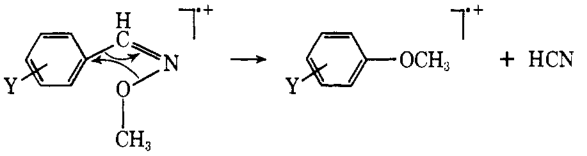
NO loss from nitrobenzenes. Using these data and Brown's appearance potential values[22] ϵ_{excess} has been calculated for each of these compounds (Table III). While no definite trends with substituent can be discerned, ϵ_{excess} is generally small (average value 0.7 eV) as are the corresponding energy 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 $\epsilon_0{}^r$, T determinations could overcome this difficulty.



(7)

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

J. H. Beynon, M. Bertrand, and R. G. Cooks*

Contribution from the Department of Chemistry,
Purdue University, Lafayette, Indiana 47907. *Received June 19, 1972*

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.

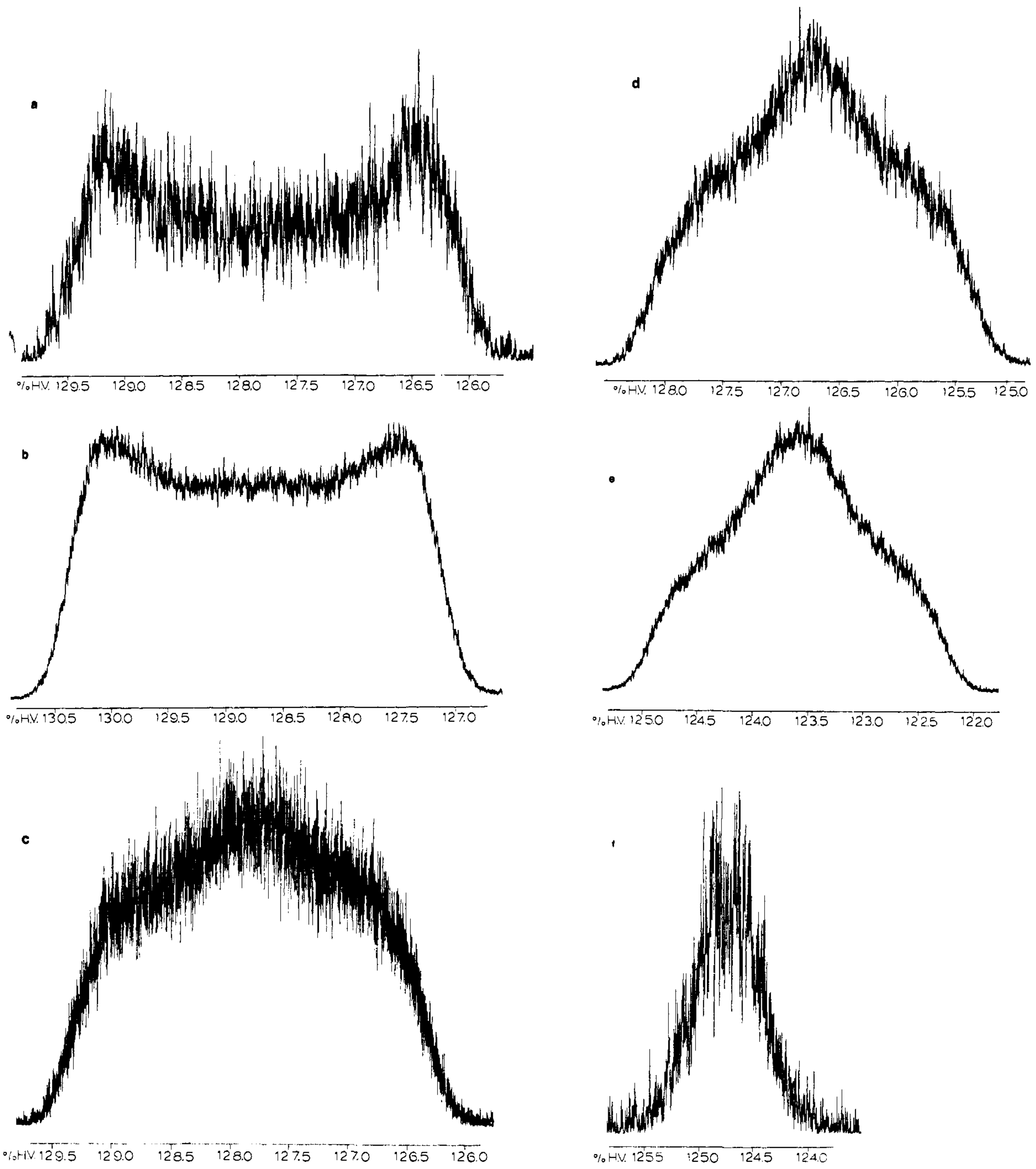


Figure 1. Composite metastable peak for loss of NO· from para-substituted nitrobenzenes: (a) p-NH_2; (b) p-OH; (c) p-CH_3; (d) p-F; (e) p-Cl; (f) p-HCO. The sequence a to f shows clearly that the central component of the peak is favored going to electron-withdrawing groups.

