HYDROGEN PEROXIDE – MATERIAL COMPATIBILITY STUDIED BY MICROCALORIMETRY*

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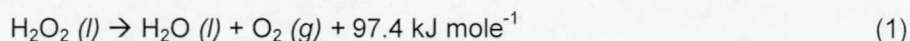NASA Marshall Space Flight Center
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ABSTRACT

Environmental and toxicity concerns with current hypergolic propellants have led to a renewed interest in propellant grade hydrogen peroxide (HP) for propellant applications. Storability and stability has always been an issue with HP. Contamination or contact of HP with metallic surfaces may cause decomposition, which can result in the evolution of heat and gas leading to increased pressure or thermal hazards.

The NASA Johnson Space Center White Sands Test Facility has developed a technique to monitor the decompositions of hydrogen peroxide at temperatures ranging from 25 to 60 °C. Using isothermal microcalorimetry we have measured decomposition rates at the picomole s^{-1} g^{-1} level showing the catalytic effects of materials of construction. In this paper we will present the results of testing with Class 1 and 2 materials in 90 percent hydrogen peroxide.

APPROACH

For hydrogen peroxide, the decomposition reaction:

$$H_2O_2 \ (l) \rightarrow H_2O \ (l) + O_2 \ (g) + 97.4 \ kJ \ mole^{-1} \tag{1}$$

can be followed by several techniques including measurement of the pressure or volume of the product gas, decrease in the chemical assay, weight loss or by calorimetric measurements. In an uncontaminated, stabilized sample this decomposition reaction is slow, being on the order of 1 – 2 percent per year. To do a parametric evaluation of the decomposition reaction often involves intensifying a reaction variable such as temperature to provide measurable changes in short real-time. For example, the MIL-Spec stability test involves studying the decomposition at 100 ºC for 24 hours.[1] An alternate approach is to exploit the use of ultra-sensitive techniques at or near room temperature. One such ultra-sensitive technique is microcalorimetry[2,3] which measures heat flow at the microWatt (μW or μJoule s^{-1}) level. Decomposition rates measured in the range of 25 to 60 °C show significant heat flows due to the background rates of HP decomposition in a passivated container. In order to determine the effect of added materials it was necessary to characterize the decomposition of the HP in the container and correct for this background rate when testing with materials. The material tests were then performed at three temperatures to establish the temperature dependence of the reaction rate.

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EXPERIMENTAL

MATERIALS

The hydrogen peroxide used in this study were commercial samples of 90 percent HP provided by FMC Corp (Pasadena, TX). Analysis by permanganate titration showed the solutions to contain 90.5 percent hydrogen peroxide. Aluminum 5254 was in the form of coupons 1.0 x 3.0 x 0.15 cm. The passivation was performed per FMC Bulletin 104 and consisted of mechanical surface preparation with 600 grit metallographic paper, followed by ultrasonic cleaning in water for at least 1 minute, cleaning with 1 percent by weight detergent heated to 49 °C (120 °F), then an ultrapure water rinse. The surface was chemically passivated by exposure to a 0.25 percent sodium hydroxide solution for 20 minutes at room temperature, an ultrapure water rinse, 35 percent nitric acid for 1 hour at room temperature, ultra pure water rinse, and a final conditioning with 90 percent HP for at least 4 hours. The coupons were then rinsed with ultrapure water and oven dried at approximately 100 °C. Before use the coupons were inspected for corrosion. If corrosion was noted the passivation process was repeated.

Stainless Steel 316 was purchased in the form of 0.635 cm (0.25 inch) OD tubing with 0.12 cm (0.049 inch) wall thickness. The tubing was cut to 2 cm (0.79 inch) lengths using a metallurgical diamond saw. The tubing sections were passivated per FMC bulletin 104 and consisted of an ultrasonic cleaning in water for at least 1 minute, followed by degreasing with 1 percent detergent solution heated to approximately 49 °C (120 °F), then an ultrapure water rinse. The samples were then immersed in 70 percent nitric acid for a minimum of 4 hours at room temperature, an ultrapure water rinse and then immersion in 90 percent HP for 4 hours. Finally the tubes were rinsed with ultrapure water and oven dried. Before use the tubing sections were inspected for corrosion. If corrosion was noted the sample was discarded.

A portion of the 316 stainless steel samples was commercially electropolished by Delstar Metal Finishing Inc. of Houston TX. After electropolishing the samples were cleaned with 1 percent detergent solution heated to 49 °C (120 °F), rinsed with ultrapure water, then immersed in 90 percent HP for 4 hours followed by an ultrapure water rinse and oven drying. Before use the surfaces of the samples were inspected and if any corrosion was noted the samples were discarded.

