CLVIII.—*The Velocity of Decomposition of High Explosives in a Vacuum. Part I.*

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PREVIOUS work on the stability of explosives has been devoted almost entirely to the nitric esters. The methods used depend for the most part on the detection and estimation of the oxides of nitrogen evolved on heating, and are not, in general, applicable to nitro-aromatic compounds or to mercuric fulminate, azides, etc. In order to meet the need for a simple quantitative stability test for such compounds, the vacuum test described below was developed. This has been widely used for high explosives, more particularly for trinitrophenylmethylnitroamine. It has proved itself so simple in use after some thousands of tests that it may be of interest for the investigation of other reactions in which gases are evolved. Some measurements of the rate of decomposition in a vacuum have been made on guncotton (Obermüller, *Mitt. Berl. Bezirksver.*, 1904, **1**, 30; Dupré, *Ann. Rep. Insp. of Explosives*, 1903, 26; 1904, 28; 1905, 29; Hodgkinson and Coote, *Chem. News*, 1905, **91**, 194; Robertson and Napper, *T.*, 1907, **91**, 764; Willcox, *J. Amer. Chem. Soc.*, 1907, **30**, 271; Pleus, *Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1910, **5**, 121), on silver oxalate (Hoitsema, *Zeitsch. physikal. Chem.*, 1896, **21**, 137), trinitrotoluene (Verola, *Mém. poud. Salp.*, 1911—1912, **16**, 40), and tetryl (Knowles, *J. Ind. Eng. Chem.*, 1920, **12**, 246). The methods described were not, however, convenient as standard tests for high explosives.

From measurements on a large number of explosives, it appears that these are in all cases subject to a gradual decomposition, with evolution of gas, at temperatures below their ignition points. The velocity decreases strongly as the temperature is lowered, but there can be little doubt that a very slow decomposition must occur even at the ordinary temperature.

As in the case of nitric esters (Farmer, this vol., p. 811), the decomposition is partly catalytic and partly non-catalytic; when catalytic influences are eliminated, the velocity sinks to a minimum. In many cases, the catalytic decomposition outweighs the intrinsic decomposition of the pure substance, and it is frequently difficult to purify the explosive to such a degree that the catalytic influences are completely removed. For the same reason, different preparations of the same substance often differ considerably in their rates of decomposition. Frequently the evolution of gas proceeds

with an acceleration due to autocatalysis, whilst in other cases it becomes slower after a time, owing to the decomposition and consequent elimination of impurities. In many cases the presence of moisture gives rise to very erratic results, and special steps are therefore taken to eliminate this influence. As a rule, the decomposition has been carried only to the extent of a small evolution of gas. The measurement of small volumes of gas has, it is true, the disadvantage that the measurements are more affected by traces of volatile matter, etc., but if the decomposition is carried further, the products formed are liable to have a very disturbing effect, and frequently a very rapid evolution of gas sets in.

The nitro-aromatic compounds are, in general, very much more stable than the nitric ester explosives. Whilst guncotton shows a marked decomposition in Will's test at 135° in four hours, and nitroglycerin at a lower temperature, the trinitrobenzene derivatives require, in general, temperatures of 140° to 180° in order to give readily measurable volumes of gas on heating for 100 hours. The dinitro-compounds show scarcely any measurable decomposition. The nitroamines, such as tetryl, on the other hand, are less stable, and decompose sufficiently rapidly for measurements at 120° .

