Gas-Phase Nitrosation of Benzene. Implications for Solution Electrophilic Aromatic Substitution Reactions

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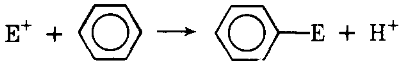
Abstract: The structures of nitrosated benzene, $C_6H_6NO^+$, and protonated nitrosobenzene, $C_6H_5NOH^+$, in the gas phase were examined and compared to similar species in solution. Gas-phase ion structures were determined from chemical reactivity studies as well as from photodissociation spectra utilizing ion cyclotron resonance spectroscopy (ICR). Protonated nitrosobenzene was observed to have a photodissociation maximum at 355 ± 5 nm (for the process $C_6H_5NOH^+ + h\nu \rightarrow C_6H_6^+ + NO$) in comparison to the solution absorption maximum at 360 ± 5 nm. The structure in both cases was found to be the substituent protonated species. In a similar comparison, nitrosated benzene has a photodissociation maximum at 327 ± 5 nm (for the process $C_6H_6NO^+ + h\nu \rightarrow C_6H_6^+ + NO$) and a solution absorption maximum at 332 ± 5 nm. The structure in both cases was observed to be a weakly bound charge-transfer π complex. The solution-phase intermediate in the nitrosation reaction, a σ complex, is found to exist as a high-energy species in the gas phase which prevents the gas-phase substitution reaction from occurring. The results suggest a charge-transfer mechanism for nitrosation and nitration in solution.

Introduction

Nitrosation is one type of electrophilic aromatic substitution (EAS) reaction where an electrophile, E^+, substitutes into an aromatic position (eq 1). A great deal of work on nitrosation



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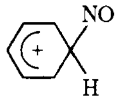
in solution has come from Challis and co-workers.[1] Their observation of a deuterium isotope effect demonstrated that the rate-determining step involves proton loss from the benzenonium ion (a σ complex), I. The presence of a π complex in the mechanism was found to be kinetically insignificant.



I

This contrasts with a similar electrophile, NO_2^+, which is involved in nitration. Although nitration proceeds through a benzenonium ion intermediate, the actual rate-determining step occurs earlier as evidenced by the lack of a deuterium isotope effect.[2]

There has been some controversy concerning the actual mechanism of nitration. Olah has observed anomalous reaction rates for several EAS reactions including nitration and benzylation.[3] These systems appeared to violate the reactivity–selectivity relationship, which states that the more reactive an electrophile is, the less selective it is for either substrate or position. Olah observed cases of nitration reactions displaying low substrate selectivity yet high positional selectivity. To explain this, he involved a π complex prior to formation of the σ complex. Thus, formation of the π complex would be rate determining, thereby specifying substrate selectivity, whereas rearrangement to the σ complex would determine positional selectivity. However, the anomalous reaction rates have been shown by Ridd and co-workers[4] to be invalid. Their work on nitration of bibenzyl demonstrated incomplete mixing prior to reaction. Thus the inclusion of a π complex in the nitration mechanism is unsubstantiated.

Additional evidence against the π complex comes from Rys and co-workers.[5] Competitive nitrations were found to correlate poorly with either various π-complex stabilities or with σ^+ values. Thus there is no reason to prefer π complexes over σ complexes at the rate-determining step.

In addition, theoretical calculations (STO-3G) by Santiago and co-workers[6] have been performed on "early" (π-complex type) and "late" (σ-complex type) transition states. Using attack of a proton upon benzene and toluene as a model, the authors found that the "late" transition state is lower in energy.

Another mechanism for nitration reactions which has been little studied involves a charge-transfer step in place of the π complex or encounter pair previously mentioned. One version, proposed by Brown,[7a] involves formation of a charge-transfer π complex prior to formation of a σ complex. Another version, formulated by Nagakura and Tanaka,[7b-d] involves charge transfer without π-complex formation. In support of this mechanism, Pedersen and co-workers[8] found a correlation between the logarithm of the rate constants for nitration of aromatics compared with the ionization potentials of the aromatics derived from excitation energies of charge-transfer bands. The positional selectivities were found to agree qualitatively with the spin density as determined by the proton hyperfine splitting at each carbon atom of the radical cation. Therefore substrate reactivity would be determined by charge-transfer π-complex formation and positional selectivity by the subsequent formation of the σ complex by the two radical moieties.

The generally accepted view for the mechanism of nitration[9] was proposed by Coombes and co-workers.[10a] They observed that reactive aromatics reached a limiting rate of nitration which is close to the diffusion-controlled limit. In order to explain this, they suggested that formation of an encounter pair, prior to σ-complex formation, is the rate-limiting step. In a subsequent study, Moodie and co-workers[10b] observed that, in spite of a diffusion rate reaction, positional selectivity is maintained. This indicated that formation of the σ complex determines positional selectivity. They envision that the encounter pair initially formed requires no attractive interaction between the aromatic substrate and the electrophile.

