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A TG STUDY OF THE SOLVOLYTIC BREAKDOWN OF A CROSSLINKED DOUBLE BASE PROPELLANT

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ABSTRACT

The solvolytic breakdown and dissolution of obsolete crosslinked propellants may be carried out with surprising ease with subsequent recovery of expensive constituents in high yields. An approach was adopted in which degradation was initiated in composites while they were swollen in an appropriate solvent containing additives capable of reacting with and cleaving chemical bonds located in the polymer chain. A kinetic study of the solvolysis reaction of the urethane linkages in a crosslinked double base propellant in ethanolamine solution was followed by thermogravimetry. Kinetic data were obtained using the propellant fraction reacted, which was expressed as the product of the TG fraction at 200°C and the molarity of the ethanolamine solution. First-order rate constants for the reaction were found to be higher in the mixed solvent of toluene–isopropanol compared with isopropanol probably because of their differences in swelling behavior. Activation energies for solvolysis were about 5 kcal mole^{-1} in toluene–isopropanol and about 8 kcal mole^{-1} in isopropanol. Nitroglycerin present as a plasticizer in double base propellants was extracted prior to kinetic analysis because it was found to react with the ethanolamine. The solvolytic degradation of the propellant binder with nitrocellulose was about three times as fast as the binder without nitrocellulose. A variable heating rate study showed that the binder with or without nitrocellulose had the same activation energy for thermal decomposition. Kinetic data indicates that nitrocellulose appears to catalyze the solvolytic degradation but not the thermal degradation of a crosslinked double base propellant binder.

INTRODUCTION

Large amounts of ordnance must be disposed of every year because of deterioration or obsolescence. Most of this is burned. Critics, of whom there are many, point out that this procedure releases hydrogen chloride and oxides of nitrogen into the atmosphere as well as quantities of smoke. A further objection is the complete waste of the large amounts of energy which go into the production of some of the high energy constituents in propellants. Accordingly, a program was initiated to develop chemical methods for the safe disposal of propellants in a non-polluting process and the reclamation of energetic constituents. It was found that the solvolytic breakdown

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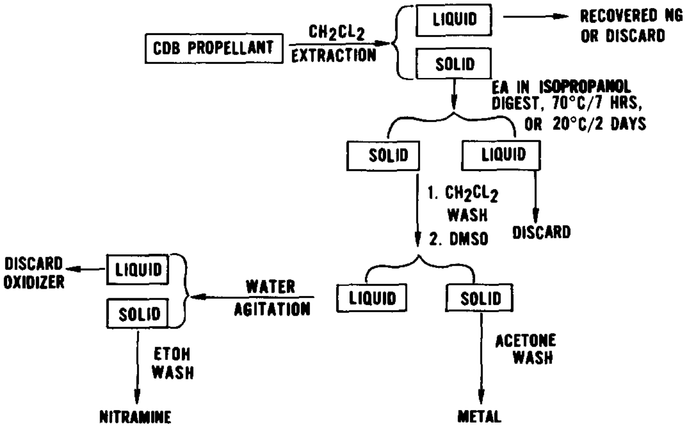

Fig. 1. Separation scheme for crosslinked double base propellant.

and dissolution of obsolete crosslinked propellants may be carried out with surprising ease with subsequent recovery of expensive constituents in high yields. An approach was adopted in which degradation was initiated in composites while they were swollen in an appropriate solvent containing additives capable of reacting with and cleaving chemical bonds located in the

