Journal of Chromatography, 387 (1987) 171–186
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

CHROM. 19 088

RESPONSE OF THE NITROGEN MODE OF THE THERMIONIC IONIZATION DETECTOR TO SUBSTITUTED NITROBENZENES

C. S. JONES and E. P. GRIMSRUD*
Department of Chemistry, Montana State University, Bozeman, MT 59717 (U.S.A.)
(Received August 18th, 1986)

SUMMARY

The response of the nitrogen mode of the thermionic ionization detector to a large number of substituted nitrobenzenes has been studied. The effects of detector temperature, emitter heating current, bias voltage, and changes in the detector gas on the responses of 36 compounds is reported. An attempt is made to interpret these results in terms of three candidate models for the mechanism of the nitrogen mode of the thermionic ionization detector response. Of particular importance in this study is a comparison of the observed responses with recently reported gas phase electron affinity values of the substituted nitrobenzenes. The results tend to support a mechanism in which the initiating step is thermal decomposition of the analyte molecule at the surface–gas interface, followed by electron transfer from the emitter surface to a gas phase species (probably nitrogen dioxide). For some molecules, a mechanism involving direct electron transfer to the intact parent molecule may also be operative.

INTRODUCTION

Thermionic ionization detectors which use heated alkali-impregnated sources have been widely used for the selective gas chromatographic (GC) detection of nitrogen- and phosphorus-containing compounds[1–7]. In these applications a thermionic emitter is heated either by a hydrogen–air flame or electrically in a flameless atmosphere containing hydrogen and oxygen. With the flameless version of the thermionic ionization detector, it is thought that a response occurs due to electron transfer from the low work function surface to highly electronegative species, possibly CN, NO_2, and PO_2, which are thought to be produced in the reactive gaseous boundary layer adjacent to the hot surface[5]. The selective response of the flameless thermionic ionization detector to nitrogen to phosphorus-containing compounds has been explained in terms of a lowering of the effective "work-function" of the emitter surface due to the presence of electronegative species at the gas–solid interface. More recently, Patterson and co-workers[8–9] have shown that a flameless thermionic ionization detector can also be used for the detection of certain electronegative molecules in an inert nitrogen atmosphere. Using a highly cesium-enriched ceramic emitter and a relatively low surface temperature of about 400–500°C, selective responses to certain classes of

0021-9673/87/$03.50

molecules, such as dinitrotoluenes, was demonstrated. Subsequent use of this detector for the specific analysis of nitrated polycyclic aromatic hydrocarbons in environmental samples has been reported[10]. In this version of the thermionic ionization detector the analyte molecule, by itself, appears to carry with it all of the ingredients necessary for occurrence of a surface-to-gas phase electron transfer. Beyond this general deduction, however, no more precise description of the surface ionization mechanism of this detector has been offered. The study of the nitrogen mode of the thermionic ionization detector to be related here was designed specifically to explore this question concerning the fundamental basis of this detector's response to electronegative molecules.

On first consideration, one can envision several potential mechanisms by which nitrogen mode responses might occur. The first and simplest one is by direct electron transfer from the surface to the molecule, as shown in mechanism 1,

$$\text{e(surface)} + \text{M} \rightleftharpoons \text{M}^- \tag{1}$$

to form a molecular negative ion, M^-. This possibility is a reasonable one in view of the fact that the compounds to which the nitrogen mode is known to respond have positive electron affinities. Another possibility, shown as mechanism 2,

$$\text{M} \rightarrow \text{N} + \text{X} \xrightarrow{\text{e(s)}} \text{X}^- \tag{2}$$

is that the analyte molecule is thermally decomposed on the hot surface (s) of the emitter to form species N and X, one of which has a high electron affinity and abstracts an electron from the surface to form the negative ion, X^-. This possibility is attractive in view of the very high electron affinity of NO_2 (refs. 11 and 12) and the specificity of response previously demonstrated to nitroaromatic hydrocarbons[8-10]. An additional possibility seems worthy of consideration since it is thought to be operative in other modes of the thermionic ionization detector[4,5]. That is, gas phase radicals at the solid–gas interface might chemically alter the analyte molecule so as to again form an intermediate species, X, which abstracts a surface electron, as shown in mechanism 3.

$$\text{M} + \text{R}^\bullet \rightarrow \text{N} + \text{X} \xrightarrow{\text{e(s)}} \text{X}^- \tag{3}$$

While the presence of reactive species, R, might seem unlikely in an atmosphere of pure nitrogen, it is nonetheless possible due either to the presence of impurities in nitrogen or due to the generation of reactive species from the analyte itself.

An attempt is made here to interpret the nitrogen mode responses for the thermionic ionization detector of 36 compounds, most of which are substituted nitrobenzenes, in terms of the above candidate mechanisms. Of particular significance here is a comparison of the responses of the substituted nitrobenzenes to their gas phase electron affinity values, which have recently been reported[12]. Also, the effects on the responses to all compounds of variations in detector temperature, source heating current, bias voltage, and detector gas dopants (methane, isobutane, oxygen, nitrous oxide, carbon dioxide, and argon) are reported.

EXPERIMENTAL

A thermionic ionization detector with nitrogen mode was purchased from Detector Engineering and Technology (Walnut Creek, CA, U.S.A.) and was used without modification. This detector has been described in detail by Patterson[8]. It contains a low work-function cathode made of cesium sulfate-enriched ceramic. This thermionic emitter is electrically heated and negatively biased with respect to a surrounding anode which is attached to an electrometer. The chromatographic effluent (10 ml/min nitrogen) is mixed at the base of the detector with additional detector gas (usually nitrogen) so that the total gas flow-rate through the detector is 100 ml/min.

