

# POSITIVE AND NEGATIVE ION MASS SPECTRA OF RING-SUBSTITUTED NITROBENZENES

S. Rahman - Setayesh and M. R. Arshadi

*Department of Chemistry, Sharif University of Technology, Tehran, Islamic Republic of Iran*

## Abstract

The 70 eV positive and negative ion mass spectra of ring-substituted nitrobenzenes were studied. The influence of the substituent group on the fragmentation modes of the molecular ions is discussed. The effect of pressure in the formation of negative ions was also studied. As expected, the ratio of fragment ions to negative molecular ions decreased with increasing pressure in ion source.

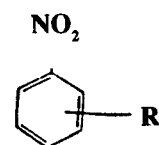
## Introduction

Negative ion mass spectrometry is often used to complement the information obtained from positive ion mass spectra. In the early days of mass spectrometry, there was not much interest shown in the field of negative ion spectra. This was partly due to the difficulties in production and detection of the negative ions. With rapid advancement in the field, and the design and production of more and more powerful detection systems in the last twenty years, negative ion mass spectrometry has finally received its due attention.

There have been a number of mass spectrometric studies of nitro-aromatic compounds published in recent years. Most of them, however, have employed very specialized techniques, such as negative ion chemical ionization [1, 2], high pressure [3], laser [4, 5] and fast atom bombardment [6, 7] mass spectrometry. The present investigation has been carried out using conventional electron impact ionization methods, available to almost all organic chemists, for comparing positive and negative spectra and identification purposes.

In this paper, we present the results of an investigation made on the positive and negative ion mass

spectra of some ring-substituted nitrobenzenes. We were particularly interested in the effect of the substituted group on the fragmentation patterns of both positive and negative ion spectra of these compounds. These compounds can be represented by the following structure.



## Results and Discussion

### Dinitro Benzenes

#### a) Positive Ions

The positive ion mass spectra of the three isomers of dinitrobenzenes are shown in Figure 1.

As can be seen, the molecular ion is the base peak in the spectra of meta and para isomers but 60% of the base peak in the ortho spectra.

The loss of O and NO group which is a common feature of all aromatic nitro compounds is also observed here at low intensities. Among the various mechanisms suggested for elimination of NO is [8].

