Electron Transfer Processes. XV. Addition of Nitric Oxide and Nitrogen Dioxide to Anions of Nitro Alkanes and Oximes

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Abstract: Nitrogen dioxide and nitric oxide react in basic solution with the aci anions of primary aliphatic nitro alkanes (nitronates) to give the gem-dinitro dianion radicals of the form [R-C(NO2)2]. gem and gem-nitronitroso radicals of the form [R-C(NO2)N(NO)]. With R = H, D, CH3, and CH2CH3. The production of the latter radicals in the reaction of NO2 with nitronates (R = Me, Et) is also noted and a source proposed. Nitromethane at low base concentration gives with NO2 the dinitronitrosomethyl dianion radical. Formaldoxime gives with both NO and NO2 the dinitrosomethyl dianion radical. The dinitrosethyl dianion radical anion has also been prepared by reduction of aqueous solutions of potassium acetonitrosolate (CH3C(NO)2 = NO-K+). Acetaldoxime gives the nitronitrosomethyl dianion radical with NO2. Deuterium exchange for the radicals where R = H is found to be rapid, but does not occur in the dinitrosomethyl dianion radical.

The aci anions of nitro alkanes (nitronates) have been used to trap several short-lived radicals, namely the hydroxyl radical,3-5 the amino radical,6 the methyl radical,6 radicals derived from alcohols by loss of an α-hydrogen atom,4 and the phenyl radical7 according to eq 1.

\[
\text{X}^- + \text{RCH(NO}_2\text{)}^- \xrightarrow{\text{glucose}} [\text{RCH(NO}_2\text{)}^-]^- + \text{H}^+ \tag{1}
\]

Lagercrantz and coworkers have prepared the dianion radicals of various aliphatic6 and aromatic3 dinitro compounds using glucose in aqueous alkali (eq 2). Further reduction to dianion radicals of the gem-nitronitroso compounds is also observed.8,9

\[
\text{RCH(NO}_2\text{)}^- + [\text{RCH(NO}_2\text{)}^-]^- \xrightarrow{\text{glucose}} [\text{RCH(NO}_2\text{)}^-]^- + \text{H}^+ \tag{2}
\]

A similar series has been prepared by electrolytic reduction of dinitro compounds in DMF.10 In light of these observations it was considered worthwhile investigating the system in which X- in eq 1 was either NO2 or NO. In the presence of alkali, the originally formed radical anion could be converted to the stable radical dianions as outlined in eq 3 and 4.

Table I. Hyperfine Splitting Constants of Dinitro Dianion Radicals

<table>
<thead>
<tr>
<th>R</th>
<th>aH(NO₂)</th>
<th>aH(R)</th>
<th>aH(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>9.65</td>
<td>13.01</td>
<td>4.03</td>
</tr>
<tr>
<td>D</td>
<td>9.65</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>Me</td>
<td>10.00</td>
<td>13.85</td>
<td>3.23</td>
</tr>
<tr>
<td>Et</td>
<td>10.05</td>
<td>14.03</td>
<td>1.84</td>
</tr>
</tbody>
</table>

Results and Discussion

Reaction of Nitronates with Nitrogen Dioxide. The anions from nitromethane, nitroethane, and 1-nitropropane all reacted in 5-10 M sodium hydroxide solutions with nitrogen dioxide to produce the corresponding dinitro dianion radicals whose hyperfine splitting constants (hfsc) are reported in Table I. These hfsc are in good agreement with those reported by Lagercrantz for the dinitromethyl and dinitroethyldianion radicals. The esr spectrum of the 1,1-dinitropropyl dianion radical is shown in Figure I.

The methanenitronate anion was found to be a more efficient trap for nitrogen dioxide than the ethane-nitronate and 1-propanenitronate anions. Whereas the methanenitronate in 2.5 M sodium hydroxide readily gave a very strong esr signal from small amounts of nitrogen dioxide gas (1-2 ml; see Experimental Section), the other nitronates gave no reaction even on prolonged passage of NO2 through the solution. Higher base concentration gave strong signals with all the nitronates and using 10 M base, only small amounts of NO2 gas (1-4 ml) were required to give strong signals. At low base concentrations and even at high base concentrations with aged solutions, solutions which were not agitated vigorously during addition of the NO2 gas,
or with an excessive amount of NO₂, considerable (often major) amounts of the gem-nitronitroso dianion radicals were formed from ethanenitronate and propanenitronate solutions. This phenomenon can be attributed to the consumption of base by side reactions (in the case of aged solutions) or by local pH variations (in the case of poorly mixed solutions) which would allow formation of nitrolic acids, which in turn are reduced to the nitronitrosaalkyl dianion radicals (1; \( R = \text{CH}_3 \) or \( \text{CH}_3\text{CH}_2 \)) by the nitro alkane anion. The ability of nitro alkane anion to transfer one electron to a wide variety of unsaturated systems has been previously documented.  

