

THE EFFECT OF SOME DISSOLVED METAL-ION CONTAMINANTS ON THE HOMOGENEOUS DECOMPOSITION RATE OF ANHYDROUS HYDRAZINE*

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Summary

Experiments are described which seek to establish the effects of dissolved manganese and chromium species on the rate of homogeneous decomposition of anhydrous hydrazine into nitrogen and ammonia. Decomposition rates at 43°C and 50°C were determined from pressure measurements made over a period of time on hydrazine samples contained in closed vessels fitted with pressure transducers. Results indicate that the addition of soluble manganese and chromium complexes to hydrazine, both individually and together, does not bring about an increase in decomposition rate and may even reduce it. However, the addition of a small amount of acid to hydrazine containing these two metals leads to a significant increase in rate, well above that found from the addition of acid alone. It is concluded that the homogeneous decomposition of anhydrous hydrazine may be catalysed by trace chromium and manganese species acting in conjunction with the hydrazinium ion ($N_2H_5^+$).

Introduction

During long-term storage anhydrous hydrazine undergoes slow decomposition to produce mainly nitrogen and ammonia. The decomposition reaction ($3 N_2H_4 \rightarrow N_2 + 4 NH_3$) is subject both to heterogeneous catalysis at containment vessel surfaces and to homogeneous catalysis within the bulk liquid [1] and therefore an understanding of each of these processes is essential if improvements are to be made in hydrazine system lifetimes. This paper reports the results of experiments aimed at identifying species responsible for catalysing the decomposition of anhydrous hydrazine at moderate temperatures in the homogeneous liquid-phase.

Previous work on the storage of hydrazine [2] has shown that an increased homogeneous decomposition rate is observed in samples of the

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propellant containing carbon dioxide (carbamic acid) which have been in contact with stainless steel. It has been suggested [3] that the increase is due to the onset of homogeneous catalysis involving metal-ions leached from the stainless steel surface by the corrosive effect of carbamic acid. To date no firm evidence for the involvement of particular metal-ions has emerged. However, experiments reported herein indicate that a significant increase in the rate of hydrazine decomposition is observed following the addition of an acid to hydrazine samples containing dissolved manganese and chromium.

Experimental

Hydrazine used in the decomposition rate studies conformed to the U.S. Monopropellant Grade specification [4]. $\text{Cr}(\text{N}_2\text{H}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ was prepared as previously described [3]. All other reagents and chemicals were A.R. grade and were used without further purification.

All manipulations involving the addition of solids to hydrazine in glass vessels were conducted in a nitrogen-filled glove-box.

Decomposition rate measurements on hydrazine were carried out using closed glass vessels fitted with strain-gauge pressure transducers and housed in thermostatically-controlled hot-air ovens. These assemblies and the method by which the decomposition rate (as standard cm^3 of nitrogen per day) was calculated from the observed rise in ullage pressure have been described previously [5].

Results and discussion

Previous studies have identified a linear correlation between hydrazinium ion (N_2H_5^+) concentration and the homogeneous decomposition rate of anhydrous hydrazine in contact with stainless steel. This has led to the view that a catalytic cycle for the homogeneous decomposition of hydrazine may involve a metal-ion and an acidic species acting together. It was subsequently found [3] that iron in the form of the carbazato complex $\text{Fe}(\text{N}_2\text{H}_3\text{CO}_2)_2(\text{N}_2\text{H}_4)_2$ has no effect on the homogeneous decomposition rate of hydrazine in glassware at 43°C , even in the presence of an added acid. Similar experiments involving the addition of soluble manganese and chromium compounds to hydrazine are now reported.

Manganese was added to hydrazine in the form of manganese(II) chloride tetrahydrate, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$.

Decomposition rate measurements on the manganese-doped sample were carried out in glass vessels at 43°C and the results (Fig. 1) show that successive additions bring about a decrease in the decomposition rate of hydrazine for manganese concentrations up to 0.0035 M . From the small number of results obtained the relationship appears to be: $\text{rate} \propto [\text{Mn}]^{-1/2}$.

Chromium was added to hydrazine as the carbazato-complex

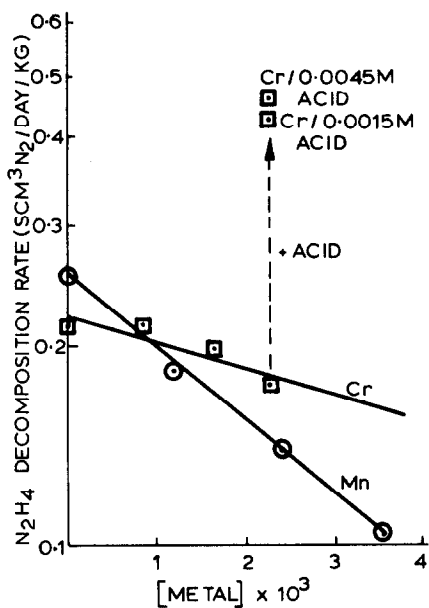


Fig. 1. Effect of Mn, Cr and Cr/acid on the decomposition rate of hydrazine at 43°C.

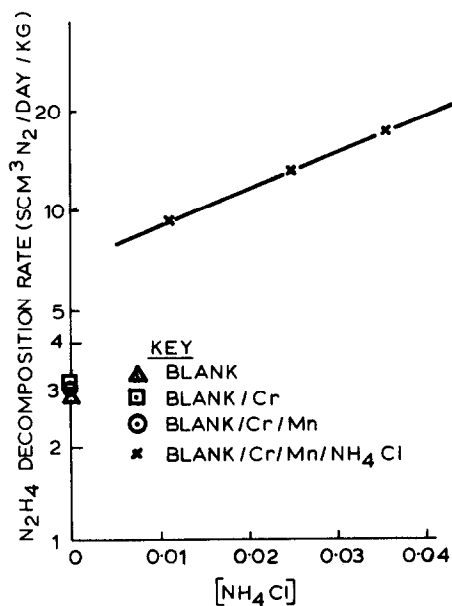


Fig. 2. Effect of Mn/Cr/acid on the decomposition rate of hydrazine at 50°C.

$\text{Cr}(\text{N}_2\text{H}_3\text{CO}_2)_3 \cdot 2\text{H}_2\text{O}$ and decomposition rate measurements on the resulting solutions were carried out as described above. Results are shown in Fig. 1. The effect of chromium alone on the decomposition rate is slightly negative up to a concentration of 0.002 *M*. However, the addition of an acid (2-naphtol) to the final chromium solution produces an almost 3-fold increase in the hydrazine decomposition rate and the rate is further increased by a second acid addition.

In the final series of experiments an acid (which, alone, has previously been shown [3] to have no significant effect on the homogeneous decomposition rate of hydrazine) was added to a sample of hydrazine containing both manganese (0.0034 *M*) and chromium (0.0020 *M*) in the forms described above. Decomposition rate measurements as depicted in Fig. 2 were carried out in a titanium vessel at 50°C. The results (Fig. 2) show that the blank rate and those determined following addition of chromium and then manganese have similar values. However, there is a significant increase in rate on the addition of acid (NH_4Cl) and the relationship under these conditions approximates to: $\text{rate} \propto [\text{H}^+]^{1/2}$

Conclusions

A significant increase in the homogeneous decomposition rate of hydrazine at 50°C is observed on the addition of an acid to samples of hydrazine containing dissolved manganese and chromium. This behaviour may be simulating the observed increase in rate which follows contact between acidified hydrazine and stainless steel.

Further work is in hand to investigate the effects of other acids on the homogeneous decomposition rate of hydrazine in the presence of dissolved manganese and/or chromium.

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