The detector was mounted on a Varian 3700 gas chromatograph which also housed an electron-capture detector. A wide-bore fused silica column (10 m × 530 μm I.D., 50% phenylmethyl silicon stationary phase) was used with a 1-μl splitless injection and isothermal operation of the oven. The end of this column was threaded through a transfer line and into the base of the detector in order to minimize exposure of the sample to metallic surfaces. All chemicals studied were purchased from commercial suppliers. Standard solutions of them were made by the successive dilution of weighed quantities into toluene. The detector gases argon, carbon dioxide and nitrous oxide were obtained from Chemetron Co. (Chicago, IL, U.S.A.). Methane and isobutane were obtained from Linde Co. (Danbury, CT, U.S.A.) and nitrogen from Liquid Air Co. (San Francisco, CA, U.S.A.). All of these were first passed through oxygen-removing and water-removing traps. A specially prepared tank of 0.31% oxygen in nitrogen was obtained from Airco (Montvale, NJ, U.S.A.).

The chromatographic retention times of all compounds were first established using a flame ionization detector. Column temperatures required for the convenient elution of all chemicals ranged from 75 to 180°C. Injection reproducibility as measured by peak area was routinely better than ±10%.

RESULTS

The responses of 36 compounds were determined over a wide range of concentrations. Peak-height calibration curves determined using two different levels of emitter heating current are shown in Fig. 1. Generally, a region of near-uniform molar response was observed only for the first decade or two of concentration change above the lowest detectable concentration. The molar responses to most substances increased or decreased significantly with further increases in sample concentrations. The peak area response observed for the lowest concentration of each compound in Fig. 1A are listed in Table I as the absolute response (C/mol) of that substance. Also, listed in Table I is the observed detection limit at which the response to each compound was about five times the noise level.

The effect of temperature of the detector housing on the response to each compound was determined over the range 270 to 370°C. Typical results are shown in Fig. 2 for five compounds. The absolute response to all compounds is increased by temperature in a nearly linear manner as shown. Therefore, it is possible to describe the temperature dependence of response for each compound by the ratio of responses observed at 370 and 270°C. This is done in the fourth column of data of Table I. The result is that the relative responses of almost all of the compounds are

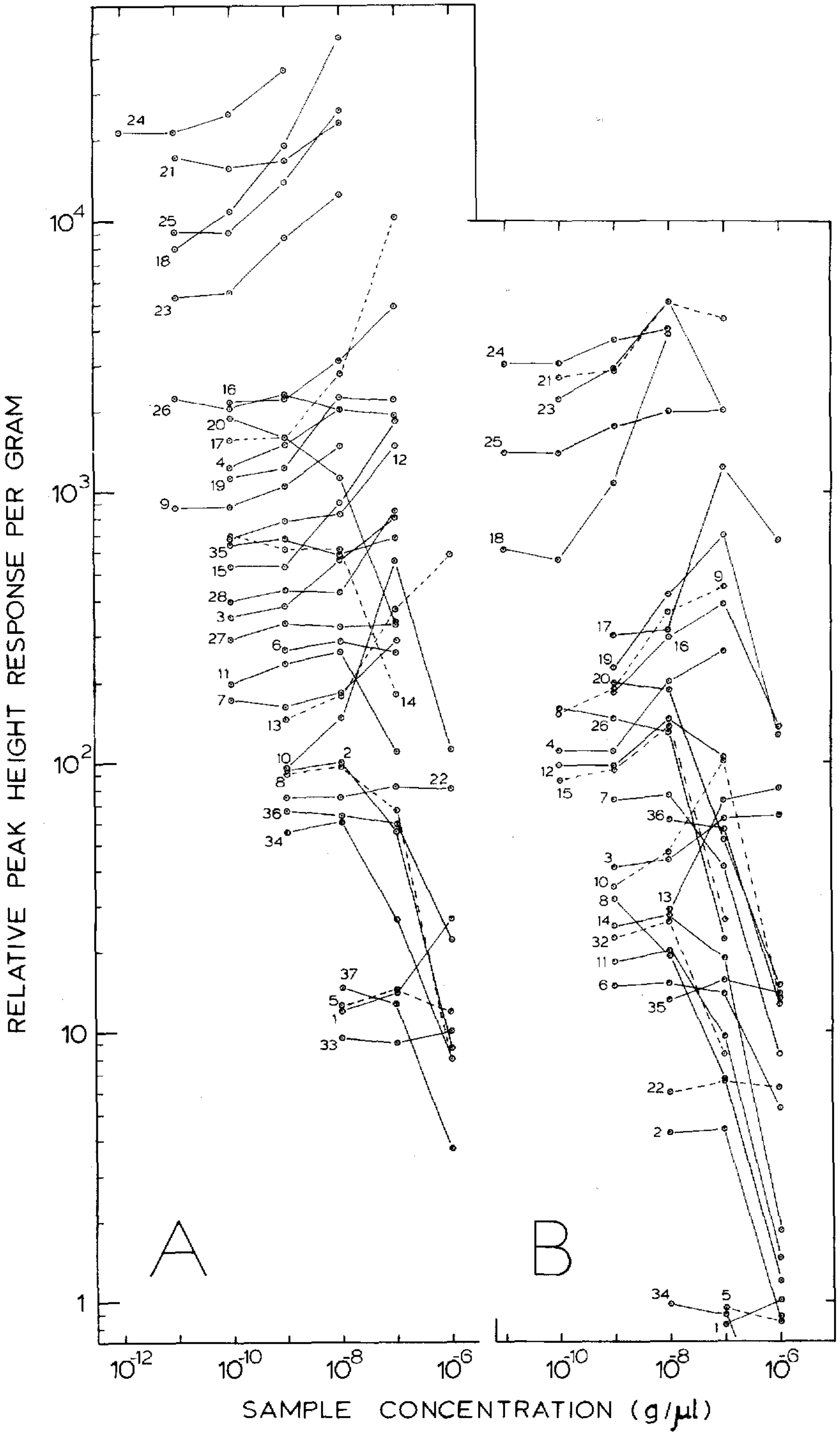


Fig. 1. Thermionic ionization detector with nitrogen mode peak height responses to varied amounts of substituted nitrobenzenes. The compound associated with each calibration curve is indicated by the number assigned in Table I. Detector conditions are: temperature, 320°C; gas flow, 100 ml/min nitrogen; bias voltage, −45 V; source heating current: (A) 2.30 A and (B) 2.10 A.

increased in a similar manner, about three to five times, by this 100°C temperature increase. Also shown in Fig. 2 is the baseline current observed at various detector temperatures. The baseline current rises proportionately with responses between 270 and 320°C and then increases more sharply than relative responses at higher detector temperatures. Therefore, maximum signal-to-noise responses to all compounds were observed in the 270 to 320°C temperature range.

