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REAL TIME LOW TEMPERATURE DECOMPOSITION OF EXPLOSIVES - PETN

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ABSTRACT

Chemiluminescence NO/NO_x analyzers have been used to make real-time measurements of PETN decomposition products near storage temperatures. Over the 326-393 K (53-120°C) temperature range the NO_x evolution rate from PETN is described by $4.3 \times 10^9 \exp(-16500/T)s^{-1}$ and $6.3 \times 10^{11} \exp(-18000/T)s^{-1}$ in moles NO_2 per mole PETN for samples having surface areas of 1500 $cm^2\ g^{-1}$ and 14000 $cm^2\ g^{-1}$, respectively. NO_2 is readily absorbed by both PETNs and is desorbed at a rate corresponding to an activation energy of 15 kcal mol^{-1}.

INTRODUCTION

This work describes the application of chemiluminescence techniques to the measurement of the decomposition rates of PETN. The lack of sufficiently sensitive gas analysis techniques has limited previous decomposition measurements either to high temperatures where different decomposition mechanisms might be operative than at the lower temperatures of interest, or to long (decomposition product) accumulation times in which primary decomposition products are likely to be lost due to secondary reactions.

In the present work NO and NO_2 production from PETN is determined by passing a carrier gas through sample cells containing small amounts of PETN and analyzing the effluent with a high sensitivity chemiluminescence NO/NO_x analyzer. An analyzer sensitivity has been achieved in this work which is at least a factor of 10 better than commercially available instruments; this sensitivity has made it possible to obtain decomposition data at temperatures as low as 53°C. Due to the high thermal stability of PETN, even higher sensitivity would be required to extend these measurements to lower temperatures.

EXPERIMENTAL

The experimental arrangement is shown in Fig. 1. N_2 carrier gas is passed over the PETN samples which are maintained at a constant temperature, between

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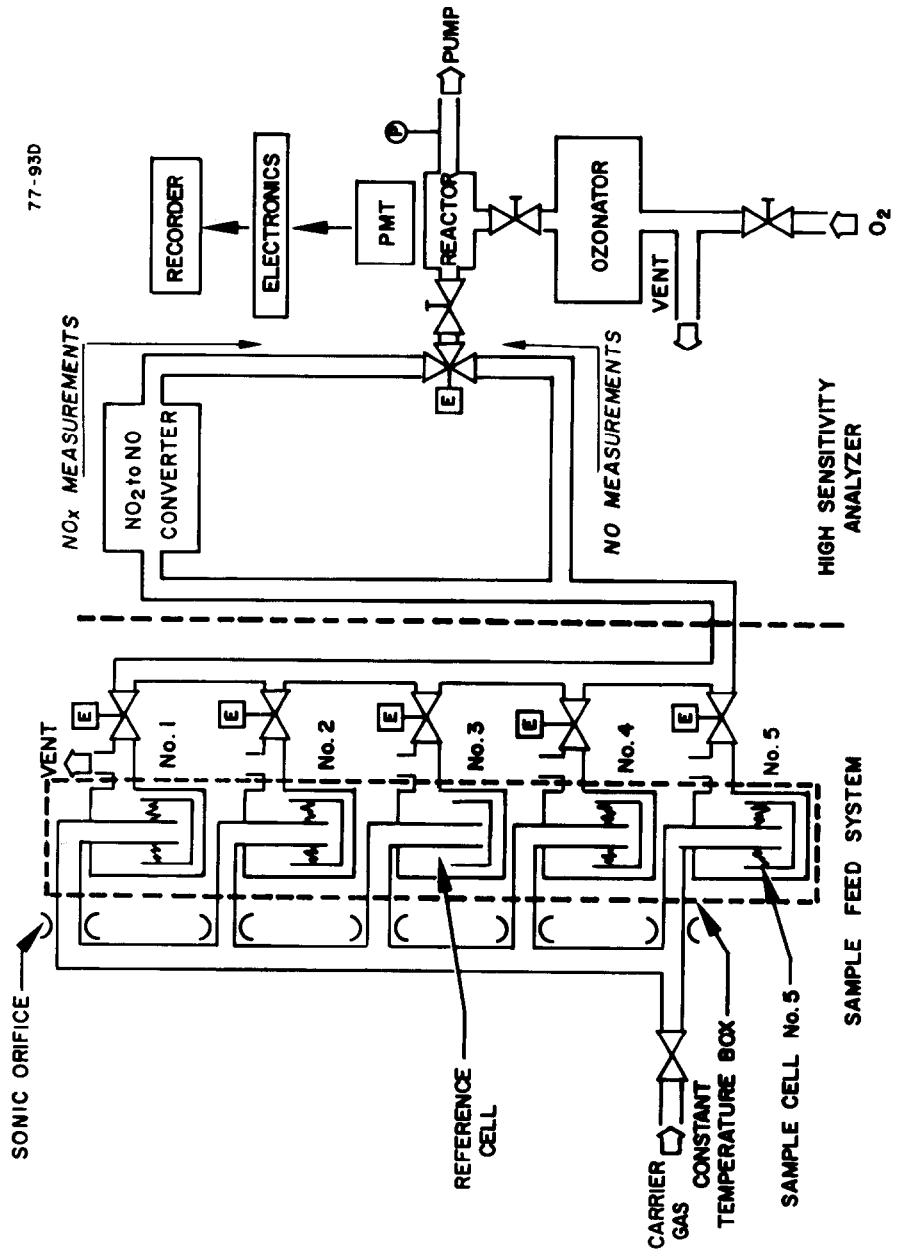

