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Electrophilic Aromatic Nitration in the Gas Phase

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Abstract: Aromatic nitration by $MeO^+(H)NO_2$, in essence a nitronium ion solvated by one methanol molecule, has been studied in the gas phase by using an integrated approach, based on the coordinate application of ICR, CI, and CID mass spectrometric methods with a highly complementary radiolytic technique. The latter can be used in gases at atmospheric pressure and allows direct evaluation of key mechanistic features, in particular of substrate and positional selectivity. The results resolve early discrepancies between gas-phase and liquid-phase studies, characterizing the reaction as a typical, well-behaved electrophilic substitution of moderate selectivity. The data from the gas-phase nitration of ten monosubstituted benzenes fit a Hammett's type linear plot, characterized by a ρ value of −3.87. The correlation does not extend to highly activated substrates, such as anisole and mesitylene, since the nitration rate tends to a limiting value that cannot be increased by further enhancing the activation of the substrate, exactly as in "encounter-rate" nitrations occurring in solution. The mechanism and the energetics of the gas-phase nitration have been investigated, and the relative stability of the charged intermediates involved, in particular of the isomeric protonated nitrobenzenes, has been estimated by theoretical approaches at two different levels, using STO-3G minimal basis and 4-31G split-valence basis sets.

Nitration plays a central role in the theory of aromatic reactivity and is quoted in the textbooks as the canonical example of a mechanistically well-defined electrophilic substitution.[2–5]

Yet, despite the overwhelming amount of attention received, and the huge body of data accumulated in many decades, important aspects of the nitration mechanism are far from defined and remain the focus of active interest.

The most serious problems arise from the profound influence of the reaction medium, ineluctable in condensed-phase studies, which affects and diversifies the reactivity pattern to such an extent as to void the very notion of a single nitration mechanism.[6]

An effective approach to overcome the above difficulties, and progress toward a general theory of aromatic nitration directly comparable with theoretical results, is the extension of the study to the gas phase, an environment largely free of solvation, ion pairing, and other complicating factors, provided of course that the gas-phase experiments are capable of furnishing mechanistic information comparable to that derived from condensed-phase investigations.

Such a requirement can hardly be met by purely mass spectrometric approaches, whose results have so far delineated reactivity patterns, typical of the low-pressure domain experimentally accessible, hardly consistent with common experience in liquid-phase nitration. Thus NO_2^+, long recognized as *the* nitrating species in solution, fails to add to aromatics under mass spectrometric conditions, reacting instead according to charge exchange and oxygen atom transfer processes.[7–9] Other gaseous cations, $CH_2ONO_2^+$ and $EtO(NO_2)_2^+$, display a peculiar selectivity, nitrating *deactivated* substrates at *higher* rates, an anomaly traced to the incursion of competitive charge-exchange processes.[10,11] Quite apart from these specific problems, any approach to gas-phase aromatic nitration based esclusively on mass spectrometric techniques is bound to evoke unfavorable comparison with condensed-phase studies, since the lack of discrimination among isomeric nitrated ions prevents the mechanistically crucial evaluation of key parameters, such as orientation and partial rate factors, readily measurable in solution.

In a preliminary communication we have recently outlined an approach to gas-phase aromatic nitration aimed at providing mechanistic information fully comparable with that from condensed-phase studies.[12] The approach, successfully applied in other areas of gas-phase ion chemistry,[13] is based on the combination of mass spectrometric methods, including chemical ionization (CI), ion cyclotron resonance (ICR), and collisionally induced dissociation (CID) spectrometry, with a radiolytic technique. The preliminary results have identified the reagent used, protonated methyl nitrate, as the first example of a well-behaved nitrating cation, showing that its substrate and positional selectivity fully conform to reaction patterns long established in solution.[12]

This account reports the full details of the study, which has been extended to a much larger number of substrates, and a more comprehensive mechanistic analysis, including theoretical calculations on experimentally inaccessible aspects of the reaction energetics.

Experimental Section

Materials. The gases, having a stated purity in excess of 99.9 mol %, were obtained from Matheson Gas Products Inc. The chemicals used as reference standards in the analyses, or as substrates in the nitration experiments, were obtained from commercial sources, or prepared according to unexceptional procedures, their purity being established by GLC and GLC/MS on the same columns used for the analysis of the products.

Radiolytic Experiments. The gaseous samples were prepared by using a greaseless vacuum line, as described in earlier reports,[13] except for the introduction of $MeNO_3$, accomplished with a microsyringe, rather than in fragile glass bulbs that must be shattered. The irradiations were carried out at doses ranging from 5×10^3 to 3×10^4 Gy, at a dose rate of 1×10^4 Gy h^{-1} in a 220 Gammacell (Nuclear Canada Ltd.) at a temperature of 37.5 °C.

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[1] (a) Università "La Sapienza". (b) Universidad Autònoma.

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[7] Benezra, S. A.; Hoffman, M. K.; Bursey, M. M. *J. Am. Chem. Soc.* **1970**, *92*, 7501.

[8] Hoffman, M. K.; Bursey, M. M. *Tetrahedron Lett.* **1971**, 2539.

[9] Morrison, J. D.; Stanney, K.; Tedder, J. M. *J. Chem. Soc., Perkin Trans. 2* **1981**, 967.

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[13] For a discussion of the principles and the experimental aspects of the radiolytic technique, cf.: (a) Cacace, F. *Radiat. Phys. Chem.* **1982**, *20*, 99. (b) Speranza, M. *Gazz. Chim. Ital.* **1983**, *113*, 37. For recent applications to gas-phase aromatic substitution, cf.: (c) Cacace, F.; de Petris G.; Fornarini, S.; Giacomello, P. *J. Am. Chem. Soc.* **1986**, *108*, 7495. (d) Cacace, F.; Ciranni, G. *J. Am. Chem. Soc.* **1986**, *108*, 887 and references therein.

