January, 1979] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (1), 65—68 (1979) 65

Chemical Ionization Mass Spectrometry of Alkyl Nitrates and Nitrites[†]

Rebati C. Das,[††] Osamu Koga, and Shin Suzuki*
Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 260

(Received May 23, 1978)

The mass spectrometry of alkyl nitrites and alkyl nitrates with chemical ionization using methane and isobutane as reagent gases produces quasi-molecular ions, $(M+1)^+$ and/or $(M-1)^+$. These ions have maximum abundance for lower nitrates and nitrites. The chemical ionization mass spectrometry, in conjunction with gas chromatography, can be used for quantitative estimation of alkyl nitrates and nitrites in very low amounts.

The behaviors of nitrogeneous compounds formed in the photochemical reactions of NO$_x$–hydrocarbon–O$_2$ system in the atmospheric smog as well as in the chamber model have recently gained much interest.[1–3] Unfortunately, all compounds have not been completely and unequivocally identified.[1–3] Alkyl nitrates and nitrites, present in the above system, have been analyzed in low quantities by GC method using ECD detector,[4] but many other compounds *e.g.* chloride interfere in the method. Independent confirmation is, therefore, necessary. Mass spectrometry is a very convenient method of analysis but conventional electron impact ionization (EI)method is not always suitable due to easy fragmentation of unstable compounds by electron beams producing structurally insignificant low mass fragments. Chemical ionization (CI) mass spectrometry, recently developed,[5] has been used to obtain quasi-molecular peaks [$m/e=(M+1)$ or $(M-1)$] of many organic compounds of high abundance, thus making their identification more confirmatory.

This paper reports our results on the CI mass spectrometry of alkyl nitrates and nitrites as a part of our overall program of complete identification and analysis of all the products formed in the NO$_x$–hydrocarbon–O$_2$ system.

Experimental

A Shimadzu GC-MS apparatus was used. Mostly commercially available alkyl nitrates and nitrites were used. Ethyl nitrate, pentyl and isopentyl nitrate (Tokyo Kasei Kogyo) were directly used after having checked their purity chromatographically. All other compounds were separated from the constituents present with them in the GC column consisting of PEG 400 at room temperature using helium as carrier gas (flow rate 8—11 ml/min) before introduction to the ionization chamber. Ethanolic solutions of ethyl nitrite (Wako), pentyl and isopentyl nitrite (Tokyo Kasei Kogyo) were used. Ethyl nitrite being a gas at room temperature is market as solution in ethanol. Pentyl and isopentyl nitrite are market in the mixed form. Methyl nitrate is not commercially available. It was prepared by gas phase photolysis of ethyl nitrite-O$_2$ system[6] and separated from other products in the above manner.

Results and Discussion

Figures 1 to 8 give the EI and CI mass spectral patterns of some common alkyl nitrates and nitrites.

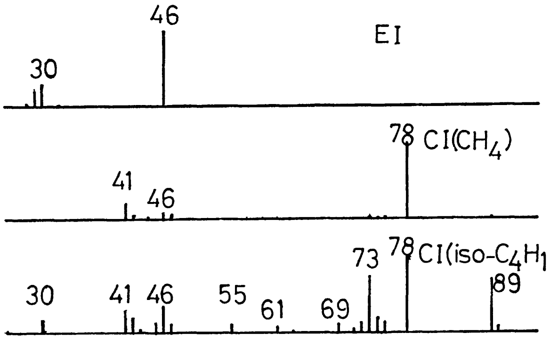

Fig. 1. Mass spectra of methyl nitrate (MW 77).

