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Photochemical Decay Reactions of N_2O_5 , HNO_3 , ClNO_3 and BrNO_3 in the Energy Range 10–20 eV.

H.-W. Jochims, W. Denzer, H. Baumgärtel

Institut für Physikalische und Theoretische Chemie der Freien Universität Berlin, Takustraße 3, W-1000 Berlin 33

O. Lösking and H. Willner

Institut für Anorganische Chemie der Universität Hannover, Callinstraße 9, W-3000 Hannover 1

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The photochemical behaviour of gaseous N_2O_5 , HNO_3 , ClNO_3 and BrNO_3 has been investigated in the energy range 10–20 eV by photoionization mass spectrometry using monochromatized synchrotron radiation. The decay reactions are analyzed using the photoion yield curves of fragment ions and their appearance energies. Hitherto unknown photochemical reactions and thermochemical data have been evaluated.

Introduction

The photodissociation of the neutral compounds has been studied in some detail [1,2] because of their wellknown presence in the earth atmosphere and their occurrence in the halogen and NO cycles causing ozone depletion [3]. These experiments primarily have been focused on reactivity, gasphase equilibria and reaction kinetics of these compounds.

Otherwise only a few photoelectron spectra [4,5] and electron impact mass spectra [6,7] of the nitroxy compounds are available from the literature. Appearance energies (AE) of ionic fragments on which thermochemical considerations are based have not been measured so far. This partly may result from the difficulties in preparing pure samples of this very reactive molecules and in handling them without decomposition.

Experimental

Substances

Anhydrous *nitric acid*, HNO_3 , was prepared through addition of conc. sulfuric acid (7 mL) to dry sodium nitrate (3 g) under reduced pressure. The product was collected at 77 K and purified by repeated fractional condensation in vacuo.

Dinitrogen pentoxide, N_2O_5 , was produced from dry lithium nitrate LiNO_3 (4 g) and nitrylfluoride, FNO_2 (1.8 g) according to [8] in a passivated 500 mL stainless steel cylinder equipped with a tungsten carbide needle valve (HOKE, Cresskill, USA). The reac-

tion was accomplished by slowly warming up the reactor from 77 K to 273 K. Unreacted FNO_2 and decomposition products (e.g. NO_2) were removed in vacuo at 243 K.

Chlorine nitrate, ClNO_3 , was obtained by the reaction of ClF (4.9 g) with dry sodium nitrate (8.5 g) in a similar way as described for N_2O_5 [9]. The crude product was purified by repeated fractional condensation in vacuo in traps held at 163/147/77 K. The pure compound was collected in the 147 K trap.

Bromine nitrate, BrNO_3 , results from the reaction of dry bromine and chlorine nitrate successively condensed into a passivated stainless steel cylinder and slowly warmed up from 77 K to 298 K [10]. Volatile materials and byproducts were separated by trapping (241/228/77 K) under reduced pressure. The final purification was performed by multiple fractional condensation of the 228 K fraction.

All the substances were analyzed by means of IR- and UV-spectroscopy, respectively. Their purity was greater than 98%.

Experimental Setup

A detailed description of the photoionization mass spectrometer has been given in a previous paper [11].

The vapors of HNO_3 , N_2O_5 , ClNO_3 , BrNO_3 held at 283/253/183/243 K respectively are directly fed into the ionization source of a quadrupole mass filter via a glass inlet system and ionized by monochromatized synchrotron of the Berlin storage ring BESSY using a 1 m-McPherson monochromator (1200 l/mm Al-grating, wavelength resolution 0.2 nm). In order to prevent thermal or photon-induced decomposition of the compounds the reservoir was stored at dry ice temperature and the whole inlet systems including the Young needle valve was wrapped by aluminum foil. Traces of decomposition products were eliminated by an additional vacuum pump by-pass. Only in the mass spectra of BrNO_3 traces of bromine have been detected.