Fig. 1 Apparatus for NO and NO_2 evolution rate measurements.

326 to 393 K (53 to 120°C). The NO and NO_x(= NO + NO_2) picked up by the carrier gas from the decomposing PETN is then measured with the high sensitivity NO/NO_x chemiluminescence analyzer. The N_2 carrier flows continuously at 1 to 3 ml(STP)s^{-1} through all five cells; with the aid of solenoid valves the effluent from one cell at a time is directed toward the NO/NO_x analyzer while the remainder flows out through the vent lines as shown in Fig. 1. An electronic control system, consisting of a microprocessor and interface circuitry, allows continuous measurements over extended time periods. This control system selects the sample to be analyzed, the temperature of the samples, and the analyzer reading range (determined in preliminary experiments).

For individual measurements 1-15 min is generally allowed. Any one of 16 temperatures and 10 instrument ranges can be selected. The reference cell is used to measure the NO and NO_x content of the carrier gas which usually contains a few ppb NO_x (v/v), an order of magnitude larger than the minimum amount of NO_x to be measured.

Standard NO/NO_x chemiluminescence analyzers in use for ambient air monitoring typically have a limit-of-sensitivity of one to a few ppb. Such instruments measure NO directly and NO_2 by conversion to NO, cf. Fig. 1. For the present work an increase in sensitivity of about a factor of 10, at a 1 ml(STP)s^{-1} flow rate, was achieved by modifying an AeroChem Model AA-3 analyzer. The NO_2 to NO converter is a high temperature (≈ 1300 K) noble metal catalytic type which is > 95% efficient in converting NO_2 to NO.

PETN samples were obtained from Dr. H. Golopol of LLL.

RESULTS

When "fresh" PETN is first heated, it gives off much more NO and NO_x than when it has been maintained at, e.g., 70°C for several days. The initial high NO_x evolution rates are not representative of the decomposition process and are ignored (they are presumably due to NO_2 absorption by the PETN--similar behavior was observed with NC[1]).

