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Cluster ions: Gas-phase stabilities of $NO^+(CH_3CN)_n$ and $NO_2{}^+(CH_3CN)_n$ with $n=1$–5

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Abstract

The gas-phase equilibria of the clustering reactions of NO^+ and $NO_2{}^+$ with CH_3CN were measured with a pulsed electron-beam high-pressure mass spectrometer. Thermodynamic quantities, $\Delta H°_{n-1,n}$ and $\Delta S°_{n-1,n}$, of the $NO^+(CH_3CN)_n$ and $NO_2{}^+(CH_3CN)_n$ clusters with $n=1$–5 were determined. It was found that both clusters with $n=3$ are relatively more stable toward dissociation. For $n=1$–4, the thermochemical stabilities of $NO^+(CH_3CN)_n$ were observed to be slightly higher than those of corresponding $NO_2{}^+(CH_3CN)_n$. The results suggest a switch of the attacking site on the core ion for the fifth ligand molecule of these clusters at $n=4 \rightarrow 5$. (Int J Mass Spectrom 203 (2000) 93–100) © 2000 Elsevier Science B.V.

Keywords: Gas-phase equilibria; Bond enthalpies; Cluster ions; High-pressure mass spectrometer

1. Introduction

There has been growing interest in the physicochemical properties of the NO and NO_2 molecules in many fields. These species play an important role in the chemistry of the upper Earth's atmosphere and directly or indirectly are responsible for ozone destruction, formation of nitric acid, creation of organic nitrate compounds, and other significant effects [1–3]. Furthermore, it has been recognized that NO and its redox forms (NO^+ and NO^-) can play a key bioregulatory function and are of considerable interest in connection with human health [4–7]. Chemical ionization studies indicate that interesting reactivities can be obtained from the use of NO^+ as a reagent ion to characterize and locate double [8–10] or triple [11,12] bonds, cyclopropanes [13], and epoxides [14–17]. In addition, NO^+ may be an interesting reagent in the trace gas analysis of air [18] and the development of mass spectrometric techniques to monitor $NO_{n=1,2}$ in the atmosphere [19]. Ion-clustering processes form a sensitive basis for the stratospheric measurement of compounds that are present in the stratosphere using in situ mass spectrometry [20]. As the stabilities of cluster ions may play an important role in determining their relative concentrations and the composition of the upper atmosphere, the study of the binding energies (BEs) in the cluster ions is an important step for the understanding of atmospheric ion chemistry and nucleation processes.

In this article, the thermochemical stabilities of cluster ions $NO^+(CH_3CN)_n$ and $NO_2{}^+(CH_3CN)_n$ were determined by measuring the gas-phase equilibria of the clustering reactions (1) and (2):

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$$NO^+(CH_3CN)_{n-1} + CH_3CN+M$$

$$=NO^+(CH_3CN)_n+M, \qquad (1)$$

$$NO_2^+(CH_3CN)_{n-1}+CH_3CN+M$$

$$=NO_2^+(CH_3CN)_n+M, \qquad (2)$$

Acetonitrile, CH_3CN, has been chosen because of its relevance to atmospheric chemistry [21,22]. The BEs of gaseous NO^+ and $NO_2{}^+$ ions to different molecules, as well as the structures for some of ion-molecule complexes formed by these species, have been the subject of numerous experimental and theoretical studies [23–39]. So far, relatively few studies [34–39] have been performed on clustering reactions of NO^+ and $NO_2{}^+$ with neutral molecules (N_2, O_2, NO, N_2O, H_2O, CO_2, CH_3NO_2) that extended the measurements of BEs to higher-order clustering reactions. Knowledge of stepwise solvation energies as a function of degree of solvation may be helpful in understanding how the energetics evolves from that of the microscopic world toward that of solution.

2. Experimental

The experiments were performed with a pulsed electron-beam high-pressure mass spectrometer (PHPMS) and standard techniques that have been described previously [40]. Reactions in the ion source gold-plated on the inside were initiated by a 80-μs pulse of 500–1000eV electrons, and equilibria in the clustering reactions were observed for reaction times of 1–6 ms, in channels 10–60 μs wide. The ions escaping from the field-free ion source into an evacuated region were magnetically mass analyzed and collected in a multichannel analyzer as a function of their arrival time after the electron pulse.