The effect of heating current supplied to the source emitter was also determined for each component from heating current (I) = 2.1–2.4 A. Typical results are shown in Fig. 3. Again, a near-linear positive dependence of response on heater current was observed for all compounds. This dependence for each compound is expressed in Table I as the ratio of responses observed at 2.4 and 2.1 A heating current. For this variable a somewhat wider range of response dependencies is observed than was noted for variations in detector temperature. Response amplifications from about 2 to 8 are observed for most of the compounds by this 0.3 A increase in source current. Also, shown in Fig. 3 is the effect of heating current on the baseline current. For our detector the relative increase in baseline current is roughly equal to relative response increases up to about 2.25 A, after which baseline current and aossiciated noise level increase more sharply than do molar responses.

The effect of variation in the bias voltage, from −5 to −45 V applied to the central emitter, on responses is shown in Fig. 4 for several arbitrarily selected cases. The clear result here is that responses are continuously and linearly increased by an increasingly negative bias voltage. For all compounds the ratios of responses observed with bias voltages of −45 and −15 V are listed in Table I. Most of these fall

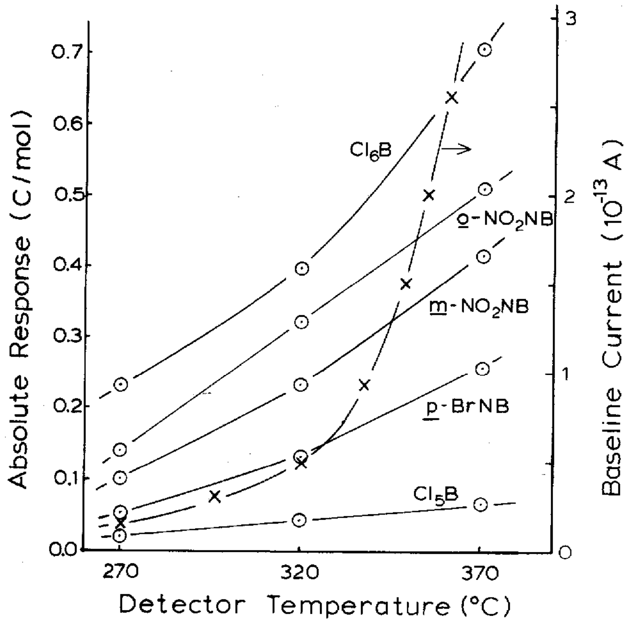


Fig. 2. Absolute thermionic ionization detector with nitrogen mode response of five compounds and detector baseline current as a function of the detector block temperature. Source heater current, 2.1 A; bias voltage, −45 V. See Table I for abbreviations.

TABLE I

THERMIONIC IONIZATION DETECTOR WITH NITROGEN MODE RESPONSES AND AFFECTS OF EXPERIMENTAL PARAMETERS ON RESPONSES TO VARIOUS ELECTRONEGATIVE MOLECULES

*Compound**	*EA*** (*kcal/mol*)	*Absolute molar response**** (*C/mol*)	*Detection limit* (*pg*)	*Effect*§ *of detector temp.*	*Effect*§§ *of heater current*	*Effect*§§§ *of bias voltage*	*Different detector gases*†					
							0.3% O_2	*90%* CO_2	*90%* N_2O	*15%* CH_4	*15% Iso-butane*	*90% Ar*
1 NB	22.1	$2.2 \cdot 10^{-4}$	$12 \cdot 10^3$	4.2	8.4	2.3	0.37	0.80	0.77	0.18	0.10	6.1
2 *m*-CH_3ONB	22.7	$5.5 \cdot 10^{-3}$	780	4.9	7.4	2.8	0.59	0.73	0.43	0.32	0.24	4.6
3 *p*-CH_3ONB	19.6	0.08	125	4.5	14	2.5	0.57	0.88	0.20	0.45	0.31	4.0
4 *o*-CH_3NB	20.0	0.29	65	2.6	4.0	2.7	0.53	1.06	0.36	0.75	0.58	2.3
5 *m*-CH_3NB	21.4	$1.1 \cdot 10^{-3}$	$4 \cdot 10^3$	4.3	8.9	2.6	0.36	0.73	0.43	0.35	0.11	3.7
6 *p*-CH_3NB	20.5	0.03	250	4.4	5.0	2.8	0.50	0.75	0.41	0.71	0.59	3.2
7 *o*-FNB	23.5	0.11	115	3.2	2.2	2.7	0.72	1.54	0.54	1.1	0.76	1.3
8 *m*-FNB	27.5	0.018	165	4.9	9.3	2.4	0.40	0.73	0.32	0.65	0.45	1.9
9 *p*-FNB	24.3	0.51	65	3.75	4.0	2.7	0.80	1.50	0.32	1.00	0.71	1.5
10 *o*-ClNB	25.0	0.018	470	3.4	2.1	2.6	0.41	1.1	0.32	0.50	0.47	1.5
11 *m*-ClNB	28.1	0.018	340	5.5	6.3	2.2	0.52	0.77	0.33	0.62	0.52	1.70
12 *p*-ClNB	27.5	0.060	105	5.2	4.9	2.7	0.67	0.90	0.30	0.59	0.41	1.50
13 *o*-BrNB	25.5	0.043	260	3.7	4.6	2.5	0.82	1.00	0.50	0.35	0.45	1.8
14 *m*-BrNB	28.8	0.035	140	3.3	3.9	2.8	0.75	0.92	0.40	0.47	0.45	1.56
15 *p*-BrNB	28.3	0.13	150	5.0	3.8	2.9	0.67	0.88	0.27	0.49	0.33	1.3
16 *o*-CNNB	35.1	0.39	25	4.2	4.2	2.9	0.51	0.88	0.25	0.40	0.35	2.1
17 *m*-CNNB	34.1	0.49	14	4.8	5.6	2.7	0.34	0.84	0.19	0.55	0.52	1.8
18 *p*-CNNB	38.1	1.4	9	4.0	4.1	2.7	0.27	0.78	0.12	0.57	0.57	1.7

