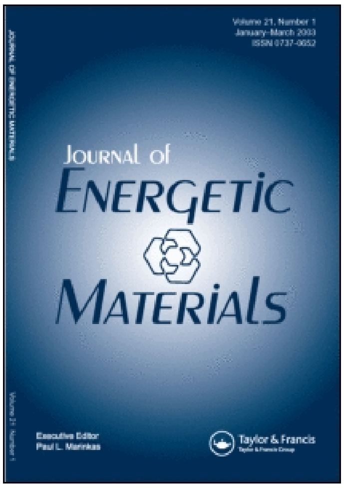

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Stability and Degradation Processes of 2,4,6-Trinitrotoluene (TNT) on Metal Oxide Surfaces

Melissa Mileham[a]; A. E. Stiegman[a]; Michael P. Kramer[b]
[a] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL [b] Air Force Research Laboratory, Munitions Directorate, Ordnance Division, Energetic Materials Branch, (AFRL/MNME), Eglin, AFB FL

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Stability and Degradation Processes of 2,4,6-Trinitrotoluene (TNT) on Metal Oxide Surfaces

MELISSA MILEHAM
A. E. STIEGMAN

Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL

MICHAEL P. KRAMER

Air Force Research Laboratory, Munitions Directorate, Ordnance Division, Energetic Materials Branch, (AFRL/MNME), Eglin, AFB FL

The chemical stability of 2,4,6-trinitrotoluene (TNT) when placed in physical contact with metal oxide surfaces is investigated. The TNT is deposited at 1–3 monolayers of coverage on the surface of microcrystalline MnO_2*,* CuO*,* WO_3*,* MoO_3*,* Bi_2O_3*,* SnO_2*, and* Fe_2O_3 *by wet impregnation. The samples were placed in a 50°C oven and allowed to react over a period of 11 months. Periodically, samples were removed and analyzed chromatographically to determine whether products were being formed at the surface of the oxide. TNT proved to be inert to most oxides; however, both* CuO *and* MnO_2 *effected a clean decomposition of the TNT into tri-nitrobenzene.*

Keywords: trinitrotoluene (TNT), metal oxides, degradation

Address correspondence to A. E. Stiegman, Dept. of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306.

Introduction

A new approach to the development of high output explosives and pyrotechnics is the use of binary inorganic solid-state reactive materials in combination with traditional organic high explosives such as 2,4,6-trinitrotoluene (TNT), cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX), and 1,3,5,7-tetramethylene-2,4,6,8-tetranitramine (HMX). These binary energetic materials are stoichiometric mixtures of metal (fuel) and metal-oxide (oxidant) particles, which react through a solid-state redox reaction that is typified by the well-known thermite reaction.

$$\mathrm{Fe_2O_3 + 2Al \rightarrow\ Al_2O_3 + 2Fe} \quad \Delta\mathrm{H} = 3.97\ \frac{\mathrm{kJ}}{\mathrm{g}}$$

The advantage to these inorganic materials is that the energy density can be several times higher than conventional explosives; however, the rate of energy release is usually significantly lower.

To overcome this problem, a new generation of composite materials has been developed in which inorganic fuel/oxidant systems are mixed with conventional explosives (e.g., TNT, RDX and HMX). In these systems, the energy release of the binary metal/oxide system is driven by the conventional explosive, thereby releasing energy much more rapidly and in a controlled fashion. Studies to date have indicated that this approach affords great promise in exploiting the high energy density provided by binary inorganic energetic compositions. In the case of TNT it has been studied with various oxidant phases and fuels (e.g., MnO_2 and Al, Al-Zr and Mg-Al alloys) as high-energy-density explosives for high penetration applications and as components for boosters and primers and, in fact, patents exist on this technology [1–3].