**Keywords:** Positive; Negative; Ion EI mass spectra

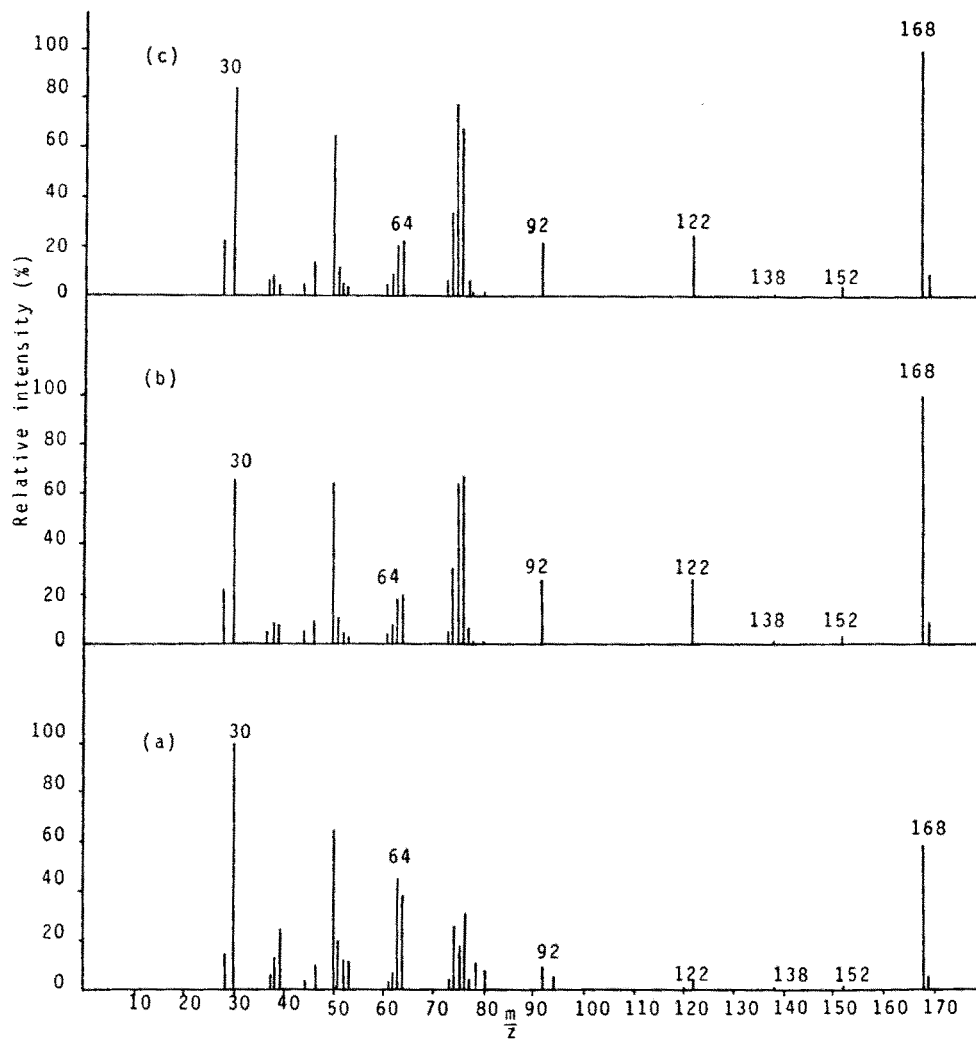
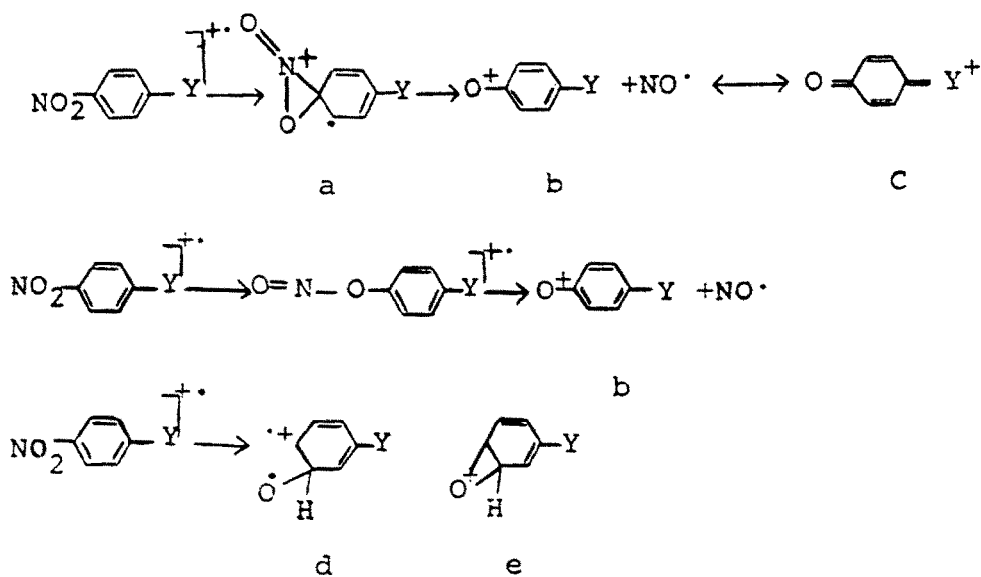


Figure 1. Positive ion mass spectra of (a) ortho dinitrobenzene; (b) meta dinitrobenzene; (c) para dinitrobenzene

Obviously, the existence of an electron withdrawing group on the ring will destabilize cation (b), thus the second nitro group will destabilize cation (b).