19 o-NO$_2$NB	36.2	0.32	10	3.6	2.0	2.8	0.60	1.3	0.36	0.74	0.67	1.7
20 m-NO$_2$NB	36.2	0.23	6	4.3	6.6	3.0	0.51	0.61	0.24	0.51	0.43	1.9
21 p-NO$_2$NB	43.6	3.9	3	1.9	3.6	2.5	0.85	1.2	0.30	0.87	0.65	1.6
22 m-CF$_3$NB	30.9	0.011	200	3.1	4.3	2.5	0.42	0.62	0.27	0.44	0.33	1.7
23 2,3-DNT		4.4	8	3.4	3.3	2.7	1.27	0.55	0.37	0.60	0.49	1.56
24 2,4-DNT		23	2	4.5	4.2	2.7	1.3	0.64	0.50	0.69	0.59	1.7
25 2,6-DNT		6.5	7	3.3	2.9	2.6	0.42	0.75	0.22	0.44	0.35	2.0
26 3,4-DNT		1.6	50	4.4	3.2	2.7	0.83	1.00	0.59	0.67	0.50	1.5
27 2,4-Cl$_2$NB		0.18	90	3.0	3.1	1.9	0.72	0.86	0.58	0.65	0.45	2.1
28 3,4-Cl$_2$NB		0.21	130	2.7	3.2	3.1	0.96	0.77	0.75	0.56	0.38	2.1
29 2,3,4-Cl$_3$NB		0.28	90	3.6	3.2	3.0	0.93	0.60	0.83	0.37	0.37	3.2
30 2,3,5-Cl$_3$NB		0.30	120	3.6	4.3	2.6	0.73	0.77	0.76	0.36	0.34	3.0
31 2,3,4,5-Cl$_4$NB		0.33	200	2.5	3.5	2.7	1.08	0.79	1.15	0.44	0.44	3.3
32 2,3,5,6-Cl$_4$NB		0.27	170	2.9	5.0	2.5	0.75	0.84	1.25	0.30	0.28	5.6
33 1,2,3,4-Cl$_4$B		$3.2 \cdot 10^{-3}$	$8 \cdot 10^3$	4.4	5.1	2.6	1.08	0.87	1.3	0.48	0.55	2.0
34 Cl$_5$B		0.037	720	3.7	4.5	2.86	1.12	0.84	0.92	0.40	0.44	2.02
35 Cl$_6$B		0.38	60	3.1	2.2	2.5	0.88	1.1	0.56	0.71	0.75	1.26
36 Perfluorobenzoquinone	60.2	0.15	$1 \cdot 10^3$	2.6	3.7	2.6	0.56	0.75	0.47	0.54	0.54	4.0
Baseline current[††]							0.46	1.9	1.1	0.74	0.55	8.8

[*] B = Benzene; NB = nitrobenzene; DNT = dinitrotoluene.

[**] Electron affinity values taken from ref. 12.

[***] Determined from peak areas using following conditions: detector temperature, 320°C; emitter heater current, 2.30 A; flow-rate, 100 ml/min nitrogen.

[§] Ratio of molar response observed at 370°C to that at 270°C; emitter heating current, 2.1 A.

[§§] Ratio of molar response observed with heater current 2.4 A to that with 2.1 A; detector temperature, 320°C.

[§§§] Ratio of molar responses observed using bias potentials of −45 and −15 V applied to the emittor; detector temperature, 320°C; emitter heating current, 2.3 A.

[†] These detector gases were mixed at the base of the detector with nitrogen so that the total detector gas flow-rate was 100 ml/min. Values listed are ratio of responses relative to responses in nitrogen gas.

[††] I_X/I_{N_2}.

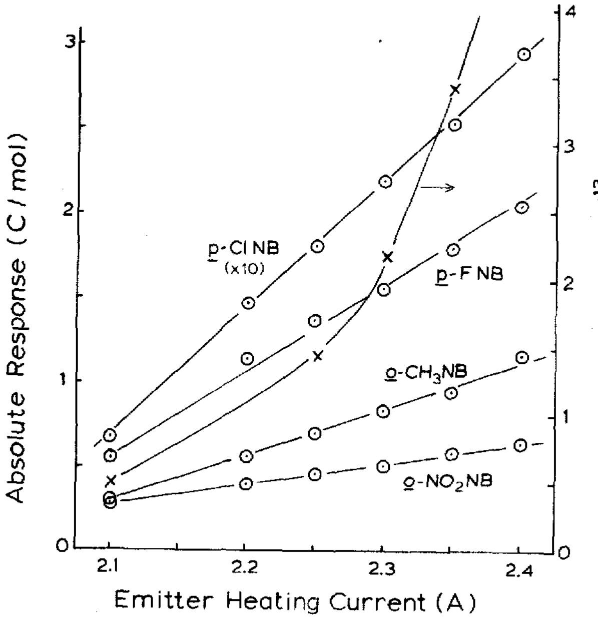


Fig. 3. Absolute thermionic ionization detector with nitrogen mode response of four substituted nitrobenzenes and baseline current as a function of emitter heating current. Detector temperature, 320°C; bias voltage −45 V.

