

# Is NO (Nitric Oxide) an Electron Acceptor or an Electrophile? A Detailed Thermodynamic Investigation on the Mechanisms of NO-Initiated Reactions with 3,6-Dibromocarbazolidine Anion and Related Carbanion

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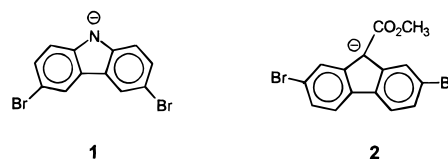
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In recent years, especially after the discovery of its roles in acting as the endothelium-derived relaxing factor (EDRF) in human bodies,<sup>1</sup> NO (nitric oxide) has received much more intense attention than ever before. Although recent research has exhibited that NO, an important biradical, has a wide range of physiological and pathological activities,<sup>2–5</sup> up to now little is known about its fundamental chemistry in relation to these biological functionalities.<sup>6</sup> Recently, Janzen et al.<sup>7</sup> found that NO can react with phenolic antioxidants to generate phenoxyl radicals. Ohsawa and co-workers reported that NO can nitrosate amides and oxidize Hantzsch dihydropyridines to give the corresponding pyridine derivatives.<sup>8</sup> These results displayed some significant biologically related chemical properties of NO, but in no case has sufficient evidence been gathered to allow an explicit statement of mechanism for the NO-initiated reactions.

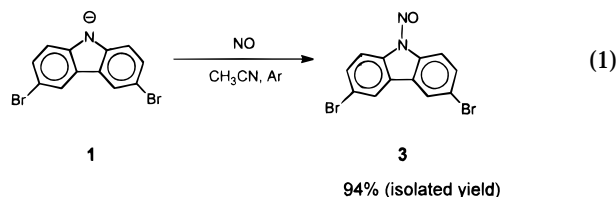
We have recently carried out an investigation on some NAD(P)H model-mediated reactions utilizing detailed thermodynamic analysis to differentiate various possibilities of feasible mechanisms.<sup>9</sup> Thermodynamic approaches of a related kind have also been applied by this group<sup>10</sup> and by others<sup>11</sup> to derive information regarding the energetics of biologically or chemically important systems. Because the mechanism of NO-mediated reactions is currently of great interest and, to our knowledge,

no detailed thermodynamic analysis has been reported for this category of reactions, we in this work conducted research of this kind to derive detailed information on the energetics of the title reactions. The mechanism-probing substrates chosen to examine the role of NO were 3,6-dibromocarbazolidine nitraneion (**1**) and a structurally similar carbanion, 2,7-dibromo-9-(methoxycarbonyl)fluorenone (**2**), whose basicity (or nucleophilicity) and electron-releasing property are in a comparable range with those of some biologically important species (e.g., phenoxides) under a physiological environment<sup>12</sup> and therefore can serve as models for NO-mediated reactions. Furthermore, both the carbazole derivatives themselves and some N-nitrosated aromatic amines are known to be biologically active compounds,<sup>16,17</sup> so the information gathered in the present work may provide hints for understanding the relevant NO-involving biotransformations for relevant systems.



## Results and Discussion

**Reaction of NO with Nitraneion 1.** The reaction of 3,6-dibromocarbazolidine (**1**) with excess NO gas in dry acetonitrile was found to give the corresponding *N*-nitroso product (**3**), a member of the important carcinogen family (*N*-nitrosoamines), in nearly quantitative yield (eq 1).



It was the basic concern of the present work to investigate the thermodynamic details of this NO-initiated reaction in order to understand the possible roles of NO in living bodies. The two most conceivable mechanisms for reaction 1 are illustrated in Scheme 1, in

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(12) The  $pK_a$ s of 3,6-dibromocarbazole, 2,7-dibromo-9-(methoxycarbonyl)fluorenone, and phenol are 17.1<sub>s</sub>, 10.3<sub>s</sub>, and 18.0 in DMSO,<sup>13</sup> respectively (note that the  $pK_a$  of phenol in H<sub>2</sub>O is 9.99<sup>14</sup>), whereas the corresponding anion oxidation potentials in MeCN are -0.148 V (this work), -0.310 V (this work), and -0.344 V<sup>15</sup> vs ferrocenium/ferrocene, respectively.

