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Gas-Phase Ion–Molecule Nitration Chemistry: The Nitration of Aromatic Radical Cations by Nitrogen Dioxide

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Abstract: We have observed in gas-phase work at 10 torr that aromatic radical cations ($ArH^{+}\cdot$) readily react with NO_2 to give the σ-bonded $ArH–NO_2^+$. Under the same conditions the reactions of nitronium ion (NO_2^+) with neutral ArH yield only $ArH^{+}\cdot$ and $ArH–O^{+}\cdot$, products of electron or oxygen transfer. The radical cations giving the σ intermediate were those from benzene, methylbenzenes up to mesitylene and 1,2,4-trimethylbenzene, phenol, and several fluorobenzenes up to 1,2,4-trifluorobenzene. In contrast tetrafluorobenzenes, furan, and pyridine did not yield the σ intermediate. Naphthalene reacted to give the σ-bonded $C_{10}H_8–NO_2^+$, but surprisingly slowly. The parallels to condensed-phase nitration are yet to be fully demonstrated, but it is clear that the odd-electron system NO_2 + $ArH^{+}\cdot$ yields the σ-bonded intermediate leading to nitration.

We recently reported our preliminary results[1] on the gas-phase ion–molecule chemistry of aromatic radical cations reacting with nitrogen dioxide. This account describes the full details of the study and further results concerning the mechanism of aromatic nitration. To our knowledge, the gas-phase ion chemistry of these odd-electron systems has not been previously reported.

The generally accepted mechanism for aromatic nitration in solution is shown in eq 1 through 4:[2]

$$H^+ + HNO_3 \rightarrow H_2NO_3^+ \qquad (1)$$

$$H_2NO_3^+ \rightarrow NO_2^+ + H_2O \qquad (2)$$

$$NO_2^+ + ArH \rightarrow \underset{\sigma\ \text{complex}}{ArHNO_2^+} \qquad (3)$$

$$ArHNO_2^+ + \text{base} \rightarrow ArNO_2 + \text{base}H^+ \qquad (4)$$

Nitronium ion is first formed by protonation of nitric acid in an acidic medium. Nitronium ion reacts with the aromatic to yield a π complex, which isomerizes to a σ (or Wheland) intermediate, which then gives up a proton to the medium to yield the nitroaromatic product. The π complex is invoked to explain the selectivity observed in this reaction[3] although the nature of the complex is still not completely agreed upon.[2a] For aromatics that are more easily oxidized than toluene, Perrin[4] has suggested electron transfer takes place in the reaction of nitronium ion with the aromatic, followed by a recombination of the resulting $NO_2/ArH^{+}\cdot$ pair.

$$NO_2^+ + ArH \rightarrow ArH^{+}\cdot + NO_2 \qquad (5)$$

$$ArH^{+}\cdot + NO_2 \rightarrow ArHNO_2^+ \qquad (6)$$

In earlier gas-phase work on aromatic nitration, researchers studied the even–even electron NO_2^+/ArH systems and observed only charge transfer and oxygen atom transfer from nitronium ion.[5-8]

$$NO_2^+ + ArH \rightarrow NO_2 + ArH^{+}\cdot \qquad (7)$$

$$NO_2^+ + ArH \rightarrow NO + ArHO^{+}\cdot \qquad (8)$$

These studies were both done at 10^{-5} torr in an ICR spectrometer. Nitration of aromatics was accomplished only when the nitronium ion was bound, as in $CH_2ONO_2^+$.

$$CH_2ONO_2^+ + ArH \rightarrow ArHNO_2^+ + CH_2O \qquad (9)$$

No information on the structure of the product ion was obtained. Moreover, under these conditions, the formation of $ArHNO_2^+$ product was favored for aromatic systems containing electron-withdrawing substituents, in distinct contrast to the common experience in condensed-phase nitrations.

Finally, Reents and Freiser[9] have investigated the nitrosation of benzene in the gas phase, with a nitrite ester as the source of NO^+.

$$C_6H_6 + RO–NO^+ \rightarrow C_6H_6–NO^+ + RO\cdot \qquad (10)$$

From a study of proton transfer, NO^+ transfer, and UV–Vis photodissociation results, they determined that the product (eq 10) was a π complex rather than a σ complex. Their result is consistent with condensed-phase studies in which nitrosation of benzene gives only a reversible π complex, not a σ complex. We have also studied the reactions of aromatic radical cations with NO[1] and have observed results in agreement with Reents and Freiser, obtaining only a reversible complex as the product.