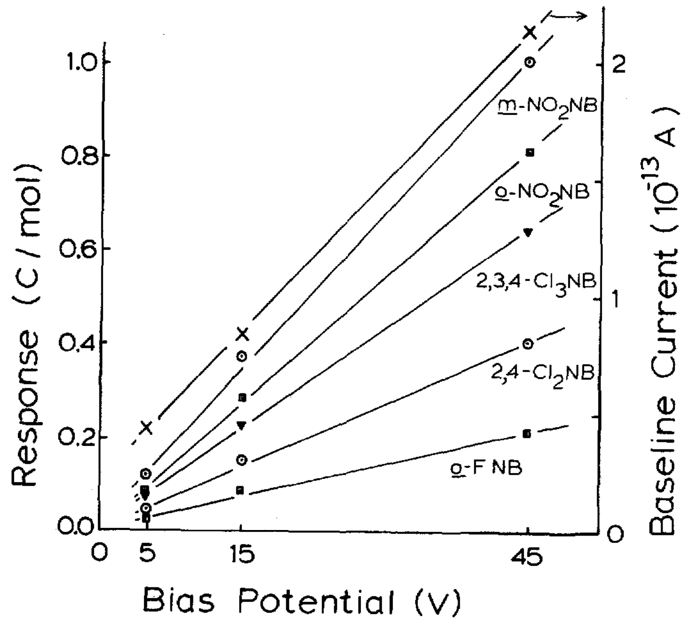


Fig. 4. Absolute thermionic ionization detector with nitrogen mode response of five substituted nitrobenzenes and baseline current as a function of emitter bias potential. Source heating current, 2.3 A; detector temperature, 320°C.

within the narrow range 2.5 to 3.0, which is nearly equal to the voltage ratios. It is significant to point out that these results differ distinctly from those of analogous experiments with the thermionic ionization detector operated in the nitrogen, phosphorus mode[5], where a saturation level of response to analyte was observed with only −12 V applied to the emitter in a source of similar dimensions. In Fig. 4 the baseline current is also shown to vary linearly with bias voltage. However, since this plot approaches a non-zero origin, the ratio of response to baseline current is somewhat superior with use of the greater bias voltage.

Absolute responses to all compounds were also determined using altered detector gases. These included oxygen, carbon dioxide, argon, nitrous oxide, isobutane, and methane which were mixed in various proportions into nitrogen. These results and accompanying affects on standing current are shown in the last six columns of Table I. For all detector gases tested, relatively minor changes in responses were observed.

DISCUSSION

If the mechanism for the response of the thermionic ionization detector with nitrogen mode involves a reversible electron transfer from the low work-function surface to the analyte molecule, as shown in mechanism 1, to form a gas phase molecular negative ion, one might then expect the responses to bear a predictable dependence on the electron affinity (EA) of the molecule. More precisely, the observed current response to a molecule, M, might then be given by eqn. 4, which is a variation of Richardson's equation[13] for the limiting magnitude of current by thermionic emission, which assumes that all negative charges formed at the surface–gas interface are rapidly swept to the anode by an applied electric field.

$$I = AT^2 \exp[-(W - \mathrm{EA_M})/T] \tag{4}$$

In this equation, W is the work function for thermionic emission of an electron from a heated surface at temperature T, $\mathrm{EA_M}$ is the electron affinity of M, and A is a constant for a given surface. Therefore, if this mechanism is operative, the relative responses observed within a closely related group of molecules such as the substituted nitrobenzenes might be expected to increase exponentially with increased $\mathrm{EA_M}$. Fortunately, electron affinity values for all of the mono-substituted nitrobenzenes shown in Table I have recently been measured[12] and are listed in the table. In Fig. 5, the logarithm of the nitrogen mode absolute response to each substituted nitrobenzene is plotted as a function of $\mathrm{EA_M}$. If eqn. 4 applies to our system, a straight line of positive slope is expected. This figure indicates, however, that over the entire group of substituted nitrobenzenes, the observed relative responses do not bear a strict exponential dependence on $\mathrm{EA_M}$. Therefore, mechanism 1 and the factor of molecular electron affinity does not, by itself, explain the responses of all of the substituted nitrobenzenes. If the data in Fig. 5 is considered in parts, one set of isomers at a time, select portions of the data might be taken to suggest that reaction 1 may be partially involved or that reaction 1 may be one of several mechanisms involved. For example, the cyanonitrobenzenes and the dinitrobenzenes have the highest EA values and they do, indeed, have responses which are as great or greater than the rest.

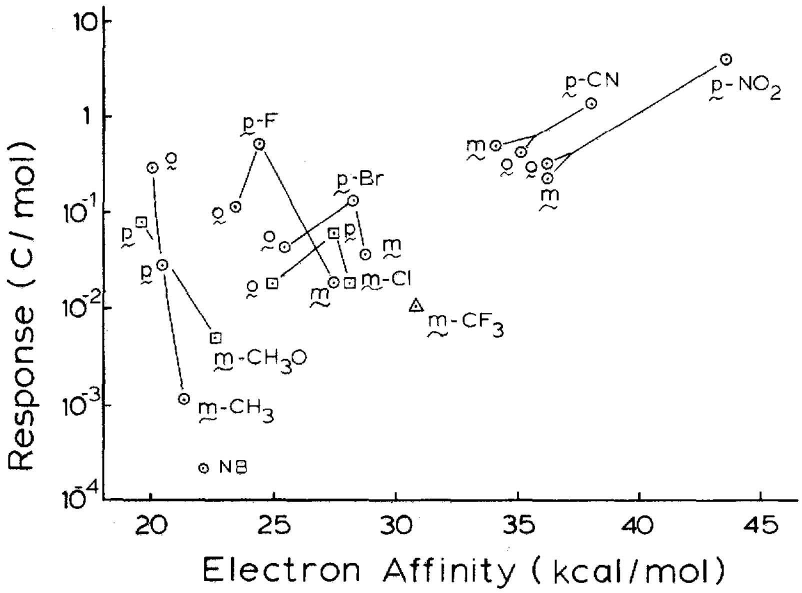


Fig. 5. Comparison of thermionic ionization detector with nitrogen mode molar responses with electron affinity values for substituted nitrobenzenes.

Moreover, within each of these compound types, the isomeric variations of response appear to correlate reasonably well with EA_M; that is, the *para* isomers of cyanonitrobenzene and dinitrobenzene have distinctly larger responses and EA values than the *meta* and *ortho* isomers. It can also be seen that unsubstituted nitrobenzene has the lowest molar response observed and also has one of the lowest EA_M values. On the other hand, the methyl and methoxy nitrobenzenes both exhibit a distinct reverse response dependence on EA_M. Also, within each isomeric group of halogenated nitrobenzenes, the relative nitrogen mode responses of the thermionic ionization detector do not correlate with their EA_M values. For these halogenated compounds the *para* isomers always have the greatest response even though the *meta* isomers have the highest EA values.