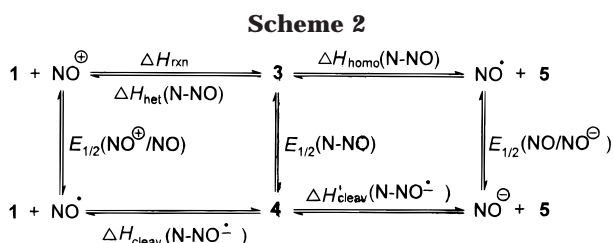
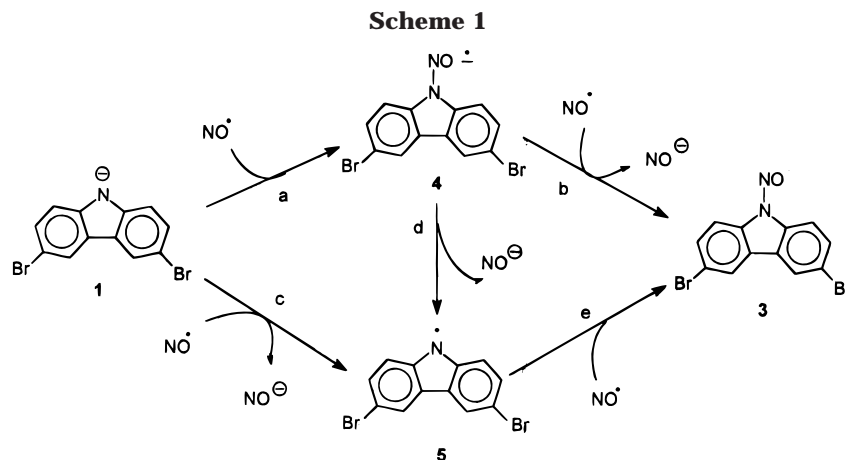
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which path **a–b** represents an initial electrophilic attack of NO to nitranion **1** followed by a subsequent electron transfer from the incipient radical anion **4** to NO, whereas path **c–e** represents an initial electron transfer (ET) of **1** to NO followed by coupling of the incipient nitrogen radical **5** with an NO radical. As shown, the common product from either path is *N*-nitroso carbazole **3**.

Because attempts to trap and experimentally distinguish intermediates **4** and **5** were unsuccessful, it was necessary to invoke other analytical strategy such as thermodynamic driving force analysis to aid in solving the mechanistic problem. For this purpose, a detailed investigation on the driving force for each mechanistically feasible step in Scheme 1 has been carried out. A thermodynamic approach of a similar kind has also been successfully applied recently by this group to other biologically important systems.<sup>9</sup> The appropriate cycles necessary in the present work for evaluating the energetics of the elementary processes in Scheme 1 are illustrated in Scheme 2. The equations accordingly derived are shown below (eqs 2–4),

$$\Delta H_{\text{hom}}(\text{N-NO}) = \Delta H_{\text{het}}(\text{N-NO}) - F[E_{1/2}(\text{NO}^+/\text{NO}) - E_{\text{ox}}(\text{N}^-)] \quad (2)$$

$$\Delta H_{\text{cleav}}(\text{N-NO}^-) = \Delta H_{\text{het}}(\text{N-NO}) + F[E_{1/2}(\text{N-NO}) - E_{1/2}(\text{NO}^+/\text{NO})] \quad (3)$$

$$\Delta H_{\text{cleav}}(\text{N-NO}^-) = \Delta H_{\text{hom}}(\text{N-NO}) + F[E_{1/2}(\text{N-NO}) - E_{1/2}(\text{NO}/\text{NO}^-)] \quad (4)$$

where  $\Delta H_{\text{hom}}$ ,  $\Delta H_{\text{het}}$ ,  $\Delta H_{\text{cleav}}$ , and  $\Delta H_{\text{cleav}}^-$  represent heat of homolysis, heat of heterolysis, heat of homolytic cleavage of radical anion (to form NO radical), and heat of heterolytic cleavage of radical anion (to form NO<sup>-</sup> anion), respectively. The basic data necessary for calculating the thermodynamic quantities in eqs 2–4 are listed in Tables 1 and 2, respectively.

