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THE THERMAL DECOMPOSITION OF 2,3,4,6-TETRANITROMETHYL BETA-D-GL--ETC(U)
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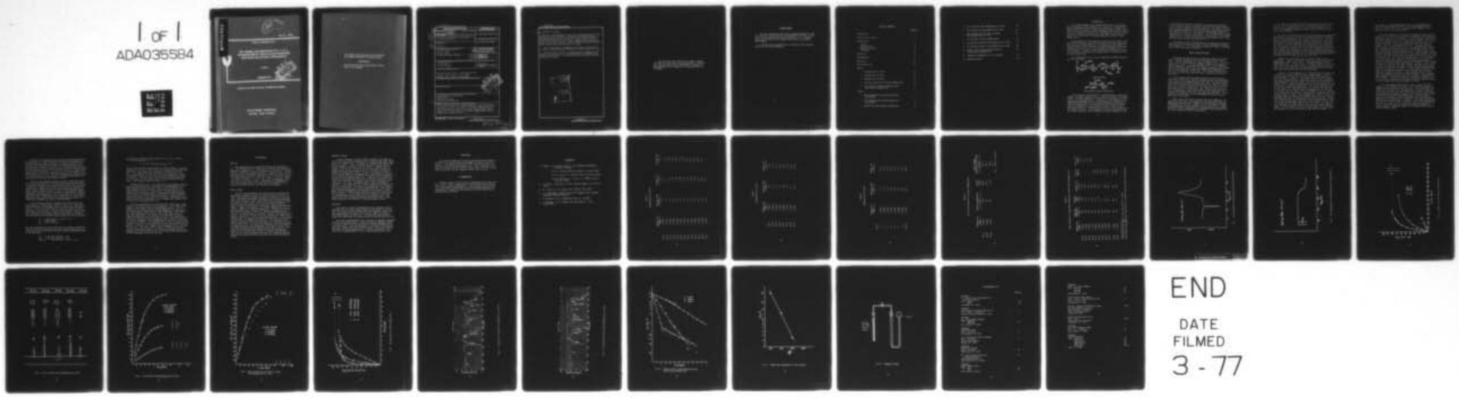

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TECHNICAL MEMORANDUM 2223

THE THERMAL DECOMPOSITION OF 2, 3, 4, 6-TETRANITRO-METHYL BETA-D-GLUCOPYRANOSIDE (BETA-METHYLGLUCOSIDE TETRANITRATE)

T. HIRATA

JANUARY 1977

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An initial study of the thermal decomposition of beta-methylglucoside tetranitrate (beta-megt) has been made. Although a number of experiments were carried out in a static system, the most useful information was obtained from manometric measurements of volume changes during the thermal decomposition. Decomposition was carried out at 120°C, 130°C, 140°C, and 150°C for various time intervals. → over

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20. ABSTRACT (Continued)

Thin layer chromatography (TLC) was used to follow the change in nitrate substituents in the solid residue. There are four trinitrate isomers of beta-methylglucoside; however, the TLC analysis only showed three spots at the expected positions for the trinitrates. Rarely was there a clear-cut evidence for the fourth trinitrate. As the decomposition proceeded further, the three "trinitrate" spots also became less intense and other nitrate spots began to appear at lower positions on the TLC strips.

Above its melting point, decomposition of beta-megt as followed manometrically, resembled the thermal decomposition of other nitrate esters.

The plot of time vs log (V_f - V) indicated that the decomposition consisted of at least two parts. An activation energy of 32 kcal/mole and a frequency factor of log A = 13 were obtained from the Arrhenius relationship for the initial section.

ACKNOWLEDGMENT

This investigation was based on an original proposal to study the synthesis, characterization, and decomposition of the nitrate esters of beta-methylglucoside initiated by Dr. Y. P. Carignan whose continuing advice and helpful discussions are gratefully acknowledged.

A special note of appreciation is expressed to Mr. Nathaniel Gelber for the nitrate analyses.

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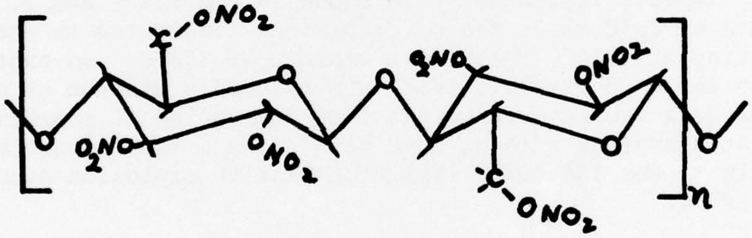
INTRODUCTION

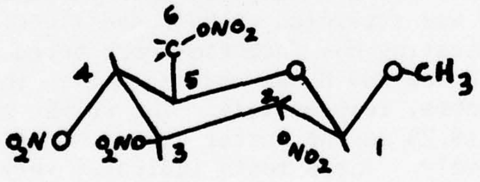
The thermal decomposition of mononitrate esters in the vapor phase are complex and the complexities increase for the polynitrate esters decomposing from the liquid and solid phases. Despite the difficulties, the kinetics of these decompositions have been studied because of theoretical and practical considerations since the nitrate esters are energetic materials and a knowledge of their mode of decomposition is essential for understanding their behavior under thermal stress.

The decomposition of polynitrate esters has been studied in the past (Ref 1); however, there does not appear to be any studies made on the thermal decomposition of 2,3,4,6-tetranitro-methyl beta-D-glucopyranoside, or more commonly beta-methylglucoside tetranitrate (hereafter beta-megt) which closely models the monomeric unit of nitrocellulose. A kinetic study of beta-megt is obviously of value in the effort to understand the decomposition of nitrocellulose at elevated temperatures.

The relationship of beta-megt to completely nitrated nitrocellulose is shown below:



Nitrocellulose



beta-methylglucoside tetranitrate

As can be seen, nitrocellulose is polymer having a simple beta-D-glucose structure joined at the 1,4 carbon positions by an oxygen bridge. The model compound was chosen for study because of its possible use as an energy source. In addition, it was thought that a thorough understanding of its thermal decomposition would give insight to the behavior of the more complex nitrocellulose polymer. The model compound has nitrate groups attached to the 2,3 and 6 carbon positions as in nitrocellulose as well as a nitrate group in the carbon-4 position. The end groups of nitrocellulose would have the nitrate functions at the carbon-1 and carbon-4 positions. The

C-1 position in beta-megt is blocked with a methoxy group whereas in nitrocellulose the C-1 position is joined by an oxygen bridge to the C-4 carbon of another anhydroglucose unit. The totally nitrated, beta-D-glucose pentanitrate is less stable and slowly decomposes at room temperature (Ref 2). The 4-methyl beta-methylglucoside 2,3,6-trinitrate is a colorless syrup (Ref 3). On the other hand the model compound chosen is readily obtainable by the nitration of the parent compound and is a stable solid melting at approximately 116°C. (Uncorrected capillary melting point (Ref 4).)

The purpose of this investigation was to explore the thermal decomposition of beta-megt and obtain the kinetic parameters defining its decomposition. The liquid phase decomposition above its melting point was the first area of interest.

RESULTS AND DISCUSSION

Preliminary thermal data on beta-megt were obtained by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA). Typical thermograms are shown in Figures 1 and 2. At a heating rate of 20°C min^{-1} the DSC thermogram indicated an endotherm commencing at 100°C, reaching a minimum at 120°C. An exotherm was seen to commence at about 145°C and reached a maximum at about 195°C. The TGA data indicated a weight loss commencing at approximately 155°C at a heating rate of 20°C min^{-1}. At a faster heating rate of 30°C min^{-1}, the TGA curve indicated that an explosion occurred at about 195°C.

It was assumed from the thermal profiles that beta-megt was stable up to about 150°C. However, when purification by sublimation of this nitrate was attempted at 90°C and 110°C in a closed system, brown fumes indicating NO_2 formation were noted. Therefore, decomposition at 90°C and 100°C was carried out in the static system for nine and four hours, respectively. The weight loss was 61.6% in the former and 19.2% in the latter case. Nitrate loss was 78% and 33.1%, respectively. These tests indicated very definitely that substantial decomposition could occur from the solid phase. It was decided, for this study, that the decomposition from the liquid phase would be followed.

