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Gas-phase clustering reactions of NO_2^-, $C_2H_3NO_2^-$, $C_2H_4NO_2^-$, $C_2H_5NO_2^-$ and $C_2H_5NO_4^-$ with $C_2H_5NO_2$

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Abstract

The gas-phase negative ion–molecule reactions of $C_2H_5NO_2$ have been investigated by pulsed electron-beam high-pressure mass spectrometer. Association of $C_2H_5NO_2$ with O_2^- leading to $C_2H_5NO_4^-$ and its clusters was observed, increasing in relative importance with decreasing temperature. The clustering reactions $A^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows A^-(C_2H_5NO_2)_n$ for A = NO_2, $C_2H_3NO_2$, $C_2H_4NO_2$, $C_2H_5NO_2$ and $C_2H_5NO_4$ were studied, and the thermochemical data, $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$, for these reactions were determined. The decay rates found for $CH_3NO_2^-(CH_3NO_2)_n$ and $C_2H_5NO_2^-(C_2H_5NO_2)_n$ are significantly higher than those of other clusters studied. We consider the influence of the dipole-bound states of the core anions, $CH_3NO_2^-$ and $C_2H_5NO_2^-$, on the transport dynamics of their clusters.

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

1. Introduction

Nitroalkanes are interesting in various respects. From a practical point of view, interest in aliphatic nitro compounds arises because of their explosive and propellant significance as well as their relevance to the atmospheric chemistry. From the fundamental point of view, nitroalkanes are of interest since they have large dipole moments. It is well known that if the dipole moment of the system exceeds ~2.5 Debye, then the "dipole-bound anion" may be formed [1–3]. Much attention has been directed recently to the formation and properties of the dipole and valence states of nitromethane anion, $CH_3NO_2^-$, and its clusters [4–9].

In a recent work [10], we studied the gas-phase clustering reactions $X^-(CH_3NO_2)_{n-1} + CH_3NO_2 \rightleftarrows X^-(CH_3NO_2)_n$ (X = Cl, NO_2, CH_2NO_2, CH_3NO_2 and CH_3NO_4) and thermochemical stabilities for $X^-(CH_3NO_2)_n$ with $n \leq 4$ were determined. It has been shown that the dynamics of the decay of $CH_3NO_2^-(CH_3NO_2)_n$ is remarkably faster than those of other clusters studied [10]. This effect is discussed in terms of a mechanism in which interconversion between valence and dipole states of $CH_3NO_2^-$ acts as a gateway to intra-cluster and intermolecular transfer of an excess electron in $CH_3NO_2^-(CH_3NO_2)_n$ providing more efficient loss of these clusters.

In the present paper, we report the first (to our knowledge) studies of the clustering reactions of $C_2H_5NO_2$ with a number of anions produced in $C_2H_5NO_2/N_2$ gas mixtures. Contrary to the wealth of information on the properties of $CH_3NO_2^-$ anions, the investigations on $C_2H_5NO_2^-$ are rather scarce. Lunt et al. [11] measured absolute total integral and total backward scattering cross-sections for $C_2H_5NO_2$ in the energy range from 50 meV to 1.2 eV. Dissociative electron attachment to $C_2H_5NO_2$ has been the subject of several investigations [12–14]. In a recent study, Märk and co-workers [14] reported the absolute partial cross-sections for the formation of eight fragment negative ions (NO_2^-, $C_2H_3NO_2^-$, O^-, OH^-, CN^-, CNO^-, HCN^- and NO^-) by electron attachment to $C_2H_5NO_2$ in the gaseous phase under collision-free conditions.

The main objective of the present study is to obtain information on the thermochemical stability of the cluster ions $A^-(C_2H_5NO_2)_n$ (A = NO_2, $C_2H_3NO_2$, $C_2H_4NO_2$, $C_2H_5NO_2$ and $C_2H_5NO_4$), by measuring the equilibria of the gas-phase clustering reaction

$$A^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows A^-(C_2H_5NO_2)_n \qquad (1)$$

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As a continuation of a previous study [10], we also report on the formation of a stable ion product, $C_2H_5NO_4^-$. Furthermore, we focused our attention on the dynamics of the decay of the observed ions. We believe the results to be of fundamental chemical significance and also to have implications for atmospheric ion chemistry as well as detonation chemistry in the context of a possible role of the ionic intermediates in the shock initiation and detonation mechanism of nitroalkanes.

2. Experimental

The measurements were performed with a pulsed electron-beam high-pressure mass spectrometer (PHPMS) utilizing standard techniques. The apparatus was the same as that used in our previous work [10]. The reagent gas in the ion source was ionized by 500–1000 eV electron beam. The ions produced were sampled through a slit (15 μm × 2 mm) and were magnetically mass analyzed. Ion detection was provided by a channeltron equipped with a conversion dynode. Mass spectra were registered by scanning the spectrometer electromagnet with continuous electron ionization. Thermodynamic data were obtained using an electron beam pulsed with periods of 95 μs for reaction times 1–6 ms, during which the intensity of a selected ion was collected in a multichannel analyzer as a function of its arrival time after the electron pulse. The surface of the ion source was coated with colloidal graphite to prevent charging of the surface of the ion exit slit and so resulting in a decrease of the ion intensities in the low-temperature region. All the experimental data presented here were obtained using graphite-coated ion source surface.

The carrier gas (N_2 at 1–5 mbar) was purified by passing it through a liquid N_2 cooled 4 Å molecular sieve trap. The partial pressure of $C_2H_5NO_2$ introduced into the carrier gas was varied over 0.2–0.4 mbar range, dependent on the experimental conditions.

The equilibrium constants, $K_{n-1,n} = (I_n/I_{n-1}P)$, where I_n/I_{n-1} is the measured ion intensity ratio of the respective ionic species at equilibrium and P is the partial pressure of $C_2H_5NO_2$. The thermodynamic values, $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$, were derived from the temperature studies of the equilibrium constants using the van't Hoff equation $\ln K_{n-1,n} = (\Delta S^\circ_{n-1,n}/R) - (\Delta H^\circ_{n-1,n}/RT)$. The measured $K_{n-1,n}$ for all clustering reactions studied were found to be independent of the change of the partial pressures of $C_2H_5NO_2$ in the range 0.2–0.4 mbar.

The reactant ion NO_2^- was produced by dissociative electron capture, reaction (2),

$$e^- + C_2H_5NO_2 \rightarrow (C_2H_5NO_2^-)^* \rightarrow NO_2^- + C_2H_5 \quad (2)$$

of the electrons slowed down to energy of about 0.73 eV [14] by the gas in the reaction chamber. As discussed below, NO_2^- can also arise from the ion–molecule reaction of the $O_2^-/C_2H_5NO_2$ system.