**Table 1. Heterolytic and Homolytic Dissociation Energies (kcal mol<sup>-1</sup>)<sup>a</sup> of the N–NO Bonds in **3** and **4** and Redox Potentials (V vs Fc<sup>+</sup>/Fc)<sup>b</sup> of the Relevant Species in CH<sub>3</sub>CN at 25 °C**

$\Delta H_{\text{het}}(\text{N-NO})$	51.6	$E_{1/2}(\text{NO}^+/\text{NO})$ <sup>c</sup>	0.863
$\Delta H_{\text{hom}}(\text{N-NO})$	28.3	$E_{1/2}(\text{NO}/\text{NO}^-)$ <sup>d</sup>	-0.287
$\Delta H_{\text{cleav}}(\text{N-NO}^-)$	3.0	$E_{1/2}(\text{N-NO})$ <sup>e</sup>	-1.243
$\Delta H_{\text{cleav}}(\text{N-NO}^-)$	6.3	$E_{\text{ox}}(\text{N}^-)$ <sup>f</sup>	-0.148
		$E_{\text{ox}}(\text{C}^-)$ <sup>g</sup>	-0.310

<sup>a</sup> The N–NO bond heterolysis energy ( $\Delta H_{\text{het}}$ ) was measured by titration calorimetry in CH<sub>3</sub>CN at 25 °C (experimental error: 0.3 kcal mol<sup>-1</sup>). Other bond energies were calculated from eqs 2–4. Estimated uncertainties: 2 kcal mol<sup>-1</sup>. <sup>b</sup> Measured by cyclic voltammetry (CV) in CH<sub>3</sub>CN at 25 °C. Reproducibility:  $\leq 0.005$  V. <sup>c</sup> Reference 10a. <sup>d</sup> Reference 20. <sup>e</sup> Redox potential of compound **3**. <sup>f</sup> Oxidation potential of nitranion **1**. <sup>g</sup> Oxidative peak potential of carbanion **2**. The  $E_{1/2}$  would be -0.343V assuming an anodic shift of 33 mV (see: Bausch, M. J. Ph.D. Dissertation, Northwestern University, Evanston, IL, 1984).

**Table 2. Energetics (kcal mol<sup>-1</sup>) of Each Mechanistic Steps Shown in Scheme 1<sup>a</sup>**

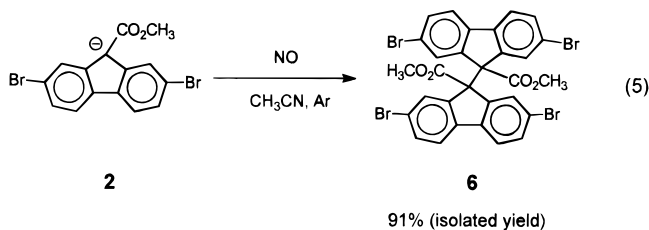
step	<b>a</b> <sup>b</sup>	<b>b</b> <sup>c</sup>	<b>c</b> <sup>c</sup>	<b>d</b> <sup>d</sup>	<b>e</b> <sup>e</sup>
$\Delta H$	-3.0	-22.0	+3.2	+6.3	-28.3

<sup>a</sup> All values were derived in CH<sub>3</sub>CN at 25 °C. <sup>b</sup> From eq 3. <sup>c</sup> From the difference of electrode potentials of related species using the data in Table 1. <sup>d</sup> From eq 4. <sup>e</sup> From eq 2.