An additional argument against the importance of EA_M on response is provided by *p*-fluoranil (perfluorobenzoquinone in Table I). Its electron affinity is very high, 60.2 kcal/mol (ref. 12). Yet its nitrogen mode response is lower than about half of the responses for the substituted nitrobenzenes shown in Fig. 5. Also, one might have expected that successive additions of chlorine on Cl_2NB to form Cl_3NB and Cl_4NB, would have significantly increased EA_M and, therefore, the nitrogen mode response, if mechanism 1 is operative. As shown in Table I, however, the molar responses of the di- to tetra-chlorinated nitrobenzenes are almost constant. Finally, eqn. 4 predicts that the responses of compounds which have low EA_M values will have greater temperature dependence than those of higher EA_M. Again, inspection of the data in Table I under the two headings concerning detector temperature and source heating current provide no convincing support for this expectation. From the above considerations of electron affinities and responses, it appears that if mechanism 1 is involved at all in the nitrogen mode responses of the thermionic ionization detector, it is definitely not the only mechanism involved nor is it a dominant one in many instances. If it can be assumed that only one mechanism is operative in the nitrogen mode, that mechanism does not appear to be mechanism 1.

The nitrogen mode is related to the electron capture detector by virtue of the fact that both provide selective responses to molecules by the formation of negative ions. It is interesting, therefore, to compare the relative responses obtained with each in order to see if any additional similarities of mechanism are suggested. Relative electron-capture detection (ECD) responses were also measured and this comparison is made for the substituted nitrobenzenes and dinitrotoluenes in Fig. 6. From this comparison it appears that absolutely no correlation exists between the rates of electron-capture by the nitrobenzenes on a heated, low-work function surface and in a gaseous medium. We have also compared the electron-capture detector and thermionic ionization detector with nitrogen mode responses of other molecules not shown in Table I, and have found with these, also, little correlation of response magnitudes. For example, perfluoromethylcyclohexane, is known[14] to have a very large gas phase electron-capture rate coefficient. Yet, the response of the nitrogen mode of the thermionic ionization detector to this molecule ($4 \cdot 10^{-3}$ C/mol) is lower than that of almost every compound listed in Table I. It is not necessarily surprising that no correlation between electron-capture detector and thermionic ionization detector with nitrogen mode responses exists, unless the sought-for mechanism for the nitrogen mode involves gas phase electron-capture near the low-work function surface. This possibility, which would constitute a slight alteration of candidate mechanism 1, appears also not to be operative.

The second mechanism proposed in the introduction was mechanism 2 in

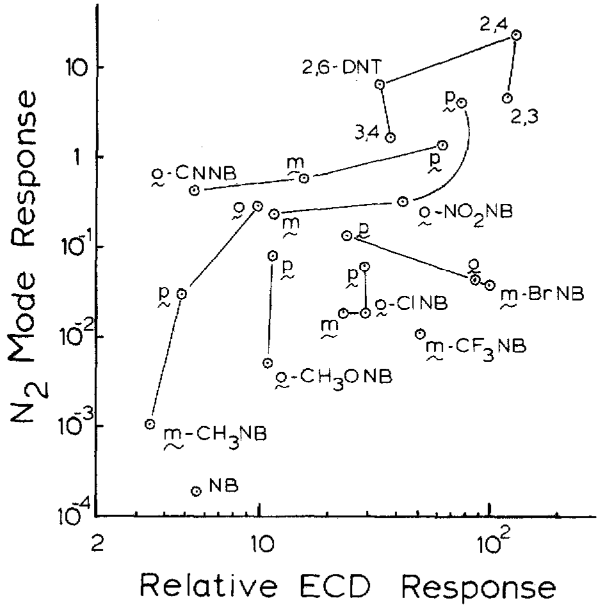
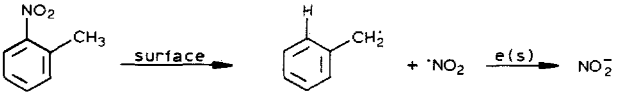


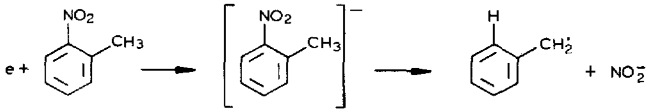
Fig. 6. Comparison of absolute thermionic ionization detector with nitrogen mode responses of substituted nitrobenzenes (NB) and dinitrotoluenes (DNT) with their relative molar electron-capture detector responses.

which thermal decomposition of the analyte is envisioned to occur at the solid–gas interface followed by electron transfer to one of the decomposition products. This possibility is difficult to prove conclusively because little is known of the possible elementary steps in this process. As mentioned earlier, however, it is an attractive alternative because, if nitrogen dioxide is formed by such a surface or temperature assisted decomposition, electron transfer to it would be facilitated by its very high EA value [53 kcal/mol (refs. 11 and 12)]. Another attractive feature of mechanism 2 is that it offers the following plausible explanation for the anomalous relative responses of the nitrotoluene isomers and nitrobenzene, previously shown in Fig. 5. The *ortho* isomer responds ten times more strongly than the second-most strongly responding *p*-nitrotoluene. This might be explained by the following reaction:



in which a benzyl rather than a phenyl radical is formed by hydrogen atom transfer to the reaction site from the adjacent methyl group. The formation of a benzyl rather than a phenyl radical lowers the energy of the decomposition by 23 kcal/mol (as deduced from benzyl versus phenyl C–H bond strengths[15]. The same type of radical stabilization is possible with the *meta* and *para* isomers of nitrotoluene during their decomposition on the hot surface, but the decomposition of these molecules would not occur as rapidly due to the increased distance between their methyl group and the reaction site. With nitrobenzene, no such assistance by a methyl group is possible as the molecule comes in close contact with the surface and, according to this model, its initial decomposition to nitrogen dioxide requires the formation of a higher energy phenyl radical and, therefore, is not as fast at a given temperature of the surface. In Table I, the relative responses to four dinitrotoluenes are also reported. Again, it is noted that the one isomer among these which does not have a methyl group adjacent to a nitro group, 3,4-dinitrotoluene, also has the lowest nitrogen mode response.

