THE DECOMPOSITION, BOILING AND EX-PLOSION OF TRINITROTOLUENE AT HIGH TEMPERATURES.

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The instability of 2 : 4 : 6-trinitrotoluene (TNT.) at high temperatures, as exemplified by its spontaneous explosion, is well known, but few detailed observations of the thermal decomposition and vaporisation preceding the explosion are to be found in the literature. Such data are, however, of some interest in the fundamental study of the thermal sensitiveness of explosives.

Experimental.

Material.—A commercial TNT., m.p. 80·5° c., containing approximately 99 % of α-TNT. was used for the decomposition and ignition experiments. α-TNT. was prepared from this by repeated recrystallisation from conc. H_2SO_4.

Measurement of Decomposition Rate.—The decomposition preceding explosion was examined in Pyrex glass reaction bulbs, nitrogen, hydrogen or air being present at atmospheric pressure to reduce distillation of the liquid from the hot zone. The methods for rapid heating of the sample of explosive and for recording rapid pressure changes were those described previously.[1]

Measurement of Boiling-point.—The induction period before the explosion of TNT. at its boiling point is sufficiently long (about 20 sec.) to enable a direct measurement of the b.p. to be made before the explosion. The sample of TNT. was introduced by an electromagnetic arrangement into a vertical Pyrex tube 1·5 cm. internal diam. immersed to a depth of 2-3 cm. in a bath of fused nitrates maintained at a temperature usually about 30° c. above that of the boiling point to be measured, and containing air or nitrogen at the required pressure. The hot junction of a platinum-platinum-rhodium thermocouple was fixed about 3 mm. above the surface of the TNT. to measure the temperature of the condensing vapour. This particular thermocouple has no catalytic effect on the decomposition of TNT. The E.M.F. was measured with a potentiometer and short-period galvanometer, the thermocouple being calibrated by direct immersion in a nitrate bath, and the resulting curve checked at four points by determining the boiling points of benzoic acid, phthalic anhydride, benzophenone and anthracene by the method used with the TNT., the values found being within 1½° c. of the accepted values. The b.p. of benzoic acid was also found at 12 cm. pressure and a value obtained in close agreement with the vapour pressure

[1] Robertson, *Trans. Faraday Soc.*, 1948, **44**, 677.

measurements of Kahlbaum.[2]   The possibility of making the measurements in 15 sec. was established with these substances.

A convenient quantity of TNT. was 50 mg., but the b.p. values remained unaltered on varying the quantity from 10-100 mg.   The temperature of the heating bath could be varied from 15 to 60° c. above the b.p. without altering the readings.   The accumulation of decomposition products in the TNT. did not appreciably alter the readings ; thus at 267° c. the liquid could be steadily boiled for 15 min. without change of b.p.   This was also the same in air and nitrogen.

Decomposition of TNT.

Pressure-time curves for the thermal decomposition of TNT. in a closed system showed first a rapid pressure rise due to partial vaporisation of the liquid, followed by a quiescent period in which no appreciable gas evolution occurred. This merged somewhat indefinitely into a period of accelerating gas evolution
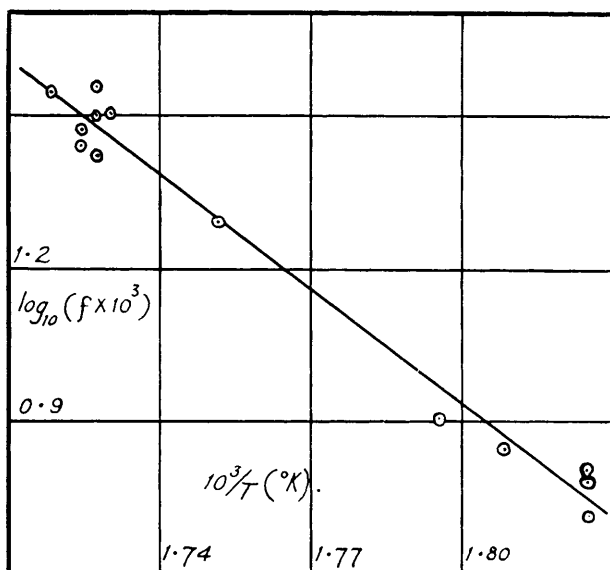

FIG. 1.—Decomposition of TNT.