In order to give an approximate idea of the relative stability, the temperatures may be calculated by extrapolation, at which the gas evolution amounts to 1 c.c. per gram in 100 hours:

Trinitrobenzene	190— 195°
Trinitrophenol	150— 155°
2 : 4 : 6-Trinitrotoluene	135— 140°
2 : 3 : 4- "	135— 140°
3 : 4 : 6- "	130— 135°
Trinitrophenylmethylnitroamine	115— 120°
Cellulose nitrate (N=13 per cent)	Approx. 100°

Trinitrotoluenes gave 0.8 to 1.8 c.c. of gas per gram in 100 hours at 140° . The differences in velocity between different samples indicated the presence of traces of catalysts, although most of the samples were very pure. There was practically no parallelism between the melting point and stability. The rate of evolution showed no acceleration; hence no autocatalysis occurred within limits measured. From the results obtained, it is evident that pure trinitrotoluene could be kept indefinitely at the ordinary temperature, but the actual rate of decomposition cannot be ascertained by direct extrapolation, as the results obtained in the case of tetryl have shown that a great increase in stability occurs on passing from the molten to the solid condition.

The isomeric trinitrotoluenes which accompany the symmetrical compound in small proportion on nitration of toluene were also

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examined. The commercial products contained impurities which decreased their stability. When these were removed by crystallisation, 2:3:4-trinitrotoluene showed about the same stability as the 2:4:6-isomeride, whilst 3:4:6-trinitrotoluene was somewhat less stable. The stability of 2:4:6-trinitrotoluene was not sensibly affected by the addition of 1 per cent. of the other pure isomerides, but 5 per cent. of the 3:4:6-isomeride caused a slight increase of velocity.

Mixtures of picric acid and trinitrotoluene showed a lower rate of decomposition at 140° than trinitrotoluene alone. This was somewhat surprising, since the general experience is that acids decrease the stability. It is possible that the trinitrotoluene exists as an equilibrium in which a small quantity of an *isonitro*-compound is present, the latter being the cause of the instability observed. Picric acid might readily cause the *isonitro*-compound to revert to the normal nitro-compound, thus increasing the stability.

As an example of an unsaturated substance, castor oil was mixed with trinitrotoluene and with picric acid, and the mixtures were tested. The castor oil depressed the stability very strongly in both cases.

Trinitrophenol showed a stability intermediate between that of trinitrobenzene and that of trinitrotoluene. Trinitrobenzene showed extreme stability, even at the boiling point of aniline, and the stability was not perceptibly affected by wet and dry storage trials. This is of interest as showing that, notwithstanding the difficulty of introducing the third nitro-group, the trinitro-compound, when once prepared, is very stable.

EXPERIMENTAL.

Apparatus.—The thermostat (Fig. 1) consists of a cylindrical copper bath, which is maintained at the required temperature by a boiling liquid. The cover consists of a thin brass casting with six orifices for the heating tubes, and a short column to support the condenser. These all form part of the casting, thus avoiding joints, which are otherwise very apt to leak during protracted tests. The connexion with the condenser is made by a conical joint surmounted by a cap, which can be filled with vaselin or other material to lute the joint. The brass column also projects about 0.5 cm. into the interior of the bath, and is connected with a cylinder of coarse copper gauze of the same diameter as the tube and about 15 cm. in length. The object of this is to convey the condensed liquid down the centre of the bath and ensure uniform

heating. The lid has also a small opening for filling the bath. This is fitted with a cap and a cup for luting. A cylinder of lagging material surrounds the bath. The top of the bath is also

FIG. 1A.

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covered with a loose cake of asbestos lagging material about 3 cm. thick, with holes corresponding with those in the brass cover.

The condenser (Fig. 2) is of the multitubular pattern, and the water inlet tube is fitted with a funnel, as shown, so that the flow of water can be seen.

For temperatures from 80° to 100° , mixtures of alcohol and water were used. From 100° to about 135° , solutions of calcium chloride were generally taken. In the latter case, the addition of a little lime is advisable to avoid corrosion of the copper.

The temperature of the boiling calcium chloride solution is

FIG. 1B.

readily adjusted by adding water if too high, or by allowing water to evaporate if too low. The level of the liquid should be maintained at about 5 cm. from the lid of the bath.

