the computation of ϵ_{excess} for reaction 2 and hence the energy partitioning quotient T/ϵ_{excess}. It is striking that this quotient (Table I) is independent of substituent. Such a finding would be unlikely if any of the above assumptions were grossly in error[29] and this result, therefore, supports the association of T_l with the four-centered hydrogen transfer reaction 2. The meta-substituted anisoles also show T/ϵ_{excess} approximately independent of substituent although the value of the quotient is lower than that for the para-substituted compounds. These results are in marked contrast to those found for the oxime ethers[6] which are also believed to undergo a four- or five-centered rearrangement at threshold,[30] but for which the energy partitioning quotient T/ϵ_{excess} varies from 0.20 for the *p*-cyano substituent to 0.73 for the *p*-methoxy group.

Since the heat of formation of ion e is not known, the thermochemistry of reaction 3 cannot be determined. It is still possible, however, to get some idea of whether this reaction is a reasonable possibility for the process leading to the narrow component of the $(M - H_2CO)\cdot^+$ metastable peak. The difference $T_l - T_s$ is approximately 300 meV in the para series. This difference represents some fraction of the difference in product enthalpies and if approximately the same fraction (16%) of ϵ_{excess} is partitioned to kinetic energy in the reaction leading to ion e (as in the case for reaction leading to ion b) then the difference in product enthalpies is of the order of 1.8 eV.[31] A similar argument for the meta compounds where the average $T_l - T_s$ values is 180 meV, also yields an enthalpy difference of 1.8 eV. This seems entirely reasonable in view of the formulation of e as an ionized carbene.

The experimentally determined energy partitioning quotient, T/ϵ_{excess} will only give information on the potential energy surface and hence, the reaction mechanism, if it approximates the quantity of real interest T^e/ϵ_0^r where T^e is that portion of the experimentally determined kinetic energy release which is due to the reverse activation energy, ϵ_0^r. The relationship $T/\epsilon_{excess} \approx T^e/\epsilon_0^r$ requires that $T \approx T^e$ and $\epsilon_{excess} \approx \epsilon_0^r$, or, equivalently, that $T^e \gg T^{\ddagger}$ and $\epsilon_0^r \gg \epsilon^{\ddagger}$. If this last

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(28) (a) R. G. Cooks and J. H. Beynon, *Chem. Commun.*, 1282 (1971); (b) T. R. Govers and J. Schopman, *Chem. Phys. Lett.*, **12**, 414 (1971).

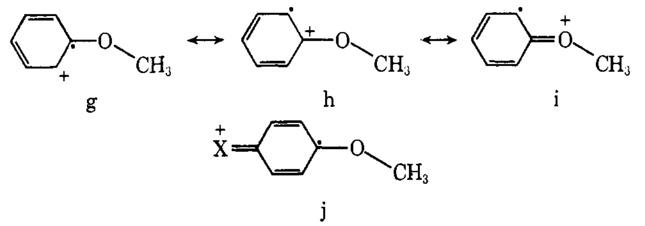
(29) If T/ϵ_{excess} had varied the assumptions would not necessarily have been erroneous.

(30) Compare ref 23. This question is taken up in ref 6b.

(31) The assumption that 16% of the energy is partitioned to kinetic energy represents a gross approximation. However, the same result can be obtained by a slightly different argument. The magnitude of T_s suggests that ϵ_0^r must be rather small, but the activation energy for this process is similar to that of the four-membered cyclic transfer (*vide supra*). Hence, the product enthalpy difference must approximately equal ϵ_{excess} for the four-member cyclic transfer; *viz.*, the enthalpy difference must be approximately 2 eV.

inequality is satisfied, then $T^e \gg T^{\ddagger}$ will also be satisfied.[32] Hence, provided $\epsilon_0^r \gg \epsilon^{\ddagger}$, then $T/\epsilon_{excess} \approx T^e/\epsilon_0^r$. Recent evidence[9] shows that for simple bond cleavages in molecular ions of about 10 atoms $\epsilon^{\ddagger}$ is of the order of 0.1 eV or less. In larger molecules and for rearrangement reactions, values of a few tenths of an electron volt are therefore probable.[33] Hence, in cases such as the $M\cdot^+ \rightarrow (M - H_2CO)\cdot^+$ reaction where ϵ_{excess} is several volts the approximation of $\epsilon_0^r \approx \epsilon_{excess}$ is justified.