Examination of Table 2 shows that the energy changes in the reaction steps **a** and **b** are both negative (-3.0 and -22.0 kcal mol<sup>-1</sup>, respectively), suggesting that coordination of NO with nitranion **1** to form a radical anion intermediate **4**, followed by electron transfer of **4** to another NO molecule to generate product **3**, is an energetically favorable path and therefore would most likely be the mechanism for the reaction. On the other hand, the energy changes in steps **c** and **d** are both positive (3.2 and 6.3 kcal mol<sup>-1</sup>, respectively), so the pathways **c** and **d** would be energetically less favorable. The fact that neither the carbazolyl radical (**5**) in the ESR experiment nor the carbazole dimer product was observed in our reaction system seems indeed to be more in favor of the **a–b** pathway.

**Reaction of NO with Carbanion **2**.** The second step of the above reaction (i.e., **b** in Scheme 1) indicates that NO may serve as an electron acceptor when reacting with electron-rich species (e.g., **4**), a property for which direct evidence is insufficient in the literature. Although the thermodynamic analysis presented above does suggest that this must be the case for reaction **1**, more explicit evidence still needs to be further explored. To examine such possibility, it was of interest to investigate the

reaction of NO with a better electron donor of similar structure, e.g., the 2,7-dibromo-9-(methoxycarboxy)fluorene carbanion **2**. It was found (see Experimental Section) that when carbanion **2** was treated with an excess amount of NO, the 9,9'-dimer **6** was isolated as the sole product in nearly quantitative yield (eq 5).



It is immediately realized that the most reasonable precursor of product **6** should be the 2,7-dibromo-9-(methoxycarbonyl)fluorenyl radical (**7**). According to the mechanisms proposed for the reaction of nitranion **1** (Scheme 1), radical **7** could result either from removal of an electron from carbanion **2** to NO (similar to path **c** in Scheme 1) or from heterolytic dissociation of the C–NO bond in 2,7-dibromo-9-nitroso-9-(methoxycarbonyl)fluorene radical anion (**8**), an intermediate formed upon a direct coordination of carbanion **2** with NO (similar to paths **d** and **a** in Scheme 1, respectively).

To address the preference of the mechanism, the detailed thermodynamics of the relevant primary processes are the quantities necessary. Unfortunately, the instability of the 2,7-dibromo-9-nitroso-9-(methoxycarbonyl)fluorene compound (**9**)<sup>21</sup> has prevented both a direct determination of the C–NO bond heterolysis energy by titration calorimetry and an electrochemical measurement of the reduction potential of **9**. However, the energetic quantities can be reasonably estimated by comparisons with some relevant thermodynamic data available. A parallel examination of the heterolytic dissociation energetics for all the Y–NO/Y–H bond pairs (~40 of them) determined earlier in this laboratory<sup>10a,22</sup> shows that the Y–NO bonds are 12.0–34.5 kcal mol<sup>-1</sup> weaker in strength than the corresponding Y–H bonds. Also, comparison of all the known pairs of the reduction potentials ( $E_{\text{red}}$ ) of Y–H and its nitrosated compounds Y–NO<sup>22</sup> indicated that these two values are in fact very close to each other ( $\Delta E = 0.009 \pm 0.017$  V). If the  $E_{\text{red}}$  (Y–NO) of **9** is assumed to be the same as that of its parent 2,7-dibromo-9-(methoxycarbonyl)fluorene (**10**) [ $E_{1/2}(\mathbf{10}) = -1.282$  V, this work], and also keeping in mind the above-mentioned energy differences (12.0–34.5 kcal mol<sup>-1</sup>) and the  $pK_a$  of 6.5 (or 8.9 kcal mol<sup>-1</sup>) for **10**,<sup>13</sup> the range of  $\Delta H_{\text{cleav}}(\text{C–NO}^-)$  for **8** can then be estimated using eq 3 to be -6.1 to -28.6 kcal mol<sup>-1</sup>. Therefore, the reverse process of this bond fission (i.e., a process similar to path **a** in Scheme 1) would be energetically *unfavorable* by at least 6.1 kcal mol<sup>-1</sup>. On the other hand, a simple calculation using the appropriate redox data in Table 1