The question arises as to whether the nitrosation reaction is as simple as it appears or if it more closely resembles the nitration scheme. Even though σ-complex formation controls the reaction rate and orientation of the products, an earlier association of the reactants may occur.

With this in mind, we decided to examine the nitrosation of benzene in the gas phase. There have been very few studies of EAS reactions in the gas phase compared to solution. Previous gas-phase studies include the rates of nitration[11,12] and acetylation,[12] relative stabilities of nitrosated and nitrated aromatics,[13] and the structures of intermediates in acetylation of anisoles and cresols.[14]

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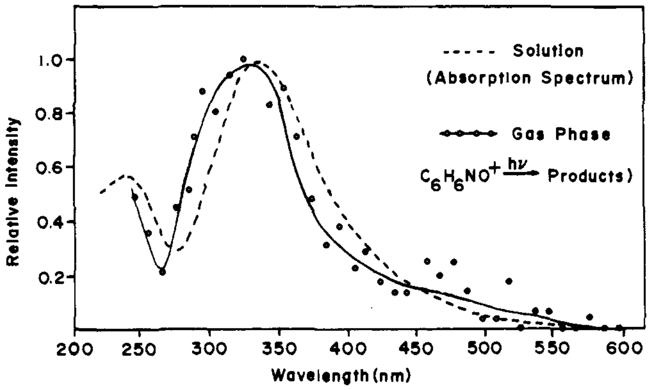


Figure 1. Solution-phase absorption spectrum of $C_6H_6NO^+$ compared to its gas-phase photodissociation spectrum.

In the absence of stabilizing effects due to a ubiquitous solvent, we may obtain as a product an intermediate in the solution mechanism. Since there is no solvent to remove the proton from the substitution product, this ion—in this instance protonated nitrosobenzene—would be isomeric with a reaction intermediate, e.g., the σ complex. A structural study must be made to determine if substitution occurred or, instead, a σ complex or even a π complex, which occurs as an intermediate in the acetylation of anisole and cresol,[14] is formed. This paper presents a study—the gas-phase nitrosation product of benzene, $C_6H_6NO^+$, is compared to protonated nitrosobenzene, $C_6H_5NOH^+$, in the gas phase. Utilizing the dual capabilities of an ion cyclotron resonance spectrometer (ICR) for both chemical and photochemical examinations of gas-phase ions,[15] an extensive comparison of these ions to each other and corresponding ions in solution was made. The results yield significant implications for the solution-phase mechanism.

Experimental Section

Gas-phase chemistry and photochemistry were studied using an ion cyclotron resonance spectrometer (ICR)[16] in conjunction with a 3.5-kW mercury-xenon arc lamp and a 0.25-m Schoeffel monochromator set for 10-nm resolution.

The collision-induced dissociation (CID) spectra were recorded using a modified AEI MS 902 mass spectrometer.[17] For $C_6H_6NO^+$, conditions follow: source pressure, 0.083 Torr (10:1 CH_3ONO-C_6H_6); source temperature, 150 °C; accelerating voltage, 7 kV; collision gas pressure, 3.8×10^{-5} Torr (N_2). For $C_6H_5NOH^+$, conditions follow: source pressure, 0.453 Torr (CH_4); <1 mg of nitrosobenzene inserted via probe; source temperature, 135 °C; accelerating voltage, 7 kV; collision gas pressure, 3.6×10^{-5} Torr (N_2).

The ^1H NMR spectra were obtained using a Perkin-Elmer R-32 NMR equipped for low-temperature studies. The solution-phase UV spectra were acquired using a Cary 10-11M recording spectrophotometer with short path length quartz cells (0.0015-0.000 15 cm path lengths). The molar extinction coefficients are the average of at least two measurements. Their deviations (±10-30%) reflect the uncertainties in the path lengths. Utilizing a Varian E109 X-band EPR recording spectrometer equipped for low-temperature studies, the EPR spectrum of the $C_6H_6NO^+$ species was obtained at a temperature of −150 °C.

The π complex between NO^+ and benzene, $C_6H_6NO^+$, was generated in solution via the method of Allan and co-workers[18] by addition of benzene to 1.2 M $NOHSO_4$ in H_2SO_4. The $NOHSO_4$ solution was prepared according to the literature[18] using $NaNO_2$ which had been twice recrystallized from water to yield white crystals. Both the UV spectrum and the ^1H NMR spectrum were obtained with a 1 M benzene concentration in the 1.2 M $NOHSO_4$ solution.

Protonated nitrosobenzene was generated in solution by addition of nitrosobenzene to distilled FSO_3H at −78 °C. Both the UV spectrum and the ^1H NMR were obtained using a 1 M nitrosobenzene solution.

Methyl nitrite was prepared according to the literature.[19] All other chemicals were commercially available and used without further purification except for two freeze-pump-thaw cycles to remove noncondensable gases prior to gas-phase studies.

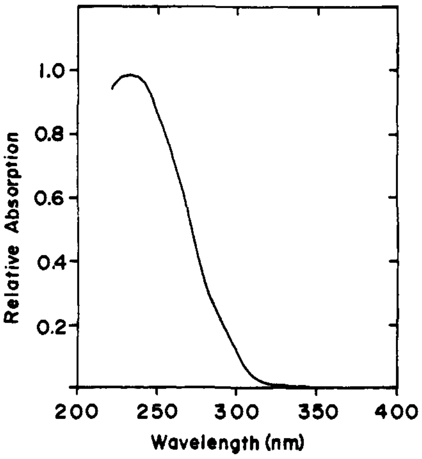


Figure 2. Solution-phase absorption spectrum of NO^+ in H_2SO_4.

Results

Solution. The $C_6H_6NO^+$ species, formed by addition of benzene to 1.2 M $NOHSO_4$ in H_2SO_4, has the absorption spectrum illustrated in Figure 1 with a maximum at 332 ± 5 nm (ϵ 18 000 M^{-1} cm^{-1} ± 30%) and with a weaker absorption maximum at 240 ± 5 nm. For comparison, the absorption spectrum of $NOHSO_4$ in H_2SO_4 is shown in Figure 2; the maximum is at 232 ± 5 nm.

Bandlish and Shine[20] have observed the formation of aromatic radical cations from their neutral precursors by reaction with $NOBF_4$. Although the possibility of forming the benzene radical cation by reaction with NO^+ is slight, this was verified by obtaining an EPR spectrum for the $C_6H_6NO^+$ species. No signal was obtained for $g = 1.8$-2.4, indicating that the benzene radical cation was not present.

The ^1H NMR of the $C_6H_6NO^+$ species produced a singlet at 4.76 ppm vs. internal tetramethylammonium cation (TMAC) (7.89 ppm vs. Me_4Si).[21] The signal varied less than 0.10 ppm as the benzene:NO^+ mole ratio was varied from 1:10 to 1:1. In contrast, Allan and co-workers[18] have reported singlets at 1.45 and 1.74 ppm downfield from external benzene (8.65 and 8.94 ppm vs. Me_4Si, corrected) for benzene:NO^+ mole ratios of ~1:1 and ~1:2, respectively. The signal variation as a function of mole ratio which they report is unexplainable. However, the discrepancy in the proton shift appears due, in part, to the diamagnetic susceptibility correction. The large amount of benzene present alters the solution's diamagnetic susceptibility, which they did not take into account. This was shown by comparing the proton shift of external benzene to internal TMAC in a 1 M benzene-1.2 M NO^+-H_2SO_4 solution. The measured proton shift of external benzene (3.55 ppm vs. internal TMAC, corrected) differed significantly from the expected value (4.07 ppm). Thus, the shift of $C_6H_6NO^+$ was too far downfield when compared to external benzene. However, there is still a discrepancy of ~0.5 ppm which may be due to the more concentrated $NOHSO_4$ solution (1.8 M) which they used. This would result in a higher concentration of benzene, thus affecting the solution's diamagnetic susceptibility even more.

Protonated nitrosobenzene, formed by addition of nitrosobenzene to FSO_3H at −78 °C, has the absorption spectrum illustrated in Figure 3 with a maximum at 360 ± 5 nm (ϵ 47 000 ± 10% M^{-1} cm^{-1}). This spectrum is in general agreement with the result of Belyaev and co-workers,[22] who also observed a maximum at 360 nm. The ^1H NMR, shown in Figure 4, has aromatic protons at 7.8-9.0 ppm vs. Me_4Si (based upon internal TMAC)[21] and a signal at 16 ppm vs.

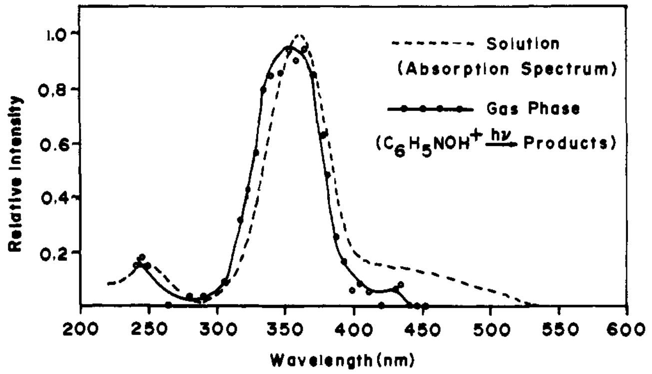


Figure 3. Solution-phase absorption spectrum of $C_6H_5NOH^+$ compared to its gas-phase photodissociation spectrum.

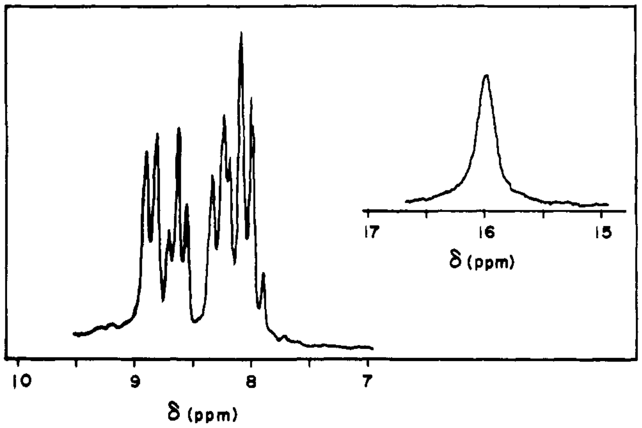


Figure 4. ^1H NMR of $C_6H_5NOH^+$ in FSO_3H.

Me_4Si due to protonation on the nitroso group. The integrated signals yielded the expected proton ratios of 5:1, respectively. The spectrum was unchanged from −65 to −30 °C. Although significant broadening occurred up to 10 °C, the protonated nitrosobenzene was stable at this temperature for 10 min as demonstrated by the reversion to the original spectrum upon cooling to −30 °C.

Gas Phase. Nitrosobenzene was protonated in the gas phase by the use of methane (reaction 2a). The $C_6H_5NOH^+$ thus formed was found to undergo photoreaction 2b exclusively, yielding the photodissociation spectrum which is shown in Figure 3 together with the solution spectrum for comparison. The photodissociation observed has an onset at 445 ± 5 nm (the use of diethyl ether as a mild protonating agent was found to have no effect upon threshold value) and a maximum at 355 ± 5 nm. The photoappearance spectrum of $C_6H_6^{+}\cdot$ was found to match the photodissociation spectrum of $C_6H_5NOH^+$, confirming reaction 2b.

$$C_6H_5NO + CH_5^+ \rightarrow C_6H_5NOH^+ + CH_4 \qquad (2a)$$

$$C_6H_5NOH^+ + h\nu \rightarrow C_6H_6^{+}\cdot + NO\cdot \qquad (2b)$$

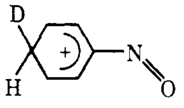
Recent work by Freiser and Beauchamp[23] determined the change in proton affinities and Li^+ affinities between the ground state and excited state of various monosubstituted benzenes. From their study, they obtained a relation

$$\Delta PA(B) = 0.76\Delta D(B\text{-}Li^+) + 15 \qquad (3)$$

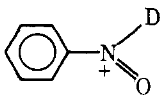
correlating the change in the binding energy of Li^+ of a species in its ground and electronically excited state, $\Delta D(B\text{-}Li^+)$, to the similar change in proton affinity. The value of $\Delta D(B\text{-}Li^+)$ for nitrosobenzene (20 kcal/mol) which they reported yields an estimate using eq 3 for the ΔPA(nitrosobenzene) of 30 kcal/mol, which is in good agreement with the observed value of 27 kcal/mol. The correspondence suggests that H^+ and Li^+ are bonded to the same position, presumably the nitrogen.[24]

The structure of $C_6H_5NOH^+$ was probed by studying its ion chemistry. Reaction with pyridine, both a stronger proton acceptor than nitrosobenzene and a stronger NO^+ acceptor than benzene, demonstrated proton transfer (confirmed by double resonance) but no NO^+ transfer. Since the presence of a small amount of the pyridine/NO^+ species (*m/e* 109) may be obscured by the ^{13}C peak of $C_6H_5NOH^+$ (*m/e* 108), toluene, a stronger NO^+ acceptor than benzene, was reacted but again no NO^+ transfer was observed. These results indicate that protonated nitrosobenzene retains its initial structure rather than rearranging to a π complex, which would be expected to transfer NO^+ exclusively, or to a σ complex, which would be expected to transfer both NO^+ and H^+.

The site of protonation was examined by deuteration of nitrosobenzene. Deuteration on the ring (species II) would lead



II



III

to both deuteron and proton transfer as in the case of anisole.[25] However, if deuteration occurs on the substituent (species III), then only deuteron transfer is possible. Thermoneutral deuteron transfer (reaction 4) yielded no protonated nitrosobenzene. In addition, $C_6H_5NOD^+$ was found to deuterate but not protonate pyridine, confirming the first observation that nitrosobenzene is substituent protonated (species III).

$$C_6H_5NOD^+ + C_6H_5NO \rightarrow C_6H_5NO + C_6H_5NOD^+ \qquad (4)$$

The proton affinity of nitrosobenzene was found to lie between NH_3 (PA = 208.4 ± 2.0 kcal/mol)[26] and isopropyl ether (PA = 209.1 ± 2.0 kcal/mol),[27] yielding an estimate for the PA of nitrosobenzene = 208.8 ± 2.0 kcal/mol.

A collision-induced dissociation (CID) spectrum of $C_6H_5NOH^+$, illustrated in Figure 5a, was obtained to independently compare its structure with that of $C_6H_6NO^+$. Fragmentations involving loss of hydrogen as well as yielding products identical with photodissociation are common.[28] The charge stripping peak (*m/e* $54^+ = 108^{2+}$), although of low intensity, is significant, as will be discussed later.

An attempt to nitrosate benzene by direct reaction of NO^+ with benzene resulted in reaction 5. This reaction has been observed by Lias and Ausloos,[29a] who measured an equilibrium constant of 119.0 ± 17.9 at 35 °C. The extent of the reaction is due to a favorable entropy of reaction (ΔS = +8.8 eu).[29b]

$$NO^+ + C_6H_6 \rightarrow NO\cdot + C_6H_6^{+}\cdot \qquad (5)$$

Benzene was successfully nitrosated by the Williamson and Beauchamp[30] sequence of reactions 6–8 which utilize nitric oxide and isopropyl chloride.

$$NO^+ + C_3H_7Cl \rightarrow C_3H_6NO^+ + HCl \qquad (6)$$

$$C_3H_6NO^+ + C_3H_7Cl \rightarrow C_3H_6 + C_3H_7ClNO^+ \qquad (7)$$

$$C_3H_7ClNO^+ + C_6H_6 \rightarrow C_3H_7Cl + C_6H_6NO^+ \qquad (8)$$

A drawback to this system is the presence of *m/e* 43^+, a major fragment ion from isopropyl chloride, which protonates the various species present. This greatly complicated the subsequent structural analysis by ion-molecule reactions.

A second method utilized methyl nitrite as the nitrosating agent. Double resonance of the resultant nitrosated benzene indicated precursor ions of *m/e* 30 (NO^+), 60 (CH_2ONO^+), 62 (CH_3ONOH^+), and 91 (CH_3ONONO^+), as well as *m/e*

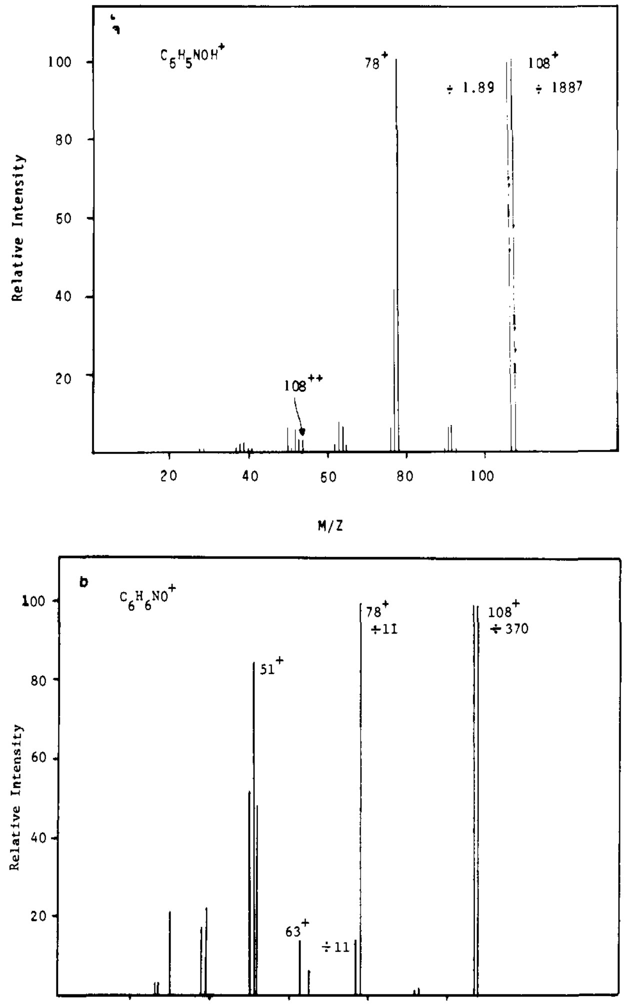


Figure 5. (a) CID spectrum of $C_6H_5NOH^+$. (b) CID spectrum of $C_6H_6NO^+$.

78 ($C_6H_6^+$). Relevant reactions of methyl nitrite, from studies by McAllister and Pitman[31] as well as Farid and McMahon,[32] are given in eq 9-12. The reactions producing $C_6H_6NO^+$ are presented in reactions 13-16. This system proved more desirable because nitrosated benzene readily became the base peak in the mass spectrum without the problems of an acidic ion being present.

$$NO^+ + CH_3ONO \rightarrow CH_2ONO^+ + HNO \qquad (9)$$

$$CH_2ONO^+ + CH_3ONO \rightarrow CH_2O + CH_3ONONO^+ \qquad (10)$$

$$CH_2ONO^+ + CH_3ONO \rightarrow CH_3ONOH^+ + \text{products} \qquad (11)$$

$$CH_3ONOH^+ + CH_3ONO \rightarrow CH_3OH + CH_3ONONO^+ \qquad (12)$$

$$CH_2ONO^+ + C_6H_6 \rightarrow CH_2O + C_6H_6NO^+ \qquad (13)$$

$$CH_3ONOH^+ + C_6H_6 \rightarrow CH_3OH + C_6H_6NO^+ \qquad (14)$$

$$CH_3ONONO^+ + C_6H_6 \rightarrow CH_3ONO + C_6H_6NO^+ \qquad (15)$$

$$C_6H_6^{+\cdot} + CH_3ONO \rightarrow C_6H_6NO^+ + CH_3O\cdot \qquad (16)$$

The photodissociation spectrum of nitrosated benzene ($C_6H_6NO^+$), generated by either of the methods described above, is illustrated in Figure 1 together with the solution spectrum for comparison. Photoreaction 17 was observed exclusively with an onset at 580 ± 5 nm and a maximum at 327 ± 5 nm. The photoappearance spectrum of $C_6H_6^{+\cdot}$ was found to match the photodissociation spectrum of nitrosated benzene, confirming reaction 17.

$$C_6H_6NO^+ + h\nu \rightarrow C_6H_6^{+\cdot} + NO\cdot \qquad (17)$$

Ion-molecule reactions were used to interrogate the ion's structure. Reaction with pyridine, a stronger base than nitrosobenzene, yielded no proton transfer. Reaction with toluene, a stronger NO^+ acceptor,[33] indicated transfer of NO^+ from $C_6H_6NO^+$ to toluene and was confirmed by double resonance. These results indicate that $C_6H_6NO^+$ retains the structure of a π complex rather than rearrange to a σ complex or to protonated nitrosobenzene.

The strength of the [benzene/NO]$^+$ bond was found to be >39 kcal/mol, the bonding energy between ethanol and NO^+,[34] by the occurrence of reaction 18. An upper limit of 49 kcal/mol is obtained from the threshold of photodissociation of $C_6H_6NO^+$ (reaction 17).

$$C_2H_5ONOH^+ + C_6H_6 \rightarrow C_2H_5OH + C_6H_6NO^+ \qquad (18)$$

The CID spectrum of $C_6H_6NO^+$, shown in Figure 5b, was obtained to independently compare the ion's structure with that of $C_6H_5NOH^+$. Fragmentation involving loss of hydrogen and loss of NO· was found which was also observed for $C_6H_5NOH^+$. However, the charge stripping peak, which was observed in the case of $C_6H_5NOH^+$, was absent here, suggesting a structural dissimilarity between the two ions.

Discussion

The two gas-phase ions—$C_6H_6NO^+$ and $C_6H_5NOH^+$—are obviously distinct species. This was shown by differences in their chemical reactivity and their photodissociation spectra. Also, the charge stripping peak (*m/e* $54^+ = 108^{2+}$) present in the CID spectrum of $C_6H_5NOH^+$ but absent in the CID spectrum of $C_6H_6NO^+$ indicated a structural difference, although the nature of the difference is not discernible. As would be predicted, $C_6H_5NOH^+$ is protonated nitrosobenzene—the expected nitrosation product of benzene in solution before H^+ loss. Conversely, $C_6H_6NO^+$ must represent a stable intermediate in the reaction pathway. The chemical reactivity suggests that $C_6H_6NO^+$ is a π complex. The similarity of its spectroscopic properties to the solution $C_6H_6NO^+$ species, which was postulated to be a π complex by Allan and co-workers,[18] supports this. In addition, the large extinction coefficient in solution (ϵ ~18 000 M^{-1} cm^{-1}) coupled with the broad, featureless absorption band suggests that the species is a charge-transfer complex as formulated by Mulliken.[35] The charge-transfer reaction 5 suggests that the charge in the π complex resides predominantly on the benzene moiety (species IV) with a transfer of charge to the NO moiety upon electronic excitation. With this formulation, the process of "NO^+ transfer" from benzene to toluene involves a simultaneous $2e^-$ transfer (cf. Scheme I).

Although $C_6H_6NO^+$ and $C_6H_5NOH^+$ are distinct species,

Scheme I

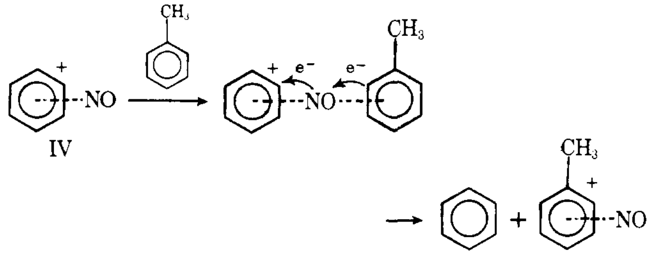


Table I. Thermochemical Data

compd	ΔH_f, kcal/mol	ref
$C_6H_6^{+}\cdot$	233	*a*
NO^+	235.1	*a*
$C_6H_5NO^{+}\cdot$	252	*d*
H^+	365.2	*a*
C_6H_6	19.8	*b*
$H\cdot$	52.1	*b*
$NO\cdot$	21.6	*b*
$C_6H_5\cdot$	70	*b*
HNO	24.6	*b*
$HNO^{+}\cdot$	261.9	*e*
C_6H_5NO	47	*c*
$C_6H_5^+$	270	*f*

[a] Rosenstock, H. M.; Drakl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977,** *6.* [b] Karapet'yants, M. K.; Karapet'yants, M. L. "Thermodynamic Constants of Inorganic and Organic Compounds"; Ann-Arbor-Humphrey Science Publishers: Ann Arbor, Mich., 1970. [c] Average of three values: 41 kcal/mol, Carmichael, P. J.; Gowenlock, B. G.; Johnson, C. A. F. *Int. J. Chem. Kinet.* **1972,** *4*, 339–343. 48.1 kcal/mol, Choo, K. Y.; Golden, D. M.; Benson, S. W. *Ibid.* **1975,** *7*, 713–724. 51.5 kcal/mol, Pepekin, V. I.; Lebedev, V. P.; Balepin, A. A.; Lebedev, Y. A. *Dokl. Phys. Chem.* (*Engl. Transl.*) **1975,** *221*, 370–373. [d] Sum of $\Delta H_f(C_6H_5NO)$ and $IP(C_6H_5NO)$. IP = 8.87 eV, footnote *a*. [e] Sum of $\Delta H_f(HNO)$ and $IP(D^{15}NO)$. IP = 10.29 eV. Kohout, F. C.; Lampe, F. W. *J. Chem. Phys.* **1966,** *45*, 1074–1075. [f] Beauchamp, J. L. *Adv. Mass Spectrom.* **1974,** *6*, 717–723.

Table II. Thermodynamics of Photodissociation Reactions

	ΔH_{rxn}, kcal/mol	
possible photoproducts	$C_6H_5NOH^+$	$C_6H_6NO^+$
$C_6H_6^{+}\cdot + NO\cdot$	52	44
$C_6H_6 + NO^+$	52	44
$C_6H_5NO^{+}\cdot + H\cdot$	101	84
$C_6H_5^+ + HNO$	92	93
$C_6H_5\cdot + HNO^{+}\cdot$	128	121
$C_6H_5\cdot + H\cdot + NO^+$	154	133
$C_6H_5^+ + H\cdot + NO\cdot$	141	147
$C_6H_5NO + H^+$	208.8	201
$C_6H_5\cdot + H^+ + NO\cdot$	253	246

their ion photoproducts are equivalent—$C_6H_6^{+}\cdot$. Utilizing the thermochemical data in Table I, various postulated photoproducts and the corresponding heats of reaction are presented in Table II. At moderate energies (<360 nm, 79 kcal/mol), only the first two photoproducts are possible. However, $C_6H_6^{+}\cdot$ is the sole ionic product due to the entropy considerations previously mentioned. At higher energies (e.g., 250 nm, 114 kcal/mol), although more dissociation channels are accessible, they do not compete effectively.

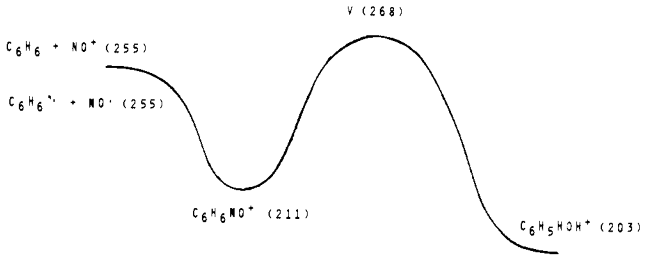
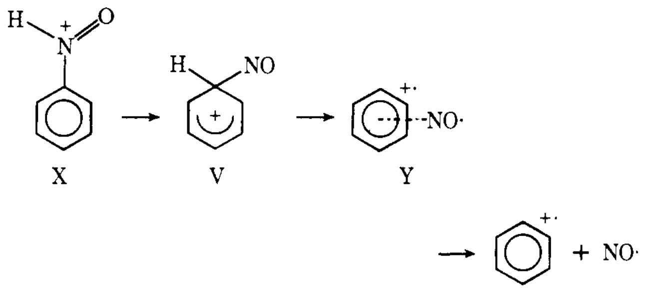


Figure 6. Reaction coordinate for gas-phase nitrosation of benzene (values in parentheses are ΔH_f's). Species V is postulated to be the σ-complex intermediate as discussed in the text.