Table 1 shows the results obtained from the decomposition at 120°C using the static system except for TD-30 and TD-31 where the manometric system was used. Sample size was approximately 30 mgs and decomposition was for intervals of one to six hours. Attempts to quantitatively isolate unreacted starting material after decomposition by various techniques were unsuccessful and therefore only the total weight loss could be ascertained.

The weight loss ranged from 1% for 60 minutes of reaction time (TD-13, -14, -20) to about 15% for a 360 minute run (TD-22, -23). TD-21 was also decomposed for 360 minutes but the weight loss of 23.2% seems anomalous compared to the 13.5% and 15.7% loss in the other two experiments.

The loss of analyzable nitrate from the decomposition ranged from approximately 4% (TD-14 and -20) for decomposition of one hour duration to the neighborhood of 30% (TD-22) after six hours. The 49.4% loss of nitrate obtained in TD-21 appears anomalous as did the loss of weight for the same experiment mentioned previously. Experiments TD-30 and TD-31 were followed by the volume of gases evolved; however, the weight loss after 120 and 170 minutes was only about four and seven percent, respectively. Since this temperature (120°C) was only slightly above the melting point (116°C), more extensive data were obtained from experiments at 130°C where decomposition proceeded at a more reasonable rate and kinetic calculations were made from experiments where the weight losses were above 20%.

Weight loss at 130°C and 140°C is shown in Tables 2 and 3, respectively. Figure 3 depicts the weight loss data from the three temperatures (120°C, 130°C, 140°C). The maximum weight loss was approximately 80%. At 140°C, this was reached in about 10 hours; at 130°C, this occurred beyond 16 hours. The data obtained for decomposition at 120°C indicates that maximum decomposition would occur only after considerable time at this temperature.

Progress in the decomposition as evidenced from the residue can be seen in the results from thin layer chromatography. Typical chromatograms of residue after various periods of decomposition at 130°C are shown in Figure 4. The topmost spot is due to unreacted beta-megt as determined from comparison with pure starting material chromatographed in the same manner. The three spots which follow were the first to appear upon decomposition of starting material and a fourth spot occasionally appeared in this area as decomposition of the original sample progressed further. No further spot appeared in this region. At longer periods of decomposition, not only was the starting material almost entirely consumed but also the quantity of the three spots was reduced. Simultaneously, materials with lower R_f values began to appear. The prominant spots (three or four) immediately below the beta-megt are probably due to the trinitrates of beta-methylglucoside as indicated from denitration studies. Futhermore, there are only four trinitrates of beta-methylglucoside, which is also the maximum number appearing in this region. If these are the trinitrates, the implication is that one of the $O\text{-}NO_2$ bonds behaves differently from the others since only three spots normally appear. All the carbons with nitrate substituents in the beta-megt are secondary (C2, C3, C4) except one (C6) which is primary. In this respect, beta methlyglucoside reacts with triphenylmethyl chloride to give almost exclusively the 6-triphenylmethyl ether (Ref 5); however, the cause of this difference, whether steric or electronic, has not been investigated.

Since the separation of unreacted beta-megt from other nitrate isomers has not yet been satisfactorily accomplished, the thermal decomposition could not be followed by loss of sample but could be followed most conveniently by observing a physical change in the system. Using the manometric system, the volume increase due to gas evolution was observed. Typical gas volume-time curves are shown in Figures 5 and 6 for decomposition at 130°C. The curves have the familiar shape found for other nitrate ester decompositions indicating a continuous volume increase until the maximum or final values were reached, then remaining constant up to 75 and 100 hours. The gas phase gradually became brown due to NO_2, passed through a maximum intensity and then became colorless. The presence of NO in the colorless gas phase was shown by the reappearance of the brown color from the reaction $2NO + O_2 = 2NO_2$ upon introduction of air. The sample sizes were varied from 0.0260 g to 0.1029 g and, as expected, a family of curves were obtained wherein proportionately larger volumes of gases were obtained from larger samples. However, as can be seen in Figure 6, based on a unit mass of sample the rates of gas evolution were the same when the sample size was increased approximately twofold from 0.0545 g to 0.1029 g. The same figure also shows that there was considerable deviation from the normal curve when the sample was reduced to 0.0260 g. Larger samples were not tried because of equipment limitation and possible hazard. This parameter (mass/volume or degree of filling) was not further examined or verified although it is important from the standpoint of autocatalysis in the reaction. Sample sizes between 50 mg and 100 mg were used in all other experiments using the manometric system.

It is quite apparent from Figure 7 that at 130°C the final volume, V_f, was obtained only after 75 hours although complete decomposition had probably occurred earlier. On the other hand, the reaction at 140°C and 150°C had progressed to the point where the volume did not further increase after about 25 hours. The dotted line extrapolation appears to indicate that V_f was attained in about 15-20 hours at the two higher temperatures. The data shown in Figure 7 and tabulated in Table 4 represents those runs where decomposition was carried out to completion. The total gas evolution per unit mass obtained from the average at these three temperatures was 340 ± 10 cc gm^{-1} at STP. Using this value, the theoretical V_f values for all runs were calculated from the known quantity of initial samples. Subsequent graphs and calculations were based on these calculated values.

The infrared absorption spectra of gases from the decomposition are informative. A good spectrum with definitive absorptions was obtained after more than seven hours of reaction at 130°C (Fig 8). The same spectrum with minor changes in absorption bands was also obtained after 25 hours at 150°C (Fig 9). The major differences are the reduction of the band centered at about 1875 cm^{-1} and an increase of the band between 1100 cm^{-1} to 1225 cm^{-1} for the gas sample from decomposition at the lower temperature (Fig 8) to the sample at the higher temperature (Fig 9). The noncorrespondence of band positions was found to be due to a malfunction in the spectrometer where the drum speed did not match the frequency readout.

Except for the infrared absorption spectra indicating similarities, the gaseous products have not been quantitatively identified in detail and therefore it is not possible at this time to correlate a theoretical volume increase from the stoichiometric equation of decomposition. However, since the infrared data did show that the gases at final volume (25 hours at 150°C) at two different temperatures (130°C and 150°C) were very similar to the sample at shorter decomposition time where V_f was not reached (130°C), it was assumed that at the three temperatures and for reactions not carried out to completion, the V_f value could be calculated from the results obtained from decompositions where V_f was determined.

On the assumption that the decomposition followed the first order rate law, a typical plot of time vs log $(V_f - V)$ shows that the decomposition of beta-megt follows at least a two stage process (Fig 10). This is not apparent from either the volume vs time or weight loss vs time curves. This two stage process has been found for nitrate esters previously studied in this manner. The specific rate constants for the initial period of reaction was calculated from the slope of the foregoing graph obtained from the relationship:

$$kt = 2.303 \log [(V_f - V_o)/(V_f - V)]$$

V_f = final volume
V = volume at time t
V_o = 0

For those experiments at 130°C which were not carried to completion, the V_f value was calculated as previously indicated and k_{sp} was calculated for various time intervals from the above equation rewritten in the form below:

$$kt_1 = 2.303 \log [(V_f)/(V_f - V_1)]$$
$$kt_i = 2.303 \log [(V_f)/(V_f - V_i)]$$
$$k(t_i - t_1) = 2.303 \log [(V_f - V^1)/(V_f - V_i)]$$

Calculations were made at time intervals $\Delta t = (t_i - t_1)$, setting $t_1 = 0$ and therefore $U_1 = 0$.

$$k = (1/\Delta t)\ 2.303 \log [(V_f)/(V_f - V)]$$

These results from both calculations are shown in Table 5. Note the constancy of the rate at 130°C with loss of weight which ranges from 20% to 80%. The average rate constant at 130°C was 4.36×10^{-5} sec^{-1}. The constants at 140°C and 150°C are also given in Table 5. The Arrhenius plot of log k vs the reciprocal temperature is shown in Figure 11. From the slope of the line an activation energy of 32 k cal $mole^{-1}$ for the initial portion of the reaction was calculated. The frequency factor was log A = 13.

Although the log $(V_f - V)$ vs time plot (Fig 10) appears to indicate an acceleration in the second part of the decomposition after approximately four hours at 130°, there is no acceleration or a slight decrease after four hours at 140°C and a decrease in rate after two hours at 150°C. Autocatalysis is always possible at NO_2 accumulates in the decomposition. Furthermore, the DSC thermogram (Fig 1) indicates that the exothermic portion of the beta-megt decomposition occurs in the vicinity of 140-150°C. Therefore an acceleration would not be unexpected in this decomposition; however, the data does not convincingly show this.

