

# Explosion and Ion Association Chemistry of the Anion Radicals of 2,4,6-Trinitrotoluene, 2,6-Dinitrotoluene, and Trinitrobenzene

Matthew L. Batz, Paul M. Garland, Richard C. Reiter, Michael D. Sanborn, and Cheryl D. Stevenson\*

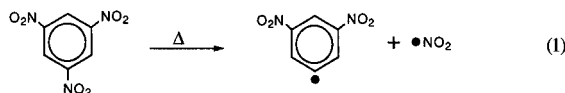
Department of Chemistry, Illinois State University, Normal, Illinois 61790–4160

Received November 26, 1996

EPR analysis shows that the anion radical of 2,6-dinitrotoluene (DNT) in liquid ammonia exists with the counterion (either  $K^+$  or  $Na^+$ ) associated with one of the two nitro groups. This tight association ( $-NO_2^{\cdot-}M^+$ ) persists after solvent removal, and it renders the anion radical very susceptible to loss of metal nitrite. The slightest agitation of the solid potassium salt of  $DNT^{\cdot-}$  leads to detonation, and formation of  $KNO_2$  and polymer (in the solid phase) and  $CH_4$ ,  $HCN$ ,  $H_2$ , and  $N_2O$  (in the gas phase). Trapping experiments suggest that the methane comes from carbenes, and it is suggested that the  $HCN$  comes from an anthranil radical intermediate. The potassium anion radical salts of 1,3-dinitrobenzene, 2,6-dinitrotoluene, 1,3,5-trinitrobenzene, and 2,4,6-trinitrotoluene all readily lose  $KNO_2$ , and the ease of  $C-NO_2^{\cdot-}M^+$  bond rupture increases with the degree of nitration. In the cases of the two trinitrated systems dissociation takes place immediately upon anion radical formation in liquid ammonia. This observation is consistent with the fact that only the systems with two nitro groups vicinal to a methyl group yield  $HCN$  upon detonation.

## Introduction

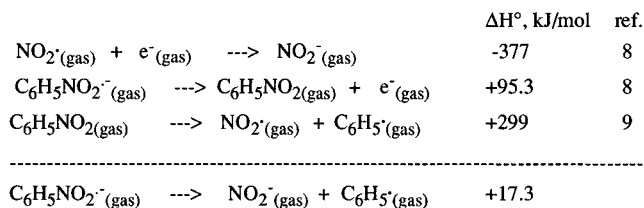
The initial reaction leading to the ignition of solid state field explosives is endothermic.<sup>1</sup> This helps render the explosive material able to be handled in the absence of strong shock or impact. In the cases of nitroaromatic field explosives, which include 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), and 2,6-dinitrotoluene (DNT),<sup>2</sup> the endothermic homolytic cleavage of the  $C-NO_2$  bond (e.g. reaction 1) is the key primary step leading to explosion.<sup>3,4</sup>



The resulting free radicals then initiate the subsequent exothermic reactions leading to the sudden consumption of all of the solid explosive. The elegant work from Brill's and Tsang's groups has unraveled much of the mechanistic detail concerning these explosive reactions.<sup>3–6</sup>

However, there remains confusion over the great variability in the impact and shock sensitivity of nitroaromatic explosives, despite a wide number of correlations having been made. Some of these correlations have been called absurd,<sup>1</sup> and an excellent review of these matters, with some historical content, was published 4 years ago by Brill and James.<sup>3</sup> In spite of the unclear nature of this variability, it is known that ignition sites occur in local heated regions of the material called "hot spots".<sup>1</sup> It is known that these hot spots are normally formed mechanically, yet prediction of the sensitivity of

## Scheme 1



an explosive remains elusive, as we still have insufficient knowledge of hot spot conditions.<sup>1</sup> Here we wish to propose the possibility of "chemically induced hot spots."