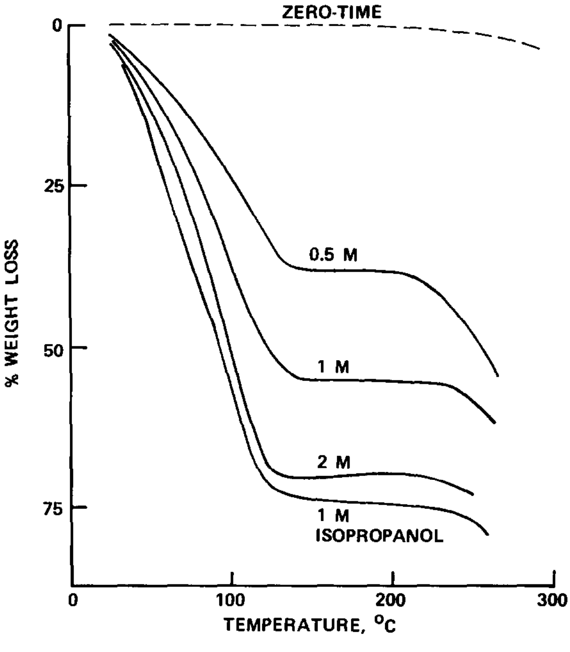

Fig. 2. TG curves of crosslinked double base propellant after reaction in various concentrations of ethanolamine in toluene–isopropanol for 240 min at 60°C.

polymer chain. A kinetic study was done of the solvolysis reaction in ethanolamine (EA) solution of the urethane linkage in a crosslinked double base (CDB) propellant. The overall separation scheme is shown in Fig. 1. In this study, only the reaction of the solid propellant in isopropanol or in the mixed solvent of toluene–isopropanol is of interest. The kinetic information permits one to optimize the solvolysis reaction. As the reaction proceeds, reactants are converted into products and the products are measured quantitatively by the plateau at 200°C in the thermogravimetric (TG) curve (Fig. 2). In solution after the reaction is completed is the solvent and the soluble degraded propellant binder. In the TG analysis it was found that the solvent volatilized prior to 200°C leaving the binder which was measured as the plateau in the 200°C region; the degraded binder itself decomposed above 250°C. The untreated propellant binder decomposed above 350°C. The kinetic data were analyzed by making use of the function α, which is the fraction of the CDB propellant binder reacted and is expressed by

$$\alpha = \mathrm{TG}_{200^\circ\mathrm{C}} \times M_{\mathrm{EA}}$$

where $\mathrm{TG}_{200^\circ\mathrm{C}}$ is the TG fraction at 200°C and M_{EA} is the molarity of the ethanolamine solution.

EXPERIMENTAL

The CDB propellant was cut into pieces about 1/4 × 1/4 × 1/16 in. The nitroglycerin (NG) present as a plasticizer in the propellant was extracted with methylene chloride and the sample was then allowed to air dry in the hood. The propellant mass-to-solvent ratio was 30g/100 ml. The reaction solvent was mainly toluene–isopropanol, 1 : 1 by volume and in some cases isopropanol. The concentration of the ethanolamine used as an additive to sever the crosslinks in the binder was 0.5, 1.0 and 2.0 M.

The reactions were carried out in 400 ml round bottom resin flasks equipped with a three-neck top for an air stirrer, reflux condenser, and a nitrogen purge. The water bath was steam heated to 40, 50, and 60°C and was located in a steel cubicle. The reaction mixture was analyzed every 40 min up to 240 min. A new sample/solvent mixture was used for each reaction time. At the end of each reaction, the solution was filtered, allowed to evaporate down to 5 ml in the hood, filtered again, and heated in an oven for 2 h at 60°C. The filtrate is a free flowing colored liquid that contains mostly ethanolamine and degraded propellant binder.

A DuPont 990 Thermal Analyzer and a 951 Thermogravimetric Analyzer were used to obtain the TG curves at a heating rate of 10°C min^{-1} on 5–7 mg samples in a nitrogen atmosphere. The ethanolamine concentration was determined by adding an aliquot to 100 ml 1 : 1 isopropanol–water, titrating with 0.1 N HCl to the methyl red endpoint and back titrating, if necessary, with 0.1 N NaOH.

