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Analysis of Explosives by Negative Ion Chemical Ionization Mass Spectrometry

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ABSTRACT: Negative ion chemical ionization (NCI) mass spectrometry using isobutane as a reagent has been applied to the analysis of explosives. The method is evaluated as complementary to positive ion CI, as both methods can be applied to the same sample. We used a magnetic-sector-type mass spectrometer without changing the electron multiplier voltage. Under these conditions NCI mass spectra of explosives have been obtained at a sensitivity similar to that of positive ion CI mass spectra.

KEY WORDS: criminalistics, explosives, spectroscopic analysis

The analysis of explosives is of major importance in several analytical fields.

Forensic identification of explosive residues in debris after a bombing can provide important information as to the type and origin of the explosive used. The decomposition products being gases, only trace amounts of the original material are left on the scene of the explosion.

In environmental trace analysis, the search for contamination from explosives in seawater as a result of obsolete munitions dumps and the control of explosive pollutants that may find their way into groundwater and surface water are important.

In environmental health hazards prevention, periodical analysis of body fluids of personnel working in explosives manufacturing plants should be made for the detection of traces of explosives in blood and urine.

All these applications need a highly sensitive and specific analytical technique. Mass spectrometry (MS), which contains these two features, has become during the last few years a widely used tool for the analysis and identification of explosives. The earlier works on MS of explosives were done with an electron impact (EI) ionization source [1-7]. Most explosives undergo considerable EI fragmentation but do not produce a molecular ion.

Chemical ionization (CI) MS [8], being a mild ionization technique, has become commonly used for the analysis of explosives [9-15]. Various reagent gases have been used: hydrogen [9], water [10], methane [12,13,15], isobutane [11,12,13], and ammonia [14]. Although direct CI-MS is being used for forensic identification of explosives [16], there are still several compounds that are characterized by considerable fragmentation. Also, field ionization [17] and field desorption [18] mass spectra of most explosives produce many fragment ions.

It has, therefore, become common practice to use two different analytical techniques [19] for the positive identification of an unknown explosive or explosives mixture, for example, CI-MS and EI-MS [16].

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In mass spectrometers with dual CI/EI sources in which the slits cannot be widened in the EI mode, there is a decreased sensitivity compared to CI or to open-source EI. Moreover, in closed EI sources an effect of "self-CI," producing $(MH)^+$ ions [20], has been observed in the EI mode.

In an effort to find a sensitive MS method that can be complementary to CI and can be applied to the same sample, we have investigated the use of negative ion chemical ionization (NCI) using isobutane as the reagent gas for the analysis of explosives.

The application of NCI has been pioneered in several fields by various workers [21-26]. Several reaction types may occur in the negative ion source [27]. The most likely to occur with isobutane as reagent are these:

- (1) electron resonance capture $AB + e^- \rightarrow AB^-$, the isobutane acting primarily as a moderator in producing high concentrations of low-energy electrons;
- (2) dissociative electron capture $AB + e^- \rightarrow A + B^-$, producing fragment ions;
- (3) proton transfer reactions $AH + B^- \rightarrow A^- + BH$, producing $(M-H)^-$ ions. The H^- ion, produced from isobutane, is a gas-phase base capable of abstracting a proton from organic compounds that are strong gas-phase acids; and
- (4) ion-molecule reactions, occurring mainly between the ions and molecules of the sample, producing ions of the type $(M+R)^-$.

This paper reports the negative ion CI mass spectra with isobutane as reagent gas of several commonly encountered explosives. The use of isobutane as CI reagent facilitates the alternate recording of positive and negative CI mass spectra of the same sample by simply switching the polarity of the ion source and electromagnet voltages.

Experimental Procedure

General

Mass spectra were recorded on a Varian MAT CH7 single-focusing mass spectrometer modified for CI and for negative-ion mode operation. The CI modifications included a gas-tight dual EI/CI source, a special reagent gas inlet system, a quartz direct insertion probe, and a differential pump on the ion source. Originally the repeller was operated at 0 to -30 V with respect to the ionization chamber. A 9-V battery was added between the circuit and the repeller to increase the voltage of the repeller to $+9$ V. Electron energy was 105 eV. The source could be operated at a pressure² range up to 133.3 Pa (1.0 torr). The modifications for negative-ion operation included:

- (1) reversion of the electromagnet current polarity by the activation of a relay having two sets of contacts that connect the current supply to the magnet either in the positive or negative mode;
- (2) reversion of the polarity of the repeller battery voltage by a switch; and
- (3) a Fluke 408 B high voltage power supply for the accelerating voltage, which replaces the internal high voltage power supply. The Fluke 408 B power supply can be operated in either the positive or negative mode by reversing a switch.