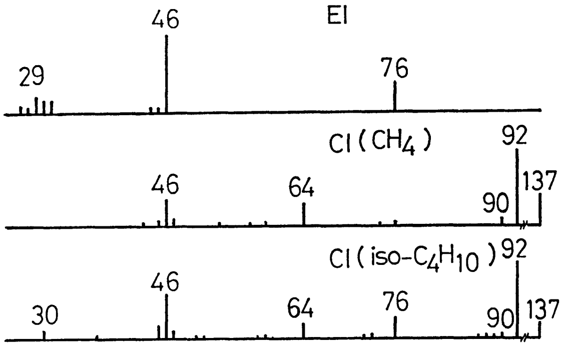

Fig. 2. Mass spectra of ethyl nitrate (MW 91).

The CI patterns are for CH$_4$ and i-C$_4$H$_{10}$ as reagent gases. The conditions of the mass spectra presented in Figs. 1 to 8 are as follows. EI spectrum: Ion-source temperature 170 °C, Electron energy 70 eV, Pressure[†††] 7×10^{-7} Torr. CI(CH$_4$) spectrum: Ion-source temperature 170 °C, Electron energy 500 eV, Pressure[†††] 3×10^{-5} Torr. CI(i-C$_4$H$_{10}$) spectrum: Ion-source temperature 170 °C, Electron energy 500 eV, Pressure[†††] 0.75×10^{-5} Torr.

The main reactant ions are known to be CH_5^+ and $C_2H_5^+$ when methane is used as the reagent gas.[5] Similarly with i-C$_4$H$_{10}$ as the reagent gas, t-$C_4H_9^+$ is the main reactant ion.[5,7] The proton and hydride transfer reactions of these ions are important for analytical purpose, because they generate the quasi-molecular $(M+1)^+$ and $(M-1)^+$ ions respectively.

[†] Presented at the 37th National Meeting of the Chemical Society of Japan, Yokohama, April 1978.

[††] Present address: Department of Chemistry, University College of Engineering, Burla, Orissa, India.

[†††] Pressure is monitored between the ionization chamber and the vacuum pump in the apparatus. This pressure relates only to the reagent gas pressure.

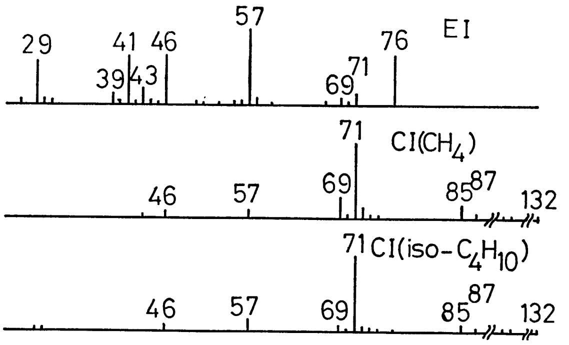

Fig. 3. Mass spectra of pentyl nitrate (MW 133).

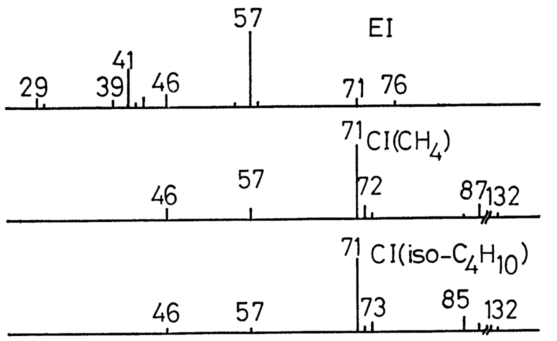

Fig. 4. Mass spectra of isopentyl nitrate (MW 133).