This proposal is a result of two recent empirical considerations:<sup>7</sup> (1) innocuous nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ) can be rendered a very shock and impact sensitive explosive via the one-electron reduction to its anion radical ( $M^+, \text{C}_6\text{H}_5\text{NO}_2^{\cdot-}$ ) and (2) the explosions of the solid alkali metal salts are sufficiently hot to result in the pyrolysis of any neutral nitrobenzene present. This latter fact was deduced from the observation of  $\text{NO}_2$  in the product gasses from explosions involving  $M^+\text{C}_6\text{H}_5\text{NO}_2^{\cdot-}$ , contaminated with  $\text{C}_6\text{H}_5\text{NO}_2$ , while  $\text{NO}_2$  is absent when no neutral nitrobenzene is present in the anion radical explosive.<sup>7</sup> The extreme sensitivity of the anion radical salt is a result of the tight association of the cation with the electronegative nitro group making it a good leaving group leading to potassium nitrite. The normally very endothermic nature of the initial homolytic bond cleavage is also compromised (by more than 281 kJ/mol), Scheme 1.

Adding to the possibility of the presence of "chemically induced hot spots" is the fact that nitroaromatic anion radicals are very thermodynamically stable. Further, they can form via electron transfer from hydroxide ion. Can the presence of small amounts of anion radical salt contaminants in bulk TNT, DNT, or TNB pose a realistic premature explosion hazard?

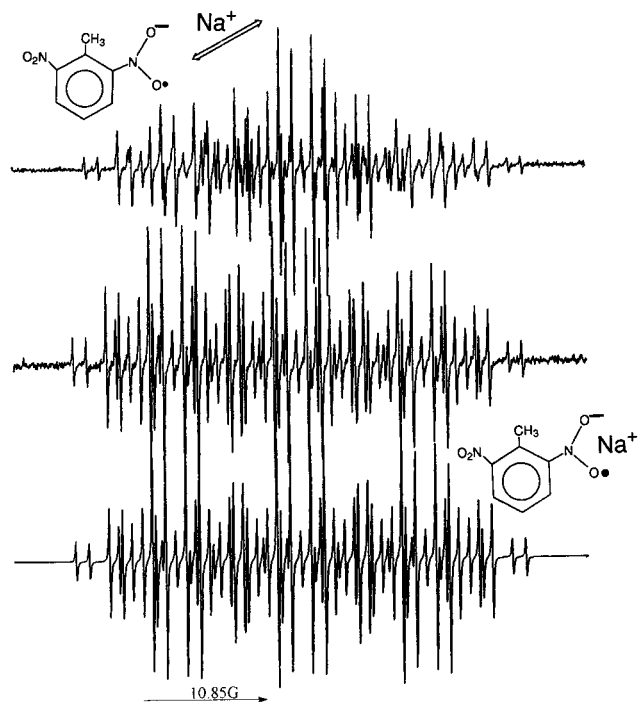
(7) Stevenson, C. D.; Garland, P. M.; Batz, M. L. *J. Org. Chem.* **1996**, *61*, 5948.

\* Abstract published in *Advance ACS Abstracts*, March, 15, 1997.  
(1) Traver, C. M.; Chidester, S. K.; Nichils, A. L., III. *J. Phys. Chem.* **1996**, *100*, 5794.

(2) Kohler, J.; Meyer, R. *Explosives*; VCH: Weinheim, 1993.  
(3) Brill, T. B.; James, K. J. *J. Phys. Chem.* **1993**, *97*, 8752.  
(4) Tsang, W.; Robaugh, D.; Mallard, W. G. *J. Phys. Chem.* **1986**, *90*, 5968.

(5) (a) Brill, T. B.; James, K. J. *J. Phys. Chem.* **1993**, *97*, 8759. (b) Brill, T. B.; Brush, P. J.; James, K. J.; Shepherd, J. E.; Pfeiffer, K. J. *Appl. Spectrosc.* **1992**, *46*, 900. (c) Brill, T. B.; James, K. J. *Chem. Rev.* **1993**, *93*, 2667.

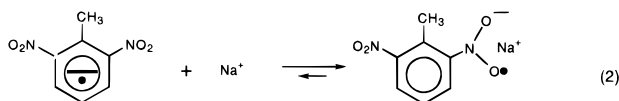
(6) He, Y. Z.; Cui, J. P.; Mallard, W. G.; Tsang, W. *J. Am. Chem. Soc.* **1988**, *110*, 3754.



