XXXIV.—*The Products of Nitration of Toluene.*

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EARLY in 1915 it became necessary to accelerate and increase the output of trinitrotoluene used in filling high explosive shell, and on this account purification by crystallisation was abandoned, the crude product being substituted. In these circumstances it was found essential to study the nitration of toluene quantitatively at each stage, especially as little information could be obtained from the literature. One of us, therefore, outlined a programme of work designed to give the information desired on the proportions of mono-, di-, and tri-nitrotoluenes produced at each stage of manufacture and on the behaviour of the crude trinitrotoluene under varying temperature conditions. A summary of the results is now given, the method of thermal analysis being used throughout. The details of manipulation followed closely those of Philip (T., 1903, **83**, 814), and so are not further described.

Mononitration.

Previous workers are Holdermann (*Ber.*, 1906, **39**, 1256), Friswell (*J. Soc. Chem. Ind.*, 1908, **27**, 258), and van der Arend (*Verslagen K. Akad. Wetensch. Amsterdam*, 1908, 208).

Reference Curves.—As the product of mononitration is mainly *o*- and *p*-nitrotoluenes, the binary fusion curve for *o*- and *p*-nitrotoluenes was first plotted from the data given in Table I and Fig. 1.

TABLE I.

<i>p</i> -Nitrotoluene per cent.	Crystallisation point.	<i>p</i> -Nitrotoluene per cent.	Crystallisation point.
100	51.5°	50	16.7°
90	45.5	35	— 0.4
75	36.75	25	— 14.33
60	25.2	0	— 4

These values agree with results obtained by Holleman (*Rec. trav. chim.*, 1914, **33**, 1), which were not available at the time of our investigation. Bell and Spry (*J. Ind. Eng. Chem.*, 1921, **13**, 60) have since published similar figures.

The fusion curve for *m*- and *p*-nitrotoluenes, not previously investigated, was plotted from the results given in Table II and Fig. 1.

TABLE II.

<i>m</i> -Nitrotoluene per cent.	Crystallisation point.	<i>m</i> -Nitrotoluene per cent.	Crystallisation point.
0	51.5°	73	-2.9°
25	36.2	75	-1.0
40	24.4	80	2.8
50	15.4	90	10.0
67	— 2.9	100	16.0

The ternary fusion diagram for *o*-, *m*-, and *p*-nitrotoluenes was partly studied, about thirty observations being made, chiefly in

FIG. 1.

the regions where small percentages of *m*-nitrotoluene are present. The results taken from this diagram and given in Table III were used in analysis.

TABLE III.

Addition of *m*-nitrotoluene to a mixture of 75 per cent. of *o*- and 25 per cent. of *p*-nitrotoluene.

<i>m</i> -Nitrotoluene per cent.	Crystallisation point.	<i>m</i> -Nitrotoluene per cent.	Crystallisation point.
1.03	- 15.3°	4.1	- 16.9°
2.04	- 15.9	5.08	- 17.4
2.93	- 16.3	8.85	- 19.3

Methods of Analysis.—I. Special Method for Mononitrotoluene.

When commercial nitrotoluene is cooled, the initial crystallisation point is rather difficult to determine, as it is not very far removed from the eutectic and there is a great risk of overcooling. The second crystallisation point is well defined, however, as the eutectic represents about 85 per cent. of the mixture.

The method adopted to obtain greater accuracy was to determine the second crystallisation point of the original mixture and then to add an equal quantity of pure *p*-nitrotoluene and determine the initial crystallisation point; as the mixture was quite rich in *p*-nitrotoluene, a well-defined halt was then obtained. The percentage of *p*-nitrotoluene *P* in this mixture is read off from the *o-p*-curve (Fig. 1), the small quantity of *m*-nitrotoluene present having, judging by the ternary diagram, much the same effect as the same quantity of *o*-nitrotoluene in depressing the crystallisation point. The percentage *p* of *p*-nitrotoluene in the mixture under investigation is consequently $p = 2(P - 50)$. The percentage *m* of *m*-nitrotoluene in the eutectic of the original mixture is read off from the curve drawn from Table III. Then, if *x* is the required percentage of *m*-nitrotoluene in the mixture and *p* the percentage of *p*-nitrotoluene,