Experimental Procedures

A block diagram of the flow discharge mass spectrometer used for these experiments is shown in Figure 1. The helium carrier/buffer gas is purified by passage through a liquid-nitrogen-cooled 0.75-in.-o.d. copper trap filled with Davidson 3A molecular sieves. The reactive neutrals are mixed with the helium in a vacuum line by bleeding small quantities of the neutrals through a Whitey RS22 stainless steel metering valve. The premixed helium/neutral gas flow enters the upstream end of a 0.5-in.-o.d. by 6-in.-long flow tube. Generally, 10 to 15 torr of helium and 0.01 torr of the reactive neutrals are used. This gives a helium/argon concentration of 10^{17} molecules cm^{-3}, reactive neutrals at approximately 10^{14} molecules cm^3, and an ion density of approximately 10^8 cm^{-3}. The ion source can be used at pressures from 5 to 100 torr and over a temperature range of 30 to 200 °C. The mass spectrometer region is differentially pumped by 6-in. diffusion pumps equipped with cold traps in both the ion-focusing and quadrupole regions. This provides adequate pumping capacity to handle pressures up to 100 torr in the ion source with a sampling orifice of 100 μm.

A small argon flash lamp is used as a photoionization source for the mass spectrometer. The design of the ion source is shown in Figures 2 and 3. The flash lamp is an open-ended, $^1/_8$-in.-o.d. Pyrex tube into which a $^1/_{16}$-in.-o.d., two-hole ceramic insulator has been inserted. Two 10-mil molybdenum wires protrude about $^1/_{16}$ in. beyond the end of the

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[1] Schmitt, R. J.; Buttrill, S. E., Jr.; Ross, D. S. *J. Am. Chem. Soc.* **1981**, *103*, 5265–5267.

[2] (a) Schofield, K. "Aromatic Nitration"; Cambridge University Press: London, 1980. (b) Hughes, E. D.; Ingold, C. K.; Reed, R. I. *J. Chem. Soc.* **1950**, 2400–2440.

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[9] (a) Reents, W. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1980**, *102*, 271–275. (b) Reents, W. D.; Freiser, B. S. *Ibid.* **1981**, *103*, 2791–2797.

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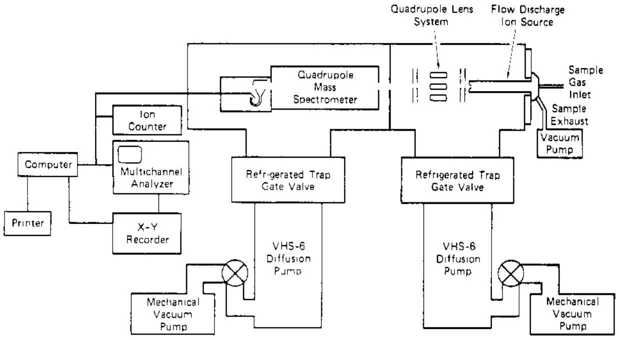

Figure 1. Schematic of the flow discharge mass spectrometer.

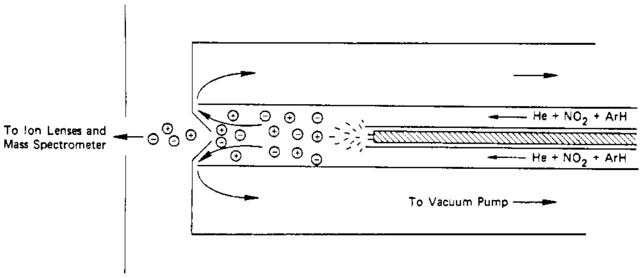

Figure 2. Schematic of the flow discharge ion source.

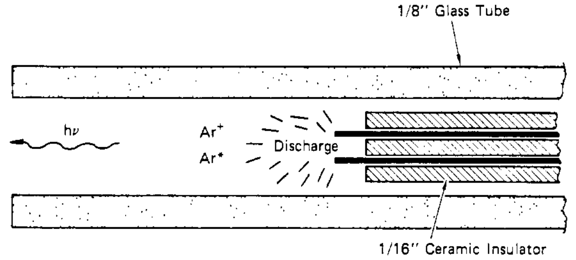

Figure 3. Blowup of the ion source.

insulator and about $^1/_8$ in. from the opening of the glass tubing (Figure 3). A steady flow of argon is maintained in the flash lamp, contributing approximately 0.5 torr to the total pressure in the ion source. The lamp is pulsed at about 100 Hz at a potential of 2500 V with use of a simple spark gap.