MICROCALORIMETER

The microcalorimeter used in this study was a commercial instrument provided by Hart Instrument Co., now Calorimetry Sciences Corp. (Spanish Fork, UT). The lowest level at which a confident measurement of the difference between the sample and empty (blank) heat rates is estimated to be approximately 5 μW. For this minimum heat rate reading, the minimum detectable chemical reaction rate for Equation 1 is approximately 5 picomoles $s^{-1} g^{-1}$. Microcalorimeter reaction vessels were glass crimp top vials, which had been cleaned by immersion in 10 percent nitric acid for 2 days, rinsed in ultrapure water and then immersed in 30 percent hydrogen peroxide for 2 days. The peroxide cleaned vials were then rinsed repeatedly in ultrapure water and oven dried. The vials had a capacity of 28.5 mL. They were sealed using a thin film of fluorinated ethylene-propylene, covered by a polytetrafluoroethylene-lined butyl rubber gasket held on by a crimp seal. All tests were run at least in triplicate.

During operation it was found the pressure buildup due to the formation of oxygen in the decomposition reaction would be periodically vented by deformation of the PTFE-lined butyl rubber gasket. This was evidenced by small dip in the heat evolution rate data followed by a return to the previous level. The reaction vessel was loaded with a weighed amount of HP. The total volume of the samples was approximately 20 mL. The vessels were pre-equilibrated to test temperature in the airbath of the microcalorimeter. The heat flow activity of an empty cell was recorded for a minimum of 4 hours and then a temperature equilibrated reaction vessel was transferred to the cell from a heating block or the microcalorimeter airbath. The heat evolution rates were measured for periods greater than 48 hours. After a cell-background correction, observed heat rates were converted to chemical reaction rates using Equation 1. The heat of reaction was corrected to the assay value as indicated in FMC Handbook.[4] The rates of decomposition of the peroxide are reported in units of μW (μJoules s^{-1}) which are the

instrumentally reported units or in picomoles s^{-1} g^{-1} of contained hydrogen peroxide. A decomposition rate of 10 picomole s^{-1} g^{-1} corresponds to an active oxygen loss (AOL) rate of 1.07 percent per year. A picomole is 10^{-12} moles.

RESULTS AND DISCUSSION

Decomposition rates of HP measured in real-time in the microcalorimeter have been shown to change with time. For HP decomposition rates in passivated containers, the rate drops from an initial high level when measurements begin to a limiting value at longer times. This is presumably due to continued passivation or cleaning of the surface after the start of testing. In the case of HP in contact with a sample material, the real-time behavior begins with the same drop from the initial heat rate, but at longer times the rate tends to increase with time at a rate dependant on the material. In order to make the analysis workable, the decomposition rate after 200 hours of exposure was tabulated for this testing, allowing for the exclusion of the initial high heat rate and any long-term increases in the decomposition rate.

The background decomposition rate of HP in a passivated container was determined in triplicate at temperatures between 25 and 60 °C. These background heat rates are due to the decomposition of the HP on the surface of the glass container and bulk homogeneous decomposition. This background rate was normalized to the mass of peroxide. The average heat of decomposition rate per gram and the corresponding molar decomposition rate for each temperature are given in Table 1. These background rates range from 21 picomoles s^{-1} g^{-1} at 25 °C to 300 picomoles s^{-1} g^{-1} at 60 °C.

When measuring heat rates from a reaction vessel with a sample immersed in HP the overall measured rate in μW is the sum of the background rate and the sample rate:

Overall measured rate (μW) = Sample rate (μW) + Background rate (μW)   (2)

These background rates were subtracted from the overall measured rate to yield the sample rate. This sample rate was then converted to a mole rate and normalized to the surface area of exposed sample to obtain a material rate. This material rate should then be a system-independent measure of the effect of exposure on the decomposition rate of the peroxide.

The temperature dependence of the reaction rate can be expressed in terms of the activation parameters used in the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

Table 1. Background Decomposition Rates of Hydrogen Peroxide as a Function of Temperature

	25 °C	35 °C	40 °C	55 °C	60 °C
Heat Rate μW g^{-1}	2.1	6.17	9.1	19.91	29.58
Mole Rate Picomoles $s^{-1}g^{-1}$	21	70	92	227	303

Table 2. Decomposition Rates for Hydrogen Peroxide on Materials, Background Corrected Picomoles s^{-1} cm^{-2}

Material	25 °C	40 °C	60 °C
Al 5254	71	348	640
316 SS	643	4516	56200
316 SS, Electropolished	556	1610	30860

Where k is the molar decomposition rate, A is the pre-exponential term, E_a is the activation energy, R is the universal gas constant (8.314×10^{-3} kJ $mole^{-1}$) and T is the absolute temperature (K). Figure 1 plots the logarithm of the background-corrected rate versus the inverse of the temperature for each of the three materials. The replicate data used to generate the average values in Table 2 are plotted individually in Figure 1. The slope of the line is $-E_a/R$ and the intercept is Ln(A). Least squares analysis of the rate-temperature data was used to calculate the mole-rate based activation energy parameters E_a and A which are given in Table 3. Because this is a nonlinear function, the E_a and A values calculated from the individual data points will differ form the E_a and A values calculated from the averages.

