# "Ipso" Aromatic Nitration in the Gas Phase

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Nitration of selected dialkylbenzenes, including *o*- and *p*-cymene, *p*-*tert*-butyltoluene, *p*-diisopropylbenzene, and *p*-di-*tert*-butylbenzene, by protonated methyl nitrate,  $(CH_3OH-NO_2)^+$ , has been investigated in the gas phase in the pressure range from  $10^{-8}$  to 720 Torr by Fourier transform ion cyclotron resonance (FT-ICR) and collisional activated dissociation (CAD) mass spectrometry and by the radiolytic technique. The results provide the first demonstration of gas-phase electrophilic aromatic nitrodealkylation and a quantitative evaluation of its efficiency relative to the competing nitration process. Dealkylation of the alkyl substituent to the nitro group, yielding O-alkylated or O-protonated ions. The positional selectivity of the nitration, and the relative rate of the "ipso" attack by  $(CH_3OH-NO_2)^+$  are discussed, especially as regards the role of the intrinsic steric requirements of the alkyl group, which in the gas phase is unaffected by the many complicating factors, e.g., solvation, ion pairing, etc., operative in solution. The results are compared with those concerning condensed-phase nitrodealkylation and the related nitrodealkylation reaction.

## Introduction

Aromatic nitration at a ring position carrying a substituent other than H has long been deduced from the formation of products characterized by the loss of the substituent attached to the nitrated site,<sup>1-3</sup> but its nature was fully recognized only in 1971 by Perrin and Skinner,<sup>4</sup> who coined the prefix "ipso" currently used to denote the reaction. Ipso nitration has since been the subject of extensive studies, whose results opened up new perspectives in the theory of aromatic substitution.<sup>5–7</sup> The mechanistic picture outlined by the above studies, all performed in solution, is complicated by the influence of the medium especially as concerns the fate of the primary ipso nitrated Wheland intermediate, generally denoted as the W<sub>i</sub> adduct. Depending on the nucleophilicity of the medium, the presence of specific anions and other nucleophiles, etc., the W<sub>i</sub> adduct can react in different ways, e.g., by migration of the ipso group, by capture by the nucleophile, by substituent modification, or by return to reactants.

A considerable simplification can be expected by the extension of the study to the gas phase, an environment largely free of the complicating effects typical of condensed media and one which allows, in addition, more direct correlation of the experimental results with those from theoretical approaches.

We report here on the gas-phase nitrodealkylation of selected dialkylbenzenes promoted by protonated methyl nitrate,  $(CH_3-OH-NO_2)^+$ , whose most stable isomer, protonated on the methoxy oxygen, is in essence a nitronium ion solvated by a methanol molecule, as shown by mutually supporting theoretical and experimental results.<sup>8–10</sup> The reactivity of  $(CH_3OH-NO_2)^+$  toward aromatics has been previously investigated by a combination of mass spectrometric and radiolytic techniques,<sup>11–13</sup> complemented by a recent theoretical study.<sup>14</sup> We have followed the same experimental approach<sup>15</sup> to investigate the gas-phase nitration of substrates selected for their recognized ability to undergo nitrodealkylation in condensed media.

#### Results

**Radiolytic Experiments.** The nitrating cation has been obtained according to the well-established reaction sequence

$$\operatorname{CH}_4 \longrightarrow \operatorname{C}_n \operatorname{H}_5^+ \quad (n = 1, 2)$$
 (1)

$$C_nH_5^+ + CH_3ONO_2 \rightarrow C_nH_4 + (CH_3OH - NO_2)^+$$
 (2)

promoted by the radiation-induced ionization of methane containing a small mole fraction of methyl nitrate.<sup>11</sup> Following thermalization by multiple collisions with  $CH_4$  molecules, the cation reacts with the aromatic substrate S, present in trace amounts in the system, yielding arenium ions, e.g.