Safety Precautions.—To guard against damage by explosion, steel tubes with closed bottoms were provided; these fitted loosely into the brass orifices, and were packed round with fine copper fillings to give good contact with the bath. They were made rather short (Fig. 3), since it was found that if they extended nearly to the surface of the bath, they became cooled by radiation, and irregular temperatures were obtained.

The thermostats were surrounded by screens and placed in a fire-proof shed. A cistern was provided to guard against failure of the water supply, and an automatic ball-cock tap was fitted to cut off the gas supply in case the cistern became empty.

FIG. 2.

Heating Tubes.

— The glass apparatus passed through numerous modifications in the course of a large number of measurements. The earlier patterns were fitted with glass taps for exhaustion, but it was found much better to avoid these, and the simple device shown in Fig. 3 was found to be a great improvement. In order to exhaust the tube, a quantity of mercury sufficient to fill the upright limb of the capillary tube is placed in the lower cup. This cup is connected with the pump by means of a rubber stopper. The apparatus is then inclined so that the cup is horizontal and the mercury lies in a pool in the cup, leaving a free passage between the pump and the capillary tube.

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After exhaustion, the apparatus is returned to the upright position, and, on releasing the vacuum, the mercury rises in the

FIG. 3.

capillary tube, which acts as a manometer during the test. The cup at the top of the heating tube is luted with mercury, and the apparatus is then ready to be transferred to the thermostat. It is important that the stopper be very well ground, and lubricated as thinly as possible with a non-reactive lubricant.

The thermometer is embedded in sand in a similar heating tube, which is introduced into one of the steel tubes and placed in the bath. Accuracy of the temperature readings is of great importance in view of the high temperature-coefficients of the decompositions.

Method of Working.—

Very thorough cleaning of the apparatus is necessary, as traces of foreign matter have a marked catalytic effect. The tubes were cleaned successively with acetone, benzene, and hot chromic acid, and were then subjected to prolonged washing with water. The manometers were similarly cleansed. The com-

plete removal of moisture is also of importance, since this frequently gives rise to abnormal accelerations. The explosive is dried at a temperature well below its decomposition point, and weighed quantities are introduced into the test-tubes. These are

then connected with the capillary tubes, the ground stoppers being thinly lubricated. The apparatus is then exhausted to about 5 mm. of mercury by means of a Geryk pump, and is heated to a temperature at which no measurable decomposition will occur (generally 80°) for some hours to remove water.

The apparatus is then again exhausted, dry air is allowed to enter through a three-way cock attached to the pump, and removed once more by the pump, and the apparatus is inserted in the thermostat. A little asbestos wool is packed round the stopper.

The time at which the heating commences is noted, and an arbitrary period is allowed to permit the pressure to settle down before the first reading is taken. This is necessary, on account of minute traces of residual volatile matter, and in some cases the volatility of the compound itself. In general, one and a-half hours have been found sufficient. The height of the mercury column is then read at intervals, in comparison with the barometric height. It is convenient to use, as barometer, a similar tube exhausted and placed near the apparatus. This automatically corrects the reading for temperature of the mercury and capillary depression.

To avoid differences in the level of the mercury in the lower cup, it is convenient to fill this up, so that it overflows into a dish as the mercury descends in the capillary tube.

In taking a number of readings, a sliding scale may be used with advantage. The zero is set to the mercury level in the barometer, and the difference between manometer and barometer can then be read off directly.

Calculation of Gas Volume.—The calibration of the apparatus includes measurements of the volume of the test-tube, the volume of unit length of the capillary, and the total length of the three limbs of the capillary tube from the stopper to a point on the capillary-tube level with the average height of mercury in the cup. The volume of explosive is deducted from the volume of the heating tube to obtain the net volume.

In calculating repeated readings with the same explosive and the same bath temperature, the following shortened method of calculation is useful: The bath temperature is practically constant; the ordinary temperature alters somewhat, but as this only affects the correction of the volume in the capillary tube, it may also be taken as constant (it was, in general, about 30°).

