

The hydrothermolysis of the picrate anion: kinetics and mechanism

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Abstract

The hydrothermolysis of the picrate anion in aqueous solution has been studied at 260–325 °C in liquid water. At starting pH values above 12, the disappearance of picrate begins immediately and is first order in OH⁻. At lower pH, there is an induction period preceding the disappearance, and over the pH range 6.7–11.9 there is no pH dependence in the developed reaction phase. Added borate and silicate salts promote the reaction, suggesting their acting as nucleophiles at hydrothermal conditions. Nitrite is an initial product, while acetate is a final product and reflective of a vigorous oxidative sequence consuming the intermediate products. A reaction sequence consistent with the results at the lower pH includes initiation of a chain process by displacement of nitrite by water, followed by nucleophilic displacement of nitrite by nitrite such that a nitro group is replaced by an O–N=O group. The ester then rapidly hydrolyzes, and the net reaction is the production of an additional nitrite with each cycle. A simple modeling of this system satisfactorily fits the experimental findings. © 2002 Elsevier Science B.V. All rights reserved.

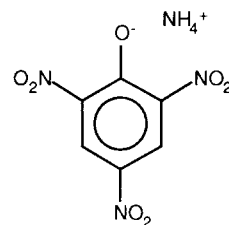
Keywords: Hydrothermolysis; Ammonium picrate ; Nucleophilic displacement; Hazardous waste disposal

1. Introduction

The disposal of large quantities of excess and obsolete energetic materials remains a major problem in both the government and private sectors [1]. Open burning, open detonation, and controlled incineration are the currently preferred methods of destruction, and their utilization continues to escalate. That growth proceeds in the face of increasing political and public pressure fostered by ever-rising concerns over safety and environmental soundness of the operations.

Alternatives to combustion have been sought accordingly, and among the more promising of those considered are processes involving near critical and supercritical water [2]. The discussion here describes studies in very hot water with ammonium picrate,

commercially referred to as Explosive D. The virgin material is insensitive to shock and can be safely handled, but old, stored samples that have been in contact with metals and atmospheric moisture can become highly sensitive and their handling can be hazardous. Since the material is water-soluble and can be safely handled in solution, its thermal decomposition to innocuous products in water was considered a possible route to its safe disposal.



Ammonium Picrate

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We are unaware of any reported studies of the decomposition of aqueous picric acid or the picrate anion, although kinetics studies of the decomposition of the neat acid have been reported over the range 180–270 °C [3,4]. In that case, the process is complex, proceeding in possibly five distinct stages, and an induction period is present to 230 °C. At higher temperatures the induction period vanishes. No product data were provided, nor apparently were there any attempts to probe the induction process with added substances.

The study described here follows the large body of innovative work in hydrothermal media by Brill and coworkers featuring a variety of kinetics monitoring techniques [5–7]. The picrate chromophore made it an excellent candidate for spectrophotometric monitoring of its thermal behavior in very hot water. Studies were conducted in a high pressure/temperature spectrophotometer cell in liquid water at 260–320 °C. The products of the decomposition were also determined in conversions conducted in small bomb reactors.

2. Experimental procedures

2.1. Material preparation

Stock solutions of ammonium picrate were prepared by neutralizing solutions of picric acid with stoichiometric quantities of ammonium hydroxide. The final pH was 6.7. The picric acid was used as received from Altech Chemical Co. as a moist solid containing 35% water. All reactant solutions were prepared with degassed Millipore water.

2.2. Kinetics studies

2.2.1. Spectrophotometry

The picrate anion offers a convenient chromophore for studying the reaction kinetics spectrophotometrically at about 360 nm. The spectrophotometer used in this work was a Hewlett-Packard Model HP 8452A diode-array instrument interfaced with an HP Vectra VL2 computer operating HP8532 UV–VIS software. The designs for cell and oven used in geochemical studies by Susak et al. [8] were adapted for this study, and a sketch of the cell is presented in Fig. 1. The cell body is 316 stainless steel, and the internal volume is