during which the TNT. gradually darkened, and above 275° c. (with 50 mg. TNT) the decomposition became sufficiently rapid after a time to give rise to an explosion.   Above 350° c., however, no explosion occurred with this quantity of TNT. since the bulk of the material distilled from the hot zone leaving a dark residue.   Larger quantities than 50 mg. were then required for explosion.   The pressure (p) due to the decomposition of the TNT. after the quiescent period (that is the observed pressure increment minus the increment due to the vaporisation) followed the equation,

$$\log_{10} p = ft + \text{constant,}$$

where t is time and f a constant measuring the acceleration of the gas evolution. The temperature variation of f was given by the equation,

$$f \text{ (sec.}^{-1}) = 10^{11\cdot4} e^{-34\cdot4 \text{ kcal.}/\boldsymbol{R}T},$$

the experimental results for 50 mg. TNT. being shown in Fig. 1.   The value for the apparent activation energy lies between that of 46 kcal./g. mol. which may be deduced from the temperature coefficient given by Robertson[3] for the very early stages of decomposition, and the value of 27 kcal./g. mol. given by

[2] Kahlbaum, *Z. physik. Chem.*, 1898, **26**, 577.
[3] Robertson, *J. Chem. Soc.*, 1921, 1.

Roginsky[4] from experiments in closed ampullæ, when autocatalysis is greatly facilitated.

Below the explosion temperature the rate of gas evolution, after attaining a maximum, finally diminished with time approximately in accordance with an exponential law. No difference in the pressure-time curves was observed with the different inert gases present. An increase in the quantity of TNT. used to over 100 mg. diminished both the quiescent period and the induction period before explosion, and increased f. This was considered to be due to self-heating and autocatalysis. The importance of autocatalysis in the decomposition could be shown by obtaining from the partially decomposed TNT. a strongly catalytic substance of low volatility. Addition of 10 % of this to TNT. completely removed the quiescent period and increased f. The quiescent period could also be removed by previous exposure of the sample to ultra-violet light (a quartz mercury lamp was used) for a few hours.
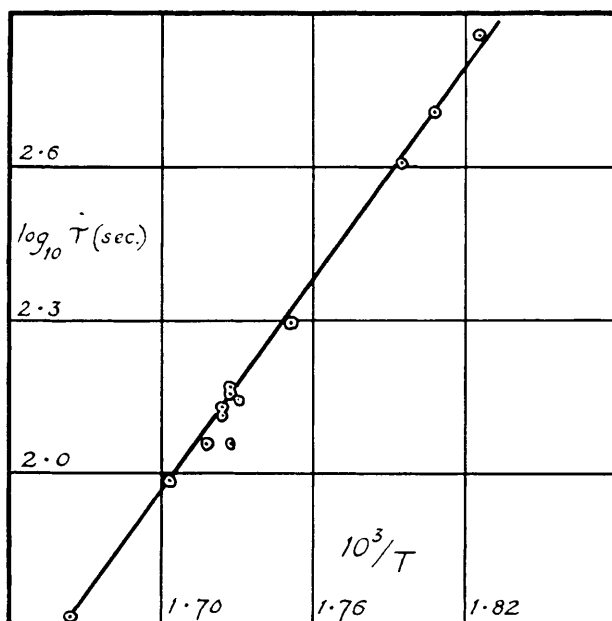

FIG. 2.—Induction period before explosion of TNT.

The induction period (τ) before explosion for 50 mg. TNT. was 12 min. at 275° c. and 50 sec. at 328° c. It followed the equation

$$\log_e \tau = E/RT + \text{constant},$$

E having a value of 32 kcal./g. mol. from the straight line shown in Fig. 2. The experimental error in the activation energies for f and τ was estimated as 2·5 kcal./g. mol., the small difference between them being considered insignificant.

Effect of Additions.—A considerable number of foreign substances when added to TNT. in small quantities increased f and diminished τ, but no substance was found which inhibited the decomposition to any large extent. Generally, the rise in f was in line with the fall in τ, as may be seen from Table I. With added explosives, two distinct types of behaviour were observed. The nitro-amines and nitric esters decomposed first in solution in the TNT. leaving it to undergo its normal accelerative decomposition with some modification in f and τ. With added explosives containing the NO_2 group linked to carbon, the behaviour of the mixture was similar to that of TNT. alone. Ammonia present in the gas phase (with nitrogen to give a total pressure of 1 atm.) accelerated the decomposition of TNT. at 300° c. according to the equations,

$$\tau = \tau'(1 + 0\cdot11p)$$
and
$$f' = f(1 + 0\cdot06p),$$

[4] Roginsky, *Physik. Z. Sowjet.*, 1932, **1**, 640.

where p is the partial pressure of ammonia (o·9 cm.) and τ' and f' are the modified constants which with ammonia present replace the normal ones τ and f.