If the difference between barometer and manometer reading be p mm., the corrected volume of gas in the heating tube is equal to:

$$\text{Net gas space} \times \frac{273}{273 + \text{bath temp.}} \times \frac{p}{760}.$$

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The corrected volume of gas in the capillary tube is equal to (total length - 760 + p) $\times$ (vol. of 1 mm.) $\times \frac{273}{303} \times \frac{p}{760} = p$ (total length - 760) $\times$ (vol. of 1 mm.) $\times \frac{1}{843} + p^2$ (vol. of 1 mm.) $\times \frac{1}{843}$.

Hence the corrected volume is equal to

$$p(a + b) + p^2c,$$

where $a = \frac{\text{net gas space} \times 273}{760(273 + \text{bath temp.})}$;

$$b = \frac{1}{843} (\text{length of capillary tube} - 760) \times (\text{vol. of 1 mm.})$$

$$c = \frac{1}{843} (\text{vol. of 1 mm.}).$$

These constants can be determined for the whole series of measurements, and the calculation is then very simple. The constants b and c depend only on the calibration of the apparatus; a depends also on the volume of explosive and the bath temperature.

Correction for Fluctuations in Bath Temperature.—The fluctuations due to alteration of boiling point with variations of the barometric pressure are of importance, as the velocity of decomposition usually increases approximately 100 per cent. for each 5 degrees, or 15 per cent. per degree. It is better to apply the correction to the time readings rather than to correct the

FIG. 4.

2:4:6-Trinitrotoluene (various samples) at 140°.

volume of gas from the individual tubes in the bath. If the deviation of temperature is within about 0.3°, it is generally sufficient to calculate a time correction for each day's readings, based on the mean temperature of the bath. Thus a deviation of 0.1° corresponds with a difference of 1.4 per cent. in the velocity, or 0.34 hour per day.

Measurements of Gas Evolution.

2:4:6-Trinitrotoluene.—Measurements at 120° gave very low results (about 0.15 c.c. in 100 hours). At 180° the evolution was too rapid and gave erratic accelerations, which made the measurements untrustworthy for comparison. Convenient velocities were obtained at 140°, and the following measurements were made on trinitrotoluenes from different sources (Fig. 4).

FIG. 5.

Trinitrotoluene isomerides at 140°.

Gas Evolution at 140° (c.c. per gram).

Melting point.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours
81.1°	0.35	0.69	1.04	1.31	1.56
81.05	0.39	0.78	1.16	1.47	1.75
81.05	0.12	0.33	0.70	0.94	1.13
81.0	0.14	0.28	0.54	0.85	1.13
81.0	0.16	0.32	0.55	0.85	1.13
81.0	0.16	0.35	0.58	0.78	0.99
81.0	0.12	0.22	0.37	0.57	0.77
80.95	0.25	0.50	0.86	1.21	1.50
80.95	0.14	0.28	0.52	0.83	1.10
80.75	0.33	0.68	0.86	1.01	1.26
80.65	0.26	0.54	0.85	1.13	1.36
80.65	0.33	0.71	0.90	1.07	1.24
78.80	0.36	0.71	1.09	1.45	1.80

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Comparative measurements on dinitrotoluene gave no perceptible decomposition in 100 hours.

2:3:4-*Trinitrotoluene*.—The following figures show the gas evolution after one and two crystallisations respectively. The purification reduced the rate of decomposition slightly.

Gas Evolution at 140° (c.c. per gram).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	
One crystallisation ...	0.44	0.78	1.07	1.40	1.75	Fig. 5 (4)
Two crystallisations ...	0.18	0.46	0.76	1.05	1.36	„ (3)
„ „ „	0.22	0.37	0.67	1.01	1.38	„ (2)
2:4:6-T.N.T. (mean)	0.24	0.49	0.77	1.04	1.29	„ (1)

3:4:6-*Trinitrotoluene*.—The commercial product was much less stable than the above, and decomposed so rapidly at 140° that the measurement had to be made at 120°. The results after one crystallisation are given at both temperatures.