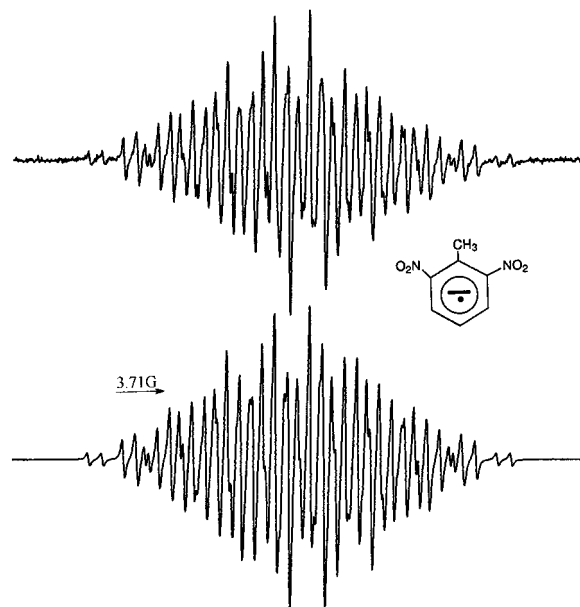
**Figure 1.** (Top): EPR spectrum of the sodium anion radical salt of DNT in liquid ammonia recorded at 200 K. (Middle) EPR of the same sample but with 0.2 M added NaI. (Bottom): Computer simulation generated using the following parameters:  $a_{\text{H}} = 3.78$  G (2H),  $a_{\text{H}} = 2.93$  G (3H),  $a_{\text{H}} = 1.16$  G (1H),  $a_{\text{N}} = 10.85$  G (1N), peak to peak line width = 0.095 G.

## Results and Discussion

The addition of a small amount of solvated electron, produced by dissolving sodium metal in liquid ammonia, to a  $10^{-3}$  M liquid  $\text{NH}_3$  solution of DNT results in the immediate formation of the anion radical of DNT, as evidenced by the very persistent EPR signal. The EPR signal of  $\text{DNT}^{\cdot-}$  prepared in this manner is well resolved and exhibits the coupling constants shown in Figure 1. Two important features exhibited by Figure 1 are the facts that the electron spin is interacting with only a single nitrogen and that the single nitrogen has a modulating hyperfine splitting resulting in the obvious line width alternation. This is most likely due to the very rapid formation and dissociation of a tight ion pair between the sodium cation and one of the two  $\text{NO}_2$  groups, reaction 2. If the equilibrium is shifted far to



the right, the charge and spin density would be localized in the associated nitro group, and this nitrogen would exhibit the broad-sharp-broad pattern shown in Figure 1, top. The high-field line is further broadened by  $g$ -tensor anisotropy due to slow molecular tumbling in solution. If this analysis is correct, the addition of sodium iodide to the ammonia solution should shift the equilibrium all the way to the right and eliminate the line width alternating pattern and simultaneously increase the nitrogen splitting. These expectations were, indeed realized, Figure 1, middle. To further support this analysis the Na reduction of DNT was carried out in hexamethylphosphoramide (HMPA), where ion associa-



**Figure 2.** (Top) EPR spectrum of the sodium anion radical salt of DNT in HMPA recorded at 298 K. (Bottom): Computer simulation generated using the following parameters:  $a_{\text{H}} = 4.46$  G (2H),  $a_{\text{H}} = 2.75$  G (3H),  $a_{\text{H}} = 1.085$  G (1H),  $a_{\text{N}} = 3.712$  G (2N), peak to peak line width = 0.21 G.

tion is greatly reduced.<sup>10</sup> In HMPA two equivalent nitrogens are observed, and there is no evidence of modulating line widths, Figure 2.

Reduction with potassium metal in liquid ammonia leads to analogous EPR results. Removal of the solvent under reduced pressure leaves the dark red crystalline salt,  $\text{K}^+\text{DNT}^{\cdot-}$ . After exposure to high vacuum for about 1 h, the solid anion radical salt is free of residual ammonia. This was evidenced by the fact that the addition of  $\text{H}_2\text{O}$  to this solid yields a water solution that is free of ammonia. This is in contrast to the anion radical alkaline earth metal salts which do retain ammonia in a complex, e.g.,  $\text{Ba}^{2+}(\text{NH}_3)_2(\text{naphthalene}^{\cdot-})_2$ .<sup>11</sup>

The  $\text{K}^+\text{DNT}^{\cdot-}$  salt exhibits extreme thermal and shock sensitivity. This material is much more sensitive to agitation than even  $\text{K}^+\text{C}_6\text{H}_5\text{NO}_2^{\cdot-}$ . Even the vibrations from the mechanical pump next to the vacuum line can result in the detonation of  $\text{K}^+\text{DNT}^{\cdot-}$ . In all cases a gentle agitation of the evacuated reaction vessel containing the salt resulted in a violent detonation concomitant with a yellow flash of light and the production of a dark cloud inside of the reaction vessel. To avoid the shattering of the reaction vessel, care was taken to use small amounts of salt (<200 mg) and large glass reaction vessels (100 mL), which could accommodate the volume of evolved gas. It should be noted that even under these conditions, the apparatus was occasionally shattered.