DISCUSSION

TG fractions

Figure 2 shows the TG curves for the solvolysis reactions of CDB propellants after 240 min at 60°C and the effect of the ethanolamine concentrations on the TG plateaus in the 200°C region; also shown is the zero-time TG curve for the propellant binder. As the degradation reaction proceeds, the TG fraction at 200°C continuously increases. When the initial ethanolamine concentration was increased in the solvolysis reaction, the TG plateau at 200°C decreased. At first, this observation appears to be contradictory, as one might expect that as the ethanolamine concentration increases the TG fraction would also increase. However, it is the propellant binder fraction reacted and not the TG fraction by itself that is of primary importance in following the extent of reaction.

Binder fraction reacted

The propellant binder fraction reacted, α, was found to increase as the ethanolamine concentration increases and also as the mass of CDB propellant increases in the solvolysis reaction (Fig. 3). Figures 2 and 3 also show that, in isopropanol solution, the TG fraction and the fraction of the CDB propellant reacted in 1 M ethanolamine is less than in the mixed solvent of

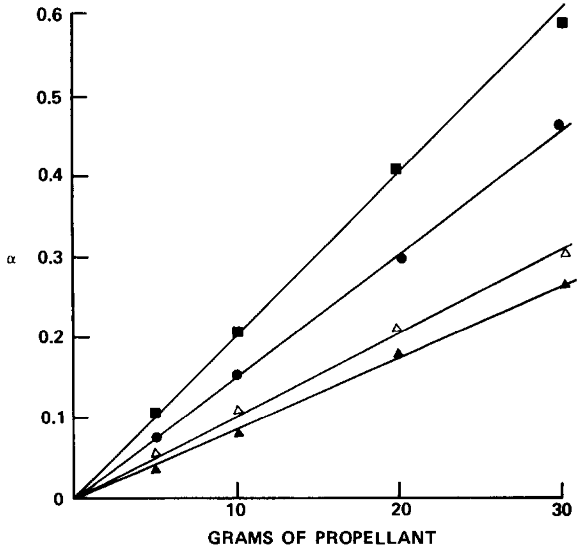

Fig. 3. Crosslinked double base propellant fraction reacted after 240 min at 60°C vs. mass of propellant in various concentrations of ethanolamine in toluene–isopropanol. ■, 2 M; ●, 1 M; Δ, 0.5 M; ▲, 1 M in isopropanol.

toluene–isopropanol. This is because toluene causes the propellant to swell more and consequently it is easier for the ethanolamine in the mixed solvent to diffuse into the swollen propellant binder network and attack the cross-link bonds and thereby break the binder down.

Effect of temperature

Figure 4 shows that, as the temperature of the solvolysis reaction increases from 40 to 50 to 60°C, the propellant binder fraction reacted also increases.

Effect of nitroglycerin

Normally, the NG was extracted prior to the degradation reaction. However, a series of experiments was performed to observe what effect, if any, NG would have on the solvolysis. Figure 5 shows the relationship between the percent ethanolamine reacted and pH of the solution with the mass of CDB propellant with and without NG after the solvolysis reaction. NG was found to react with the ethanolamine and thereby lower the pH of the solution. With NG present in the experiment nearly all the ethanolamine (1 M) was found to react and the pH was lowered nearly three units; in the absence of NG, only half of the ethanolamine (1 M) reacted and the change in pH was only one unit. The product of the solvolysis reaction as given by the TG plateau at 200°C was found to be less after a given reaction time when NG was present because of the competing reaction of ethanolamine