$$(CH_3OH - NO_2)^+ + C_6H_5X \rightarrow CH_3OH + C_6H_5XNO_2^+ \quad (3)$$

In the case of alkylbenzenes a fraction of the arenium ions can undergo dealkylation. Eventually, the gaseous cations are quenched by a gaseous base, B. The nature, yields, and isomeric composition of the neutral end products are established by GC or GC/MS. The absolute yields of the products reported in Table 1, expressed by their  $G_{(+M)}$  values, i.e., the number of molecules formed per 100 eV, are affected by a relatively large uncertainty, estimated to be as high as  $\pm 20\%$ , owing to the many sources of errors, especially as regards the radiation dose actually absorbed by the gas, the presence of adventitious or radiolytically formed impurities, etc. Nevertheless, consideration of the absolute yields is of interest, showing that nitration and/or nitrodealkylation are indeed major reaction channels in the gas phase, the combined  $G_{(+M)}$  values of their products ranging from 0.7 to 1.5 in systems containing no deliberately added bases. On the basis of the G value for the formation of the  $C_nH_5^+$  primary ions from the irradiation of  $CH_4$ ,<sup>16</sup> the above  $G_{(+M)}$  values correspond to yields of 25–50%. The ionic origin of the nitrated and nitrodealkylated products is suggested by their very nature, by the presence of radical and thermal electron scavengers, and especially by the depression of their yields

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TABLE 1: Aromatic Nitrodealkylation by Radiolytically Fomed (CH<sub>3</sub>OH-NO<sub>2</sub>)<sup>+</sup> Ions in Methane at 720 Torr



<sup>*a*</sup> All systems contained CH<sub>3</sub>ONO<sub>2</sub> (10 Torr), a thermal electron scavenger (SF<sub>6</sub>, 5 Torr) and a radical scavenger (O<sub>2</sub>, 10 Torr). <sup>*b*</sup> Standard deviation of the results, 10%. <sup>*c*</sup> Apparent substrate/mesitylene reactivity ratio. <sup>*d*</sup> Evaluated indirectly from the  $k_{(p-tert-butyltoluene/k_{(p-di-tert-butyltoluene)})}$  ratio.

caused by addition of a base, e.g.,  $(C_2H_5)_3N$ , that competes with the substrate for the  $(CH_3OH-NO_2)^+$  cation, besides intercepting a small fraction of the primary  $C_nH_5^+$  ions. The experimental dependence of the nitration yields on the base concentration quantitatively fits the trend predicted by a simple model which takes into account only the competition between the base and the substrate,<sup>17</sup> as illustrated in Figure 1, that refers to nitration of *p*-diisopropylbenzene. Remarkably, even in the presence of a 3-fold excess (0.70 Torr vs 0.24 Torr) of  $(C_2H_5)_3N$ over the substrate, which reduces the lifetime of the nitrated arenium ions down to ca.  $10^{-8}$  s, the relative rates of nitration and nitrodealkylation are unaffected.

The isomeric composition of the nitrated products shows a significant bias for substitution ortho to a methyl, rather than to an isopropyl group, e.g., *o*-cymene yields the following isomers, where the position of the NO<sub>2</sub> group is italicized: 3 = 6%, 4 = 42%, 5 = 21%, 6 = 31%, close to that obtained using NO<sub>2</sub><sup>+</sup>BF<sub>4</sub><sup>-</sup> in sulfolane, i.e., 3 = 1%, 4 = 42%, 5 = 19%, 6 = 37%, whereas a somewhat different composition is obtained from mixed-acids nitration.<sup>19</sup> The same trend characterizes the gas-phase nitration of *p*-cymene and *p*-tert-butyltoluenes, as apparent from Table 1.



**Figure 1.** Dependence of the yields on the concentration of added  $(C_2H_5)_3N$  in the nitration of *p*-diisopropylbenzene in CH<sub>4</sub> at 720 Torr, 315 K. *G*° is the yield measured in the absence of added bases.

Salient features of the isomeric composition of the nitrodealkylated products is that the nitro group is invariably found at a ring position formerly occupied by one of the alkyl substituents and that the relative position of the latter ones is unchanged.

In addition to nitrated products, alkylated products were detected, e.g., nitration of p-diisopropylbenzene gave triisopropylbenzenes, whose yields accounted for ca. 50% of the  $i-C_3H_7^+$ lost in the nitrodeisopropylation, suggestive of intermolecular R<sup>+</sup> transfer from the ipso-nitrated arenium ion. This inference is supported by the effect of a gaseous base, (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>N, that almost entirely suppresses the alkylated products. To verify the mechanistically informative evidence for the occurrence of transalkylation, experiments were performed where the gaseous system contained mesitylene, a highly activated arene that was expected to efficiently trap any R<sup>+</sup> ions from the ipso-nitrated arenium ions. In a typical experiment, nitration of p-diisopropylbenzene (0.32 Torr) in the presence of mesitylene (0.41 Torr) gave equal amounts of p-nitrocumene ( $G_{(+M)} = 0.18$ ) and of isopropylmesitylene, showing that the  $i-C_3H_7^+$  ions from the nitrodeisopropylation were quantitatively trapped by mesitylene.