On pulsing, excited argon atoms and argon ions are produced. The argon ions are lost to the walls of the glass tube while the excited argon atoms give off photons of 11.6 and 11.8 eV, ionizing anything with an IP below 11.8 eV throughout the length of the flow tube. Hence a plug of gas from the end of the Pyrex tube to the sampling orifice is ionized. The mixture of neutrals and ions is sampled as it flow past the sampling orifice. The neutrals are pumped away, and the ions are mass analyzed and recorded as a function of elapsed time since the argon lamp flash.

Housing the electrodes within the Pyrex tubing prevents pyrolysis of the reactive neutrals by shielding them from the high-energy pulses. Pressure in the ion source is measured by an MKS Baratron Model 220-BHS, 0–100 torr. Most of the gas flow is exhausted to a 200 L min^{-1} Leybold-Heraeus pump with a small fraction being sampled through a 100-μm orifice.

The ion signal is focused into the quadrupole via a series of lenses. Two flat plates are followed by a set of quadrupole focusing lenses to steer the ion beam, and then two more flat plates are used to direct the beam into the quadrupole. The ion source is held at +25 V. Mass discrimination effects are minimized, but the ion signals are not corrected for these effects.

Mass analysis is done with a Extranuclear quadrupole with $^5/_8$ in. rods. The signal is then collected, ion counted, and analyzed in a DEC VT 105 terminal equipped with an LSI 11/2 microprocessor. The data are recorded on either an *X–Y* plotter or a line printer. For the time-resolved data, data points are taken every 100 μs after the start pulse for a period up to 5 ms, the maximum residence time of ions in the flow tube.

We performed experiments using the benzene radical cation–dimer system to check whether the ions in the source were at thermal equilibrium. An example of our results is shown in Figure 4. Previous work established a $\Delta H = -14.7$ kcal mol^{-1} and a $\Delta S = -22.5$ eu for the reaction.[10] We have measured this equilibrium at six temperatures ranging from room temperature up to 150 °C and calculated a $\Delta H = -15.0$ kcal mol^{-1} and a $\Delta S = -23.2$ eu, which are in good agreement with the literature values.

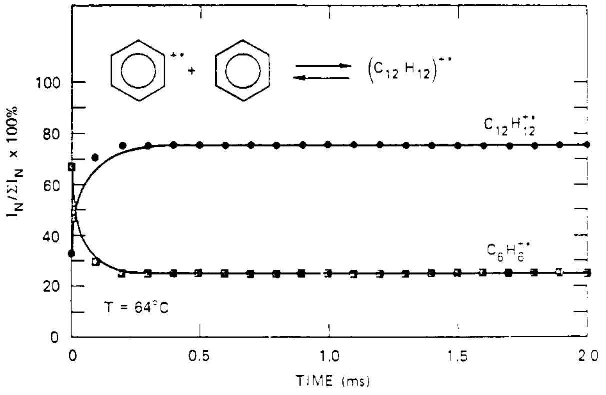

Figure 4. Time-dependent plot of benzene dimerization.

Materials. We used helium (99.999%), argon (99.9995%), and NO (99.99%). NO$_2$ was purified by distilling the cylinder gas into a 10-L storage bulb; then several freeze–thaw cycles were employed to remove the lower oxides of nitrogen. The bulb was then pressurized with oxygen and allowed to stand for 1 week to remove the remaining NO. The oxygen was pumped off, the NO$_2$ pressure was measured, and the bulb was pressurized with helium to dilute the NO$_2$. Despite these precautions, evidence of nitrosation (presumably due to some NO impurity or possibly formed by photolysis of NO$_2$ by the argon resonance radiation) was always observed. The organics for this study were obtained from commercially available sources and were distilled into the system from lithium aluminum hydride or calcium hydride whenever possible. Toluene-d_3 (99% D) and toluene-d_8 (99.5% D) were obtained from Stohler Isotope Chemical, and benzene-d_6 (99.5% D) was obtained from Aldrich Chemical Co.

Rate Constant Calculation. The rate of reaction of a radical cation or any other ion, A$^+$, with a neutral is described by:

$$-d[A^+]/dt = k[A^+][N] \qquad (11)$$

where k is the bimolecular rate constant in cm^3 molecule^{-1} s^{-1}. Because $[N] = 10^{14}$ molecules cm^{-3} and $[A^+] \sim 10^8$ ions cm^{-3}, pseudo-first-order kinetics apply. The reactive neutral concentration, N, is calculated at room temperature as

$$N = \frac{(P_{He})(3.26 \times 10^{16})(F_N)}{F_{He}} \qquad (12)$$

where P_{He} = the pressure of the helium buffer gas (torr), 3.26×10^{16} = the number of particles (cm^{-3} torr^{-1}), F_N = the flow of the reactive neutral (atm cm^{-3} s^{-1}), and F_{He} = the flow of the helium buffer gas (atm cm^{-3} s^{-1}).