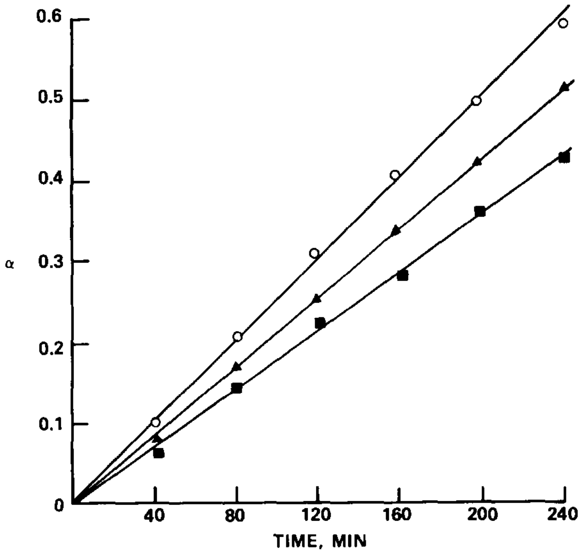

Fig. 4. Crosslinked double base propellant fractions reacted vs. time in 2 M ethanolamine solution at 60°C (○), 50°C (▲) and 40°C (■).

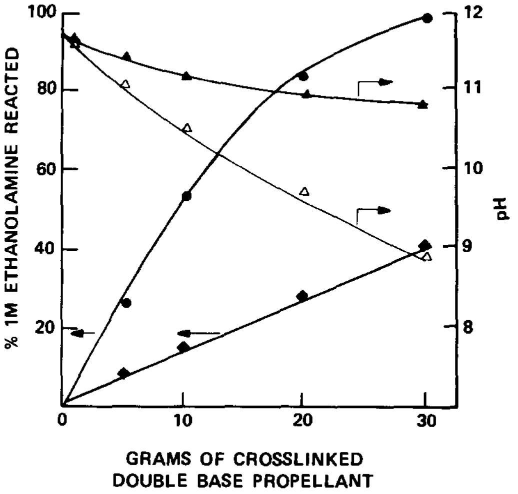

Fig. 5. Relationship between % ethanolamine reacted and pH with mass of crosslinked double base propellants with and without NG after degradation in ethanolamine solution. ▲, pH without NG; △, pH with NG; ●, EA with NG; ◆, EA without NG.

with NG. Evidently, two liquids react faster than a liquid with a solid. From the slope of the percent ethanolamine reacted vs. mass of CDB propellant without NG in Fig. 5, it was found that 100 ml of 1 M ethanolamine solution could degrade nearly 75 g of CDB propellant; the reaction mixture is only 30 g/100 ml.

Reaction rates for propellant

If a first-order or pseudo-first-order reaction is assumed for the solvolytic breakdown of the urethane crosslinks in a CDB propellant, then by making use of the fraction reacted (α) as a function of time and temperature, typical first-order plots of log(1-α) vs. time as shown in Figs. 6 and 7 are obtained. Two straight-line plots may be drawn with a change in slope occurring near 160 min. The slope of the lines are equivalent to the rate constants (K_1, K_2). It is apparent that $K_1 < K_2$; usually, $K_1 > K_2$ (Table 1). This indicates that the reaction rate increases as the concentration of reactant decreases. This is possible if the products formed during the degradation process contribute to the rate of the reaction. This may be possible in the present case because the CDB propellant binder contains nitrocellulose (NC) along with a polyglycol and a difunctional isocyanate curing agent such as hexamethylene diisocyanate (HDI). It is believed that the initial reaction occurring is the decomposition of the nitrocellulose, which has a catalytic effect on the solvolysis of the polyglycol moiety. Thus, the probable sequence of events occurring in the solvolysis reaction of a CDB propellant is an induction time, during which the propellant swells accompanied by penetration of the