Also, $C_2H_3NO_2^-$ is produced by dissociative electron capture at ∼0 eV [14].

$$e^- + C_2H_5NO_2 \rightarrow (C_2H_5NO_2^-)^* \rightarrow C_2H_3NO_2^- + H_2 \quad (3)$$

Märk and co-workers [14] in low-pressure (∼10^{-6} mbar) of $C_2H_5NO_2$ studies found that the cross-section for formation of $C_2H_3NO_2^-$ is about two order of magnitude lower than that of NO_2^-. In the present high-pressure experiments, the yield of $C_2H_3NO_2^-(C_2H_5NO_2^-)_{n=0,1}$ was found to be about 15% of the total ion intensity at ∼420 K, but with a decrease of temperature the intensity of these ions rapidly decreased (see Fig. 2). This prevented measurements of the thermochemical properties of $C_2H_3NO_2^-(C_2H_5NO_2)_n$ with $n > 2$.

The $C_2H_4NO_2^-$ ion is not observed under collision-free conditions [12–14]. In the present study, this species is assumed to be produced by several exothermic proton transfer reactions, such as

$$O^- + C_2H_5NO_2 \rightarrow C_2H_4NO_2^- + OH \quad (4)$$

$$OH^- + C_2H_5NO_2 \rightarrow C_2H_4NO_2^- + H_2O \quad (5)$$

$$NO^- + C_2H_5NO_2 \rightarrow C_2H_4NO_2^- + HNO \quad (6)$$

The experiments with $CH_3CD_2NO_2$ show that $C_2H_4NO_2^-$ is produced in these reactions by the elimination of H^+ from α-C. As mentioned above, the O^-, OH^- and NO^- ions involved in the reactions (4)–(6) can be formed by electron capture to $C_2H_5NO_2$ [14]; O^- and OH^- may also arise from a trace amounts of impurities, O_2 and H_2O.

The parent anion, $C_2H_5NO_2^-$, is probably produced in a three-body capture of thermal electrons by the reactions (7) and (8a):

$$e^- + C_2H_5NO_2 + M \rightarrow C_2H_5NO_2^- + M \quad (M:\ \text{third body}) \quad (7)$$

$$e^- + 2C_2H_5NO_2 \rightarrow [(C_2H_5NO_2)_2^-]^* \leftrightarrow C_2H_5NO_2^- + C_2H_5NO_2 \quad (8a)$$

$$e^- + 2C_2H_5NO_2 \rightarrow [(C_2H_5NO_2)_2^-]^* \xrightarrow{M} (C_2H_5NO_2)_2^- \quad (8b)$$

In this study, as in the $CH_3NO_2^-$ case [10], the intensity of the monomer $C_2H_5NO_2^-$ was negligibly small and was observed only occasionally. This is most likely due to a short lifetime of this species with respect to autodetachment and/or dissociation into thermodynamically stable fragments.

The chemicals, N_2 (99.999%), $C_2H_5NO_2$ (99.5%, Aldrich) and $CH_3CD_2NO_2$ (99% atom D, Aldrich), were purchased from commercial sources. The $C_2H_5NO_2$ sample used was checked by GC/MS analysis which showed a trace amounts of nitropropane.

3. Results and discussion

3.1. General description

When 5 mbar N_2 buffer gas containing small amounts (~0.4 mbar) of $C_2H_5NO_2$ was ionized by an 800 eV electron beam at an ion source temperature of 353 K, $NO_2^-(C_2H_5NO_2)_n$ and $C_2H_5NO_4^-(C_2H_5NO_2)_n$ were produced as major negatively charged cluster ions. As shown in Fig. 1, a significant amounts of ions at *m/z* 224 and 225, which correspond to $C_2H_4NO_2^-(C_2H_5NO_2)_2$ and $C_2H_5NO_2^-(C_2H_5NO_2)_2$, respectively, were observed under these experimental conditions. At temperatures above ~350 K, small amounts of $C_2H_3NO_2^-(C_2H_5NO_2)_n$ with $n = 1$ and 2 were formed (not shown). The general formulas of these ions are deduced from the *m/z* values and confirmed by the correct mass shifts observed with $CH_3CD_2NO_2$ (see inset of Fig. 1).

As shown in Fig. 2, with a decrease of temperature below ~385 K, the $C_2H_5NO_4^-$ ion and its clusters started to be formed, and these species became the dominant product ions at the low-temperature end of the experiments. It is noteworthy that the growth of the total intensity of $C_2H_5NO_4^-(C_2H_5NO_2)_n$ with a decrease of temperature is accompanied by a decrease of $NO_2^-(C_2H_5NO_2)_n$. Variations in relative intensities of these series of cluster ions are similar to those found [10] for the analogous systems, $CH_3NO_4^-(CH_3NO_2)_n$ and $NO_2^-(CH_3NO_2)_n$. Thus, in line with the previously described concept for the formation of the core anion $CH_3NO_4^-$ in the CH_3NO_2/N_2 mixture [10], we adopt here the analogous mechanistic scenarios for $C_2H_5NO_4^-$ formation in the $C_2H_5NO_2/N_2$ system. Scheme 1 depicts the most likely mechanism involving an S_N2-type displacement reaction channel (9a) leading to NO_2^- and the termolecular addition path (9b) to form $C_2H_5NO_4^-$.

The O_2^- anion involved in this reaction mechanism is thought to be originated from trace amounts (~1 ppm) of O_2 present in the buffer gas as an impurity. Note that the effects of trace levels of the O_2 impurity on high-pressure mass spectra have been reported in several previous studies [15,16]. Also, a strong nucleophilic character of O_2^- in gas-phase ion–molecule reactions with a variety of organic compounds has been demonstrated [17].

The pathway (9a) is exothermic by 12.2 kcal/mol [18] (assuming $\Delta H_f(C_2H_5OO) = -1.8$ kcal/mol, see Ref. [17]) and it is expected to occur through the formation of an intermediate ion–neutral complex **I**, which may undergo charge migration and rearrangement to **II**, for NO_2^- displacement. Because the electron affinity of NO_2, $EA(NO_2) = 2.30$ eV (if not stated otherwise, all thermochemical data have been taken from Ref. [18]) is higher than that of C_2H_5OO, $EA(C_2H_5OO) = 1.186$ eV [19], the formation of NO_2^- is favored over $C_2H_5OO^-$. The anion product $C_2H_5NO_4^-$ may be treated as a collisionally stabilized ion–neutral intermediate complex **II**, pathway (9b). This pathway is presumed to occur in competition with the unimolecular dissociation of **II** via (9a). It is possible that the intermediate **II** may rearrange to the ethylperoxynitrate structure, $C_2H_5OONO_2^-$. However, due to experimental limitations, we were unable to verify this possibility.