The electron multiplier is an EMI 9643/4 B multiplier operated at a first dynode voltage of -2500 V. The accelerating voltage of the mass spectrometer is 3000 V, and therefore negative ions can be recorded without any change of the multiplier voltage. However, the lower kinetic energy of the impacting negative ions, 0.5 keV (3.0 - 2.5), results in a decrease in sensitivity by at least a factor of 10 [28] relative to positive ion detection.

²Original data were reported in English customary units.

Source pressure in the NCI mode was in the range of 26.7 to 66.7 Pa (0.2 to 0.5 torr) unless otherwise specified. Samples were admitted into the source through the direct insertion probe.

Samples and Reagent Gas

Explosives were obtained in pure form from the Analytical Laboratory of the Israel Police Headquarters. Isobutane (99.97%) was purchased from Matheson Gas Products, Inc., East Rutherford, N.J.

Results and Discussion

Five explosives were examined in this study: 2,4,6-trinitrotoluene (TNT); nitroglycerin (NG); pentaerythritol tetranitrate (PETN); 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX); and 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX).

Mass Spectra of TNT

Figure 1 shows the NCI mass spectra of TNT with isobutane at two different reagent gas pressures: (a) at a pressure of 10.7 to 13.3 Pa (0.08 to 0.1 torr) and (b) at a pressure of 26.7 to 53.3 Pa (0.2 to 0.4 torr). In both cases the $(M-H)^-$ ion peak at m/e 226 is the base peak. In the lower pressure mass spectrum typical fragmentation peaks are observed at m/e 26 (CN^-) and at m/e 46 (NO_2^-), which are abundant in low pressure negative ion mass spectra [29,30] and in the negative ion field ionization mass spectrum [31] of TNT. In both the lower and higher pressure NCI mass spectra of TNT, the ions m/e 197 ($M-NO^-$), m/e 210

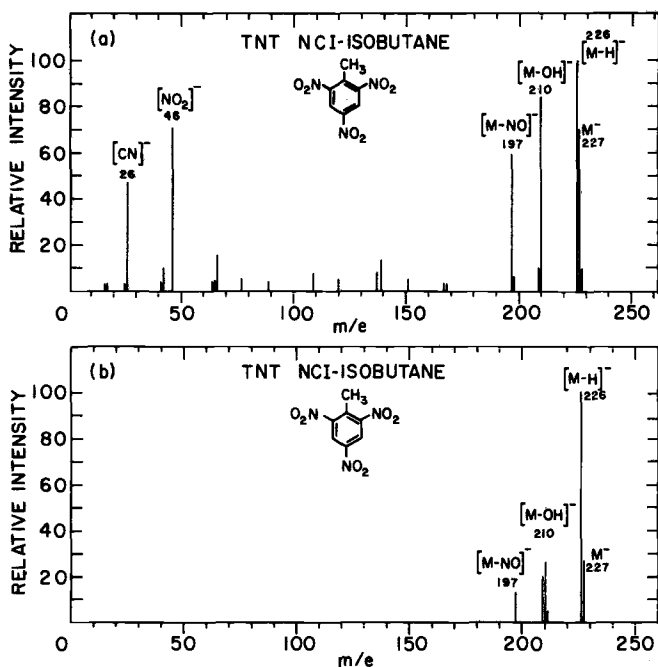


FIG. 1—Negative ion chemical ionization mass spectra of TNT with isobutane as reagent. Ion source temperature, 150°C and probe temperature, 120°C. (a) Source pressure 10.7 to 13.3 Pa (0.08 to 0.1 torr) and (b) source pressure 26.7 to 53.3 Pa (0.2 to 0.4 torr).