For the measurements of the equilibria of the clustering reactions (1) and (2), a known amount of CH_3CN was introduced into 4–6 mbar of bath gas N_2 containing a small amount of NO or NO_2. Trace amounts of $CHCl_3$ were added as an electron capture agent to increase ion residence times. The ion source pressure was measured with a 10-mbar MKS capacitance manometer placed in the gas inlet line just before the ion source.

In the N_2/NO/CH_3CN mixture, the reactant ion NO^+ was mainly produced by the charge-transfer reactions (3) and (4)

$$N_2^+ + NO=NO^+ + N_2 \qquad (3)$$

$$N_4^+ + NO=NO^+ + 2N_2 \qquad (4)$$

For the studies of the equilibria of reaction (2), together with those of reaction (1), the $N_2/NO_2/CH_3CN$ gas mixture was used from which both $NO_2{}^+$ and NO^+ ions were produced. At relatively high temperatures ($T>450$ K), the ratio of ion intensities $\Sigma NO_2{}^+(CH_3CN)_n/\Sigma NO^+(CH_3CN)_n$ was observed to decrease with an increase in ion source temperature. This effect can be attributed to the well-known reaction $2NO_2 \leftrightarrow 2NO+O_2$. In the $N_2/NO_2/CH_3CN$ system, production of $NO_2{}^+$ was accomplished mainly by charge-transfer reactions analogous to (3) and (4).

The equilibrium constants, $K_{n-1,n}$, were evaluated at each temperature from the expression $K_{n-1,n}=I_n/I_{n-1}P$, where I_n/I_{n-1} is the measured ion intensity ratio of the corresponding clusters at equilibrium and P is the partial pressure of CH_3CN. The thermodynamic values, $\Delta H°_{n-1,n}$ and $\Delta S° n-1,n$, were derived from the temperature studies of the equilibrium constants using the van't Hoff equation: $\ln K_{n-1,n}=-\Delta H°_{n-1,n}/RT+\Delta S°_{n-1,n}/R$. The measured $K_{n-1,n}$ were found to be independent of the change of partial pressures of CH_3CN in the range 0.03–0.5 mbar.

The bending over in the van't Hoff plots was not observed in the present experiments. This indicates that the decomposition of cluster ions outside the ion source caused by the collision-induced dissociation was negligible. The clustering reactions (1) and (2) were measured down to the temperature just above the condensation point of the CH_3CN vapor ($\sim$230 K for 0.15 mbar of CH_3CN at a source pressure of 5 mbar).

N_2 (Polish product, 99.999%), NO (Aga, 99%), and CH_3CN (Roth, 99.9%) were used without further purification. NO_2 was prepared by thermal decomposition of $Pb(NO_3)_2$ according to reaction (5) and then purified.

$$2Pb(NO_3)_2 = 2PbO + 4NO_2 + O_2 \tag{5}$$

The sample gas NO_2 was passed over P_2O_5 to remove traces of moisture that may have been present in the system and was further purified by freeze-thaw cycles and by evacuating the sample at −77°C (dry ice) in order to eliminate O_2 and NO that were produced during the course of preparation of NO_2. The sample was stored in the dark to prevent photolysis.

3. Results and discussion

Examples of the temporal profiles of the $NO^+(CH_3CN)_n$ and $NO_2^+(CH_3CN)_n$ clusters with $n=2$–4 are shown in Fig. 1. The equilibria for reactions (1) and (2) are found to be established during ~100–400μs after the pulse, depending on the experimental conditions. The results of the measured equilibrium constants for these reactions are displayed as van't Hoff plots in Figs. 2 and 3. The measurement of the equilibrium constants could not be done for the cluster ions with $n>5$ because of the condensation of CH_3CN vapor on the wall of cold ion source below ~230 K.

