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KINETIC STUDIES OF THE THERMAL DECOMPOSITION OF TETRYL USING ACCELERATING RATE CALORIMETRY. PART II. PRODUCTS AND MECHANISM OF THE REACTION

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ABSTRACT

The products trinitroanisole and picric acid form the decomposition of tetryl in the ARC were measured at several stages during the complete decomposition. At the minimum self-heat rate after the first decomposition peak, tetryl had almost completely disappeared. Trinitroanisole and picric acid accounted for 62% of the tetryl decomposed, the remainder being gaseous products and some residue insoluble in ethanol. The second peak described the decomposition of the product picric acid. The total weight loss in the complete decomposition was 67%. The relation of the yields of the products to the kinetics of the decomposition suggests that picric acid may not be the source of autocatalysis, suggested to occur during the early stages of the decomposition. The activation energy and frequency factor for the second stage of the decomposition were substantially lower than those derived for the first stage, showing that autocatalysis is not important in the second stage of the decomposition.

INTRODUCTION

The kinetics of the decomposition of tetryl are complex and it is generally agreed that the reaction is autocatalytic [1]. The source of the autocatalysis is, however, not firmly established. The products of the decomposition include gases, principally CO_2, CO, N_2, NO and NO_2, and condensed-phase products, mainly trinitroanisole, picric acid and small amounts of *N*-methyl-2,4,6-trinitroaniline.

Detailed studies of the kinetics of the isothermal reaction were made by Dubovitskii and co-workers [2,3], which included analysis of both condensed-phase and gaseous products during the complete course of the decomposition. They concluded that decomposition occurred both by loss of nitrogen and loss of NO_2. The results showed that the latter contributed to acceleration of the rate as well as the condensed-phase picric acid, as had been suggested earlier [4]. More recent work by Hara and Osada [5], using a variety of analytical techniques, confirmed the simultaneous and independent formation of trinitroanisole and picric acid in the initial stages and the subsequent conversion of trinitroanisole into picric acid. An induction period was observed for the formation of both products. They suggested that radicals formed in the initial stages, rather than picric acid could promote the decomposition and thus cause an autocatalytic effect.

Studies by DSC and DTA generally showed two decomposition peaks but kinetic analysis has usually been confined to the first main peak [6–8]. As discussed in Part I [9], the activation energies measured from these techniques are usually considerably higher than those measured isothermally. In their DTA study Hara and Osada [5] found three peaks and identified the first peak with the simultaneous formation of both trinitroanisole and picric acid. They suggested that the second and third peaks were caused by conversion of trinitroanisole to picric acid and decomposition of picric acid, respectively.

Kinetic analyses of the rates of decomposition are far from satisfactory. Because of the observed induction periods, with possible autocatalysis, rate constants are difficult to define and depend on the stage of the decomposition at which measurements are made. The mechanism of the decomposition is not yet understood to the point where a measured activaton energy can be related to a particular step. It has been suggested [10] that the true rate constant for decomposition should refer to the initial rate of decomposition, before autocatalysis becomes important. Even if this could be measured, however, as seems doubtful, the rate of the total decomposition, including autocatalysis under various conditions, is still important in an assessment of the thermal hazard in handling and storage. The measurements obtained from the ARC cover the complete decomposition of the reactant and the use of these measurements to derive rate constants and activation energies for the decomposition were described in Part I [9]. In Part II we describe measurements of the formation of the condensed-phase products during the course of the decomposition and their relation to the self-heat rate. Analysis of the products was achieved by thin-layer chromatography and UV-VIS spectrophotometry. Activation energies derived by these and other methods are discussed in relation to the mode of decomposition of tetryl.

EXPERIMENTAL

Apparatus

The accelerating rate calorimeter (ARC) and its method of operation were described in Part I [9]. The UV-VIS spectroscopic analysis of the decomposition products was performed using a Shimadzu Model 200UV double-beam spectrophotometer with 1-cm cells and 1-nm slit width. Pre-coated TLC plates, silica gel 60F-254, with layer thickness 0.25 mm, were obtained from Canadawide Scientific Co.