The nitrosation of alkyl nitronates by nitrosating agents, including N₂O₄, is well established (eq 5) and the electron transfer step (eq 6, \( R = \text{CH}_3 \)) was confirmed by mixing equal volumes of 1 M nitroethane and 1 M acetonitrolic acid (CH₃(NO₂) = NOH) in 5 M sodium hydroxide (deoxygenated using nitrogen). A very strong signal from the radical I (\( R = \text{CH}_3 \)) was produced (in the absence of the nitroethane there was no radical produced). The use of \(^{15}\text{N} \text{NO}_2\) with a poorly mixed solution of 1 M nitropropane in 10 M sodium hydroxide gave a mixture of the radicals 2 and 3 but no detectable amount (<5%) of the radical 4.

\[
\text{CH}_3\text{CH}_2\overset{\text{NO}_2}{\longrightarrow} \quad \text{CH}_3\text{CH}_2\overset{\text{NO}}{\longrightarrow}
\]

of 1 M nitroethane and 1 M acetonitrolic acid (CH₃C-(NO₂)=NOH) in 5 M sodium hydroxide (deoxygenated using nitrogen). A very strong signal from the radical I (\( R = \text{CH}_3 \)) was produced (in the absence of the nitroethane there was no radical produced). The use of \(^{15}\text{N} \text{NO}_2\) labeled nitrogen dioxide with a poorly mixed solution of 1 M nitropropane in 10 M sodium hydroxide gave a mixture of the radicals 2 and 3 but no detectable amount (<5%) of the radical 4.

This indicates that nitrosation, with specific introduction of the \(^{15}\text{N}\) in the nitroso group (cf. eq 5), occurs prior to radical formation, i.e., elimination of water from such symmetrical intermediates as a dinitro radical anion is not the pathway for formation of nitro-nitroso alkanes (eq 7), since this would be expected to give rise to a 50:50 mixture of \(^{15}\text{N}\) in the nitro and nitroso groups. The addition of \(^{15}\text{NO}_2\) to methanenitratone and ethanenitratone anions gave the corresponding dinitro dianion radicals (see Figure 2) with one nitro group labeled with \(^{15}\text{N}\).

Nitromethane in solutions of low base concentration (1–2.5 M) with an excess of NO₂, or in 5 M base which had been aged, gave a very strong signal, poorly resolved in aqueous sodium or potassium hydroxide solution but having good resolution in tetramethylammonium hydroxide solution which has been attributed to the dinitronitrosomethyl dianion radical (5). This radical exhibits line width variation phenomena, a detailed discussion of which has been presented elsewhere.  

The radical (5) was also produced when either acetylacetone or the potassium salt of dinitromethane was treated with a large excess of NO₂ in 5 M base. The formation of the radical from dinitromethane may be formulated as a nitrosation followed by electron transfer (from the dinitromethyl anion). The formation from nitromethane in 2.5 M base is probably the result of nitrosation followed by trapping of NO₂ by the resulting nitro oxime. The specific labeling of the nitroso group when \(^{15}\text{NO}_2\) was allowed to react with

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Table II. Nitronitroso Dianion Radicals

<table>
<thead>
<tr>
<th>R</th>
<th>$\alpha_{R}^{\text{NO}}$</th>
<th>$\alpha_{R}^{\text{NO}_2}$</th>
<th>$\alpha_{R}^{\text{H}}$</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>6.23</td>
<td>11.47</td>
<td>2.77</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>6.23</td>
<td>11.47</td>
<td>2.73</td>
<td>$\alpha_{D}^{\text{H}} = 0.43$</td>
</tr>
<tr>
<td>Me</td>
<td>5.93</td>
<td>12.25</td>
<td>2.77</td>
<td></td>
</tr>
<tr>
<td>Et</td>
<td>5.95 ($\alpha_{\text{Me}}^{\text{NO}} = 8.25$)</td>
<td>12.30</td>
<td>1.55</td>
<td></td>
</tr>
<tr>
<td>CN</td>
<td>6.70</td>
<td>10.00</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>NO$_2$</td>
<td>5.80</td>
<td>10.75</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>$^{15}$NO$_2$</td>
<td>$\alpha_{\text{N}}^{\text{NO}} = 8.25$</td>
<td>$\alpha_{\text{N}}^{\text{NO}_2} = 15.03$</td>
<td>$\alpha_{\text{N}}^{\text{H}} = 0.90$</td>
<td>$\alpha_{\text{NO}}^{\text{CN}} = 0.35$ $\alpha_{\text{NO}}^{\text{NO}_2} = 0.65$</td>
</tr>
</tbody>
</table>