$$x = 4m \frac{(100 - p)}{300 + m},$$

for in 100 parts of the mixture there are *p* parts of *p*-, *x* parts of *m*-, and $(100 - p - x)$ parts of *o*-nitrotoluene; the eutectic of this mixture, since the composition of the eutectic of *o*- and *p*-nitrotoluenes is 75 per cent. of *o*-nitrotoluene and 25 per cent. of *p*-nitrotoluene, will contain *x* parts of *m*-, $100 - p - x$ parts of *o*-, and $25/75 (100 - p - x)$ parts of *p*-nitrotoluene, and the percentage of *m*-nitrotoluene in the eutectic is

$$m = \frac{100 x}{\frac{4}{3} (100 - p - x) + x}.$$

II. General Method Applicable to Ternary Mixtures.

This depends on obtaining known and unknown mixtures of the same second crystallisation point.

In Fig. 2 a ternary composition diagram is shown, in which *O*, *P*, and *M* represent 100 per cent. of each of the isomerides in triangular co-ordinates, *A* represents the composition of the eutectic mixture of *O* and *P*, and *T* the ternary eutectic composition. *B* represents a known mixture of *O* and *P*, and

BM a known curve of compositions obtained by adding M to B . The second crystallisation points of this series of mixtures are taken, corresponding with compositions along the boundary curve AT . Then let C represent any unknown mixture in the region APT ; its second crystallisation point E , corresponding with that of the known mixture D , is determined, a known percentage of M is added, and the new second crystallisation point F , corresponding with that of the known mixture G , is determined. The composition of the mixture C may then be calculated as follows:

Let x be the required percentage of O , and z the required percentage of M in the mixture C . Let h be the percentage of M added to 100 parts of C in the determination. Let d be the

FIG. 2.

percentage of M added to 100 parts of the known mixture B which gives the same second crystallisation point as C , and g the percentage of M added to 100 parts of B which gives the same second crystallisation point as C after the addition of h parts of M (d and g correspond with D and G in the diagram and are read off from the curve BM , plotted as second crystallisation point against added percentage of M). Also let p be the percentage of O in the mixture B .

Then
$$\frac{x}{p} = \frac{z}{d} = \frac{z + h}{g}$$

hence
$$z = \frac{d h}{g - d} \text{ and } x = \frac{p h}{g - d}.$$

The percentage of P in the mixture is $100 - x - z$.

If the substance M is not available for addition to the unknown mixture C , a definite percentage of the known mixture B may be added. Then, by similar reasoning, if x , z , p , and d have the same significance as before, but k is the percentage of O added to C when a quantity of mixture B is added for the second determination of the crystallisation point, and g the percentage of M added to 100 parts of B which gives the same second crystallisation point as the mixture formed by this addition of B to C ,

$$\frac{z}{x} = \frac{d}{p} \text{ and } \frac{z}{x+k} = \frac{g}{p}.$$

hence

$$x = \frac{k g}{d - g} \text{ and } z = \frac{d k g}{p(d - g)}.$$

TABLE IV.

Curve BM .—The percentage of m -nitrotoluene added to a mixture of 70 per cent. of o - and 30 per cent. of p -nitrotoluene, and the corresponding second crystallisation points.

Added m -nitro- toluene per cent.	Second crystal- lisation point.	Added m -nitro- toluene per cent.	Second crystal- lisation point.
0.5	— 14.9°	2.6	— 16.1°
1.1	— 15.3	3.4	— 16.5
1.7	— 15.65	4.3	— 17.0
2.2	— 15.9	5.1	— 17.4
		9.05	— 19.3

Examination of Mononitrotoluene.—Samples of mononitrotoluene were prepared under varying conditions of nitration as detailed in Table V, and the resulting products analysed by method I. The effect of conditions on the composition is not large, although low temperature reduces the proportion of m -nitrotoluene and increases the proportion of p -nitrotoluene. When a small bulk of mixed acid is used, the nitration appears to proceed too vigorously for the temperature effect to be obtained.