The temperature has a measurable effect on the nitrodealkylation rate, that is enhanced at higher temperatures with respect to that of nitration. A detailed study has been performed only in the case of *p*-diisopropylbenzene, where the ratio of the rate constants for nitration ( $k_N$ ) and for nitrodealkylation ( $k_{ND}$ ) in CH<sub>4</sub> at 720 Torr has been measured at 315, 323, 333, 343, and 353 K. The Arrhenius plot obtained fits the linear equation  $\ln(k_N/k_{ND}) = -4.09 + 1331/T$ , whose correlation coefficient *R* = 0.989 is consistent with the analytical errors.

Fourier Transform Ion Cyclotron Resonance (FT-ICR) Mass Spectrometry. In the low-pressure range typical of FT-ICR experiments, the study of the nitration and nitrodealkylation reactions promoted by  $(CH_3OH-NO_2)^+$  is complicated by the incursion of predominant, often overwhelming, charge-transfer and proton-transfer processes, favored by the low ionization potential and the high proton affinity (PA) of the dialkylbenzenes, and whose rate critically depends on the excess energy of the nitrating cation. For instance, (CH<sub>3</sub>OH-NO<sub>2</sub>)<sup>+</sup> ions obtained according to reactions 1 and 2 from the CI of CH<sub>4</sub>/ CH<sub>3</sub>ONO<sub>2</sub> mixtures in the external source of a FT-ICR spectrometer, driven into the resonance cell and allowed to react with *p*-diisopropylbenzene undergo almost exclusively charge exchange, yielding but traces of the expected nitrated and nitrodealkylated adducts. A definite improvement was achieved by application of the collisional thermalization technique developed by Thölmann and Grützmacher.<sup>20</sup> Accordingly, the  $(CH_3OH-NO_2)^+$  ions formed in the external CI source were driven into the resonance cell, containing *p*-diisopropylbenzene at pressures ranging from  $10^{-8}$  to  $10^{-7}$  Torr. Following a 2-s delay, the  $(CH_3OH-NO_2)^+$  ions were isolated by ejecting all other ions by low-power radiofrequency "shots" and CH<sub>4</sub> was introduced via a pulsed valve, reaching a peak pressure up to  $10^{-4}$  Torr for a short time (1–5 ms). Under such conditions, appreciable intensities of ions whose m/z ratios correspond to those of the C<sub>12</sub>H<sub>18</sub>NO<sub>2</sub><sup>+</sup> nitrated adduct(s) (m/z = 208.13375) and of the C<sub>9</sub>H<sub>12</sub>NO<sub>2</sub><sup>+</sup> nitrodealkylated adduct(s) (m/z =166.086 80) ions were detected and identified by exact mass measurement.

Remarkably, the relative abundance of the nitrodealkylated adduct(s), ca. 3% after the reaction time of 3 s in *p*-diisopropylbenzene at  $10^{-7}$  Torr, exceeds by an order of magnitude that of the nitrated adduct, pointing to the facile dealkylation of the latter under the low-pressure conditions prevailing in the FT-ICR experiments. No  $C_3H_7^+$  or (CH<sub>3</sub>-OC<sub>3</sub>H<sub>7</sub>)H<sup>+</sup> ions were detected, suggesting that dealkylation involves loss of a neutral species, most likely  $C_3H_6$ . To verify such a hypothesis and to ascertain the nature of the species undergoing dealkylation, nitrated adducts were prepared by a different route according to the reaction

$$RC_{6}H_{4}NO_{2} + i \cdot C_{3}H_{7}OH_{2}^{+} \rightarrow H_{2}O + RC_{6}H_{4}N(O)^{+}O \cdot i \cdot C_{3}H_{7}$$
(4)