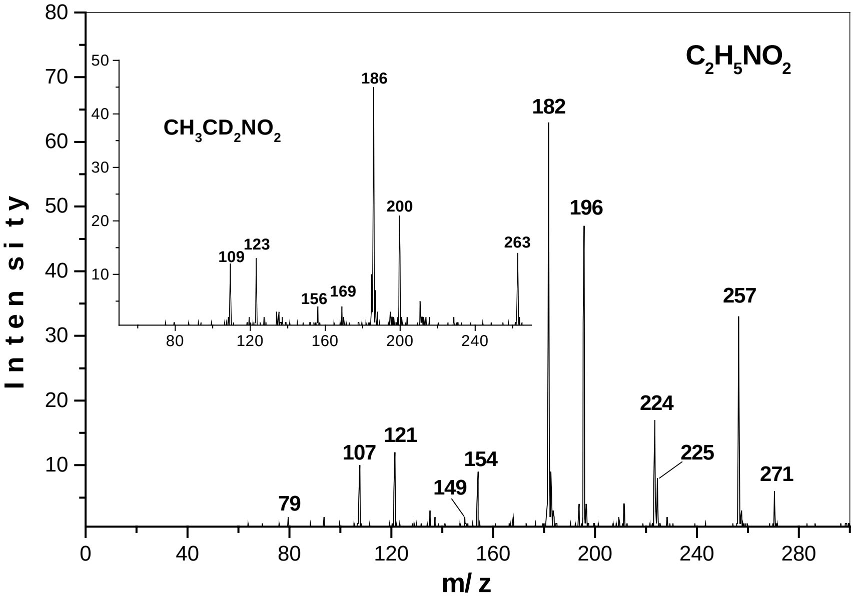


Fig. 1. Anion mass spectrum of the 7.8% $C_2H_5NO_2/N_2$ gas mixture recorded at source pressure of 4.8 mbar and $T = 306$ K. The inset shows partial mass spectrum of the mixture 6.9% $CH_3CD_2NO_2/N_2$ at 5 mbar and $T = 353$ K. The peaks at *m/z* 121, 196, 271 assigned to $NO_2^-(C_2H_5NO_2)_n$ ($n = 1$–3); *m/z* 107, 182, 257—$C_2H_5NO_4^-(C_2H_5NO_2)_n$ ($n = 0$–2); *m/z* 149, 224—$C_2H_4NO_2^-(C_2H_5NO_2)_n$ ($n = 1, 2$); *m/z* 225—$C_2H_5NO_2^-(C_2H_5NO_2)_2$; *m/z* 79, 154—$HNO_4^-(C_2H_5NO_2)_n$ ($n = 0, 1$); *m/z* 123, 200—$NO_2^-(CH_3CD_2NO_2)_n$ ($n = 1, 2$); *m/z* 109, 186, 263—$CH_3CD_2NO_4^-(CH_3CD_2NO_2)_n$ ($n = 0$–2); *m/z* 156—$HNO_4^-(CH_3CD_2NO_2)$.

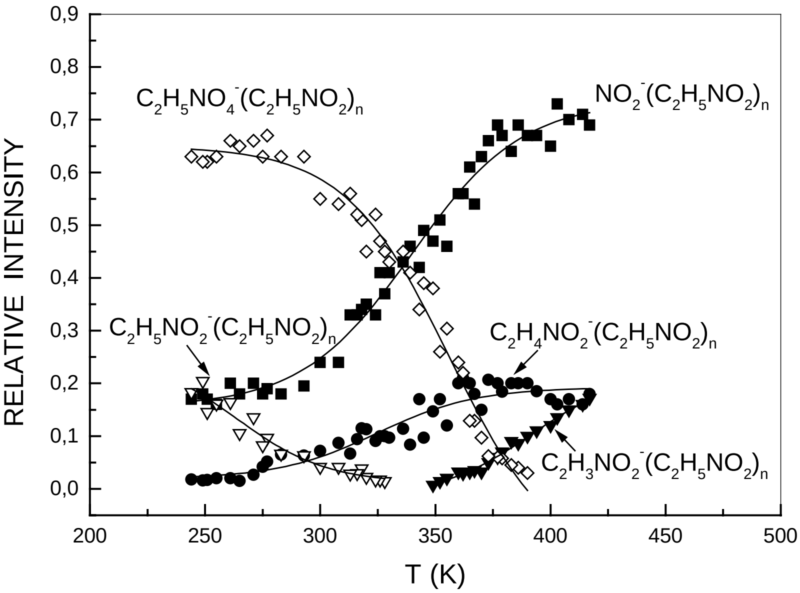


Fig. 2. Temperature dependence of the normalized total intensities of the cluster ions observed in the mass spectra of the 7.8% $C_2H_5NO_2/N_2$ mixture at a source pressure of 5 mbar.

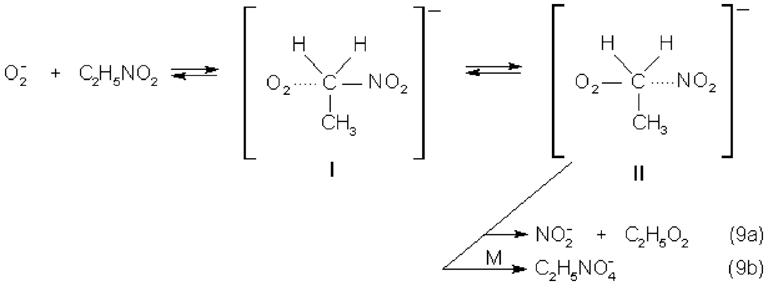
The proposed mechanism (Scheme 1) is in agreement with the results of temperature dependence measurements that show the increase in efficiency of $C_2H_5NO_4^-(C_2H_5NO_2)_n$ formation with decreasing of temperature (Fig. 2). This trend can be satisfactorily accounted for by consideration of the lifetime of the ion–neutral complex **II**: the lifetime of such complex and the probability of its termolecular stabilization is expected to increase with decreasing temperature. Similarly, the increase of lifetime of the excited $[(C_2H_5NO_2)_2^-]^*$ with decreasing temperature explains the observed trend in the growth of $C_2H_5NO_2^-(C_2H_5NO_2)_n$ whose formation is assumed to be initiated by the reaction channel (8b). The temperature dependence behavior of the relative intensities of $C_2H_3NO_2^-(C_2H_5NO_2)_n$ and $C_2H_4NO_2^-(C_2H_5NO_2)_n$, as shown in Fig. 2, is most likely a consequence of the influence of temperature on the internal energy of the excited $(C_2H_5NO_2^-)^*$ and other species involved in the production of the precursors of the core anions, $C_2H_3NO_2^-$ and $C_2H_4NO_2^-$ (see Section 2).