TABLE V.

Toluene.	Weight of nitrating acid.			Temp.	Crystallisation points.		Calculated composition.		
	H ₂ SO ₄ .	HNO ₃ .	H ₂ O.		Initial.	Second.	Ortho.	Meta.	Para.
75		282	18	40°	30.8°	— 17.35°	60.7	4.3	35
"		282	18	0	31.7	— 16.4	60.3	2.5	37.2
35	58.7	23.8	17.5	50	30.3	— 17.3	62.2	4.3	33.5
"	"	"	"	40	29.8	— 17.2	63.6	4.2	32.2
"	"	"	"	20	30.35	— 17.4	61.9	4.5	33.6
"	"	"	"	0	30.6	— 17.45	61.1	4.5	34.4
"	112	"	38.2	40	30.25	— 17.1	62.7	3.9	33.4
36	"	"	"	0	31.3	— 16.8	60.5	3.3	36.2

Mononitrotoluene prepared under the conditions recorded for the fifth sample in Table V was examined by method II (both variants).

(a) The second setting point, -17.4° , corresponds with 5.1 on the curve BM (Table IV).

After the addition of 2 per cent. of *m*-nitrotoluene, the second setting point, -18.5° , corresponds with 7.4 on curve BM .

Here $p = 70$, $d = 5.1$, $g = 7.4$, and $h = 2$.

Hence $z = \frac{5.1 \times 2}{2.3} = 4.4$, and $x = \frac{70 \times 2}{2.3} = 61$.

Therefore the composition is *o*- 61, *m*- 4.4, and *p*- 34.6.

(b) The second setting point, -17.4° , corresponds with 5.1 on curve BM (Table IV).

After the addition of an equal part of mixture *B* (70 per cent. of *o*- and 30 per cent. of *p*-) the second setting point, -16° , corresponds with 2.4 on curve BM .

Here $p = 70$, $d = 5.1$, $g = 2.4$, and $k = 70$.

Hence $x = \frac{kg}{d - g} = \frac{70 \times 2.4}{2.7} = 62.2$

and $z = \frac{dkg}{p(d - g)} = \frac{5.1 \times 70 \times 2.4}{70 \times 2.7} = 4.5$.

Therefore the composition is *o*- 62.2, *m*- 4.5, and *p*- 33.3.

Remarks.—Mononitrotoluene prepared under the usual conditions of nitration will contain approximately

o-nitrotoluene 62 per cent. ± 1 .

p-nitrotoluene 33.5 to 32 per cent.

m-nitrotoluene 4.5 to 4.2 per cent.

These proportions do not appear to be affected sufficiently by variations in the process to make the suppression of *m*-nitrotoluene feasible, and therefore the influence of all three isomerides must be considered in the subsequent stages of nitration.

Dinitration.

Previous Work.—There appears to be in the literature no account of quantitative work on the dinitration of *o*-nitrotoluene. It is usually stated, without reference, that *p*-nitrotoluene gives 2:4-dinitrotoluene only. Sirks (*Rec. trav. chim.*, 1907, 27, 208) found that *m*-nitrotoluene gave more than 50 per cent. of 3:4-dinitrotoluene, and more 2:3- than 2:5-dinitrotoluene.

Reference Curves.—As *o*-nitrotoluene gives on nitration 2:4-

and 2:6-dinitrotoluenes, the binary fusion curve for these two isomerides is important.

Giua (*Ber.*, 1914, 47, 1721) gives results which do not agree well with ours, given below in Table VI and Fig. 3.

TABLE VI.

2 : 6-Dinitro- toluene per cent.	Crystallisation point.	2 : 6-Dinitro- toluene per cent.	Crystallisation point.
0	69.8°	61.8	37.15°
9.83	64.5	65.2	39.95
27.89	53.95	70.9	44.55
33.43	49.95	73.6	46.25
39.5	45.0	77.5	49.0
44.63	39.75	81.7	52.25
48.14	35.95	83.9	53.95
50.0	34.75	90.8	59.05
51.95	33.15	95.2	61.45
55.75	32.05	100	64.65

FIG. 3.