* Data obtained from two isomers.12

Nitromethane in 2.5 M base was again observed giving rise to the equilibrium mixture of the radicals 6 and 7,13 both of which have $^{15}$N in the nitroso group.

The formation of 5 from acetylacetone may follow several routes but essentially the central carbon atom is converted to nitromethane by the action of base and NO$_2$ and the nitromethane then reacts as above. The reaction of acetylacetone in the absence of solvent (and alkali) gave rise to the radical 8, which gave a triplet splitting for one nitrogen of 28.0 G. This result is as expected in view of the results obtained with other carbonyl compounds having active methyl groups.14

$$\text{CH}_3\text{CO}-\text{C}=\text{COCH}_3$$

8

Reaction of Nitronates with Nitric Oxide. Nitric oxide was found to react with nitrate anions in 5 M base to give the corresponding nitronitroso dianion radicals. The hfsc are reported in Table II. The data for the nitronitrosomethyl dianion radical are in good agreement with that reported by Lagercrantz.8 The spectrum of the nitronitrosomethyl dianion radical is shown in Figure 3. On long standing of the alkaline solution of nitromethane prior to addition of NO the cyano-nitronitrosomethyl dianion radical16 was produced (for hfsc, see Table II). This was shown to be derived from the self-condensation product of nitromethane, methazonic acid, since the spectrum obtained from methazonic acid was identical. Presumably the first formed radical loses water as shown in eq 8.

$$\text{CH}_3\text{CO}-\text{C}=\text{COCH}_3 + \text{NO} \rightarrow \text{CH}_3\text{CO}=\text{CH}_3 + \text{NO}_2$$

8

Reaction of Nitric Oxide and Nitrogen Dioxide with Acetaldoxime and Formaldoxime. Formaldoxime in 5 M base was found to give a very weak esr signal when treated with nitric oxide, consisting of an approximate 1:2:3:2:1 quintet of doublets which can be interpreted as arising from interaction with two equivalent nitrogens ($\alpha^N = 8.05$ G) and one hydrogen ($\alpha^H = 3.15$ G). The radical is presumably the novel dinitrosomethyl dianion radical and its mode of formation is given in eq 9. The very weak esr signal decayed fairly rapidly.

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that obtained above. The mode of formation of the product was a quite strong (and stable) signal identical with reaction formulated in eq 10, since the reaction of radical, eq 11 (no mechanism is implied or suggested) when treated with nitrogen dioxide. The initial product gave a series of products in (4-8 min) and was replaced by the esr signal of the nitronitrosomethyl dianion radical.

Figure 4. First derivative esr X-band spectrum of the dinitrosoethyl dianion radical in 5 M sodium hydroxide at 25°C.

\[
\begin{align*}
\text{CH}_3 & \equiv \text{N} - \text{O}^- + \text{NO}^+ \\
\left[ \text{CH}_3\text{NO}^- \right]^{-} & \rightarrow -\text{H}^+ \rightarrow \left[ \text{H} - \text{C} = \text{N} \text{NO}^- \right]^{-2} \quad (9)
\end{align*}
\]

(4-8 min) and was replaced by the esr signal of the nitronitrosomethyl dianion radical.

Acetaldoxime was found to be unreactive toward nitric oxide in the base concentration range 1-10 M. Formaldoxime gave a series of products in 5 M base when treated with nitrogen dioxide. The initial product was a quite strong (and stable) signal identical with that obtained above. The mode of formation of the dinitrosomethyl dianion radical cannot be the simple reaction formulated in eq 10, since the reaction of formaldoxime with \(^{15}\text{NO}_2\) gives rise to the same radical,

\[
\begin{align*}
\text{H} - \text{C} \equiv \text{N} - \text{O}^- - \text{NO}^+ & \rightarrow \text{H} - \text{C} = \text{N} \text{NO}^- \\
\left[ \text{H} - \text{C} = \text{N} \text{NO}^- \right]^{-2} & \quad (10)
\end{align*}
\]

i.e., no \(^{15}\text{N}\) is incorporated. A possible explanation of this observation is that an oxidative cleavage by \(\text{NO}_2\) is taking place on the formaldoxime trimer giving rise to a C-1 fragment bearing two \(^{14}\text{N}\) atoms. Subsequent electron transfer steps result in the observed radical, eq 11 (no mechanism is implied or suggested for the first step). Addition of excess nitrogen dioxide gave first the nitronitrosomethyl dianion radical and then complex mixtures which included the dinitrosoethyl dianion radical.