Another possible contribution to the $C_2H_5NO_4^-$ ion product is the third-body reaction

$$NO_2^- + C_2H_5O_2 + M \rightarrow C_2H_5NO_4^- + M \qquad (10)$$

The required precursor, the ethylperoxy radical $C_2H_5O_2$, may be formed in the ion source in the reaction of $C_2H_5 + O_2$ [20]; the C_2H_5 radicals are produced under the electron irradiation of nitroethane ($e^- + C_2H_5NO_2 \rightarrow NO_2^{\pm} + C_2H_5$). However, as previously stated for the CH_3O_2 system [10], due to the expected very low concentrations of both reactants $C_2H_5 + O_2$, and the product, $C_2H_5O_2$, the contribution of reaction (10) to the production of $C_2H_5NO_4^-$ should be negligible under the present experiments. On the other hand, we cannot exclude the possibility that the $C_2H_5 + O_2$ species adsorbed on the ion source walls lead to the formation of $C_2H_5O_2$, which after desorption to the gas phase can undergo reaction (10).

Finally, it should be mentioned that besides the series of the cluster ions discussed above, small amounts



Scheme 1.

of the $B^-(C_2H_5NO_2)_n$ clusters, where B^- stands for the core ion of *m*/*z* 79, are observed in both $C_2H_5NO_2/N_2$ and $CH_3CD_2NO_2/N_2$ mixtures (Fig. 1). These clusters started to be formed with a decrease in temperature below 350 K and the efficiency of their formation, as in the case of $C_2H_5NO_4^-(C_2H_5NO_2)_n$, increases with a decrease in temperature (not shown). Presumably, the *m*/*z* 79 ion corresponds to the HNO_4^- ion product from the termolecular addition reaction $[O_2^- + HNO_2] + M$, where the HNO_2 is either a minor impurity present in the nitroethane or a product of some reaction occurring in the ion source.

3.2. Stabilities of cluster ions

As an example, Fig. 3 shows the time profiles of the concentrations of clusters $C_2H_5NO_2^-(C_2H_5NO_2)_n$ and $C_2H_5NO_4^-(C_2H_5NO_2)_n$ observed in the 4.4% $C_2H_5NO_2/N_2$ gas mixture at the indicated temperatures. An approach to equilibrium for the clustering reactions (1) was observed ~200–400 μs after the electron pulse, depending on the experimental conditions. The results for the measured equilibrium constants for these reactions are displayed in the van't Hoff plots in Fig. 4. The lower limits of temperatures for the measurement of the equilibrium con-

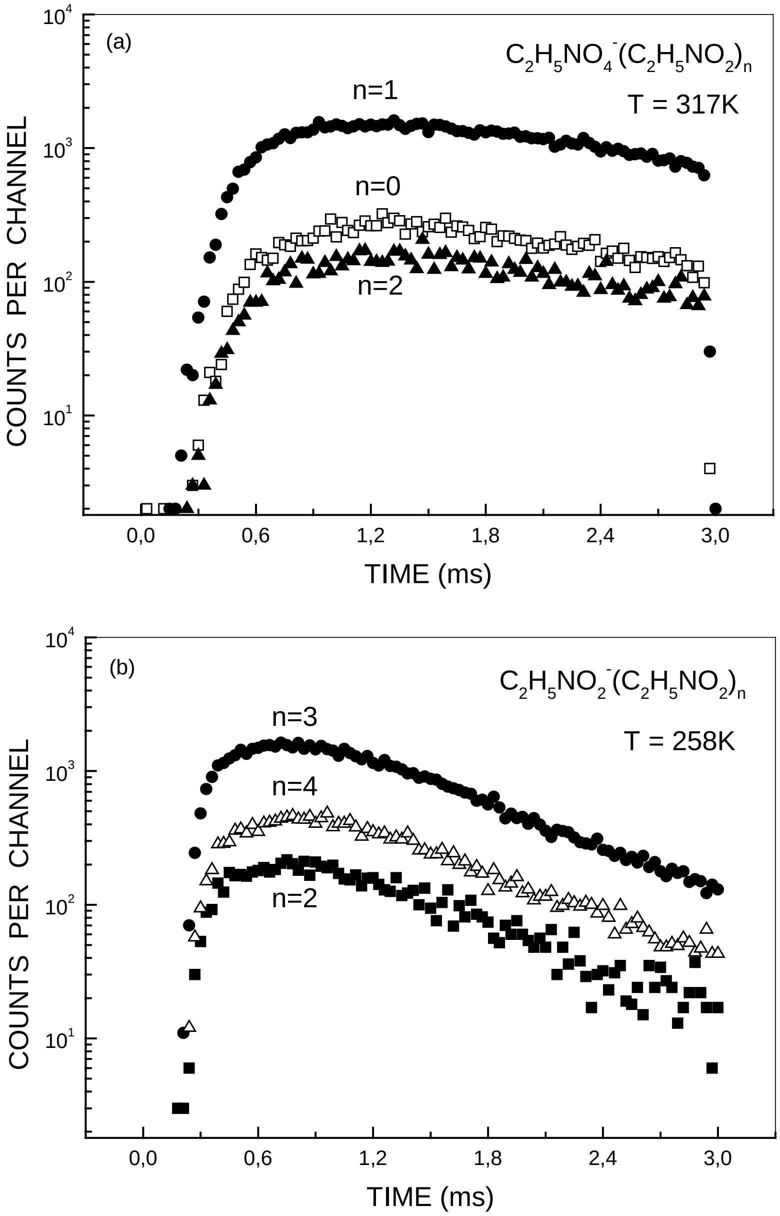


Fig. 3. The time profiles of the cluster ions: (a) $C_2H_5NO_4^-(C_2H_5NO_2)_n$ (n = 0–2) and (b) $C_2H_5NO_2^-(C_2H_5NO_2)_n$ (n = 2–4) observed in the 7% $C_2H_5NO_2/N_2$ mixture at indicated temperatures and a source pressure of 5.6 mbar. Electron pulse width, 95 μs; channel dwell time, 30 μs; energy of incident electrons = 600 eV. At 3 ms, a short (90 μs) pulse (−50 V) is applied to the repeller electrode in order to annihilate all ions produced in the ion source.

