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The formation of chloride adducts in the detection of dinitro-compounds by ion mobility spectrometry

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Abstract

The formation of chloride adducts by dinitro-alkanes in the gas phase has been studied by ion mobility spectrometry. Special emphasis was placed on the association of chloride with 2,3-dimethyl-2,3-dinitrobutane (DMNB), a prospective taggant for plastic explosives, but the reactions of chloride with 1,4-dinitrobutane (DNB) and with 2,3-dimethyl-2,4-dinitropentane (DMDNP) were also studied briefly. The thermal stabilities of the chloride adducts as shown by the effect of temperature on the mobility spectra were found to decrease in the order $DNB{\cdot}Cl^- > DMDNP{\cdot}Cl^- > DMNB{\cdot}Cl^-$. The equilibrium $Cl^- + DMNB = DMNB{\cdot}Cl^-$ was set up in the drift tube and by monitoring the drift time of the single peak due to the equilibrium mixture of Cl^- and $DMNB{\cdot}Cl^-$ as the DMNB concentration was varied, the equilibrium constant was determined. Measurement of the equilibrium constant at a series of temperatures gave $\Delta H^0 = -92.1 \pm 3.1$ kJ mol^{-1} and $\Delta S^0 = -92.1 \pm 7.4$ J K^{-1} mol^{-1} for the association. The enthalpy change for the formation of the most stable of the dinitro adducts, $DNB \cdot Cl^-$, is estimated to be 20 kJ mol^{-1} more negative than that for the DMNB adduct. The order of the stabilities of the chloride complexes is consistent with the number of very acidic hydrogen atoms on the carbon atoms in positions α to the nitro groups viz. DNB, 4; DMDNP, 2; DMNB, 0. The determined vapor pressures of DMNB and DNB over the respective ranges −20 to +50 °C and −10 to +30 °C respectively, are described by the equations $\log P = 19.82 \pm 0.09 - (4\,878 \pm 26)/T$ (K) and $\log P = 18.08 \pm 0.29 - (4\,274 \pm 81)/T$ (K), where P is the vapor pressure in parts per billion by volume, T is temperature in kelvin, and the quoted uncertainties are the standard errors. (Int J Mass Spectrom 209 (2001) 185–195) © 2001 Elsevier Science B.V.

Keywords: Ion mobility spectrometry; Chloride adducts; Dinitro compounds; Dimethyldinitrobutane; Enthalpy of association

1. Introduction

Ion mobility spectrometry (IMS) is an analytical technique that is used extensively for, amongst other things, the field detection of narcotics and explosives [1,2]. The advantages that favor its use are the simplicity of the equipment and of its operation, with detection limits in the ppb and ppt range. The detection of organic explosives such as dynamite, TNT, and smokeless powder is sometimes carried out by sampling and preconcentrating ambient air followed by IMS analysis, in a search for the presence of traces of the vapors of nitrate esters or nitro-compounds. This approach is feasible when the vapor pressure of

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the chemical is relatively high. For example, the 100 ppm vapor pressure of ethylene glycol dinitrate at room temperature, the most volatile effluent of dynamite formulations, enables ion mobility spectrometry to be employed for the detection of this explosive [3]. However, plastic explosives such as RDX and PETN, with very low vapor pressures of around 10 ppt at 25 °C [4] are not amenable to detection by ambient air sampling. Consequently it has been proposed that a taggant should be added in the manufacture of plastic explosives that has a vapor pressure sufficiently high to enhance the delectability of the explosives by IMS [5,6].

2,3-dimethyl-2,3-dinitrobutane (DMNB) has been suggested as having suitable properties as a taggant [5,6]. It is readily available and has a suitable vapor pressure at 25° C. However, there is a major drawback to the detection of nitro compounds by ion mobility spectrometry since in both negative and positive ion modes at ambient temperature, ionization is partly or wholly dissociative. This results in the formation of small ions with high mobilities that are not separable from the reactant and other ions present in the spectrum of ambient air. For example, in the negative ion mode of operation, NO_2^- is a major ion in the spectra of nitro and dinitro paraffins [7]. Also, in many cases when an ion mobility spectrometer is employed as a detection device it is advantageous to operate at temperatures above ambient since this simplifies the spectrum by removing slowly desorbing molecules and also reduces ion solvation by water and other background molecules. Unfortunately, at elevated temperatures the dissociative component of ionization increases, causing peaks representative of the molecules of interest to diminish in importance or to completely vanish from the spectrum. In order to circumvent this problem of thermal instability, ion/molecule association reactions may be used to generate more thermally stable ions that are well separated from reactant and other peaks in the mobility spectrum.

Mass spectrometric chemical ionization studies over many years have demonstrated the gas phase stability and hence analytical usefulness of adducts formed by the attachment of chloride to neutral molecules [8]. For example, Bouma and Jennings showed that chloride attachment leads to abundant adducts of organonitrates [9]. Hence, not surprisingly, chloride has been shown to be a useful reactant ion in several areas of analysis by IMS [3,10]. A major advantage of its use is its selectivity in forming stable adducts with molecules having acidic hydrogens. Such adducts have much larger collision cross sections and therefore much lower mobilities than the reactant chloride ion. The adduct peaks are then well resolved from the reactant and other ions.

In this paper we report on an IMS study of the association of the chloride ion with dinitro-alkanes. Special emphasis has been placed on an investigation of the association of chloride with DMNB but the association of chloride with 1,4-dinitrobutane (DNB) and with 2,3-dimethyl-2,4-dinitropentane (DMDNP) have also been studied briefly. IMS has been employed to determine the standard entropy and standard enthalpy for the association of chloride with DMNB by measurement of ion mobilities over a range of temperatures.