In order to test the above and other mechanistic proposals, it would be desirable to be able to measure and identify the negative ions being formed under nitrogen mode conditions. While such experiments have not yet been performed, it is interesting to consider the high temperature negative ion spectra shown in Fig. 7 of the nitrotoluenes and nitrobenzene which result from gas phase electron-capture at 300°C. Ions due to the species M^-, $(M - O)^-$, and NO_2^- are observed for all four compounds. At 200°C (spectra not shown), only the M^- ion is formed in significant abundance for all four compounds. The distinct feature of the spectra in Fig. 7 is that the intensity of the NO_2^- ion at $m/e = 46$ is greatly increased by temperature only for the *ortho* isomer, so that at 300°C, it becomes the base peak in the spectrum of *o*-nitrotoluene. The cause for this may be closely related to the mechanism just proposed for the surface ionization of the nitrotoluenes except that in gas phase electron-capture, the decomposition step would be expected to follow, rather than precede, the ionization step, as shown:



In this case the second step may again be facilitated by an adjacent methyl group which allows a benzyl rather than a phenyl radical to be formed. Moreover, in the gas phase it may be possible to form the more stable benzyl radical only for the ortho isomer. That is, without the assistance of a surface, phenyl radicals probably are formed in the production of NO_2^- from *m*- and *p*-nitrobenzene, as they must be in the case of nitrobenzene. This may explain why, in Fig. 7 at 300°, the relative rates of NO_2^- production for *m*- and *p*-nitrotoluene and nitrobenzene appear to be identical. The above considerations of the relative thermionic ionization detector responses of the nitrotoluenes and nitrobenzene leads us to the tentative conclusion that mechanism 2 is operative for, at least, these molecules.

Because of its acknowledged importance in other modes of the thermionic ionization detector, we are obliged to also consider whether proposed mechanism 3 is important. In that mechanism the initial breakdown of the analyte molecule is thought to be caused by reactions with reactive species, R, which are continuously formed at the surface–gas interface by the decomposition of either permanent components of the detector gas or the analyte, itself. If the detector gas is a very stable

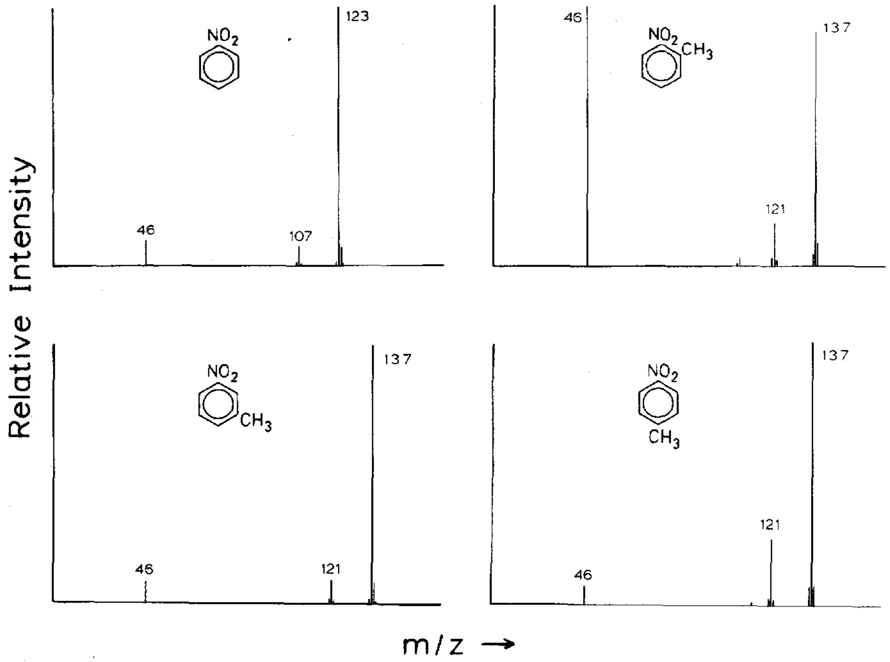


Fig. 7. High temperature, negative ion electron-capture mass spectra of nitrobenzene and three isomers of nitrotoluene. Ion source gas, 0.3 torr methane; source temperature, 300°C; sample introduction by capillary GC.

molecule, such as nitrogen, or is an atomic gas, such as argon, any reactive species present would have to be formed from either carrier gas impurities or the analyte.

In order to assess the potential participation of detector gas in the thermionic ionization dector with nitrogen mode, the responses to all compounds were measured using a variety of different detector gases. The results of these experiments, which included detector gases 0.3% oxygen, 90% carbon dioxide, 90% argon, 90% nitrous oxide, 15% isobutane and 15% methane in nitrogen, are reported in Table I. The most striking feature of these data is that these wide variations of detector gas cause only relatively minor alterations of the absolute responses. With the exception of argon, the vast majority of responses in the various gases fall within factors of about 0.4–1.0 of the responses observed in nitrogen. If reactive species were important as suggested in mechanism 3, one might have expected their production, as well as their destruction rates, to have been very different in these varied detector gases. Our conclusion, therefore, is that mechanism 3 is not generally operative at concentration levels near the detection limits. It remains possible, however, that for higher concentrations of certain compounds, mechanism 3 may be operative where the reactive intermediate species is produced by the destruction of the analyte molecule, itself. This may provide an explanation of why, in several cases shown in Fig. 1, the molar responses increase with higher concentrations of analyte. This trend was particularly apparent, for example, for all isomers of cyanonitrobenzene.