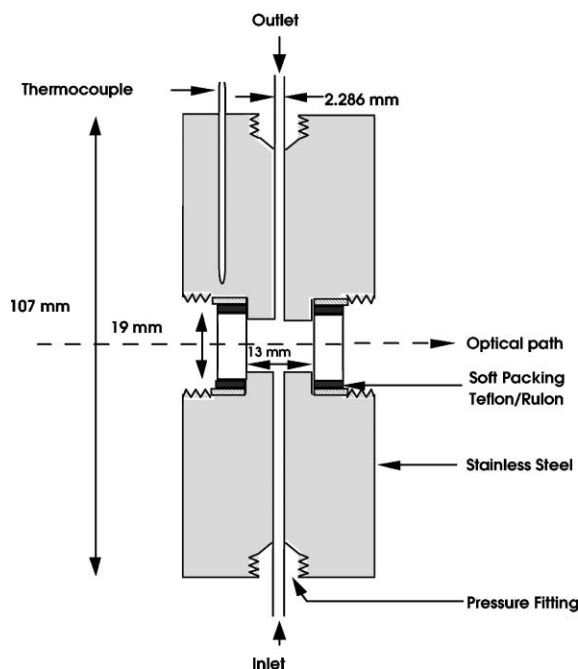


Fig. 1. Spectrophotometric cell for kinetics studies in hydrothermal media.

about 3 ml. The quartz windows are sealed against the cell body with Rulon/Teflon packing. Temperature of the cell is monitored with a NiCr/NiAl (K-type) thermocouple. The cell inlet is connected to an HPLC Pump (WATERS, M-45) through the inlet valve (Whitey, SS-ORS2). The outlet side of the cell is mated to an Autoclave Engineers high temperature valve (Model no. HT-A13280), which is followed by a NOSHOK pressure gage, a pressure relief valve (Cajon Model no. SS-4R3A, 300–5000 psi), and a shutoff valve (Whitey, SS-ORS2).

The cell is heated in a snugly fitting resistance tube furnace with circular openings in the optical path. The furnace core is a stainless steel tube wrapped with 5 m of insulated Nichrome wire (0.280 Ω/m). The core is then wrapped with Kaowool insulation and housed within a thin-walled brass tube capped on either end with transite. To provide thermal protection for the spectrophotometer the brass housing is then wrapped with a water jacket of soft copper tubing. The entire furnace assembly is mounted on an aluminum plate fashioned to replace the standard sample holder in the spectrophotometer. The temperature is controlled by

an Eurotherm temperature controller (808 L1 NO NO QS AKKC 100).

In operation, the system began at room temperature with the cell flushed with mill-Q water, and a spectrum was obtained to serve as the blank. Heating was then begun and when the temperature of the cell reached the selected set point, the study solutions were pumped through the cell. Picrate concentrations of about 3.2 mM were used. The pressure of the system was set by adjusting the relief valve. Once a stable spectrophotometer signal was recorded at the desired wavelength, the run was initiated by closing the inlet and outlet valves.

2.2.2. Batch studies

We conducted a small number of runs in a batch mode. Solutions were heated in quartz reactors as described in the following sections, and removed from a thermostated oven at selected intervals for analysis using a Hewlett-Packard 1090 HPLC equipped with a Hypercil C18 column.

2.3. Product studies

Reactions for product studies employed 6.0 mM ammonium picrate solutions in 5 ml sealed quartz reactors. The reactors were cleaned initially with acetone and baked at 260 °C for a few hours. Once loaded, the reactors were torch-sealed under argon. Care was taken not to heat the solution as the vial was being sealed. The reactors were then placed inside stainless steel bombs with enough water present to mimic the head space/liquid volume ratio in the reactor tube, minimizing the pressure stress across the quartz walls.

The bombs were heated in a thermostated oven heated at selected temperatures. In one series, samples were removed at various times and quenched in an ice bath. Remaining picric acid and other organics were determined using a Hewlett-Packard 1090 HPLC equipped with a Hypercil C18 column. Inorganic products were determined with a Dionex 2000i ion chromatograph equipped with a conductivity detector. When product gases were determined, the reactions were conducted in stainless steel bombs with quartz inserts.