An important issue related to the incorporation of conventional organic high-energy materials with metal/metal-oxide binary compositions is one of inherent incompatibility between the organic and inorganic phases. This incompatibility arises from deleterious surface chemistry between the organic and metal or metal-oxide phase in the composite. These deleterious processes arise from interfacial chemical processes including, but not exclusively, reduction at the metals (fuel) surface and oxidation at the oxide surface. The magnitude of these processes will likely be exacerbated by the degree of contact between the organic materials and the metal or metal-oxide surfaces and will be affected by temperature, humidity and other ambient conditions of storage and handling.

This report is the first in a series describing the results of a comprehensive study of the compatibility of organic high-energy materials with metal oxide oxidant phases. In this report the compatibility of 2,4,6-trinitrotoluene (TNT) when placed in physical contact with a range of metal oxides is assessed from the degree of chemical degradation observed over time. The metal oxides were chosen based on their use or proposed use in composite energetic materials.

Experimental

Materials

MnO_2 (Aldrich, reagent grade, $>90\%$ purity, $\sim 10\,\mu m$ particle size), CuO (Aldrich, nanopowder, $\sim 33\,nm$), Fe_2O_3 (Fisher, anhydrous) MoO_3 (nano and micron, Climax Molybdenum), SnO_2 (Keeling & Walker Ltd.), WO_3 (Atlantic Equipment Engineering) and Bi_2O_3 (Aldrich), were used as received from the manufacturer. 2,4,6-Trinitrotoluene (TNT) was obtained from Chemservice and sublimed prior to use. Acetonitrile (Acros, reagent grade) was used as received.

Long-Term Surface Reactivity Studies

Samples for long-term reactivity studies were prepared using a wet impregnation technique. Sixty milligrams of TNT, dissolved in acetonitrile, was slurried with 1 g of the metal oxide, after which the acetonitrile was pumped off under vacuum (10^{-3} torr) to leave a dry powder. The approximate coverage area of TNT is $986\,m^2/g$, based on an estimated area of a TNT molecule obtained from treating the molecule as a disk with the outer circumference defined by the oxygen atoms of the nitro groups (obtained from the crystal structure of

1,3-dinitrotoluene) with a radius extending from the center of the aromatic ring.

Sealed containers containing the samples were placed in an oven held at 50°C. Periodically, a small portion of the powder (~0.10 g) was withdrawn and stirred into 1 mL of acetonitrile. The solids were allowed to settle and supernatant liquid containing the organic species was analyzed by HPLC using a 60:40 H_2O/CH_3OH solution as the mobile phase at a flow rate of 0.75 mL/min. A UV detector was used and set to a fixed wavelength of 254 nm. The detector response was calibrated with known concentrations of TNT and trinitrobenzene (TNB). Notably, the two compounds show a negligible difference (1.86%) in the integrated peak areas per molar quantity, indicating an almost identical detector response (extinction coefficient). The presence of new compounds formed from interfacial chemistry was evident in the chromatograph by comparison to control samples. The percent degradation was determined from the ratio of the integrated peak area of the TNT in the HPLC with the sum of all the peak areas. For samples that showed only minimal degradation, no attempt was made to determine the products. For oxides that induced significant amount of degradation the product was characterized by GC-MS.

Thermal Analysis

Differential scanning calorimetry (DSC) was performed on a TA Instruments DSC Q1000 under both O_2 and an inert (N_2) environment at a flow rate of 40 mL/min. Samples were prepared using the wet impregnation technique described above. A 2-mL aliquot of TNT (0.13 M in acetonitrile) was added to 1 g of MnO_2 or CuO and the solvent was removed under vacuum. The dry powder containing TNT deposited on the surface of the metal oxide was then analyzed. Samples of pure TNT and TNT deposited on silica gel and on LiF and KBr were also analyzed to differentiate surface chemistry specific to the metal oxides. The samples were all placed in sealed aluminum pans for DSC analysis; however, the pure TNT sample pan had a pin-prick for ventilation purposes.

