

# Communications to the Editor

## Ambident Aniline Reactivity in Meisenheimer Complex Formation

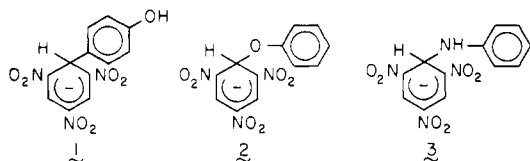
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Received November 16, 1982

We reported previously on the first instance of ambident nucleophilic reactivity in Meisenheimer ( $\sigma$ -) complex formation. Thus phenoxide ion was found to react with 1,3,5-trinitrobenzene (TNB) to yield the carbon-bonded adduct **1**;<sup>1</sup> up to that time only the oxygen-bonded adduct **2** had been reported.<sup>2</sup>

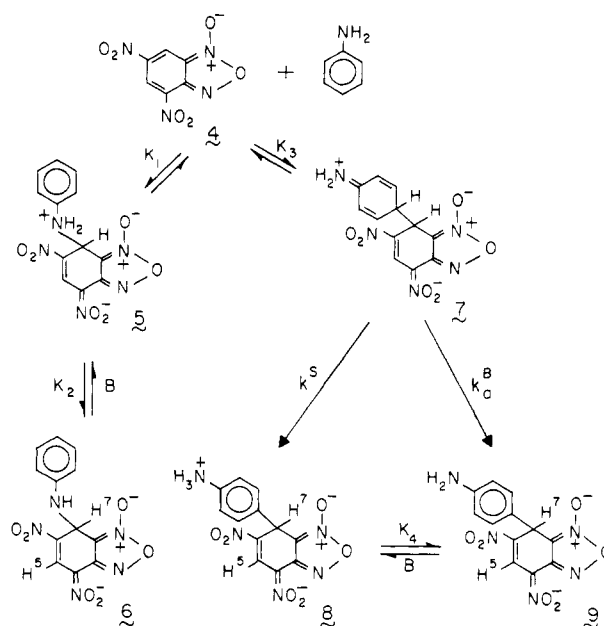


There has been no report so far that aromatic amines could act as potential carbon nucleophiles in  $\sigma$ -complex<sup>3</sup> formation with nitroarenes.<sup>4</sup> TNB was found to react with aniline in the presence of triethylamine or 1,4-diazabicyclooctane (DABCO) to yield the nitrogen-bonded adduct **3**.<sup>5</sup> We now report that aniline reacts with 4,6-dinitrobenzofuroxan (**4**) to yield the carbon- as well as the nitrogen-bonded  $\sigma$  complexes. Moreover, the carbon-bonded adduct can be obtained as the anionic  $\sigma$  complex as well as the zwitterionic species.

The following key observations have been made: (1) The addition of aniline to 1 equiv of **4** in  $(\text{CD}_3)_2\text{SO}$  resulted in the rapid formation of the zwitterionic carbon-bonded adduct **8** as shown by its NMR spectrum.<sup>6</sup> **8** was also rapidly and nearly quantitatively obtained through reaction of equimolar quantities of aniline and **4** in methanol, the product precipitating within 1 min of mixing the reagents. To our knowledge, this is the first isolation of such a zwitterionic complex.

(2) The addition of 2 equiv of aniline to a  $(\text{CD}_3)_2\text{SO}$  solution of **4** resulted in the formation of both the carbon- and nitrogen-bonded adducts. An NMR spectrum obtained within 2 min of mixing the reagents showed an approximately 50/50 mixture of

Scheme I



**9** and **6**.<sup>6</sup> However, the signals for **9** increased quickly at the expense of those for **6**, and the conversion was complete after 30 min.

(3) The addition of **4** to equivalent amounts of aniline and triethylamine in  $(\text{CD}_3)_2\text{SO}$  resulted in the formation of a greater proportion (ca. 90%) of the nitrogen-bonded adduct **6** and required a considerably longer period (ca. 36 h) for conversion to **9**.

The above observations are uniquely consistent with the formulations shown in Scheme I. A key point in relation to this scheme is that when aniline acts as a nitrogen nucleophile, the initially formed zwitterionic intermediate **5** will be present in very small concentration and reaction with a second mole of base is required in order to form the stable adduct **6**.<sup>5,7</sup> On the other hand, the quinoid intermediate **7** formed from carbon attack by aniline can rearomatize spontaneously ( $k^S$  step, i.e., via a solvent-assisted pathway)<sup>8</sup> to yield the stable zwitterionic adduct **8**. Observations 1 and 2 above follow directly from these considerations. The third observation is in accord with (a)  $K_2^{\text{PhNH}_2} > (>>) K_2^{\text{Et}_3\text{N}}$  and (b) that base-catalyzed deprotonation of **5** to **6** occurs more rapidly than the base-promoted rearomatization of **7** to **9** ( $k^B$  step) or the spontaneous aromatization of **7** ( $k^S$  step) and subsequent equilibrium deprotonation of **8** to **9**.

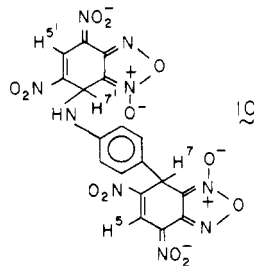
Thus the essential features of Scheme I are that the formation of **6** tends to be kinetically favored but is reversible, while formation of **9** is slower but occurs irreversibly; hence **9** is obtained as the thermodynamically controlled product. A noteworthy difference between the present system and the TNB-aniline system

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- (6) The  $\sigma$  complexes showed the following  $^1\text{H}$  NMR parameters ( $\text{Me}_4\text{Si}$  as internal standard): (a) **6**:  $\delta$  8.95 (s, 1 H, H-5), 6.23 (s, 1 H, H-7), 7.1 (m, 5 H, ArH). (b) **8**:  $\delta$  9.00 (s, 1 H, H-5), 5.53 (s, 1 H, H-7), 7.59, 7.43 ( $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz, 4 H, Ar H), 9.95 (br, s, 3 H,  $\text{NH}_3^+$ ). (c) **9**:  $\delta$  8.99 (s, 1 H, H-5), 5.30 (s, 1 H, H-7), 7.13, 6.77 ( $\text{A}_2\text{B}_2$ ,  $J = 9$  Hz, 4 H, Ar H). (d) **10**:  $\delta$  8.93 (s, 1 H, H-5), 6.20 (d,  $J = 9$  Hz, 1 H, H-7), 9.00 (s, 1 H, H-5'), 5.29 (s, 1 H, H-7'), 7.11, 6.80 ( $\text{A}_2\text{B}_2$ ,  $J = 9$  Hz, 4 H, Ar H), 6.50 (d,  $J = 9$  Hz, 1 H, NH).

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- (8) (a) Although the  $k^S$  step in the solvent-assisted pathway could be analogous to the  $k^B$  step with the solvent acting as the base, other possibilities also exist. One such possibility is that the solvent assists in transfer of a proton from carbon to nitrogen by a process similar to the "conducted tour" mechanism described in ref 8b and 8c. (b) Cram, D. J. "Fundamentals of Carbanion Chemistry"; Academic Press: New York, 1965; Chapter 5. (c) Buncel, E. "Carbanions, Mechanistic and Isotopic Aspects"; Elsevier: Amsterdam, 1975; Chapter 2.

studied previously<sup>5</sup> is that in the latter case a tertiary base ( $\text{Et}_3\text{N}$  or DABCO) is required for transformation to the  $\sigma$  complex to be effective; formation of the zwitterionic intermediate is sufficiently disfavored such that the overall process with aniline alone does not occur. This contrasting behavior reflects the greater stability of  $\sigma$  complexes in the 4,6-dinitrobenzofuroxan system.<sup>9</sup>

Following the characterization of complexes **6**, **8**, and **9**, it became of interest to determine whether a  $\sigma$  complex containing both carbon- and nitrogen-bonding functions could be prepared. In fact, we found that the diadduct **10** can easily be prepared by



addition of **4** to a  $(\text{CD}_3)_2\text{SO}$  solution of **8**, followed by 2 equiv of  $\text{Et}_3\text{N}$ . The NMR spectrum of the product is completely in accord with the structural formulation in **10**.<sup>6</sup>

We intend to further investigate the reactions of aromatic amines with various nitroaromatic compounds in order to attempt to delineate the structural/electronic factors with respect to the nucleophile and electrophile on ambident reactivity in such systems.

**Acknowledgment.** Support of this research by grants from the Naval Surface Weapons Center at Silver Springs, MD (M.J.S.), and the Natural Sciences Research Council of Canada (E.B.) is gratefully acknowledged.

**Registry No.** **4**, 5128-28-9; **6**, 84802-77-7; **8**, 84802-78-8; **9**, 84802-79-9; **10**, 84802-80-2; aniline, 62-53-3.

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## Formation of the $\text{NH}_4^-$ Ion in the Gas Phase

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Received November 29, 1982

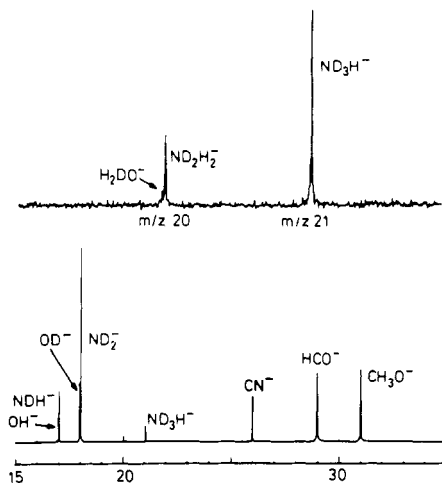
As part of our interest in gas-phase hydride-transfer reactions<sup>1</sup> we recently observed  $\text{H}_3\text{O}^-$  formed by oxidation of formaldehyde by  $\text{OH}^-$ .<sup>2</sup> Deuterium-labeling experiments have shown that the structure of the  $\text{H}_3\text{O}^-$  ion can best be described as a hydride ion solvated by a water molecule, in agreement with recent ab initio molecular orbital calculations at the 4-31++G level.<sup>3</sup> Equation

<sup>†</sup> Visiting scientist from the Department of Chemistry and Biochemistry, University of Turku, SF-20500 Turku 50 Finland.

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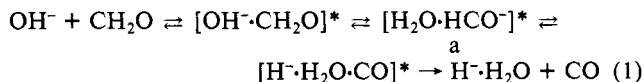
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(3) Squires, R. R., personal communication.



**Figure 1.** FT ICR spectrum of an  $\text{ND}_2^-/\text{ND}_3/\text{CH}_2\text{O}$  system. Experimental conditions:  $p(\text{ND}_3) = 70 \mu\text{Pa}$ ,  $p(\text{CH}_2\text{O}) = 30 \mu\text{Pa}$ , magnetic field strength 1.4 T, electron energy 4.5 eV, emission current 800 nA. The spectrum is taken at a trapping time of 150 ms (i.e., 150 ms after the electron beam pulse started), 2350 transients accumulated. The expanded graph on top shows the mass region from  $m/z$  19 to 22. The  $\text{OH}^-$  and  $\text{OD}^-$  ions observed are due to background water but do not interfere with the measurements as can be seen from the low abundance of the  $\text{H}_2\text{DO}^-$  ions.

1 rationalizes the formation of this species via a two-step process in the collision complex.<sup>2</sup> The first step is proton transfer from



formaldehyde to  $\text{OH}^-$ , but the resulting complex a does not dissociate, because water is more acidic than formaldehyde.<sup>4</sup> The second step is transfer of a hydride from  $\text{HCO}^-$  to water, resulting in  $\text{H}_3\text{O}^-$  and  $\text{CO}$ .

The observation of  $\text{H}_3\text{O}^-$  raises the question whether  $\text{NH}_4^-$  can also be generated as a stable species in the gas phase. The reaction between  $\text{NH}_2^-$  and formaldehyde has been examined earlier by drift cell ion cyclotron resonance spectrometry,<sup>4</sup> but no ion corresponding to  $\text{NH}_4^-$  has been reported. However, under the improved experimental conditions of our Fourier transform ion cyclotron resonance (FTICR) spectrometer<sup>6,7</sup> we have been able to observe ions at  $m/z$  18. Although our instrument does not yet have the capability of performing high-resolution experiments, the mass of these ions can be measured with sufficient accuracy:  $18.0350 \pm 0.0037$  daltons (exact mass of  $\text{NH}_4^-$  is 18.0344 daltons). Support for the formation of  $\text{NH}_4^-$  is derived from the observation that ions at  $m/z$  19 are formed if  $^{15}\text{NH}_3$  is used.<sup>8</sup> The mass of these ions is measured to be  $19.0316 \pm 0.0041$  daltons (exact mass of  $^{15}\text{NH}_4^-$  is 19.0314 daltons). This clearly shows that  $\text{NH}_4^-$  is a stable species in the gas phase.

The mechanism of formation of  $\text{NH}_4^-$  appears to be different from that of  $\text{H}_3\text{O}^-$  (see eq 1) in the following sense: the proton abstraction from formaldehyde by  $\text{NH}_2^-$ , which is a stronger base than  $\text{OH}^-$ , is now exothermic and results in the formation of  $\text{HCO}^-$  ions (eq 2).<sup>4</sup> Ejection of these  $\text{HCO}^-$  ions<sup>9</sup> results in removal

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(8)  $^{15}\text{NH}_3$  was generated from  $^{15}\text{N}_2$  ammonium sulfate (label content 96.5 atom %  $^{15}\text{N}$ ).