2. Experimental

Initial studies on the thermal stability of the chloride adducts of dinitroalkanes were conducted with a Phemto-Chem MMS-160 ion mobility spectrometer-mass spectrometer (PCP Inc., West Palm Beach, FL). The signal from the IMS was averaged with a Nicolet 1170 signal averager. The analog-to-digital converter resolution used with the Nicolet was 12 bit, with a full-scale setting of ±4V. The basic measurement with this instrument was the drift time, which could be measured to ±0.02 ms. Ion mobility peaks in the spectra were identified by mass spectral scans when the shutter to the drift region was opened to allow a continuous flow of ions through the drift region to the mass spectrometer.

Most measurements of the chloride adduct formation with DMNB were performed using a Phemto-Chem MMS-390HT ion mobility spectrometer-mass spectrometer. The data acquisition systems for both the ion mobility and the mass spectrometer sections of

Table 1
Instrument parameters

Instrument	Phemto-Chem MMS-160 (analytical)	Phemto-Chem MMS-390HT (equilibrium studies)
cell length	14 cm	15 cm
drift length	8 cm	5 cm
carrier gas (UHP nitrogen with $\sim$5% dichloromethane,	200 mL/min	80–200 mL/min (introduced via IMS exhaust)
drift gas	UHP nitrogen, 600 mL/min	UHP nitrogen, 300–800 mL/min with 0–70 ppm DMNB
inlet and drift temperature:		
DMNB experiments	50 °C	100 °C to 190 °C
DMDNP	100 °C	n/a
DNB	150 °C	n/a
mode of operation:	negative ions	negative ions
drift field (V cm^{-1})		
DMNB	250	167
DMDNP	214	
DNB	193	
dwell time	55 μs/channel	70 μs/channel
data points	512	256
gate width	0.2 ms	0.2 ms
number of scans	256	1200
IMS pressure	atmospheric	atmospheric
mass spectrometer pressure	n/a	6×10^{-5} Torr
MS scanning speed	n/a	1000 amu/s

this instrument were built in house, and utilized an IBM-compatible PC operating on an MS Windows 3.11 platform. The mobility data were collected by means of LabView (National Instruments) software in combination with an Atlanta Signal Processing Inc. Chimera DSP card fitted with a Texas Instrument TMS320C25 microprocessor and an AD16 analog-to-digital and digital-to-analog daughter board; the resolution was 16 bits and the full-scale amplitude was ±4V. The MS data were acquired via an MCS-plus multichannel scaler card (EG&G Ortec) controlled by an A68-BI MCS emulation software; the card was operated in a single-channel analyzer input mode with 12-bit resolution.

Mass-identification of ions responsible for particular IMS peaks resulted from a threefold approach. First, an ion mobility spectrum was obtained by gating the shutter grid of the ion mobility spectrometer cell and allowing the ion mobility electrometer to collect data; under these conditions, the quadrupole mass filter was not used. Second, a mass spectrum was obtained by holding the shutter grid of the ion mobility spectrometer open, thus allowing all ions formed to drift through the tube and into the mass spectrometer. Finally, mass-identified ion mobility spectra were recorded by gating the shutter grid as in the first procedure but with the mass spectrometer tuned to a specific *m/z* value. The mass spectrometer detector then responded to only one ionic species and, consequently, the mobility spectrum contained a peak corresponding only to ions of that particular *m/z* value. The experimental parameters used to operate the two ion mobility spectrometer-mass spectrometer instruments are presented in Table 1.

For the equilibrium study of the association of chloride with DMNB, different concentrations of DMNB were introduced into the drift region of the Phemto-Chem 390-HT. To accomplish this, the flow regimen of the instrument was slightly modified, as depicted schematically in Fig. 1 and described in Table 1. The purpose of this modification was to accurately control the concentration of DMNB in the drift region and to alter the flow pattern in the ionization region of the IMS so that both the drift gas with DMNB and the carrier gas with dichloromethane