Results and Discussion

Degradation Studies

The long-term degradation studies were designed to simulate long-term ambient storage of multicomponent high-energy materials where TNT would be in intimate contact with metal oxide surfaces. Relatively low concentrations (~1–3.5 monolayers) of TNT were deposited on the oxide surfaces to isolate specific interfacial chemistry and to allow sensitive detection of reaction products relative to the TNT (i.e., without the chromatogram being overwhelmed by large amount of TNT). Table 1 shows the oxides surveyed in the study and their TNT surface coverage in the prepared samples.

A chromatogram of the samples was taken immediately upon preparation to establish the initial purity. They were then placed in a 50°C oven under the ambient atmosphere and allowed to react over the course of ~11 months with samples withdrawn periodically over that time and analyzed by HPLC. The amount of decomposition of the TNT over time for each oxide surface where measurable decomposition is observed is shown in Fig. 1.

Table 1

Coverage levels (monolayers) of TNT on metal oxides

Metal oxide	BET surface area (m^2/g)	TNT coverage (monolayers)
MnO_2	40.2477	1.49
CuO	31.9157	1.88
WO_3	17.0450	3.52
MoO_3 (large)	24.9929	2.40
MoO_3 (nano)	55.1272	1.09
Bi_2O_3	25.9291	2.31
SnO_2	21.3088	2.82
Fe_2O_3	32.9970	1.82

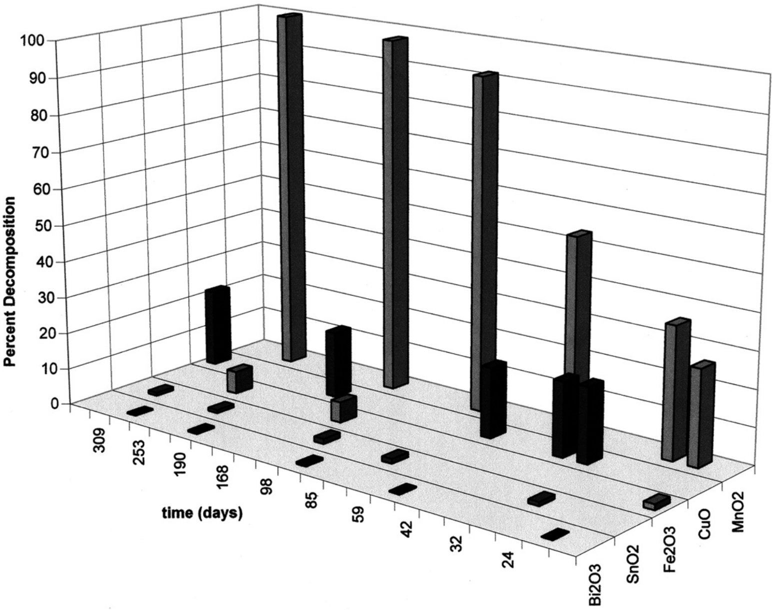


Figure 1. Percent decomposition over time of TNT deposited on various metal oxide substrates.

TNT proved to be inert or only slightly reactive on the majority of oxide surfaces. In particular, no detectable decomposition was observed for MoO_3 and WO_3. As indicated in Fig. 1, small amounts of decomposition ($<10\%$) were observed for Bi_2O_3, Fe_2O_3, and SnO_2. over the duration of the study. For two of the oxides, CuO and MnO_2, more extensive decomposition was observed with 21% of the TNT consumed over CuO and essentially complete (100%) consumption observed for MnO_2. For the case of CuO, the decomposition reached its maximum after about one month (Fig. 1) but did not react further after that. This suggests that that reaction is stoichiometric with a specific surface site, which, once consumed, ceases to react further. Conversely, for MnO_2, the reaction proceeds to completion, suggesting either a large amount of surface sites on the MnO_2 or that the reaction is catalytic. An important aspect of

TNT reactivity on both of these surfaces is that the HPLC data indicates that the reaction is quite clean, going primarily to a discrete product as opposed to decomposition into multiple species with MnO_2 being somewhat cleaner than the CuO. Moreover, based on a comparison of the retention times, the product is the same for both oxides.