Results

The photoion spectra of N₂O₅, HNO₃, ClNO₃ and BrNO₃ in the energy range of 10–20 eV are displayed in Figs. 1–4. The ion yield curves have been corrected for photon flux variations during the monochromator scan. The relative ion intensities obtained at 20.7 eV excitation energy are enlisted in Table 1. For comparison the results of the electron impact mass spectrum of HNO₃ [7] and of N₂O₅ [6] have also been included in Table 1.

Table 1

Relative photoion intensities (PIMS) at 20.7 eV in comparison to available electron impact mass spectroscopic (EIMS) data in % according to Refs. [6, 7]

	N ₂ O ₅		HNO ₃		ClNO ₃	BrNO ₃
	PIMS	EIMS	PIMS	EIMS	PIMS	PIMS
M ⁺	(0)	(0)	(0)	(2)	(0)	(1)
NO ₂ ⁺	(100)	(20)	(95)	(100)	(100)	(100)
O ₂ ⁺	(0)	(0)	(1)	(4)	(0)	(0)
NO ⁺	(30)	(100)	(100)	(85)	(36)	(30)
OH ⁺	(–)	(–)	(9)	(25)	(–)	(–)
O ⁺	(1)	(0)	(2)	(21)	(0)	(0)
N ⁺	(0)	(0)	(1)	(10)	(0)	(0)
ClO ⁺	(–)	(–)	(–)	(–)	(9)	(–)
Cl ₂ ⁺	(–)	(–)	(–)	(–)	(3)	(–)
Cl ⁺	(–)	(–)	(–)	(–)	(3)	(–)
BrO ⁺	(–)	(–)	(–)	(–)	(–)	(7)
Br ₂ ⁺	(–)	(–)	(–)	(–)	(–)	(15)
Br ⁺	(–)	(–)	(–)	(–)	(–)	(6)

The heats of formation ΔH_f^{298} used in the discussion of the results have been compiled in Table 2.

Table 2

Compilation of enthalpy of formation values at 298 K in kJ/mol according to [16] and literature cited therein, if not stated otherwise

N ₂ O ₅ :	11 [16]	NO ₂ :	33.2 [16]	NO:	91.3 [16]
N ₂ O ₄ :	1159 [*]	N ₂ O ₃ :	1051 [*]	N ₂ O:	9 [16]
HNO ₃ :	–134.3 [16]	NO ₂ ⁺ :	974.0 [16]	NO ⁺ :	984.6 [16]
HNO ₃ ⁺ :	1018 [16]	HO ₂ ⁺ :	1105.5 [16]	HO ₂ :	10.5 [16]
NO ₃ :	71.1 [22]	OH:	39.0 [16]	OH ⁺ :	1293.3 [16]
ClONO ₂ :	26.5 [23]	ClO:	101.9 [16]	ClO ⁺ :	1158.0 [*]
ClNO:	52 [16]	ClNO ⁺ :	1101 [16]	Cl:	121.3 [16]
ClNO ₂ :	13 [16]	ClNO ₂ ⁺ :	1155 [*]	ClO ₂ :	97 [16]
BrONO ₂ :	70.8 [*]	BrO:	125.8 [16]	BrO ⁺ :	1110.0 [*]
BrONO ₂ ⁺ :	1083.9 [*]	Br:	111.9 [24]	H:	217.9 [16]
O(³ P):	249.2 [16]	O ⁺ :	1563.1 [16]		

* This work.

Discussion

N₂O₅

The photoionization mass spectra of N₂O₅ show the signals $m/e = 46$ (NO₂⁺), $m/e = 30$ (NO⁺) and a very small one at $m/e = 16$ (O⁺).

The ion yield curve of the nitrogendioxid cation shows a smooth onset at 11.8 eV. This value may be compared with the photoelectron spectrum of N₂O₅ [5] which shows the lowest adiabatic ionization potential at 11.4 eV and the corresponding vertical value at 12.3 eV. From the thermochem-

ical data [12] one calculates AE (N₂O₅⁺) = 11.91 eV. This result indicates that the parent ion is not stable in its electronic ground state and it explains that no N₂O₅⁺ could be observed.