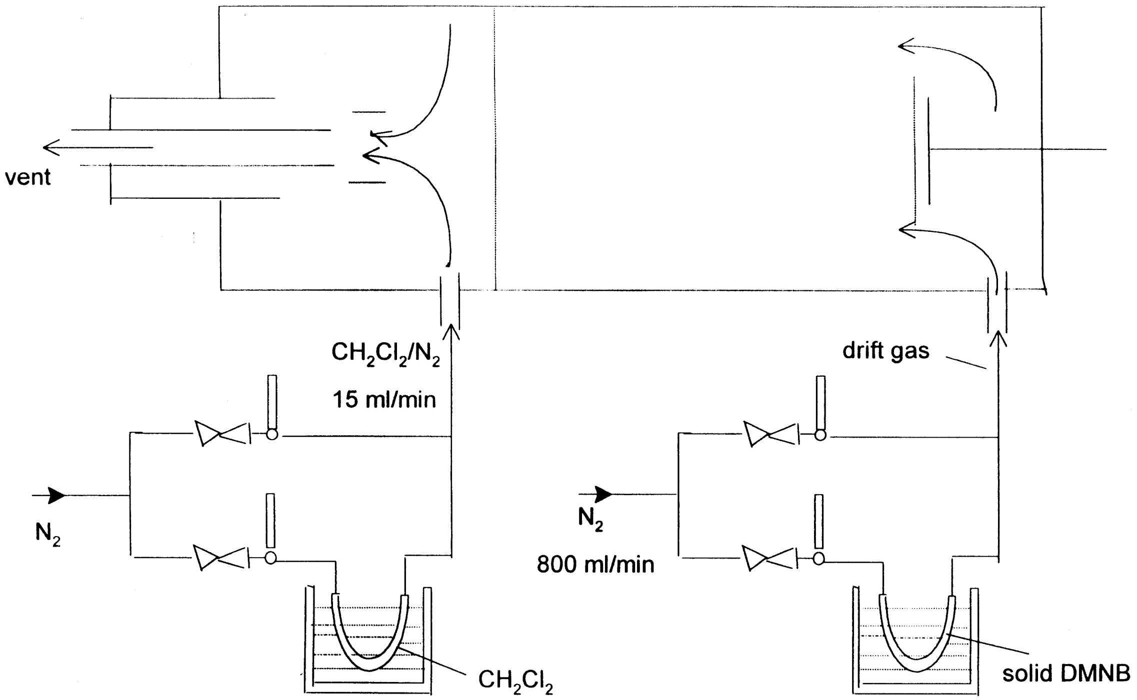

Fig. 1. The flow patterns of the carrier and drift gases in the in the study of equilibrium of the association of chloride with DMNB.

(the source of chloride ions) would pass through the ionization region together. Dynamic gas blending systems similar to those used for the vapor pressure measurements described previously [3] were utilized for generating the known concentrations of DMNB and CH_2Cl_2 in the appropriate streams.

2,3-Dimethyl-2,3-dinitrobutane (DMNB) was purchased from Aldrich and used without further purification. 2,3-Dimethyl-2,4-dinitropentane (DMDNP) and 1,4-dinitrobutane (DNB) were synthesized by CYE (Box 443, Bath, Ontario, Canada K0H 1G0). The purity of the materials was >98% as estimated by gas chromatography. Dichloromethane was distilled-in- glass grade from Caledon (Georgetown, Ontario, Canada). Ultrahigh purity nitrogen was used for both sample introduction and drift gas. For the determination of the thermodynamic parameters for the binding of chloride to DMNB the moisture content of the nitrogen was reduced to a low but unknown level by passage through activated molecular sieve and anhydrous calcium sulfate.

3. Results and discussion

3.1. Vapor pressure measurements

In order to carry out the experiments it was necessary to feed into the ion mobility spectrometer known gas-phase concentrations of DMNB. This necessitated knowledge of the vapor pressure of DMNB over a range of temperatures. The vapor pressure of DMNB has been determined over the temperature range −20 to +50 °C using a continuous-flow vapor generator in combination with a preconcentration/thermal desorption technique and gas chromatographic analysis. The experimental setup has been described [11]. The vapor pressure of DNB over the temperature range −10 to +30 °C, was also determined by the same method. An electron capture detector was used for the gas chromatographic determination of DMNB and a nitrogen specific detector was used for DNB. The data obtained are plotted according to

$$\text{Log P (ppb)} = A + B/T \quad (1)$$

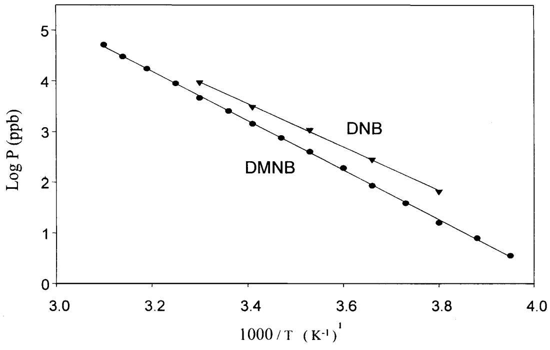

Fig. 2. The temperature dependences of the vapor pressures of DMNB and DNB.

as log P versus 1/T, in Fig. 2, where P is the vapor pressure in ppb (parts per billion by volume), and T is the temperature in kelvin. Linear regression analysis of the data yielded the parameters in Table 2; the quoted errors are standard errors.

At 25 °C, the equilibrium vapor concentration of DNB, 5.6×10^3 ppb, is greater than that of DMNB, 2.7×10^3 ppb, by slightly more than a factor of two.

3.2. Chloride adduct formation in the ion mobility spectra of dinitro alkanes

When the MMS-160 was used as an analytical instrument with Cl^- as reactant ion, dinitro compounds were allowed only in the mobility spectrometer source region. Under this condition, chloride adducts of DMNB, DNB, and DMDNP were observed in the ion mobility spectra of each of the compounds at 50 °C. A typical mobility spectrum obtained from a sample of the headspace above solid DMNB is shown in the inset of Fig. 3. The associated mass spectrum of all ions in the mobility spectrum is also shown. There are two major peaks in the mobility spectrum that mass spectrometry, in the absence and presence of DMNB, proved to be due to Cl^- and its hydrate, $H_2O{\cdot}Cl^-$ (first peak) and $DMNB{\cdot}Cl^-$ (later peak). The small peaks in the mobility spectrum with mobilities intermediate between those of $H_2O{\cdot}Cl^-$ and $DMNB{\cdot}Cl^-$ have counterparts in the mass spectrum but were not identified. Similar spectra, showing the presence of $DNB{\cdot}Cl^-$ and $DMDNP{\cdot}Cl^-$ were obtained when the headspaces above the other two dinitro compounds were sampled.