Thus, the second-order rate constant is calculated from

$$k = \frac{-d \ln [A^+]}{dt} \, \frac{F_{He}}{(P_{He})(F_N)(3.26 \times 10^{16})} \qquad (13)$$

The helium flow and pressure and the flow of the neutral are measured by their pressure change in a calibrated volume. The d ln [A$^+$]/dt term is obtained from the slope of a plot of ln [A$^+$] vs. time. We assume that the cross-sectional ion density in the flow tube is of the plug-flow type rather than the laminar flow encountered in a flowing afterglow; hence, the average ion velocity should be the same as the buffer gas velocity.[11] Therefore, the term α, which is normally used to correct for the increased flow velocity of the ions in a flowing afterglow, is neglected for this calculation.[11]

Results

To explore the scope of reaction 14, we examined the gas-phase

$$ArH^{+\cdot} + NO_2 \rightarrow ArHNO_2^+ \qquad (14)$$

ion chemistry of the radical cations of 18 aromatic compounds

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(10) (a) Jasinski, J. M.; Rosenfeld, R. N.; Golden, D. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 2259–2265. (b) Anicich, V. G.; Bowers, M. T. *Ibid.* **1974**, *96*, 1279–1286. (c) Field, F. H.; Hamlet, P.; Libby, V. F. *Ibid.* **1969**, *91*, 2839–2342.

(11) Ferguson, E. E.; Fehsenfeld, F. C.; Schmeltekopf, A. L. *Adv. At. Mol. Phys.* **1969**, *5*, 1–49.

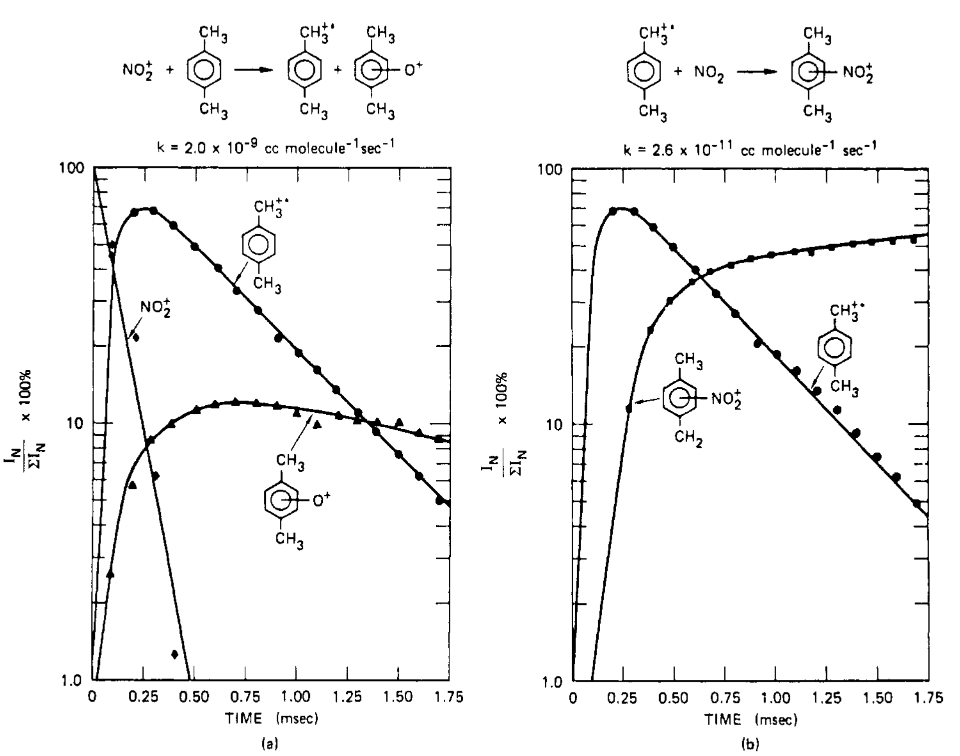

Figure 5. Time-resolved plots showing the reaction of (a) the nitronium ion with *p*-xylene and (b) *p*-xylene radical cation with NO_2.

with NO_2. The results are summarized in Table I. The electron-rich naphthalene cation reacted only very slowly with NO_2 while the electron-poor tetrafluorobenzenes showed no detectable reaction ($k < 10^{-13}$ cm^3 molecule^{-1} s^{-1}).