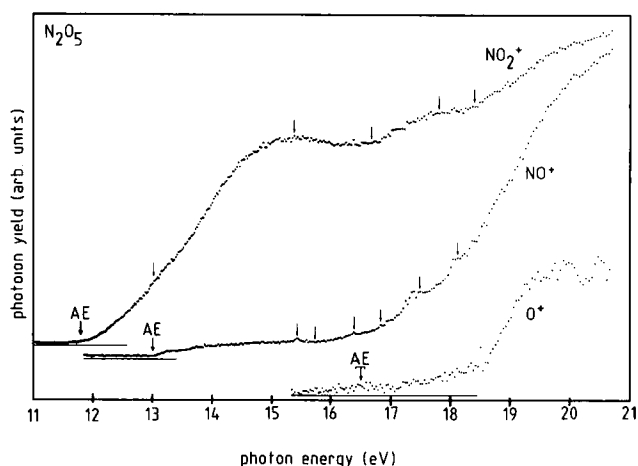
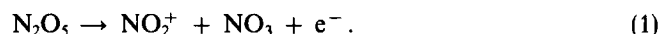


Fig. 1

Photoion yield curves of the fragment ions of N₂O₅. Features discussed in the text are marked by arrows

The formation of NO₂⁺ has to be assigned to the reaction



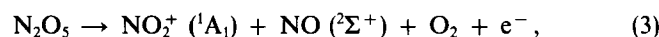
Taking into account the thermochemical data given in Table 2 the calculated appearance energy of this reaction comes to 10.73 eV. Therefore about 1 eV excess energy is involved in the NO₂⁺ formation at the threshold. But it should be mentioned that the accuracy of some of the thermochemical data used for this calculation may be not very high.

A careful inspection of the NO₂⁺ yield curve reveals an inflection near 13 eV, a broad maximum around 15.5 eV and small but clearly distinguishable onsets at 16.5 eV and 17.7 eV. Finally the ion yield curve increases again beyond 18.2 eV.

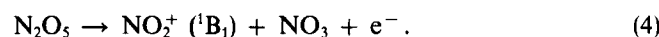
The inflection near 13 eV correlates with the onset (12.92 eV) of the reaction



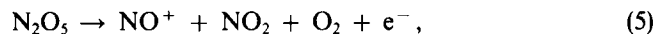
indicating the dissociation of NO₃. The NO₂–O bond energy obtained from this experimental value and the calculated appearance energy of reaction (1) comes to 2.28 eV (220 kJ/mol). The assignment of the higher onsets is difficult, they may be correlated with the formation of higher electronic states either of NO₂⁺ or the neutral fragments. By energetical arguments the onset near 16.5 eV may be due to the process



and the onset at 18.2 eV could arise from

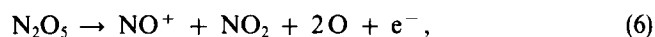


The NO⁺ yield curve shows the first smooth onset at around 12.95 eV and increases around 15.8 eV. Several weak resonant features are superposed on the ion yield curve at 15.43 eV, 16.38 eV, 16.83 eV, 17.62 eV and around 18 eV. The formation of NO⁺ is expected to occur according to the following reaction



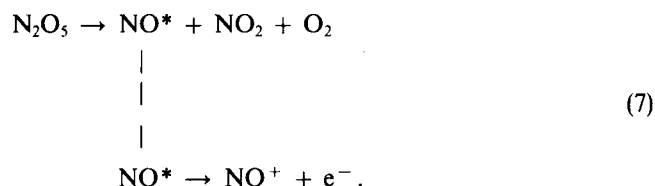
with an onset energy of 10.45 eV calculated from thermodynamic values given in Table 2. This indicates considerable amounts of excess energy (2.5 eV) to be involved in this reaction. Considering a sequential process for the formation of NO⁺, i.e. the dissociation of excited NO₂⁺ into NO⁺ + O one would expect the onset at 13.42 eV which is about 0.5 eV above the experimental value and therefore dismisses this process.