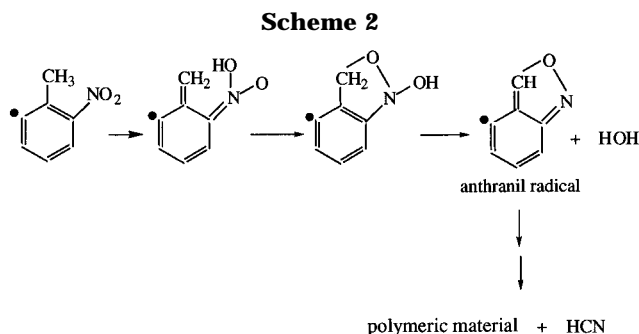
IR spectra of the noncondensable (liquid nitrogen) gasses indicated that  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{HCN}$  are the only IR active gasses generated in the explosion. With the exception of  $\text{HCN}$  these are the same gasses gener-

(8) Chowdhury, S.; Kishi, H.; Dillow, G. W.; Kebarle, P. *Can. J. Chem.* **1989**, *67*, 603.

(9) McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(10) (a) Stevenson, C. D.; Echegoyen, L.; Lizardi, L. R. *J. Phys. Chem.* **1972**, *76*, 1439. (b) Leven, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Am. Chem. Soc.* **1970**, *92*, 2268.

(11) (a) Stevenson, C. D.; Schock, L. E. *J. Am. Chem. Soc.* **1983**, *105*, 3742. (b) Stevenson, C. D.; Schock, L. E.; Concepcion, R.; Peterson, R. A. *J. Phys. Chem.* **1985**, *89*, 175.



ated in the explosions of  $K^+C_6H_5NO_2^{\cdot-}$ s and the potassium salts of the *o*-, *m*-, and *p*-nitrotoluene anion radicals. The difference in the decomposition chemistry of the  $DNT^{\cdot-}$  system is accounted for by the fact that a nitro group remains vicinal to the methyl group after the loss of nitrite. The presence of the  $CH_3$  group next to the remaining  $NO_2$  group facilitates the breakdown of the radical ( $\{CH_3\}\{NO_2\}C_6H_3^{\cdot}$ ), just as it facilitates the decomposition of *o*-nitrotoluene over that of nitrobenzene.<sup>4,12</sup>

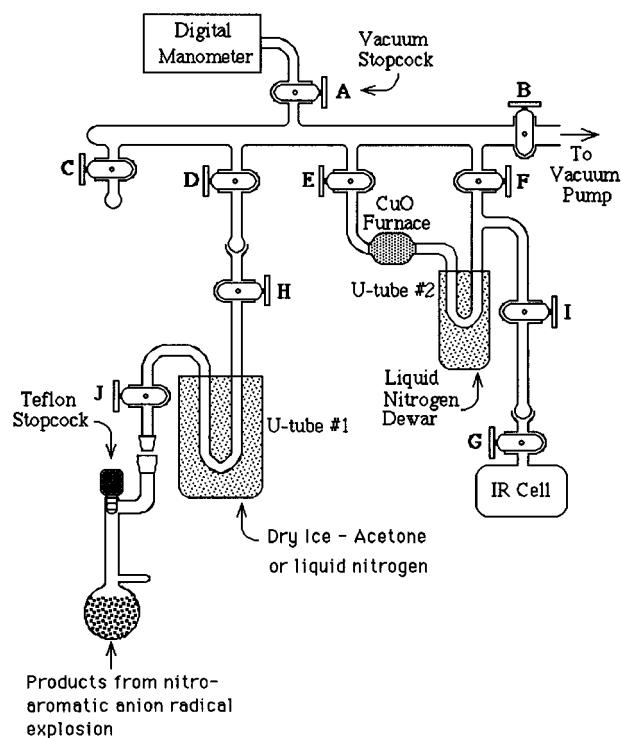
The pyrolysis of *o*-nitrotoluene (*o*- $CH_3$ - $C_6H_4NO_2$ ) follows a different mechanism than that of  $C_6H_5NO_2$  as evidenced by the formation and destruction of anthranil during the decomposition of the former.<sup>12</sup> Anthranil (a stable intermediate) provides a pathway with a lower energy of activation. It also leads to the formation of cyano compounds. A proposed mechanism for the formation and breakdown of the anthranil radical that is analogous to that proposed for anthranil is shown in Scheme 2.