All the aromatic radical cations tested react with NO to give nitrosoaromatic products. This nitrosation result parallels that

$$ArH^{+\cdot} + NO \rightarrow ArHNO^+ \quad (15)$$

of Reents and Freiser,[9] who nitrosated a wide variety of compounds and obtained a set of relative nitroso cation affinities.

In addition to nitration and nitrosation products, phenolic products are observed for every aromatic tested. These products result from the reactions of nitronium ion with the aromatic to yield NO and $ArHO^{+\cdot}$ (eq 8). They are not a product of aromatic radical cation reactions (see below).

Discussion

Role of Nitronium Ion in Gas-Phase Nitrations. In mixed acid nitrations, nitronium ion, NO_2^+, is believed to be the nitrating agent (eq 1 through 4). From our results, which are consistent with earlier work obtained at lower pressures,[5-7] we found that NO_2^+ does not nitrate aromatics to give a σ or Wheland intermediate C_6H_6–NO_2^+ in the gas phase but instead reacts by either O^+ or electron transfer (eq 16 through 18):

$$NO_2^+ + C_6H_6 \not\rightarrow C_6H_6NO_2^+ \quad (16)$$

$$NO_2^+ + C_6H_6 \rightarrow C_6H_6O^+ + NO \quad (17)$$

$$NO_2^+ + C_6H_6 \rightarrow C_6H_6^{+\cdot} + NO_2 \quad (18)$$

This result is clearly illustrated in Figure 5a,b. Figure 5a shows a time-resolved plot of the reaction of NO_2^+ with *p*-xylene. The NO_2^+ concentration decays exponentially via electron transfer from or via O^+ transfer to *p*-xylene with a rate constant of 2.0×10^{-9} cm^3 molecule^{-1} s^{-1}. Figure 5b shows a time-resolved plot of the formation of the nitrated xylene coming from the xylene radical cation. The much lower formation of protonated nitroxylene ion from the xylene radical cation does not begin until the vast majority of NO_2^+ is consumed (nitration is slower than either electron transfer or O^+ transfer). Thus, we can rule out NO_2^+ as the nitrating agent in these gas-phase experiments.

Product Structure. It has been proposed that the reaction of an aromatic radical cation with NO_2 should give a σ complex rather than a π complex (vide supra). The earlier ion–molecule work did not address the question of the structure of the nitration product, π or σ complex.[5-8]

Table I. Reactions of Aromatic Radical Cations with NO_2[a]

ArH	nitration via aromatic radical cation	k,[b] cm^3 molecule^{-1} s^{-1}
C_6H_6	yes	2.4×10^{-11}
$C_6H_5CH_3$	yes	1.2×10^{-11}
p-$C_6H_4(CH_3)_2$	yes	1.7×10^{-11}
mesitylene[c]	yes	
1,2,4-trimethylbenzene	yes	
phenol	yes	
C_6H_5F	yes	3.7×10^{-11}
C_6H_5Cl	yes	
o-$C_6H_4F_2$	yes	
m-$C_6H_4F_2$	yes	1.2×10^{-12}
p-$C_6H_4F_2$	yes	2.9×10^{-12}
1,2,4-$C_6H_3F_3$	yes	
1,2,3,4-$C_6H_2F_4$	no	
1,2,4,5-$C_6H_2F_4$	no	
furan	no	
pyridine	no	
m-$FC_6H_4CF_3$	yes	
naphthalene	very slow	

[a] Nitration by NO_2^+ results in $ArHO^+$ or electron transfer as product, eq 7 and 8. [b] Forward rate constant for $ArH^{+\cdot}$ includes $ArHNO^+$ (from NO impurity). [c] See discussion for explanation of unusual behavior.

To probe the structure of the benzene nitration product $C_6H_6NO_2^+$, we studied a mixture of benzene-d_6, NO_2, and a base, pyridine (py). Because the proton affinity (PA) of py (PA = 218 kcal mol^{-1})[12] is greater than that of nitrobenzene (PA = 191.6 kcal mol^{-1})[12] and assuredly greater than the PA of any σ-bonded intermediate that might be formed, deuteron transfer from $C_6H_6NO_2^+$ to py would establish that the reaction of an aromatic radical cation with NO_2 gives a σ-bonded product (structure II or III). However, a π complex (I) would not transfer a deuteron (proton) to py because this structure lacks acidic protons.