Reagents

The tetryl sample used in this study was provided by Defence Research Establishment, Valcartier, Quebec (DREV) and used without further purification. Sodium ethoxide solution, 0.1 M, was prepared by dissolving sodium ethoxide, 97% (Aldrich Chemical Company), in ethanol. Picric acid (ACS grade) was obtained from Anachemica Chemical Company. A standard solution of 100 ppm was prepared and used in further dilutions. A standard tetryl solution, 100 ppm, was also prepared. All solvents were reagent grade.

Procedure

A 0.15 g sample was introduced into the titanium spherical bomb with 3/16 × 1 in. tube stem. The start temperature was 100 °C and the step-heat interval was 5 °C. The heat-wait-search sequence was performed as described in Part I [9] until the exothermic reaction was detected. The measurements of temperature, pressure, time and self-heat rate were then collected and stored in the microprocessor. Each test was stopped at a particular end temperature and cooled immediately. End temperatures were selected corresponding to the various stages in the formation of the products.

After cooling, the sample was dissolved in ethanol and transferred to a volumetric flask. The spherical bomb was rinsed with ethanol until the solution was colourless. Because complete removal with ethanol was difficult, acetone was used to dissolve any remaining solids. The acetone solution was transferred into a beaker and air dried. What remained was dissolved in ethanol, combined with the first ethanol solution and diluted to volume. The fraction of the residue insoluble in ethanol was determined by the weight difference of a filter paper before and after filtering the final ethanol solution. The weight loss was determined from the difference in weight before and after reaction.

Analysis of products

The two major products which have been reported from the decomposition of tetryl are trinitroanisole and picric acid. Analysis for the former product was considerably hindered by the inability to obtain a sample of trinitroanisole, due to restriction on its sale. Nevertheless by a combination of TLC analysis and UV-VIS spectrophotometric analysis and making use of published values for the absorption coefficient for trinitroanisole, a quantitative analysis for the reaction products was obtained.

TLC analysis

The solution of tetryl decomposition products was applied on two silica gel TLC plates. Each plate was developed in benzene and a solution of benzene/methanol/acetic acid (90/16/8 by volume) for 10 cm and air dried. Three components of the mixture were observed, of which bands (2) and (3) were identified as tetryl and picric acid, respectively, by comparison of retention times of the pure compounds.

Further identification of the components of the mixture was made by recovery of the separated bands on the TLC plates. Two ml of the ethanol solution was used for the separation. After development in benzene followed by air drying, each band, 1 cm width, was scraped off and extracted five times, each in 5 ml of ethanol. The extracts were centrifuged, combined and diluted to 25 ml. A plate was treated in the same way using the pure solvent to serve as blank.

UV-VIS spectrophotometric analysis

Calibration curves for tetryl and picric acid were obtained using ethanol solutions of 20, 15, 10, 5 and 4 ppm, prepared from the stock solution of 100 ppm. Each solution was scanned from 800 to 200 nm. For tetryl the absorption maxima was at 220 nm, while picric acid showed maxima at 215 and 360 nm. Figure 1 shows the spectra of tetryl, picric acid and trinitroanisole in ethanol. A linear relation between absorbance and concentration was obtained at the wavelengths shown in Table 1 where the values for the absorption coefficients are given. The absorbance of mixtures of tetryl and picric acid was measured to confirm that no chemical interaction occurred under the conditions of the measurements. The absorbances of the mixtures at the wavelength indicated were given by the following equations:

$$A_{400} = 53[\text{picric acid}]$$

$$A_{230} = 62[\text{picric acid}] + 81[\text{tetryl}]$$

where the concentrations are expressed as g l^{-1}.

Identification of bands (2) and (3) as tetryl and picric acid, respectively, was confirmed by the individual spectra. Identification of band (1) as trinitroanisole was made through its reaction with sodium ethoxide solution to form the σ-complex with strong absorption maxima at 410 and 490 nm [11,12]. Figure 2 shows a spectrum of this complex. The concentration of trinitroanisole was determined using the published value for ϵ at 490 nm (15850 l mol^{-1} cm^{-1}) [13], where the other products do not absorb, from the following equation:

$$A_{490} = 65[\text{TNA}]$$

where the concentration is expressed in g l^{-1}.