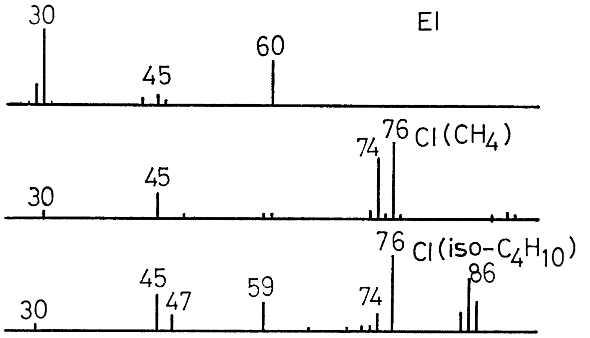

Fig. 5. Mass spectra of ethyl nitrite (MW 75).

$$RH + CH_5^+/C_2H_5^+/t\text{-}C_4H_9^+ \longrightarrow RH_2^+ + CH_4/C_2H_4/C_4H_8 \quad (1)$$

$$RH + C_2H_5^+/t\text{-}C_4H_9^+ \longrightarrow R^+ + C_2H_6/C_4H_{10} \quad (2)$$

A perusal of the figures shows that the mass spectral patterns obtained with CH_4 as the reagent gas are generally simpler (less fragments) and therefore, CH_4 is more suitable for the identification and analysis of alkyl nitrates and nitrites by CI mass spectrometry.

Almost all the compounds produce $(M+1)^+$ ion, but only in the lower homologues of nitrates and nitrites(with 1 and 2 C-atoms), it is the most abundant one. There may be two reasons for this *viz.*(i) with the increase of chain length of the molecule, the bond energy decreases causing easy fragmentation of the quasi-molecular ion and (ii) Reaction 1 producing $(M+1)^+$ ion may be sufficiently exothermic in higher homologues to exceed the bond dissociation energies. The latter explanation is more reasonable, because the decrease of bond dissociation energy from 1-C to 5-C compounds is not likely to be high.[8)] Thus, the proton

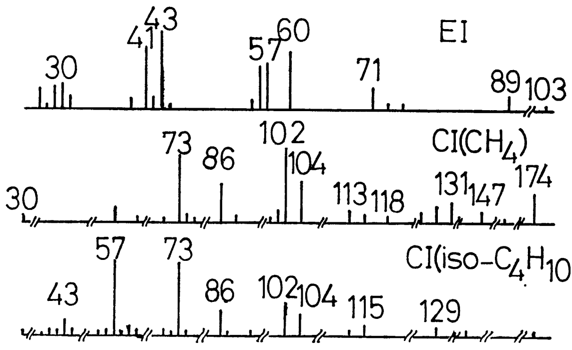

Fig. 6. Mass spectra of butyl nitrite (MW 103).

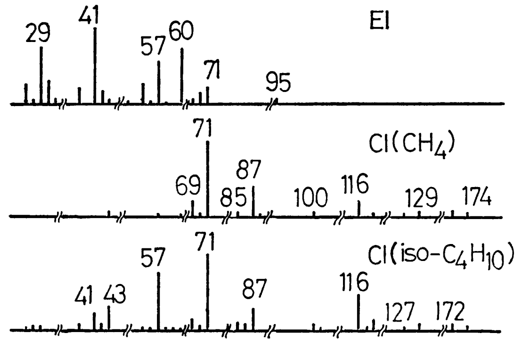

Fig. 7. Mass spectra of pentyl nitrite (MW 117).

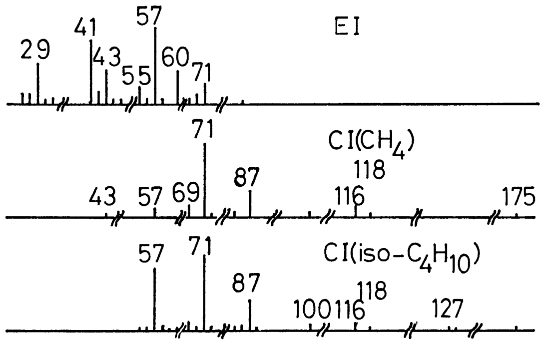

Fig. 8. Mass spectra of isopenthyl nitrite (MW 117).

affinity of ethyl nitrates and nitrites may be higher for higher homologues, because heat of Reaction 1 is given by the following equation.[7)]

$$\Delta H_1 = PA(CH_4/C_2H_4/C_4H_8)\text{-}PA(RH) \quad (3)$$

(PA stands for proton affinity)

The $(M-1)^+$ ions generally do not have high abundance. It is also observed with our limited data that these ions are present in relatively greater abundance in the nitrite spectra than in the corresponding nitrate spectra with any particular reagent gas.