(M-OH)⁻, and the parent ion at *m/e* 227 are observed, but their intensity with respect to the base peak is much lower in the higher pressure mass spectrum. It seems that at a higher reagent gas pressure the dominant reaction of negative-ion formation in TNT is proton transfer. TNT is a strong gas-phase acid and therefore can be ionized by proton transfer to an ion like H⁻ (produced from isobutane), which is a strong gas-phase base.

Mass Spectrum of NG

Because of its high volatility, the mass spectrum of NG has to be recorded at the lowest source and probe temperatures possible. Even under such conditions the positive ion CI mass spectrum of NG with isobutane as reagent is known to be problematic (Refs 11, 14, and our own experience). In the NCI mode, reproducible mass spectra of NG were obtained by using isobutane as reagent (Fig. 2). Important fragment ions are (NO₂)⁻ and (ONO₂)⁻ (base peak at *m/e* 62) and [O(NO₂)₂]⁻ at *m/e* 108 and (ONO₂)₂⁻ at *m/e* 124. Two other fragment ions are *m/e* 181 (M-NO₂)⁻ and *m/e* 197 (M-NO)⁻. A parent ion appears at *m/e* 227, probably formed by electron resonance capture and two adduct ions, at *m/e* 243 (M+O)⁻ and at *m/e* 289 (M+ONO₂)⁻, which are formed by ion-molecule reactions in the sample.

Mass Spectrum of PETN

The NCI mass spectrum of PETN is shown in Fig. 3. Like NG, the base peak is at *m/e* 62 (ONO₂)⁻ and a major fragment ion is at *m/e* 46 (NO₂)⁻, which is the base peak in EI and in CI-methane analysis of PETN [12]. As in the NCI spectrum of NG, a fragment ion (M-NO)⁻ and an adduct ion (M+ONO₂)⁻ are observed. No molecular ion, but an (M-H)⁻ ion at *m/e* 315 and an (M+H)⁻ ion at *m/e* 317 are observed, as are the corresponding oxygen addition peaks (M-H+O)⁻ at *m/e* 331 and (M+H+O)⁻ at *m/e* 333. An adduct peak at *m/e* 362 (M+NO₂)⁻ is observed as in positive-ion CI-water [10], where it is the base peak.

Mass Spectra of RDX

Figure 4 shows the NCI mass spectra of RDX with isobutane at two different reagent gas pressures: (a) at a pressure of 10.7 to 13.3 Pa (0.08 to 0.1 torr) and (b) at a pressure of 26.7 to 53.3 Pa (0.2 to 0.4 torr). Typical fragment ions in both spectra are at *m/e* 46 (NO₂)⁻; *m/e*

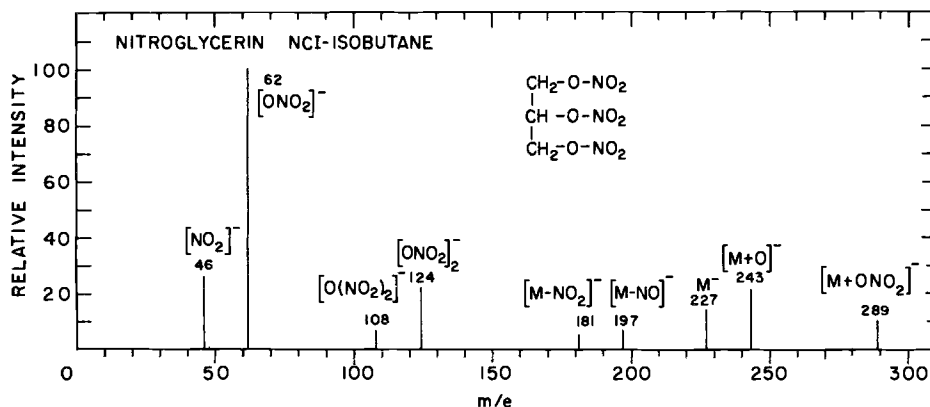


FIG. 2—Negative ion chemical ionization mass spectrum of NG with isobutane as reagent. Ion source temperature, 80°C; probe temperature, 25°C; and source pressure, 26.7 to 66.7 Pa (0.2 to 0.5 torr).