Reactivity of TNT on MnO_2

Thermal Analysis. Thermal analysis of pure trinitrotoluene using differential scanning calorimetry (DSC) is shown in Fig. 2.

The thermal scan shows a sharp endotherm at 80°C, which corresponds to melting, and an exotherm whose observed peak at this scan rate (10°/min) is at 306°C, which corresponds to the decomposition of the molecule. This thermal decomposition process has been studied previously and was found to initially involve oxidation of the methyl group but, even in the early stages of reaction, it is quite complex and ultimately yields

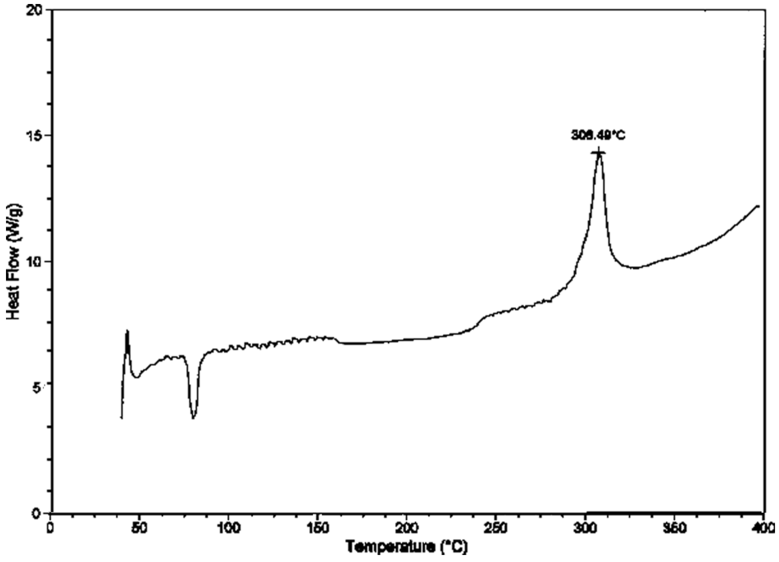


Figure 2. Differential scanning calorimetry trace of pure TNT (note exothermic processes are above the baseline).

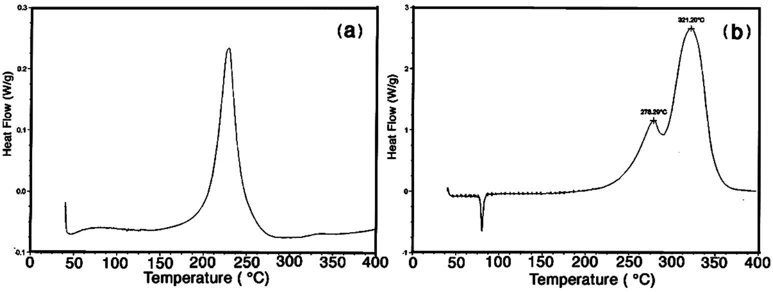


Figure 3. DSC of (a) 1.4 and (b) 4 monolayers of TNT deposited on MnO_2.

telomeric or polymeric materials [4–7]. When the sample is analyzed in a sealed container, the decomposition becomes an explosive event with an abrupt release of energy. When considering composites of TNT with inorganic oxides, the effect of the organic–inorganic interface on these well-known thermal processes is of interest. The DSC plot of TNT deposited at ~1.4 monolayer loadings on MnO_2 is shown in Fig. 3.

At these coverage levels, the melting endotherm is not observed. This is expected since no crystalline bulk phase is present. More importantly, however, the thermal decomposition process occurs at 229°C, which is significantly lower than the bulk. When the amount of TNT is increased to >4 monolayers, two exothermic processes are observed, one whose peak is close to that resolved in the bulk (321°C) and a low-temperature exothermic process at 278°C. Our preliminary interpretation of this complex thermal behavior is that it represents the superposition of interfacial and bulk processes observable at the higher loadings of TNT though it may reflect a more complex decomposition process than is initiated at the surface. A similar, but less dramatic, interfacial effect is observed on CuO with monolayer coverage yielding a decomposition exotherm at 280°C and excess loadings showing interfacial and bulk decomposition at 294 and 318°C, respectively.