A second series of experiments involved exhaustive decomposition at pH 13. Similar analytical techniques were used in this case.

3. Results

3.1. Chemical kinetics

The results of several experiments at 300 °C are shown in Fig. 2. The figure presents points representing picrate concentrations over periods of tens of minutes, and shows a range of behavior with changing pH and the addition of salts. The figure also includes first order curves developed from the decay behavior.

The hydrothermolysis of ammonium picrate alone at a starting pH of 6.7 showed an initial flat, or induction, period followed by an abrupt decline in concentration in the developed phase of the process. A pH boost to 11.9 with the addition of KOH substantially reduced the induction phase, but did not fully eliminate it. It is seen that the developed phases are sensibly accommodated by the first order curves, and it is notable that the increase in basicity of about five orders of magnitude did little to change the rate of the developed reaction. A further pH increase to 12.7 (conducted in sealed quartz tubes), both fully eliminated the induction period and substantially increased the reaction rate.

The next experiments included the addition of borate and silicate salts. They were conducted following some unexpected preliminary results with ammonium picrate and other NO₂-containing energetic materials in hydrothermal studies performed in both sealed Pyrex and sealed quartz tubes. In the Pyrex cases the apparent rates of decomposition were strikingly greater than those in the quartz tubes. This result led to the suspicion that borate and silicate were in some manner promoting the reactions, and that effect was subsequently demonstrated in the quantitative work with the hydrothermal cell.

(These results, including those for a broader range of energetic materials, are described in recently issued patents [9,10].)

Sodium borate and sodium silicate solutions are themselves basic, and the starting pH of the salt-added runs are noted in the figure. It is clear from the figure that the salts provide substantial promotion of the overall rates of reaction. The major effect, however, is the elimination of the induction period, with an immediate first order decay of picrate levels. It is seen in the cases of the salt-free runs that once they enter the developed phases, the loss rates are within an order of magnitude of those with the added salts.

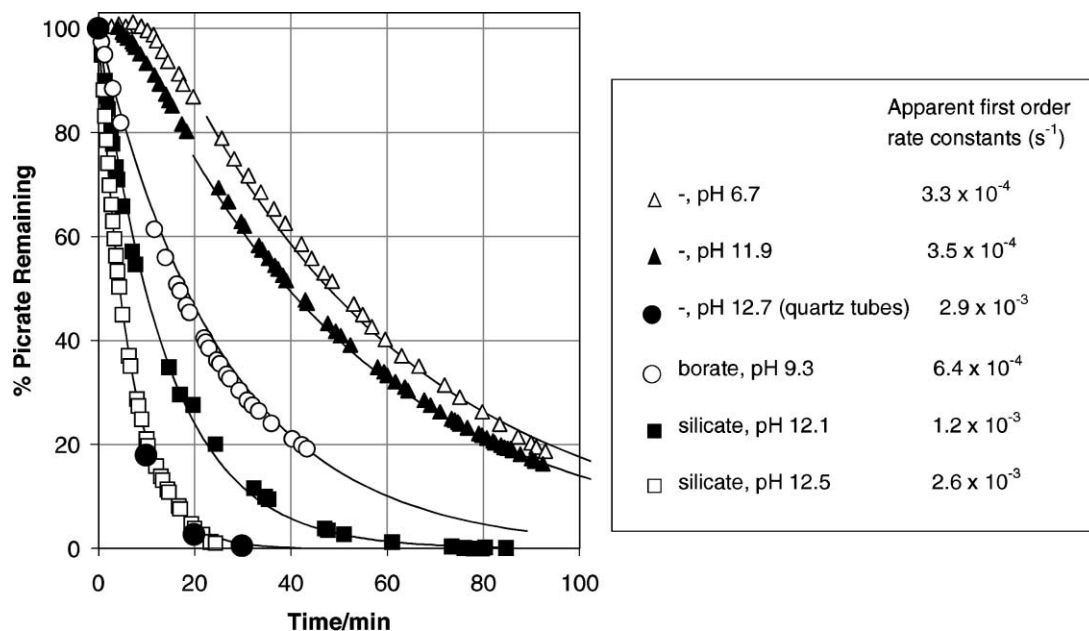


Fig. 2. Picrate loss as a function of time over a range of conditions. The smooth curves correspond to the respective apparent first order rate constants.