A possible explanation for the second part of the curve is the oxidative reactions of NO_2 at room temperature. The reactor volume immersed in the thermal bath was approximately four ml. The remainder of the volume increase during decomposition was due to mercury displacement in the burette at room temperature. Therefore, as the volume increased above four ml, most of the gases were at or near room temperature. The fading of the brown color as the decomposition progressed indicated that the rate of NO_2 formation decreased and also that NO_2 was disappearing due to oxidative reactions with organic components of the decomposition as well as reaction with mercury in the burette. The increased rate at 130°C may mean that the secondary reaction at room temperature was more rapid than the decomposition. At 150°C, the secondary reaction appears to be at the same rate at 130°C. The data at 140°C cannot be rationalized from the available information; however, the IR spectra of gases from the decomposition at 130°C and 150°C were similar whereas the spectrum from the 140°C decomposition was not the same.

EXPERIMENTAL

Material

Beta-methylglucoside was obtained from K and K Laboratories, Inc. The tetranitrate was synthesized according to the method of Honeyman and Morgan (Ref 6). The product was dissolved in a minimum quantity of methanol and reprecipitated in distilled water. Several reprecipitations and washings were made to remove all traces of acid. The final product indicated a melting point of 115°C and the following elemental analysis: C = 22.5%, H = 2.79%, N = 14.79%. Theory: C = 22.4%, H = 2.69%, N = 14.97%. Thin Layer Chromatography (TLC) indicated only one nitrate spot. Purification by sublimation at 110°C was attempted but it was later found that decomposition occurred even at 90°C and this was therefore discontinued.

Static System

The first few experiments were carried out in a vacuum system where gaseous products could be continuously removed from the reaction site; however, beta-megt was seen to sublime out of the hot zone. Sublimation experiments indicated that there was appreciable sublimation pressure at 100°C and therefore the following procedure was used in a static system. Samples were placed in ampoules with bulb ends blown from pyrex tubes, evacuated, and flame sealed. Sample weights were obtained by weighing the ampoules empty and with samples. Samples were immersed in a constant temperature bath previously brought up to operating temperature. The bath consisted of Dow Corning 550 fluid, silicone oil, heated and temperature controlled by a knife heater via a Precision Scientific Electronic Relay Control. The thermal lag was such that, visually, the temperature appeared constant to ± 1.0°C but may have been better. After a given reaction time, the ampoule was removed from the bath and cooled with liquid nitrogen to terminate the reaction. The long neck of the ampoule was scored with a file and attached to a vacuum system with a short rubber hose. The system and connecting lines were evaluated, the ampoule broken at the scored mark and the gases were separated into the condensible and noncondensible fractions at -196°C. Both CO and NO were qualitatively identified mass spectroscopically. Sample size was usually about 30 mg or 0.08 moles of beta-megt. At 120°C and six hours of decomposition time, the condensible gaseous products were insufficient to show distinctive infrared absorption spectra.

Manometric System

A simple manometric system as shown in Figure 12 was also set up to follow the thermal decomposition by observing the volume change during the decomposition. The sample was weighed in NMR sample tubes of 2.5 ml volume. A layer of dodecane was placed on the mercury to prevent immediate reaction of NO_2 with mercury. However, NO_2 was soluble in the oil and eventually the attack on mercury produced enough scum to obscure the mercury level. When this occurred, the mercury was removed and cleaned. The entire system was cleaned, dried and reassembled for subsequent runs. The sample was inserted in the reactor which was attached to the capillary 3-way stopcock by way of the 10/30 standard taper joint. After the entire system was flushed with nitrogen, the mercury in the burette was raised to the "zero" level with the 3-way stopcock open to the system and to the atmosphere. This gave a minimum reaction volume at atmospheric pressure. A gas pressure in the system was necessary to prevent sublimation of the sample. The reactor with sample was then inserted into the previously heated constant temperature bath. The volume of gases from the decomposition was measured on the burette at atmospheric pressure by equalizing the mercury levels in the burette and in the reservoir. At the termination of the reaction, the reactor was withdrawn from the oil bath, the gases sampled via the 3-way stopcock and their infrared absorption spectra were noted. Atmospheric pressure was recorded on a separate manometer system.

Analytical

The weight loss from the decomposition was calculated from the difference of the original sample weight and the weight of the residue. The nitrate loss was obtained from the difference between the calculated amount of original nitrate and the amount of nitrate in the residue found by wet analysis. Infrared, mass spectroscopic, weight loss and nitrate loss analyses were carried out where possible.

Thin Layer Chromatographic (TLC) analysis was frequently employed to follow the decomposition. A drop of acetone or methanol solution of solubles from the residue was placed on Eastman Chromagram 13179 silica gel (6061). This was developed in a solution of 75% ethylene chloride, 20% methylene chloride and 5% ether. The various nitrates were made visible by spraying the air dried TLC sheets with a solution of 0.2 g diphenylamine in 100 cc concentrated sulfuric acid.

CONCLUSION

The thermal decomposition of beta-methylglucoside tetranitrate consists of at least two parts which appear to follow first order kinetics. The decomposition between 130°C and 150°C proceeds at a rate which can be followed manometrically. Under conditions of the present investigation, the activation energy for the initial process was 32 kcal $mole^{-1}$ and the frequency factor, log A, was 13.

RECOMMENDATION

Detailed studies should be made at temperatures above 150°C and below 130°C in order to determine the fit of the kinetic constants over a wider range of temperatures. Further studies should be made at a wider range of mass/volume ratios to study the possibility of autocatalysis. Quantitative determinations should be made of the gaseous reaction products.

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Table 1

Decomposition at 120°C

	Sample size (gm)	Reaction time (hr)	Weight loss (%)	Nitrate loss (%)
TD-13	0.0320	1.0	0.6	--
TD-14	0.0310	1.0	0.9	3.92
TD-20	0.0342	1.0	1.47	3.83
TD-15	0.0330	2.0	2.70	6.80
TD-16	0.0328	2.0	3.35	8.56
TD-30	0.1019	2.0	3.83	9.10
TD-31	0.0522	2.8	6.71	16.50
TD-17	0.0351	4.0	5.70	14.0
TD-18	0.0357	4.0	9.24	22.8
TD-19	0.0343	4.0	9.62	24.6
TD-21	0.0345	6.0	23.2	49.4
TD-22	0.0349	6.0	13.5	31.1
TD-23	0.0353	6.0	15.7	--

Table 2

Decomposition at 130°C

	Sample size (gm)	Reaction time (hr)	Weight loss (%)
TD-26	0.0970	0.9	14.5
TD-32	0.0606	2.0	21.75
TD-25	0.0935	2.1	23.1
TD-28	0.1016	2.0	25.9
TD-27	0.0969	3.0	33.9
TD-29	0.1018	7.6	53.5
TD-35	0.1029	16	64.8
TD-41	0.0545	75.5	81.8

Table 3

Decomposition at 140°C

	Sample size (gm)	Reaction time (hr)	Weight loss (%)
TD-37			
A	0.0503	1.0	25.2
B	0.0489	2.0	47.6
C	0.0543	3.0	58.3
D	0.0531	4.0	65.5
E	0.0360	5.0	68.4
F	0.0499	6.0	72.5
G	0.0536	9.0	79.8
TD-38	0.0542	25.7	80.0

Table 4

Total gas evolution at various temperatures

				Final volume
	Sample size (gm)	Reaction temperature (°C)	V_f(STP) (cc)	V_f(STP) per unit mass (cc gm^{-1}
TD-41	0.0545	130	18.05	331.2
TD-38	0.0542	140	19.01	350.7
TD-39	0.0504	150	17.14	340.0
			Avg	340.0 ± 10cc gm^{-1}

Table 5

Rate constants of beta-methylglucoside tetranitrate decomposition

	Sample size (gm)	Reaction temperature (°C)	Reaction time (hr)	Weight loss (%)	*K x 10^5 (sec^{-1})	**K x 10^5 (sec^{-1})
TD-26	0.0979	130	0.99	14.5	--	4.77
TD-32	0.0935	130	2.0	21.75	--	4.41
TD-25	0.0935	130	2.1	23.1	--	4.23
TD-28	0.1016	130	2.0	25.9	--	4.28
TD-27	0.0969	130	3.0	33.9	4.30	
TD-29	0.1018	130	7.67	53.5	4.49	
TD-36	0.0515	130	14	--	4.35	
TD-35	0.1029	130	16	64.8	4.33	
TD-41	0.0545	130	75.5	81.8	4.11	
TD-38	0.0542	140	25.7	80	12.63	
TD-39	0.0504	150	25	85.7	29.48	

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*Calculated from slope of Log $[(V_f)/(V_f-V)]$ vs time.