which is known to occur selectively at the nitro group, yielding an O-alkylated ion.<sup>21</sup> In a typical case, the ions ( $R = CH_3$ ) were prepared in the external source according to reaction 4 from the CH<sub>4</sub>/*i*-C<sub>3</sub>H<sub>7</sub>OH CI of *o*-nitrotoluene, introduced into the resonance cell, isolated, and allowed to react with selected bases/nucleophiles. Although kinetic measurements were prevented by the low intensity of the O-alkylated ions, the nature of the charged products, and their dependence on the strength of the base proved informative.  $CH_3C_6H_4NO_2H^+$  ions, m/z =138, were formed in the presence of bases of relatively low PA, e.g.,  $C_6H_6$ , PA = 181.3 kcal mol<sup>-1.22</sup> Stronger bases, such as mesitylene,  $PA = 200.7 \text{ kcal mol}^{-1}$ , were protonated but not alkylated, whereas an exceptionally strong base/nucleophile.  $(CH_3O)_3PO$ , PA = 212.0 kcal mol<sup>-1</sup>, was observed to undergo both protonation and alkylation by  $CH_3C_6H_4N(O)^+O_i-C_3H_7$ ions. All the above observations point to the propensity of the ions from (4) to undergo dealkylation, either unimolecularly by loss of propene or upon reaction with gaseous bases/ nucleophiles, under conditions typical of FT-ICR experiments.

The structure of the nitrated adducts from reaction 3 was also probed by FT-ICR techniques, e.g., the (CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>-*i*-C<sub>3</sub>H<sub>7</sub>)NO<sub>2</sub><sup>+</sup> ions obtained from the CH<sub>4</sub>/CH<sub>3</sub>ONO<sub>2</sub> CI of *o*-cymene in the external ion source were isolated and allowed to react with gaseous bases, e.g., (CH<sub>3</sub>O)<sub>3</sub>PO. Efficient proton transfer was observed, which, according to the criterion customarily used to discriminate between ion-neutral complexes and covalently bound intermediates,<sup>23</sup> provides strong evidence that the species being probed contain a covalently bound nitro group and hence have the arenium-ion and/or the O-alkylated ion structure.

**Collisionally Activated Dissociation (CAD) Spectrometry.** Additional structural insight was sought by recording the CAD spectra of the nitrated adducts obtained from selected dialkylbenzenes according to reaction 3. In general, the CH<sub>4</sub>/CH<sub>3</sub>-ONO<sub>2</sub> CI spectra of typical dialkylbenzenes such as the cymenes, *tert*-butyltoluenes, diisopropylbenzenes, di*tert*-butylbenzenes, etc., recorded at 100–150 °C at total pressures of 0.1-0.4 Torr display significant (M + NO<sub>2</sub>)<sup>+</sup> peaks.

Attention was focused on *p*-cymene, recording the CAD spectra of populations of  $C_{10}H_{14}NO_2^+$  ions obtained from three different reactions. Population A was prepared from the CH<sub>4</sub>/ CH<sub>3</sub>ONO<sub>2</sub> CI of *p*-cymene according to reaction 3, as previously established by the FT-ICR results outlined in the previous section. Population B consisted of  $C_{10}H_{14}NO_2^+$  ions from the CH<sub>4</sub>/*i*-C<sub>3</sub>H<sub>7</sub>OH CI of *p*-nitrotoluene, according to the O-alkylation process (eq 4). Population C was obtained by the CH<sub>4</sub> CI of *o*-nitro-*p*-cymene according to the unselective proton-transfer process

$$iC_{3}H_{7}$$
  $\longrightarrow$   $NO_{2}$   $CH_{3} + C_{n}H_{5}^{+}$   $\longrightarrow$   $C_{n}H_{4} + \begin{bmatrix} VO_{2} \\ VO_{2} \\ VO_{3}H_{7} \\ VO_{2} \\ VO_{3} \end{bmatrix} H^{+}$  (5)

which is expected to yield O-protonated ions, as well as arenium ions, some of which are protonated at the ring position carrying the i-C<sub>3</sub>H<sub>7</sub> group.

The spectra, compared in Table 2, are qualitatively similar, the only conspicuous difference concerning the abundance of the charged fragment at m/z = 91, much higher from population B. This is hardly surprising, in that the fragment is likely arising from the O-isopropylated ion, the most abundant C<sub>10</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> isomer in population B, according to the simple bond-fission process

TABLE 2: CAD Spectra of  $C_{10}H_{14}NO_2^+$  Ionic Populations from Different Reactions

	rel intensities (%) <sup>a</sup>		
fragment $m/z$	$A^b$	$\mathbf{B}^{c}$	$\mathbf{C}^d$
39	3.1	2.9	1.8
41	2.6	2.5	2.5
43	3.8	8.0	2.0
51	3.1		1.8
63	3.6	3.8	1.9
65	4.0	8.2	2.7
77	5.6	2.3	4.9
91	12.7	30.6	11.9
103	4.8		4.4
105	10.8	3.7	11.3
107	3.7	4.5	2.7
115	10.4		10.7
117	13.7		15.8
121	М	31.1	М
148	4.9		3.7
162	6.2		8.3