When the temperature of the mobility spectrometer was raised to 60 °C $DMNB{\cdot}Cl^-$ was no longer observable, but $DNB{\cdot}Cl^-$ and $DMDNP{\cdot}Cl^-$ were still present. At 110 °C the $DMDNP{\cdot}Cl^-$ was no longer observable but $DNB{\cdot}Cl^-$ was still present. This peak finally vanished at a temperature of 160 °C. The thermal stabilities of the chloride adducts of the three dinitro compounds therefore decrease in the order $DNB{\cdot}Cl^- > DMDNP{\cdot}Cl^- > DMNB{\cdot}Cl^-$.

The appearance or nonappearance of a chloride adduct in the ion mobility spectrum may be understood through a combination of thermodynamic and kinetic arguments. In the ion source region before the shutter, on the assumption that the concentration of the dinitro-compound (A) is significantly greater than that of the chloride ions, the association reaction

$$A + Cl^- + M \Leftrightarrow A{\cdot}Cl^- + M \tag{2}$$

will attain equilibrium, i.e. the forward and backward reactions proceed at the same rate. M is a third body required to thermalize the nascent complex and to activate the complex for its dissociation. However, since reaction at constant temperature and pressure occurs with a constant concentration of M, its presence will be ignored in the following discussion. The forward and backward reactions of Eq. (2) may therefore be treated respectively as second and first order processes. The equilibrium constant, K, for the reaction and the rate constants for the forward and backward reactions, k_+ and k_-, are related by

$$K = \frac{[A{\cdot}Cl^-]c^o}{[A][Cl^-]} = \frac{k_+c^o}{k_-} \tag{3}$$

in which c^o is the standard concentration corresponding to the standard pressure of one atmosphere.

In the drift region, where no A is present, the reaction can only proceed in the backward direction for which the lifetime of $A{\cdot}Cl^-$ is $1/k_-$. The drift time, t_1, for $DMNB{\cdot}Cl^-$ at 50 °C was 11.4 ms and since this ion was not observed at or above 60 °C, its backward rate constant, k_-, at 50 °C must have been $\sim 10^2\ s^{-1} = 1/t_1$. If it is assumed that a complex is

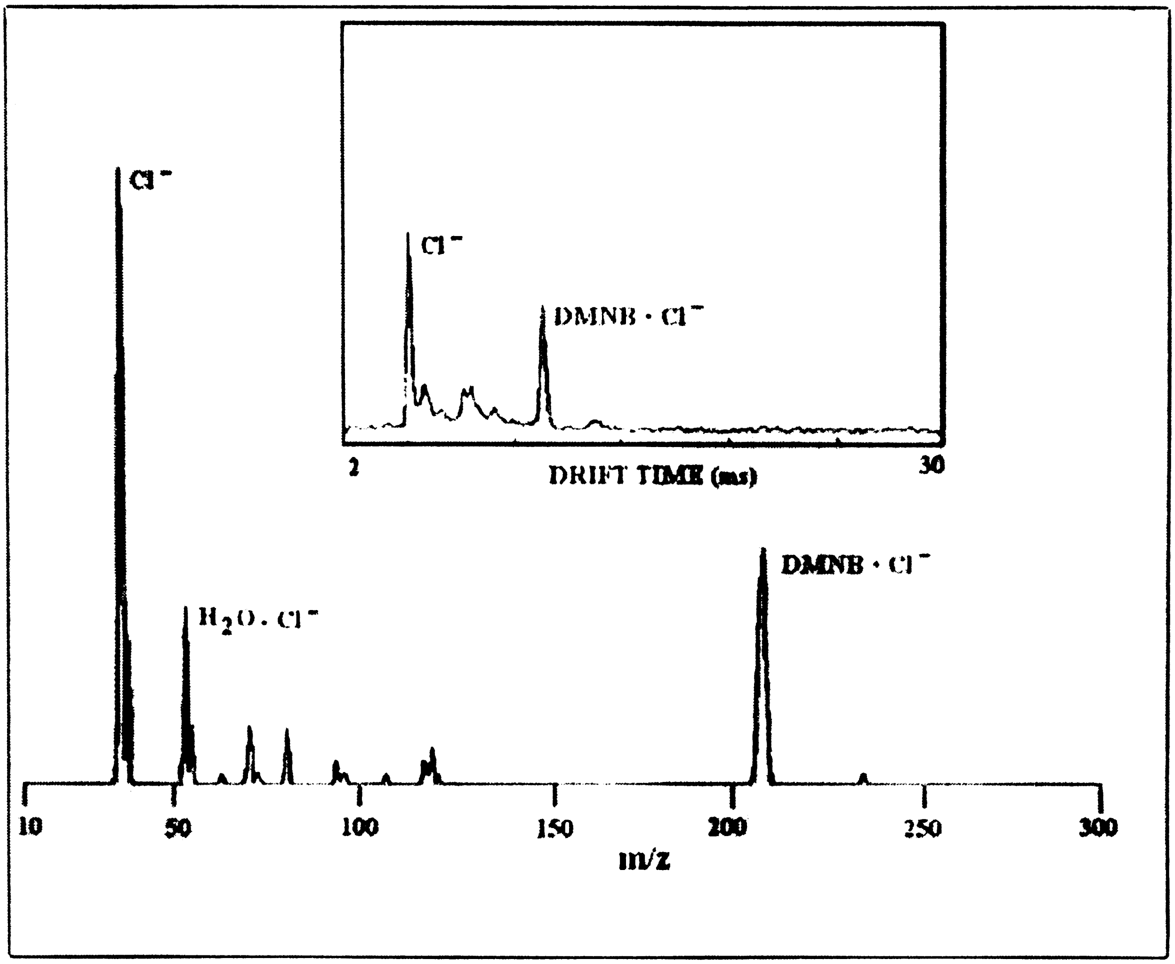

Fig. 3. The ion mobility spectrum at 323 K (inset) and the associated mass spectrum for a system in which DMNB is present only in the ion source region.