TABLE I.—EFFECT OF ADDITIONS ON THE DECOMPOSITION OF TNT.

Addition.	%.	Temp. (°c.).	Increase in f.	Decrease in τ.
Ferric oxide	1·9	297	2·2	3·9
Manganese dioxide	12	298	16	17
Hopcalite	10	278	—	57
Hopcalite	1·9	297	2·8	2·3
Potassium permanganate . . .	10	298	12	9·9
Benzophenone	11	300	5·0	3·1
Quinol	11·5	305	2·3	2·7
Triphenylcarbinol	9·5	299	—	8·0
Paraffin wax	7·5	284	4·1	5·1
α-Nitroso-β-naphthol	9	301	8·9	10
α-Nitroso-β-naphthol iron complex .	11	276	—	45
Diphenylamine	9	287	10·5	14
p-Toluidine	10	297	7·0	6·1
m-Aminobenzoic acid	8	302	6·1	6·3
Thiocarbamide	10	301	—	7·5
m-Nitroaniline	9	302	2·8	2·8
p-Nitroaniline	11·5	299	3·8	4·0
Hexanitrodiphenylamine . . .	9	299	2·0	1·1
Trinitroanisole	11·5	299	4·2	3·4
Trinitroxylene	10·5	301	0·86	0·71
Dinitrophenol	7	307	1·4	1·1
Cyclotrimethylenetrinitramine . .	13	301	5·1	4·3
Cyclotetramethylenetetranitramine .	10	299	2·8	2·0
Tetryl	10·5	302	2·6	3·6
Pentaerythritol tetranitrate . .	11·5	302	3·1	1·4

The Boiling-point of TNT.

A knowledge of the boiling-point of TNT. is useful in interpreting the results of experiments on its behaviour at high temperatures. Belajev and Yusephovich [5]
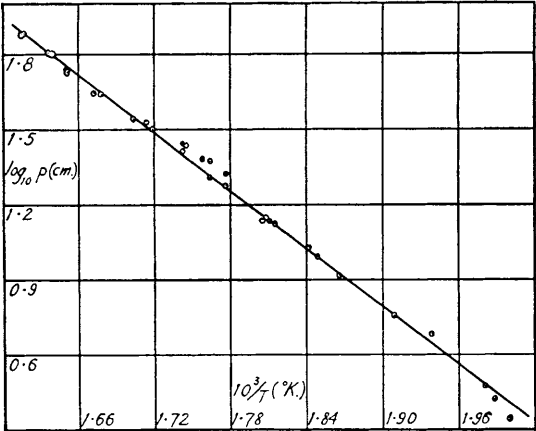

FIG. 3.—Vapour pressure of TNT.

give the boiling-point at 2 mm. as 190° c. and at 50 mm. as 245-250° c., finding by extrapolation 300 ± 10° c. at atmospheric pressure. Extrapolation of the

[5] Belajev and Yusephovich, *Compt. rend.*, *U.R.S.S.*, 1940, **27**, 133.

vapour pressure measurements of Menzies [6] for the range 82-102° c., using a value derived from his results of 12 kcal./g. mol. for the latent heat of vaporisation, and neglecting the temperature variation of this quantity, gives for the b.p. 530° c. To clarify this discrepancy, a direct measurement of the temperature of condensation of α-TNT. vapour was made at various pressures. At 76 cm. pressure this was $345° \pm 2°$ c., and at 3 cm. 232° c. Identical results were obtained with the commercial sample and α-TNT. On representing the b.p. results by plotting the logarithm of the vapour pressure (p) against $1/T$ the points shown in Fig. 3 were obtained, the equation for the vapour pressure from the straight line shown being

$$\log_{10} p \text{ (cm.)} = 8\cdot 11 - 3850/T° \text{ K.}$$

This gives a latent heat of vaporisation of 17,500 cal./g. mol. with an error estimated at 1000 cal./g. mol. The results are not sufficiently accurate to justify the addition to the equation of another term allowing for the difference in specific heat between the liquid and the vapour. Menzies gives the vapour pressure at 100° c. as $1\cdot 06 \times 10^{-2}$ cm. whereas the value calculated from the equation, above is $0\cdot 62 \times 10^{-2}$ cm. The discrepancy could arise from the presence of volatile impurity in the sample used by Menzies.