Gas Evolution at 120° (c.c. per gram).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
Original (sample a)	2.2	3.3	—	—	—
One crystallisation	0.55	1.08	1.58	2.05	2.48

Gas Evolution at 140° (c.c. per gram).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	
Sample (a) One cryst.	4.7	7.9	—	—	—	Fig. 5 (8)
„ Two „	1.50	3.00	—	—	—	„ (7)
Sample (b) One cryst.	0.89	1.80	2.80	4.10	5.70	„ (6)
„ Two „	0.76	1.38	1.99	2.60	3.23	„ (5)

Even after purification, this isomeride was much less stable than 2:3:4-trinitrotoluene.

Mixtures of the Isomeric Trinitrotoluenes.—In order to ascertain whether the unsymmetrical isomerides, which always accompany 2:4:6-trinitrotoluene in small quantity in the crude product, affect the stability, the following mixtures were examined.

Gas Evolution at 140° (c.c. per gram).

2:3:4- T.N.T., per cent.	3:4:6- T.N.T., per cent.	Sam- ple.	Puri- fica- tion.	2:4:6- T.N.T., per cent.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
—	—	—	—	100	0.16	0.34	0.57	0.78	0.99
1	—	a	coml.	99	1.03	1.55	2.12	2.60	3.01
1	—	b	coml.	99	0.23	0.80	1.40	2.01	2.53
1	—	b	2 crysts.	99	0.15	0.33	0.55	0.79	0.98
5	—	a	coml.	95	2.23	3.34	4.21	4.99	5.78
5	—	a	1 cryst.	95	0.31	0.77	0.98	1.23	1.52
5	—	b	1 cryst.	95	0.54	0.87	1.10	1.36	1.69
5	—	b	2 crysts.	95	0.17	0.44	0.52	0.78	0.98
—	1	b	1 cryst.	99	0.48	1.11	1.61	2.10	2.53
—	1	a	2 crysts.	99	0.10	0.67	1.02	1.37	1.62
—	1	b	2 crysts.	99	—	—	—	—	1.28
—	5	a	2 crysts.	95	2.01	2.85	3.45	4.02	4.60
—	5	a	2 crysts.	95	1.56	2.51	3.22	3.85	4.44
—	5	b	2 crysts.	95	—	—	—	—	2.71

Influence of Picric Acid on the Stability of 2:4:6-Trinitrotoluene.—A trinitrotoluene was tested alone and in admixture with picric acid. The evolution from the mixture was less than from trinitrotoluene alone.

C.c. of gas (corr.) (140°).

Picric acid.	2:4:6- T.N.T.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	150 hours.	200 hours.
2	—	0.14	0.25	0.29	0.35	0.44	0.62	0.83
2	2	0.14	0.22	0.25	0.32	0.42	0.62	0.81
2	2	0.15	0.23	0.28	0.34	0.43	0.68	0.95
—	2	0.25	0.50	0.74	0.96	1.19	1.94	2.88

Influence of Unsaturated Compounds.—To avoid a disturbing effect on the gas volume due to vapour pressure, castor oil was chosen, as a fairly non-volatile, unsaturated substance. This increased the rate of decomposition very strongly; even at 120°, the gas evolution from trinitrotoluene containing 5 per cent. of castor oil was readily measurable.

C.c. of gas (corr.) (120°).

2:4:6- T.N.T.	Castor oil.	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.	150 hours.	200 hours.
5	0.25	0.65	1.00	1.90	2.80	3.75	7.60	11.10

Naphthalene under similar conditions gave no measurable gas evolution in admixture with trinitrotoluene, even when present to the extent of 40 per cent.

Picric Acid.—Measurements were made at 140° and 183° on picric acid crystallised from water. The gas evolution was very rapid at the higher temperature, but showed some decrease in velocity as the decomposition proceeded, from which it would

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appear that some catalyst was being gradually eliminated. The successive crystallisations did not reduce the rate of decomposition at 183° , but at 140° some stabilisation was noticeable in the latter crystallisations.