The EI spectra of the compounds reported in this paper are consistent with those documented in the literature.[9,10)] Two characteristic ions present in the EI spectra of the nitrates are, NO_2^+ ($m/e=46$) and $CH_2ONO_2^+$ ($m/e=76$).[‡,10)] The corresponding ions,

---

[‡] Present in normal-type alkyl nitrates and nitrites except in CH_3ONO_2 and CH_3ONO.

NO^+(m/e=30) and CH_2ONO^+ (m/e=60)‡ are also present in the EI spectra of the nitrite esters. In addition to the above characteristic ions, many fragments from the alkyl carbon chain are also present. In higher homologues of the nitrate and nitrite compounds, these mass fragments from the carbon chain have relatively high abundance. Details of the EI spectra are not intended to be discussed in this paper.

Influence of Temperature and Pressure. The influence of temperature and pressure on the CI mass spectral pattern was studied in detail with ethyl nitrate as the substrate. Figure 9 shows the fraction of the relative abundance of the main ion (m/e=92) *vs.* temperature of the ionization chamber and pressure. It can be seen that the quasi-molecular ion has got maximum abundance at low temperature (170 °C) and pressure of $\approx 3\times10^{-5}$ Torr and $\approx 0.8\times10^{-5}$ Torr respectively for CH_4 and i-C_4H_{10} as reagent gases. The CI mass spectral patterns presented in this paper have, therefore, been taken at 170 °C and the above mentioned pressures.

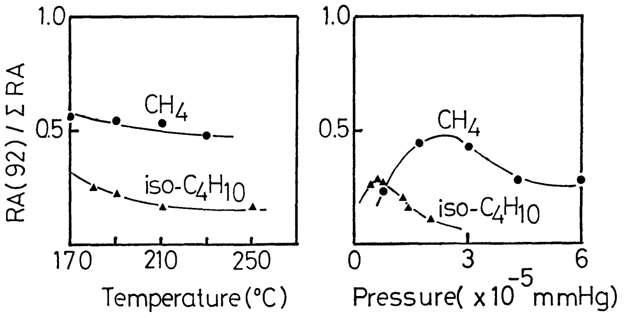

Fig. 9. Pressure and temperature dependence of mass fragments of ethyl nitrate.

Identification of Major Fragmentation Products. Complete identification of all fragments could not be made and is difficult. However, some speculations may be useful.

Methyl Nitrate (MW 77)(Fig. 1). $(M+1)^+$ is the ion with maximum abundance. Other major ions present are m/e=41, 46 (NO_2^+), and 47(NO_2H^+) for CH_4 as reagent gas and m/e=30 (NO^+), 41, 42, 45 (CH_3ON^+), 46 (NO_2^+), 47 (NO_2H^+), 55, 61 (CH_3ONO^+), 69, 72, 73 ($C_4H_9O^+$), 74, 75, and 89($C_4H_9O_2^+$) for i-C_4H_{10} as reagent gas. m/e=73 and 89 ions may be formed by the separation of CH_3ONO (m=61) and CH_3ON (m=45) groups from the cluster ion, $(RH+C_4H_9)^+$. Such cluster ions are very common in CI mass spectra with i-C_4H_{10}.[11] Unfortunately there are many unassigned ions, but only m/e=41 ion has relatively high abundance.