formed at every collision between Cl^- and DMNB then k_+ is approximately 10^{-9} cm^3 $molecule^{-1}$ s^{-1} [12] and from Eq. (3), K is approximately 2×10^8. Since $-RT\ln K = \Delta G^o = \Delta H^o - T\Delta S^o$ and taking ΔS^o for a typical association reaction as 100 J K^{-1} mol^{-1} [13], then $\Delta H^o \sim -88$ kJ mol^{-1} for the association of $Cl-$ with DMNB. Using the same arguments, together with the temperatures above which the adducts first failed to appear, 110 °C for DMDNP and 160 °C for DNB, the predicted enthalpy changes for the formation of the more stable Cl^- adducts are: for $DNB{\cdot}Cl^-$, -109 kJ mol^{-1} and for $DMDNP{\cdot}Cl^-$, -96 kJ mol^{-1}.

3.3. The enthalpy and entropy of association of chloride ion with 2,3-dimethyl-2,3-dinitrobutane

When an ion mobility spectrometer is operated in the analytical mode, an equilibrium which may be set up in the source region according to Eq. (2) cannot be sustained once the ions enter the drift region where no dinitro-compound is present. If, however, the dinitro-compound is introduced with the drift gas and exits past the ion source then its constant concentration allows the maintenance of equilibrium at all times. The Cl^- and $A{\cdot}Cl^-$ ions will then not appear as separate peaks in the mobility spectrum but will constitute a composite peak whose drift time, t_{obs}, is the sum of the drift times of the two ions, weighted according to their equilibrium mole fractions. This effect was noted in the early days of mobility spectroscopy [14]. The setting up of equilibria between ions generated in an IMS source and neutral molecules contained in the drift gas has been used to study the formation of several proton bound complexes containing nitrogen and oxygen bases [15] and of chloride/alkyl halide complexes [16,17].

If X_0 and t_0 and X_1 and t_1 are the respective equilibrium mole fractions and drift times of Cl^- and $A{\cdot}Cl^-$ then, provided there are no other interfering reactions:

$$X_o+X_1=1 \tag{4}$$

$$X_o t_o \div X_1 t_1 = t_{obs} \tag{5}$$

In Eq. (5), t_{obs} is the arrival time of the maximum of the composite peak. Using Eqs. (4) and (5) to solve for X_1 and X_0 leads to their ratio defined by

$$\frac{X_1}{X_o}=\frac{t_{obs}-t_o}{t_1-t_{obs}}=\frac{[A{\cdot}Cl^-]}{[Cl^-]} \tag{6}$$

At a fixed temperature, t_{obs} will increase from the value t_o to the value t_1 as the concentration of the dinitro compound is increased. If there is no addition of a second dinitro molecule to the chloride then the drift time will maximize when $t_{obs}=t_1$, i.e. when the the dinitro compound concentration is such that Cl^- spends all its time associated with the dinitro compound. The ion mobility spectra in Fig. 4 exemplify the increase of drift time of the peak as the concentration of DMNB throughout the spectrometer was increased. The mobility spectra in the figure were obtained at a fixed temperature of 170 °C with concentrations of DMNB ranging from 0 to 50 ppm. The mobility spectra are much simpler than the one shown in Fig. 3 because the drift tube operating temperature is much higher, resulting in a cleaner, degassed instrument, and also because the nitrogen gas used was more highly purified. These two factors decrease the concentrations of impurities in the system and minimize spurious peaks associated with their presence. In Fig. 5 are plotted the values of t_{obs} as a function of the DMNB concentration and it is seen that the drift time is indeed tending towards a limiting value at high concentration.

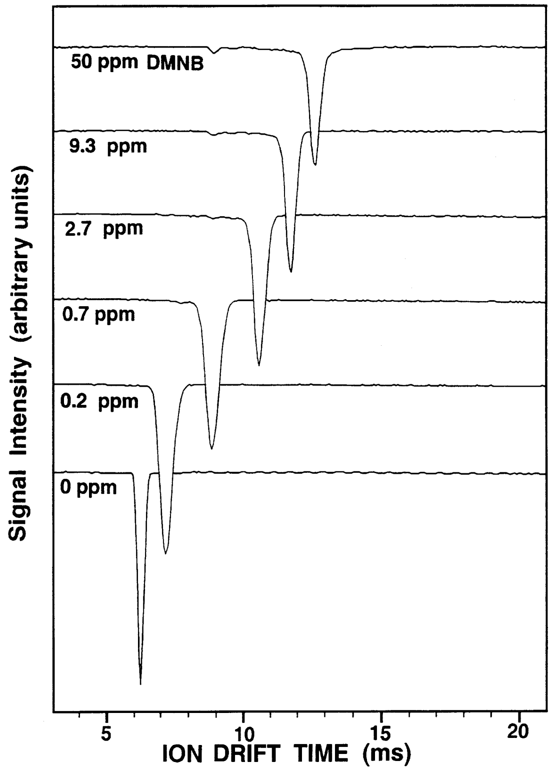

Fig. 4. Ion mobility spectra as functions of the concentration of DMNB at 443 K; the peak at 0 ppm DMNB is due to the noncomplexed Cl^- ion. DMNB is present throughout the spectrometer.