Gas Evolution at 140° (c.c. per gram).

	100 hours.	150 hours.	200 hours.	300 hours.
Original	0.11	0.27	0.44	0.88
Cryst. No. 2	0.13	0.35	0.51	0.92
„ „ 4.....	0.04	0.12	0.23	0.50
„ „ 5.....	0.06	0.21	0.31	0.58

Gas Evolution at 183° (c.c. per gram).

	1 hour.	2 hours.	3 hours.	5 hours.	10 hours.	15 hours.	20 hours.
Cryst. No. 1	2.90	4.50	5.45	6.45	—	—	—
„ „ 2	2.95	4.85	6.10	7.30	—	—	—
„ „ 3	2.30	3.95	5.20	6.15	8.35	10.60	12.80
„ „ 4	1.90	3.80	5.50	6.65	9.00	11.35	13.65
„ „ 5	2.05	3.90	5.65	6.95	9.20	11.50	13.80

As in the case of trinitrotoluene, castor oil increased the decomposition. Whereas picric acid alone gave practically no measurable decomposition at 120° , a mixture of picric acid with 5 per cent. of castor oil gave the following evolution:

Picric Acid, 5 grams. Castor Oil, 0.25 gram.

	50 hours.	100 hours.	150 hours.	200 hours.
C.c. at 120°	0.85	2.50	4.70	6.85

1:3:5-Trinitrobenzene.—The gas evolution from this compound was very low, even at 183° (boiling aniline bath). The following rates of decomposition were obtained with different samples:

Gas Evolution at 183° (c.c. per gram).

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0.05	0.14	0.20	0.27	0.33
	0.04	0.09	0.13	0.18	0.23
	0.03	0.07	0.10	0.14	0.19
	—	0.10	0.13	0.15	0.18
	—	0.10	0.13	0.15	0.18
	—	0.15	0.19	0.25	0.30
Mean.....	0.04	0.11	0.15	0.19	0.23

In order to ascertain the effect of storage on the stability, samples were kept for a year at 50° , and tested as above at 183° .

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0.07	0.13	0.18	0.24	0.30
	0.08	0.13	0.17	0.23	0.28
	0.06	0.10	0.17	0.22	0.27
	0.06	0.07	0.16	0.22	0.26
Mean.....	0.07	0.11	0.17	0.23	0.28

The influence of hydrolysis was examined by keeping samples for a year in a saturated atmosphere at 45° and testing at 183°.

	20 hours.	40 hours.	60 hours.	80 hours.	100 hours.
	0.04	0.08	0.13	0.17	0.17
	0.02	0.04	0.12	0.25	0.24
	0.01	0.02	0.10	0.11	0.15
Mean.....	0.02	0.05	0.12	0.18	0.19

The effect of an admixture of picric acid on trinitrobenzene was tried at 150°, as the decomposition of picric acid itself is too rapid at 183°.

Gas Evolution at 150°.

	100 hours.	200 hours.	300 hours.	400 hours.	500 hours.
Picric acid, 0.2 gram	}... 0.07	0.26	0.86	1.45	2.22
Trinitrobenzene, 1.8 grams					
Trinitrobenzene 1.8 grams					
	0.07	0.07	0.20	0.28	0.60

Summary.

An apparatus is described for the determination of stability of high explosives by the velocity of evolution of gas on heating in a vacuum.

All explosives appear to be liable to a gradual decomposition at temperatures considerably below their ignition points. The velocity is highly affected by temperature and by the catalytic action of impurities.

Trinitrotoluene and the isomerides which accompany it on nitration of toluene do not differ greatly in stability when purified. Trinitrobenzene is much more stable, notwithstanding the difficulty with which it is prepared by nitration, and trinitrophenol shows an intermediate stability.

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