The use of 90% argon as detector gas caused consistently greater responses, ranging from 1.3 to 4 times that in pure nitrogen. Also, the baseline emission current was significantly higher with use of argon. This result may be more easily explained in terms of physical rather than chemical effects of the detector gas if one assumes that the detailed nature of the emitter surface and its work function, W, can be altered slightly by the nature of its surrounding gas. Argon, being the most chemically inert of the gases used, interacts least with the cesium-enriched surface and may allow the lowest effective work function to be established. Another possible physical explanation of the variations of responses with different detector gases has been considered, that due to their differences in thermal conductivities which, in turn, might cause differences in the temperature of the emitter surface. The thermal conductivities are: nitrogen, 65.7; oxygen, 68.2; carbon dioxide, 43.8; argon, 45.5; nitrous oxide, 46.1; isobutane, 44.2; and methane, 89.3 units[16] at 49°C. While this factor could explain why responses and baseline current are greater in argon due to its lower thermal conductivity than that of nitrogen, and an expected hotter surface, it does not explain the lower responses observed in carbon dioxide, nitrous oxide, and isobutane. For carbon dioxide, nitrous oxide, isobutane, and probably methane, it appears that chemical modification of the surface and an accompanying increase in the effective work function is the cause of the slightly lowered responses observed in these detector gases.

One additional physical effect on response is worthy of discussion. This is the effect shown in Fig. 4 of emitter bias voltage on responses. As shown in this figure and in Table I, this effect is clearly a physical one which is relatively insensitive to the chemical differences which exist among the 36 compounds studied. The continuous and linear dependence of response on bias voltage shown in Fig. 4 was unexpected. As has been reported for the nitrogen, phosphorus-mode of the thermionic ionization detector[5], we had expected to observe a saturation level of response with the application of -15 V or even -5 V since the field thereby induced was expected to be sufficient to collect essentially all gas phase negative ions. This expectation is supported by calculations of expected ion velocities in the direction of the anode relative to the linear velocity of ions due to ventilation through the cell. For example, for the following values of our experiments: bias voltage, 15 V; cathode-to-anode distance, 0.12 cm; total flow-rate, 100 $cm^3 min^{-1}$; cross sectional area of flow path, 0.11 cm^2; and conservatively assuming the mobility of the ion in question in atmospheric pressure nitrogen to be at least 1.0 $cm^2 s^{-1} V^{-1}$ (ref. 17); the radial velocity of ions along the applied field is predicted to be 125 cm/s while the longitudinal velocity due to detector gas flow is only 15 cm/s. Since the length of our detector is several times greater than the radial dimension, all negative ions are expected to be collected, if the applied field serves only to transport negative ions to the anode. Since the experiments of Fig. 4 indicate that the response is continuously proportional to relatively large applied electric fields, the remaining explanation for this observation is that the rate of emission of negative ions from the emitter surface is directly proportional to the electric field in that vicinity. While it is not clear whether this deduction favors any one of the proposed mechanisms discussed here over the others, it does provide another significant characterization of the mechanism of the nitrogen mode response of the thermionic ionization detector.

CONCLUSIONS

The nature of the nitrogen mode response of the thermionic ionization detector to 36 electronegative molecules has been reported here. An attempt has been made to interpret these data in terms of three proposed mechanisms for the nitrogen mode response. One mechanism considered (mechanism 3) involved initial reaction of the analyte molecule with gaseous reactive species at the solid–gas interface. This mechanism is similar to that thought to be responsible for the response of the nitrogen and phosphorus specific mode of the thermionic ionization detector. This mechanism was not supported here by experiments in which a variety of detector gases were used. Another mechanism (mechanism 1), involving simple electron transfer from the emitter to the analyte molecule, was tested by a comparison of responses with the known electron affinities of individual molecules. These experiments did not lend universal support to mechanism 1. Nevertheless, its possible importance for some compounds cannot be ruled out. It was also shown that the relative rates of electron transfer in the nitrogen mode of the thermionic ionization detector bear no correlation with relative gas phase electron-capture responses. Another mechanism considered (mechanism 2) involved thermal decomposition of the analyte on the hot emitter surface, as the initiating step, followed by electron transfer from the surface to one of the decomposition products. This mechanism offered a plausible explanation for the otherwise anomalous responses of the three isomers of nitrotoluene and nitrobenzene. Mechanism 2 is the only candidate model which is not in contradiction with any experiments reported to date. Therefore, if only one mechanism is operative in the nitrogen mode, it might be concluded that it is mechanism 2. It remains possible, however, that both mechanisms 1 and 2 are operative and that their relative importance is compound-dependent.

ACKNOWLEDGEMENT

This work is supported by the National Science Foundation under Grant No. CHE-8514029.

REFERENCES

1 A. Karmen, *Anal. Chem.*, 36 (1964) 1461.
2 G. R. Verga and F. Roy, *J. Chromatogr.*, 116 (1976) 17.
3 V. V. Brazhnikov and E. B. Shmidel, *J. Chromatogr.*, 122 (1976) 527.
4 B. Kolb, M. Auer and P. Pospisil, *J. Chromatogr. Sci.*, 15 (1977) 53.
5 P. L. Patterson, *J. Chromatogr.*, 167 (1978) 381.
6 P. L. Patterson and R. L. Howe, *J. Chromatogr. Sci.*, 16 (1978) 275.
7 G. R. Verga, *J. Chromatogr.*, 279 (1983) 657.
8 P. L. Patterson, *Chromatographia*, 16 (1982) 107.
9 P. L. Patterson, R. A. Gatten and C. Ontiveros, *J. Chromatogr. Sci.*, 20 (1982) 97.
10 C. M. White, A. Robbat and M. H. Randall, *Anal. Chem.*, 56 (1984) 232.
11 E. Herbst, T. A. Patterson and W. C. Lineberger, *J. Chem. Phys.*, 61 (1974) 1300.
12 E. P. Grimsrud, G. Caldwell, S. Chowdhury and P. Kebarle, *J. Am. Chem. Soc.*, 107 (1985) 4627.
13 M. Thewlis (Editor), *Encyclopaedic Dictionary of Physics*, Vol. 7, Pergamon Press, New York, 1962, p. 252.
14 L. G. Christophorou, *Adv. Electron. Electron Phys.*, 46 (1978) 55.
15 D. F. McMillen and D. M. Golden, *Annu. Rev. Phys. Chem.*, 33 (1982) 493.
16 *Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL, 62nd ed., 1981, p. E-2.
17 W. Lindinger and D. L. Albritton, *J. Chem. Phys.*, 62 (1975) 3517.