Acetaldoxime in 5 M base was far less reactive and prolonged passage of nitrogen dioxide gave the nitrosoethyl dianion radical (I; \(R = \text{CH}_3\)) with no formation of a dinitroso species. Excess nitrogen dioxide gave oxidation to the dinitrosoethyl dianion radical.

The dinitrosoethyl dianion radical is capable of reductive cleavage by NO to give first the nitronitrosomethyl dianion radical and then complex mixtures which included the dinitrosoethyl dianion radical.

Deuterium Exchange in the Radical Derived from Nitromethane and Formaldoxime. The dinitromethyl and nitrotrinitrosomethyl dianion radicals were both found to undergo deuterium exchange extremely rapidly (<2 min) upon the addition of deuterium oxide presumably by the following mechanism

\[
\text{RH}^- + \text{D}_2\text{O} \rightarrow \text{HRD}^- + \text{OD}^- \rightarrow \text{HOD} + \text{RD}^- \quad (12)
\]

The ratio of \(a_{\text{H}}/a_{\text{D}}\) for the radicals was 6.4 and 6.5, respectively (cf. Tables I and II).

The dinitrosomethyl dianion radical did not exchange deuterium even after 2 hr at 30°C. The protonation–deprotonation process must be taking place almost exclusively on oxygen, rather than on carbon, as indicated in eq 13.

\[
\begin{align*}
\left[ \text{H} - \text{C} = \text{N} \text{NO}^- \right]^{-2} & + \text{D}_2\text{O} \rightarrow \left[ \text{H} - \text{C} = \text{N} \text{D} - \text{O}^- \right]^{-2} \quad (13)
\end{align*}
\]

Experimental Section

Preparation and Purification of Materials. Nitromethane, nitroethane, and 1- and 2-nitropropane were distilled prior to use. Phenylacetaldimine, \(^{15}\)formaldehyde hydrochloride, \(^{15}\)benzaldehyde were prepared by oximation of the corresponding aldehydes. Ethanenitrosic acid was prepared by nitrosation of nitroethane. The potassium salt of dinitromethane was prepared by reduction of dibromodinitromethane. Methazonic acid was prepared by the method of Armand, and was reduced electrolytically over mercury.

Gas Trapping Procedure. The appropriate neutral compound (2 mmol) (or potassium salt for dinitromethane and hydrochloride for formaldoxime) was dissolved or suspended in the requisite amount of water in one arm of an H tube stoppered with septum.
caps and attached to a flat fused-silica esr cell. The appropriate volume of 10 M sodium hydroxide was then placed in the remaining arm and both solutions were deoxygenated using nitrogen for 10-20 min. The solutions were then mixed (total volume 2 ml) and the appropriate gas was bubbled or syringed into the system. Spectra were recorded on either a Varian E-3 or 4500 esr spectrometer.

Cation–Anion Combination Reactions. VIII. Reactions of Tropylium Ions in Methanol Solution

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Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received December 18, 1971

Abstract: Rate and equilibrium constants for the reactions of tropylium ion and of several aryltropylium ions with nucleophiles in methanol solution have been determined by stop-flow spectrophotometry. The $pK_a$ values, rate constants for reaction with methanol, and rate constants for reaction with methoxide ion, respectively, for the cations studied are tropylium ion, 2.15, 150 sec$^{-1}$; phenyltropylium ion, 2.92, 71 sec$^{-1}$; $p$-chlorophenyltropylium ion, 2.30, 92 sec$^{-1}$; $p$-methoxyphenyltropylium ion, 4.09, 13 sec$^{-1}$; $p$-dimethylaminophenyltropylium ion, 6.68, 0.22 sec$^{-1}$; 2,3,10$^8$ sec$^{-1}$. The reactions of all of these cations with azide ion reached equilibrium at rates too fast to measure by our techniques. Equilibrium constants for formation of the aryltropyl azides are phenyltropylium ion, 1.8 x 10$^{-8}$ M; $p$-chlorophenyltropylium ion, 4.8 x 10$^{-8}$ M; $p$-methoxyphenyltropylium ion, 8.8 x 10$^{-8}$ M; $p$-dimethylaminophenyltropylium ion, 1.9 x 10$^{-8}$ M. The reaction rates of all of the cations with thiophenoxide ion are very nearly diffusion controlled. In the case of $p$-dimethylaminophenyltropylium ion the equilibrium and rate constants for formation of the thioether are 9.1 x 10$^{-8}$ M and 6.4 x 10$^{-8}$ sec$^{-1}$, respectively. Although the reactivities of these cations differ greatly from those of Malachite Green derivatives, the selectivities of the different cations are the same.