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The radiolytic products were analyzed by GLC, using Sigma 1 and Sigma 3 chromatographs, equipped with flame ionization or photoionization detectors, and by GLC/MS, using a Hewlett-Packard 5892A quadrupole mass spectrometer. The identity of the products was established by comparison of their capacity factors with those of authentic samples, as well as from their mass spectra. The amounts of products formed were deduced from the areas of the corresponding elution peaks, using the internal-standard calibration method.

The following columns were used: (i) a 3.3-m long, 3-mm i.d. glass column packed with SP-2100 (20% w/w) and Carbowax 1500 (1%) on 100–120 mesh Supelcoport, operated at 110–130 °C, (ii) a 25-m long, 0.25-mm i.d. fused silica column, coated with methylsilicone fluid, operated from 80 to 120 °C, and (iii) a 25-m long, 0.53-mm i.d. fused silica column, coated with OV-101, operated from 60 to 120 °C.

Mass Spectrometric Measurements. The protonation of $MeNO_3$ and of $MeNO_3/C_6D_6$ mixtures was studied in the Hewlett-Packard quadrupole instrument, operated in the CI mode. The pressure within the source was measured with a ionization manometer, whose readings had been previously calibrated with a Bourdon-type mechanical gauge. The protonation experiments were carried out at a source temperature of 150 °C, at CH_4 pressures up to 1 Torr. The same set of experiments was repeated in the ion source of a ZAB-2F spectrometer (VG Micromass Ltd.), operated in the CI mode and fitted with a MKS Baratron Model 221A capacitance manometer. Typical experimental conditions were as follows: electron current 1 mA, electron energy 50 V, mass resolving power 2×10^3, energy resolution 4×10^3, methane or isobutane pressure from 0.2 to 0.4 Torr, ion source temperature 180 °C. The CID spectra of the nitrated adducts from PhH and of the model protonated adducts from $PhNO_2$ and the isomeric nitrotoluenes were taken by admitting He into the collision cell of the ZAB-2F spectrometer and increasing its pressure to ca. 10^{-6} Torr, which caused a 30% reduction of the main beam.

The proton affinity (PA) of methyl nitrate was estimated by measuring the equilibrium constant of the proton transfer from $MeNO_3H^+$ to $CH_2(CN)_2$ and making the customary assumptions about the entropy change of the reaction. The measurements were carried out in a pressure range from 5×10^{-7} to 1×10^{-6} Torr, at 30 °C, in a Nicolet FT-MS 1000 ICR mass spectrometer equipped with a 2-T superconducting magnet and a 2.54-cm^3 cell.

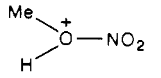
Warning: Methyl nitrate is a dangerous compound and should be used only in minute amounts, since it may explode if overheated. Attempts to shatter fragile glass ampules containing liquid $MeNO_3$ occasionally resulted in explosions. Inhalation of the vapors causes adverse physiological effects.

Results and Discussion

The Nitrating Reagent. Radiolysis of gaseous NO_2 does not represent a convenient approach to the study of the NO_2^+ reactivity, owing to the incursion of free radical processes. Among bound forms of nitronium ion, attention was focused on protonated methyl nitrate, which belongs to a class of nitrating agents well-known in solution[14] and is conveniently obtained in the gas phase from exothermic proton-transfer reactions

$$MeNO_3 + AH^+ \rightarrow MeNO_3H^+ + A \qquad (1)$$

Evaluation of the proton affinity (PA) of methyl nitrate from proton-transfer equilibrium constants led to an approximate value of 176 kcal mol^{-1},[15] not inconsistent with the known PA of $EtNO_3$, 178.5 kcal mol^{-1}.[16] The exothermicity of (1) can accordingly be calculated around 44 and 13 kcal mol^{-1} respectively for the protonation of $MeNO_3$ by CH_5^+ and $C_2H_5^+$, the major Brønsted acids in ionized methane. While the relative stability of the two conceivable structures of protonated methyl nitrate cannot be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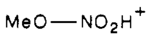
II

established experimentally, theoretical results suggest that I should be more stable by ca. 20 kcal/mol^{-1},[17] which is not inconsistent with the remarkable nitrating ability of the cation demonstrated by the present work. The experimentally measured heat of formation and PA of $MeNO_3$ allow evaluation of the $H_f°$ value of I, ca. 161 kcal mol^{-1}.