Figure 1 illustrates the that the decomposition rates for both the passivated and electropolished 316 stainless steel are more sensitive to changes in temperature than Al5254 due to the steeper slope of the curves.
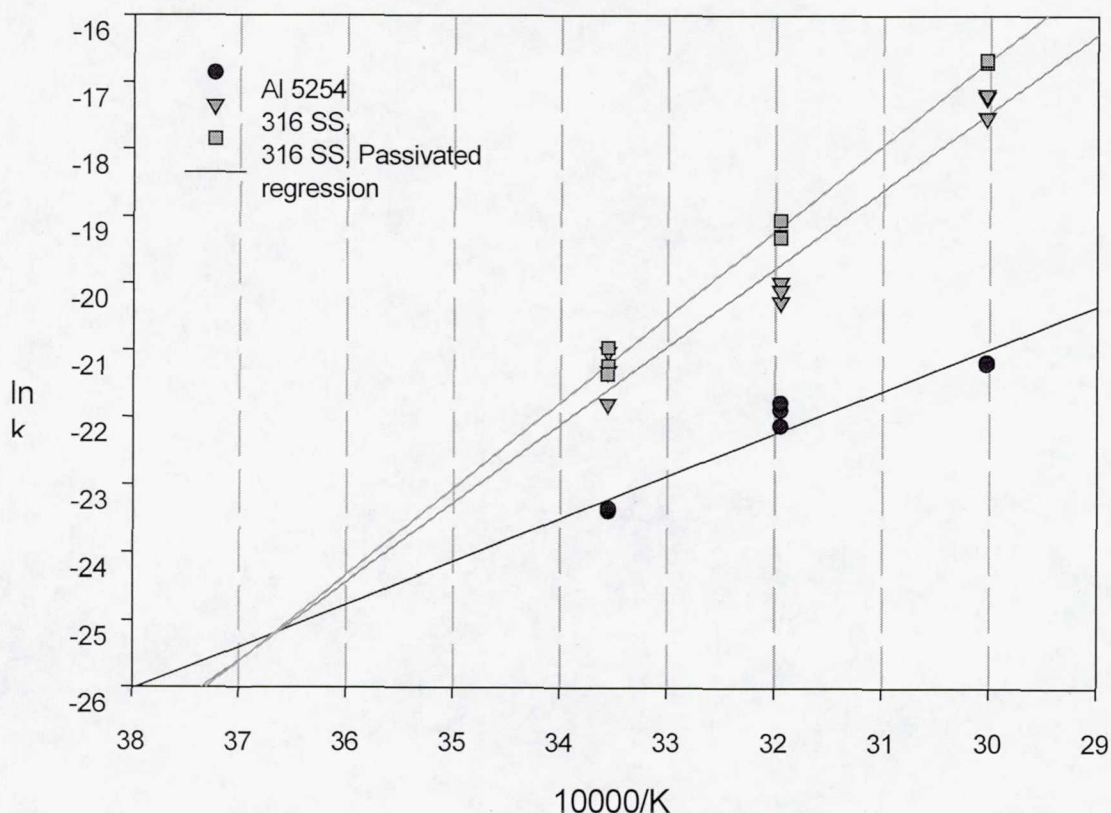

Figure 1.
Arrhenius Plot for Hydrogen Peroxide Decomposition on Al 5254, Electropolished 316 Stainless Steel, and Passivated 316 Stainless Steel

Electropolishing produces a smoother surface on a microscopic scale as well as changing the relative amounts of the constituent metals at the surface. For stainless steels the surface becomes chromium enriched, usually at the expense of the iron content. The changes in rate are most likely due to a combination of these two factors. The result is a surface with different chemical properties and a lower surface area. This effect accounts for the difference in both the intercept (A value) and the slope (E_a) in the Arrhenius plot.

The steeper slopes (increased E_a) for the passivated and electropolished 316 stainless steels over Al 5254 illustrate the decomposition rates for both the passivated and electropolished 316 stainless steel are more sensitive to changes in temperature than Al 5254 due to the steeper slope of the curves. Raising the temperature of peroxide in contact with materials have been generalized as having the effect of increasing the reaction rate by a factor of 2.3 times for each 10 °C (18 °F). Using the Arrhenius parameters from Table 3 and calculating the rate increase from 25 to 35 °C for each of the materials gives the rate increases and factors shown in Table 4. The relative increases range from a factor of 2.1 to 4.2.

One interesting feature of the plot in Figure 1 is the isokinetic temperature, the temperature at which the background corrected rates of reaction for all the materials are equal. This occurs at a temperature of 0.2 °C with a corresponding rate of 9.6 picomoles s^{-1} cm^{-2}.

Table 3. Mole-Rate Activation Parameters

	A picomoles s^{-1} cm^{-2}	E_a J $mole^{-1}$
Al 5254	2.10	59275
316 SS	2.2×10^9	105909
316 SS Electropolished	4.06×10^7	97126

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