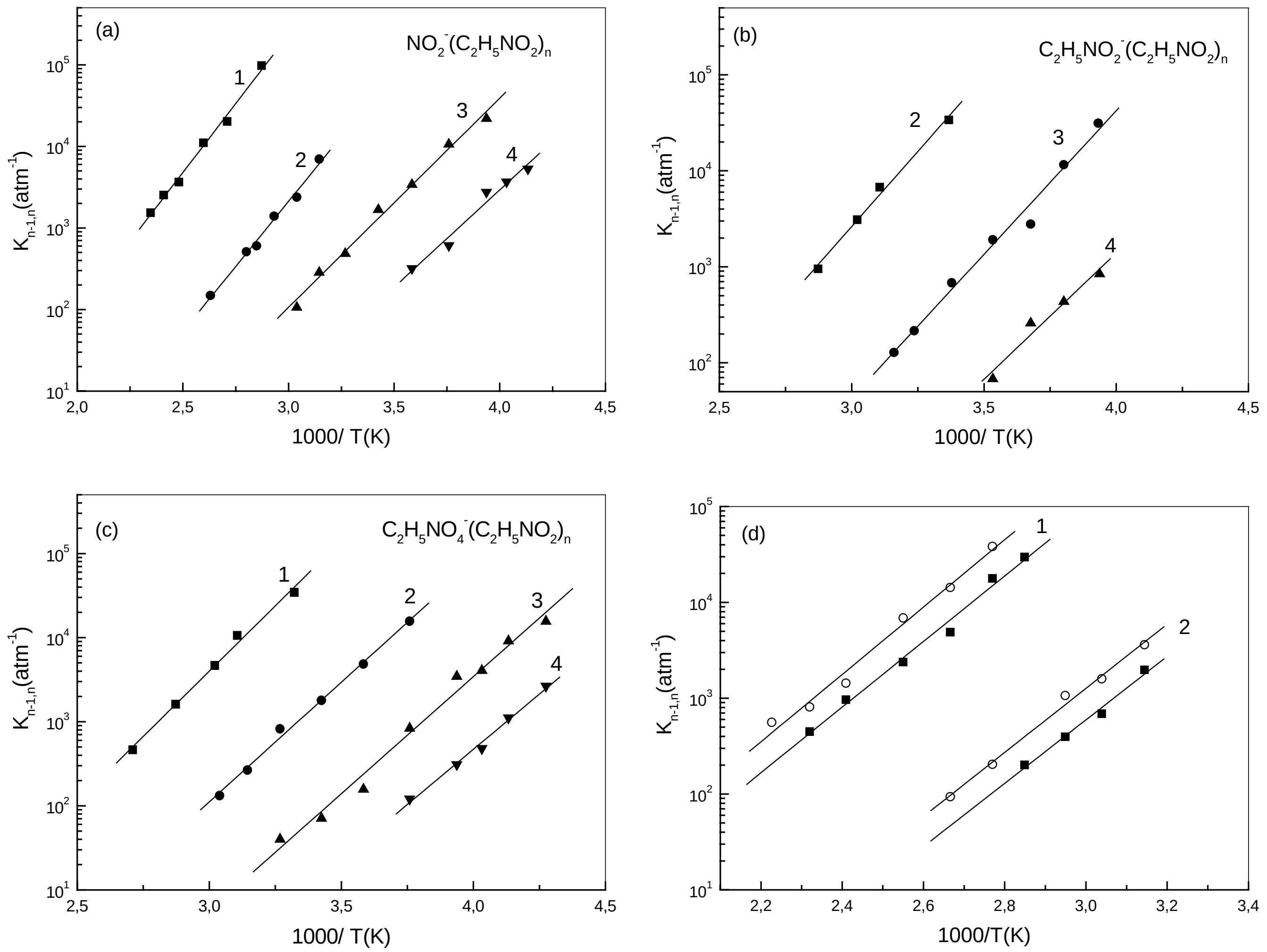


Fig. 4. van't Hoff plots for the equilibria $A^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows A^-(C_2H_5NO_2)_n$, A = (a) NO_2; (b) $C_2H_5NO_2$; (c) $C_2H_5NO_4$; (d) $C_2H_3NO_2$—solid symbols; $C_2H_4NO_4$—open symbols. The numbers shown in the figures correspond to the value of n.

stants correspond to the start of condensation of $C_2H_5NO_2$. The enthalpy and entropy changes derived from such plots for all the systems studied are listed in Tables 1 and 2. The reported $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ values are averages of several measurements, each obtained from a weighted least-squares fit of the van't Hoff plots. The error limits show the statistical fluctuations; the absolute error from an uncertain true value may be greater. It is likely that the core–ligand bonding in the clusters studied is mainly electrostatic in nature, dominated by the ion-dipole and the ion-induced dipole interactions.

Fig. 5 shows the n dependence of $\Delta H^\circ_{n-1,n}$ for $A^-(C_2H_5NO_2)_n$, A = NO_2, $C_2H_5NO_2$ and $C_2H_5NO_4$, together with those of $X^-(CH_3NO_2)_n$, X = NO_2, CH_3NO_2

Table 1

Thermochemical data, ΔH° (kcal/mol) and ΔS° (cal/mol K)[a], for the gas-phase clustering reactions: $NO_2^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows NO_2^-(C_2H_5NO_2)_n$, $C_2H_5NO_2^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows C_2H_5NO_2^-(C_2H_5NO_2)_n$ and $C_2H_5NO_4^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows C_2H_5NO_4^-(C_2H_5NO_2)_n$

n	NO_2^-		$C_2H_5NO_2^-$		$C_2H_5NO_4^-$	
	$-\Delta H^\circ_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$	$-\Delta H^\circ_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$	$-\Delta H^\circ_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$
1	15.8 ± 0.5	23 ± 2			14.3 ± 0.8	26 ± 3
2	14.9 ± 0.5	27 ± 3	14.6 ± 0.2	28 ± 2	12.7 ± 0.8	28 ± 3
3	11.8 ± 0.5	26 ± 2	13.6 ± 0.3	30 ± 3	11.3 ± 0.9	30 ± 3
4	11.0 ± 0.5	28 ± 2	11.9 ± 0.5	33 ± 3	10.5± 0.9	33 ± 4

[a] Standard state 1 atm. Results given to the temperature of the van't Hoff plot. However, since the ΔS° dependence upon the temperature is small, ΔS° values are approximately equal to those at 298 K.