and its ring-substituted derivatives.[1b] The method utilizes the energy partitioning parameter $T/\epsilon_{\text{excess}}$, where T is the kinetic energy released in the metastable reaction in question and ϵ_{excess} is the sum of the reverse activation energy (ϵ_0^{r}) and the nonfixed (internal) energy ($\epsilon^{\ddagger}$) of the activated complex. In the anisole case, H_2CO loss occurs by two competitive mechanisms, each of which is associated with a particular T value.[2] From the energy partitioning data, the variations in kinetic energy release with substituent and the variation, with substituent, of the relative proportions of the two processes, it was concluded that H· transfer from the methoxyl group to the ring occurs competitively through four- and five-membered cyclic transition states.[1b]

The loss of NO· is a characteristic reaction of aromatic nitro compounds in the mass spectrometer and it has been the subject of many studies.[3] The reaction is particularly interesting because it is accompanied by uniquely large kinetic energy releases in some compounds. This has been ascribed[3b] to the formation of the stable (M − NO)$^+$ ion d, which in the para series includes the quinonoid ion e as a resonance contributor.

---

(2) Throughout this paper the T value calculated at half the peak height is quoted. A distribution of T values of which this is merely the most probable value is actually involved.

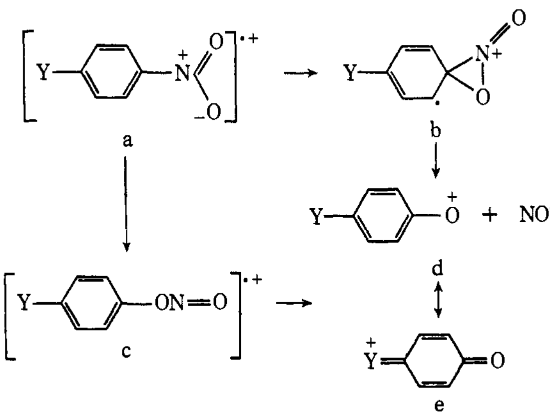
(3) (a) J. H. Beynon, R. A. Saunders, and A. E. Wiliams, *Ind. Chim. Belge*, **29**, 311 (1964); (b) M. M. Bursey and F. W. McLafferty, *J. Amer. Chem. Soc.*, **88**, 5023 (1966); (c) S. Meyerson, I. Puskas, and E. K. Fields, *ibid.*, **88**, 4974 (1966); (d) H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Ions," Holden-Day, San Francisco, Calif., 1967, p 575.

Table I. Kinetic Energy Release for NO· Loss from Para-Substituted Nitrobenzenes[a]

	Y = NH_2	OCH_3[b]	OH	CH_3	H	Cl	F	CN	HCO
T_l[c]	1.24 (>95%)	1.22 (>95%)	1.23 (>95%)	0.96 (90%)	0.55 (50%)	0.83 (60%)	0.84 (70%)	0.35 (40%)	
T_s	*d*	*d*	*d*	0.13[c,e](10%)	0.09 (50%)[f]	0.11 (40%)[f]	0.09 (30%)[f]	0.07 (60%)[f]	0.07 (~100%)

[a] All data are given in electron volts. [b] This compound can also lose CH_2O which also has mass 30; however, the magnitude of *T* as well as the shape of the metastable peak suggest that NO· loss is by far the most important process. Furthermore, Brown has estimated the $(M - NO)^+$ process to be >97% (see ref 12). [b] The estimated error in T_l is ±5%; that in T_s is ±10%. [d] Present, but *T* could not be estimated. [e] The estimated error in relative abundances is ±30%. [f] The estimated error in relative abundances is ±10%.

The accepted view is that nitro–nitrite isomerization a → c precedes or accompanies fragmentation.[3a]



Experimental Section

All measurements of kinetic energy release were performed on the Hitachi RMH-2 mass spectrometer[4] modified as previously described.[5] Standard operating conditions were ionizing electron energy 70 eV, electron current (total emission) 1 mA, ion source temperature 130°, and ion accelerating voltage 8–10 kV. A narrow energy resolving β-slit was used for maximum energy resolution and the accelerating voltage scan method[6] was used to plot metastable peaks. The metastable peak width at half-height was used to derive *T* in the usual way,[7] after deconvolution and correction for the energy spread in the main beam.[1b]

Results and Discussion

We have examined the peak shapes associated with metastable loss of NO· from a series of para-substituted nitrobenzenes. As is the case for CH_2O loss from anisoles,[1b] these peaks are composite for most substituents (see Figure 1) indicating that NO· loss occurs by two discrete processes. The relatively high-energy resolution of our instrument ($E/\Delta E > 8000$) explains why previous investigators were unable to detect the composite nature of these metastable peaks.[8] This new observation requires that the entire mechanistic question be reexamined.