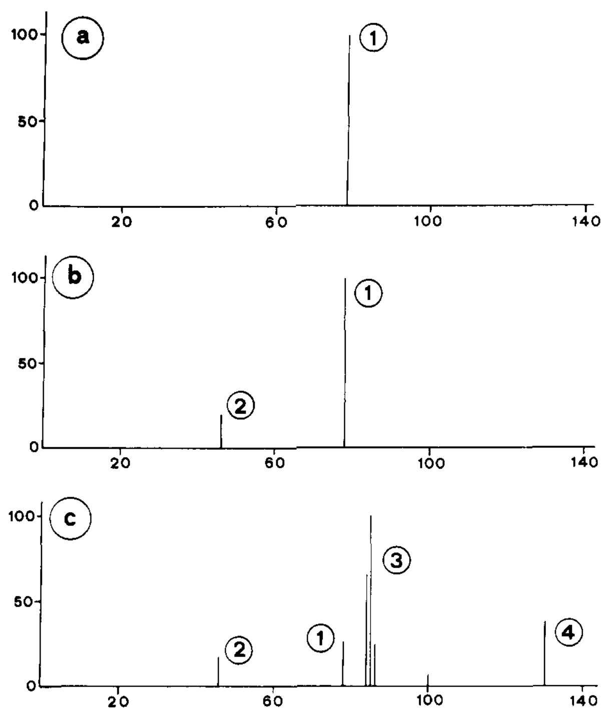

Figure 1. Methane CI of (a) $MeNO_3$, low partial pressure (<0.1 mTorr), (b) $MeNO_3$, ca. 0.1 mTorr, and (c) $MeNO_3/C_6D_6$. Major methane peaks (CH_5^+ and $C_2H_5^+$) not reported. (1) $MeO^+(H)NO_2$ at m/z 78. (2) NO_2^+ at m/z 46. (3) $C_6X_7^+$ (X = H, D) at m/z 84, 85, 86. (4) $C_6D_6NO_2^+$ at m/z 130.

Chemical Ionization Mass Spectra. The CH_4 CI spectra of $MeNO_3$, recorded at 1 Torr and 160 °C, display the $(M + H)^+$ quasimolecular ion at m/z 78 as the only significant peak, provided that the nitrate pressure is sufficiently low (<0.1 mTorr) to prevent its direct ionization (Figure 1a). At somewhat higher $MeNO_3$ pressures, NO_2^+ is formed in relatively low abundances by direct ionization processes, as shown by Figure 1b. At still higher $MeNO_3$ concentrations, the CI spectra clearly denote the occurrence of direct ionization, yielding NO_2^+ and $CH_2ONO_2^+$ ions, and of ion–molecule reactions, giving $MeO(NO_2)_2^+$ ions. The CI spectra of benzene, recorded under the same CH_4 pressure, display a predominant $(M + H)^+$ peak (ca. 80%), together with smaller abundances of $(M + C_2H_5)^+$, $(M + C_3H_5)^+$, and $(M + C_3H_7)^+$ ions.[18] Figure 1c illustrates the methane CI spectrum of a 1:1 $MeNO_3/C_6D_6$ mixture, recorded under conditions comparable to those of Figure 1b. Use of the deuteriated arene was aimed at detecting the possible formation of the molecular ion of benzene, which could not be accomplished with C_6H_6, since both I and $C_6H_6^+$ are characterized by the same m/z ratio. The most interesting feature of the spectrum, which displays three major $C_6X_7^+$ (X = H, D) ions, is undoubtedly the formation of a $C_6D_6NO_2^+$ adduct, whose significant abundance roughly accounts for the decrease of I, while the abundance of NO_2^+ is nearly unaffected. Despite their qualitative nature, the CI results lend themselves to the following considerations:

(i) The spectra of neat $MeNO_3$ show that CH_5^+ and $C_2H_5^+$ ions efficiently protonate methyl nitrate, yielding an adduct that is effectively stabilized, even at the relatively low pressure and the relatively high temperature prevailing in the ion source.

(ii) The spectra of the $C_6D_6/MeNO_3$ mixture are consistent with the view that I is the only effective nitrating species. In fact,

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[14] Raudnitz, H. *Chem. Ber.* **1927**, *69*, 738. See also ref 6, p 94.

[15] All PA values are taken from, or adjusted to, the scale given by: (a) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695. The thermochemical data of neutral species are taken from: (b) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970. The heat of formation of $MeNO_3$ is taken from: (c) Gray, P.; Williams, A. *Chem. Rev.* **1959**, *59*, 239.

[16] Kriemler, P.; Buttrill, S. E., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 1123. Their value is adjusted to the PA scale of ref 15a.

[17] Dewar, M. J. S.; Shanshal, M.; Worley, S. D. *J. Am. Chem. Soc.* **1967**, *89*, 3590.

[18] Munson, M. S. B.; Field, F. H. *J. Am. Chem. Soc.* **1967**, *89*, 1047.

Table I. CID Mass Spectra of $C_6H_6NO_2^+$ Ions

	relative intensities[a]		
m/z	A[b]	B[c]	C[d]
107	13.20	11.88	10.64
94	15.78	13.85	17.69
78	9.33	8.35	9.33
77	44.48	48.28	44.28
65	2.23	2.09	2.69
63	1.60	1.56	1.68
51	10.10	10.98	10.25
38	1.83	1.72	1.91
30	1.00	0.88	1.04
27	0.45	0.39	0.49

[a] The intensities are normalized with respect to the sum of the intensities of a spectrum which represents the average of 30 scans. The spectra are corrected for the contributions due to the unimolecular decomposition of metastable ions at *m/z* 94 and 78. [b] Protonation of $PhNO_2$ with *t*-Bu^+ ions. [c] Protonation of $PhNO_2$ with $C_nH_5^+$ ions (n = 1, 2). [d] Nitration of PhH with $MeO^+(H)NO_2$ ions.

under comparable conditions, a $CH_4/MeNO_3$ plasma does not contain significant concentrations of other potentially nitrating species, except NO_2^+, whose inability to add to aromatics under mass spectrometric conditions is well-documented.[7-9]

In this connection, it is worthy of mention that direct evidence on the ability of I to add to benzene in the gas phase is independently provided by earlier double-resonance ICR experiments on $C_6D_6/MeNO_3$ mixtures.[7] As is usually the case, the CI and ICR results provide no evidence on the nature of the nitrated adduct detected, in particular on the crucial question of whether a C–N bond has actually been formed. This aspect of the problem is addressed in the following section.