The Explosion of TNT.

The Vapour.—The vapour alone exploded less readily than the liquid, for it was heated in bulbs of 2 cm. diam. up to 357° c. without explosion, although extensive decomposition was noted, this being less subject to autocatalysis than that of the liquid. Mixtures of the vapour with air, nitrogen or hydrogen propagated a flame readily once this was initiated, but the necessary concentration of vapour was not determined. These flames could be initiated by exposing the vapour to cold ferric oxide, when a reaction occurred and some of the oxide particles became incandescent. Thus if TNT. was heated rapidly in a test tube and iron oxide brought to the mouth of the tube a flame was initiated at the oxide which passed down the tube and ignited the liquid TNT. At lower temperatures flames could be produced in the vapour which did not suffice to ignite the liquid : thus, cold TNT. brought into contact with iron oxide at 200° c. produced almost immediately a small flame confined to the vapour, the bulk of the liquid TNT. exploding many seconds later after accelerative decomposition.

The Liquid.—The lowest temperature at which liquid TNT. in equilibrium with vapour exploded spontaneously after thermal decomposition depended on the quantity of liquid present, being lower for larger quantities. The lowest ignition temperature for a given initial quantity of TNT. could, therefore, be raised by increasing the proportion vaporising by altering the volume available to the vapour or by diminishing the inert gas pressure. An apparent upper temperature limit of explosion was observed if all the liquid disappeared from the hot zone by vaporisation or boiling before the thermal decomposition accelerated to explosion. The upper temperature limit of 380° c. for deflagration of TNT. reported by Andreew [7] can probably be interpreted in this way.

Observations of the explosion of TNT. after the induction period revealed that the liquid attained a bright red heat and a flame was propagated through the vapour above it, considerable quantities of carbon being deposited. The survival without damage of the glass bulb used showed clearly that no detonation occurred under the conditions used. The rate of decomposition of the liquid before ignition was greater at higher temperatures, and also greater in the presence of the more efficient accelerators of reaction : the results, in general, led to the conclusion that the condition satisfied before ignition was the attainment of a certain extent of decomposition (such that the pressure had risen to about half the final non-explosive thermal decomposition value) and not the attainment of a certain rate of gas evolution. This was also true in general for TNT. containing up to 10 % of foreign substances such as metallic salts and oxides, organic compounds, other explosives and various waxes. The four substances, hopcalite, ammonium dichromate, ferric oxide and barium hydroxide, however, present to the extent of 10 % in TNT. caused ignition at 300° c. with no perceptible prior decomposition, probably as a result of vigorous exothermic reaction between the TNT. and the added substance. Catalytic substances which could be isolated from partially decomposed TNT. also greatly facilitated the ignition of fresh samples of TNT. One may also note in this connection the well-known effect of alkalis in increasing the ease of ignitability of TNT.

[6] Menzies, *J. Amer. Chem. Soc.*, 1920, **42**, 2218.
[7] Andreew, *Acta Physicochim.*, 1935, **3**, 119.

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Discussion.

Although the acceleration of the decomposition of TNT. with time proceeds in accordance with the mathematical formulation for branching-chain reactions, there is as yet no clear evidence for the actual existence of reaction chains : in fact, the acceleration of the reaction by quinol, benzoquinone and diphenylamine might be considered to point to the absence of free-radical chains. Furthermore, if the final stages of the TNT. decomposition below the explosion temperature are treated some-what arbitrarily as a first-order reaction of activation energy 34 kcal., the actual rate of reaction can then be represented by an Arrhenius equation $B\,e^{-E/RT}$ with a value for B of about 10^{11} sec.$^{-1}$. The view of Semenoff[8] that chain reactions in TNT. lead to an abnormally large value for B is not supported. It seems probable that the primary reactions lead to the formation of substances of higher molecular weight which catalyse subsequent decomposition and may be involved in bimolecular reactions.