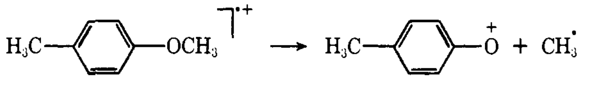
The thermochemical data are, therefore, consistent with the suggestion that reactions 2 and 3 are indeed involved in formaldehyde loss from substituted anisoles. The present experimental results also provide another means of testing this hypothesis. The relative proportions of the processes leading to T_l and T_s follow this generalization: in the para series electron-donating substituents increase the relative contribution of the process associated with the larger T, electron-withdrawing substituents decrease it. In the meta series there are smaller substituent effects upon the relative proportions of the processes. Substituents also show very little effect upon the magnitude of either the larger or the smaller T values. These facts are all accommodated if the process leading to the larger T value involves the four-center hydrogen transfer mechanism and that leading to the small T value involves the five-center hydrogen transfer mechanism and both hydrogen transfers occur to radical sites.[34] The unsubstituted anisole molecular ion includes the resonance forms g, h, and i which, among others, account for the occurrence of both the four- and five-membered hydrogen transfer processes. Introduction of an electron-donating para substituent adds the new relatively stable form j and should, therefore, promote the four-membered cyclic hydrogen transfer to the radical site. The contribution of the process leading to the larger T values should, therefore, increase and this was observed to be the case. An electron-withdrawing para-substituent, on the other hand, decreases the electron density and, hence, the radical density in the ring, but does so more effectively at the para than at the meta position. Hence, the reaction involving hydrogen transfer from the methoxyl group to the adjacent position through a five-membered cyclic transition state should occur relatively more readily, as observed. Electron-withdrawing meta substituents will tend to cancel the effect of the methoxyl group and give small effects, relative to anisole itself. Electron-donating meta groups will reinforce the buildup of electron (radical) density ortho to the methoxy group and will promote reaction by the five-membered cyclic transition state. It is found (Table II) that the meta substituted compounds give smaller proportions of the process leading to the larger energy release than the corresponding para-substituted compounds and this, together with the variation in peak shape with change in meta substituent, is in agreement with the predication based on the radical site mechanism.



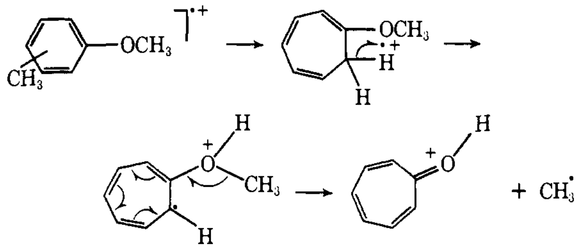
g h i

j

Finally, some discussion of the methyl elimination reactions is warranted. Of principal interest is the fact that only one of the para-substituted compounds, *p*-methylanisole, gave a composite metastable peak. The smaller T value is comparable to that observed for methyl loss from the other compounds (Table III), indicating that the simple cleavage mechanism, eq 5, is probably responsible. (Evidence that methyl loss normally involves simple cleavage has been reported.[11,22]) The larger energy release involves a process unique to the methyl-substituted compound. Moreover, within experimental error, the energy release accompanying this process is identical with that observed for *o*-methylanisole (Table III). This suggests that ring expansion precedes the process accompanied by the larger energy release. The formation of the very stable protonated tropone would account for these observations and for the magnitude of the energy release. The mechanism can be depicted as eq 6.