CID Spectrometry. Table I reports the CID mass spectrum of the $(PhHNO_2)^+$ adduct from the reaction of I with PhH (spectrum C), compared to those of model ions from the protonation of $PhNO_2$ by CH_5^+ and $C_2H_5^+$ ions (methane CI, spectrum B) and respectively by *t*-$C_4H_9^+$ ions (isobutane CI, spectrum A). The latter reaction is particularly useful, in that *t*-$C_4H_9^+$ is a mild Brønsted acid, capable of protonating $PhNO_2$ exclusively at the substituent,[19] according to a slightly *endothermic* process, which yields a pure Ph–NO_2H^+ model ion, without excess kinetic internal energy.[20]

Even a cursory examination of Table I reveals the striking similarity of the spectra, which contain the same fragments in nearly equal abundances. A more quantitative comparison, based on the similarity indexes (SI) of the relevant pairs of spectra,[21,22] gave the following results:

Spectra A vs. B, SI = 10.6

Spectra A vs. C, SI = 11.4

Spectra B vs. C, SI = 17.8

It is worth noting that the larger the difference between two CID spectra *the higher* the value of the corrisponding SI and that unavoidable instrumental fluctuations introduce small differences even into consecutive scans of *the same* CID spectrum. The above SI values are far below the threshold indicative of actual structural differences among the ionic populations assayed.[23] This finding is of interest, since the model ion from the protonation of $PhNO_2$ with *t*-$C_4H_9^+$ (spectra A) can be assigned with a high degree of confidence to the O-protonated nitrobenzene structure, consistent, inter alia, with the significant abundance of the fragment at *m/z* 107 resulting from the loss of a OH group from the nitrated adduct.

The CID results show that the adduct formed from the reaction of I with PhH does indeed contain a C–N bond, having the Ph–NO_2H^+ structure (vide infra).

The Radioltyic Nitration. Irradiation of a gaseous system formed by CH_4 as the bulk component, together with $MeNO_3$ and aromatic substrates, leads to formation of nitrated products in high yields. Table II illustrates the composition of the radiolytic systems and the nature, the isomeric composition, and the yields of the products. While the results refer specifically to the competitive nitration of PhH and PhMe, they are sufficiently representative of the whole set of experiments. The composition of the irradiated systems deserves a brief comment. In addition to CH_4 (720 Torr in most cases), O_2 (10 Torr) was used as a radical scavenger and SF_6, an effective interceptor of thermal electrons, was used to prevent their conceivable attachment to nitrated products. In fact, addition of SF_6 (5 Torr) was found to cause slight changes in the isomeric composition of certain products, as in the case of nitrotoluenes illustrated in Table II. Very low concentrations of the aromatic substrates were used, generally in the range from 0.5 to 1 Torr, owing frequently to vapor-pressure limitations and, more generally, in order to minimize direct radiolysis.

In the radiolytic experiments, the absolute yields of the products are measured by the corrisponding $G_{(+M)}$ values, which express the number of molecules formed per 100 eV absorbed by the gas. In evaluating the absolute yields reported in Table II, one should bear in mind that the combined $G_{(+M)}$ values of the CH_5^+ and $C_2H_5^+$ protonating ions from the radiolysis of neat CH_4 in the pressure range of interest amount to ca. 3.[24] Thus, under the assumption that nitration requires preliminary protonation of $MeNO_3$ (vide infra), the experimental results, however approximate, point to nitration as a major reaction channel.

Nature of the Nitration Process. Before proceding to discuss the results, the preliminary problem must be addressed as to whether the radiolytic nitration is an ionic process and to identify the specific reagent(s) effective in the irradiated systems. As to the first question, it appears that a convincing case for the ionic character of the nitration can be based on the presence of an effective radical scavenger (O_2), as well as on the depressing effects of a gaseous base (NMe_3) on the yields.

Furthermore, negligible yields of nitrated products ($G_{(+M)} <$ 0.02) are obtained from the radiolysis of systems where CH_4 is replaced by *i*-C_4H_{10}. This is particularly significant in view of the inability of *t*-$C_4H_9^+$ ions from *i*-C_4H_{10} to protonate $MeNO_3$.[25]

The Nitrating Reagent. The mass spectrometric evidence and the very composition of the irradiated systems point to I as the reagent effective in radiolytic nitration. However, intervention of other potentially nitrating species, such as NO_2^+, $CH_2ONO_2^+$, and $MeO(NO_2)_2^+$ that conceivably could be formed in the radiolytic systems, deserves detailed consideration. The problem can conveniently be addressed considering the inefficiency of the nitration reaction in the "blank" experiments that involve *i*-$C_4H_{10}/MeNO_3$/arenes mixtures. This observation denies the role of nitrating agents whose formation does not proceed via $MeNO_3$ protonation. Consequently, the problem boils down to ascertain whether nitrating species other than I are formed from the protonation of methyl nitrate under the conditions prevailing in the

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(19) $PhNO_2$ is an oxygen base, cf.: (a) Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452. (b) Kruger, T. L.; Flammang, R.; Litton, F.; Cooks, R. G. *Tetrahedron Lett.* **1976**, 4555.

(20) The PA values of isobutene and nitrobenzene are respectively 195.9 and 193.4 kcal mol^{-1}, the corresponding gas-phase basicities being 187.3 vs. 185.6 kcal mol^{-1}. The basicity difference (ca. 2 kcal mol^{-1}) is just about the maximum value that still allows an endothermic proton-transfer reaction to be observed.