Both NO· loss reactions were shown to be due to unimolecular fragmentation of the nitrobenzene molecular ion by taking measurements over a range of pressures (2×10^{-7} to 5×10^{-5} Torr) in the first field-free (drift) region of the mass spectrometer. In no case was a change in peak shape detectable and neither component peak was enhanced in intensity on addition of collision gas. At the high pressure extreme some decrease in total signal was observed and this is associated with scattering of the main ion beam.

Table I gives the kinetic energy release (*T* value) associated with each of the NO· loss processes, the composite signal having been resolved into two components as described in the Experimental Section. The larger kinetic energy release is designated T_l and the smaller T_s. The relative contributions of the processes leading to T_l and T_s are also given in Table I. These relative abundances show a pronounced substituent effect, electron-withdrawing groups favoring the reaction leading to T_s. Only *p*-dinitrobenzene (omitted from Table I) is anomalous;[9] it gives for the reaction in which $M\cdot^+$ loses NO· a very weak, apparently noncomposite peak, $T \approx 0.6$ eV. This peak may well be due to a collision-induced process, since the abundance of the metastable peak was more than two orders of magnitude lower than that for any other substituent and consequently high source pressures were necessary to observe the transition. This led to considerable sample leakage into the first field-free region and, hence the usual check on the unimolecularity of the reaction by varying the field-free region pressure could not be performed.

The results of Table I suggest that T_s is independent of substituent although experimental error may mask a tendency for T_s to increase as the para substituent becomes more electron donating. On the other hand, T_l shows a definite substituent dependence, being largest for substituents which are most effective as resonance electron donors. There is not, however, a simple linear relationship between T_l and σ^+ (or any of the common σ constants), nor would one be expected since the substituent presumably affects the enthalpy of both activated complex and products and, possibly, the manner of energy partitioning (*vide infra*). The absence of a simple Hammett correlation is seen clearly in the results for the powerful amino, hydroxyl, and methoxyl electron donors, which give T_l values that are identical within experimental error. This result is in disagreement with an earlier claimed Hammett correlation.[3b] The strong electron donors are particularly suitable for investigating substituent effects because errors arising from the deconvolution procedure are minimal, T_l being >95% of the total metastable signal in each of these cases. For two of the transitions the metastable peak due to fragmentation in the second field-free region was unobscured by normal mass ions and sufficiently abundant to allow the accurate determination of *T*. The values found were 1.21 eV for *p*-

---

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

(5) (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).

(6) (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).

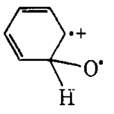
(7) (a) J. H. Beynon, R. M. Caprioli, W. E. Baitinger, and J. W. Amy, *Org. Mass Spectrom.*, 3, 661 (1970); (b) J. H. Beynon, R. M. Caprioli, and T. Ast, *ibid.*, 5, 229 (1971).

(8) This also accounts for the fact that the kinetic energy release measurements found in this study are higher than those reported earlier.[3b]

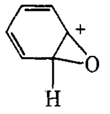
(9) Dinitroaromatics in general tend to lose $NO_2\cdot$ rather than NO· from the molecular ion.[3a]

methoxyanisole and 1.00 eV for *p*-methylanisole. Both values are within a few hundredths of an eV of the T_l value observed in the first field-free region (Table I).

The foregoing results suggest that NO· loss from para-substituted nitrobenzenes occurs by two competitive mechanisms which have similar activation energies yet lead to products of very different stabilities. The fact that no detectable change in the relative abundance ratios occurred as the ionizing electron energy was lowered to a nominal 13 eV is in line with the suggestion that both processes have similar activation energies. The difference in product enthalpies is thought to be large since $T_l - T_s$ is large. Since the first excited state of the neutral NO· lies some 4.7 eV[10] above the ground state, the possibility of forming an excited neutral can be dismissed. It thus seems that the enthalpy difference is due to the formation of the product ion in two isomeric forms, in analogy to the situation encountered for formaldehyde elimination from anisole molecular ions. These considerations are all accommodated by the proposal that one of the NO· loss mechanisms is the accepted process a → b → d. The stability of the product ion d ↔ e indicates that this process is associated with T_l. This line of argument is supported by the fact that T_l generally increases as the substituent is made more electron donating and also by the fact that the relative contribution of the process leading to T_l increases as Y is made a better electron donor.



