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by

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Abstract

TNT was destroyed in a small batch reactor, using uncatalyzed 4 N ammonium peroxydisulfate at 95 °C. The material was destroyed below limit of detection in less than 15 minutes, indicating a formal first order rate constant of 0.06 min⁻¹. A crude estimate of scaleup rates indicates a throughput of 1 tonne/m³-day.

Experimental. Tests were conducted on the oxidative destruction of 2,4,6-trinitrotoluene using uncatalyzed 4 N ammonium peroxydisulfate at 95 °C. A 1-L batch reactor vessel with reflux column was loaded with 100 ml of 0.1 M H₂SO₄ and preheated to 95 °C. One gram (1 g) of granular TNT was injected; the TNT immediately melted to form a dispersion of fine globules.

Using a peristaltic pump, 4N (NH₄)₂S₂O₈ was introduced at a rate of 5.5 ± 0.5 ml/minute. After 10 minutes, the TNT separate phase had vanished, and a sample was taken, chilled, and analyzed for total carbon using a calibrated TOC machine. The experiments were repeated twice, with oxidant injection terminated after 15 and 30 minutes, and residuals analyzed as before.

The peroxydisulfate concentration was determined by reduction by excess Fe(II), followed by titration with a standardized solution of 0.1 N KMnO₄. The TOC was calibrated using 25 ppm solutions of sucrose.

Results and analysis. TNT has a molecular weight of 227.13 g/mol, a weight fraction of carbon of 0.37, and an equivalent weight of 6.31 g/equiv, based on the stoichiometry oxidation half reaction:

Initially 1 g (0.159 equivalents) were added to 100 ml of acid, thus producing a carbon concentration of 3627 ppm (as C) and a total amount of carbon of 0.37 g in the vessel. After 10 minutes, 55 ml of oxidant were added (containing 0.22 equivalents), the TNT separate phase had vanished, and analysis of the product showed 0.045 g of carbon remaining in the solution, or 87.7% destroyed--an apparent oxidant utilization of 63%. After 15 minutes of oxidation, the carbon content of the resultant liquid fell below the limit of the TOC analyzer (~0.5 ppm), or <2 ppm when corrected for dilution prior to test, with an apparent utilization of oxidant of 0.159/0.33 = 48%. This indicates that more than 99.9% of the material had been destroyed in 15 minutes at 95°C by 4 N peroxydisulfate, with a utilization of between 48 and 63%.

We can calculate a formal rate constant, based on the assumption of first-order reaction kinetics. Using concentrations expressed in equivalents, the rate constant is

$$k_a \sim (0.159 \cdot 0.877 / 0.22) / 10 = 0.06 \text{ min}^{-1}.$$

This value is in the midpoint of values measured for destruction of bulk ethylene glycol, triethylamine, oxalic acid, etc., and supports the general model that uncatalyzed peroxydisulfate oxidation is controlled by the thermal decomposition of the oxidant to form the sulfate radical

anion. [1-3]. The Attached chart shows the rate superimposed on data for trace-level organic compounds as well as data taken from destruction of bulk organic compounds, with rates extrapolated from rate data for formation of the free radical.

Projections of throughput. We can make a crude estimate of the throughput of a waste destruction technique, simply by scaling the rate data to a 1 m³ vessel fed with 4 N oxidant and TNT. Based on this rate, the projected throughput of the process (using 4 N ammonium peroxydisulfate, 50% utilization) is roughly 1.1 tonne/m³/day, as computed from:

$$\text{throughput} \sim 50\% * 0.06 \text{ min}^{-1} * 4 \text{ equiv/L} * 6.3 \text{ g/equiv} = 0.756 \text{ g-TNT/L-min}$$

Table 1. Destruction of 1 g of TNT in experiments lasting 10,15, and 30 minutes, using 4N ammonium peroxydisulfate (uncatalyzed) at 95 °C.

<i>Time min</i>	<i>oxidant added equiv</i>	<i>total weight, g</i>	<i>ppm-C determined</i>	<i>carbon remaining, g</i>	<i>Fraction C destroyed</i>
0	0	102 g	3627	0.37	(0)
10	0.22	168	269	0.045	0.877
15	0.33	201	<2*	<0.0004	>0.999
30	0.66	301	<2*	<0.0006	>0.998

*below limit of detection, corrected for dilution of aliquot; actual measurement 0.19 ppm, 30 minutes.

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Figure 1. Given are rates of destruction of 20 diverse organic substances at trace levels, TNT at bulk concentrations 1% (circle), and other test chemicals (ref [1]) are plotted against reciprocal absolute temperature. The rate of formation of the sulfate free radical from uncatalyzed thermal decomposition of peroxydisulfate are also given, supporting the theory that peroxydisulfate destruction of organic compounds is determined by the initial formation of the sulfate radical anion [4,5].