<sup>*a*</sup> The intensities are normalized with respect to the sum of the intensities of a spectrum that represents the average of 50 scans. The intensities of fragments containing metastable contributions (M) have not been taken into account. <sup>*b*</sup> From reaction 3. <sup>*c*</sup> From reaction 4. <sup>*d*</sup> From reaction 5.

$$CH_{3}C_{6}H_{4} \xrightarrow{i} N(O)\dot{O}iC_{3}H_{7} \longrightarrow C_{7}H_{7}^{+} + C_{3}H_{7}NO_{2}^{+}$$
(6)  
m/z = 180 m/z = 91 m/z = 89

Remarkably, however, the fragment of m/z = 91 is present as well, if in lower abundances, in the CAD spectra of population A and C, obtained from reactions 3 and 5 which are not expected to yield, at least as primary ionic intermediates, O-isopropylated ions. A plausible explanation is that a fraction of the arenium ions from nitration (eq 3) and protonation (eq 5) isomerizes into the O-isopropylated ion structure in the time interval, ca. 10  $\mu$ s, between formation and structural assay:



#### Discussion

Previous mass spectrometric and radiolytic studies have shown that the efficient gas-phase nitration reaction promoted by protonated methyl nitrate involves formation of arenium ions

$$CH_3 \rightarrow 0 - NO_2 + O = CH_3OH + R + (+) O(2)$$
(8)

which subsequently undergo intramolecular proton transfer to the nitro group, considerably faster than the competing intraannular migration, e.g.,  $k_0/k_r = 22.5$  in the nitration of toluene in CH<sub>4</sub> at 720 Torr and 315 K:<sup>13</sup>

$$R \xrightarrow{k_{0}} R \xrightarrow{k_{0}} R \xrightarrow{H} NO_{2}$$

$$R \xrightarrow{k_{0}} R \xrightarrow{H} NO_{2}$$

$$H \xrightarrow{H} H \xrightarrow{H} NO_{2}$$

$$R \xrightarrow{+B} R \xrightarrow{NO_{2}} (9)$$

Passing to nitrodealkylation, two mechanistic problems deserve consideration, namely, the detailed course of the alkyl group removal from the ipso-nitrated ring position and the evaluation of the efficiency of the process relative to nitration, particularly as regards the effect of steric factors.

Mechanism of the Alkyl Group Removal. The scheme outlined in Chart 1 provides a satisfactory rationalization of the results. Formation of the Wi intermediate from (CH3OH- $NO_2$ )<sup>+</sup> is necessarily accompanied by formation of CH<sub>3</sub>OH, whose local concentration is very high, the two species being initially contained in the same ion-neutral complex. Methanol,  $PA = 181.9 \text{ kcal mol}^{-1},^{22}$  is undoubtedly capable of promoting exothermic dealkylation of Wi according to reactions 10a and 10b. No evidence for these processes has been provided by the mass spectrometric and radiolytic experiments, whose results suggest instead that dealkylation requires bases/nucleophiles stronger than CH<sub>3</sub>OH, e.g., mesitylene in the case of pdiisopropylbenzene. A reasonable explanation, independently supported by the evidence from CAD spectrometry, can be based on the fast  $R^+$  migration (eq 13a) to the NO<sub>2</sub> group, a process which is strongly exothermic, owing to the much higher basicity/ nucleophilicity of the nitro group than of the ipso position of the ring. The exothermicity of migration (eq 13a) can promote fragmentation (eq 13b) of the O-alkylated ion, the only process observable under the low-pressure conditions typical of FT-ICR experiments.

There is no evidence for intraannular  $NO_2^+$  migration (eq 11) nor for R<sup>+</sup> migration (eq 12), which is ruled out by the failure to detect products where the relative position of the R and R' substituents has changed. In summary, the radiolytic and mass spectrometric results suggest intramolecular migration of the alkyl group bound to the ipso-nitrated carbon to the nitro group, the same process undergone by the H atom of the nitrated ring position in gas-phase nitration.<sup>13</sup> Both processes reflect the strong tendency, typical of isolated ions in the gas phase, to achieve the most efficient intramolecular solvation of the charge, which in the case of interest favors binding of the R<sup>+</sup> cation to more nucleophilic nitro group rather than to the strongly deactivated aromatic ring.