In order to use the relationship between the ratio of mole fractions of chloride and adduct and the ratio of differences in drift times, the value of t_1 must be determined for each temperature. This can be most readily accomplished in the manner described by Giles and coworkers [16,17]. The equilibrium expression, Eq. (3), may be combined with Eq. (6) to give

$$K=\frac{t_{obs}-t_o}{t_1-t_{obs}}\cdot\frac{10^9}{[DMNB]} \tag{7}$$

which rearranges to

$$(t_{obs}-t_o)^{-1}=(K(t_1-t_o)[DMNB]/10^9)^{-1} + (t_1-t_o)^{-1}. \tag{8}$$

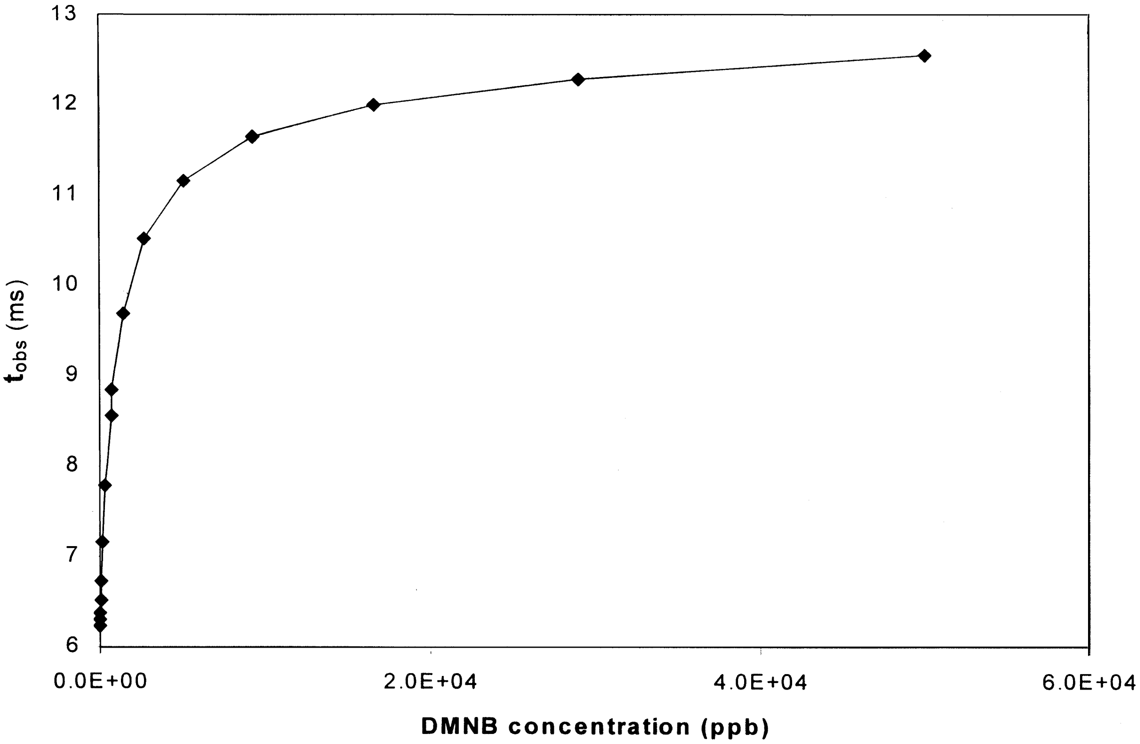

Fig. 5. t_{obs} for the composite Cl^-/DMNB · Cl^- ion mobility peak as a function of the concentration of DMNB, showing the approach to a limiting value at high concentration. Temperature 443K.

In these latter two equations [DMNB]=[A] is in units of ppb.

If Eq. (8) holds, then at each experimental temperature, a plot of $(t_{obs}-t_o)^{-1}$ vs. $[DMNB]^{-1}$ should yield a straight line of slope $[K(t_1-t_o)]^{-1}$ and intercept $(t_1-t_o)^{-1}$. Since t_o, the drift time of the chloride ion, is determined at each temperature in the absence of DMNB, the value of $t_1$may be obtained from the value of the intercept for each temperature. The plot shown in Fig. 6 for the association of chloride with DMNB at 170 °C has an intercept of 0.1594 ms^{-1} which yields $t_1=12.69$ ms. From the slope of the graph, the derived equilibrium constant is 9.95×10^5. The equilibrium constant was determined for five temperatures between 100 and 190°C and the results, presented in Fig. 7, show that the graph of ln K vs. 1/T is linear. The error bars in the figure are derived from the standard errors of the slopes and intercepts of the $(t_{obs}-t_0)^{-1}$ vs. $[DMNB]^{-1}$ plots. The thermodynamic data obtained from the slope and intercept of the van't Hoff plot are: $\Delta H^o=-92.1\pm3.1$ kJ mol^{-1} and $\Delta S^o=-92.1\pm7.4$ J K^{-1} mol^{-1}. The measured t_0 values and the derived t_1 values for the five temperatures are summarized in Table 3.