**Calculated from $\frac{2.303}{\Delta t}$ log $[(V_f)/(V_f-V)]$ at several time intervals and averaged.

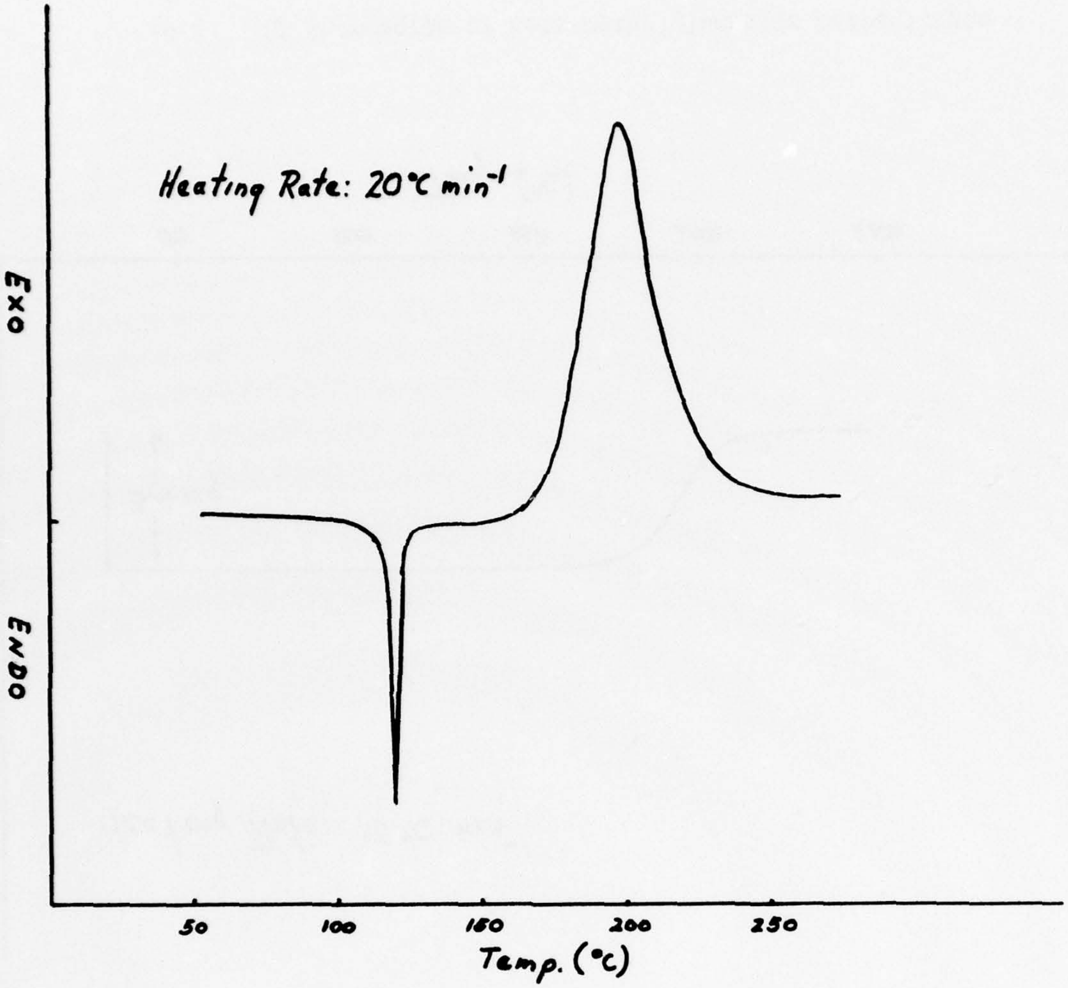

Fig 1 DSC thermogram of beta-methylglucoside tetranitrate

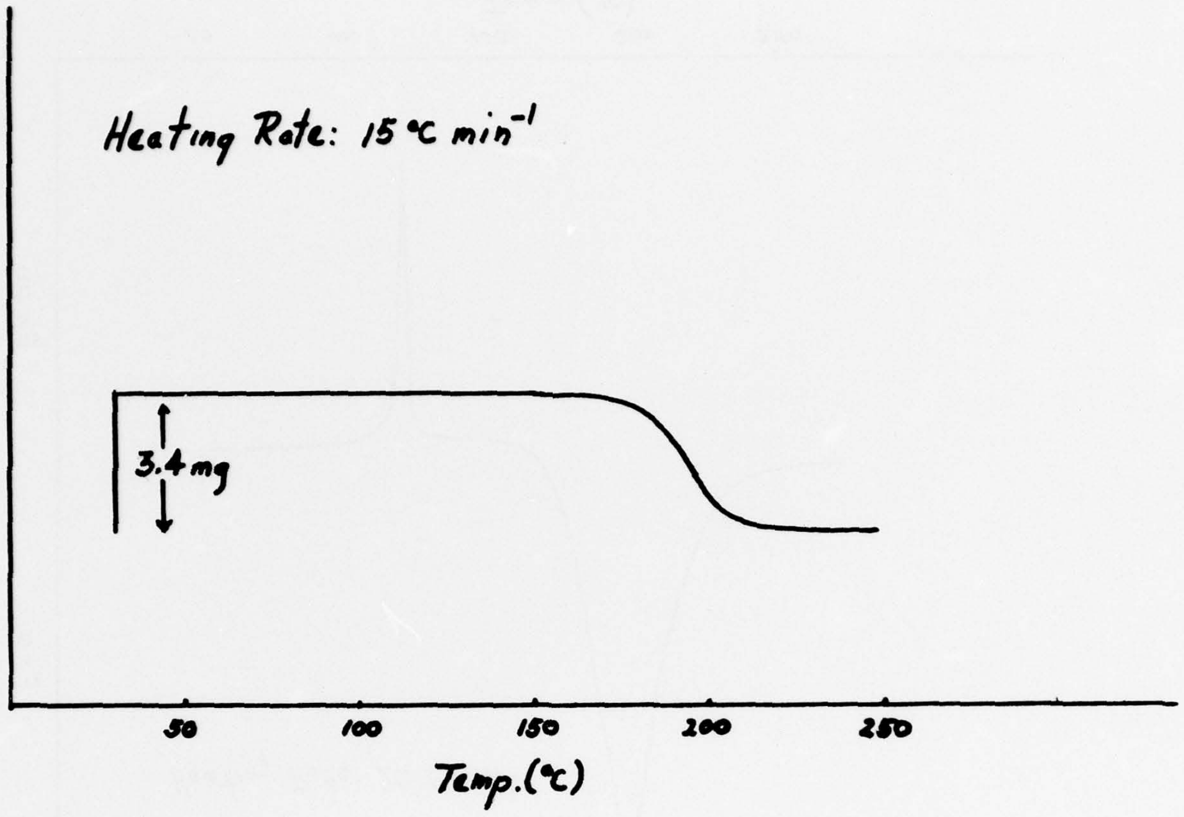