To support the conclusion that the HCN comes from the anthranil radical, samples of the solid potassium salt of the *m*-dinitrobenzene anion radical were generated in an identical manner. These red crystals also explode upon gentle agitation, and the explosion gasses are the same as those observed in the  $K^+DNT^{\cdot-}$  explosions with the exception of HCN. HCN is not a product of the explosion of  $K^+m-C_6H_4(NO_2)_2^{\cdot-}$ .

The noncondensable (in dry ice-acetone) gasses for all salts, which amount to about 1.0 mol/mol of solid salt, were allowed into a high-vacuum system, Figure 3. The vacuum system was equipped with a CuO oven and an IR cell. Heating of the CuO furnace resulted in an immediate drop in the total pressure to 38% of its original value ( $CuO + H_2 \rightarrow Cu + H_2O$ ), indicating that 62% of the gas was hydrogen. The simultaneous deposition of water ice in the frozen U-tube was also observed.

When the deep blue solvated electron solution in liquid  $NH_3$  comes in contact with TNT dissolved in liquid ammonia, a white precipitate is immediately formed, and the clear ammonia solution proved to be diamagnetic upon EPR analysis. Evaporation of the ammonia leaves an off-white solid which explodes upon agitation. Water was distilled onto the solid through the vacuum system, and the water soluble portion was separated. IR analysis of this water soluble material proved it to be potassium nitrite. The remaining material appeared to be polymeric in nature and was very sensitive toward explosion upon agitation. The explosion gasses were  $CO$ ,  $CO_2$ ,  $CH_4$ , and HCN.

The sensitivity toward loss of an  $NO_2^-$  group increases as more  $NO_2$  groups are added to the nitrotoluene anion



**Figure 3.** Vacuum apparatus used for the analysis of the gasses produced from the detonation of the solid nitroaromatic anion radical salts. The system was pumped down to  $10^{-6}$  Torr prior to opening the Teflon stopcock allowing the gasses into the vacuum line.

radical systems:  $K^+o-(CH_3)C_6H_4(NO_2)^{\cdot-} < K^+DNT^{\cdot-} < K^+TNT^{\cdot-}$ . This latter system is so sensitive toward loss of a nitrite that  $KNO_2$  splits off immediately upon one electron reduction. Since the  $C-NO_2^{\cdot-}M^+$  bond ruptures while the anion radical is dispersed in solution, no detonation is experienced. The remaining radical  $[(CH_3)C_6H_4(NO_2)_2^{\cdot}]$  polymerizes and apparently incorporates some  $K^+TNT^{\cdot-}$  into the resulting polymer. It is probably a solid TNT anion radical salt contaminant that gives rise to the sensitive explosive nature of the polymer.

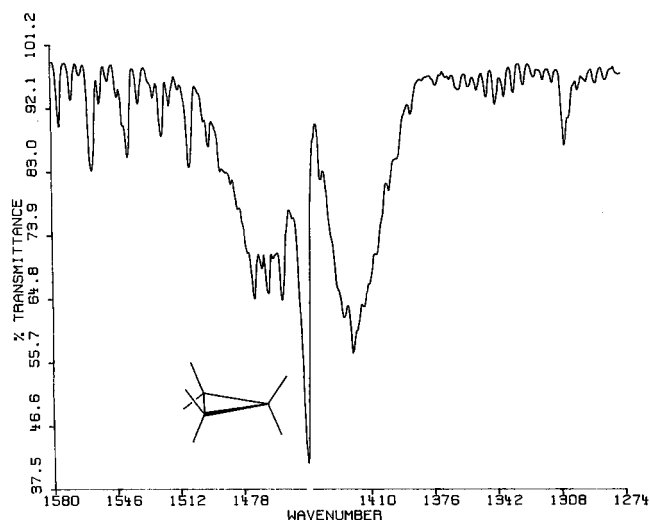
The rapid loss of  $NO_2^-$  from  $TNT^{\cdot-}$  must mean that a very tight ion pair between one of the nitro groups in the anion radical and the potassium counterion exists upon reduction. This species does not have a sufficient lifetime (prior to loss of  $KNO_2$ ) in liquid ammonia for EPR observation. However, the trinitrobenzene anion radical has been observed in tetrahydrofuran, with a sodium counterion which is, indeed, tightly associated with one of the nitro groups as evidenced by the EPR hyperfine splittings:  $a_N = 7.86$  G (1N) and  $a_N = 0.31$  G (2N).<sup>13</sup>