The increasing ion yield beyond 15.8 eV may be explained by the reaction

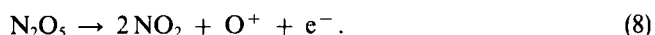


for which an onset of 15.62 eV has been calculated.

The small resonances indicate, that besides direct dissociative ionization small amounts of NO⁺ may result via autoionization of superexcited neutral NO, according to processes like



The ion yield of O⁺ is very weak and has its onset between 16 eV and 17 eV. The assignment to a specific process of formation seems ambiguous. There is only reaction (8) which may contribute to the formation of oxygen ions at threshold,



The calculated appearance energy of this reaction is 16.8 eV.

HNO₃

The photoionization mass spectra of nitric acid show signals $m/e = 46$ (NO₂⁺), $m/e = 30$ (NO⁺) and $m/e = 17$ (OH⁺). The ion yield curves are shown in Fig. 2. No parent ions are detected.

The NO₂⁺ yield curve arises at 11.90 eV. In the following increasing region steps at 12.48, 12.86 and 13.28 eV are recognized. In the range 15–17 eV four additional onsets are observed at 15.24, 15.76, 16.33 and 16.66 eV. Behind the broad maximum at 17 eV the ion yield decreases, interrupted by two maxima at 17.66 eV and 18.24 eV. Nitric acid has an ionization potential of 11.96 eV which is well established [4]. By comparison of the onset energy of NO₂⁺ and the ionization potential it becomes understandable, that no par-

ent ions have been observed. This result is in contradiction to the electron impact spectrum where small amounts of the molecular ion have been monitored [7].

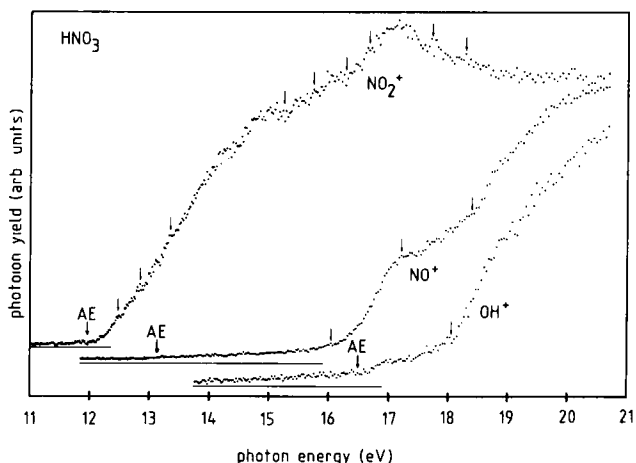
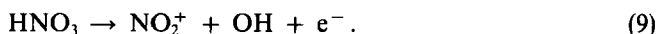


Fig. 2 Photoion yield curves of the fragment ions of HNO₃. Features discussed in the text are marked by arrows

The most probable process for the formation of NO₂⁺ is



The thermodynamic calculation of the appearance energy results in 11.90 eV which is in good agreement with the experimental value. Therefore we assume that NO₂⁺ is produced in the electronic ground state and that reaction (9) is practically free of excess energy. The steplike features in the ascending part of the ion yield curve can be assigned to vibrationally excited OH radicals. The OH vibration is 0.46 eV [13] which fits well into the observed steps.