f



g

Little direct evidence is available to indicate the mechanism of the second process by which NO· is lost from the molecular ion. Comparison with the anisole system in which radical initiated reactions involve both the carbon bearing the substituent and that ortho to it suggests O–C bond formation *via* a four-membered cyclic transition state. The structure of the (M − NO)$^+$ ion generated by such a route might be f or g, both relatively unstable species. This would account for the observed small energy release. An alternative possibility is that the second reaction gives a small energy release because it involves simple cleavage and that nitro → nitrite isomerism precedes NO· loss.

The energy partitioning method can be applied in further investigating the mechanism of NO· loss. (See the preceding paper for a discussion of the basis and assumptions of this method.) First ϵ_{excess} must be calculated from eq 1 where $YC_6H_4NO_2$ and $YC_6H_4O\cdot$

$$\epsilon_{\text{excess}} = \text{AP}((\text{M-NO})^+) - \text{IP}(YC_6H_4O\cdot) + \Delta H_f{}^\circ(YC_6H_4NO_2) - \Delta H_f{}^\circ(YC_6H_4O\cdot) - \Delta H_f{}^\circ(NO\cdot) \quad (1)$$

represent the aromatic nitro compound and the aryloxyl radical, respectively. Unfortunately, the ionization potential of only one aryloxyl radical has been determined; phenoxyl radical has an IP of 8.84 eV.[11] This value and the reported appearance potential of the corresponding (M − NO)$^+$ ion (10.35 eV)[12] were obtained by electron impact using the semilog plot technique[13] and are therefore uncertain to perhaps 0.2 eV or more. The heat of formation of NO· has been measured as 21.57 kcal mol^{-1} (0.94 eV),[14] that of nitrobenzene has been calculated as 15 kcal mol^{-1} (0.65 eV)[15] by the group equivalent technique of Franklin, while that of the phenoxyl radical has been determined to be 10 kcal mol^{-1} (0.43 eV).[16] Substituting in eq 1 one calculates $\epsilon_{\text{excess}} = 0.79$ eV for $C_6H_5NO_2\cdot^+ \rightarrow C_6H_5O^+ + NO\cdot$. Even though the uncertainty in this value is considerable, perhaps 0.3 eV, the data are reasonable in that $\epsilon_{\text{excess}} > T$. Moreover, it yields an energy partitioning parameter $T/\epsilon_{\text{excess}}$ of 0.70, a reasonable number in the light of the parameters found in other systems.[1,18]

In spite of the fact that the ionization potentials of other aryloxyl radicals have not been measured, it is still possible to calculate ϵ_{excess} for these reactions. In doing this the preceding evidence that the reaction leads to ion d is accepted as adequate to define the reaction and an attempt is now made to assess the behavior of this reaction with regard to energy partitioning. It must be emphasized that the available thermochemical data are not highly precise, but it must also be recognized that they may be adequate to suggest several important trends.

The limiting factor in determining ϵ_{excess} for the substituted nitrobenzenes is the evaluation of the heats of formation of the substituted aryloxy cations. This quantity is related to two of the unknowns in eq 1 as shown in eq 2

$$\Delta H_f(YC_6H_4O^+) = \text{IP}(YC_6H_4O\cdot) + \Delta H_f{}^\circ(YC_6H_4O\cdot) \quad (2)$$

hence, substituting in eq 1

$$\epsilon_{\text{excess}} = \text{AP}((\text{M} - \text{NO})^+) + \Delta H_f{}^\circ(YC_6H_4NO_2) - \Delta H_f(YC_6H_4O^+) - \Delta H_f{}^\circ(NO\cdot) \quad (3)$$

Now, $\Delta H_f(YC_6H_4O^+)$ can be estimated from the appearance potential for formation of this fragment ion in reactions of the type

$$YC_6H_4OX \longrightarrow YC_6H_4O^+ + X\cdot + e^-$$

All such reactions involve excess energy terms, including the kinetic shift and a reverse activation energy,[19]

---

[10] F. R. Gilmore, *J. Quant. Spectrosc. Radiat. Transfer*, **5**, 369 (1965).

[11] I. P. Fisher, T. F. Palmer, and F. P. Lossing, *J. Amer. Chem. Soc.*, **86**, 2741 (1964).

[12] P. Brown, *Org. Mass Spectrom.*, **4**, 533 (1970).

[13] F. P. Lossing, A. W. Tickner, and W. A. Bryce, *J. Chem. Phys.*, **19**, 1254 (1951).