The TNB system also yields a precipitate and formation of potassium nitrite upon reduction in liquid ammonia. The solids remaining after solvent removal behave in nearly an identical manner to that of the TNT system. However, in the case of TNB, no HCN is observed in the postexplosion gasses of the polymeric solid. This was the expected result, as there is no methyl moiety to interact with a remaining  $NO_2$  group.

Methane is a product resulting from the explosion of all of the nitroaromatic anion radicals investigated (including those of nitrobenzene, *o*-, *m*-, and *p*-nitrotoluene,<sup>7</sup> *m*-dinitrobenzene, DNT, TNT, and TNB). It has

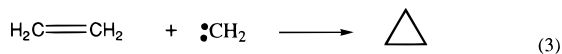
(12) Gonzalez, A. C.; Larson, C. W.; McMillen, D. F.; Golden, D. M. *J. Phys. Chem.* **1985**, *89*, 4809.

(13) Berzaghi, M.; Oliva, C.; Simonetta, M. *J. Phys. Chem.* **1981**, *85*, 1799.



**Figure 4.** Gas phase FT-IR spectrum of the reaction product that was frozen out at  $-142\text{ }^{\circ}\text{C}$  resulting from the explosion of  $\text{K}^+\text{DNT}^-$  anion radical solid salt under 530 mm of ethylene. The strong peak at  $1444\text{ cm}^{-1}$  is due to a  $\text{CH}_2\text{-CH}_2$  bending mode in cyclopropane (see: Pinchas, S.; Lauticht, I. *Infrared Spectra of Labelled Compounds*; Academic Press Inc.: New York, 1971; p 80).

been proposed, for the nitrobenzene system, that the  $\text{CH}_4$  results from a carbene intermediate.<sup>7</sup> To add support to the proposal of carbene intermediates, the explosions of the potassium anion radical salts of nitrobenzene, *o*-nitrotoluene, and DNT were carried out in a flask charged with 530–600 Torr of ethylene. In each case, cyclopropane (Figure 4) was found to be present in the gaseous products. Cyclopropane is the expected product from the reaction between carbene and ethylene, reaction 3.



### Conclusions

Nitrobenzene, nitrotoluene, dinitrobenzene, dinitrotoluene, trinitrobenzene, and trinitrotoluene all form anion radicals in liquid ammonia upon reduction with potassium, and the potassium counterion is tightly associated with just one of the nitro groups. Upon removal of the solvent, the potassium ion remains tightly associated with a single  $\text{NO}_2$  moiety. This association renders the anion radical very sensitive toward breakage of the  $\text{C-NO}_2\text{-K}^+$  bond. If this bond rupture takes place in the solid state (where many anion radicals and nitroaromatic molecules are in close proximity), an explosion results. The ease of nitrite loss is increased with  $\text{NO}_2$  substitution, and it takes place in the TNT and TNB systems prior to solvent (liquid ammonia) removal. The cleavage of the  $\text{C-NO}_2\text{-M}^+$  bond follows the “regio-conserved” or heterolytic (mesolytic) mode, as observed for other anion radical systems.<sup>14</sup>

In view of the above, it seems likely that small amounts of anion radical contamination in nitroaromatic field

explosives represent “chemically induced hot spots” that could lead to inadvertent explosion.

### Experimental Section

Samples of each anion radical were generated via reduction of the corresponding nitroaromatic in an evacuated apparatus. A glass bulb containing an alkali metal mirror suspended above a bulb containing 30–40 mL of liquid ammonia at ca.  $-30\text{ }^{\circ}\text{C}$  containing the 1.5–2.5 mmol of nitroaromatic was cooled to  $-78\text{ }^{\circ}\text{C}$ . This resulted in the condensation of ammonia onto the metal mirror. The blue solvated electron could then drip down into the nitroaromatic solution. After formation of the desired amount of anion radical, the tube containing the metal mirror was sealed from the apparatus. EPR samples were then taken by pouring a portion of this solution into an attached sample tube. The EPR analysis was carried out with a Bruker ER-200 spectrometer.