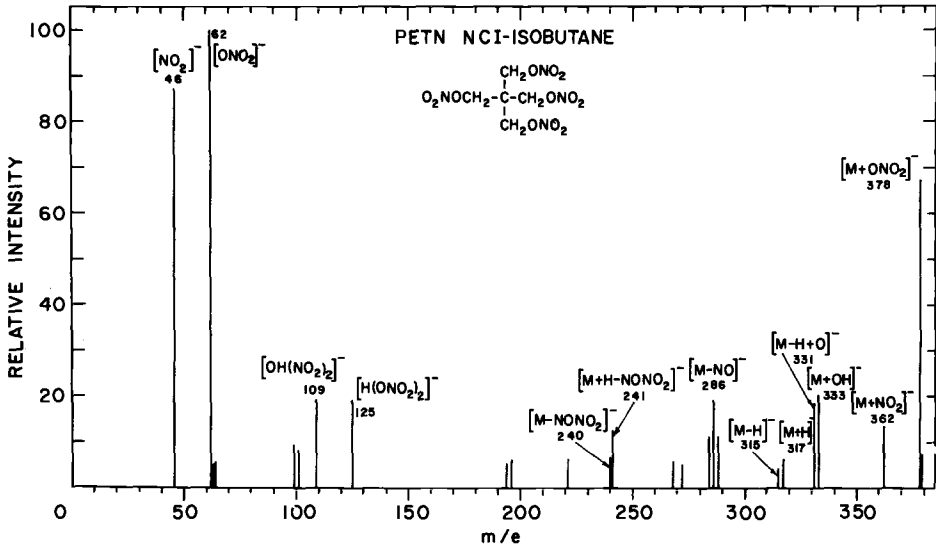


FIG. 3—Negative ion chemical ionization mass spectrum of PETN with isobutane as reagent. Ion source temperature, 125°C; probe temperature, 75°C; and source pressure, 26.7 to 66.7 Pa (0.2 to 0.5 torr).

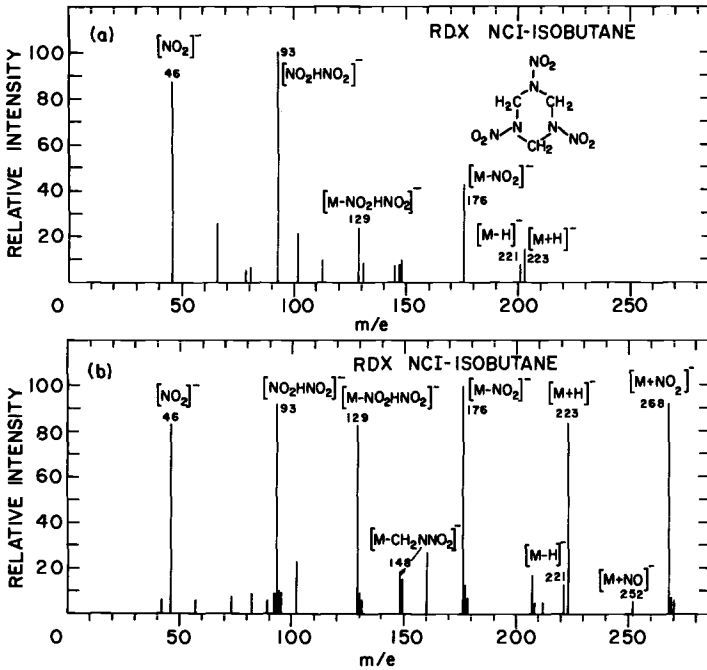


FIG. 4—Negative ion chemical ionization mass spectra of RDX with isobutane as reagent. Ion source temperature, 150°C and probe temperature, 100°C. (a) Source pressure, 10.7 to 13.3 Pa (0.08 to 0.1 torr) and (b) source pressure, 26.7 to 53.3 Pa (0.2 to 0.4 torr).