The nitration of *m*-nitrotoluene gives 3:4-, 2:3-, and 2:5-dinitrotoluenes. The binary fusion curves for these substances

(Fig. 3) were drawn from the data in Tables VII, VIII, and IX and used in the examination of the nitration of *m*-nitrotoluene.

TABLE VII.

2 : 3- and 3 : 4-Dinitrotoluenes.		
3 : 4-Dinitro- toluene per cent.	Crystal- lisation point.	Eutectic.
20	45.75°	
40	30.05	
45	26.9	22.5
50.5	22.5	22.5
55	26.5	22.5
60	29.5	
80	46.5	

TABLE VIII.

3 : 4- and 2 : 5-Dinitrotoluenes.		
2 : 5-Dinitro- toluene per cent.	Crystal- lisation point.	Eutectic.
0	58.4°	
20	45.95	
40	31.9	
60	22.85	20.75
80	37.15	
100	50.1	

FIG. 4.

Ternary setting-point diagram. Mixtures of 2 : 3-, 3 : 4-, and 3 : 6-dinitrotoluenes.

TABLE IX.

2 : 3- and 2 : 5-Dinitrotoluenes.

2 : 5-Dinitrotoluene per cent.	Crystallisation point.	Eutectic.
0	59.15°	
20	45.85	
40	30.4	19.65
60	26.1	19.85
80	38.45	
100	50.1	

The ternary diagram for these three isomerides was also prepared (Fig. 4)

Examination of Dinitrotoluene.—The nitration of each of the isomeric mononitrotoluenes, and of the mononitration product of toluene obtained under the conditions described in Table V, to dinitrotoluene was carried out as follows :—

Fifty grams of mononitrotoluene were nitrated with 240 grams of a mixed acid of composition : sulphuric acid 77, nitric acid 11·3, and water 11·7 per cent.

The mononitrotoluene was added at 40—45°, and the temperature was finally raised to 70° and maintained for thirty minutes. The acid was then diluted with 40 c.c. of water, and the product separated, washed, and dried. The yield was about 91 per cent. The results obtained were as follows : *p*-nitrotoluene gave 2 : 4-dinitrotoluene only, crystallisation point 69·7°; *o*-nitrotoluene gave a mixture of 2 : 4- and 2 : 6-dinitrotoluenes, crystallisation point 50° (reference to the curve in Fig. 3 gives 66·6 parts of 2 : 4- and 33·3 parts of 2 : 6-dinitrotoluene from *o*-nitrotoluene); and *m*-nitrotoluene gave a mixture of 3 : 4-, 2 : 3-, and 2 : 5-dinitrotoluenes of crystallisation point 22·8°. The last mixture was not extensively studied, but the single sample prepared corresponded in crystallisation point with a mixture of 55, 25, and 20 per cent. of 3 : 4-, 2 : 3-, and 2 : 5-dinitrotoluenes respectively.

The crude mononitrotoluenes on nitration gave a crystallisation point varying from 55·6° to 56·7°.

A moderate-scale nitration of mononitrotoluene manufactured at a Government factory gave a dinitrotoluene of crystallisation point 56°. This, on the curve in Fig. 3, corresponds with 74·8 per cent. of 2 : 4-dinitrotoluene. The composition of commercial dinitrotoluene may therefore be taken as 2 : 4-dinitrotoluene 74·8 per cent., 2 : 6-dinitrotoluene 20·7 per cent., 3 : 4-dinitrotoluene 2·5 per cent., 2 : 3-dinitrotoluene 1·1 per cent., and 2 : 5-dinitrotoluene 0·9 per cent.

Trinitration.

Examination of Trinitrotoluene.—The nitration of each of the isomeric mononitrotoluenes was carried out as follows : 100 grams of mononitrotoluene were nitrated with 1000 grams of acid of the composition : sulphuric acid 78, nitric acid 17·5, and water 4·5 per cent.