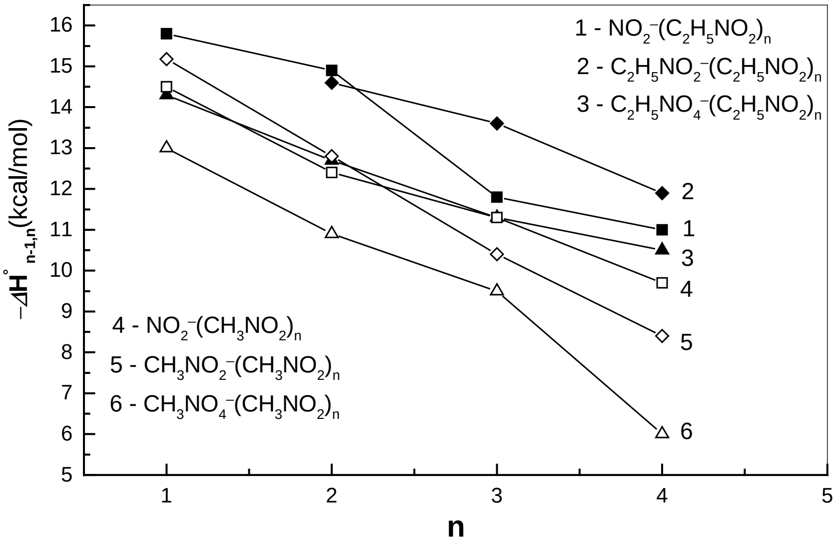


Fig. 5. The n dependence of the bond energies $-\Delta H^\circ_{n-1,n}$ (kcal/mol) of the indicated clusters. The $-\Delta H^\circ_{n-1,n}$ values for $X^-(CH_3NO_2)_n$, X = NO_2, CH_2NO_2 and CH_3NO_4, taken from Ref. [10]; for $CH_3NO_2^-(CH_3NO_2)_{n=1}$, see Ref. [4].

and CH_3NO_4, from the previous studies [4,10]. In general, the $-\Delta H^\circ_{n-1,n}$ values for $A^-(C_2H_5NO_2)_n$ are greater than those for the analogous $X^-(CH_3NO_2)_n$. These differences in $-\Delta H^\circ_{n-1,n}$ values may be due to the larger polarizability ($\alpha = 9.63\,Å^3$) and dipole moment ($\mu = 3.65$ Debye) of $C_2H_5NO_2$ than CH_3NO_2 ($\alpha = 7.37\,Å^3$ and $\mu = 3.46$ Debye) taken from the CRC Handbook, 66th edition.

The positive end of the dipole of $C_2H_5NO_2$ is mainly localized on the CH_3 group whose hydrogens are expected to interact with the negative charge site of anions in the clustering reactions. In the case of $NO_2^-(C_2H_5NO_2)_n$, the $-\Delta H^\circ_{1,2}$ value is little smaller than that of $-\Delta H^\circ_{0,1}$. This result most likely reflects the hypothesis that the first two $C_2H_5NO_2$ molecules hydrogen bond to the negatively charged O atoms in NO_2^-. The observed drop in $-\Delta H^\circ_{n-1,n}$ at $n = 3$, may be attributed to an increase of the exchange repulsion between ligands accommodated by the core anion in $NO_2^-(C_2H_5NO_2)_n$ at $n \geq 3$.

For $C_2H_3NO_2^-(C_2H_5NO_2)_n$ and $C_2H_4NO_2^-(C_2H_5NO_2)_n$, the thermochemical properties could not be measured for $n > 2$ due to reduced intensities of the ions with three and more ligand molecules at low temperatures (<350 K). The $-\Delta H^\circ_{n-1,n}$ and $-\Delta S^\circ_{n-1,n}$ values for $n = 1$ and 2 of these cluster ions are given in Table 2. These results show that the bonding energies of both core anions, $C_2H_3NO_2^-$ and $C_2H_4NO_2^-$, to $C_2H_5NO_2$ at $n = 1$ and 2 are similar and close to those of $NO_2^-(C_2H_5NO_2)_{n=1,2}$, respectively. This indicates that the nature of these core anions does not significantly affect the strength of their interaction with the first two $C_2H_5NO_2$ molecules, thus supporting the notion that the ion–molecule bond formation in the clustering reactions of these ions is mainly dictated by the electrostatic interactions of the anionic site located on the NO_2^- moiety.

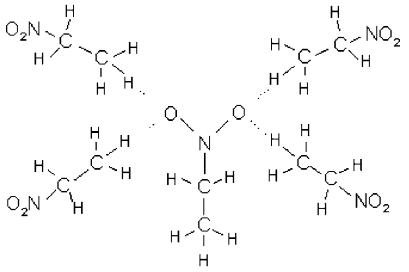
Table 2
Thermochemical data, ΔH° (kcal/mol) and ΔS° (cal/mol K)[a], for the gas-phase clustering reactions: $C_2H_3NO_2^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows C_2H_3NO_2^-(C_2H_5NO_2)_n$ and $C_2H_4NO_2^-(C_2H_5NO_2)_{n-1} + C_2H_5NO_2 \rightleftarrows C_2H_4NO_2^-(C_2H_5NO_2)_n$

n	$C_2H_3NO_2^-$		$C_2H_4NO_2^-$	
	$-\Delta H^\circ_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$	$-\Delta H^\circ_{n-1,n}$	$-\Delta S^\circ_{n-1,n}$
1	15.7 ± 0.8	24 ± 3	16.2 ± 0.8	24 ± 3
2	15.2 ± 0.8	32 ± 3	15.4 ± 0.8	31 ± 3

[a] Standard state 1 atm. Results given to the temperature of the van't Hoff plot. However, since the ΔS° dependence upon the temperature is small, ΔS° values are approximately equal to those at 298 K.

In the case of $C_2H_5NO_4^-(C_2H_5NO_2)_n$, the $-\Delta H^\circ_{n-1,n}$ values for $n = 1$ and 2 are smaller than those of other clusters studied with $n = 1$ and 2 (Tables 1 and 2). The slightly smaller bond energies in $C_2H_5NO_4^-(C_2H_5NO_2)_{n=1,2}$ most likely are due to the lower charge density localized on the anionic sites of the core ion $C_2H_5NO_4^-$. At present, however, it is difficult to speculate on the structures of the $C_2H_5NO_4^-$ system without the background of theoretical calculations and further experiments using other mass spectrometric techniques, e.g., collision-induced dissociation and neutralization reionization.

The $C_2H_5NO_2^-$ ion is not observed as an isolated compound under collision-free conditions [12–14]. In the present high-pressure experiments, a very small amount of $C_2H_5NO_2^-$ was detected occasionally. We anticipate that the formation of $C_2H_5NO_2^-(C_2H_5NO_2)_n$ is initiated by termolecular reaction (8b). By analogy to the observed location of an excess charge in the $CH_3NO_2^-(CH_3NO_2)_{n=0\text{–}2}$ anions on a single CH_3NO_2 molecule [4], the same situation for $C_2H_5NO_2^-(C_2H_5NO_2)_n$ might be expected. As in the $CH_3NO_2^-$ case [4], it is likely that both valence and dipole-bound forms of $C_2H_5NO_2^-$ can be initially produced: however, the dipole-bound states are presumably collisionally relaxed. In the valence state, the excess electron is mostly located on the NO_2^- group, and it is reasonable to suggest that the formation of $C_2H_5NO_2^-(C_2H_5NO_2)_n$ proceeds similarly as $NO_2^-(C_2H_5NO_2)_n$ by the interaction of the CH_3 group of $C_2H_5NO_2$ with the O atoms of $C_2H_5NO_2^-$. A possible structure for $C_2H_5NO_2^-(C_2H_5NO_2)_n$ with $n = 4$ is shown in **III**.