Ethyl Nitrate (MW 91)(Fig. 2). As in the case of methyl nitrate, the $(M+1)^+$ ion has maximum abundance. Other ions present are m/e=30 (NO^+), 45 ($C_2H_5O^+$), 46 (NO_2^+), 47 (NO_2H^+), 64 ($H_2NO_3^+$), 76 ($CH_2ONO_2^+$), and 137. The m/e=64 ion may be formed by the reaction between the reactant ions and RH or RH_2^+ by intramolecular rearrangement and fragmentation. The m/e=137 ion may also be speculated as $[(2M+1)-NO_2]^+$ ion, derived from $(2M+1)^+$ ion very often seen in the CI spectra.

Pentyl and Isopentyl Nitrate (MW 133)(Figs. 3 and 4). Quasi-molecular $(M-1)^+$ ion is present in very low abundance. $(M+1)^+$ ion has still less abundance. The base peak is due to $C_5H_{11}^+$ (m/e=71). Other ions produced in significant amounts are m/e=46 (NO_2^+), 57 ($C_4H_9^+$), 69 ($C_5H_9^+$), 72 ($C_5H_{12}^+/C_4H_8O^+$), 73 ($C_4H_9O^+$), 85 ($C_5H_9O^+$), and 87 ($C_5H_{11}O^+$).

Ethyl Nitrite (MW 75)(Fig. 5). As in the case of ethyl nitrate, $(M+1)^+$ ion has got maximum abundance. The $(M+1)^+$ peak is more prominent in this compound than in ethyl nitrate. The other major ions are m/e=30 (NO^+), 45 ($C_2H_5O^+$), 47 (NO_2H^+), 59 ($C_2H_5ON^+$), 85 ($C_6H_{13}^+$), 86 ($C_6H_{14}^+$), and 87 ($C_4H_9ON^+$). The last three ions are seen mainly in the i-C_4H_{10} spectrum. They may be formed by the separation of NO_2H (m=47), NO_2(m=46), and C_2H_5O (m=45) groups respectively from the cluster ion $(RH+C_4H_9)^+$.

Butyl Nitrite (MW 103)(Fig. 6). Quasi-molecular $(M-1)^+$ and $(M+1)^+$ ions are present in fairly good abundance. In the CH_4-spectrum, the former is the base peak. Other major ions present are m/e= 30 (NO^+), 43 ($C_3H_7^+$), 57 ($C_4H_9^+$), 73 ($C_4H_9O^+$), 86 ($C_4H_8ON^+$), 88 ($C_3H_6ONO^+$), 113, 115, 118, 129, 131, 147, and 174. The last seven ions are obviously cluster ions whose origins are difficult to speculate. However, except m/e=131 and 174 ions, all of them are present in relatively low abundance.

Pentyl and Isopentyl Nitrite (MW 117)(Figs. 7 and 8). Both $(M+1)^+$ and $(M-1)^+$ ions are present in low abundance, but the latter ion has comparatively greater abundance. Other major ions present are, m/e=41 ($C_3H_5^+$), 43 ($C_3H_7^+$), 57 ($C_4H_9^+$), 69 ($C_5H_9^+$), 71 ($C_5H_{11}^+$), 85 ($C_5H_9O^+$), 86 ($C_4H_8ON^+$), 87 ($C_5H_{11}O^+$), and 100 ($C_5H_{10}ON^+$). Many cluster ions are also formed in very low abundance.

Quantitative Analysis by Mass Fragmentography. To study the possibility of quantitative analysis of alkyl nitrates and nitrites in trace amounts by CI mass spectrometry, mass fragmentography was attempted. This was measured at m/e=76 and 92 respectively for ethyl nitrite and ethyl nitrate using CH_4 as the reagent gas. PEG 400 at room temperature was used as the column material. It has earlier been successfully used for the separation of many organic materials, including PAN, in the atmospheric smog.[12] This

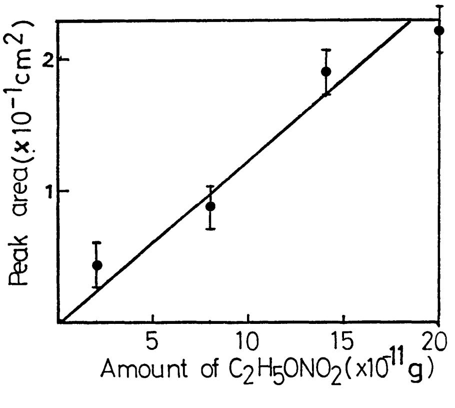

Fig. 10. Calibration curve for the analysis of ethyl nitrate by GC-CI-MF.