Table 3 Electronic excitation energies $\Delta E(\text{NO}_2^+)$ resulting from differences of the ionization energies

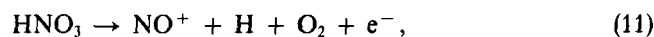
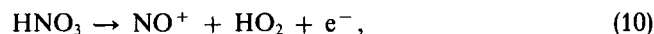
IP _{ad} (NO ₂ ⁺ /A ₁) = 9.75 eV [16]			
IP	$\Delta E(\text{NO}_2^+/\text{eV})$	Ion state	Ref.
12.85	3.10	³ B ₂	[15]
13.60	3.85	³ A ₂	[15]
14.07	4.32	¹ A ₂	[15]
14.37	4.62	¹ B ₂	[15]
16.99	7.24	³ A ₁	[15]
17.06	7.31	³ B ₁	[15]
17.13	7.38	¹ B ₁	[14]

The higher onsets in the ion yield curve can be interpreted more or less tentatively. Using the higher ionization potentials of NO₂ reported in the Refs. [14,15] and the first adiabatic IP(NO₂) = 9.75 eV [16] one can estimate at which energy the formation of NO₂⁺ in higher electronic states may occur. In this way the onset at 15.24 eV can be correlated with the formation of NO₂⁺ (³B₂) (s.a. Table 3). The other

onsets may be assigned as follows: NO₂⁺ (³A₂) (15.76 eV), NO₂⁺ (¹A₂) (16.33 eV) and NO₂⁺ (¹B₂) (16.58 eV). The two maxima in the decreasing region point to autoionization effects, but it has not been possible to correlate them with distinct states of NO₂.

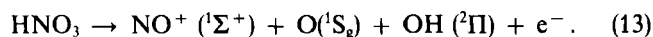
The NO⁺ yield rises very smoothly in the range between 13 and 16 eV. The onset may be taken at 13.07 eV. At about 16 eV the ion yield increases considerably. This range is interrupted by a small plateau at around 17.1 eV, where a higher onset might be placed. Finally at about 18.3 eV an inflection in the NO⁺ yield curve is recognized.

The formation of NO⁺ in the low energy range of the ion yield curve is somewhat questionable. Three different reactions may be discussed



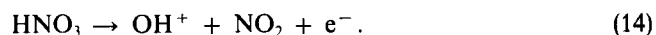
Considering the calculated appearance energies of these reactions one has to conclude, that only reaction (10) (AE = 11.72 eV) may contribute to the NO⁺ yield at the onset and in addition considerable excess energy has to be postulated. Reaction (11) (AE = 13.87 eV) and reaction (12) (AE = 14.60 eV) have to be excluded by energetical reasons. Therefore the assumption remains that at the onset reaction (10) has to be taken into account. This process includes an oxygen migration in the molecular cation. This rearrangement may have a considerable activation barrier which would explain as well the low ion yield as the excess energy of 1.3 eV observed at threshold.

The increasing ion yield in the range between 16 and 17 eV may be partly due to dissociation of excited NO₂⁺. It seems to be not unlikely that NO₂⁺ (¹A₂) and NO₂⁺ (¹B₂) dissociate into NO⁺ (¹Σ⁺) and O(³P) or O(¹D). This tentative assumption is described by Eq. (12). It is of course only based on energetic arguments. The onset around 17.2 eV in the NO⁺ yield curve correlates with the begin of the decreasing region in the NO₂⁺ curve, therefore a process competing with the NO₂⁺ formation should be assigned to the NO⁺ production at energies $E > 17.2$ eV. Considering the high onset energy it is not possible to find processes from which the fragments result in their electronic ground state we assume by energetic arguments that one possible process could be



Of course from this equation no further conclusions can be drawn concerning the mechanism of NO⁺ formation.

The simplest reaction, which can be taken into consideration to explain the very low OH⁺ yield is



The appearance energy calculated for Eq. (14) is 15.20 eV, thus large amounts of excess energy have to be postulated

if the first onset is taken to be at 16.6 eV. The steep ascend beginning at 18.2 eV can be assigned to the reaction



for which the calculated appearance energy is 18.35 eV.