It is important to determine whether the interfacial mediation of the decomposition temperature is specific to those oxides

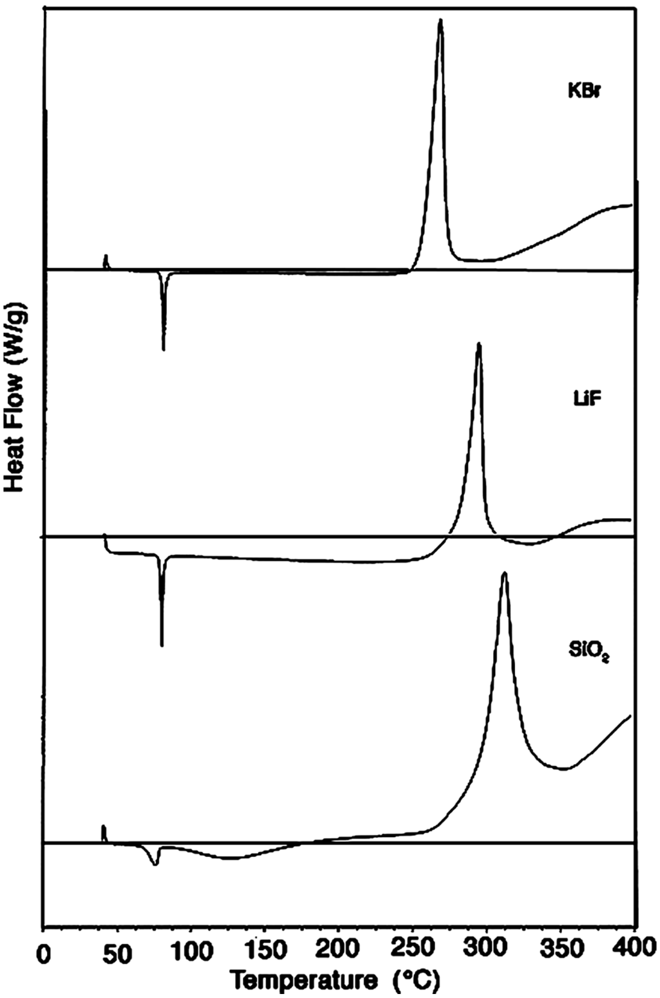


Figure 4. DSC traces of TNT deposited on KBr, LiF, and SiO_2 (note: exotherms are above the line).

or constituted a general surface effect. Thermal analysis of monolayers of TNT deposited on inert oxides and salts indicates (Fig. 4) that in almost all cases the decomposition temperature is modified. On fumed silica the decomposition temperature is very close to the bulk at 310.8°C, indicating that the silica surface is inert. Interestingly, on simple salts the interfacial effect is pronounced. Specifically, LiF shows a decomposition temperature of 293.0°C, and KBr shows an even stronger surface effect, with a decomposition temperature of 270.9°C.

These results do not provide a chemical rationale for the interfacial effect, nor do they provide any specifics on the decomposition pathway(s) on the surface. However, it is clear from the thermal analysis data that there is a pronounced and surprisingly general surface effect between TNT and solid surfaces. This effect might well mitigate energy release processes or affect long-term stability of heterogeneous composite mixtures.

Kinetics and Product Analysis. Reaction processes and decomposition pathways of trinitrotoluene deposited on the surface of microcrystalline MnO_2 were monitored by HPLC. Initial chromatographic data (Fig. 5) shows only a sharp peak at a retention time (RT) of 18.57 min, which is assigned to TNT itself by comparison to a standard solution of TNT in acetonitrile. No other significant products are observed.