Table I. Reactions of Cations in Methanol at 23 ± 1°C

<table>
<thead>
<tr>
<th>Cation</th>
<th>$pK_a$</th>
<th>$k_{MeOH}$ sec$^{-1}$</th>
<th>$k_{MeO} M^{-1}$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$-(CH$_3$)$_2$NC$_6$H$_4$C$_7$H$_6$+</td>
<td>6.68</td>
<td>0.22</td>
<td>2.3 x 10$^8$</td>
</tr>
<tr>
<td>$p$-CH$_3$OC$_6$H$_4$C$_7$H$_6$+</td>
<td>4.09</td>
<td>13</td>
<td>6.8 x 10$^8$</td>
</tr>
<tr>
<td>C$_6$H$_5$C$_7$H$_6$+</td>
<td>2.92</td>
<td>71</td>
<td>1.8 x 10$^8$</td>
</tr>
<tr>
<td>C$_7$H$_7$+</td>
<td>2.50</td>
<td>92</td>
<td>1.9 x 10$^8$</td>
</tr>
<tr>
<td>C$_5$H$_5$NMe$_2$+</td>
<td>2.15</td>
<td>1.5 x 10$^1$</td>
<td>5.4 x 10$^{-4}$</td>
</tr>
<tr>
<td>$p$-Nitro(MG)$^+$</td>
<td>6.79</td>
<td></td>
<td>6.0 x 10$^{18}$</td>
</tr>
</tbody>
</table>

* $p$-Nitro(Malachite Green), bis-$p$-dimethylaminophenyl-$p$-nitrophenylmethyl cation. † Data from ref 2.

The work leading to the present series of papers was initiated in an effort to understand the peculiar order of nucleophilic reactivities observed toward derivatives of Malachite Green cations. An initial hypothesis that the order of reactivity is characteristic of any cation–anion combination reaction has been tested by studies of aryl diazonium ion reactions. These studies indeed provided substantial support for the hypothesis.

In order to provide additional data bearing on the question of nucleophilic reactivity in cation–anion combination reactions, we then turned our attention to a third class of cations, the tropylium and aryltropylium ions. The immediately preceding paper of this series detailed our studies of the reactions of these cations in aqueous solution. The present paper reports the results of the conclusion of our studies of the tropylium ions, detailing the reactions with several nucleophiles in methanol solution.

Results

The $pK_a$ values and the rate constants for reactions of the cations with methanol and with methoxide ion are reported in Table I. In the cases of the $p$-dimethylaminophenyltropylium ion and the $p$-methoxyphenyltropylium ion, the use of dichloroacetic acid–dichloroacetate and trichloroacetic acid–trichloroacetate buffers, respectively, furnished pH ranges in which the equilibria could be studied by techniques analogous to those previously reported for aqueous solutions. For all of the other cations, however, the $pK_a$ values are so low that we were forced to use dilute solutions of perchloric acid and treat the data according to the Benesi–Hildebrand equation to obtain values for $K_a$ and the molar absorbivities of the cations.

Rate constants were obtained at pH high enough that the reactions were complete and corrections for the reverse rates were not necessary. Measurements over a range of pH established the expected relationship: $k_{obsd} = k_{MeOH} + k_{MeO}-(MeO^-)$, where $k_{obsd}$ is the observed pseudo-first-order rate constant at a given pH.

Previously reported data for the reaction of $p$-nitro(Malachite Green) with methanol and methoxide ion are also shown in Table I. The rate constant for reaction of $p$-nitro(Malachite Green) with methanol was determined in the present study, using techniques analogous to those for the tropylium ions.

In our studies of the reactions of the tropylium ions with azide ion in methanol, we have succeeded in mea-
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