The results from the KOH/pH 11.9 and borate-added runs are of particular interest. For the borate case the induction phase is fully eliminated, in the face of its being at a pH almost 3 units above that for the KOH-added system. That result suggests that borate and other similar oxyanions including silicate must themselves be chemically active in the process, most likely as nucleophiles in aromatic substitution reactions.

Ammonium picrate solutions at pH 6.7 were next studied over a range of temperatures (280–325 °C) and the induction times varied from about 40 min at the lower temperatures to below 10 min at the highest. In each case, the developed phases were reasonably well fit with first order rate constants, and an Arrhenius plot of those data is presented in Fig. 3. As is discussed next, induction behavior most often precedes a chain reaction, and the first order fit is an artifact not reflecting true first order chemistry. The linear Arrhenius response shown in the figure nonetheless reveals a mechanistic consistency over the temperature range, and can be useful in projecting behavior over a broader range of temperatures.

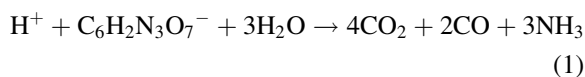
The Arrhenius parameters developed from the figure are $\log A = 12.6 s^{-1}$ and $E_a = 41.2 \text{ kcal/mol}$.

They compare sensibly well to those reported for the decomposition of neat, liquid picric acid over the range 183–270 °C of $\log A = 11.6 s^{-1}$ and $E_a = 38.6 \text{ kcal/mol}$ [3], as reflected by the Arrhenius line for those parameters in Fig. 3. These results suggest a close correspondence between the thermolytic and hydrothermolytic breakdown schemes in the neat liquid and aqueous solutions respectively.

3.2. Product studies

Product studies were conducted with aqueous picric acids solutions adjusted to pH 13.0 with KOH. The solutions were heated at 300 °C/30 min, conditions representing a period of about 15 half-lives, or well above 99% decomposition. The results are shown in Table 1.

The table shows an accounting for both C and N balances, respectively at 85 and 89%. The product slate, however, does not reflect a fully exhaustive conversion, which would have fit stoichiometry (1) and the accompanying equilibria (2) and (3):



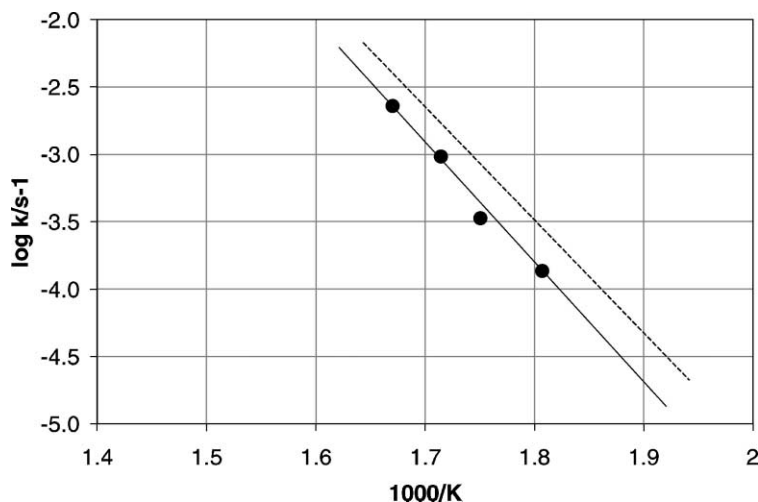


Fig. 3. Arrhenius plot of the apparent first order rate constants for the developed region of picrate loss at pH 6.7. The dashed line corresponds to the data of Andreev and Liu [3] for the pyrolysis of neat picric acid.