The enthalpy and entropy changes are summarized in Table 1, together with results of earlier investigations [29,31]. The reported $-\Delta H°_{n-1,n}$ and $-\Delta S°_{n-1,n}$ values are the averages of at least six measurements, each calculated from a weighted least-squares fit of the van't Hoff plots obtained at various partial and total pressures of the mixtures used. It is worth mentioning that essentially the same $-\Delta H°_{n-1,n}$ and $-\Delta S°_{n-1,n}$ values were found for reaction (1) from the experiments using the $N_2/NO/CH_3CN$ and $N_2/NO_2/CH_3CN$ mixtures. The error limits in Table 1 show the statistical fluctuations; the absolute error from an unknown true value may be higher. The $-\Delta H°_{n-1,n}$ values obtained in this work are in fair agreement with the NO^+ and NO_2^+ BEs of CH_3CN experimentally measured by Cacace et al. [29,31] using the FT-ICR technique (Table 1).

In Fig. 4, the enthalpy changes for reactions (1) and (2) are shown as a function of n, together with the results for other CH_3CN-solvated clusters from previous works [40,41]. The observed decreases of the $-\Delta H°_{n-1,n}$ values with n are caused by the gradual charge dispersion in the cluster ions with the addition of new clustering molecules. It is likely that the bonding in these clusters is mainly electrostatic. The results in Fig. 4 show that in the case of reactions (1) and (2) there appear breaks for $-\Delta H°_{n-1,n}$ at $n=2$ and 3, respectively. A rather rapid decrease of bond energies with $n=1\rightarrow2$ suggests some charge redistribution within the $NO^+\cdot CH_3CN$ and $NO_2^+\cdot CH_3CN$ complexes, which are assumed to be formed by the interactions of the electronegative nitrogen atom of CH_3CN with the positively charged nitrogen atom of the NO^+ and NO_2^+ ions, respectively, as indicated in the structures at I of Fig. 5.

As shown in Fig. 4, rather rapid decreases of $-\Delta H°_{n-1,n}$ for $NO^+(CH_3CN)_n$ and $NO_2^+(CH_3CN)_n$ are observed after $n=3$. These results indicate that the clusters at $n=3$ are relatively more stable than the latter ones ($n>3$). The gaps in the spacing of the van't Hoff plots between the lines for $n=3$ and 4 (Figs. 2, 3) also show that these clusters are more stable toward dissociation. All these observations may imply the "shell" fills in $NO^+(CH_3CN)_n$ and $NO_2^+(CH_3CN)_n$ at $n=3$. To gain insight into this question, the quantitative criteria developed by Meot-Ner and Speller [42], based on enthalpy sequences and the spacing of the van't Hoff plots of consecutive clustering steps, were applied to the results of the present study. For both cluster ions, these criteria suggest shell effect at $n=3$ even if one takes into consideration the experimental errors. It is interesting to compare and contrast these observations with the data for the corresponding CH_3CN-solvated clusters, $M^+(CH_3CN)_n$,(M=Na, K, Rb, Cs [41], and C_3H_4N [40]). According to the above criteria [42], the breaks in $-\Delta H°_{n-1,n}$ for the clusters of smaller central ions, $Na^+(CH_3CN)_n$ and $K^+(CH_3CN)_n$, shown in Fig. 4, suggest the apparent shell formation with $n=3$, while in the case of the clusters with larger core ions, such as $Cs^+(CH_3CN)_n$ and $C_3H_4N^+(CH_3CN)_n$, no clear shell effects occur at $n=3$. This demonstrates that the shell effect is significantly dependent on the size of a core ion whose charge density dictates the ion-molecule interaction and bond distance and, as a consequence, affects the