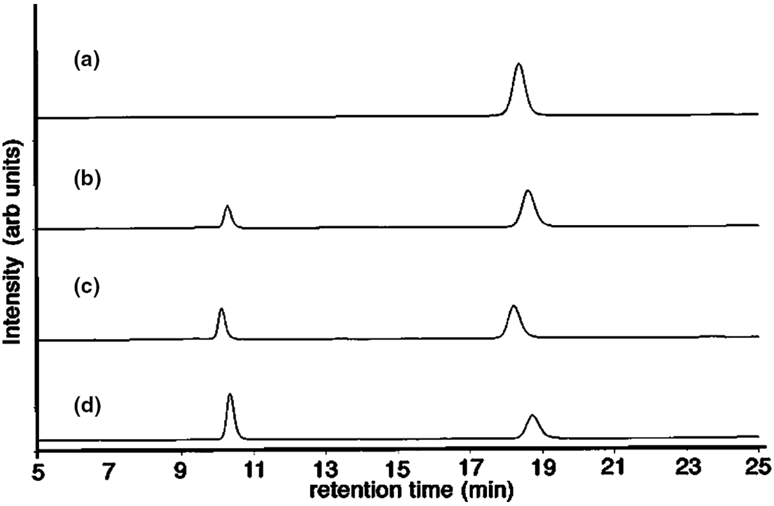


Figure 5. HPLC chromatograms of the products of 1.4 monolayer of TNT deposited on MnO_2 (a) initially and at 50°C for (b) 16, (c) 24, and (e) 42 days.

The samples were kept at a constant temperature of 50°C and reanalyzed after 16 days. The chromatogram shows two peaks, the TNT peak and a new species eluting earlier with a retention time of $\sim$10.26 min. After another 8 days of reaction, the chromatogram indicates that this species has continued to be produced and is now present in approximately equal amounts to the starting material. Also present in the chromatogram are small amounts of additional species that elute significantly faster. The observed pattern of more quickly eluting species appearing over time is suggestive of a general decomposition of the TNT into a lower molecular weight species. Notably, however, these faster eluting species represent a very small amount of the total dissolved mass and, in fact, the chromatographic data shows that TNT is actually being converted relatively cleanly into a single product in a solid-state reaction on the surface of the MnO_2. Finally, chromatograms collected after 42 days show that the new species is now predominant, suggesting that most of the TNT has been converted. The faster eluting species, while still present, has not increased significantly in concentration.

Similar observations were made from the surface reaction of TNT with CuO. Chromatographic data indicates the formation of the same species eluting at 18.57 min after 31 days of reacting at 50°C. While the species that forms is the same, the extent of reaction is much more limited and, after 39 days, there is little additional formation of this product. As with MnO_2, faster eluting species are also present which, while still minor, make up a larger fraction of the total dissolved material than they do in the MnO_2.

Characterization of the main product of the solid-state reaction was carried out by GC-MS (Fig. 6).

Injection of the product mixture, after reaction for 31 days on MnO_2, resolved two relatively intense peaks at 11.83 and 11.9 min retention time on the GC. The mass spectrum of the 11.9 min peak shows the classic fragmentation pattern for TNT with a weak parent-ion peak at 227.0 m/z and a more intense peak at 210.0 m/z corresponding to $[\mathrm{TNT{-}OH}]^+$ due to the loss of O from an o-nitro group and a H from the methyl group with ion bombardment to produce $[C_7H_4(NO_2)_2(NO)]^+$ [8]. The mass