III

The relatively large values of $-\Delta S^\circ_{n-1,n}$ with $n \geq 2$ for $C_2H_5NO_2^-(C_2H_5NO_2)_n$ and other clusters studied (Tables 1 and 2) indicate that the freedom of motion in these systems is highly restricted. This implies that intramolecular hydrogen bonding occurs in these clusters.

As can be seen directly from Fig. 6 by comparing the time dependence of the ion intensities of the three major cluster ions, the loss of $C_2H_5NO_2^-(C_2H_5NO_2)_{n=2}$ is considerably faster than that of the two other clusters. In the measurements performed under the same experimental conditions, this picture is also observed for the corresponding smaller and larger clusters of these series. A similar situation has been also found for the decay rate of $CH_3NO_2^-(CH_3NO_2)_n$ with respect to those of other clusters [10]. In this context, it should be noted that for non-reactive ions, the loss of intensity with time represents the decay due to ion diffusion to the walls of the ion source.

Although this latter observation with respect to the rapid decays of $CH_3NO_2^-(CH_3NO_2)_n$ [10] and $C_2H_5NO_2^-(C_2H_5NO_2)_n$ is attributable to their disappearance in some ion–molecule reactions with trace amounts of eventual impurities, but we cannot exclude another process which may contribute to the total loss of these clusters during the diffusion time. In the previous paper [10], we have postulated that the dipole-mediated pathway arising from the interaction between the dipole and valence states of $CH_3NO_2^-$ may be involved in the “transport” mechanism of $CH_3NO_2^-(CH_3NO_2)_n$. For the bare $CH_3NO_2^-$, both states as well as their coupling have been well documented experimentally and theoretically [4–9]. Possibly, the interconversion between these two anionic forms can open a channel for the electron loss, and in the solvated anion can open an avenue to the intracluster transfer of an excess electron and so provide a more efficient mechanism for the “transport” and the dynamics of the loss of $CH_3NO_2^-(CH_3NO_2)_n$. No data seem to be available on the binding of electrons to $C_2H_5NO_2$, but since the dipole moment of this molecule is sufficiently large, the formation of the valence and dipole-bound forms of $C_2H_5NO_2^-$ may be expected [1–3], and the transport mechanism of $C_2H_5NO_2^-(C_2H_5NO_2)_n$ is most probably similar to that proposed for $CH_3NO_2^-(CH_3NO_2)_n$.

From the experiments such as those shown in Fig. 6, the pseudo first-order rate constants, ν, obtained from the slopes of the linear portions of the ln(Intensity) versus time plots, can be used to compare the dynamics of the decay of the cluster ions during their transport to the walls. When the ion masses are close, similar rates for their diffusional loss are expected [21]. The slopes of the linear sections for the

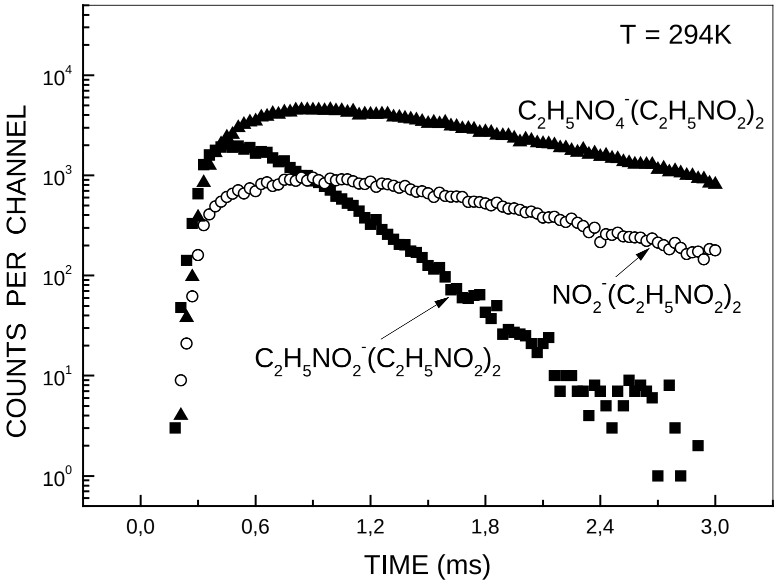


Fig. 6. Ion intensity of the indicated clusters as a function of time after 95-μs electron pulse observed in the 8.5% $C_2H_5NO_2/N_2$ mixture at a source temperature of 294 K and a constant total pressure of 2 mbar.

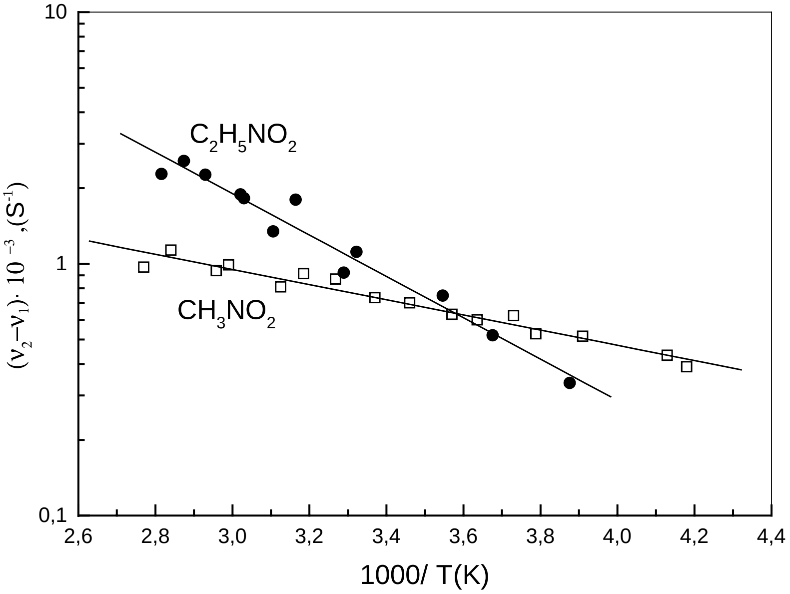


Fig. 7. Arrhenius representation of the "reactive" decays of the clusters $CH_3NO_2^-(CH_3NO_2)_n$ and $C_2H_5NO_2^-(C_2H_5NO_2)_n$ during transport to the ion source walls. $(\nu_2 - \nu_1)$ is the difference between the pseudo first-order rate constants ($\nu = \Delta\ln[\text{Intensity}]/\Delta t$) obtained from the slopes of the linear portions of runs (see Fig. 6). ν_1 represents the decay of $NO_2^-(CH_3NO_2)_n$ or $NO_2^-(C_2H_5NO_2)_n$, while ν_2 represents that of $CH_3NO_2^-(CH_3NO_2)_n$ or $C_2H_5NO_2^-(C_2H_5NO_2)_n$ for the CH_3NO_2 and $C_2H_5NO_2$ systems, respectively.