93 (NO_2HNO_2)⁻, which is the base peak in Fig. 4a; m/e 129 ($\text{M}-\text{NO}_2\text{HNO}_2$)⁻; and m/e 176 ($\text{M}-\text{NO}_2$)⁻, which is the base peak in Fig. 4b. The ($\text{M}-\text{H}$)⁻ and ($\text{M}+\text{H}$)⁻ ion peaks are observed in both spectra. However, in the higher pressure spectrum the ($\text{M}+\text{H}$)⁻ peak is much more abundant and additional adduct ion peaks at m/e 252 ($\text{M}+\text{NO}$)⁻ and at m/e 268 ($\text{M}+\text{NO}_2$)⁻ are observed. It seems that the higher reagent gas pressure enhances ion-molecule reactions in the sample to form adduct ions.

Mass Spectrum of HMX

The NCI mass spectrum of HMX (Fig. 5) includes typical fragment ions as in RDX: m/e 46 (NO_2)⁻, which is the base peak in HMX, and m/e 93 (NO_2HNO_2)⁻. Also, in the mass spectrum of HMX some fragment ions are observed that are similar to fragment ions in RDX but have an additional loss of CH_2NNO_2 , like m/e 148 ($\text{M}-2\text{CH}_2\text{NNO}_2$)⁻ and m/e 176 ($\text{M}-\text{NO}_2\text{CH}_2\text{NNO}_2$)⁻. The highest mass peak is at m/e 222 ($\text{M}-\text{CH}_2\text{NNO}_2$)⁻. Loss of one or two groups of CH_2NNO_2 from the molecular ion has been observed in EI [12] and from the MH^+ ion in positive ion CI [10].

The peak at m/e 222 is characteristic of HMX and makes differentiation between RDX and HMX in explosive residues easier, while in positive ion CI in both RDX and HMX a peak at m/e 223 is observed, but an MH^+ peak for HMX [10] is not always observed.

Conclusion

The NCI mass spectra demonstrate the usefulness of NCI as a complementary method to positive ion CI for the direct analysis of unknown explosives and explosion residues. The NCI mass spectra are simple and include M^- or ($\text{M}-\text{H}$)⁻ ions, or both, as well as some typical fragment and adduct ions. Positive ion and negative ion CI mass spectra of the same sample can be easily recorded.

Major differences in NCI mass spectra as a function of reagent gas pressure appear only in TNT and RDX. In mass spectra of NG, PETN, and HMX, no substantial changes as a function of reagent gas pressure have been observed.

The sensitivity of the NCI mass spectra of the investigated explosives is on the same order of magnitude as the positive ion CI mass spectra under the described experimental condi-

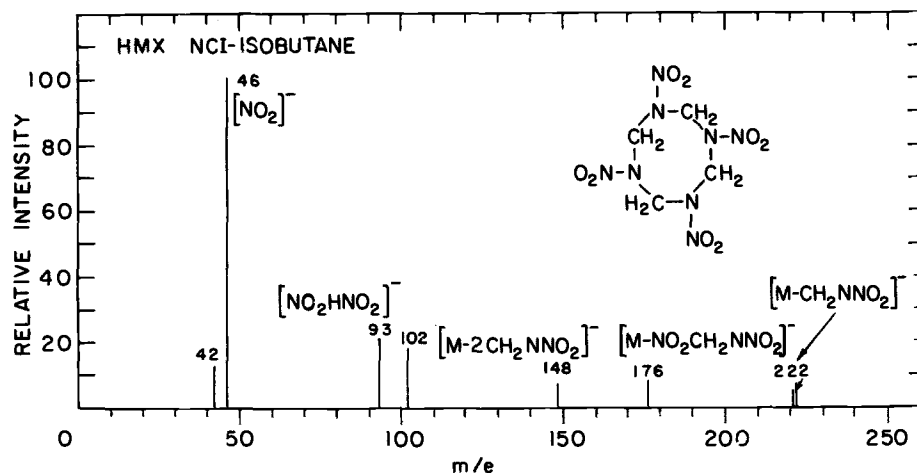


FIG. 5—Negative ion chemical ionization mass spectrum of HMX with isobutane as reagent. Ion source temperature, 155°C; probe temperature, 150°C; and source pressure, 26.7 to 66.7 Pa (0.2 to 0.5 torr).

tions. However, an increase in the kinetic energy of the impacting negative ions by applying a positive high voltage on the first dynode of the multiplier (and a higher positive voltage on the last dynode) should increase the detection sensitivity of the negative ions by one to two orders of magnitude.

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