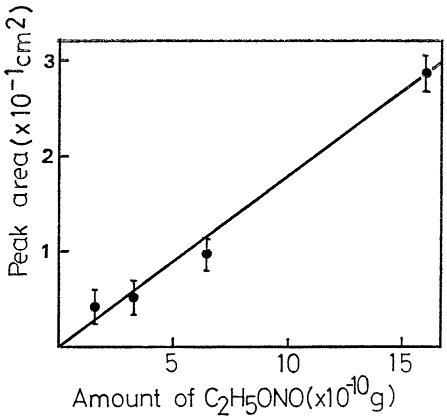

Fig. 11. Calibration curve for the analysis of ethyl nitrite by GC-CI-MF.

also has been used to separate different alkyl nitrates of low molecular weights from one another.[12] Helium was used as the carrier gas (flow rate 8—11ml/min). Standard solutions of the compounds in ethanol, in which they are stable, were injected into the column of the GC-MS apparatus and mass fragmentograms taken at appropriate GC peaks and mass numbers. The above column material could adequately separate the compounds from ethanol.

Figures 10 and 11 show the calibration curves (peak area of mass fragmentogram *vs.* amount of the compound injected into the column) at the lowest possible limits for both ethyl nitrate and ethyl nitrite respectively to give an idea about the sensitivity of the method. Qualitative detection is possible at still lower amounts of the samples (picogramme level). Quantitative analysis at picogramme level was not successful presumably due to adsorption of the samples on the glass surface of the syringe. A better sampling technique may improve the sensitivity limit.

The authors are grateful to the Japan Society for the Promotion of Science (JSPS) for award of a Senior Co-operative Fellowship to one of them (RCD). Also they wish to thank the Ministry of Education of the Government of Japan for supporting this research from the Fund for Environmental studies.

References

1) K. L. Demrjian, J. A. Kerr, and J. G. Calvert, "Advances in Environmental Science and Technology," ed by J. N. Pitts, Jr., R. I. Metcalf, and A. Leoyd., John Wiley and Sons (1974), Vol. IV, p. 1.

2) A. P. Altshuller and J. J. Bufalini, *Environ. Sci. Technol.*, **5**, 39 (1971).

3) A. P. Altshuller and J. J. Bufalini, *Photochem. Photobiol.*, **4**, 97 (1965).

4) T. Kato, "Gas-chromatographic Techniques in Air Pollution," (in Japanese), Sankyo Co., Ltd. (1975), p. 169.

5) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).

6) E. R. Stephens and M. A. Price, *J. Chem. Educ.*, **50**, 351 (1973).

7) B. Munson, *Anal. Chem.*, **43**, 28A (1971).

8) S. L. Murov, 'Handbook of Photochemistry," M. Dekker Inc. (1973), p. 79.

9) "Atlas of Mass Spectral Data," ed by E. Stenhagen, S. Abrahamsson, and F. W. McLafferty, Interscience Publ, (1969), Vol. I, pp. 97, 184, 292, 443, and 646.

10) R. T. M. Fraser and N. C. Paul, *J. Chem. Soc., B*, **1969**, 659.

11) F. Field, *J. Am. Chem. Soc.*, **91**, 2827 (1969).

12) S. Izumikawa, M. Hoyahuku, K. Nakano, K. Asakuno, and T. Ohdaira, *Ann. Rep. of the Tokyo Metropolitan Res. Inst. for Environ. Protection*, **4**, 41 (1973).