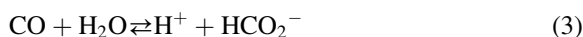
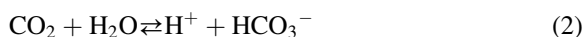


Table 1
Products of the hydrothermolysis of aqueous picrate at pH 13.0 and 300 °C/30 min

Phase	Product	Yields ^a
Carbon		
	Gas	
	CO ₂	9
	CO	11
	CH ₄	nd
Solution	Acetate	60
	Formate	5
	Glycolate	nd
	Bicarbonate	nd
Recovered solid	–	<1 ^b
Total C accounted for		85
Nitrogen		
	Gas ^b	
	N ₂ O	7
	N ₂	40
Solution	Nitrite	3
	Nitrate	<1
	Ammonium	39
Recovered solid	–	<1 ^b
Total N accounted for		89

^a Reported as final yields in percent of initial carbon and nitrogen, nd: not detected.

The nitrogen and carbon are only partially reduced and oxidized, respectively, and it is clear there is a kinetic barrier to full conversion at our conditions. The process proceeds as described, however, as evidenced by the formation of acetate as a major product. Acetate is of course a highly stable species thermodynamically [11], undoubtedly a key feature of the kinetic obstacle to full conversion. It is notable that the methyl carbon in acetate is reduced well below that of any of the carbon atoms in picrate. As a whole, however, acetate formation mirrors a net oxidation, and its presence signals the occurrence of some very highly reactive oxidation chemistry.

Broader insights into the reaction details were developed in experiments conducted in sealed quartz reactors at 260 °C/pH 2.4 and 300 °C/pH 12.7 where some of the simple products could be monitored with time. The results are presented in Table 2. Not surprisingly, at the more modest conditions, the consumption of the starting picric acid/picrate was considerably slowed. Nitrite was an initially formed product, seen in the earliest samples well before any acetate is noted, and it is noteworthy that significant, initial levels of nitrite were recorded even at pH 2.4. Acetate is a late product on the other hand, and representative of the brisk oxidation of the initial oxidation products noted

Table 2
Hydrothermolysis of aqueous ammonium picrate at 300 °C/pH 12.7^a

Temperature (°C)/pH ^b	Time (min)	Picrate (mM)	Nitrite (mM)	Acetate (mM)
260/2.4	0	6.1	nd	–
	70	5.9	0.9	–
	232	3.6	1.9	nd
	479	2.1	1.7	0.4
300/12.7	0	6.1	nd	nd
	9	1.2	8.5	nd
	20	0.3	5.6	4.9
	30	<0.1	5.8	7.0

^a nd: not detected, estimated to be <0.05 mM.

^b Starting, measured at 25 °C.

above. The nitrite levels do not climb indefinitely in accord stoichiometrically with the consumed picrate, but appear to settle at some steady-state value before falling to the low level shown in Table 1.

4. Discussion

The data collected both in the kinetics and product studies reflect a vigorous oxidation–reduction chemistry fully destroying both the picrate anion and its daughter products under hydrothermal conditions. Nitrite is an initial product, and at highly basic conditions it must be formed through nucleophilic

displacement by OH[−]. It appears, moreover, that at temperatures above 250 °C where the dielectric constant of water falls to values around 30 [12], oxyanions such as borate and silicate can also act as nucleophiles, displacing nitrite. (That quality probably applies as well to a large family of oxyanions including sulfate and phosphate.)

Fig. 4 is a logarithmic plot of the apparent first order rate constants in Fig. 2 versus the starting pH of the test solutions. The data show that there is no pH dependence at pH values from about 12 down to at least pH 6.7. A first order dependence on OH[−] at pH >12 is reflected by the regression line shown in the figure (slope = 1.09, *r*² = 0.88). Thus at these conditions the reaction rate is controlled by Eqs. (4) and (5), where O₂N–Ar–O[−] is picrate and ONu[−] represents nucleophilic oxyanions, reactions that must overcome anion–anion repulsion. We are aware of no examples of nucleophilic substitution reactions involving an anionic substrate, but the data support that supposition