(18) Enthalpy of electron transfer is assumed to be equal to free energy of electron transfer based on the observation of negligible temperature dependence of electron transfer from delocalized systems.<sup>19</sup>

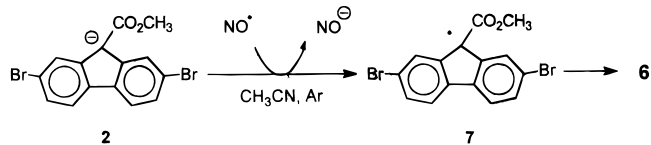
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(21) Attempts to prepare compound **9** by various ways in this work failed. Also, this compound has never been reported in the literature.

(22) Unpublished results of this laboratory.

### Scheme 3



reveals that electron transfer from carbanion **2** to NO is energetically *favorable* by 1.3 kcal mol<sup>-1</sup>. The energy difference of 7.4 kcal mol<sup>-1</sup> thus suggests that the rate of the direct ET reaction would be at least 5.4 orders of magnitude faster than the rate of coordination of **2** with NO as judged by the Arrhenius equation, showing an obvious preference of the ET mechanism (Scheme 3) over the supposedly competitive coordination mechanism.

The ET mechanism proposed here for the NO reaction with carbanion **2** may, on the other hand, provide a hint for the possible path of the NO reactions with phenolic antioxidants reported in the literature.<sup>7</sup> The phenoxide oxanion formed in the acid dissociation equilibrium ( $pK_a$  of PhOH is 10 in H<sub>2</sub>O<sup>14</sup>) is actually an even better electron donor than carbanion **2** as judged by their respective oxidation potentials (-0.344 V<sup>15</sup> vs -0.310 V). It is conceivable that NO may pull out an electron from phenoxide ion to generate the phenoxyl radical which then coupled with NO.<sup>7</sup>

To summarize, we presented here the first detailed thermodynamic analysis in terms of the driving forces for each elementary step shown in Scheme 1 for the NO-initiated reaction with nitranion **1** and showed that the most feasible mechanism should be an electrophilic combination of NO with **1** to form intermediate **4**, followed by electron transfer from **4** to NO. However, when the substrate is a better electron-providing species such as **4**, electron transfer from the electron-rich species to NO may be merged in. A more explicit example for NO to serve as electron acceptor is shown by the reaction of NO with carbanion **2**.

### Experimental Section

All reagents were of commercial quality from freshly opened containers or were purified before use. Reagent grade acetonitrile was distilled from P<sub>2</sub>O<sub>5</sub> and passed through a column containing neutral alumina to remove residual water and protic impurities. IR spectra were obtained using an FT-IR spectrophotometer. NMR spectra were taken on a 90 MHz spectrometer. MS spectra were recorded using the EI mode (70 eV). The reaction products were purified by either chromatography or crystallization. Redox potentials were obtained by CV on a BAS-100B electrochemical analyzer.

**Titration Calorimetry.** Reaction of NO<sup>+</sup> (NO<sup>+</sup>ClO<sub>4</sub><sup>-</sup>) with nitranion **1** (K<sup>+</sup> as counterion) in dry CH<sub>3</sub>CN was rapid and clean, giving coupling product **3** in nearly quantitative yield. The reaction heat ( $\Delta H_{\text{rxn}}$ ) was measured at 25 °C by a standard procedure similar to that of Arnett<sup>24</sup> on a Tranac 450 titration calorimeter. The performance of the calorimeter was checked by measuring the standard heat of neutralization of an aqueous solution of sodium hydroxide with a standard aqueous HCl solution. The MeCN solution of NO<sup>+</sup>ClO<sub>4</sub><sup>-</sup> (0.1 M) was prepared inside the argon-filled drybox with an analytical balance and volumetric flask before each calorimetric run; the calibrated motor-driven buret, filled with 2 mL of NO<sup>+</sup> solution, and the reaction vessel, containing about 40 mL of a nitranion solution (in excess), were connected to the calorimeter insert assembly.