Fig 2 TGA thermogram of beta-methylglucoside tetranitrate

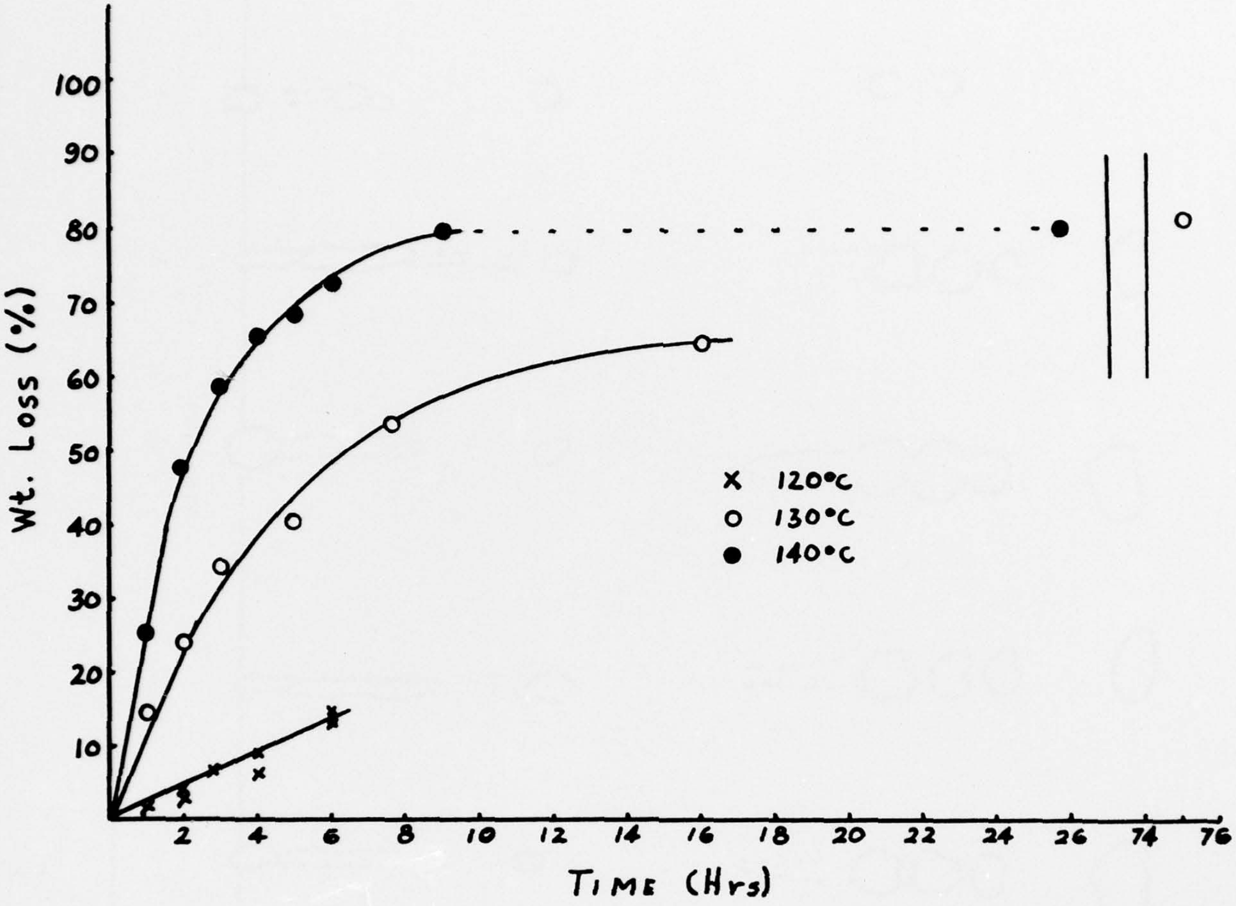

Fig 3 Weight loss from thermal decomposition

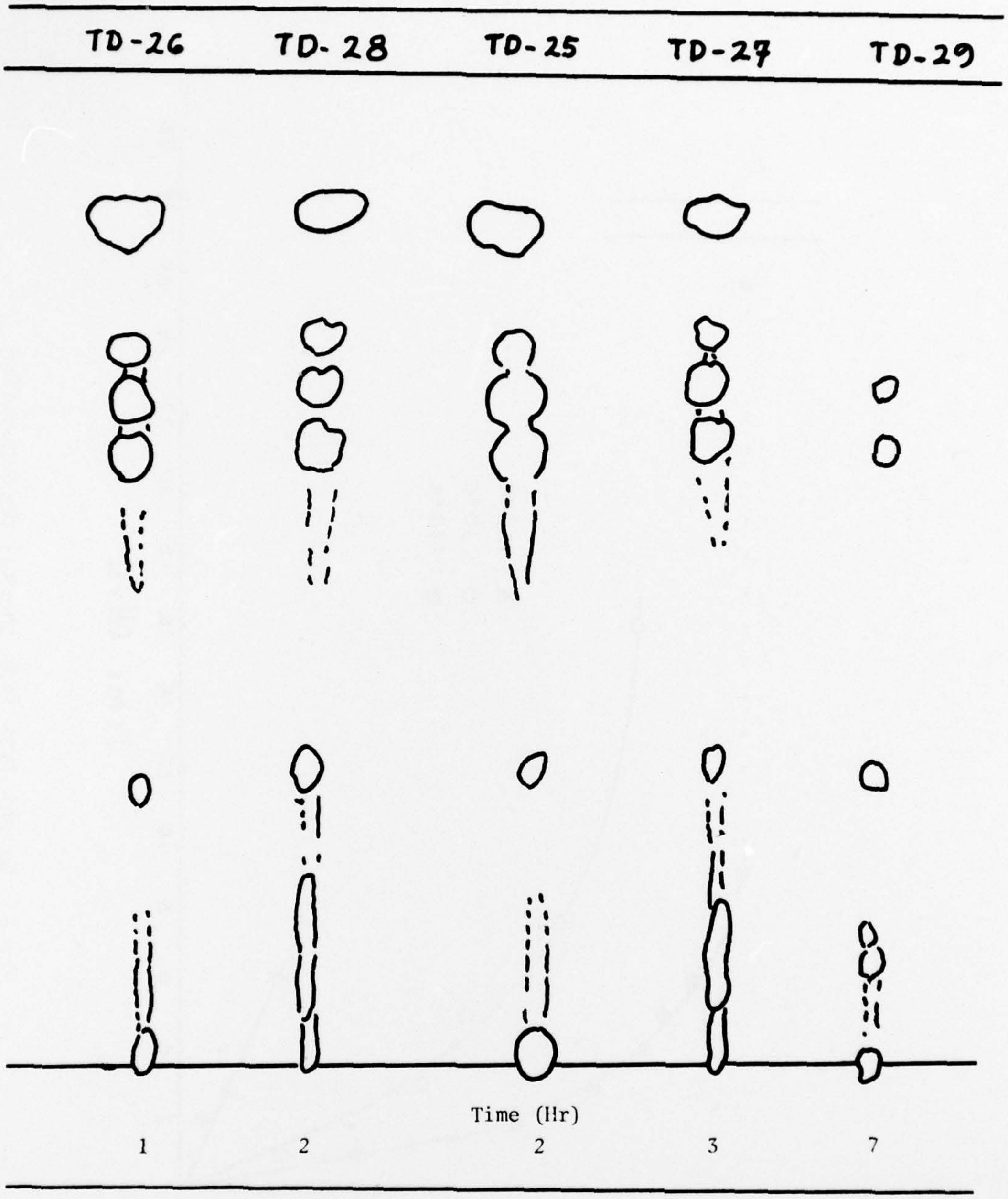

Fig 4 TLC of residue after decomposition at 130°C

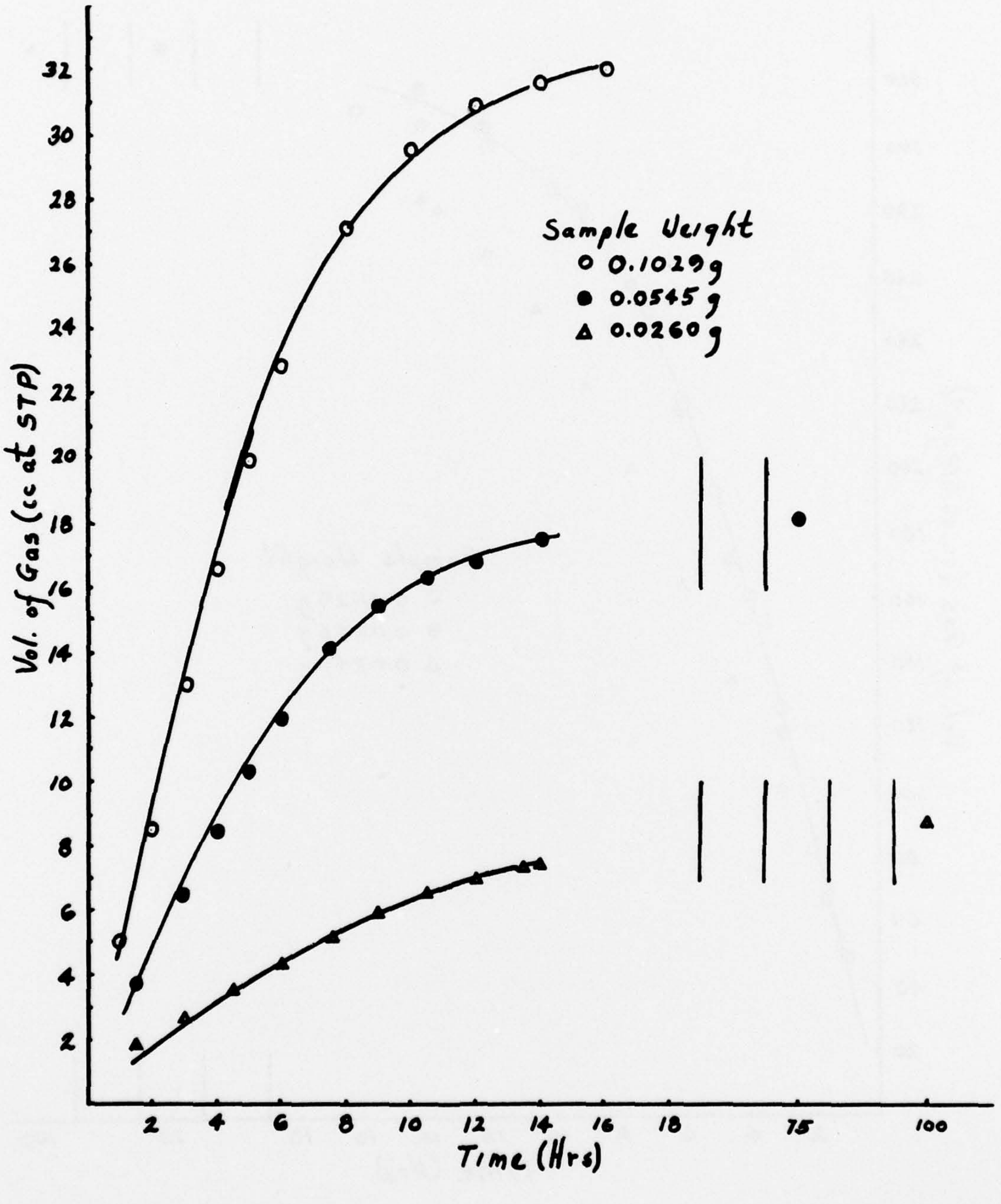