(21) Lay, J. O.; Gross, M. L.; Zwinselman, J. J.; Nibbering, N. M. *Org. Mass Spectrom.* **1983**, *18*, 16.

(22) Harrison, A. G.; Gäumann, T.; Stahl, D. *Org. Mass Spectrom.* **1983**, *18*, 517. While a definition of the minimum SI value indicative of actual structural differences is somewhat arbitrary, a conservative estimate sets the thereshold above 40, see ref 22. As a comparison, the SI values of a pair of nominally identical spectra ranged from 10 to 20.

(23) The isomeric nitrotoluenes have different cross sections for dissociative capture of low-energy electrons, cf.: Christophorou, L. G.; Compton, R. N.; Hurst, G. S.; Reinhardt, P. W. *J. Chem. Phys.* **1966**, *45*, 536. This could explain the (slight) effect of SF_6 addition on the isomeric composition of products.

(24) Ausloos, P.; Lias, S. G.; Gorden, R., Jr. *J. Chem. Phys.* **1963**, *39*, 3341.

(25) The PA of *i*-C_4H_8 exceeds that of $MeNO_3$ by ca. 20 kcal mol^{-1}.

Table II. Gas-Phase Radiolytic Nitration of Benzene and Toluene at 37.5 °C

dose (MRad)	system composition[a] (Torr)					products yields (G_{+M})			isomeric composition of nitrotoluenes		
	$MeNO_3$	additives		PhH	PhMe	$PhNO_2$	nitrotoluenes	$\frac{k_T}{k_B}$	% o	% m	% p
3.0	16.0			0.90	0.87	0.46	2.2	4.9	58	3	39
3.0	16.0			2.40	0.49	1.60	1.60	4.9	61	4	35
3.0	16.0			0.25	1.10	0.30	2.3	4.8	59	3	38
0.5	9.0	SF_6:5.0		0.20	0.22	0.32	1.8	5.1	59	7	34
0.5	9.0	SF_6:5.0	NMe_3:2.0	0.33	0.28	0.12	0.34	3	57	5	38
0.5	9.0		NMe_3 2.0	0.33	0.31	0.10	0.26	3		*b*	
0.5	9.0		NMe_3 4.0	0.38	0.33	0.06	0.08	2		*b*	
3.0	13.0[c]			1.50	1.20	1.2	2.1	2.0	51	11	38
3.0		*i*-$PrNO_3$:10,0		0.92		<0.02					
3.0	16.0[d]			1.10		<0.02					

[a] Methane (720 Torr) used as the bulk gas unless otherwise indicated. Oxygen (10 Torr) was contained in all systems as a radical scavenger. [b] Not measured. [c] Methane pressure 100 Torr, O_2 pressure 2 Torr. [d] Isobutane (720 Torr) used in the place of methane.

Table III. Substrate and Positional Selectivity of the Gas-Phase Nitration of Monosubstituted Arenes, PhX

X	k_{PhX}/k_{PhH}[a]	orientation[b]		
		% o	% m	% p
Me	5.1	59	7	34
Et	5.6	47	4	49
n-Pr	7.0	50	4	46
i-Pr	6.0	31	5	64
c-Pr	10.6	72	6	22
t-Bu	8.4	17	8	75
Ph	1.5	40	4	56
OMe	7.6	41		59
F	0.15	14	13	73
Cl	0.19	36	10	54
CF_3	0.0037		100	
(C_6D_6)	1.00 ± 0.06			
(mesitylene)	(8.1)			

[a] The standard deviation of the ratios amounts to ca. 10%, except for highly deactivated substrates. [b] Standard deviation ca. 2%.

irradiated system. A conceivable route to NO_2^+ is the dissociation of protonated I, excited by the exothermicity of (1), i.e.

$$MeNO_3 \xrightarrow[-A]{+AH^+} [I]_{exc} \rightarrow MeOH + NO_2^+ \qquad (2)$$

While the overall process is energetically allowed when A = CH_4, the CI results discussed in a previous section show that the dissociation of I is effectively prevented by collisional deactivation, even at pressures as low as 1 Torr (Figure 1a), and therefore its occurrence in CH_4 at 720 Torr is a fortiori quite unlikely. Another nitrating species could arise from protonated methyl nitrate via the process

$$I + MeNO_3 \rightarrow MeOH + MeO(NO_2)_2^+ \qquad (3)$$

However, the higher binding energy of NO_2^+ to MeOH, 24 kcal mol^{-1}, than to $MeNO_3$, <13 kcal mol^{-1},[11] makes process 3 quite unlikely on account of its appreciable endothermicity. Confirming evidence is provided by the observation that the selectivity of the nitration is unaffected by the presence in the irradiated system of MeOH, which is expected to convert NO_2^+, $CH_2ONO_2^+$, and $MeO(NO_2)_2^+$ into I.

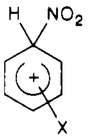
Selectivity of the Nitration. Table III portrays the reactivity of eleven monosubstituted benzenes relative to PhH, inferred from competitive nitration experiments in CH_4 gas at 720 Torr, 37 °C, and the orientation deduced from the isomeric composition of the products. In addition, mesitylene is included for comparative purposes as a typical example of a highly activated substrate, while the competitive nitration of C_6H_6/C_6D_6 mixtures has shown the lack of significant isotope effects. On inspection of the data it may be seen that the features of the gas-phase nitration are typical of an electrophilic aromatic substitution. The substrate selectivity spans more than 3 orders of magnitude, a remarkably extended range for cationic gas-phase aromatic substitution, and the reactivity order conforms to that prevailing in liquid-phase nitrations.