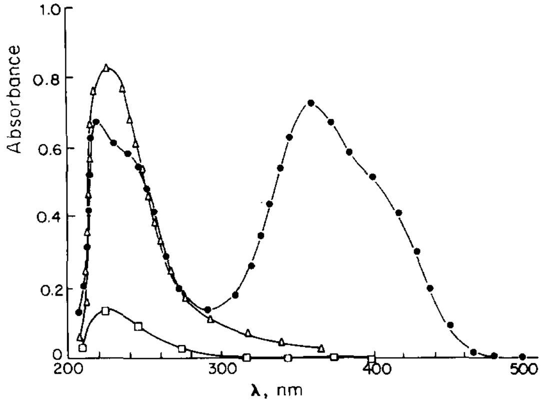

Fig. 1. Absorbance as a function of wavelength, ethanol solution. (△) Tetryl, 10 ppm; (●) picric acid, 10 ppm; (□) trinitroanisole, 2.4 ppm.

TABLE 1

Absorbance of solutions of tetryl and picric acid

Compound	Wavelength (nm)	Concentration ($g\ l^{-1}$)					ε ($l\ g^{-1}cm^{-1}$)
		0.020	0.015	0.010	0.005	0.004	
Tetryl	230	1.52	1.18	0.82	0.41	0.32	81
Picric acid	230	1.24	–	0.62	0.30	0.25	62
	400	1.06	–	0.52	0.26	0.21	53

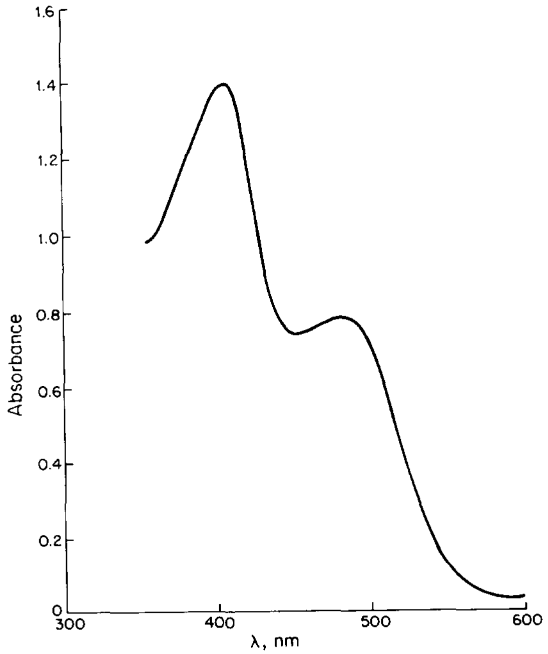

Fig. 2. Absorbance as a function of wavelength, σ-complex of trinitroanisole: 2 ml TNA, 24 ppm + 2 ml sodium ethoxide, 0.1 M ethanol solution.

TABLE 2

Condensed-phase products from the decomposition of tetryl in the ARC

Temperature (°C)	% TNA	% Picric acid	% Tetryl	% Weight loss	% Residue insoluble in ethanol
150	20.1	12.1	59.8	8.0	0
155	NA	24.9	NA	13.3	0
160	39.4	26.3	15.6	18.7	0
165	36.1	26.5	18.9	18.5	0
180	15.4	46.5	0.5	25.9	11.7
185	NA	49.0	NA	29.2	NA
200	4.4	41.2	0.7	38.5	15.2
217	NA	22.3	NA	48.1	NA
254	NA	0.03	NA	67.1	NA

NA Not analysed.