The measured enthalpy of association of DMNB with Cl^- of -92.1 kJ mol^{-1} is consistent with the value of -88 J K^{-1} mol^{-1} suggested by the observed upper temperature limit for the appearance of DMNB · Cl^- in the analytical mobility spectrum, vide supra. This value is considerably more negative than the -63 to -73 kJ mol^{-1} obtained by high pressure mass spectrometry for the binding of Cl^- to C_1, C_2, and C_3 mononitroalkanes [18], which are themselves consistent with an estimated -61 kJ mol^{-1} for the enthalpy of binding of the larger anion Br^- to nitromethane [19]. Ab initio calculations at the MP4(SDTQ) level with geometry optimization at the MP2 level show that in the bromide/nitromethane

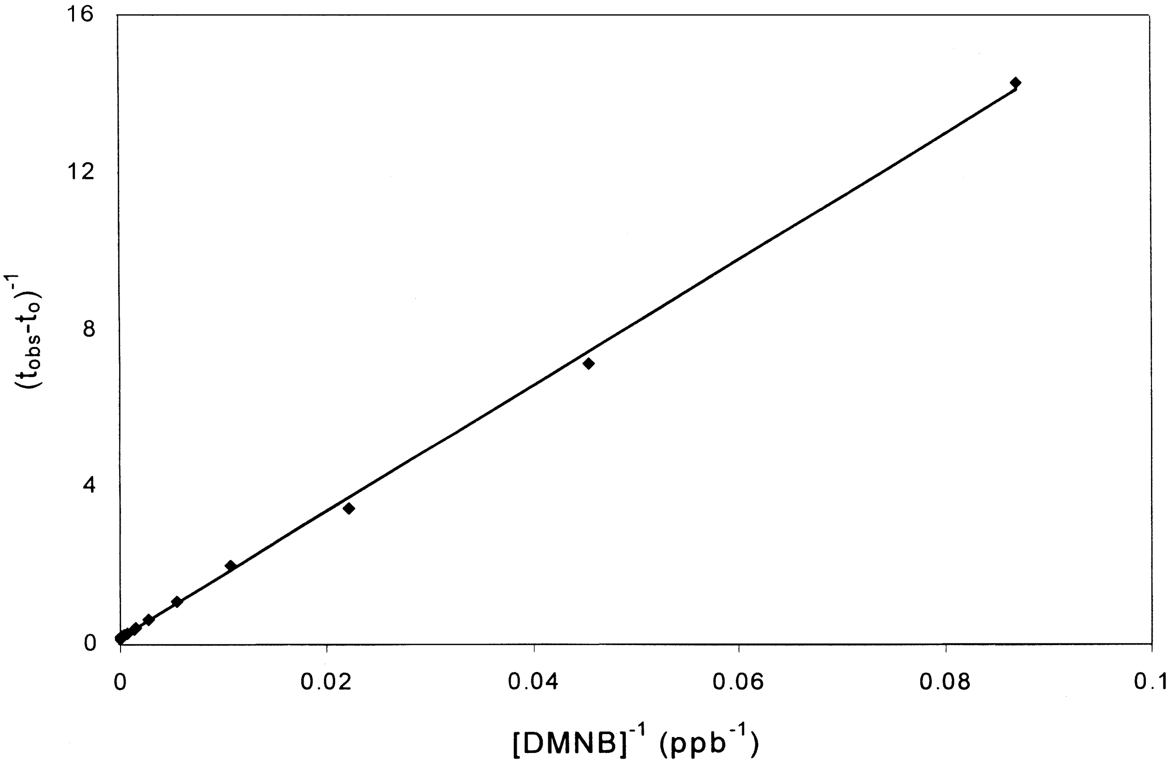

Fig. 6. $(t_{obs}-t_0)^{-1}$ as a function of $[DMNB]^{-1}$ at 443 K.

complex the Br^- is co-linear with the C–N bond and is interacting symmetrically with the three hydrogens at a distance of 3.27 Å [19]. The binding is due to hydrogen bonding with the three hydrogens augmented by electrostatic contributions from the interaction of the halide with the aligned large, 3.46 Debye [20,21], molecular dipole and with the ion-induced dipole. The enthalpy of association of the smaller Cl^- with nitromethane should be somewhat greater than that for Br^- due to a smaller X^--H distance and hence stronger hydrogen bonds and a stronger ion/dipole interaction. In concordance with this supposition, the value obtained by high pressure mass spectrometry was 65.9±1.1 kJ mol^{-1} [18].

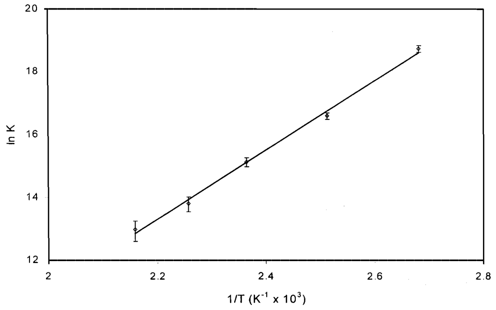

Fig. 7. Van't Hoff plot for the association reaction, $Cl^-+DMNB=DMNB\cdot Cl^-$.