**Positional Selectivity of the Nitration.** It is apparent from the foregoing that the extent of nitrodealkylation measured in the radiolytic experiments depends exclusively on the rate of ipso attack, being unaffected by the subsequent reactions undergone by the  $W_i$  intermediate, as confirmed by the insensitivity of the nitration/nitrodealkylation ratio to the addition of bases/nucleophiles. Since the gaseous  $W_i$  intermediate is bound to evolve into the nitrodealkylated product, the ratio of ipso substitution corresponds to that of ipso attack and hence, at variance with solution-chemistry studies, there is no need to worry about the effects of possible subsequent reactions that affect the composition of the products in solution, e.g., nucleophilic substitution or nucleophilic capture yielding cyclohexadienyl derivatives.

In principle, accurate evaluation of the *intrinsic* positional selectivity of nitration is possible in the gas phase, an expectation confirmed by the limited set of data from competition experiments where mesitylene was employed as a convenient secondary standard.<sup>24</sup> Although the  $f_i$  values obtained in this way should be regarded as grossly approximate, their comparison with those of unsubstituted ring positions activated to a similar extent is of interest, in that it allows evaluation of *intrinsic* steric effects in unsolvated species.

Consider, for instance, the following pairs of substrates:



It is apparent that the reactivity of the comparably activated

CHART 1

$$\mathbf{R} \stackrel{\mathbf{R}}{\longleftarrow} + (\mathbf{CH}_{3}\mathbf{OH} - \mathbf{NO}_{2})^{+} \stackrel{\mathbf{R}}{\longrightarrow} \mathbf{CH}_{3}\mathbf{OH} + \mathbf{R} \stackrel{\mathbf{R}}{\longleftarrow} \stackrel{\mathbf{NO}_{2}}{\longleftarrow} \mathbf{R} \stackrel{\mathbf{NO}_{2}}{\longleftarrow} + - \begin{bmatrix} \mathbf{CH}_{3}\mathbf{OH}_{2}^{+} + \text{olefine} & (10a) \\ (\mathbf{CH}_{3}\mathbf{OR})\mathbf{H}^{+} & (10b) \end{bmatrix}$$

$$\begin{array}{c} & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$$

$$\begin{array}{c|c} & & & \\ & & & \\ \hline \end{array}$$
(13a)

$$\rightarrow$$
 R'  $\rightarrow$  + olefine (13b)

$$\begin{array}{c} \overset{+B}{\underset{}}{\overset{+B}{\underset{}}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{}}{\overset{+B}{\underset{}}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{} & \overset{+B}{\underset{}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{} & \overset{+B}{\underset{}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{} & \overset{+B}{\underset{}} & \overset{=}}{\overset{}} & \overset{+B}{\underset{}} & \overset{=}}{\overset{}} & \overset{+B}{\underset{}} & \overset{+B}{\underset{}} & \overset$$

NO<sub>2</sub>

$$+Nu \qquad R' \qquad + NuR^+ \qquad (14b)$$

para positions is reduced by a factor of 3.3 upon replacement of H by *i*-C<sub>3</sub>H<sub>7</sub>, whereas replacement by *t*-C<sub>4</sub>H<sub>9</sub> causes a much larger, almost 200-fold, decrease of reactivity. Such effects point to the paramount role of steric hindrance of the substituent to the ipso attack by  $(CH_3OH-NO_2)^+$ , since the observed trend can hardly be traced to factors other than the *intrinsic* steric bulk of the alkyl group. By contrast, the steric acceleration noted in solution, where *o*-cymene is nitrodealkylated from 3 to 5 times faster than *p*-cymene,<sup>18,19</sup> is much less effective, if it all, in the gas phase, where the two isomers undergo nitration and nitrodealkylation at approximately the same relative rate (Table 1).

Finally, the temperature dependence of the ratio of the rate constants for nitration and nitrodealkylation of *p*-diisopropylbenzene, measured in the range from 315 to 355 K, is of interest since, based on the preceding considerations, it corresponds to the difference of the activation barriers for ipso attack and for attack to the four equivalent unsubstituted positions of the substrate. From the slope of the Arrhenius plot the  $E_a$  barrier for ipso attack is higher by  $2.6 \pm 0.4$  kcal mol<sup>-1</sup> than that of attack to each of the positions ortho to the isopropyl groups.