Fig 5 Gas evolution from decomposition at 130°C

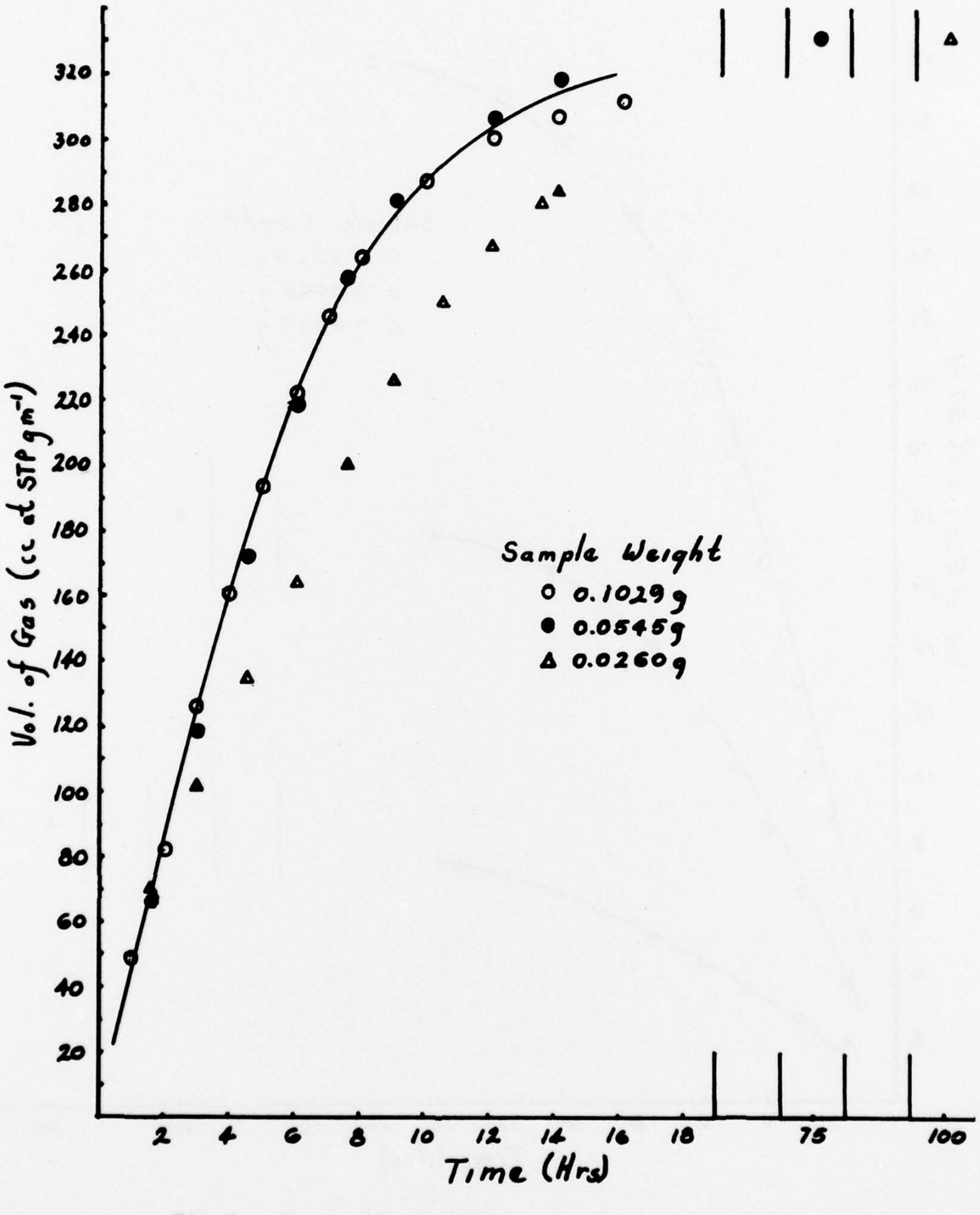

Fig 6 Gas evolution per unit mass of sample from decomposition at 130°C

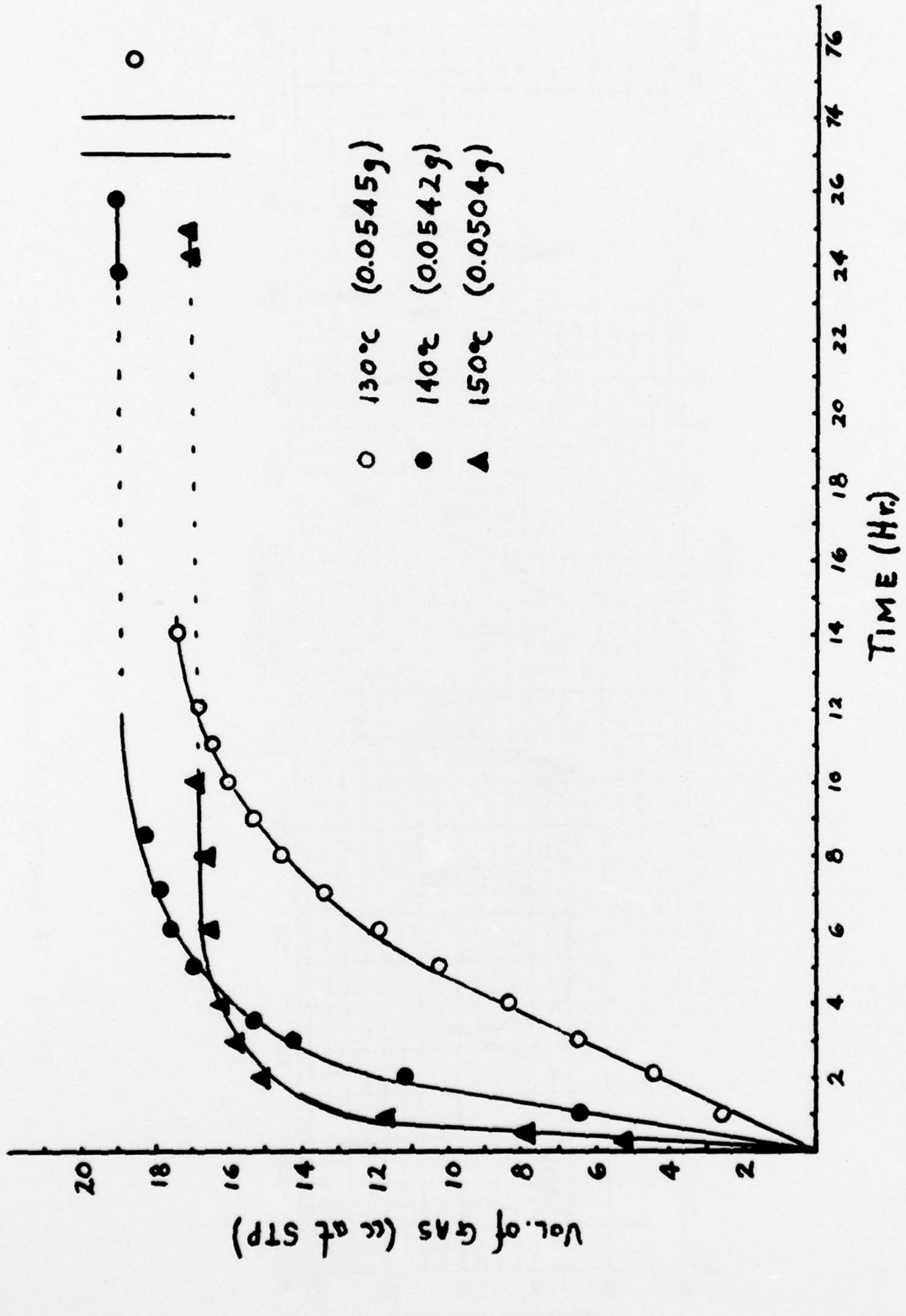

Fig 7 Gas evolution at three temperatures