The peaks at  $\frac{m}{z}$  122 and 92 can be attributed to the loss of  $\text{NO}_2$  group and the loss of  $\text{NO}$  and  $\text{NO}_2$  groups from parent ions, respectively. These peaks have a considerably lower intensity for ortho isomer.

The loss of  $\text{CO}$  from  $\text{C}_6\text{H}_4\text{O}$  like aromatic ring compounds containing oxygen is observed [9]. In addition, the peak at  $\frac{m}{z}$  30 appears in all of the three positive ion spectra, this is perhaps due to the high stability of  $[\text{NO}]^+$ .

Meyerson and Fields have also studied the positive ion spectra of dinitrobenzenes. Their results are in good agreement with this work [10]. Moreover, a comparison of the three spectra reveals that the ratio of molecular ion to the  $[\text{NO}]^+$  is smaller for the ortho isomer. These two facts can be attributed to the lower thermochemical stability of the ortho molecular ion [10].

#### b) Negative Ions

The negative ion mass spectra of ortho, para and meta dinitrobenzene are represented in Figure 2.

Owing to a high affinity for electron capture process by the  $\text{NO}_2$  radical, the highest peak in all the three spectra is at  $\frac{m}{z}$  46, corresponding to  $[\text{NO}_2]^-$  ion. The molecular anion in the spectra of the three isomers at  $\frac{m}{z}$  168 with moderate intensity was observed. As in the positive ion spectra, the loss of  $\text{O}$  and  $\text{NO}$  group from the molecular ions is also witnessed here ( $\frac{m}{z}$  152 and  $\frac{m}{z}$  138).

The peak at  $\frac{m}{z}$  138,  $[\text{M}-\text{NO}]^-$  has the highest intensity, next to  $\frac{m}{z}$  46,  $[\text{NO}_2]^-$ . This is because the remaining  $\text{NO}_2$  group on the ring has an electron withdrawing inductive effect, and thus stabilizes the resulting anion. The loss of  $\text{NO}$  occurs due to rearrangement of nitro to nitrite in molecular anion [11].