**Nitrodealkylation vs Nitrodesilylation.** Comparison of the present results with those concerning the gas-phase nitration of phenylsilanes by  $(CH_3OH-NO_2)^{+25}$  reveals significant differences. Owing to its enhanced basicity, the ring carbon bearing the SiR<sub>3</sub> group becomes an efficient proton sink, and hence desilylation of positions other than the one substituted by the nitro group can occur, e.g.



As to the ipso attack proper, the enhanced basicity/nucleophilicity of the position carrying the SiR<sub>3</sub> substituent, combined with the smaller steric hindrance of the Si(CH<sub>3</sub>)<sub>3</sub> than of the C(CH<sub>3</sub>)<sub>3</sub> group, make nitrodesilylation much more efficient than nitrode-*tert*-butylation, as apparent from a comparison of the behavior of *p*-*tert*-butyltoluene and of *p*-(trimethylsilyl)toluene. No appreciable nitrode-*tert*-butylation of the former substrate takes place (Table 1), whereas ipso nitrodesilylation accounts for over 30% of the products from the *p*-tolylsilane.<sup>25</sup> This trend is supported by a comparison of the partial rate factors for de*tert*-butylation of *p*-di-*tert*-butyltoluene,  $f_i = 0.17$ , and for desilylation of *p*-(trimethylsilyl)toluene,  $f_i = 18.3$ ,<sup>25</sup> pointing to the much higher tendency of phenylsilanes to undergo ipso attack and subsequent desilylation.

#### **Experimental Section**

**Materials.** The gases and most chemicals used in the mass spectrometric and the radiolytic experiments, or as reference standards in GC and GC/MS were research-grade products obtained from commercial sources (Matheson Gas Products, Inc. and Aldrich-Chemie GmbH). Other products e.g., isopropyl-and diisopropylnitrobenzenes were prepared according to standard procedures and assayed by the same techniques used for the analysis of the radiolytic products.

Mass Spectrometric Experiments. The FT-ICR study was performed using a Bruker-Spectrospin Apex TM 47e spectrometer equipped with an external CI ion source, a pulsed valve, two separate inlets, and a XMASS TM data system. The external CI ions source was operated at 150 °C, under a total pressure of  $10^{-5}$  Torr. The stationary pressure of the neutral reagents in the resonance cell was in the range from  $10^{-8}$ -10<sup>-7</sup> Torr. CAD spectra were recorded using a ZAB-2F instrument (VG Micromass Ltd.) operated in the CI mode. Typical experimental conditions were source temperature 180 °C, emission current 0.5 mA, repeller voltage 0 V, total pressure in the ion source 0.1-0.4 Torr. MIKE spectra were recorded at an energy resolution of ca.  $5 \times 10^3$  and represent the average of at least 40 scans. CAD spectra were taken at a lower energy resolution by admitting He into the collision cell at such a pressure to reduce the main beam intensity by ca. 30% with respect to its initial value.

**Radiolytic Experiments.** The gaseous samples were prepared according to standard procedures using a greaseless vacuum line, in 280-mL Pyrex vessels and irradiated to a total dose of  $5 \times 10^3$  Gy at a dose rate of  $2 \times 10^4$  Gy h<sup>-1</sup> in a thermostatically controlled 220 Gammacell from Nuclear Canada Ltd. The radiolytic products were extracted with methanol, containing a known amount of a suitable internal standard. The products were analyzed using a HP 5890 gas chromatograph from Hewlett-Packard and a TRIO 1 quadrupole GC/MS instrument from VG Micromass Inc., on the following columns: (i) a 50-m  $\times$  0.20 mm  $\times$  0.5  $\mu$ m capillary column, coated with a cross-linked methylsilicone phase (PONA column from HP), operated from 30 to 250 °C, and (ii) a 60-m  $\times$  0.25 mm  $\times$  0.25 µm capillary column, coated with poly(20% diphenyl-80% dimethylsiloxane) (SPB-20 from Supelco Co.), operated from 60 to 230 °C. The identity of the products was established by comparison of their retention time with those of authentic standards and/or by GC/MS, whereas their yields were calculated from the area of the corresponding elution peaks, relative to that of the reference standard, using individual calibration factors to correct for the response of the different compounds analyzed.

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