The temperature above which each of the chloride adducts of DNB, DMNB, and DMDNP was not observed in the analytical experiments would be dependent on the magnitudes of the enthalpy and

Table 2
The vapor pressures of DMNB and DNB according to the equation log P (ppb) = A + B/T

Compound	A	B	Temp. Range (°C)
DMNB	19.82 ± 0.09	−4878 ± 26	−20to+50
DNB	18.08 ± 0.29	−4274 ± 81	−10to+30

Table 3
Drift times, t, (ms) and reduced mobilities, K_0, (cm^2 V^{-1} s^{-1}) of Cl^- and DMND·Cl^-

	Cl^-		DMNB·Cl^-	
T (K)	t_0	K_0	t_1	K_0
373	7.76	2.80	14.91	1.46
398	7.05	2.89	13.82	1.48
423	6.66	2.90	2.69	1.52
443	6.24	2.93	12.1	1.51
463	5.88	2.98	11.01	1.57

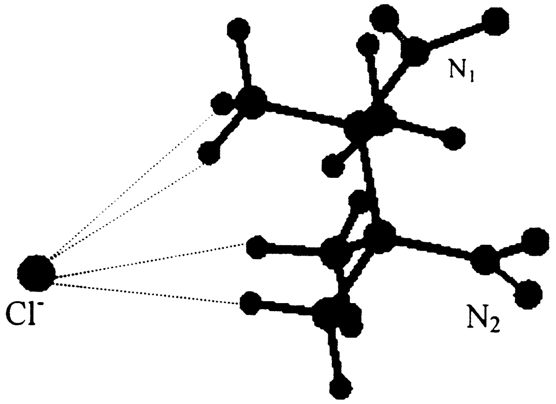

Fig. 8. A possible structure for a Cl^-/DMNB complex in which Cl^- interacts with four methyl hydrogens and with the two C–NO_2 dipoles.

entropy of binding. By analogy with the bromide adduct of nitromethane, the enthalpy of binding of chloride and dinitro compound will depend on the number and strengths of hydrogen bonds and the alignment of the two C–NO_2 dipoles. The order of increasing adduct stability is in the same order as the increasing number of hydrogens bonded to carbon in positions α to a nitro group: none in DMNB; one in DMDNP; and four in DNP. Because of the electron withdrawing strength of the nitro group such hydrogens are much more acidic than the hydrogens on other carbon atoms that possess less positive charge and hence individually have much weaker interactions with the halide. In the chloride complex of DMNB, hydrogen bonding will be through the much less acidic methyl hydrogens on the β-carbons. Simple mechanical models show that a maximum of four hydrogens can be involved. Fig. 8 is a sketch of a possible structure for the complexion which the Cl^- is interacting with two H from one methyl group and a single H from each of two other methyl groups. The two C–NO_2 dipoles, although unable to point directly to the Cl^-, do have favorable orientations.

The decrease in entropy, 92.1 J K^{-1} mol^{-1}, is too small to suggest that the association of chloride with DMNB leads to significant restriction of the motion of the molecule. The potential surface around the energy minimum is probably relatively flat as was computed for the bromide/nitromethane complex which had $H \cdots Br$ distances of 3.10 Å [19].

The mobilities, K, of the chloride ion and the chloride adduct of DMNB K were determined using

$$K = \frac{v}{E} = \frac{l^2}{Vt} \tag{9}$$

in which v is the drift velocity, E is the drift field strength, l is the length of the drift region, V is the potential drop = lE along the drift region and t is the drift time.

The reduced mobility, K_0 is defined by

$$K_0 = K\left(\frac{273}{T}\right)\left(\frac{P}{760}\right) \tag{10}$$

in which K is the mobility at temperature T (kelvin) and P is the pressure (torr) [22]. The values are presented in Table 3.

The reduced mobilities of the chloride ion, 2.80 cm^2 V^{-1} s^{-1} at 373 K and 2.93 cm^2 V^{-1} s^{-1} at 398 K, are in reasonable agreement with the values of 2.820 cm^2 V^{-1} s^{-1} and 2.883 cm^2 V^{-1} s^{-1} reported by Giles and Grimsrud for the same temperatures [16]. In agreement with the same authors, we see an increase in the reduced mobility of Cl^- with increasing temperature. The observed increases may be due, as suggested [16], to a decrease with increasing temperature of the average degree of hydration of the Cl^- by residual water. Because of a significant increase in mass, a hydrated chloride ion is less mobile than the bare ion and hence as the equilibrium concentration of the hydrate decreases the reduced mobility of the ion in the "chloride" peak should increase. The reduced mobilities of the DMNB chloride adduct also increase with increase of temperature, the percentage change between the values at the highest and the lowest temperatures being approximately the same as for the chloride ion. The hydration of the DMNB chloride adduct should be less than that of the chloride ion at any given temperature since almost invariably the addition of a second ligand to a central ion is accompanied by a smaller decrease in free energy than for the first ligand. A change in ion hydration is therefore probably not the only reason for the increases in reduced mobilities. A reduction in the ion-neutral collision cross section with increase of temperature must also play a part [22].

4. Conclusion

Dinitro-alkanes form stable gas-phase adducts at ambient temperature with chloride ions in an ion mobility spectrometer. The adducts have been identified by mass spectrometry. When the temperature of the ion mobility spectrometer was raised, the adducts disappeared from the spectra. The order of increasing stability, i.e. the order of the temperatures at which an adduct first failed to appear in the spectrum was $DMNB\cdot Cl^- < DMDNP\cdot Cl^- < DNB\cdot Cl^-$. This order coincides with the order for the total number of acidic hydrogen atoms on the two carbon atoms in position α to the nitro groups. The enthalpy and entropy of association of chloride with DMNB were obtained by following the changing drift time of the single ion mobility peak due both$\cdot Cl^-$ and $DNB\cdot Cl^-$ which were in held equilibrium throughout the drift region. The enthalpy change for the association of Cl^- with DMNB was determined as -92.1 kJ mol^{-1} and that of Cl^- with DNB is estimated to be $\sim$20 kJ mol^{-1} lower. Unfortunately, impurities in DNB, although amounting to less than 2% of the main constituent, prevented any determination of the thermodynamic parameters for the association of this compound with chloride since broad interfering impurity adducts dominated the spectrum.

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