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A dry argon atmosphere was maintained at the top of the reaction vessel to protect anion **1** from unexpected reaction. The reported  $\Delta H_{rxn}$  is the average value of two or three independent runs which consisted of up to six titrations with the same stock solution.

**Measurement of Redox Potentials.** Redox potentials were obtained by CV at 23 °C on a BAS-100B electrochemical analyzer following the procedure as described earlier.<sup>9a</sup> All sample solutions were prepared in MeCN and were 1.5 mM in concentration. The ferrocenium/ferrocene redox couple (Fc<sup>+</sup>/Fc) was taken as an internal standard. Reproducibility is usually 5 mV for ionic species and 10 mV for neutral species.

**Preparation of NO Gas.** NO gas was produced by reaction of NaNO<sub>2</sub> with sulfuric acid in the absence of oxygen and was purified by passing through 10% NaOH<sub>aq</sub> to remove higher oxides of nitrogen and finally through a solid NaOH drying tube to remove water.<sup>7</sup>

**General Procedure for Preparation of Anions **1** and **2**.** The method of E. M. Arnett et al.<sup>24</sup> was followed: the anion precursor (0.2 mmol) was dissolved in 15 mL of dry acetonitrile; then a slight excess of KH was added. The mixture was stirred at room temperature for about 40 min and then filtered directly into the reaction vessel. All the operations were carried out in an argon-filled VAC drybox.

**Product Analysis for the Reaction of NO with **1**.** The flask containing 15 mL of a CH<sub>3</sub>CN solution of substrate **1** (0.2 mmol) was degassed with argon three times by the freeze–thaw method. After it was warmed to room temperature, 25 mL of NO (in excess) was slowly bubbled into the reaction vessel with an airtight Hamilton syringe through a soda lime-filled column (to remove water). The mixture was stirred at room temperature for 30 min, and then dry Ar was bubbled in to expel excess NO. The reaction mixture was worked up followed by crystallization to afford *N*-nitroso-3,6-dibromocarbazole **3** as the sole product (94%). Product **3**: mp 150 °C (dec); *m/z* (EI, %) 352/354/356 (M/M + 2/M + 4, 12.2:24.6:11.7), 322/324/326 (47:100:51), 243/245 (12:14), 164 (71), 30 (11.6); IR (KBr, cm<sup>-1</sup>) 1592, 1582, 1570, 1470, 1447, 1420, 1400, 1325, 1276, 1240, 1230, 1200, 1135, 1075,

1059, 1040, 1030, 970, 877, 827, 808. Anal. Found: C, 41.04; H, 1.81; N, 7.86. Calcd for C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>OBr<sub>2</sub>: C, 40.67; H, 1.69; N, 7.91.<sup>25</sup>

**Product Analysis for the Reaction of NO with **2**.** The same procedure as described above was followed for this reaction. The product mixture was worked up by chromatography to give 9,9'-dimer **6** as the sole product (91% yield). Product **6**: *m/z* (EI, %) 758/760/762/764/766 (M/M + 2/M + 4/M + 6/M + 8, 0.22:1:1.41:1:0.24); 379/381/383 (45:100:51); 351/353/355 (36.5:67.2:34); 336/338/340 (32.5:60.7:30.2); 320/322/324 (6.4:14:10); 241/243 (18.6:19.4); 162(32.5);  $\delta_H$ (CDCl<sub>3</sub>) 3.84 (6H, s), 7.07~7.50 (12H, m); IR (KBr, cm<sup>-1</sup>) 1730, 1445, 1390, 1253, 1243, 1170, 1120, 1070, 1030, 1089, 924, 900, 807, 720, 680, 665. Anal. Found: C, 47.86; H, 2.51. Calcd for C<sub>30</sub>H<sub>18</sub>Br<sub>4</sub>O<sub>4</sub>: C, 47.28; H, 2.38.

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(25) Product **3** is a new compound, its structure can be easily identified on the basis of its MS spectrum. The main fragmentation pattern is shown below:

