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Communications to the Editor

Ambident Aniline Reactivity in Meisenheimer Complex Formation

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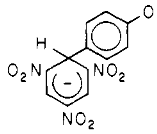
We reported previously on the first instance of ambident nucleophilic reactivity in Meisenheimer (σ-) complex formation. Thus phenoxide ion was found to react with 1,3,5-trinitrobenzene (TNB) to yield the carbon-bonded adduct **1**;[1] up to that time only the oxygen-bonded adduct **2** had been reported.[2]



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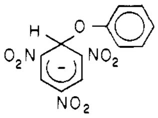

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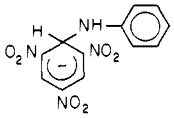

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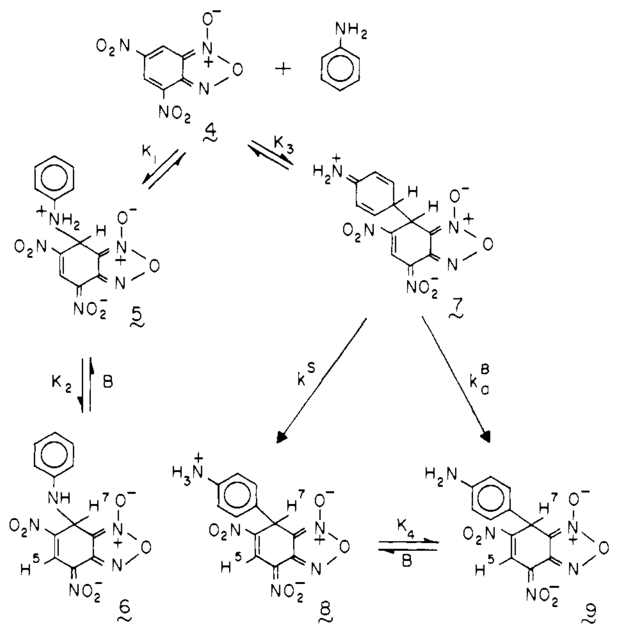
There has been no report so far that aromatic amines could act as potential carbon nucleophiles in σ-complex[3] formation with nitroarenes.[4] TNB was found to react with aniline in the presence of triethylamine or 1,4-diazabicyclooctane (DABCO) to yield the nitrogen-bonded adduct **3**.[5] We now report that aniline reacts with 4,6-dinitrobenzofuroxan (**4**) to yield the carbon- as well as the nitrogen-bonded σ complexes. Moreover, the carbon-bonded adduct can be obtained as the anionic σ 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 $(CD_3)_2SO$ resulted in the rapid formation of the zwitterionic carbon-bonded adduct **8** as shown by its NMR spectrum.[6] **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 $(CD_3)_2SO$ 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 **9** and **6**.[6] However, the signals for **9** increased quickly at the expense of those for **6**, and the conversion was complete after 30 min.

Scheme I



(3) The addition of **4** to equivalent amounts of aniline and triethylamine in $(CD_3)_2SO$ 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**.[5,7] 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)[8] 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) $K_2^{Et_3N} > (\gg) K_2^{PhNH_2}$ and (b) that base-catalyzed deprotonation of **5** to **6** occurs more rapidly than the base-promoted rearomatization of **7** to **9** (k_a^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 σ complexes showed the following ^1H NMR parameters (Me_4Si as internal standard): (a) **6**: δ 8.95 (s, 1 H, H-5), 6.23 (s, 1 H, H-7), 7.1 (m, 5 H, ArH). (b) **8**: δ 9.00 (s, 1 H, H-5), 5.53 (s, 1 H, H-7), 7.59, 7.43 (A_2B_2, $J = 8$ Hz, 4 H, Ar H), 9.95 (br, s, 3 H, NH_3^+). (c) **9**: δ 8.99 (s, 1 H, H-5), 5.30 (s, 1 H, H-7), 7.13, 6.77 (A_2B_2, $J = 9$ Hz, 4 H, Ar H). (d) **10**: δ 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 (A_2B_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_a^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.

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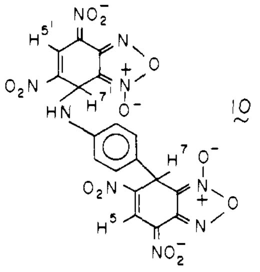
studied previously[5] is that in the latter case a tertiary base (Et_3N or DABCO) is required for transformation to the σ complex to be effective; formation of the zwitterionic intermediate is sufficiently disfavored such that the overall process with aniline alone does not occur. This contrasting behavior reflects the greater stability of σ complexes in the 4,6-dinitrobenzofuroxan system.[9]

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



10

addition of **4** to a $(CD_3)_2SO$ solution of **8**, followed by 2 equiv of Et_3N. The NMR spectrum of the product is completely in accord with the structural formulation in **10**.[6]

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.

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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 NH_4^- Ion in the Gas Phase

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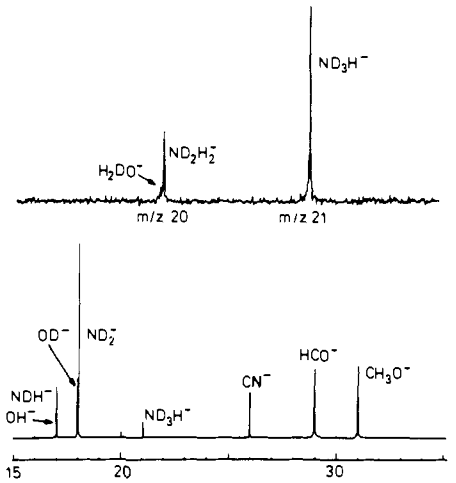

Figure 1. FT ICR spectrum of an $ND_2^-/ND_3/CH_2O$ system. Experimental conditions: $p(ND_3) = 70\ \mu Pa$, $p(CH_2O) = 30\ \mu Pa$, magnetic field strength 1.4 T, electron energy 4.5 eV, emission current 800 nA. The spectrum is taken at a trapping time of 150 ms (i.e., 150 ms after the electron beam pulse started), 2350 transients accumulated. The expanded graph on top shows the mass region from *m/z* 19 to 22. The OH^- and 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 H_2DO^- ions.

As part of our interest in gas-phase hydride-transfer reactions[1] we recently observed H_3O^- formed by oxidation of formaldehyde by OH^-.[2] Deuterium-labeling experiments have shown that the structure of the H_3O^- ion can best be desribed as a hydride ion solvated by a water molecule, in agreement with recent ab initio molecular orbital calculations at the 4-31++G level.[3] Equation 1 rationalizes the formation of this species via a two-step process in the collision complex.[2] The first step is proton transfer from

$$OH^- + CH_2O \rightleftarrows [OH^-\cdot CH_2O]^* \rightleftarrows \underset{a}{[H_2O\cdot HCO^-]^*} \rightleftarrows [H^-\cdot H_2O\cdot CO]^* \rightarrow H^-\cdot H_2O + CO \quad (1)$$

formaldehyde to OH^-, but the resulting complex a does not dissociate, because water is more acidic than formaldehyde.[4] The second step is transfer of a hydride from HCO^- to water, resulting in H_3O^- and CO.

The observation of H_3O^-[5] raises the question whether NH_4^- can also be generated as a stable species in the gas phase. The reaction between NH_2^- and formaldehyde has been examined earlier by drift cell ion cyclotron resonance spectrometry,[4] but no ion corresponding to NH_4^- has been reported. However, under the improved experimental conditions of our Fourier transform ion cyclotron resonance (FTICR) spectrometer[6,7] 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 ± 0.0037 daltons (exact mass of NH_4^- is 18.0344 daltons). Support for the formation of NH_4^- is derived from the observation that ions at *m/z* 19 are formed if $^{15}NH_3$ is used.[8] The mass of these ions is measured to be 19.0316 ± 0.0041 daltons (exact mass of $^{15}NH_4^-$ is 19.0314 daltons). This clearly shows that NH_4^- is a stable species in the gas phase.

The mechanism of formation of NH_4^- appears to be different from that of H_3O^- (see eq 1) in the following sense: the proton abstraction from formaldehyde by NH_2^-, which is a stronger base than OH^-, is now exothermic and results in the formation of HCO^- ions (eq 2).[4] Ejection of these HCO^- ions[9] results in removal

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(8) $^{15}NH_3$ was generated from $[^{15}N_2]$ ammonium sulfate (label content 96.5 atom % ^{15}N).

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