Results of a series of NO_x measurements made on 2 g samples of PETN having surface areas of 1500 cm^2 g^{-1} and 14000 cm^2 g^{-1} are shown in Fig. 2 in Arrhenius form. Carrier gas for this test was 1.8 ml(STP)s^{-1} of nitrogen. Weighted least squares fits of the data yield rate coefficient expressions of 4.3×10^9 exp(-16500/T)s^{-1} and 6.3×10^{11} exp(-18000/T)s^{-1} in moles NO_x per mole PETN for the 1500 and 14000 cm^2 g^{-1} surface area materials, respectively. These expressions predict equal NO_x evolution rates for the two samples at about 30°C. At 53°C, the lowest temperature at which measurements were made, the smaller particle PETN has about twice the NO_x evolution rate as the coarser material. If the data are extrapolated to 30°C, a half-life of 12 million years is predicted for these samples. NO evolution was also measured and the rates were found to be 5 to 10 times less than the

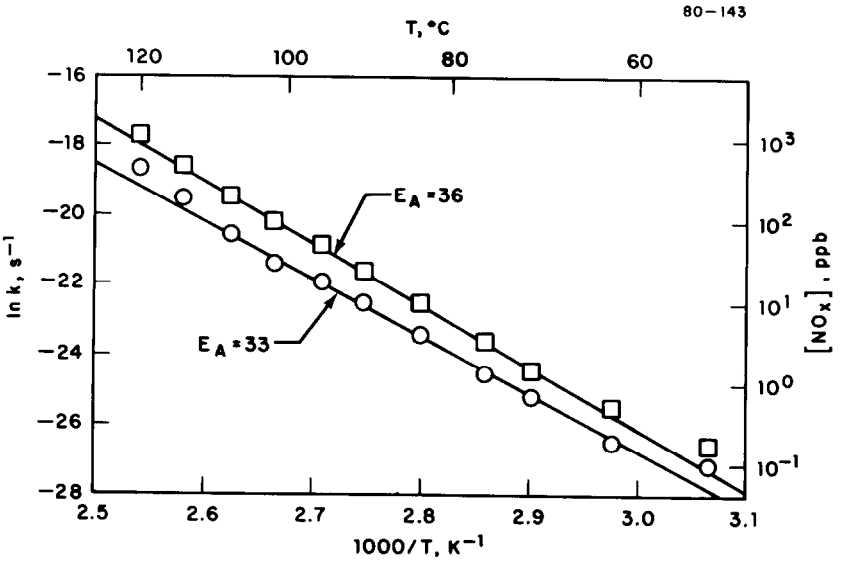

Fig. 2 NO_x evolution rate from 2 g PETN samples. N_2 flow; 2 ml(STP)s^{-1}; - 14000 cm^2 g^{-1} PETN; - 1500 cm^2 g^{-1} PETN; E_A in kcal mol^{-1}.

corresponding NO_x rates over the entire temperature range investigated. Thus 80 to 90% of the NO_x evolved is NO_2 and there appears to be little reduction of this NO_2 to NO by the PETN. This is contrary to the results obtained with NC for which essentially all the NO_x was NO[1] at temperatures above about 100°C although mostly NO_2 was observed at lower temperatures. The following additional comparisons can be made between NC and PETN:

1. Both NC and PETN readily absorb NO_2 and release it with a (desorption) activation energy of $\approx$ 15 kcal mol^{-1}.
2. A single activation energy describes the NO_x evolution due to decomposition from PETN from 53 to 120°C, while at least two different mechanisms pertain to NC decomposition. Since all the O—NO_2 bonds in PETN are equivalent while about a dozen different such bonds exist for NC, this finding is not surprising.
3. PETN is very stable towards thermal decomposition. At 30°C its NO_x evolution rate is predicted to be $\approx$ 1000 times less on a molar basis than the rate for NC (per submole).

In future tests with PETN the effect of carrier gases other than N_2 will be investigated including gases containing presumed PETN decomposition products. Longer duration tests (a few hours) will be carried out in order to reach lower temperatures of $\approx$ 30°C.

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