[14] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, NBS Tech Note 270-3 U. S. Government Printing Office, Washington, D. C., 1968.

[15] J. L. Franklin, J. G. 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, U. S. Government Printing Office, Washington, D. C., 1969.

[16] 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} > $\Delta H_f{}^\circ$(phenol). Taking $\Delta H_f{}^\circ$(phenol) as −23 kcal mol^{-1} [17] this gives a value of 9–11 kcal mol^{-1}.

[17] R. J. L. Andon, D. P. Biddiscombe, J. D. Cox, R. Handley, D. Harrop, E. F. G. Herington, and J. F. Martin, *J. Chem. Soc.*, 5246 (1960).

[18] (a) K. R. Jennings, *Org. Mass Spectrom.*, **3**, 85 (1970); (b) R. Taubert, *Z. Naturforsch. A*, **19**, 911 (1964); (c) G. Khodadadi, R. Botter, and H. M. Rosenstock, *Int. J. Mass Spectrom. Ion Phys.*, **3**, 397 (1969).

[19] See A. G. Harrison in "Recent Advances in Mass Spectrometry," A. L. Burlingame, Ed., Wiley-Interscience, New York, N. Y., 1970.

Table II. Calculated $\Delta H_f°$ and IP for $YC_6H_4O^+$ and $YC_6H_4O\cdot$[a]

Y	AP((M − NO)$^+$)[b]	$\Delta H_f°(YC_6H_4NO_2)$[c]	T_{max}	$\Delta H_f°(YC_6H_4O^+)$ (calcd)	$\Delta H_f°(YC_6H_4O\cdot)$[d]	IP($YC_6H_4O\cdot$) (calcd)
-OH	9.90	−1.40	1.78	5.78	−1.51	7.29
-NH_2	9.56	+0.65	1.77	7.58	+0.52	6.98
-OCH_3	10.03	−0.95	1.66	6.48	−1.13	7.61
-CH_3	10.34	+0.43	1.40	8.43	+0.08	8.35
-Cl	10.61	+0.29	1.36	8.60	+0.12	8.48
-F	10.64	−1.41	1.28	7.01	−1.58	8.59
-NO_2	11.10	+0.33	1.08	9.41	+0.15	9.26
-H	10.35	+0.65	0.98	9.28	+0.43	8.66
-CN	10.80	+1.98	0.70	11.48	+1.80	9.68

[a] All data in electron volts. [b] Taken from ref 17. [c] Taken from ref 15. [d] Calculated taking a group equivalence value of −0.52 eV for -O·. [e] $\Delta H_f°(NO)$ = 0.94 from ref 15.

but these terms are minimized for simple cleavage reactions. The use of appearance potential data to determine ionic heats of formation traditionally relies on the assumption that all excess energy terms equate to zero. If this is true for the loss of methyl from the substituted anisole molecular ions, then this reaction provides an independent value for $\Delta H_f(YC_6H_4O^+)$ which can be used to determine ϵ_{excess} in the nitrobenzene reaction. Data for the anisole reaction are available; for anisole itself, AP((M − CH_3)$^+$) = 11.80 eV,[20] $\Delta H_f°(CH_3\cdot)$ = 1.44 eV,[15] $\Delta H_f°(C_6H_5OCH_3)$ = −0.69. Hence, $\Delta H_f(C_6H_5O^+)$ is 9.67 eV as determined from this methyl loss reaction. Substituting this value in eq 3 for the unsubstituted nitrobenzene reaction, one obtains

$$\epsilon_{excess} = 10.35 + 0.65 - 9.67 - 0.94 \text{ eV} = 0.39 \text{ eV}$$

This value is smaller than the energy release measured from the metastable peak width for NO· loss at half-height (0.55 eV), and it is also smaller than the ϵ_{excess} value (0.79 eV) calculated directly using the experimentally determined ionization potential of the phenoxyl radical. Presumably excess energy is involved in the formation of (M − CH_3)$^+$ from anisole at threshold and this makes this method of determining ϵ_{excess} unreliable. Similar results were obtained for the substituted anisoles.

The conclusion reached above that the reaction in which NO· is lost from the molecular ion involves partition of a large proportion of the reverse activation energy into translational energy provides an alternative method for estimating ϵ_{excess} and, hence, the heats of formation of the substituted aryloxy cations. This relies on the following arguments: (i) the average energy released[2] for nitrobenzene itself represents some 70% of ϵ_{excess}, however, larger (and smaller) energy releases also contribute to the observed signal, hence the maximum energy release represents a reasonable approximation to ϵ_{excess}[21] for this reaction; (ii) NO· loss from the substituted compounds will similarly give a maximum energy release which approximates ϵ_{excess} (*vide infra* for more evidence in support of this view). The maximum energy release can be calculated from the metastable peak width measured at the base line.[22]

The estimation of ϵ_{excess} in this way allows the determination of $\Delta H_f(YC_6H_4O^+)$ from eq 3 and this in turn allows the calculation of the ionization potentials of the substituted phenoxyl radicals using eq 2. Results of these calculations are given in Table II. Comparison of the value of 9.28 eV[23] (214 kcal mol^{-1}) for $\Delta H_f(C_6H_4O^+)$ with our calculated value of 9.09 eV (209.5 kcal mol^{-1}) indicates that the above procedure is satisfactory. An indication of the internal consistency of the values obtained by this procedure lies in the fact that the estimated IP values for $YC_6H_4O\cdot$ radicals correlate fairly well with σ^+ as expected for ionization potentials[24] (see Figure 2).

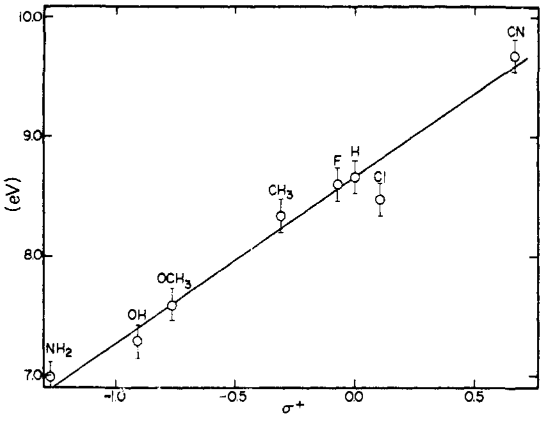


Figure 2. Relationship between the calculated IP of Y–$C_6H_4O\cdot$ and the substituent σ^+ value.

The evaluation of ϵ_{excess} in the above fashion also allows one to estimate the energy partitioning quotient, T/ϵ_{excess}, where T represents the average kinetic energy release. These values are given in Table III and, as expected, are fairly large, averaging 0.63. The mecha-

Table III. Energy Partitioning Quotient for Nitrobenzenes[a]

Y	T, eV	T_{max}, eV	T/ϵ_{excess}
-OH	1.23	1.78	0.69
-NH_2	1.24	1.77	0.70
-OCH_3	1.22	1.66	0.73
-CH_3	0.95	1.40	0.68
-Cl	0.83	1.36	0.61
-F	0.84	1.28	0.65
-H	0.55	0.98	0.56
-CN	0.29	0.70	0.42

[a] All values refer to sequence a → b → d.

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

(21) More accurately it will approximate ϵ_0^r, but $\epsilon_0^r \approx \epsilon_{excess}$ in this system.

(22) Corrected for the main beam width.

(23) Calculated from the $\Delta H_f°(C_6H_5O\cdot)$ value of 10 kcal mol^{-1} [16] and the IP($C_6H_5O\cdot$) value of 8.84 eV.[11]

(24) A. G. Harrison, P. Kebarle, and F. P. Lossing, *J. Amer. Chem. Soc.*, 83, 777 (1961).

nistic implications of these results are considered below. The conditions outlined in the accompanying paper[1b] which justify the approximation $\epsilon_{\text{excess}} \approx \epsilon_0^{\text{r}}$ are met for the NO· loss process accompanied by the larger energy release. Moreover, the agreement achieved between kinetic energy release measurements in the first and second field-free regions serves to emphasize the role of the reverse activation energy rather than excess internal energy in the phenomenon of kinetic energy release accompanying reactions of metastable ions.

Conclusions

The low energy molecular ions of aromatic nitro compounds which fragment in the field-free regions of the mass spectrometer do so by two distinct mechanisms which appear to be in competition with each other. One process involves rearrangement through a three-membered cyclic transition state b and gives the stable product ion d ↔ e. The exceptionally large energy release which accompanies this reaction is not due solely to a large reverse activation energy. Large ϵ_{excess} and, by implication, ϵ_0^{r} values have been found quite frequently.[1] Rather, this process is unique in that it occurs with partition of a major portion (63% on the average) of this energy into kinetic energy of the products.

In accounting for this observation we suggest that there may be a relationship between the "tightness"[25] of an activated complex and the constriction of intramolecular energy transfer. In "tight" activated complexes the number of degrees of freedom is severely circumscribed. Hence, the translational degree(s) of freedom which appear(s) in the activated complex configuration has little chance to interact with other modes, and so transfer the energy being forced into it as the molecular ion dissociates to products. Looser activated complexes should more effectively partition this energy to the internal modes of products. If this simple analysis is correct, it points to the NO· loss process a → d occurring *via* the concerted sequence a → b → d rather than by isomerization to the nitrite. Structure b then approximately represents the activated complex configuration and this is certainly expected to represent a "tight" complex. In this structure the ring and the nitro groups are in orthogonal planes and are bonded in a spiro type of arrangement. This suggests that coupling of the degrees of freedom of the two units will be very ineffective. It is recognized, of course, that the magnitude of the energy partitioning coefficient will also depend upon other factors, and that this analysis is very crude. For instance, our treatment does not distinguish between the "early" and "late" downhill type of surfaces encountered in exothermic ion-molecule reactions, each of which is associated with a different type of energy partitioning behavior.[26] It is nevertheless expected that the present treatment will be of some value in the study of complex ions.

The rationalization of the nitrobenzene behavior in terms of "tight" and "loose" activated complexes also extends to the anisole[1b] and oxime ether[1a,d] reactions. The four-membered cyclic transition state for H_2CO loss from the anisoles was associated with an energy partitioning parameter of 0.16 in the para series. This is much smaller than the nitrobenzene value and a looser activated complex may be at least part of the reason. The loss of HCN from benzaldoxime *O*-methyl ethers is different from the other reactions so far studied because it involves nucleophilic rather than a radical rearrangement.[1a,d] The mechanism occurs *via* a four-membered cyclic transition state when the compound possesses a strongly electron-donating para substituent and by a five-membered cyclic transition state in most other cases.[1d] In agreement with the prediction based on the loose/tight activated complex rationalization, the energy partitioning coefficient is high for strongly electron donating substituents.[1d] On the basis of the methods developed in this paper, the loss of C_2H_4 from a series of para-substituted phenetoles is accompanied by an energy partitioning parameter of only 0.01–0.02[1c] calculated for the accepted mechanism which involves formation of ionized phenol through a four-membered cyclic rearrangement. This is very low compared to all the other results obtained so far, including those for other reactions which involve four-centered rearrangements.[1] This leads one to wonder whether the phenetole reaction does indeed occur *via* a four-centered mechanism. Our doubts will be explored more fully elsewhere.[1c]

The second reaction leading to NO· loss from nitrobenzenes is that associated with the smaller energy release. This might involve isomerization to the nitrite followed by simple cleavage, but such a mechanism does not explain the large substituent dependence of the relative abundances of the processes associated with T_1 and T_s. Isomerization to the nitrite would be expected to show a similar substituent dependence to that for the three-membered cyclic rearrangement reaction. This, and the analogy with the radical rearrangements occurring in the anisoles, suggests that the mechanism involves oxygen transfer *via* a four-membered cyclic transition state. This is in accord with the observed substituent effect and with the small energy release T_s, since the product ions f or g are expected to be far less stable than d. As in the five-membered hydrogen transfer reaction in the anisoles, this process in the nitrobenzenes could be a stepwise or a concerted process. There is no direct evidence to favor one over the other mechanism. However, analogy with HCN loss from benzaldoxime *O*-methyl ethers suggests that the concerted rearrangement to the ortho position occurs. In the oxime ethers the five-membered cyclic rearrangement (to the ortho position) occurs at high energy, while, depending upon the substituent, either this process or the four-membered cyclic rearrangement is dominant in fragmenting ions of lower internal energy. If the rearrangement to the ortho position were stepwise in this case it would not be expected to compete at high internal energies with the lower activation energy four-membered cyclic rearrangement. The simplest interpretation of the rearrangements to the ortho position in anisoles (loss of H_2CO), oxime ethers (loss of HCN), and nitrobenzenes (loss of NO·) is that each of these reactions occurs by a concerted process. The majority of the high energy molecular ions which fragment in the source probably

---

(25) D. W. Setser and B. S. Rabinovitch, *Advan. Photochem.*, **3**, 1 (1964).

(26) See, for example, P. J. Kuntz, E. M. Nemeth, and J. C. Polanyi, *J. Chem. Phys.*, **50**, 4607 (1969); J. C. Polanyi, *Accounts Chem. Res.*, **5**, 161 (1972).

do so by this type of mechanism, but in the case of the anisoles and probably the nitrobenzenes rapid isomerization is expected to follow giving the product which would result from rearrangement to the substituted position. Further fragmentation would occur from this substituted ion. The rearrangement to the ortho position therefore constitutes a "hidden" mechanism in high energy ions; this explains why it has not been recognized from the analysis of normal mass spectra.

It may at first sight seem surprising to find a second case of competitive unimolecular eliminations of the same neutral so soon after the anisole study,[1b] but these two systems are rather similar in allowing radical-induced rearrangements to alternative sites on a benzene ring.