ClNO₃

The photoionization mass spectra of chlorine nitrate reveal $m/e = 46$ (NO₂⁺), $m/e = 51, 53$ (ClO⁺) and $m/e = 30$ (NO⁺) to be the most abundant fragment ions. No parent ion could be detected.

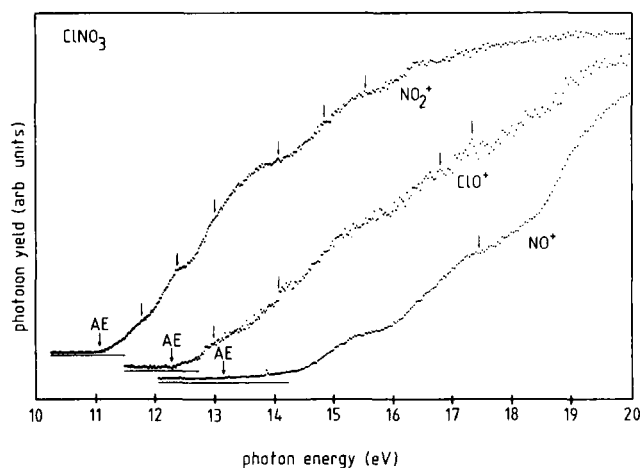
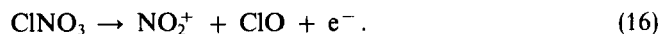


Fig. 3
Photoion yield curves of the fragment ions of ClNO₃. Features discussed in the text are marked by arrows

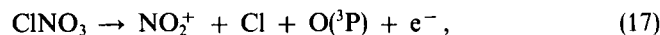
The ion yield curves rise smoothly but exhibit several clear inflections. In the NO₂⁺ yield curve the threshold is observed at 11.07 eV followed by an inflection at 11.85 eV. A second onset is observed at 12.33 eV with an inflection at 13.05 eV; further onsets can be observed around 14.1 eV, 14.9 eV and 15.3 eV. It is not clear whether at 15.8 eV an onset can be postulated in the experimental curve.

The formation of NO₂⁺ is expected to follow Eq. 16



According to (16) the expected thermodynamic onset is 10.88 eV. This value is 0.2 eV lower than the experimental onset, probably due to some excess energy, i.e. preferably kinetic energy of the fragments.

At higher excitation energies other fragmentation reactions like

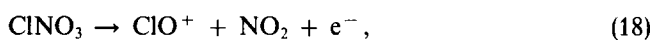


have to be discussed. The calculated appearance energy of NO₂⁺ according to Eq. (17) is 13.67 eV in good agreement with the experimental onset in the range 13.6–13.8 eV. The possible formation of excited species may be discussed using the spectroscopic data of ClO tabulated in [13] and assum-

ing that at the threshold ClO is formed in its electronic ground state including less than 0.1 eV excess energy. From energetic reasons the formation of NO₂⁺ + ClO (²A₁) is expected at 14.80 eV, i.e. above the dissociation limit of ClO. Therefore this process seems to be improbable. Furthermore no indication for this reaction is observed in the ion yield curve. At 15.3 eV an onset is registered which may be assigned to the formation of NO₂⁺ (¹A₂) (s.a. discussion for HNO₃). No interpretation of the inflection in the NO₂⁺ ion yield curve at 11.85 eV can be given at present.

A remarkable feature is the coincidence of the inflection at 12.33 eV with the onset of the ClO⁺ yield curve and of the inflection at about 13 eV with the smooth over of the NO⁺ yield curve at 13.1 eV.

The calculated appearance energy of ClO⁺ according to the unimolecular decay



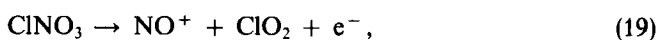
comes to 12.08 eV, i.e. about 0.2 eV below the experimental threshold. This difference may be interpreted as the excess energy involved in reaction (18).