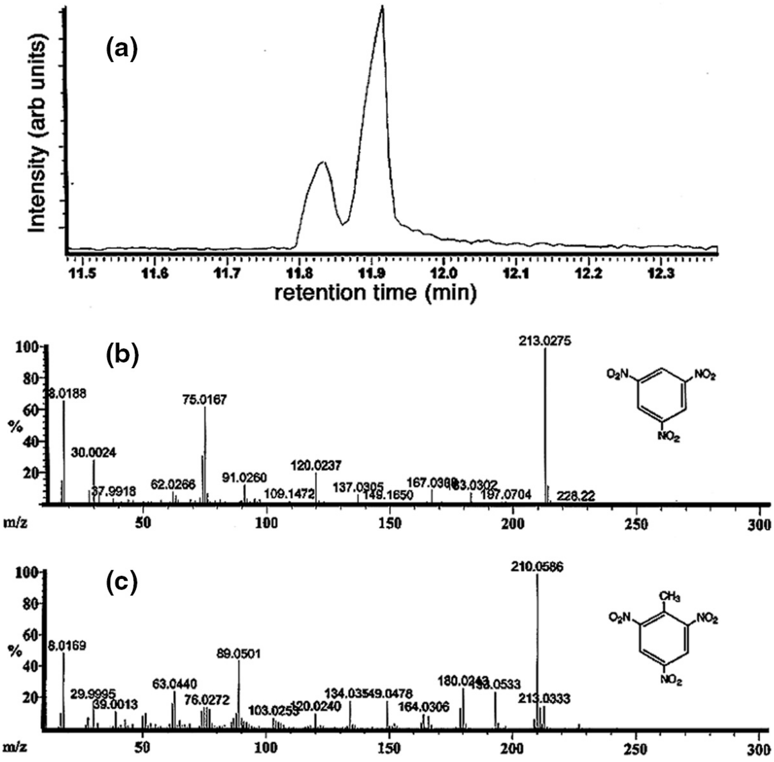
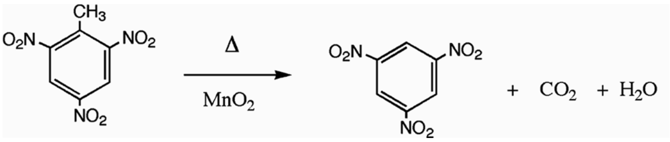


Figure 6. (a) Gas chromatogram showing two principle components at 11.83 and 11.9 min whose mass spectra identify them as (b) trinitrobenzene and (c) unreacted TNT respectively.

spectrum of the species that elutes at 11.83 min shows a strong peak at 213.0 m/z and a series of peaks at 167.0, 120.0, and 75.0 m/z. The 213.0 m/z peak can be assigned as the parent peak of trinitrobenzene (TNB), $C_6H_3(NO_2)_3$, and the progression comes from sequential loss of NO_2 (or NO_2 and H) groups. This assignment is confirmed unambiguously by comparison to the published fragmentation pattern of a trinitrobenzene. The mass spectrum was also collected on some of the minor species resolved by the gas chromatogram. They have not been fully characterized but, as would be expected, the slower eluting species appear to be higher molecular weight biphenyl species and the faster eluting species are lower molecular weight decomposition fragments. Similar data was collected for the CuO catalysis. The primary product of the solid-state reaction is TNB, though, as indicated by the HPLC data, conversion to TNB is not as extensive as it is in the case of the MnO_2. The gas chromatograph indicates that there are generally more species, both slower and faster eluting, than form with MnO_2, suggesting that conversion to TNB is less clean and that there is more net decomposition of the TNT.

While the mechanistic details of the reaction are not completely known, water has been observed forming in bulk studies. As such, this suggests that the net reaction is:



A likely pathway is the initial oxidation of the methyl group followed by a rapid decarbonylation process. Kinetically, the reaction is extremely slow and plots of the relative concentration of TNT as a function of time are qualitatively consistent with a reaction that is pseudo-first-order in TNT. Further analysis of the data using the generalized approximate rate equation (Eq. (1)) derived by Wilkinson is shown in Fig. 7 [9].