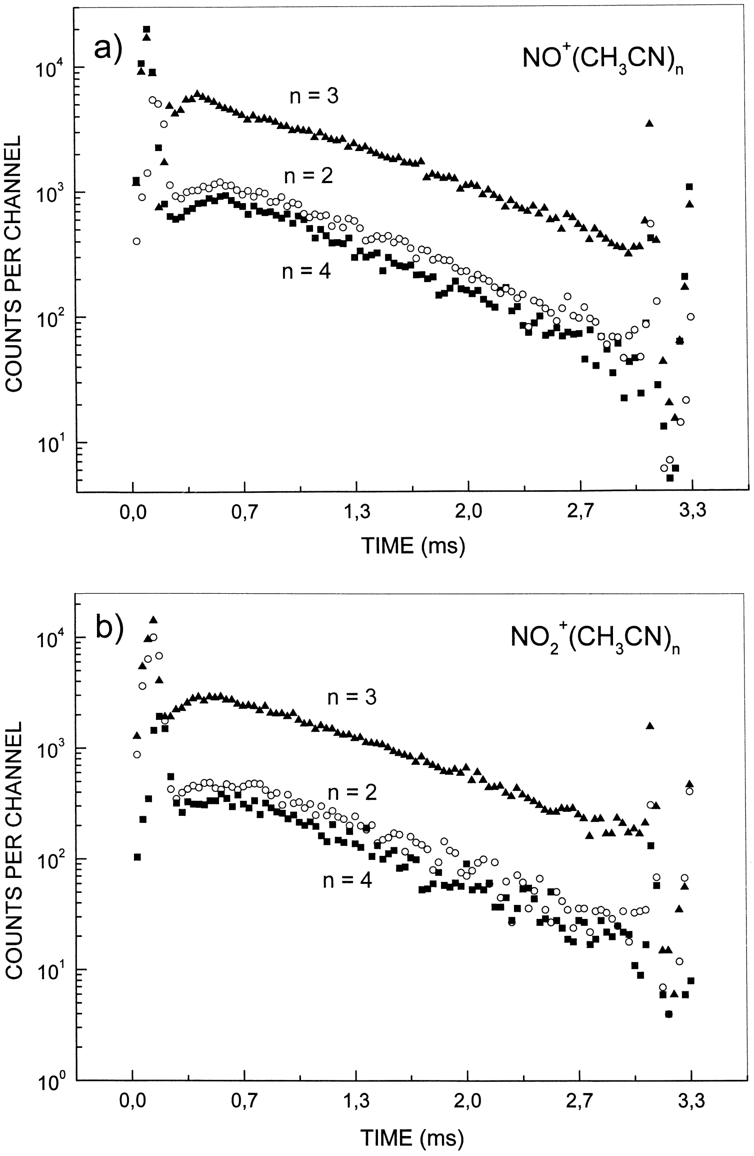

Fig. 1. The temporal profiles of cluster ions: (a) $NO^+(CH_3CN)_{n=2-4}$ and (b) $NO_2{}^+(CH_3CN)_{n=2-4}$ observed in the 2% CH_3CN/5% NO_2/N_2 gas mixture at 298 K and a source pressure of 5.1 mbar. Electron pulse width, 90 μs; channel dwell time, 30 μs; energy of incident electrons=800 eV. At 2.8 ms, a short (90 μs) pulse (+40 V) is applied to the repeller electrode in order to annihilate all ions produced in the ion source.

repulsive interaction between the ligand molecules within these clusters. The trend in the core ion size dependence of BEs ($-\Delta H°_{n-1,n}$) is clear from Fig. 4. All these results imply that the observed shell effect in the case of $NO^+(CH_3CN)_n$ and $NO_2{}^+(CH_3CN)_n$ probably reflects the CH_3CN ligand crowding in the apparent shell of $n=3$ rather than significant solvent reorganization about the new charge distribution and formation of a second solvation shell with $n=3\rightarrow4$. Interestingly, the relatively more stable clusters were also found [36,37] at $n=3$ for the $NO^+(O_2)_n$, $NO^+(CO_2)_n$, and $NO^+(N_2O)_n$ systems involving

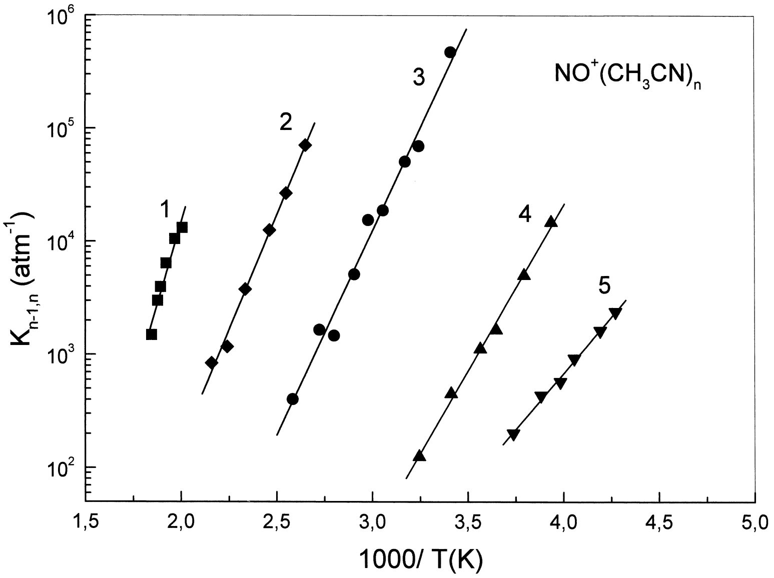

Fig. 2. Van't Hoff plots for the clustering reaction $NO^+(CH_3CN)_{n-1}$ $+CH_3CN=NO^+(CH_3CN)_n$. The number shown in the figure corresponds to the value of *n*.

smaller ligand molecules. It should be noted that the theoretical calculations [35–37] performed on the geometries of NO^+X_n ($X=N_2$, CO_2, and N_2O) and NO_2^+ $(N_2)_n$ predict that the N site of NO^+ and NO_2^+ is the most preferable for solvation by ligand molecules up to $n=4$. The observed distinct drops in the enthalpy sequences after $n=3$ for these systems were attributed to the exchange repulsion between the

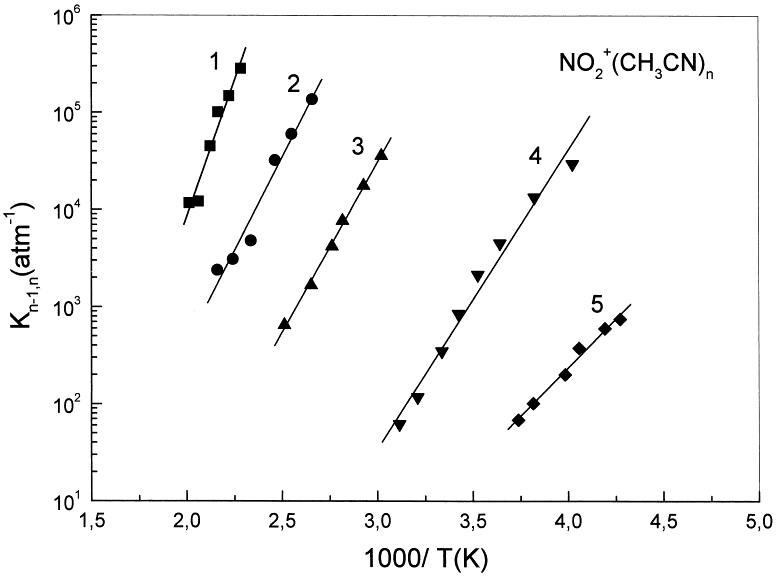

Fig. 3. Van"t Hoff plots for the clustering reaction $NO_2^+(CH_3CN)_{n-1}$ $+CH_3CN=NO_2^+(CH_3CN)_n$. The number shown in the figure corresponds to the value of *n*.

Table 1
Thermochemical data, $\Delta H°_{n-1,n}$ (kcal/mol) and $\Delta S°_{n-1,n}$ (cal/mol K) for the gas-phase clustering reactions: $NO^+(CH_3CN)_{n-1}+CH_3CN \leftrightarrow NO^+(CH_3CN)_n$ and $NO_2^+(CH_3CN)_{n-1}+CH_3CN \leftrightarrow NO_2^+(CH_3CN)_n$

	NO^+		NO_2^+	
n	$-\Delta H°_{n-1,n}$	$-\Delta S°_{n-1,n}$	$-\Delta H°_{n-1,n}$	$\Delta S°_{n-1,n}$
1	26.2 ± 1.1, 26.4 ± 2[a]	31 ± 2	24.8 ± 1.2, 25.5 ± 2.4[b]	31 ± 4
2	19.2 ± 1.1	33 ± 4	16.9 ± 0.9	25 ± 3
3	17.7 ± 1.1	33 ± 4	15.6 ± 1.1	28 ± 4
4	14.1 ± 1.1	35 ± 4	12.2 ± 1.1	30 ± 4
5	8.9 ± 0.6	24 ± 3	8.8 ± 1.1	23 ± 3

Note. $\Delta S°_{n-1,n}$ is standard state 1 atm. Results given correspond to the temperature of the van't Hoff plot. However, since the $\Delta S°$ dependence on the temperature is small, $\Delta S°$ values are approximately equal to those at 298 K.