The result, that the observed thresholds of NO₂⁺ and ClO⁺ are observed both 0.2 eV above the thermodynamic threshold and that the ClO⁺ onset is imaged in the NO₂⁺ yield curve stimulates the idea to discuss an ionic molecular aggregate ClO⁺...NO₂⁺ being involved in the decay reaction.

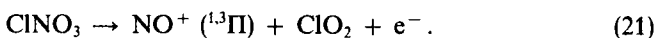
Neutral molecular aggregates of small molecules are wellknown species [17], their photoionization behaviour has been studied by many groups repeatedly in some detail. One of the most important results is that after photoionization cluster dissociation proton and electron transfer in the aggregates are often observed [18]. Another process is intracuster Penning ionization and autoionization [19]. The crucial question is: Is there any possibility for the rearrangement of the molecular ion into the corresponding ionic aggregate? It may not be excluded that an ionic aggregate with increased O–N bond length is involved in the decay of the molecular ion. It may be suggested that at higher internal energies of the aggregate intracuster electron transfer occurs leading to the fragments ClO⁺ and NO₂. This process has been observed in heterogeneous and homogeneous molecular aggregates [20]. To confirm this suggestion more theoretical calculations on ClNO₃⁺ would be helpful.

On the other side one has to take into account that the reversed charge distribution in the fragments obtained at 12.33 eV may be the consequence of an excited state of the molecular ion ClNO₃⁺. In the ClO⁺ yield curve inflections at 14.1 eV, 16.8 eV and 17.4 eV are recognized. They may be assigned by energetic reasons to the formation of the excited states A(²B₁), B(²B₂) and C of NO₂ in agreement with the spectroscopic data of NO₂ given in the Ref. [21].

The NO⁺ yield curve arises very smoothly at 13.1 eV. This appearance energy neither fits the calculated value of process (19) (AE = 10.95 eV) nor of reaction (20) (AE = 13.58 eV)



For reaction (19) a molecular rearrangement has to be postulated which may include an activation barrier leading to considerable excess energy. The first ascend of the ion yield curve beginning between 14.1–14.3 eV and the second one may be correlated with a sequential decay mechanism, i.e. the decay of NO₂⁺ (³B₂) and NO₂⁺ (¹A₂) into NO⁺ + O. The onset at 17.4 eV correlates energetically with the process



but this assignment is very tentative.

BrNO₃

The photoionization mass spectrum of BrNO₃ shows NO₂⁺, BrO⁺, NO⁺ to be the most intensive fragment ions. In contrast to chlorine nitrate the parent ion BrNO₃⁺ is observed but with very low yield. In the mass spectrum signals of Br⁺ and Br₂⁺ have been observed due to about 2% bromine resulting from decomposition of the sample.

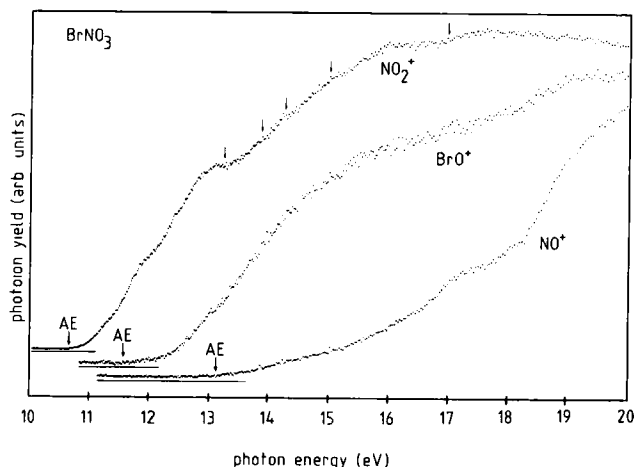
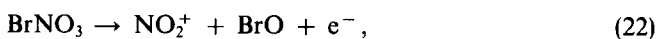


Fig. 4
Photoion yield curves of the fragment ions of BrNO₃. Features discussed in the text are marked by arrows