(5)



(6)

Thermochemical data for anisole are available to allow the calculation of ϵ_{excess} for the $M\cdot^+ \rightarrow (M - CH_3)^+$ reaction: $\Delta H_f(C_6H_5O\cdot) = 0.43$;[35] $\Delta H_f(CH_3\cdot) = 1.44$ eV;[20] $\Delta H_f(C_6H_5OCH_3) = -0.69$ eV;[20] $IP(C_6H_5O\cdot) = 8.84$ eV;[20] $AP(C_6H_5O^+) = 11.83$ eV (ref 22 gives 11.80 and 11.86 eV). Hence, using eq 4 and making the same assumptions as made for loss of H_2CO, $\epsilon_{excess} = 0.40$. With ϵ_{excess} so small, it is therefore not possible to estimate T/ϵ_0^r using T/ϵ_{excess}. The small (0.044 eV) energy release is, however, consistent with the small ϵ_{excess} value. The corresponding literature data are not available for the substituted anisoles, but in the accompanying paper[37] we report estimates of the heats of formation of aryloxy cations formed by

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(32) If this were not so the fraction of ϵ_0^r appearing as kinetic energy would have have to be much smaller than the fraction of $\epsilon^{\ddagger}$ so appearing. All available data indicate that a relatively large fraction of ϵ_0^r is partitioned into translational energy.[5,6]

(33) Compare also F. W. McLafferty, T. Wachs, C. Lifshitz, G. Innorta, and P. Irving, *J. Amer. Chem. Soc.*, **92**, 6867 (1970).

(34) The importance of radical sites in initiating hydrogen transfers in mass spectrometry is becoming more and more evident; see (a) F. W. McLafferty, "Topics in Organic Mass Spectrometry," A. L. Burlingame, Ed, Wiley-Interscience, New York, N. Y., 1970, p 223; (b) D. J. McAdoo, F. W. McLafferty, and J. S. Smith, *J. Amer. Chem. Soc.*, **92**, 6343 (1970); (c) G. Eadon, C. Djerassi, J. H. Beynon, and R. M. Caprioli, *Org. Mass Spectrom.*, **5**, 917 (1971).

(35) P. Natalis and J. L. Franklin, *J. Phys. Chem.*, **69**, 2943 (1965), estimate +9 kcal mol^{-1}; L. R. Mahoney and M. A. Da Rooge, *J. Amer. Chem. Soc.*, **92**, 890 (1970), estimate 33-35 kcal mol^{-1} greater than $\Delta H_f°$ (phenol). Taking $\Delta H_f°$ (phenol) as -23 kcal mol^{-1},[36] this gives a value of 9-11 kcal mol^{-1}.

(36) R. J. L. Andon, D. P. Biddiscombe, J. D. Cox, R. Handley, D. Harrox, E. F. G. Harrington, and J. F. Martin, *J. Chem. Soc.*, 5246 (1960).

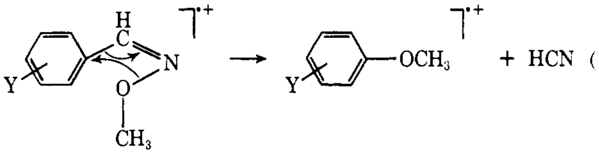
(37) J. H. Beynon, M. Bertrand, and R. G. Cooks, *J. Amer. Chem. Soc.*, **95**, 1739 (1973).

NO loss from nitrobenzenes. Using these data and Brown's appearance potential values[22] ϵ_{excess} has been calculated for each of these compounds (Table III). While no definite trends with substituent can be discerned, ϵ_{excess} is generally small (average value 0.7 eV) as are the corresponding energy releases.

Conclusion

Metastable peak shapes show that anisoles eliminate formaldehyde by two unimolecular mechanisms. Interpretation of the energy partitioning data provides evidence that one of these processes involves four-centered hydrogen rearrangement to give the substituted benzene molecular ion, b, while the results are consistent with the other reaction proceeding *via* a five-centered hydrogen transfer to give the higher energy product ion, e. The two processes apparently occur competitively from the same form of the molecular ion and both hydrogen transfers occur to radical sites. The fact that the two reactions are competitive in the metastable region does not, however, permit one to establish whether the five-membered hydrogen transfer occurs in a concerted or in a stepwise manner.