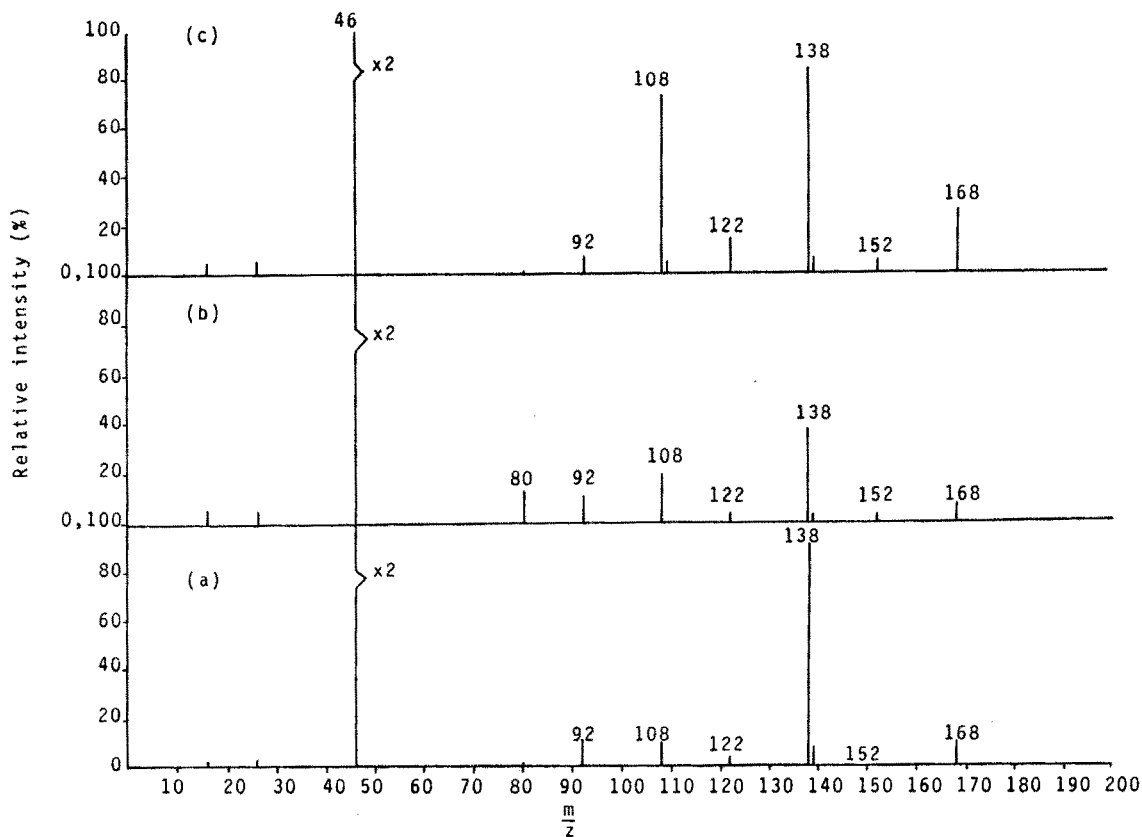
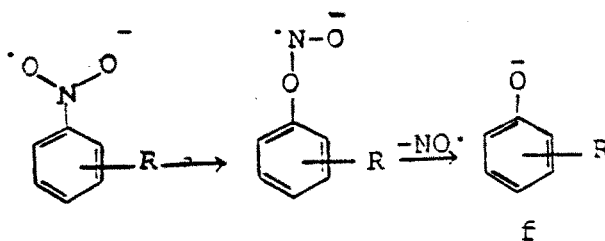


Figure 2. Negative ion mass spectra of (a) ortho dinitrobenzene; (b) meta dinitrobenzene; (c) para dinitrobenzene

The spectra in Figure 2 reveal that the peak at  $\frac{m}{z}$  138,  $[M-NO]^-$  appears with less intensity in the spectra of meta dinitrobenzene, the reason for this is due to the fact that the electron withdrawing power of  $NO_2$  substituent is more effective when it is located in the para and ortho positions.

The appearance of peaks at  $\frac{m}{z}$  122 and  $\frac{m}{z}$  92 can be attributed to the loss of the  $NO_2$  group and the loss of NO and  $NO_2$  from molecular ion, respectively.

The successive loss of two NO groups, from the molecular ion, results in the appearance of a peak at  $\frac{m}{z}$

108. The intensity of this peak in para is greater than ortho and meta isomers and can be used to differentiate this isomer from the others. This difference in the intensities can be explained by the higher stability of P-semiquinon resulting from para isomer.

In the spectra of meta isomer, there is another peak at  $\frac{m}{z}$  80. This peak is probably the result of decarboxylation of m-semiquinon, according to the following scheme:

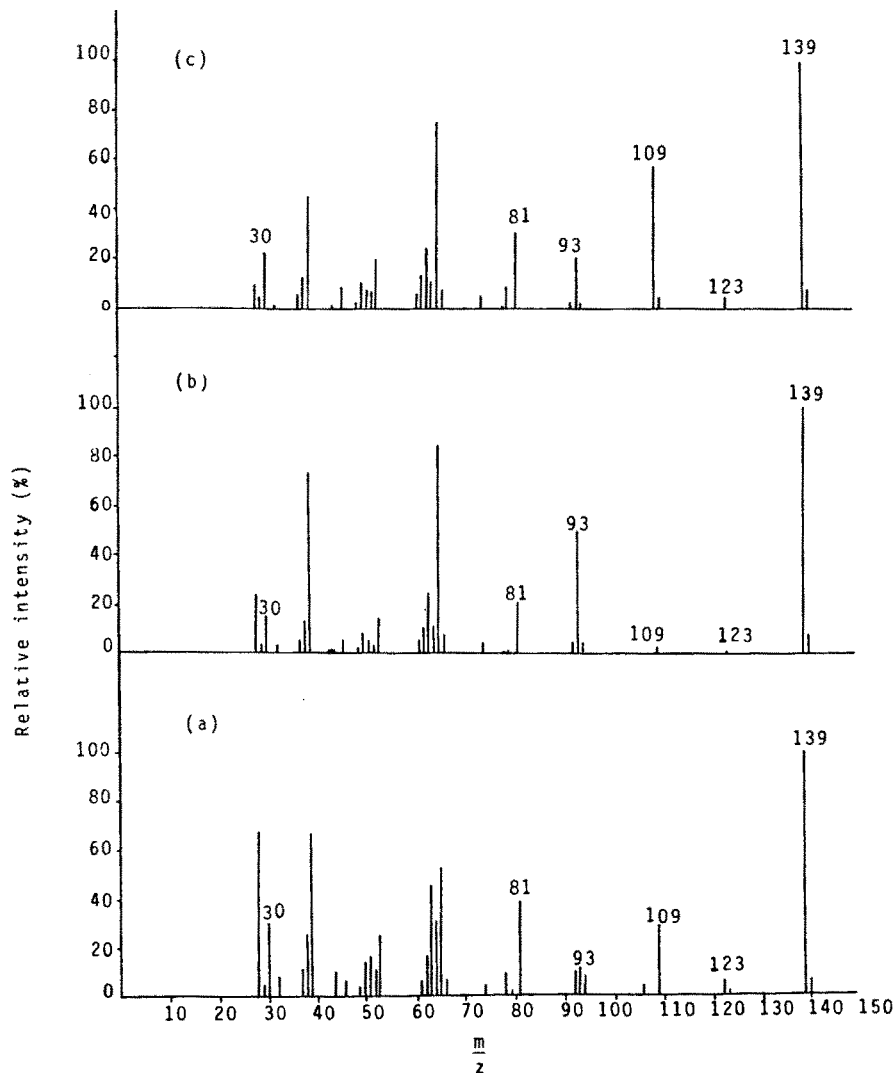
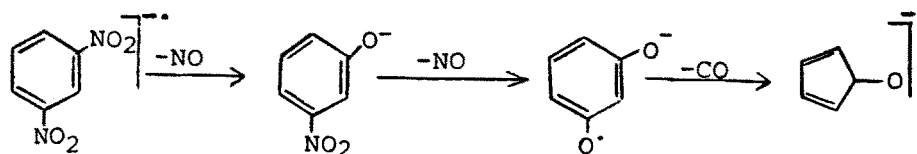


Figure 3. Positive ion mass spectra of (a) ortho nitrophenol; (b) meta nitrophenol; (c) para nitrophenol

Finally, a comparison of the positive and negative ion spectra of these three isomers reveals that, the dissimilarities between the negative ion spectra are more pronounced, thus the negative ion spectra can be used to differentiate the various isomers with more certainty.

### Nitro Phenols

#### a) Positive Ions

The positive ion mass spectra of ortho, para, meta nitrophenol are shown in Figure 3. The molecular ion is the base peak in three spectra. The loss of NO and NO<sub>2</sub> is observed at  $\frac{m}{z}$  109 and 93, respectively. The intensity of [M-NO]<sup>+</sup> in ortho and para is greater than the meta isomer due to the more stable nature of the

[M-NO]<sup>+</sup> ion in the para and ortho isomers. On the other hand, the intensity of [M-NO<sub>2</sub>]<sup>+</sup> in meta is greater than in the ortho and para isomers perhaps because of a low favorable comparative reaction, [M-NO]<sup>+</sup>.

The ion at  $\frac{m}{z}$  81 may be formed by the loss of CO from the  $\frac{m}{z}$  109 ion. The loss of CO is noted from compounds that contain oxygen [9].