[a] Ref. [31].

[b] Ref. [29].

ligand molecules but not to the shift of the attacking site from the N to the O site by the fourth ligand [37].

By analogy with the latter systems, one might expect that the first four CH_3CN molecules are able to add directly to the N site of the NO^+ and NO_2^+ central ions, with subsequent addition to form the symmetric structures like these shown in Fig. 5. Ab initio calculations [35–37,43] on the systems $M^+(CH_3CN)_n$, (M=Li and Na), NO^+X_n, ($X=N_2$, CO_2, and N_2O), and $NO_2^+(N_2)_n$ indicate that for n=2−4 the symmetric structures are expected to be most stable. The observed relatively small drops of $-\Delta H°_{1,2} \rightarrow -\Delta H°_{2,3}$ for $NO^+(CH_3CN)_n$ and $NO_2^+(CH_3CN)_n$ (Fig. 4) suggest that the complexes accommodate the next two CH_3CN molecules almost equivalently; this is in keeping with formation of the symmetric structures at II in Fig. 5.

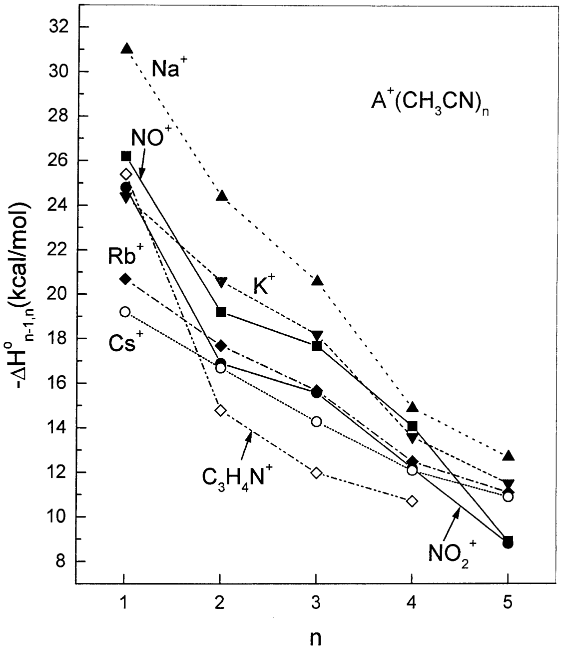

Fig. 4. The n dependence of the bond energies $-\Delta H°_{n-1,n}$ (kcal/mol) of the cluster ions: $NO^+(CH_3CN)_n$ (■), $NO_2^+(CH_3CN)_n$ (●); $Na^+(CH_3CN)_n$ (▲), $K^+(CH_3CN)_n$ (▼), $Rb^+(CH_3CN)_n$ (◆), $Cs^+(CH_3CN)_n$ (○; [41]); $C_3H_4N^+$ (◇; [40]).

As shown in Table 1 and Fig. 4, the BEs of $NO^+(CH_3CN)_{n\leq4}$ are found to be greater than those of corresponding $NO_2^+(CH_3CN)_{n\leq4}$, although the values obtained become slightly obscured if one takes the experimental errors into consideration. These observations are consistent with both the experimental [28–31,39] and calculated [25,26,28] results for singly solvated clusters, $NO^+_{n=1,2}-L$, where $L=CH_3OH$, CH_3CN, and CH_3NO_2, which show that in the case of NO^+ the BEs are larger than these of NO_2^+. This can be comprehended in terms of the smaller size and higher charge density of NO^+ compared with NO_2^+ [35]. However, the opposite prediction in this context was made by recent calculations [33], suggesting a stronger interaction for NO_2^+ than for NO^+ with several inorganic and organic molecules containing N and O heteroatoms. For example, the NO^+ and NO_2^+ affinities to CH_3OH were calculated [33] to be 23.26 and 25.18 kcal/mol, respectively. It should be noted that the experimentally measured values for NO^+ and NO_2^+ BEs to CH_3OH