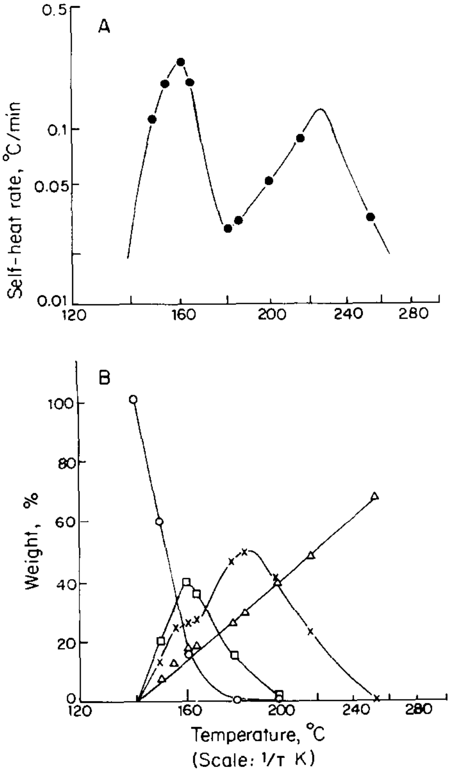

Fig. 3. Self-heat rate (A), reactant and product composition (B), as a function of $1/T$. Ti bomb; ϕ is 21. (A) Points indicate the temperature at which reaction was stopped for analysis. (B) Tetryl (○), trinitroanisole (□), picric acid (×), weight loss, $\omega_0 - \omega_F$ (△).

Analysis of the condensed-phase products by this method was made after stopping the reaction at selected temperatures throughout the course of the reaction. In some cases the recovered solution was not separated into the component fractions. From the spectrum of this solution in ethanol the concentration of picric acid only was determined from the absorbance at 400 nm. In these experiments the weight loss also was measured in the usual way. The results are given in Table 2 and Fig. 3.

DISCUSSION

The main condensed-phase products reported from the decomposition of tetryl, trinitroanisole and picric acid [2,3,5], were detected and analysed in the decomposition under the present conditions. The kinetic features of the formation and subsequent decomposition of the products were in agreement with the results of Dubovitskii and co-workers [2,3] and of Hara and Osada [5]. These independent studies both led to the conclusion that trinitroanisole and picric acid were both primary products, formed by parallel routes and that trinitroanisole subsequently decomposed to picric acid, which in turn decomposed at higher temperatures. This interpretation was most evident from the isothermal decompositions but was also supported by the DTA experiments of Hara and Osada [5] in which three exothermic peaks were observed. These were identified with the sequential decompositions described above. A similar conclusion is evident from the curves showing the product formation in Fig. 3.

In contrast to the DTA results, the self-heat rate shows only two well-defined peaks with increasing temperature. By comparison with the composition of the products, the first peak correlated with the disappearance of tetryl into both picric acid and trinitroanisole. The temperature at the maximum rate was 161°C where only about 15% of the tetryl remains. The rate constants obtained through analysis of the first peak therefore relate to the overall decomposition of the tetryl. The conversion of trinitroanisole into picric acid, evident from the analysis shown in Fig. 3B, is detectable only as an asymmetry in Fig. 3A, although data obtained using larger amounts of tetryl showed a small shoulder on this curve. The minimum between the peaks corresponds to complete disappearance of tetryl and the value of ΔT should therefore give a reasonable value for ΔH of the reaction,

tetryl → trinitroanisole + picric acid

The beginning of the second peak, 180 to 200°C refers to the decomposition of the remaining 10% of trinitroanisole into picric acid and the decomposition of picric acid. The major part of the second peak describes the decomposition of picric acid and the maximum rate (not as well defined as for the first peak) occurs at about 228°C, at which temperature about 20% of the maximum amount of picric acid remains. Kinetically these two peaks may be considered as separated, and each analysed independently. The difference in temperature between the points of maximum rates for each decomposition was about 65°C, but this difference will be a function of the rate and the ΔH of each decomposition and is not a general criterion for separation.

From the measurements of k^* as a function of temperature for the first decomposition peak, values of the activation energy, 52 kcal mol^{-1}, and the frequency factor, 10^{23} s^{-1}, were obtained and reported in Part I [9]. It was suggested that these "high" values, which cannot be interpreted in terms of passage over an energy barrier, in the usual way, were the result of autocatalysis and in particular of the enhanced importance of this effect under conditions of increasing temperature. Arrhenius parameters were also derived by kinetic analysis of the measurements of the second decomposition peak. Although less reliability is achieved from these measurements, it is evident from table 1 in Part I [9] that the activation energy, ~ 40 kcal mol^{-1}, is lower than that obtained from the first peak. With this activation energy and the measured value of k^* (fig. 3, ref. 9) a value for the frequency factor in the range 10^{14}–10^{15} s^{-1} was obtained. This decomposition therefore has Arrhenius parameters which are closer to those expected for a bond-breaking process. From Fig. 3 it appears that this decomposition begins only after tetryl has completely disappeared and trinitroanisole has almost disappeared. The self-heat rate therefore describes the decomposition of picric acid and the Arrhenius parameters obtained are in reasonable agreement with those reported for picric acid [14,15].