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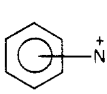
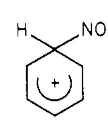
(12) Walder, R.; Franklin, E. L. *Int. J. Mass. Spectrom. Ion Phys.* **1980**, *36*, 85–112 and references therein.



I



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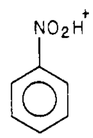


III

Benzene-d_6 was used to eliminate any possible ambiguity in the source of the proton (deuteron) transferred in the reaction. Neither $C_6D_6^{+}\cdot$ nor $(C_6D_6)_2^{+}\cdot$ transferred a deuteron to py in control experiments (eq 19 and 20), and the only product from the $C_6D_6^{+}\cdot$/py reaction is a strongly bound $(C_6D_6\text{–}Py)^{+}\cdot$ cluster. When a mixture of C_6H_6/py/NO_2 was ionized, rapid deuteron transfer to pyridine was observed from the product of the reaction of $C_6D_6^{+}\cdot + NO_2$. Figure 6 shows a time-resolved plot of the reaction, showing $C_6D_6^{+}\cdot$ rapidly dimerizing to $(C_6D_6^{+}\cdot)_2$, which reacts with NO_2. The $C_6D_6NO_2^+$ ion then proton transfers to py to give pyD^+, which dimerizes to give py_2D^+. Other cluster products, $(C_6D_6\text{–}C_5H_5N)^+$ and $(C_5H_5N\text{–}C_6D_6NO_2)^+$, are also shown in Figure 6. The deuteron transfer (eq 19) eliminates structure I as an observable product in this reaction. We cannot distinguish between structures II and III, but the only pathway to III is through II. Similar results were obtained when tetrahydrofuran (PA = 196 kcal mol^{-1})[12] was used. Furthermore, no NO_2^+ transfer reactions between aromatics are observed which would imply the formation of a reversable π complex as is seen in nitrosation chemistry (see below).

$$C_6D_6^{+}\cdot + py \nrightarrow pyD^+ + C_6D_5\cdot \quad (19)$$

$$(C_6D_6)_2^{+}\cdot + py \nrightarrow pyD^+ + C_{12}D_{11}\cdot \quad (20)$$

$$C_6D_6NO_2^+ + py \rightarrow pyD^+ + C_6D_5NO_2 \quad (21)$$

The benzene radical cation readily reacts with NO to nitrosate and give the $C_6D_6NO^+$ ion. In a manner similar to that described above, we tested for the type of complex formed. Here, ionization of a mixture of C_6D_6/NO/py resulted in no deuteron transfer to pyridine. Thus, we conclude that the $C_6D_6NO^+$ ion is a π rather than a σ complex. Our result from the radical cation–radical reaction parallels the result found by Reents and Freiser in their studies of nitrosation.[9]

In a similar manner, we also attempted to determine whether aromatic radical cations nitrate on the ring or at the side chain in the gas phase. As stated above, solution studies involving the nitration of mesitylene via NO_2 and Ce(IV) as an electron-transfer reagent have shown that a considerable amount of the reaction proceeds via side-chain nitration. α,α,α-Toluene-d_3 was chosen for these studies because it readily nitrates and forms the radical cation dimer only slowly. Unfortunately, the toluene radical cation is acidic enough to proton transfer to bases that are basic enough to accept a proton from the expected protonated nitrotoluene product (eq 22).

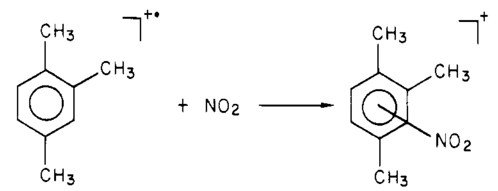
$$\begin{aligned} CD_3\text{–}C_6H_5^{+}\cdot\ \text{base} &\rightarrow \text{baseD}^+\ \text{(major)} \\ &\rightarrow \text{baseH}^+\ \text{(minor)} \end{aligned} \quad (22)$$

We can, however, determine whether the bulk of the reaction is at the ring or side chain. The results obtained from reaction of the toluene radical cation with pyridine in the absence and presence of NO_2 are compared below.

system	pyD$^+$pyH$^+$
$C_6H_5CD_3^{+}\cdot$/py	2/1
$C_6H_5CD_3^{+}\cdot$/py/NO_2	1/4

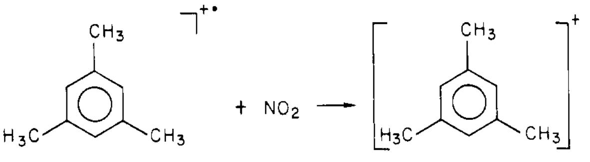
The large difference between the pyD^+/pyH^+ ratios for products of these reactions shows that the nitration is predominantly at the ring rather than on the side chain.