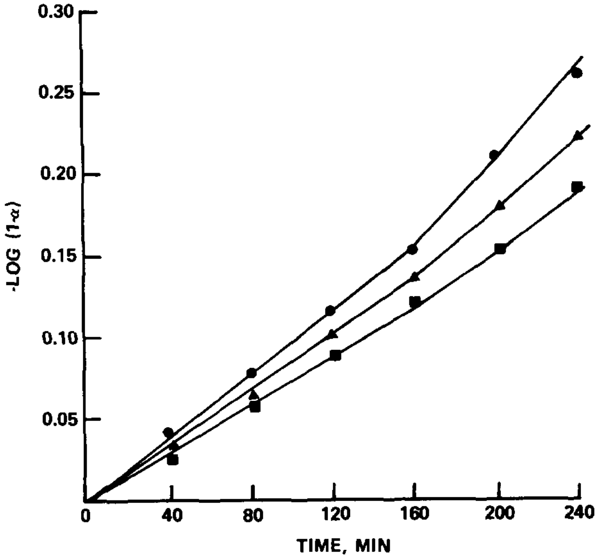

Fig. 6. First-order plots for crosslinked double base propellant in 1 M ethanolamine in toluene–isopropanol at various temperatures. ●, 60°C, $K_1 = 2.2 \times 10^{-3}$ min^{-1}; ▲, 50°C, $K_1 = 1.9 \times 10^{-3}$ min^{-1}; ■, 40°C, $K_1 = 1.7 \times 10^{-3}$ min^{-1}.

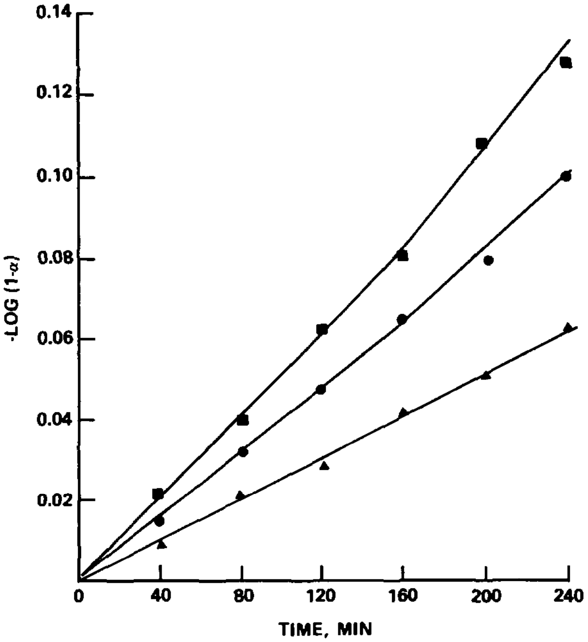

Fig. 7. First-order plots for crosslinked double base propellant in 1 M ethanolamine in isopropanol at various temperature, ■, 60°C, $K_1 = 1.2 \times 10^{-3}$ min^{-1}; ●, 50°C, $K_1 = 0.9 \times 10^{-3}$ min^{-1}; ▲, 40°C, $K_1 = 0.6 \times 10^{-3}$ min^{-1}.

TABLE 1

Kinetic data for solvolysis reaction of crosslinked double base propellant in ethanolamine solution [a]

Temp. (°C)	K_1 [b] ($\times 10^{-3}$ min^{-1})	K_2 [c] ($\times 10^{-3}$ min^{-1})
0.5 M ethanolamine in toluene–isopropanol		
40	1.0	1.1
50	1.2	1.3
60	1.4	1.8
E (kcal mole^{-1})	3.9	5.4
1 M ethanolamine in toluene–isopropanol		
40	1.7	2.0
50	1.9	2.5
60	2.2	3.3
E (kcal mole^{-1})	3.0	5.0
2 M ethanolamine in toluene–isopropanol		
40	2.1	2.8
50	2.4	3.9
60	3.2	5.0
E (kcal mole^{-1})	4.4	5.9
1 M ethanolamine in isopropanol		
40	0.6	0.6
50	0.9	1.0
60	1.2	1.5
E (kcal mole^{-1})	6.8	8.9

[a] Propellant-to-solvent ratio = 30 g/100ml.

[b] The first-order rate constant, K_1, obtained in the time period 0–160 min.

[c] The first-order rate constant, K_2, obtained in the time period 160–240 min.

ethanolamine into the binder network, followed by cleavage of the nitrocellulose bonds in the crosslinked binder, which facilitates the severing and solvolysis of the polyglycol linkages.