The solvent was removed under reduced pressure leaving deeply colored crystals. The solid anion radical salts were then left exposed to vacuum ( $10^{-3}$  Torr) to ensure the complete removal of the ammonia. The resulting crystals are extremely shock and impact sensitive. In some cases, it was necessary to support the apparatus so as to protect it from the vibration of the vacuum pump to prevent premature detonation, and the all-glass apparatuses were always kept behind explosion shields. The quantity of anion radical salt was always small, and detonation normally did not rupture the 100 mL glass bulb containing it. The detonations were initiated by simple agitation of the glass bulb.

To insure that  $\text{NH}_3$  did not remain in the solid salt, samples of the salts were quenched with  $\text{H}_2\text{O}$ , and the resulting  $\text{H}_2\text{O}$  solution was divided into two equal portions. One portion was boiled for 15 min to eliminate any dissolved ammonia, and both were titrated with a standard solution of  $\text{HCl}$ . Both titrations proved to be identical indicating the absence of ammonia.

The bulbs containing the detonation products were connected to the high-vacuum system through U-tube 1, which was cooled to  $-78$  or  $-190\text{ }^{\circ}\text{C}$ , Figure 3. After the line was pumped down to about  $10^{-6}$  Torr, the stopcock separating the bulb and the high-vacuum system (stopcock J) was opened and the gasses were allowed into the line. The pressure in the vacuum system was monitored with a Fluid Precision Inc. capacitron pressure gauge to  $\pm 0.01$  Torr. The final pressures ranged from 50 to 100 Torr. From the known volume of the vacuum system (831.6 mL), the number of moles of noncondensable gases that passed through the U-tube was obtained. The relative amounts of the gaseous products varied slightly from experiment to experiment. However, about 1 mol of noncondensable gas was obtained per mole of anion radical. Of these noncondensable gasses, about two-thirds proved to be hydrogen in each case. In no case was anything found in the chilled U-tube 1.

When the noncondensable gasses were exposed to a  $300\text{ }^{\circ}\text{C}$   $\text{Cu-CuO}$  furnace, the pressure dropped due to the oxidation of the  $\text{H}_2$  to form water, which was trapped in U-tube 2. In separate experiments mixtures of methane and hydrogen were injected into the system to verify that the hot  $\text{CuO}$  would selectively oxidize the  $\text{H}_2$  leaving the  $\text{CH}_4$ . This vacuum system was fitted with a 10 cm gas IR cell allowing us to take an IR sample of the gasses at any time. The solid ash remaining after the explosion was analyzed via LASER desorption mass spectroscopy and, in all cases, proved to be polymeric in nature.

After the detonations under ethylene, the reaction flask and U-tube 1 (Figure 3) were placed in a bath of solid-liquid methylcyclopentane ( $-142\text{ }^{\circ}\text{C}$ ). The entire system was then evacuated leaving only condensable (at  $-142\text{ }^{\circ}\text{C}$ ) materials. The melting point of ethylene is  $-169\text{ }^{\circ}\text{C}$ , and that of cyclopropane is  $-128\text{ }^{\circ}\text{C}$ . Thus, the  $-142\text{ }^{\circ}\text{C}$  U-tube will trap (freeze) cyclopropane and not ethylene under vacuum conditions. Later, warming of the U-tube and reaction flask to room temperature allowed expansion of the condensable gas into

(14) (a) Guthrie, R. D.; Shi, B. *J. Am. Chem. Soc.* **1990**, *112*, 3136.  
(b) Maslak, P.; Guthrie, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 2628.

the IR cell. Only cyclopropane was observed upon IR analysis, Figure 4.

Spectroscopic analyses were carried out using a Nicolet FT-IR and a gas cell fitted with sodium chloride windows. Matrix-assisted laser desorption time of flight mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

**Acknowledgment.** We wish to thank the National Science Foundation (Grant CHE-9011801) and the Petroleum Research Fund administered by the American Chemical Society for support of this work.

JO9622082