The same considerations hold with respect to orientation, predominantly ortho/para in activated substrates and exclusively meta in $PhCF_3$. Steric effects are also discernible in the nitration of aromatics containing bulky substituents, as shown by the increase of the para-ortho ratio which passes from 0.6 in PhMe to 2.1 in Ph-*i*-Pr to 4.4 in Ph-*t*-Bu. The selectivity data summarized in Table III lend themselves to a quantitative treatment, aimed at constructing a free-energy correlation diagram analogous to those derived from condensed-phase reactions (vide infra).

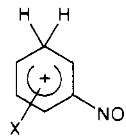
Energetics of the Nitration. Basicity of the Ipso Carbon of Nitrobenzene. The considerations developed in the previous sections suggest that nitration proceeds via the intermediacy of a protonated nitrobenzene

$$I + C_6H_5X \rightarrow [C_6H_4XNO_2]H^+ + MeOH \qquad (4)$$

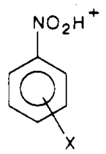
followed by deprotonation of the charged adduct by any gaseous base contained in the system, including MeOH or another molecule of substrate. The radiolytic experiments provide no direct evidence on the structure of the protonated intermediate



III



IV

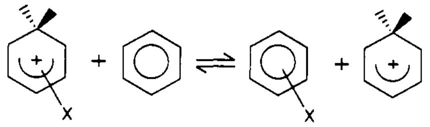


V

even though, in view of the selectivity of the reaction, it is natural to identify the most likely candidate with the "ipso"-protonated ion III, corresponding to the Wheland-type intermediate postulated in liquid-phase nitrations. The evidence from CI/CID spectrometry suggests that the protonated species has the structure V ca. 10^{-5} s after its formation. However, the long time lag before structural assay could allow extensive isomerization of the primary adduct, formed in the kinetically controlled step of the nitration. Calculations of the energetics of (4), concerning in particular formation of III, presuppose knowledge of the PA of the "ipso" carbon of $PhNO_2$, an experimentally inaccessible value whose estimate has been sought by a theoretical approach.

Although accurate calculation of absolute PA's requires very large basis sets, and explicit consideration of polarization and correlation effects,[26] relative intrinsic basicity suffices in the present case.

Accordingly, the so called isodesmic protonation process



(5)

has been used. However, the reliability of the results depends on the use of optimized structures for both the protonated and the

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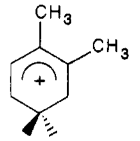
(26) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; also references therein.

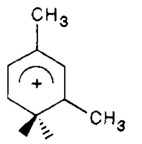
Table IV. Isodesmic Protonation Energies for Some Benzene Derivatives

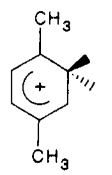
compound	position of protonation	ΔE(calcd)		$\Delta H°$- (exptl)	$\Delta H°$ (predicted) from eq 6 and 7	
		STO-3G	4-31G		STO-3G	4-31G
toluene	2	7.2	6.9	6.0[a]	6.1	6.0
	3	2.4	2.0	2.4[a]	2.3	2.4
	4	9.3	9.4	7.2[a]	7.7	7.8
o-xylene	4	11.5	11.8	9.6[a]	9.5	9.6
m-xylene	4	16.2	16.7	13.2[a]	13.2	13.2
p-xylene	2	9.5	9.4	8.4[a]	7.9	7.8
nitrobenzene	1	−27.0	−33.8		−20.8	−23.9
	2	−20.0	−26.4		−15.3	−18.5
	3	−17.9	−24.1		−13.7	−16.8
	4	−20.4	−29.0		−15.6	−20.4
fluorobenzene	4		−4.6		−0.8[b]	−2.5

[a] Values taken from ref 28. [b] Values taken from ref 30. All values in kcal mol^{-1}.

neutral species, since quite frequently protonation entails substantial geometrical distorsion.[27] The present calculations have been carried out at two different levels of accuracy, using STO-3G minimal basis and 4-31G split-valence basis sets. While both tend to slightly overestimate relative protonation energies, their results are linearly correlated with the experimental ones, which makes correction possible if a linear relationship between (relative) calculated and experimental PA's of model molecules is available. To this end, toluene and the three isomeric xylenes, whose relative gas-phase PA's are accurately known,[28] have been selected in this study as a suitable set of aromatic carbon bases. The most stable protonated species of the xylenes







have been considered, as well as all ring-protonated toluenes. The results obtained at both STO-3 and 4-31G levels are presented in Table IV, together with the available experimental data.

As expected, while calculated (relative) protonation energies slightly overstimate the experimental ones, even when a split-valence basis set is used, good linear correlations can be established between theoretical and experimental values. These linear relationships obey the least-squares fitted equations:

$$\Delta H°(\text{exptl}) = 0.788\Delta E(\text{STO-3G calcd}) + 0.417, \quad r^2 = 0.998 \quad (6)$$

$$\Delta H°(\text{exptl}) = 0.735\Delta E(\text{4-31G calcd}) + 0.920, \quad r^2 = 0.998 \quad (7)$$

The last column of Table IV reports the intrinsic basicities of the different ring positions of nitrobenzene, estimated from the appropriate ΔE values with respectively eq 6 and 7.

It can be seen that the "ipso" position of nitrobenzene is predicted to be 20.8 kcal mol^{-1} less basic than benzene at the STO-3G level and 23.9 kcal mol^{-1} at the 4-31G level. Therefore, assuming for the PA of benzene the value of 181.3 kcal mol^{-1},[15] the PA of the "ipso" carbon atom of $PhNO_2$, at the highest level of accuracy considered here, is ca. 157.4 kcal mol^{-1}. The stabilization energy of adduct III, i.e., the difference between its energy and that of the separate PhH/NO_2^+ pair, corresponds to −72.5 kcal mol^{-1} at the STO-3G level, in fair agreement with the −76.0 kcal mol^{-1} value from a previous STO-6G study.[29] However, the 4-31-G stabilization energy, −55.9 kcal mol^{-1}, is considerably lower than those determined at the minimal basis level, likely due to the much smaller basis set superimposition errors. The applicability of eq 6 and 7 to molecules containing polar substituents has been tested by calculating the PA of PhF, a carbon base in the gas phase.[30] At the highest accuracy level, the calculated relative basicity of PhF (last entry of Table IV) is underestimated by ca. 2 kcal mol^{-1}, suggesting that the PA values calculated for $PhNO_2$ may also be correspondingly underestimated.[31] The data of Table IV and the experimentally available PA of $PhNO_2$ at substituent suggest that the relative stability of the charged intermediates of interest increases in the order III < IV < V, the corresponding heats of formation being evaluated respectively around 226, 219, and 190 kcal mol^{-1}. On the basis of these values, formation of the Wheland-type intermediate III from PhH appears to be energetically allowed, even if by a narrow margin, ca. 3 kcal mol^{-1}. As an argument for the role of III as the primary intermediate, it can be pointed out that direct formation of V would require some kind of concerted mechanism, involving the fission of a C–H bond in the rate-determining step. The lack of a measurable isotope effect in the radiolytic nitration of C_6H_6/C_6D_6 mixtures (Table III) does not support a concerted pathway. As a whole, on the grounds of all available evidence from mass spectrometric, radiolytic, and theoretical sources, it seems preferable to think of III as the primary nitrated intermediate undergoing subsequent isomerization into V under the conditions typical of CI/CID experiments, characterized by a relatively long lifetime and inefficient collisional deactivation of the ionic species. In this connection, the data of Table IV show that isomerization III → V would energetically be favored, on account of the higher stability of the O-protonated isomer. By analogy with a number of similar rearrangements encountered in gas-phase ion chemistry,[32] the isomerization can be envisaged to occur within the ion–molecule complex formed by the nitrated adduct with methanol.

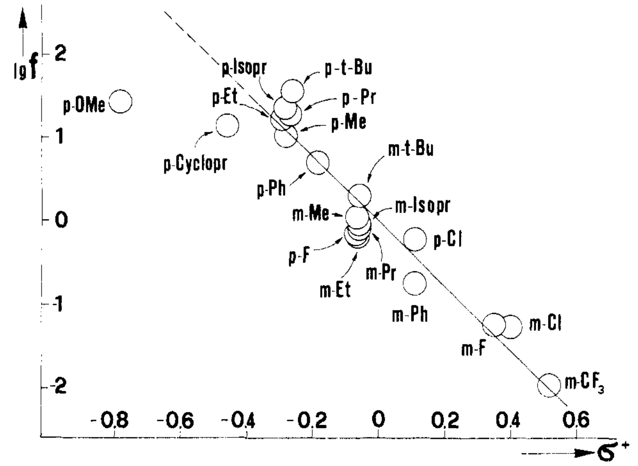


Figure 2. Logarithmic plot of the partial rate factors vs. the σ^+ constants of the substituents.

It is interesting to point out, in this connection, that the PA of MeOH, 181.9 kcal mol^{-1}, happens to be intermediate between the PA of the "ipso" carbon and that of the nitro group of $PhNO_2$, which could confer MeOH with a "catalytic" role in the apparently intramolecular proton migration involved in the III → V isomerization.

Comparison with Liquid-Phase Nitration. The data from the present gas-phase study lend themselves to useful comparison with

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[27] (a) Brown, R. S.; Tse, A. *J. Am. Chem. Soc.* **1980**, *102*, 5222. (b) Catalán, J.; Mo, O.; Pérez, P.; Yañez, M. *J. Mol. Struct. THEOCHEM* **1983**, *94*, 143.

[28] Devlin, J. L., III; Wolf, J. F.; Taft, R. W.; Hehre, W. J. *J. Am. Chem. Soc.* **1976**, *98*, 1990.

[29] Politzer, P.; Jayasuriya, K.; Sjoberg, P.; Laurence, P. *J. Am. Chem. Soc.* **1985**, *107*, 1174.

[30] Lau, Y. K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 7452.

[31] The present PA values of $PhNO_2$ are much higher than those obtained from linear correlations involving C_{1s} orbital energies, cf.: Catalân, J.; Yañez, M. *Chem. Phys. Lett.* **1979**, *60*, 499. The disagreement is particularly serious for the "ipso" carbon atom, revealing, once more, that the relationships between PA and 1s binding energies are very sensitive to details of local bonding at the protonation center.

[32] (a) Ausloos, P.; Lias, S. G. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *58*, 165. (b) Garvey, J. F.; Bernstein, R. B. *Chem. Phys. Lett.* **1986**, *126*, 394. (c) Kuck, D.; Ingemann, S.; de Koning, L. J.; Grützmacher, H. F.; Nibbering, N. M. M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 693.

liquid-phase nitrations. A logarithmic plot of the partial rate factors of monosubstituted benzenes, calculated from the data of Table III, vs. the σ^+ constants of the substituents is illustrated in Figure 2. With the exception of the two most activated substrates (vide infra) the data obey the least-squares fitted Hammett's type equation

$$\log f = \rho\sigma^+$$

characterized by a ρ value of −3.87, a negligible (<0.01) intercept, and a correlation coefficient of 0.96.