Reaction rates for binder

An additional set of experiments was run to test the postulates in the solvolysis reactions. Three reactions were carried out in 1 M ethanolamine in toluene–isopropanol at 60°C, namely (1) polyglycol (PG) by itself, (2) PG + HDI binder, and (3) PG + HDI + NC binder. The ratio of sample to solvent was only 3 g/100 ml because of the short supply of binder. Figure 8 shows that the slopes of the straight-line first-order plots of log(1-α) vs. time for the binder with NC breaks down at a rate which is three times faster than the binder without NC; the liquid PG sample undergoes solvolysis at an even faster rate, but this is not surprising because of the differences in

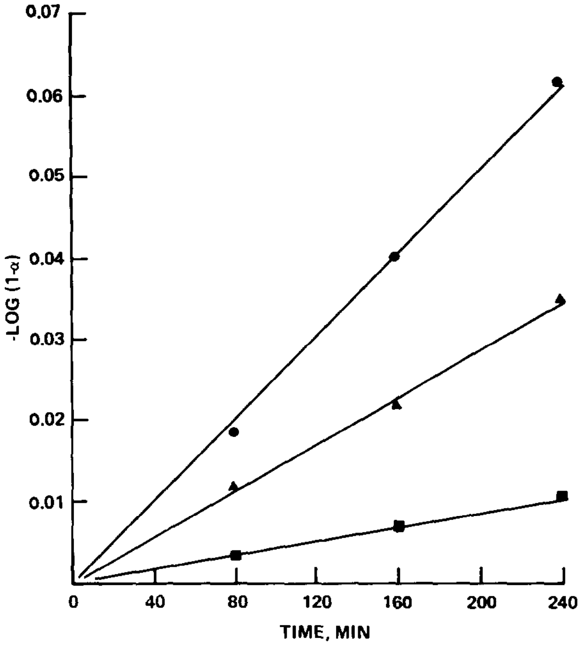

Fig. 8. First-order plots for crosslinked double base prepolymer and binders in 1 M ethanolamine in toluene–isopropanol. ●, PG, $K = 6 \times 10^{-4}$ min^{-1}; ▲, PG + HDI + NC, $K = 3 \times 10^{-4}$ min^{-1}; ■, PG + HDI, $K = 1 \times 10^{-4}$ min^{-1}.

physical state of the samples. Thus it is proved that the degradation of the nitrocellulose is the initial reaction and it accelerates the solvolytic breakdown of the binder. Apparently, the solvolysis reaction with the propellant is more complicated than with the binder because there are two rate constants with the former and only one with the latter. The rate constants for the binder breakdown cannot be compared with those for the propellant in Table 1 because the initial concentrations of each are widely different.

Activation energies

The rate constants for the solvolysis reactions are given in Table 1. The rates increase as (1) the ethanolamine concentration increases, (2) the temperature increases, and (3) after 160 min or 160/240 = 2/3 of the reaction is completed. The reaction is faster in the mixed solvent of toluene–isopropanol compared with isopropanol, probably because of the difference in swelling behavior due to the presence of toluene. A plot of K_1 or K_2 vs. ethanolamine concentration (Fig. 9) shows that there is a levelling off effect beyond 1 M ethanolamine; this indicates that 2 M ethanolamine is the optimum concentration when the ratio of propellant to solvent is 30 g/100 ml.