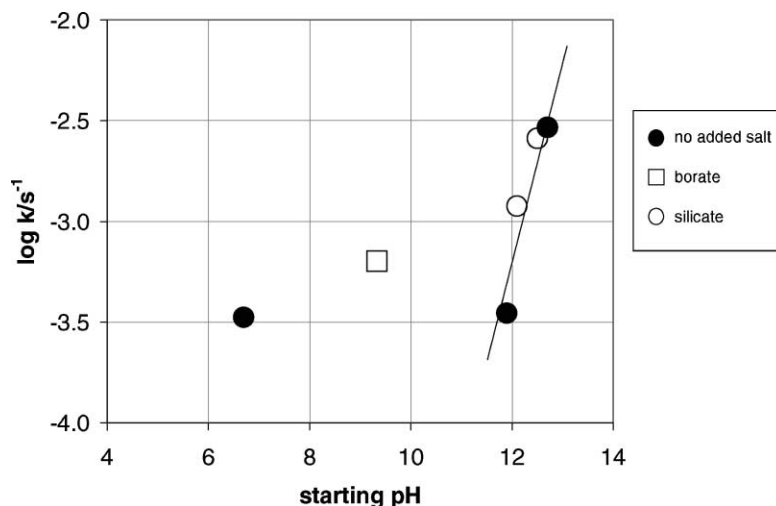
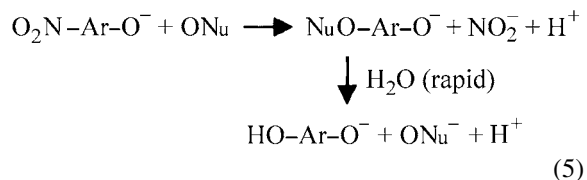
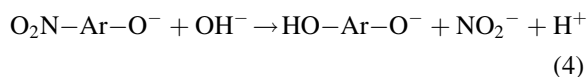
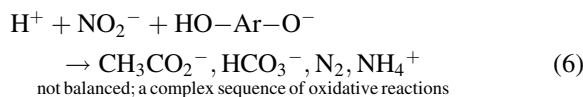


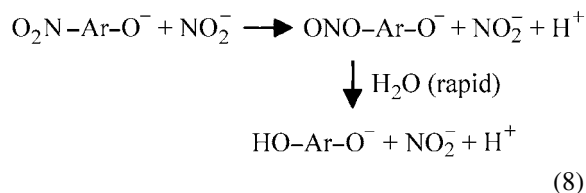
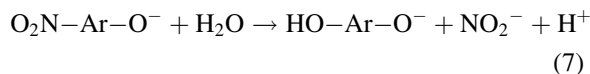
Fig. 4. Effect of starting pH and added borate and silicates salts on the reaction rate. The pH in the “no added salt” cases was adjusted by adding aqueous KOH. The regression line is shown for the points at pH 11.9 and above (slope = 1.09, *r*² = 0.88).

Exhaustive oxidation then follows in Eq. (6), in what must be a sequence of oxidations involving NO_x chemistry that cannot be simply defined:



It is significant, however, that the hydroquinone-like products from Eqs. (4) and (5) are inherently readily oxidizable, and this feature of the sequence undoubtedly promotes and stimulates its progress.

The situation at $\text{pH} < 12$ is somewhat more complex, requiring a reaction series that is overall pH independent. It must include as well an induction period and a chain process. A suitable scheme is shown in Eqs. (7) and (8):



In Eq. (7), water displaces nitrite to initiate the process; this step has precedence in polynitroarenes in the observation that the 3-nitro group in 2,3,4,6-tetrani-trophenol is replaced by an OH in boiling water [13]. The chain component is reaction (8) where NO_2^- displaces NO_2^- , but by means of O-attachment yielding a rapidly hydrolyzed nitrite ester. Reaction (8) can, in fact, be termed as a branching chain since there is a net increase of one nitrite with each cycle. The net consumption of nitrite in Eq. (6) is effectively a termination step.