loss of $NO_2^-(C_2H_5NO_2)_n$ and $C_2H_5NO_4^-(C_2H_5NO_2)_n$ were found to be similar under the same experimental conditions, as exemplified in Fig. 6 for the clusters with $n = 2$. In the previous study [10], analogous results were obtained for $X^-(CH_3NO_2)_n$, $X = NO_2$, CH_2NO_2 and CH_2NO_4. Assuming that the disappearance of $NO_2^-(CH_3NO_2)_n$ and $NO_2^-(C_2H_5NO_2)_n$ is only due to the diffusion to the walls and taking their first-order rate constants, ν_1, as the components of the diffusional loss to be involved in the rate constants, ν_2, of the decays of $CH_3NO_2^-(CH_3NO_2)_n$ and $C_2H_5NO_2^-(C_2H_5NO_2)_n$, then the differences $(\nu_2 - \nu_1)$ to a first approximation may be considered as the "reactive" contributions of these clusters to the dynamics of their loss. [Note: in the case of CH_3NO_2 the ratio ν_2/ν_1 shows essentially no temperature dependence.] The plots of the logarithm of $(\nu_2 - \nu_1)$ versus $1/T$ show a linear dependence (Fig. 7) leading to the energy barriers of 60 and 165 meV which can be associated with the "reactive" loss of $CH_3NO_2^-(CH_3NO_2)_n$ and $C_2H_5NO_2^-(C_2H_5NO_2)_n$, respectively. If we assume that the dipole-mediated mechanism is dominant in this process, then the observed temperature dependence of $(\nu_2 - \nu_1)$ may reflect the population of coupling between the dipole and valence anion states which provide a pathway to electron loss in the core anions, $CH_3NO_2^-$ and $C_2H_5NO_2^-$, of these clusters. It is worthwhile to note that the magnitude of the energy barrier of 60 meV found here for $CH_3NO_2^-(CH_3NO_2)_n$ is significantly higher than the dipole electron affinity of 12 meV reported [4] for the bare $CH_3NO_2^-$. This difference may arise from the solvation effect. This approach, however, is somewhat speculative and should be viewed with caution because a possible reactive loss of the $CH_3NO_2^-(CH_3NO_2)_n$ and $C_2H_5NO_2^-(C_2H_5NO_2)_n$ clusters due to eventual impurities cannot be excluded.

As mentioned in the Section 2, the $C_2H_5NO_2$ sample contains a trace levels of a $C_3H_7NO_2$ impurity. Inspection, however, of the mass spectra of $C_2H_5NO_2/N_2$ mixture (see, e.g., Fig. 1) registered at different temperatures reveals that peaks attributable to the series $A^-(C_2H_5NO_2)_{n-1}C_3H_7NO_2$, $A = NO_2$, $C_2H_4NO_2$ and $C_2H_5NO_2$, do not exceed the signal-to-noise level. This indicates that the possible ion–molecule reactions, such as the addition of $C_3H_7NO_2$ to $A^-(C_2H_5NO_2)_{n-1}$ and the ligand exchange of $C_2H_5NO_2$ for $C_3H_7NO_2$ in $A^-(C_2H_5NO_2)_n$ to yield $A^-(C_2H_5NO_2)_{n-1}C_3H_7NO_2$, if occur, are of very minor importance, and therefore, their influence on both the thermochemical data and the reactive loss of the cluster ions is expected to be negligible, if exists at all. In connection with the latter process, it is also useful to consider the possibility of the loss of $(C_2H_5NO_2)_n^-$ by the electron transfer reaction according to: $(C_2H_5NO_2)_n^- + C_3H_7NO_2 \rightarrow (C_2H_5NO_2)_n + C_3H_7NO_2^-$. Although no data were found for the EAs of $(C_2H_5NO_2)_n$ and $C_3H_7NO_2$, but it can safely be assumed that the EAs of the monomers, $C_2H_5NO_2$ and $C_3H_7NO_2$, are close to each other. If we further consider the following relation $\text{EA}(C_2H_5NO_2)_n \cong \text{EA}(C_2H_5NO_2)_{n-1} + \text{D}[(C_2H_5NO_2)_{n-1}^- - C_2H_5NO_2]$, where $\text{D}[(C_2H_5NO_2)_{n-1}^- - C_2H_5NO_2]$ is the dissociation energy (equivalent to $-\Delta H^\circ_{n-1,n}$) for the cluster ion, $(C_2H_5NO_2)_n^-$, it is obvious that the EAs of $(C_2H_5NO_2)_n$

with $n \geq 2$ should exhibit a considerably larger values than EA($C_3H_7NO_2$). Therefore, the electron transfer from $(C_2H_5NO_2)_n^-$ to $C_3H_7NO_2$ is not to be expected for $n \geq 2$.

4. Conclusions

In the present and previous [10] paper, we examined the negative ion chemistry of CH_3NO_2 and $C_2H_5NO_2$ which at temperatures below ∼380 K are observed to associate readily with O_2^-. The product ions $CH_3NO_4^-$ and $C_2H_5NO_4^-$ from this reaction and their clusters may have implications for the development of atmospheric chemistry and could be of interest as the elements of the mechanism in the shock initiation and detonation chemistry of nitroalkanes for which detonation properties are defined by the conditions of shock decomposition and the oxygen balance in the explosive.

The gas-phase thermochemical stabilities of $A^-(C_2H_5NO_2)_n$, $A = NO_2, C_2H_3NO_2, C_2H_4NO_2, C_2H_5NO_2$ and $C_2H_5NO_4$, were determined. The observed much higher decay rates of $CH_3NO_2^-(CH_3NO_2)_n$ and $C_2H_5NO_2^-(C_2H_5NO_2)_n$ than those of other cluster ions studied may be considered as an indication that the dipole-bound states of the core anions $CH_3NO_2^-$ and $C_2H_5NO_2^-$ may be involved in the loss of their clusters.

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