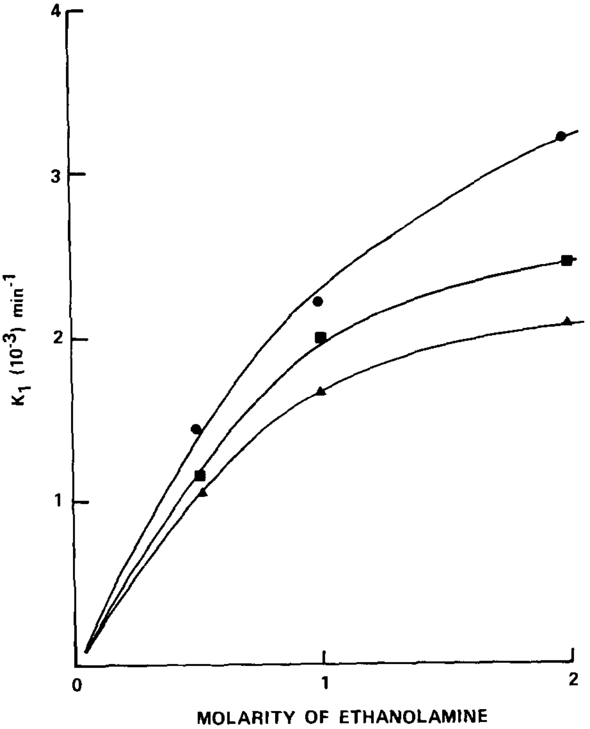

Fig. 9. Plot of K_1 vs. concentration of ethanolamine in toluene–isopropanol for the solvolysis reaction of crosslinked double base propellant. ●, 60°C; ■, 50°C; ▲, 40°C.

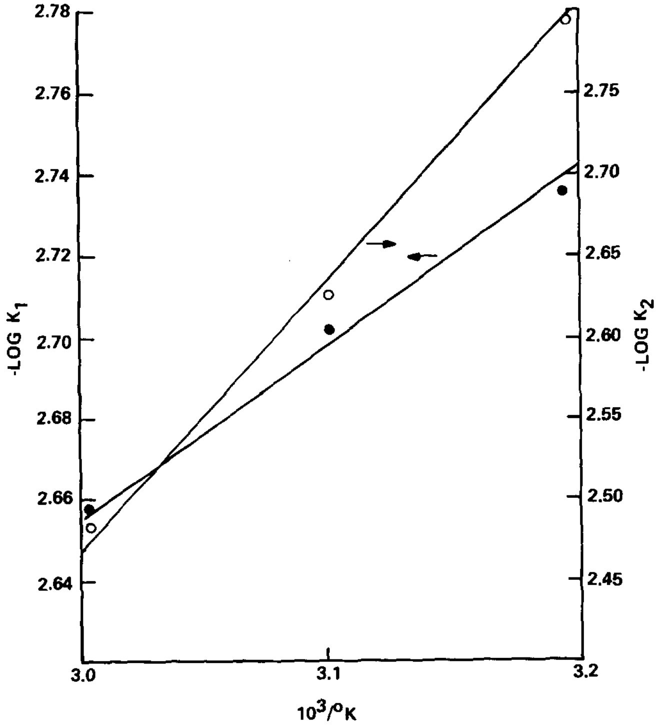

Fig. 10. Arrhenius plots for crosslinked double base propellant in 1 M ethanolamine in toluene–isopropanol. ○, $E = 3.0$ kcal mole^{-1}; ●, $E = 5.0$ kcal mole^{-1}.

A typical Arrhenius plot of log K vs. $1/T$ for the solvolysis reaction is given in Fig. 10. The activation energy is obtained from the slope of the line. Table 1 shows that the average values for the K_1 and K_2 plots for the activation energies are 5 kcal mole^{-1} in toluene–isopropanol and 8 kcal mole^{-1} in isopropanol. The lower activation energies and faster reaction rates found for the mixed solvent are in agreement with the visual observation of the solvolysis reaction wherein the sample pieces coalesce, the binder dissolves, and the fillers settle out.