$$\frac{t}{p} = \frac{nt}{2} + \frac{1}{K} \tag{1}$$

In Eq. (1), p is the fraction reacted, t the time in days, n the reaction order, and K (day^{-1}) is an apparent rate constant which is related to the true rate constant by $K = kc_o{}^{n-1}$. Evaluation of the slope for the early stages of the reaction ($p \leq 0.4$), yields a reaction order of 1.4, consistent with a first-order dependence on TNT and an apparent rate constant of 0.02/day day for MnO_2. The half-life for the reaction is 35 days. In the absence of more detailed data about the reaction products and mechanism, the kinetics analysis cannot be taken too far

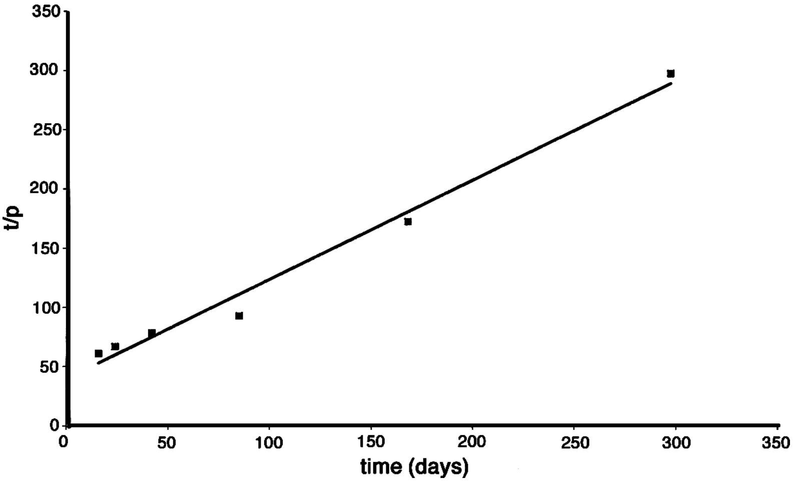


Figure 7. Plot of decomposition data of TNT on MnO_2 over time fit to Eq. (1).

and only serves to indicate the order and the relative efficiency of the reaction. It also should be noted that it is not known whether the reaction is catalytic, using O_2 as the oxidant, or whether it is stoichiometric, with oxygen taken from specific sites on the metal oxide surface.

The net reaction is of considerable interest from a synthetic standpoint, since there are, to the best of our knowledge, no previous reports of direct demethylation of aromatics. Moreover, there is no cost-effective synthesis for TNB even though, from an energetic standpoint, it is a superior high-energy material. The most direct synthesis reported to date involves the conversion of phloroglucinol into trioximes with hydroxylamine followed by oxidation to trinitrobenzene with nitric acid [10]. As such, a single-step heterogeneous synthesis may be of commercial utility in producing TNB. Unfortunately, attempts to scale up as a solution-solid reaction over MnO_2 or as a solid-state reaction involving larger amounts of TNT were not successful. From all the data obtained so far, the reaction appears to occur as a very slow interfacial reaction.

Conclusions

From the standpoint of compatibility, it is clear that the interfacial chemistry between TNT and inorganic surfaces can be pronounced. As indicated by the thermal analysis work, this involves, at one level, changes in the normal thermal decomposition pathways of the molecule, which may or may not have a net effect on stability or energy release in bulk composite materials. For redox active metal oxide phases the interfacial processes can result in a net chemical reaction that will slowly convert the TNT to another species and possibly to degradation products. For the specific oxides reported here, the interfacial reaction converts TNT to TNB relatively cleanly and quantitatively for MnO_2 and with more overall decomposition than for the case of CuO. Clearly, this result indicates that in composite energetic materials containing these components the TNT will be changing over time, which suggests that stability and energy release may also be variable. Moreover, once conversion to TNB is accomplished, further decomposition may occur and adversely affect properties.

Both MnO_2 and CuO react with TNT under relatively mild conditions. For both oxides a major product of this solid-state reaction is the demethylation of TNT to form TNB. Over CuO this reaction does not appear to be exclusive, as many other species are formed, nor does it proceed to completion.

Acknowledgments

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