Dissociative Ionization and Metastable Ions of Nitrobenzene and Nitrobenzene-d_5

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The kinetica energy released on the loss of CNO_2 from nitrobenzene and deuterated nitrobenzene ions in the second field-free region shows that this loss does not occur as a single-step process.

The apparent heat of formation of the $C_6H_5^+$ ion is found to be 270.85 kcal mol^{-1}, which is consistent with the ion having the cyclic structure.

Introduction

Unimolecular disociation, which is observed in mass-analyzed ion kinetic energy spectrometers (MIKES), results normally from ions having an internal energy slightly above the critical value. The resulting primary ionic fragment, sharing the small amount of available energy with the neutral fragment, is unlikely to undergo further dissociation. However, it was found [1 – 6] that the ions dissociating in the first field-free region (1st FFR) of a double-focusing mass spectrometer yield primary fragments with sufficient internal energy to dissociate further in the second field-free region (2nd FFR). Such consecutive dissociations require that the primary and secondary rates be competitive in the metastable range.

The utility and significance of metastable ion studies for the determination of thermochemical data of gaseous ions is well documented [7 – 10]. The heat of formation data characterize the ions in their electronic and vibrational ground state.

In the present work the mechanism of the loss of CNO_2 from nitrobenzene and nitrobenzene-d_5 ions is discussed. The study also includes a calculation of the heat of formation of $C_6H_5^+$ formed from nitrobenzene.

Experimental

The measurements were made with a Varian MAT-CH5 double focusing mass spectrometer of reversed Nier-Johnson geometry. The ions were produced in the source by bombardment with 70 eV electrons with 1 mA total emission current and 2×10^{-6} torr sample pressure. The accelerating voltage was 3 kV. A modification of the high voltage supply unit (Hochspannungsgerät BHA, OA57251) enabled us to interrupt the accelerating voltage upscan (in the defocusing mode) to carry the electrostatic – sector voltage down-scan both automatically and manually. This modification was necessary to study the consecutive metastable transitions in the way described previously [11].

The kinetic energy release T during the fragmentations has been calculated from the width of the appropriate signal in the metastable ion (MI) spectrum corrected for the width of the main beam. Thermochemical data were determined from the literature [12, 13].

Results and Discussion

Normal Mass Spectra and Fragmentation Pathways

The most intense peaks in the mass spectra of the title compounds M are due to $(M-NO_2)^+$. The ions M^+ produce the second intense peaks. The peaks due the masses 51 and 54 are also intense. They correspond to the fragments $C_4H_3^+$ and $C_4D_3^+$, respectively. Possible fragmentation pathways of the metastable ions $M^{+\cdot}$ are represented in Scheme 1.

All peak shapes are gaussian except that corresponding to $(M-NO)^+$, which is a composite peak. This composite peak indicates that two competitive unimolecular processes are operative: one involves a three – centered cyclic transition state with the

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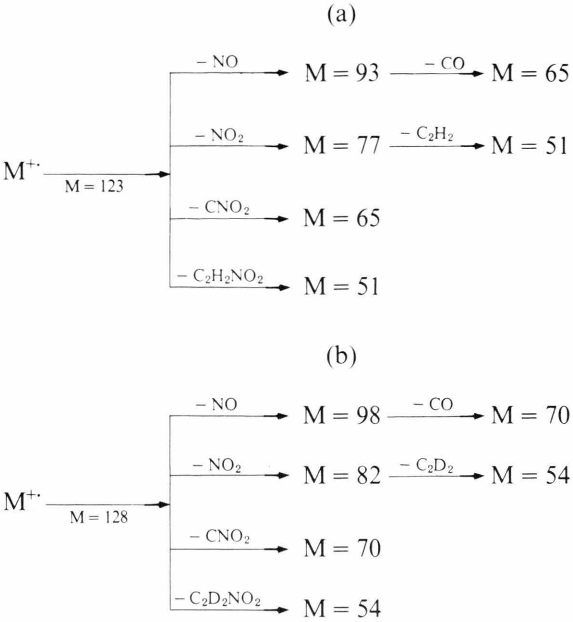

Scheme 1. Fragmentation paths of $M^{+\cdot}$ of (a) Nitrobenzene and (b) Nitrobenzene-d_5.

formation of the aryloxy cation (broad component), while the other seems to involve oxygen rearrangement to the ortho position [14] (narrow component).

It is interesting to note that the loss of NO˙ from $M^{+\cdot}$ followed by the loss of CO is an example of a consecutive fragmentation:

$$M^{+\cdot} \xrightarrow[-\mathrm{NO}]{\text{1st FFR}} [M-NO]^{+} \xrightarrow[-\mathrm{CO}]{\text{2nd FFR}} [M-CNO_2]^{+} . \qquad (1)$$

The previous study [3] of the reactivity of $[M-NO]^+$ ions showed that it is mainly the ion from the narrow component of the peak that gives the consecutive peak, whilst ions from the broad peak are generally too stable to be fragmented to form $[M-CNO_2]^+$ ions.

Kinetic Energy Release in the Consecutive Reaction

The kinetic energy released in the elimination of CO form $[M-NO]^+$ in the 2nd FFR has been calculated. The kinetic energy values $T_{50\%}$ and $T_{5\%}$, measured at 50 and 5% of the maximum peak height, are listed in Table 1. It is clear from Table 1 that the T-values are equal within the range of estimated error for the two compounds. The $T_{50\%}$-values of (56 ± 2) meV and (54 ± 2) meV found for the loss of CO are consistent with earlier work [3].

It was interesting to observe a small metastable peak corresponding to a dissociation in the 2nd FFR:

$$M^{+\cdot} \xrightarrow[-\mathrm{CNO_2}]{\text{2nd FFR}} [M-CNO_2]^{+} . \qquad (2)$$

Using the (MIKE) scan this reaction appears as a single-step process which leads to the T-values (47 ± 2) meV and (48 ± 2) meV in nitrobenzene and nitrobenzene-d_5, respectively. In a simple treatment, Harkness [15] showed that for a pair of consecutive processes having kinetic energy releases T_1 and T_2, the width of the metastable peak for the consecutive process must correspond to a kinetic energy release $T \leqq (T_1 + T_2)$. The T-values for the two steps of reaction (1) in nitrobenzene and nitrobenzene-d_5 are $T_1 = (90 \pm 10)$ meV and (98 ± 7) meV (for the narrow component of composite peak [12]) and $T_2 = (56 \pm 2)$ meV and (57 ± 2) meV, respectively. The T-value (47 ± 2) meV for nitrobenzene and (49 ± 2) for nitrobenzene-d_5 as found from reaction (2) is clearly less than either T_1 or T_2. Calculation of the T-value for reaction (2) within a single region and after correcting for the accelerating voltage gives about (54 ± 2) meV for the two ions. This value is comparable to that listed in Table 1 as a consecutive process (b). Therefore, this study indicates that reaction (2) does not occur as a single-step process.

Table 1. Energy release, in meV, in the consecutive reaction of nitrobenzene and nitrobenzene-d_5.

Compound	Transition	Energy release for transition (b)		Energy release for MIKE peak (b)	
		$T_{50\%}$	$T_{5\%}$	$T_{50\%}$	$T_{5\%}$
Nitrobenzene	$123^+ \xrightarrow{(a)} 93^+ \xrightarrow{(b)} 65^+$	56 ± 2	294 ± 10	54 ± 2	288 ± 12
Nitrobenzene-d_5	$128^+ \xrightarrow{(a)} 98^+ \xrightarrow{(b)} 70^+$	58 ± 2	299 ± 10	55 ± 2	289 ± 10

Table 2. Thermochemical data for the loss of NO_2 from the nitrobenzene ion.

Transition	I (M) eV	A (F^+) eV	E^0 eV	T_B eV	ΔH_f^* (M)	ΔH_f(N)	$\Delta H_f'$ (F^+)	$\Delta H_f'$ $(F^+)_{cor.}$
$C_6H_5NO_2^{+\cdot} \rightarrow C_6H_5^{+} + NO_2$	10.16 [a]	12.14 [a]	1.08	0.700	15 [b]	7.93 [b]	286.99	270.85

* ΔH_f's are in kcal mol^{-1}. [a] Value from [12]. [b] Value from [13].

Energetics of the Formation $(M-NO_2)^+$ from Nitrobenzene

Ion structures may be inferred from heat of formation data by comparison with reference ions [16] or molecular orbital calculations. The process to be considered is the formation from M of $M^{+\cdot}$ to give a daughter ion F^+ plus a neutral fragment $N^\cdot$:

$$M + e^- \rightarrow F^+ + N^\cdot + 2\,e^- . \tag{3}$$

For the reaction (3) the heat of formation of the daugther ion is given by

$$\Delta H_f(F^+) = A\,(F^+) + \Delta H_f(M) - \Delta H_f(N) - \varepsilon_{excess} . \tag{4}$$

If the excess energy (ε_{excess}) is ignored, an apparent heat of formation $\Delta H_f'(F^+)$ will be obtained which is an upper limit to the true value:

$$\Delta H_f'(F^+) = A\,(F^+) + \Delta H_f(M) - \Delta H_f(N) . \tag{5}$$

Most applications of the MIKES to thermochemical problems attempt to use measured values of the kinetic energy T_B [17–19] (as determined from the peak base-width) to correct $\Delta H_f'(F^+)$ for the fragmentation reaction of interest.

$$\Delta H_f'(F^+)_{cor.} = \Delta H_f'(F^+) - T_B \geqq \Delta H_f(F^+) . \tag{6}$$

However, it is not known initially whether the total ε_{excess} or only a part of it is released as T_B.

The apparent heats of formation $\Delta H_f'(F^+)$, $\Delta H_f'(F^+)_{cor.}$ and the critical energy of the $C_6H_5^+$ ion from the molecular ion of nitrobenzene are listed in Table 2.

$C_6H_5^+$ has been the subject of extensive studies [9, 20, 21] but its structure could not be established. Boyd and Beynon [9] derived $\Delta H_f(C_6H_5^+) =$ 266 kcal mol^{-1} from the phenyl-hydrogen bond dissociation energy in benzene [22] and the ionization energy of the $C_6H_5^\cdot$ phenyl radical [23]. Photoionization determinations [24] of the production threshold of $C_6H_5^+$ from C_6H_5Br gabe the same value. The present work shows that the use of T_B due to the loss of NO_2 from the nitrobenzene ion to form $C_6H_5^+$ yields $\Delta H'_{f_{cor.}} = 270.85$ kcal mol^{-1}. This is very close to the value reported before. In support of this view, it is noted that the use of $T_B = 0.88$ eV [25] for $C_6H_5^+$ formed from the dissociation of metastable $C_6H_6^{+\cdot}$ [9], equal to the reverse activation energy (ε_0^r), gives $\Delta H_f'(C_6H_5^+)_{cor.} = 269$ kcal mol^{-1}. This value is nearly equal to that found in nitrobenzene. This indicates that the $C_6H_5^+$ ions from both nitrobenzene and benzene are (cyclic) phenyl cations.

Conclusion

The kinetic energy released upon fragmentation of metastable ions gives a piece of information about the thermochemical reaction mechanism of gaseous ions.

The subtraction of the fraction of the excess energy released as kinetic energy improves the accuracy of the calculated heat of formation of the ions studied. The heat of formation thus obtained is consistent with $C_6H_5^+$ having the cyclic structure.

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[1] K. R. Jennings, Chem. Commun. **1966**, 283.
[2] L. P. Hills, F. H. Futrell, and A. L. Wahrhaftig, J. Chem. Phys. **51**, 5255 (1969).
[3] C. J. Procter, A. G. Brenton, J. H. Beynon, B. Kralj, and J. Marsel, Int. J. Mass Spectrom. Ion Phys. **35**, 393 (1980).
[4] C. J. Procter, B. Kralj, and J. H. Beynon, Org. Mass Spectrom. Lett. **15**, 326 (1980).
[5] R. K. Boyd and B. Shushan, Int. J. Mass Spectrom. Ion Phys. **37**, 355 (1981).
[6] B. Shushan and R. K. Boyd, Int. J. Mass Spectrom. Ion Phys. **37**, 369 (1981).

[7] R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, Metastable Ions, Elsevier, Amsterdam 1973.

[8] R. G. Cooks and J. H. Beynon, in A. Maccoll (Ed.), Mass Spectrometry, MTP International Review of Science, Physical Chemistry Series II, Vol. 5, Butterworths, London 1975, p. 159.

[9] R. K. Boyd and J. H. Beynon, Int. J. Mass Spectrom. Ion Phys. **28,** 163 (1977).

[10] F. H. Abd El-Kader and M. S. Abd El-Fattah, Z. Naturforsch. **38 a,** 524 (1983).

[11] H. M. Ahmed, Ph.D. Thesis, Section III.6.3 (p. 40), Cairo University.

[12] S. H. Allam, M. D. Migahed, and A. El-Khodary, Egypt. J. Phys. **13,** No. 2, 167 (1982).

[13] J. L. Franklin, J. F. Dillard, H. H. Rosenstock, J. T. Herrson, K. Droxyl, and F. H. Field, Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions, National Bureau of Standards, London 1969, p. 26.

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

[15] A. L. Harnkess, Int. J. Mass Spectrom., Ion Phys. **10,** 267 (1973).

[16] H. M. Grubb and S. Meyerson in "Mass Spectrometry of Organic Ions", Academic Press, New York 1963, Chapter 10.

[17] R. Schubert and H. F. Grutzmacher, Org. Mass Spectrom. **15,** 122 (1980).

[18] R. Schubert and H. F. Grutzmacher, J. Amer. Chem. Soc. **102,** 5323 (1980).

[19] D. V. Ramona and H. F. Grutzmacher, Org. Mass Spectrom. **16,** 227 (1981).

[20] F. Bochers and K. Levsen, Org. Mass Spectrom. **10,** 584 (1975).

[21] R. G. Cooks, J. H. Beynon, and J. F. Litton, Org. Mass Spectrom. **10,** 503 (1975).

[22] D. M. Golden and S. W. Benson, Chem. Rev. **69,** 125 (1969).

[23] Yu. Sergeev, M. E. Akopyan, and G. I. Vilesov, Opt. Spectrosk. **32,** 230 (1972).

[24] Yu. Sergeev, M. E. Akopyan, F. I. Vilesov, and V. I. Kleimenov, Opt. Spectrock. **29,** 63 (1970).

[25] M. D. Migahed and F. H. Abd El-Kader, Int. J. Mass Spectrom. Ion Phys. **28,** 225 (1978).