Considering that the σ^+ constants used for the plot are the classical ones, derived from condensed-phase studies, the success of their correlation with the present gas-phase data is remarkable. As a suitable comparison term, one can cite the nitration of nine aromatic substrates, carried out at 25 °C in nitromethane or acetic anhydride solutions, characterized by a ρ value of −6.53 with a correlation coefficient of 0.97,[6,33–36] and the nitration of 18 monosubstituted benzenes in sulfuric acid at 25 °C, characterized by a ρ value of −9.7.[37]

The less negative value of the ρ constant measured in the gas phase is suggestive of a more reactive and less selective electrophile than in liquid-phase nitrations, consistent with the free state of I, lacking both a solvation shell and a closely associated counterion, in that its charge is balanced by an electron far removed in the gas.

Another facet of the gas-phase reaction displays an intriguing analogy with liquid-phase nitrations. All highly activated substrates investigated, including mesitylene, *m*-xylene, and pentamethylbenzene, in addition to the aforementioned monosubstituted benzenes (PhOMe and c-Pr-Ph), are nitrated at significantly *lower* rates than expected from the correlation valid for less activated substrates. Such behavior is noteworthy, since it represents the gas-phase counterpart of the "encounter-rate" nitrations occurring in solution, where the two reactant molecules are held together for some time by a barrier to diffusion, related to the solvent viscosity. In the case of highly activated substrates, nitration occurs during the lifetime of such "encounter pairs" and its rate becomes diffusion-controlled, being limited by the encounter rate of the reactants.[6] It is conceivable that the "encounter-rate" nitration observed in the gas phase can involve a kinetically equivalent, if physically quite different, type of complex. In fact, ion–molecule reactions are believed to proceed in the gas phase via the preliminary formation of loose complexes, bound by strong electrostatic interactions between the unsolvated reactants.[38] When sufficiently activated aromatics are involved, nitration by I can be envisaged to occur during the lifetime of such complexes, kinetically equivalent to the "encounter pairs" postulated in solution, although the association of the reactants depends on electrostatic interactions, rather than on the solvent viscosity. Under such conditions, the rate of the gas-phase nitration would correspond to the capture rate of the ionic reactant by the neutral molecule (ADO or Langevin limit) and could not be increased by further enhancing the activation of the aromatic molecule, thus causing the observed loss of substrate selectivity.

Support for this interpretation is currently sought in our laboratory by temperature-dependence studies and by modulating the reactivity of the $RO^+(H)NO_2$ nitrating agent with appropriate modifications of the R group.

Conclusion

We have gone some way to extending the study of aromatic nitration to the gas phase, using an integrated approach which provides mechanistic information comparable to that available from solution-chemistry studies, allowing, in particular, the crucial evaluation of substrate and positional selectivity.

Resolving earlier discrepancies, the results point to the fundamental similarity of gas-phase and liquid-phase nitration, vindicating the expectation that mechanistic insight from one domain will be relevant to the other.

Acknowledgment. This work has financially been supported by the Italian National Research Council (C.N.R.) and the Ministry of Pubblica Istruzione. The authors thank G. de Petris, University of Rome "La Sapienza", for CID spectra, R. Gabrielli of the Servizio FTMS of the Area della Ricerca di Roma, C.N.R., for PA measurements, and O. Mõ for his contribution to theoretical calculations, carried out at the UAM/IBM Centers, Madrid.

Registry No. HPh, 71-43-2; MePh, 108-88-3; EtPh, 100-41-4; *n*-PrPh, 103-65-1; *i*-PrPh, 98-82-8; c-PrPh, 873-49-4; *t*-BuPh, 98-06-6; PhPh, 92-52-4; MeOPh, 100-66-3; FPh, 462-06-6; ClPh, 108-90-7; CF_3Ph, 98-08-8; C_6D_6, 1076-43-3; $MeONO_2 \cdot H^+$, 99573-80-5; $MeONO_2$, 598-58-3; mesitylene, 108-67-8.

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(38) Magnera, T. F.; Kebarle, P. *Ionic Processes in the Gas Phase*; Almoster Ferreira, M. A., Ed.; Reidel Co.: Dordrecht, 1983; p 15 and references therein.

Wavelength-Dependent Photofragmentation of Gas-Phase $Mn_2(CO)_{10}$

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Contribution from the Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0215. *Received January 2, 1987*

Abstract: $Mn_2(CO)_{10}$ is photolyzed at 350, 248, and 193 nm in the gas phase. Excitation of the σ^* state produces $Mn_2(CO)_8$ and $Mn(CO)_5$ fragments, indicating that this state is responsible for both metal–metal bond homolysis as well as ligand loss. Excitation of the π^* state at 248 and 193 nm leads to ligand loss with no evidence of metal–metal bond homolysis.

The formally single bond of dimanganese decacarbonyl was among the first metal–metal bonds to be characterized.[1] The simple structure of this molecule consisting of two $Mn(CO)_5$ subunits joined by a single metal–metal bond provides an ideal system for developing electronic structure theories.[2–4] The high quantum yield for dissociation of $Mn_2(CO)_{10}$, like that of most transition metal carbonyls, shortens the excited-state lifetimes and

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(2) (a) Levenson, R. A.; Gray, H. B. *J. Am. Chem. Soc.* **1975**, *97*, 6042. These are ionic bond dissociation energies and are used in the absence of available bond dissociation energies for the neutral molecule. (b) Levenson, R. A.; Gray, H. B.; Ceasar, G. P. *Ibid.* **1970**, *92*, 3653.

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