To a first approximation, the normal behaviour of TNT. with respect to spontaneous explosion may be represented by assuming the condition for explosion to be the attainment of a critical concentration of autocatalyst in the liquid phase, so that explosion occurs after a certain definite degree of decomposition. If the TNT. is at a temperature $T°$ K. and the reaction rate constant k for the formation of autocatalyst is given by $k = B\,e^{-E/RT}$, then if the amount of catalyst formed is small, the condition for explosion may be written

$$k\tau = C,$$

where C is the critical ratio, catalyst/TNT., for explosion and τ is the in-duction period. This equation assumes the catalyst to be formed at a constant rate and neglects the quantity of TNT. decomposed and lost by vaporisation. From this equation the temperature variation of the induction period arises from the temperature variation of k and is given by

$$\log_e \tau = E/RT + \log_e (C/B). \qquad . \qquad . \qquad . \quad (1)$$

An equation of this type with E of 32,000 cal./g. mol. is applicable to TNT. According to Urbanski and Rychter[9] this equation also applies in the temperature range 390-450° c., that is above the boiling point, but E is only 14 kcal./g. mol. Edwards[10] has also observed a diminution of E above the boiling point. This is explicable by the evaporation of the TNT. during the induction period. The volatility of the catalyst formed in the decomposition is much less than that of TNT., and its evapor-ation during the induction period may be neglected in comparison with that of TNT. If the temperature of the reaction vessel, with an area A in contact with TNT., is T, and the boiling point of TNT. is T_B, the quan-tity (q) of TNT. evaporated during the induction period τ is given by

$$qL = hA(T - T_B)\tau, \qquad . \qquad . \qquad . \qquad . \quad (2)$$

where L is the latent heat of vaporisation of TNT. and h is the appropriate heat transfer coefficient. The explosion condition, neglecting the quantity of TNT. converted into catalyst, becomes

$$(Q - \tfrac{1}{2}q)k_B\tau/(Q - q) = C, \qquad . \qquad . \qquad . \quad (3)$$

where Q is the original quantity of TNT. and k_B is the value of k at T_B. When the vessel temperature is just equal to the boiling point, the explosion condition becomes

$$k_B\tau_B = C, \qquad . \qquad . \qquad . \qquad . \quad (4)$$

[8] Semenoff, *Chemical Kinetics and Chain Reactions* (Oxford Univ. Press, 1935), Ch. 17.

[9] Urbanski and Rychter, *Compt. rend.*, 1939, **208**, 900.

[10] G. E. Edwards (private communication).

where τ_B is the induction period under these conditions. Eqn. (2), (3) and (4) give

$$\tau = \tau_B + \frac{QL}{hA(T - T_B)} - \sqrt{\tau_B^2 + \frac{Q^2L^2}{h^2A^2(T - T_B)^2}} \cdot \qquad . \qquad (5)$$

In Table II some induction periods calculated with (5) for α-TNT. at 15 lb./sq. in. air pressure when $T_B = 346°$ c. are compared with experimental figures kindly given by Dr. G. E. Edwards, the only quantity not determined by the experiments, hA/QL, being taken as 0·00065 sec.$^{-1}$ degree^{-1}. It is clear that these results are well represented by (5). Thus a value for E obtained from experiments above the boiling point with (1) cannot be interpreted as an activation energy of a chemical process. These considerations may also be of interest in the interpretation of high temperature measurements of induction periods carried out with other volatile explosives.

TABLE II.—INDUCTION PERIODS OF TNT.

Temperature (°c.).	τ (Observed) (sec.).	τ (Calculated) (sec.).
346	42·5	42·5
350	40	40·5
360	34	34·5
370	29	29·5
380	25·5	25·7
390	22·0	22·5
400	19·5	19·9
410	17·5	17·7
420	16·0	16·0
430	14·5	14·6

Summary.

The thermal decomposition of TNT. is markedly autocatalytic and can lead to spontaneous explosion after an induction period. An overall activation energy of 32-34 kcal. is obtained for the processes prior to explosion. Numerous foreign substances accelerate the decomposition. The boiling point of TNT. is 345° c. and the latent heat of vaporisation 17,500 cal./g. mol. Liquid TNT. explodes when a certain extent of decomposition is attained. The effect of boiling on the induction period before explosion can be treated quantitatively.

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