Variable heating rate

Although nitrocellulose catalyzes the solvolytic breakdown of the binder, it was found that it did not catalyze the thermal breakdown of the dry solid binder. This was determined by a variable heating rate study carried out at 0.5–20°C min^{-1} in a nitrogen atmosphere. This kinetic method was developed by Flynn and Wall [1]. As the heating rate is increased, the TG decomposition curve shifts to higher temperature (Fig. 11). The kinetic data are obtained using the equation

$$\frac{\Delta \log \beta}{\Delta(1/T)} \approx \frac{0.457\,E}{R}$$

where β is the programmed heating rate and T is the temperature at a constant TG fraction. Figure 12 shows a variable heating rate plot, the activation energies obtained were 44 kcal mole^{-1} for the binder with or

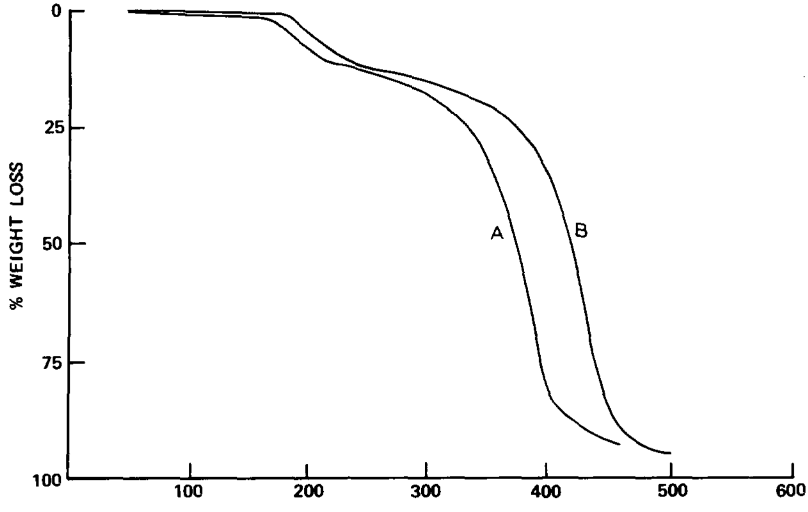

Fig. 11. Variable heating rate curves for crosslinked double base binder containing PG + HDI + NC. A, 0.5°C min^{-1}; B, 10°C min^{-1}.

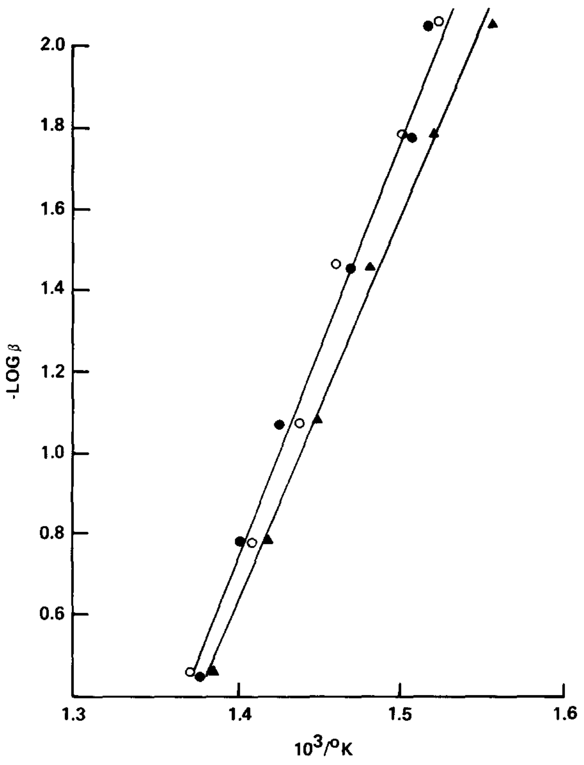

Fig. 12. Variable heating rate plots for crosslinked double base prepolymer and binders. ▲, PG, $E = 41.5$ kcal mole^{-1}; ●, PG + HDI + NC; $E = 44.4$ kcal mole^{-1}; ○, PG + HDI, $E = 44.4$ kcal mole^{-1}.

without NC and 41 kcal mole^{-1} for the liquid PG sample.

Thus it appears from the kinetic data that nitrocellulose catalyzes the solvolytic degradation but not the thermal degradation of a crosslinked double base propellant binder.

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1 J.H. Flynn and L.A. Wall, J. Res. Natl. Bur. Stand. Sect. A, 70 (1968) 478.