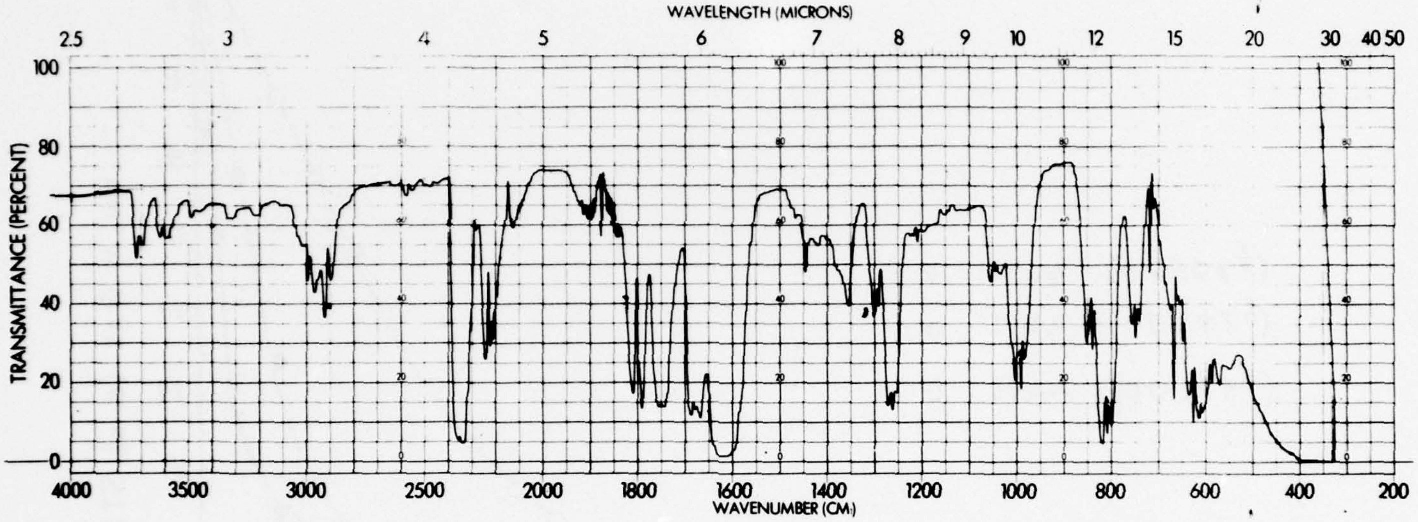

Fig 8 IR spectrum of gases from decomposition at 130°C

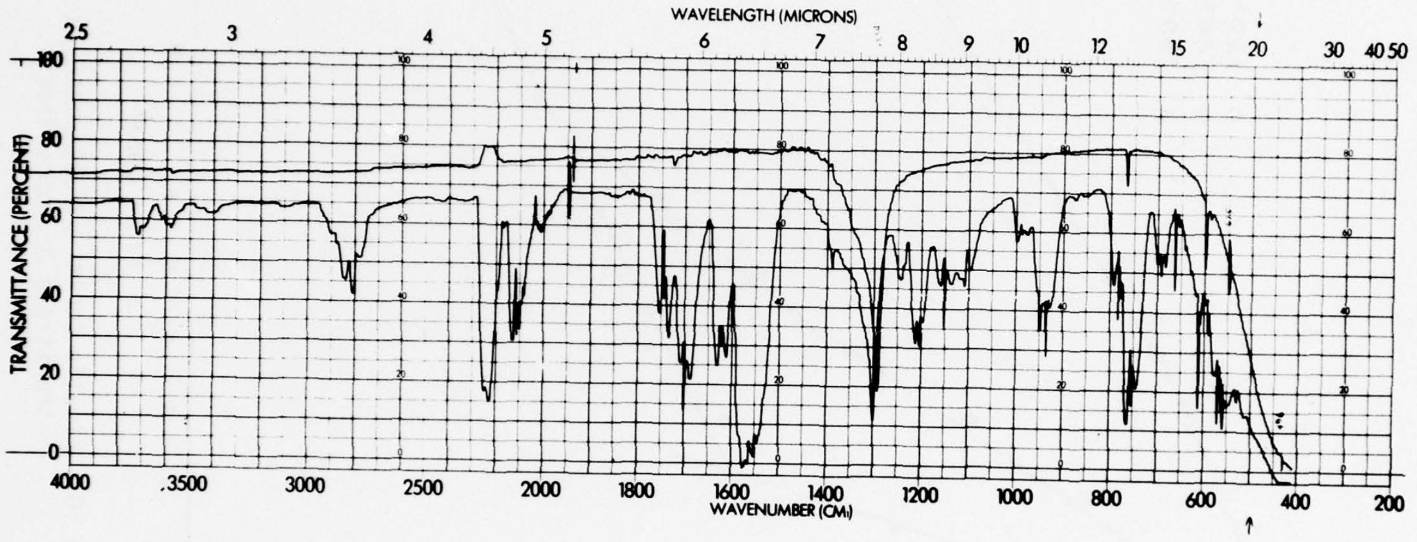

Fig 9 IR spectrum of gases from decomposition at 150°C

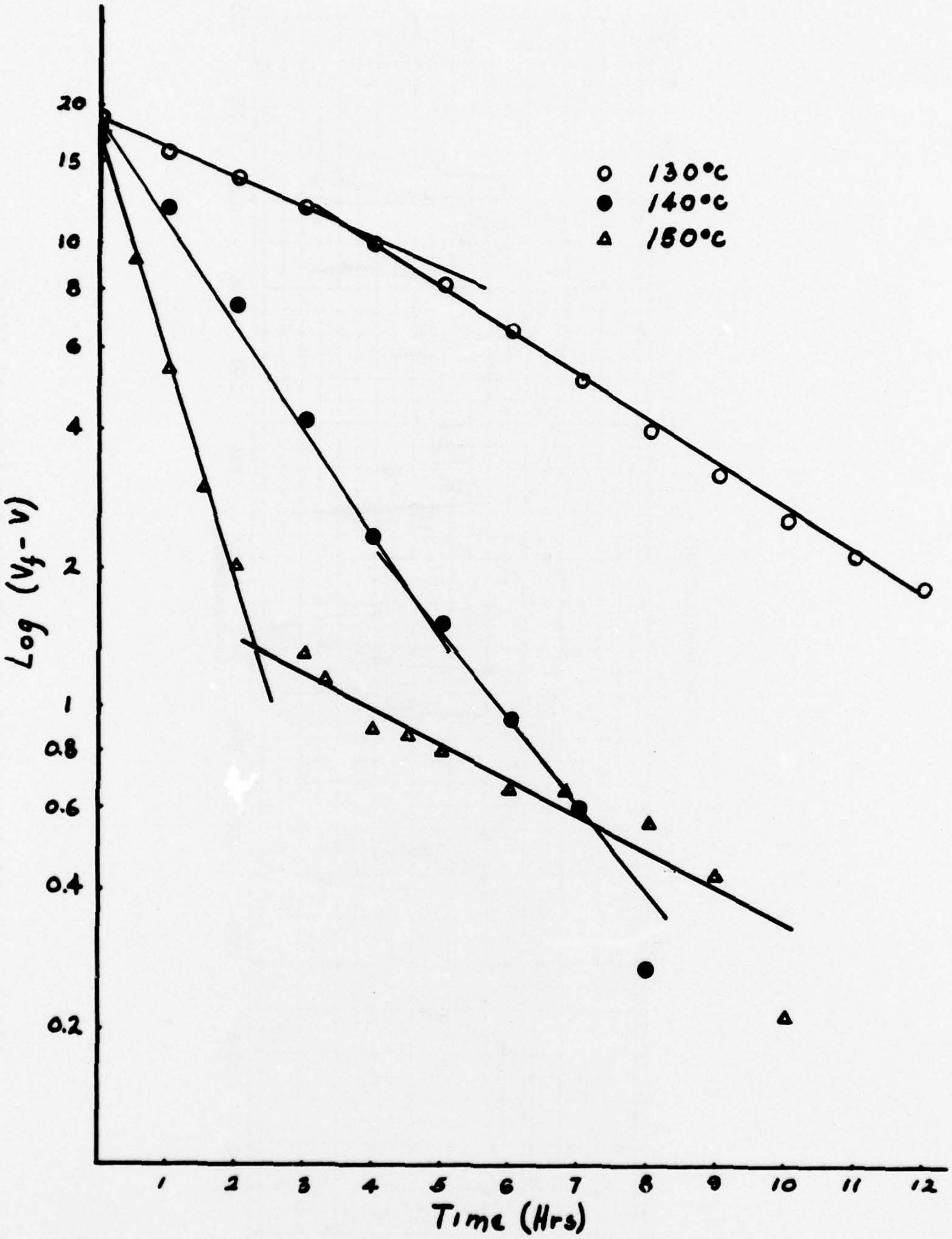