In all studies of the decomposition of tetryl reference is made to the autocatalytic character of the reaction. In several studies [16] it was suggested that picric acid may catalyse the decomposition of tetryl, possibly by a proton transfer reaction, giving a cation which is considerably less stable than the molecule. This conclusion is largely based on the results of the experiments of Hinshelwood [4] and of Dubovitskii and co-workers [2,3] in which addition of picric acid increased the rate of decomposition of tetryl and removed the induction period. The present results and those of Hara and Osada [5] as discussed in their work, do not substantiate this role of picric acid. The results of the isothermal decompositions at 150°C reported by Hara and Osada suggest that autocatalysis occurs before the formation of trinitroanisole and picric acid. The decomposition was not accelerated by either of these products. The results shown in Fig. 3, although not as extensive as the isothermal results, also do not indicate a particular acceleration of the decomposition by the formation of picric acid. This conclusion suggests that the increase in rate on addition of picric acid may be associated with the lowering of the melting point, as recognized by Hinshelwood [4] and discussed by Hall [8].

The more probable cause of autoacceleration is the formation of the reactive products, nitrogen dioxide and nitric oxide. The analysis of the gaseous products reported by Dubovitskii and co-workers [2,3] showed that both nitrogen dioxide and nitric oxide disappeared in secondary reactions and these authors recognized the importance of these reactive radicals in promoting decomposition of tetryl. Reactive gaseous products may exert their effect before diffusion from the solid phase. The effectiveness of this autocatalysis may therefore depend on a number of factors, such as the efficiency of removal of the products from the decomposing solid. Decomposition during increasing temperature may be more critically affected by the presence of these products.

SUMMARY

The two peaks in the self-heat rate as a function of temperature observed in the decomposition of tetryl in the ARC are shown to relate to the simultaneous decomposition into trinitroanisole and picric acid and to the subsequent decomposition of picric acid, respectively. From the kinetic analysis of the self-heat rate for the first peak, a "high" activation energy and frequency factor were obtained, which, it is suggested, indicates a complex mechanism of decomposition, probably involving autocatalysis. The kinetic parameters obtained from the analysis of the second peak are "normal" for a decomposition process and in agreement with previous results.

REFERENCES

1 S.M. Kaye, Encyclopedia of Explosives and Related Items, Vol. 9, U.S. Army Armament Research and Development Command, Dover, NJ 1980, p. T152.
2 F.I. Dubovitskii, V.A. Strunin, G.B. Manelis and A.G. Merzhanov, Russ. J. Phys. Chem., 35 (1961) 148.
3 F.I. Dubovitskii, G.B. Manelis and L.P. Smirnov, Russ. J. Phys. Chem., 35 (1961) 255.
4 C.N. Hinshelwood, J. Chem. Soc., 119 (1921) 721.
5 Y. Hara and H. Osada, Kogyo Kayaku, 42 (1981) 298 (English translation).
6 G. Krien, Explosivstoffe, 13 (1965) 205.
7 R.N. Rogers and E.D. Morris, Anal. Chem., 38 (1966) 412.
8 P.G. Hall, Trans. Faraday Soc., 67 (1971) 556.
9 P.P. Lee and M.H. Back, Thermochim. Acta, 107 (1986) 1.
10 M.A. Cook and M.T. Abegg, Ind. Eng. Chem., 48 (1956) 1090.
11 R. Foster, Nature (London), 183 (1959) 1042.
12 J.B. Ainscough and E.F. Caldin, J. Chem. Soc., (1956) 1269.
13 J.P. Phillips and F.C. Nachod (Eds.), Organic Electronic Spectral Data, Vol. IV, Interscience, New York, 1958.

14 Y. Hara, H. Eda and H. Osada, Kogyo Kayaku, 26 (1975) 66.
15 S.M. Kaye, Encyclopedia of Explosives and Related Items, Vol. 8, U.S. Army Armament Research and Development Command, Dover, NJ, 1978, p. P290.
16 C.E.H. Bawn, in W.E. Garner (Ed.), Chemistry of the Solid State, Butterworths, London, 1955.