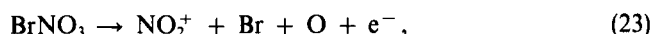
The heat of formation of BrNO₃ has not been reported hitherto. Taking the appearance energy of the process



and using the thermochemical data given in Table 2 we calculate $\Delta H_f^{298}(\text{BrNO}_3) = 71 \text{ kJ/mol}$. This value is somewhat higher than the value reported for chlorine nitrate (26.5 kJ/mol) [23], which is a reasonable result. Nevertheless it has to be mentioned that $\Delta H_f^{298}(\text{BrNO}_3)$ still may be a lower limit because nothing is known about excess energy released in (22). The heat of formation of the molecular cation can be evaluated using its appearance energy, it comes to 1100 kJ/mol.

The ion yield curves of the fragment ions show only weak diffuse structure comparable to that observed in the analogous ion yield curves resulting from chlorine nitrate.

The main fragmentation reaction produces NO₂⁺ ions with an appearance energy of 10.6 eV, close to the ionization energy of BrNO₃, resulting from the low stability of the parent ion as indicated by its weak intensity. In the NO₂⁺ yield curve a second onset around 13.2 eV is clearly expressed. Between the appearance energy and this onset only a weak inflection at about 11.7 eV appears. At higher energies inflections at 13.8 eV, 14.3 eV, 15 eV and a weak onset at 17 eV may be recognized. The second onset fits well with the appearance energy of

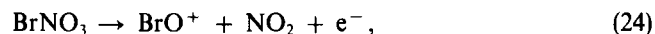


which is calculated to be 13.26 eV. The inflections at higher energies and the onset at 17 eV may be explained by the formation of electronically excited NO₂⁺ in reaction (23) as discussed above for chlorine nitrate (see Table 4).

Table 4
Calculated appearance energies of different NO₂⁺ states according to Eq. (22) using ΔE(NO₂⁺) values given in Table 3

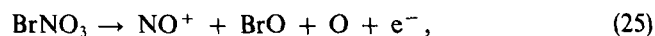
NO ₂ ⁺	¹ A ₁	³ B ₂	³ A ₂	¹ A ₂	¹ B ₂	³ A ₁	³ B ₁	¹ B ₁
AE (eV)	10.67	13.77	14.52	14.99	15.29	17.91	17.98	18.05

The BrO⁺ yield curve begins at 11.62 eV in fair agreement with the 11.7 eV inflection in the NO₂⁺ yield curve. We assign the BrO⁺ formation to

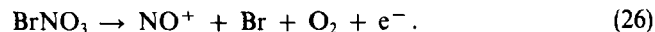


and assume that negligible amounts of excess energy are involved in this process.

The NO⁺ yield curve starts at 13.10 eV. This energy correlates with the onset in the NO₂⁺ yield curve at 13.2 eV. Therefore reaction



for which the appearance energy 13.37 eV is calculated, may be responsible for the NO⁺ formation near threshold. This value seems to be too large by 0.27 eV which points to small contributions of other processes to the NO⁺ formation. One process which is allowed energetically is



It requires 10.63 eV threshold energy which is far below the observed onset. This makes contributions of (26) rather improbable. There are some other reactions which seem to be of interest. Their discussion suffers from the lack of thermochemical data e.g. for BrO₂. By the same reason we cannot discuss the weak features at 17.2 eV and 18.2 eV properly.

Conclusion

It has been shown, that the main product of the high energy photochemistry of the discussed nitroxides are

NO₂⁺, NO⁺ and OH⁺, ClO⁺, BrO⁺ respectively. The inflections and different higher onsets in the ion yield curves of the fragment ions point to the contribution of processes from which excited species result. In many cases by comparison of spectroscopic and thermochemical data these processes could be assigned tentatively. It has been pointed out shortly that besides the classical molecular ions the formation of ionic molecular aggregates may be taken into account. As far as possible thermochemical data have been evaluated which fit well into the frame of literature data.

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