While a detailed model of the process is outside the scope of this work, we show in Fig. 5 a reaction profile for the sequence (7)–(8)–(6) employing a modeling routine described by Braun et al. [14]. The rate constants employed here were $k_7 = 1.7 \times 10^{-9} \text{ s}^{-1}$ and $k_8 = 3.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, and convenient for these purposes we presume a first order loss of nitrite in Eq. (6) with the rate constant $k_6 = 1.7 \times 10^{-4} \text{ s}^{-1}$. The figure, which includes the data from Fig. 2 for picrate at $\text{pH} 6.7$, shows a satisfactory fit and provides confidence in the proposed hydrothermolysis scheme.

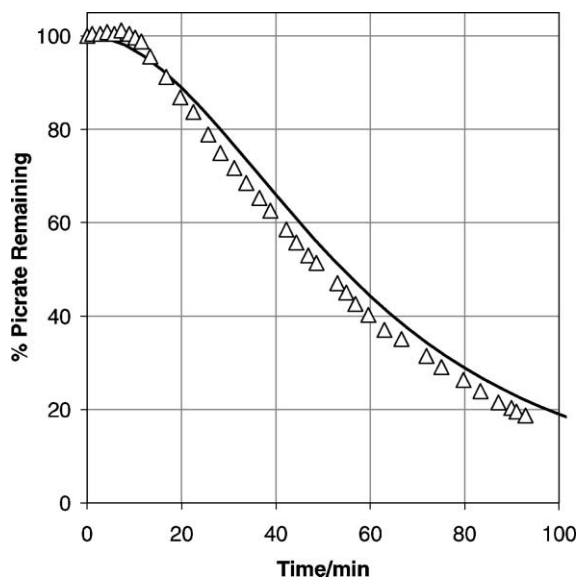


Fig. 5. Comparison of a reaction profile for the reaction sequence (7)–(8)–(6) to the observed picrate decay at $300 \text{ }^\circ\text{C}$ and $\text{pH} 6.7$. The rate constants employed in the modeling are $k_6 = 1.7 \times 10^{-4} \text{ s}^{-1}$, $k_7 = 1.7 \times 10^{-9} \text{ s}^{-1}$, and $k_8 = 3.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$.

A core feature of the scheme is the nitro-to-nitrite displacement and chain described in Eq. (8), and it is of interest to consider how broadly this reaction might be applied. The agreement shown in Fig. 3 between our Arrhenius data and those from studies in molten picric acid, as well as the fact that both systems display induction periods, strongly suggest that branching chain reactions like Eq. (8) could be prominent in the decomposition of the neat material.

That view, in turn, suggests that a similar nitro-to-nitrite displacement could be significant in the sequence of reactions leading to self-heating and abrupt energetic events for the family of polynitroarenes in general. It can be shown in simple simulations for the isothermal case that the very high concentrations of arene in the molten, neat material quickly lead to very rapidly reacting systems, with rates facilitated even further for cases where two or three starting nitro groups are converted to nitrite. This approach, emphasizing *ionic* reactions, must be viewed in the context of the broader considerations of kinetics and mechanism utilized by Brill and James [15]. In a discerning review of the topic they sought to understand energetic behavior in terms of the kinetics of the thermal decomposition of TNT, where the known chemistry is free

radical based. We would suggest that while free radical chemistry is clearly dominant in such systems once they have attained temperatures above 350–400 °C, ionic routes to that regime in the autoheating phase like those proposed here should be significant.

Finally, the findings discussed here suggest that a very hot water-based disposal of some types of energetic materials could be safe and effective. Ammonium picrate is of course, highly water-soluble at ambient temperatures, but a large range organic materials—benzene [16] and TNT [17], for example—become soluble in water in all proportions at temperatures around 300 °C. Since in a heated disposal system the hazard lies in the bulk explosive which is subject to autoheating and ultimate autoignition, it then follows that elimination of the bulk phase through its initial dissolution into a benign medium should eliminate the explosive potential.

The destructive reactions that take place in the aqueous medium described here, promoted if necessary by common oxyanions, can safely promote conversion to innocuous materials that then can be disposed of by conventional means.

Acknowledgements

This work was supported by the Air Force Research Laboratory, Tyndall Air Force Base, FL.

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