Scheme II



From the bond energy of $C_6H_6NO^+$ (44 ± 5 kcal/mol) and the PA of nitrosobenzene (208.8 ± 2.0 kcal/mol), the $\Delta H_f(C_6H_6NO^+)$ and the $\Delta H_f(C_6H_5NOH^+)$ are calculated to be 211 ± 5 and 203 ± 7 kcal/mol,[36] respectively. From this $\Delta H_f(C_6H_5NOH^+)$, we find that the onset for photodissociation (445 ± 10 nm, 64 ± 3 kcal/mol) is significantly higher in energy than either the onset for the solution absorption spectrum of $C_6H_5NOH^+$ (520 ±5 nm, 55 ± 1 kcal/mol) or the thermodynamic threshold for dissociation to products (52 ± 8 kcal/mol). This indicates a barrier to dissociation. Since this species is substituent protonated, presumably on the nitrogen,[24] this barrier could be due to the migration of the proton to the ipso carbon to form the σ complex which rearranges to the π complex. Once this barrier is surmounted, the internal energy is in excess of the bond energy and the π complex subsequently dissociates (cf. Scheme II). This barrier represents either the σ complex, V, or some other configuration between X and Y. The heat of formation for this high-energy species is calculated from the photodissociation threshold to be 267 kcal/mol. Interestingly, an estimate for the ipso proton affinity of nitrosobenzene calculated by Catalan and Yanez using C_{1s} binding energies (corrected for a new proton affinity for NH_3[26]) yields a heat of formation of V equal to 271 kcal/mol, in excellent agreement with our value for the rearrangement barrier.[37] This strongly suggests that the σ complex is at or near the barrier maximum for rearrangement and dissociation of $C_6H_5NOH^+$, resulting in a reaction coordinate illustrated in Figure 6 (the values in parentheses are heats of formation of the various species). As in solution, the highest energy step (i.e., the rate-determining step) involves formation of the σ complex, species V.

In solution, solvent effects play a considerable role in stabilizing ions. The relative energies of the various species may differ significantly from the gas phase. Since the π complex, $C_6H_6NO^+$, was stable in solution for hours—albeit under extreme conditions—this suggests that the σ complex, which was not observed, is less stable. Theoretical calculations, e.g., that of Santiago and co-workers[6] mentioned previously, which compare π- vs. σ-complex energies, consider the charge localized on the electrophile. This represents the excited state for the $C_6H_6NO^+$ species. From the onset of absorbance for the π complex the heat of formation of this "excited" π complex is calculated to be 260 ± 6 kcal/mol. This is close to the heat of formation calculated for the σ complex, V.

Thus we have found that nitrosation of benzene in the gas phase ceases with a charge-transfer π complex which is also stable in solution. This strongly suggests the occurrence of such a complex in the solution nitrosation reaction as was suggested by Brown's mechanism[7a] for nitration. Although nitrosation in solution shows no kinetically significant π complex,[1] this would mean that formation of the charge-transfer complex is in rapid equilibrium with both the reactants and the kinetically significant σ complex. Since the IP of NO_2 (9.67 eV)[38] is higher than that of NO (9.26 eV),[29b] NO_2^+ should form a charge-transfer complex more readily, thus implying that nitration may occur via a charge-transfer mechanism. In contrast with nitrosation, the charge-transfer π complex involved in nitration may be kinetically significant as demonstrated by the lack of a deuterium isotope effect.[2]

Acknowledgment. The authors thank Professor Graham Cooks and Douglas Cameron, Chemistry Department, Purdue University, for providing the CID spectra. This work was supported in part by the Research Corporation through a Cottrell Research Grant. The authors also wish to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, and Du Pont for support administered through Purdue University.

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Dimerization and Cycloaddition Reactions of a Trimethylenemethane Derivative, 2-Isopropylidenecyclopenta-1,3-diyl. Mechanistic Separation of Triplet and Singlet Reactions

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Received June 11, 1979

Abstract: Pyrolysis of 7-isopropylidene-2,3-diazanorbornene (**1**) at 60 °C in solution liberates N_2 and 2-isopropylidenecyclopenta-1,3-diyl (**2**). The diyl (**2**) dimerizes readily, but, in the presence of an olefinic trapping agent, **2** can be intercepted as either a fused adduct, F, a bicyclo[3.3.0]oct-1-ene, or a bridged adduct, B, a 7-isopropylidenenorbornane. The composition of the adduct mixture is dependent on the initial concentration of the trapping olefin, fused adducts being heavily favored at high concentrations. The concentration dependence arises from two forms of the diyl which are generated sequentially in a cascade mechanism. The first species is a singlet that can add both regiospecifically and stereospecifically, whereas the second is the triplet ground state of the diyl. Quantitative treatment of the dilution effect data for the addition of dimethyl fumarate leads to the conclusion that the rate constants for capture of the singlet and intersystem crossing to the triplet are in the ratio 7.7 M^{-1}.

The diazene **1**, 7-isopropylidene-2,3-diazanorbornene, is a source of 2-isopropylidenecyclopenta-1,3-diyl, **2**, a trimethylenemethane (TMM) derivative.[2] Diyl **2** incorporates part of the π-electron conjugated system of the parent TMM **3** in a five-membered ring, a structural feature that we believed might have useful application in fostering cycloaddition reactions.

Generation of reactive intermediates presumed to be the parent TMM, **3**, has been achieved by several routes. The two major reactions of **3** seem to be cyclization to methylenecyclopropane, **4**,[3-13] and [3 + 3] dimerization to 1,4-bismethylenecyclohexane, **5**.[6,10-12,14,15] The dimerization to **5** apparently is a characteristic reaction of the triplet form of **3**,[9,16] whereas ring closure to **4** can occur from triplet **3**[12b] and pre-

0002-7863/80/1502-0276$01.00/0