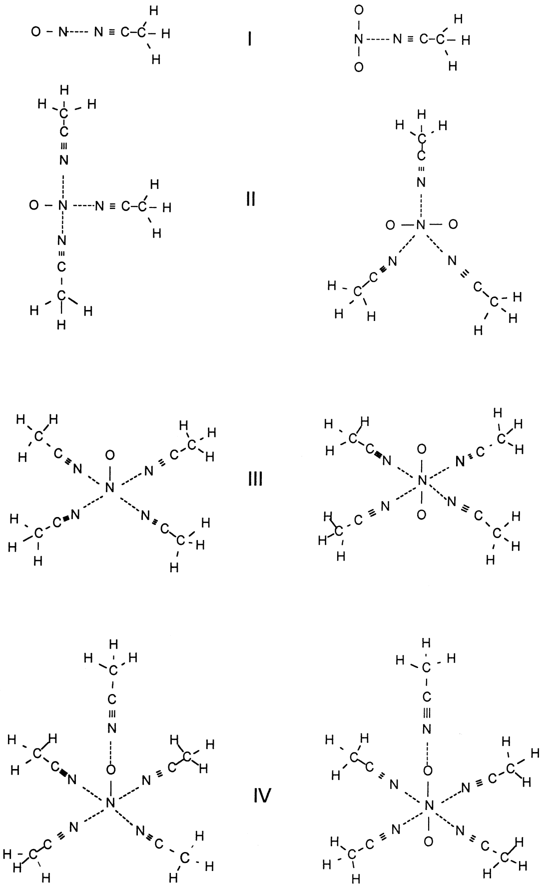

Fig. 5. Proposed structures of the $NO^+(CH_3CN)_n$ and $NO_2^+(CH_3CN)_n$ clusters, for $n=1$, 3–5.

are 23.3±2 kcal/mol [31] (for NO^+) and 19.2±2.3 kcal/mol [27], 22.3±2.4 kcal/mol [28], and 21.5±2.4 kcal/mol [29] (for NO_2^+), respectively.

As shown in Table 1, the noticeable decreases were observed in the $-\Delta S°_{n-1,n}$ values with $n=4\rightarrow5$ for $NO^+_{n=1,2}(CH_3CN)_n$. This is in marked contrast with the results obtained by Davidson and Kebarle for the alkali ion-acetonitrile clusters [41]. In the latter cases, significant increases in the $-\Delta S°_{n-1,n}$ values with $n=4\rightarrow5$ were found [41] for smaller ions. For instance, the $-\Delta S°_{3,4}$ and $-\Delta S°_{4,5}$ values are 27.9 and 41.2 eu for $Na^+(CH_3CN)_n$ and 27.5 and 33.7 eu for $K^+(CH_3CN)_n$, respectively. Such an observation can be attributed to a strong tendency of acetonitrile molecules to crowd around the core ion because of the large dipole moment of this compound (3.97 D) and relatively strong ion-molecule interaction.

The observed drops in the $-\Delta S°_{n-1,n}$ values (Table 1) with $n=4\rightarrow5$ for $NO^+_{n=1,2}(CH_3CN)_n$ suggest that the fifth ligands in the $n=5$ clusters are less crowded (have more freedom of motion) than these at $n=4$ and indicate the binding site changes (presumably from N site to O site) for the fifth ligands within the $NO^+_{n=1,2}(CH_3CN)_5$ clusters, for which the structures at IV in Fig. 5 appear probable. Ab initio calculations would be helpful in confirming this assignment. A change in the preferred binding site from nitrogen to oxygen of the NO^+ core ion was predicted for the fifth ligand molecule in the calculations [36] of the $NO^+(CO_2)_{n=1-5}$ clusters.

4. Conclusions

In this article, the gas-phase clusters $NO^+_{n=1,2}(CH_3CN)_{n=1-5}$ have been investigated. Thermochemical values, $-\Delta H°_{n-1,n}$ and $-\Delta S°_{n-1,n}$, were measured down to the condensation point of the CH_3CN vapor. The $NO^+(CH_3CN)_{n\leq4}$ clusters have binding energies slightly higher than those of the corresponding $NO_2^+(CH_3CN)_{n\leq4}$ clusters. The difference was ascribed to differences in the charge densities in the core ions, NO^+ and NO_2^+. The decreases in the $-\Delta S°_{n-1,n}$ values at $n=4\rightarrow5$ suggest a switch of the binding site for the fifth ligands within the $n=5$ clusters.

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