A notable feature of the present results is that the reverse activation energy for reaction 2 is almost independent of substituent (2.1 ± 0.2 eV). This contrasts with the situation found for HCN loss from oxime ethers (reaction 7)[6,23] and this suggests that while the present reaction is essentially a radical process the oxime ether reaction is essentially nucleophilic (at least for some substituents, see ref 6b). The contrasts between the two reaction types extend to the energy partitioning quotient, $T/\epsilon_{\text{excess}}$, which is independent of substituent in the anisoles but strongly substituent dependent in the oxime ethers. While energy partitioning can be expected to be a complex phenomenon, dependent on each individual potential energy surface, these results suggest that a general relationship may exist between the variation of $T/\epsilon_{\text{excess}}$ with substituent and the ionic or radical nature of the reaction or, at least, that the substituent should have only a minor effect on the energy partitioning quotient in radical reactions of the type under consideration. Other factors which appear to control energy partitioning in large ions are considered in the accompanying paper. If further experiments allow the determination of ϵ_{excess} from the measured energy release, then T measurements will acquire considerable value in thermochemical as well as mechanistic studies. The possible presence of a reverse activation energy constitutes a serious limitation on the determination of some thermochemical quantities by mass spectrometric methods.[38] By allowing the rapid estimation of ϵ_0^r, T determinations could overcome this difficulty.



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Acknowledgment. We thank the National Science Foundation (GP 16743) for support. One of us (M. B.) wishes to thank the N.R.C.C. for a postdoctoral fellowship.

[38] (a) A. G. Harrison in "Topics in Organic Mass Spectrometry," ref 34a, pp 121–126, and especially p 133; (b) M. Haney and J. L. Franklin, *Recent Develop. Mass Spectrosc., Proc. Int. Conf. Mass Spectrosc.*, 909 (1970).

The Metastable Loss of NO· from Aromatic Nitro Compounds

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Abstract: The loss of NO· from the molecular ions of aromatic nitro compounds has been studied by an analysis of metastable peak shapes to determine the manner in which internal energy is partitioned to the kinetic and internal energies of the products in these reactions. Two competitive unimolecular processes can be discerned: one involves a three-centered cyclic transition state with the formation of the aryloxy cation; the other seems to involve oxygen rearrangement to the ortho position. Aryloxy cation formation gives the greater kinetic energy release. Evidence for the three-membered cyclic rearrangement comes from the substituent dependence of the kinetic energy release and the substituent dependence of the relative abundances of the product ions derived from the two processes. Energy partitioning data on the elimination reaction leading to the aryloxy cation product are consistent with the assigned mechanism. These data also show that the fraction of the reverse activation energy which appears as kinetic energy is large, and a qualitative explanation in terms of the "tightness" of the activated complex is advanced. The potential of studies of this type in providing thermochemical information is noted, and the present data are used to estimate the heats of formation of a series of para-substituted aryloxy cations and the ionization potentials of the corresponding aryloxyl radicals.

Studies on energy partitioning in unimolecular ionic reactions constitute a new source of information on potential energy surfaces and, hence on the structures of gaseous ions and their unimolecular reaction mechanisms. This approach has been applied with some success in the study of several mass spectral reactions,[1] most notably formaldehyde elimination from anisole

[1] (a) R. G. Cooks, D. W. Setser, K. R. Jennings, and S. Jones, *Int. J. Mass Spectrom. Ion Phys.*, 7, 493 (1971); (b) R. G. Cooks, M. Bertrand, J. H. Beynon, M. E. Rennekamp, and D. W. Setser, *J. Amer. Chem. Soc.*, 95, 1732 (1973); (c) M. Bertrand, J. H. Beynon, and R. G. Cooks, in preparation; (d) J. H. Beynon, M, Bertrand, and R. G. Cooks, *Org. Mass. Spectrom.*, in press.