Fig 10 Kinetic curves of beta-methylglucoside tetranitrate decomposition

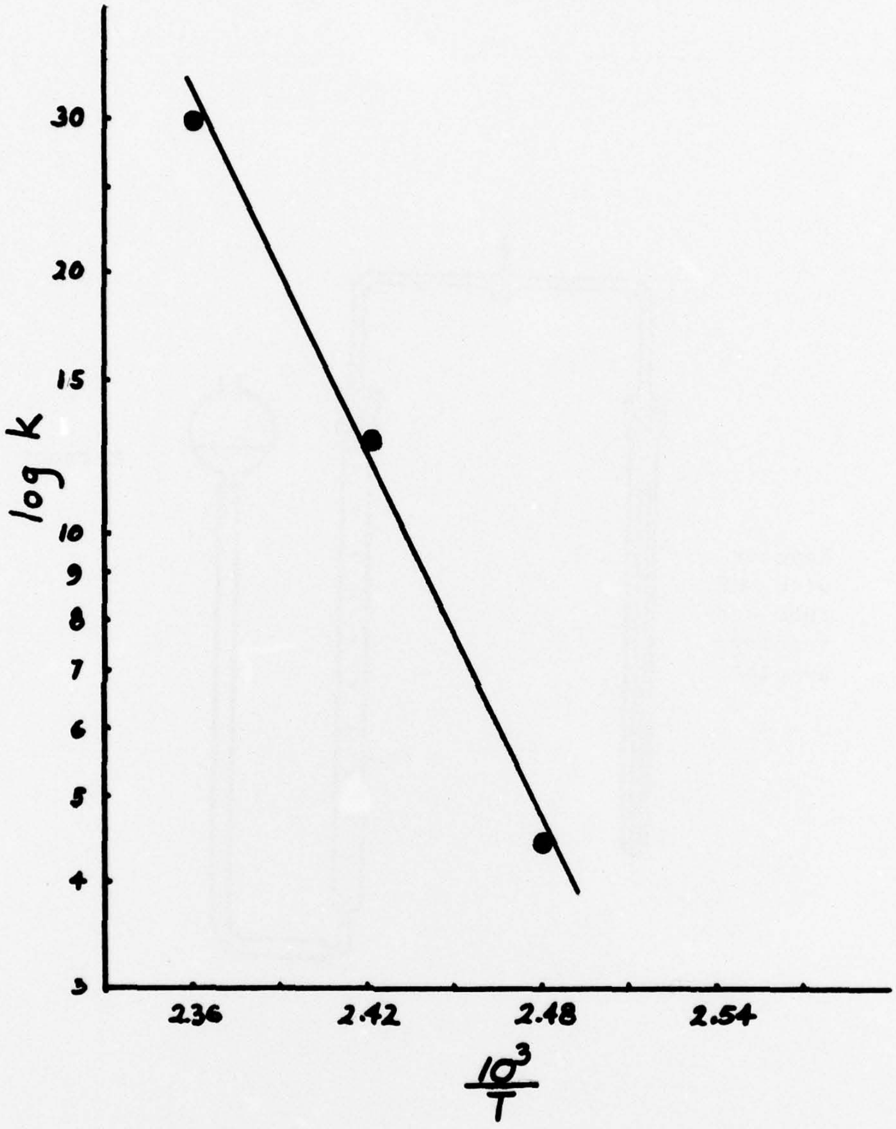

Fig 11 Temperature dependence of rate constants

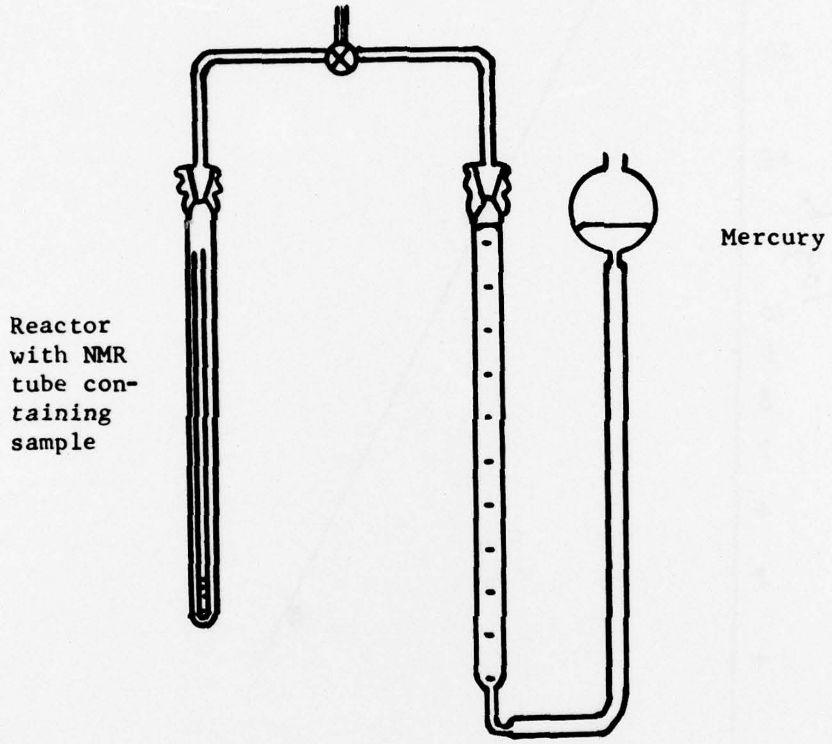

Fig 12 Manometer System

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