This study again highlights the value of the new techniques of detailed analysis of metastable peak shapes and of energy partitioning. It also suggests that correction of mass spectrometric thermochemical data for the presence of a reverse activation energy may soon be feasible. For instance, subtraction of the measured T_1 value from AP($(M - NO)^+$) would much improve the accuracy of a heat of formation value for such an ion obtained by this reaction, and the result could be extrapolated to any aromatic nitro compound. By way of contrast, the correction required in determining the heat of formation of some ion $ArH\cdot^+$ from the appearance potential of the corresponding anisole requires the subtraction of a quantity some six times the T_1 value.

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.

Kinetics of the Gas-Phase Thermal Unimolecular Elimination of Ketene or 1,1-Dimethylketene from 2,2-Dimethyl-3-ethoxycyclobutan-1-one. A Quasi-Zwitterion Transition State

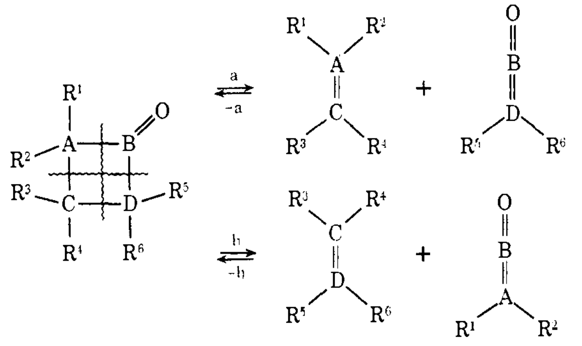
Kurt W. Egger

Contribution from the Monsanto Research S. A., 8050 Zürich, Switzerland.
Received August 31, 1972

Abstract: The kinetics of the gas-phase thermal decomposition of 2,2-dimethyl-3-ethoxycyclobutan-1-one (DEC) was studied in the temperature range 464–558 K using a static reaction system and gas chromatographic analysis. Two simultaneous concerted pathways yield the product pairs ketene + isobutenyl ethyl ether (65–80% of the total conversion) and 1,1-dimethylketene + vinyl ethyl ether (35–20%). Independent first-order total rate constants for the overall depletion of DEC were calculated based on the internal standard technique (k_{tot}) as well as the amounts of vinyl ethyl ether and isobutenyl ethyl ether observed (k'_{tot}). The rate constants were independent of the initial starting pressure in the range 5–50 Torr and of the total pressure (propylene) of up to 700 Torr and fit the Arrhenius relationships $\log (k_{tot}/\mathrm{sec}^{-1}) = 13.58 \pm 0.29 - (40.27 \pm 0.68 \text{ kcal mol}^{-1})/\theta$ and $\log (k'_{tot}/\mathrm{sec}^{-1}) = 13.61 \pm 0.22 - (40.32 \pm 0.51 \text{ kcal mol}^{-1})/\theta$, where $\theta = 2.303RT$. These activation parameters, when compared with the corresponding values observed for cyclobutanone itself, indicate a stabilizing effect of 3-alkoxy groups of 11.5 kcal mol^{-1}, which is about the same as was observed previously for substituted vinyl groups. The results of this work further substantiate the assumption of an essentially zwitterionic charge separation involved in the gas-phase $2_s + 2_a$ ketene + olefin addition–elimination reactions.

Kinetic studies of the gas-phase thermal elimination of ketenes from cyclobutanone derivatives and particularly the observed substituent effects should yield important information about the detailed nature of the reaction mechanism and the transition state involved in these systems (I), where *A*, *B*, *C*, and *D* represent carbon atoms. In principle, three extreme formulations of the transition-state structures and detailed reaction path may be envisaged: (a) a concerted synchronous process with an essentially symmetrical neutral transition state, (b) a concerted nonsynchronous path involving considerable charge separation and an asymmetric transition state, and (c) a biradical reaction path.

The first possibility (a) can be ruled out on the basis of the well-known fact that conjugated olefins add to ketenes in a four-center 2 + 2 process to the exclusion of the "allowed" six-center $4_s + 2_s$ Diels–Alder reaction.[1-4] This has been rationalized on the basis of the principle of orbital symmetry conservation, by



(I)

---

[1] J. C. Martin, P. G. Gott, V. W. Goodlett, and R. H. Hasek, *J. Org. Chem.*, 30, 4175 (1965).

[2] W. T. Brady and H. R. O'Neal, *ibid.*, 32, 2704 (1967).

[3] R. Huisgen and P. Otto, *Chem. Ber.*, 102, 3475 (1969).

[4] M. Rey, S. Roberts, A. Dieffenbacher, and A. S. Dreiding, *Helv. Chim. Acta*, 53, 417 (1970).