Nitration of Mesitylene, 1,2,4-Trimethylbenzene, and Naphthalene. We have observed surprising differences in the reactivity of the radical cations of mesitylene and 1,2,4-trimethylbenzene to NO_2. The 1,2,4-trimethylbenzene radical cation is readily nitrated (eq 23) to give a nitroaromatic cation as stable product.



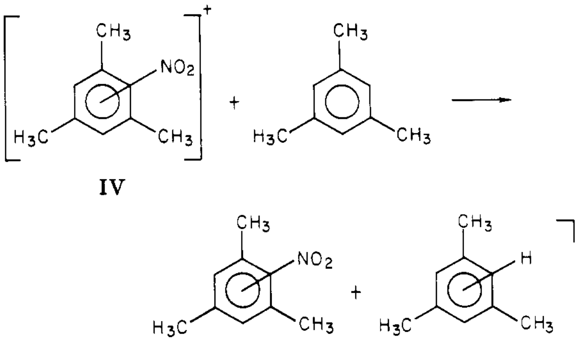
(23)

Mesitylene behaves somewhat differently. The mesitylene radical cation readily adds NO_2 to give a short-lived nitromesitylene cation (eq 24 and 25); however, the nitromesitylene cation is not stable in this environment, losing a proton to mesitylene to give protonated mesitylene as the final, stable product.



IV

(24)



(25)

The proton loss from mesitylene is quite unexpected because we assumed that the proton affinity of nitromesitylene (2-nitro-1,3,5-trimethylbenzene) would be greater than that of mesitylene as proton affinity tends to increase with increasing functionality.[12] We also expected the proton affinities of mesitylene and 1,2,4-trimethylbenzene or those of nitromesitylene and 5-nitro-1,2,4-trimethylbenzene to be approximately equal and the behavior of these two trimethylbenzene systems to parallel each other. Because of the observed proton transfer from IV to mesitylene, we believe that we are observing a lower than expected proton affinity for 2-nitro-1,3,5-trinitrobenzene that results from steric crowding of the nitro group.

The behavior of naphthalene is also somewhat unexpected. In the gas phase naphthalene nitrates very slowly. We expected that naphthalene should nitrate easily, in analogy to the ease with which it nitrates in solution, or at least behave similarly to mesitylene or 1,2,4-trimethylbenzene, which are also electron-rich systems. This failure of naphthalene to readily nitrate is still not understood.

Effect of Clustering On Reaction. Many aromatic radical cations rapidly cluster with a neutral aromatic molecule. For example, the benzene radical cation clusters with a neutral benzene with an equilibrium constant of approximately $K_{eq} \sim 10^6$ at 25 °C.[10] We have observed that the nitration[1] of aromatic radical cations proceeds whether or not the radical cation dimerizes. We do not believe that the dimer is required for the nitration reaction, but frequently the dimer formation is so rapid that the dimerization is complete before nitration can occur. For benzene, in which the equilibrium constant for dimerization is very high, we cannot tell if the monomer reacts at all with NO_2, with apparently all the reaction coming from the dimer. However, for p-xylene, for which the monomer can be easily made with little or no dimer, the reaction is observed to proceed from only the monomer. In the case of fluorobenzene, both the monomeric and dimeric forms lead to nitroaromatic product.