#### b) Negative Ions

The peak at  $\frac{m}{z}$  46 (see Figure 4) which corresponds to [NO<sub>2</sub>]<sup>-</sup> appears, to a large extent in the negative ion spectra of only meta and para isomers.

However, the peak at  $\frac{m}{z}$  122 which is the base peak

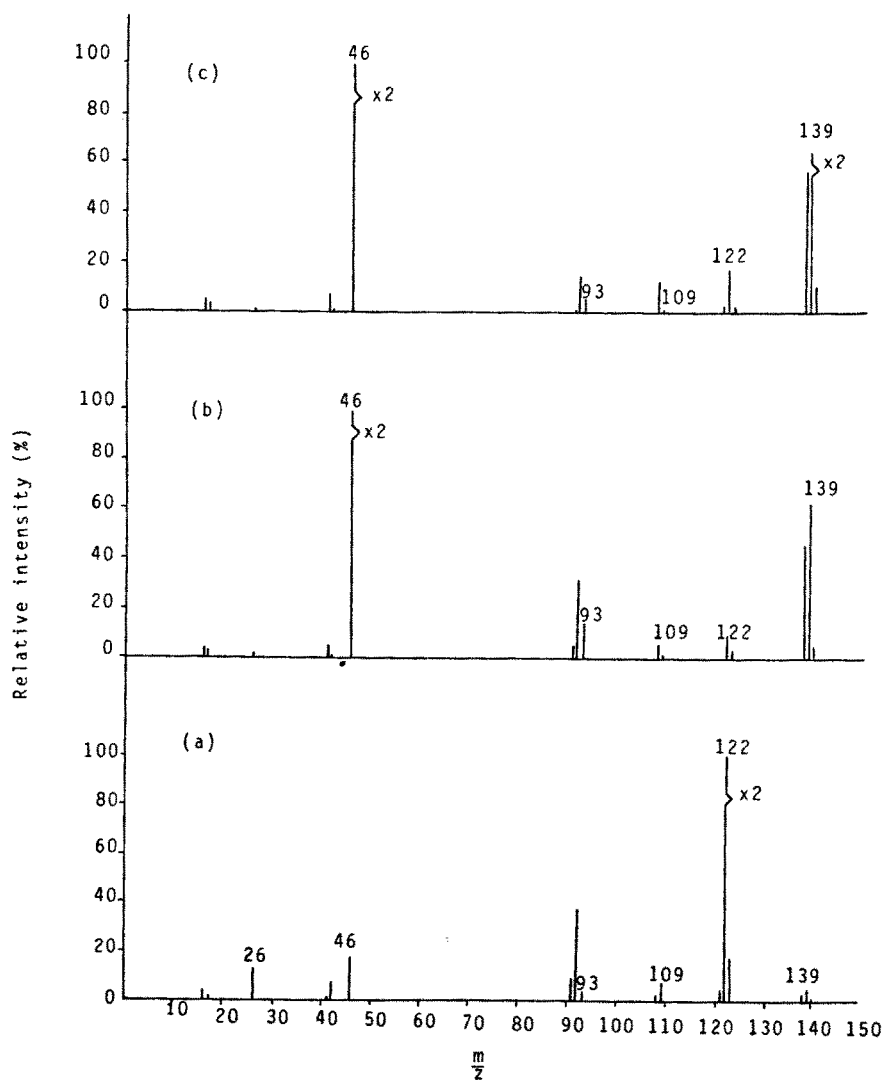
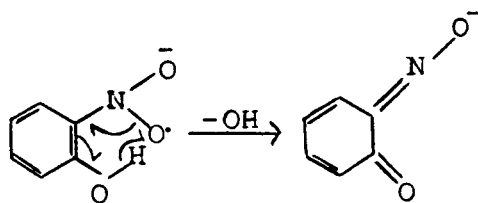