$$ArH^{+}\cdot + NO_2 \rightarrow ArHNO_2^+ \quad (26)$$

$$(ArH)_2^{+}\cdot + NO_2 \rightarrow ArHNO_2^+ + ArH \quad (27)$$

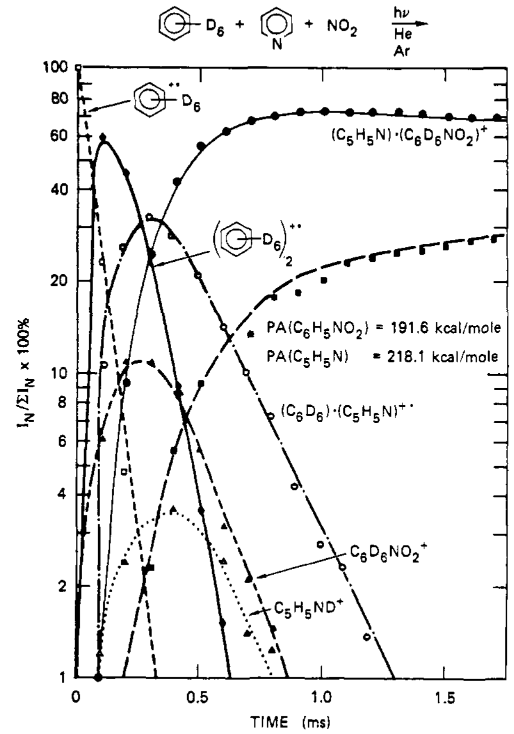


Figure 6. Resolved mass spectra of benzene-d_6, pyridine, and NO_2.

Comparison with Solution Chemistry. Some comparisons and constrasts can be drawn between the solution and the gas-phase results. It is not surprising that a highly deactivated aromatic such as tetrafluorobenzene does not nitrate in the gas phase; the same behavior is observed in solution. In solution, a difluoroquinone is the product instead of a nitroaromatic, whereas in the gas phase no reaction is observed.[13] It is surprising that a highly activated aromatic, such as naphthalene, nitrates slowly in the gas phase. Indeed, in analogy with solution results, one would expect the reaction to occur on every collision. The gas-phase results on the clustered nitronium ion[5-7] parallel our observations on both deactivated and activated aromatics. While it is apparent that there is some barrier to the reaction of activated aromatic radical cations with NO_2 in the gas phase, the origin of this barrier is not now clear.

Conclusion

We have studied the gas-phase chemistry of aromatic radical cations and that of nitronium ion. Under nonsolvated conditions, the nitronium ion plays no part in the nitration mechanism. Rather, the nitronium ion gives only O^+ or e^- transfer. Aromatic radical cations will add NO_2 to give a nitroaromatic product that has been confirmed to be a σ complex. Nitrosations of aromatic radical cations by reaction with NO give only a π complex. This is the first clear example of a reaction of an aromatic radical cation with NO_2 to give a nitroaromatic product. This work affirms that aromatic radical cations are a plausible intermediate in the mechanism for aromatic nitration.

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Registry No. $C_6H_6^{+\cdot}$, 34504-50-2; $C_6H_5CH_3^{+\cdot}$, 34504-47-7; *p*-$C_6H_4(CH_3)_2^{+\cdot}$, 34510-22-0; $C_6H_5F^{+\cdot}$, 34468-25-2; $C_6H_5Cl^{+\cdot}$, 55450-32-3; *o*-$C_6H_4F_2^{+\cdot}$, 65308-08-9; *m*-$C_6H_4F_2^{+\cdot}$, 65308-07-8; *p*-$C_6H_4F_2^{+\cdot}$, 59331-60-1; 1,2,4-$C_6H_3F_3^{+\cdot}$, 57164-22-4; 1,2,3,4-$C_6H_2F_4^{+\cdot}$, 57164-19-9; 1,2,4,5-$C_6H_2F_4^{+\cdot}$, 34528-25-1; *m*-$FC_6H_4CF_3^{+\cdot}$, 88288-93-1; NO_2, 10102-44-0; mesitylene radical cation, 34510-23-1; 1,2,4-trimethylbenzene radical cation, 65018-34-0; phenol radical cation, 40932-22-7; furan radical cation, 66429-00-3; pyridine radical cation, 16399-94-3; naphthalene radical cation, 34512-27-1.

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Gated Reactions

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Abstract: In dense materials, the initial step for many reactions is the formation of a permissive atomic arrangement within which the reaction proper can proceed comparatively rapidly. A simple but general approach is presented for analyzing the kinetics of such "gated" reactions.

For reactions in dense materials, it is not uncommon to find that the best description of the reaction path involves certain auxiliary coordinates in addition to other more obvious or primitive ones. Perhaps the simplest example is that of vacancy diffusion in a crystal.[1] Here, both for rate calculations and mechanistic descriptions, it is essential to consider displacements of the "gate" atoms between which the diffusing atom must squeeze in addition to the primitive displacement of the diffusing atom. As other examples, reactions that involve charge displacement within a solute molecule immersed in a polar solvent may be dependent upon solvent molecule reorganization,[2-4] and flexible chelating agents such as certain crown ethers may have to assume particular conformations before they can bind ions or other ligands.

Auxiliary coordinates are evidently also required in the analysis of a variety of problems in molecular biophysics. Examples include ligand binding[5,6] and side-chain isomerization[6] in proteins, both of which must in some cases be preceded by extensive structural

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