Figure 4. Negative ion mass spectra of (a) ortho nitrophenol; (b) meta nitrophenol; (c) para nitrophenol

in the spectra of the ortho isomer has a lower intensity than the other two spectra. The reason could be the occurrence of a more favorable fragmentation scheme in the case of the ortho nitrophenol. This fragmentation scheme can be represented as follows:



The expulsion of OH from molecular ion has also been reported in negative ion spectra of o-nitrobenzoic acid [12], o-nitrobenzamide [11], o-nitroacetanilide, o-nitrophenyl trifluoroacetamide [13] and o-nitrothioacetanilides [14]. As can be seen, this scheme is only possible for the ortho isomer. Furthermore, in comparison with the meta and para isomers, the intensity of the molecular ion in the ortho nitrophenol is not of any significance. This can also be attributed to the relative ease of occurrence of the above fragmentation process.

As in the case of dinitrobenzenes, a glance at the three spectra represented in Figure 4 reveals that the negative ion spectra of the three nitrophenols are distinguishable from each other, thus can be used for identification of these compounds and their derivatives.

#### The Effect of Pressure in the Formation of Negative Ions

To investigate the effect of ion source pressure on the fragmentation pattern of the negative molecular ions, the mass spectra of ortho dinitrobenzene and para nitrophenol were taken at several ion source pressures. The results are summarized in Tables 1 and 2.

Table 1. The ratio of major fragments to molecular ion of ortho dinitrobenzene

PX10 <sup>6</sup> Torr	[M-No] <sup>-</sup> [M] <sup>-</sup>	[M-No-No] <sup>-</sup> [M] <sup>-</sup>	[M-No <sub>2</sub> -No] <sup>-</sup> [M] <sup>-</sup>	[No <sub>2</sub> ] <sup>-</sup> [M] <sup>-</sup>
5	13	2	3	36
30	8.81	0.95	0.94	19.36
60	7.78	0.90	0.86	17.04

As can be seen, the ratio of the fragment ions to the molecular ions decreases with increasing pressure in the ion source. This effect has been attributed to the

Table 2. The ratio of major fragments to molecular ion of para nitrophenol

PX10 <sup>6</sup> Torr	[M-H] <sup>-</sup> [M] <sup>-</sup>	[M-OH] <sup>-</sup> [M] <sup>-</sup>	[M-HNo] <sup>-</sup> [M] <sup>-</sup>	[M-HNO <sub>2</sub> ] <sup>-</sup> [M] <sup>-</sup>	[NO <sub>2</sub> ] <sup>-</sup> [M] <sup>-</sup>
3	0.86	0.59	0.24	0.83	2.69
6	0.57	0.19	0.22	0.24	2.57
30	0.44	0.13	0.1	0.12	1.53
50	0.49	0.061	0.034	0.035	0.38

fact that as the pressure is increased, the low energy electron capture process becomes more favourable than any other process of the negative ion formation [15, 16]. This is due to the availability of a large flux of secondary electrons, which results in a more stable molecular ion [17, 18].

#### Experimental Section

The compounds investigated were obtained commercially prior to the studies of their spectra by M S However, dinitrobenzene isomers were recrystallized from absolute ethanol and nitrophenol isomers were recrystallized from distilled water, dried in an oven and their purities confirmed through melting and TLC analysis.

Mass spectra of negative ions may be obtained in the same way as positive ions with a conventional mass spectrometer after reversal of the potentials. Mass spectra were determined on a varian MAT CH-5 spectrometer. The samples were introduced directly into the ion source by the solid probe and the spectra were taken at 70 eV and 3000 volts accelerating potential for the positive ion spectra. The negative ions were taken at 70 eV and accelerating potential 5000 volts and 2-3X10<sup>-5</sup> torr pressure in ion source. The 5000 volts were provided by means of an external d. c. power supply, and resulted in a higher sensitivity and better resolution, as described in a previous publication [17].

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