The nitrations were carried out with gradual rise of temperature from 50° to 120° during five hours. The nitration product was precipitated with an excess of water, washed, and dried. *o*-Nitrotoluene gave 156 grams of 2 : 4 : 6-trinitrotoluene of crystallisation point 79·8°, *p*-nitrotoluene gave 158 grams, of crystallisation point 80·2°,

and *m*-nitrotoluene gave 144 grams of a mixture of trinitrotoluenes, of crystallisation point 73.8° .

Analysis of Crude Trinitrotoluene.—From the results obtained above, it is clear that crude trinitrotoluene may be regarded as composed of three essential components :

- (1) Pure 2 : 4 : 6-trinitrotoluene.
- (2) The mixture of trinitrotoluenes derived from *m*-nitrotoluene, and
- (3) Crude dinitrotoluene, of crystallisation point close to 56° , the presence of which is due to incomplete nitration under manufacturing conditions.

FIG. 5.
*Change of crystallisation point in course
of nitration of dinitrotoluene.*

The binary fusion curves for these three materials and the ternary fusion diagram were therefore mapped and from the ternary diagram all the desired information about any particular sample of crude trinitrotoluene could be obtained after its crystallisation point had been determined.

Information derived from the Ternary Diagram for Crude Trinitrotoluene.—The course of nitration as shown by the change in crystallisation point and the degree of completeness of nitration reached at any stage of the trinitration are given by Fig. 5, taken from the ternary diagram. If the crystallisation point or setting point is taken wet, the temperature is 5° lower.

Table X gives the composition of crude trinitrotoluene corresponding with varying crystallisation points.

TABLE X.

Crystallisation point.	Percentage composition.		
	2 : 4 : 6-Trinitro-toluene.	Other isomerides.	Dinitrotoluene.
78°	95.2	4.0	0.8
77	93.7	3.9	2.4
76	92.4	3.8	3.8
75	90.8	3.8	5.4
74	89.2	3.7	7.1

Table XI gives the composition at various temperatures of the liquid phase in crude trinitrotoluene of crystallisation point 76°. This is obtained by following the course of crystallisation of mixtures of this composition on the ternary diagram, the production of the line joining the points representing 2 : 4 : 6-trinitrotoluene and the composition in question, and reading off the composition at the isothermal lines.

TABLE XI.

	2 : 4 : 6-Tri-nitrotoluene.	Other isomerides.	Dinitro-toluenes.
Original composition	92.4	3.8	3.8
Composition of liquid phase at 60°	67.6	16.2	16.2
" " " " " 50°	57.6	21.2	21.2
" " " " " 40°	50.8	24.6	24.6
" " " " " 30°	45.0	27.5	27.5

The percentage of oil in crude trinitrotoluene of setting point 76° at various temperatures can be calculated from Table XI. Table XII gives the results obtained.

TABLE XII.

Temp.	Oil content.
60°	23.4
50	17.9
40	15.5
30	13.8

The loss on purification by such processes as centrifuging, washing with cold alcohol, or the sulphite process depends on the composition of the crude trinitrotoluene.

The last process removes only the isomeric trinitrotoluenes, raising the crystallisation point by 2.4°; the crystallisation point of the original crude material must therefore be high for this process to give purified material of a crystallisation point of 80°.

Further Investigation of the Trinitrotoluenes formed by Nitration.

Previous Work.—Molinari and Giua (*Rendiconti del Reale Istituto de Scienza e Lettere*, 1913, **46**, fasc. II) investigated the by-products of trinitrotoluene manufacture and obtained by distillation in a vacuum a product melting at 79.5° which they considered to be 2:3:5- or 2:3:6-trinitrotoluene. Will (*Ber.*, 1914, **47**, 704) states positively that as the result of exhaustive investigation and extensive modification of the conditions of nitration, nothing but

$E\alpha\beta$ = eutectic of α - and β -trinitrotoluenes.

$E\beta\gamma$ = eutectic of β - and γ -trinitrotoluenes 73.5° .

$E\alpha\gamma$ = eutectic of α - and γ -trinitrotoluenes.

$E\alpha\beta\gamma$ = ternary eutectic 44.4° . Composition α 43.5 %, β 20.0 %, γ 36.5 %.

$C\beta\gamma$ = compound $\beta\gamma$. Setting point 74.5° .

the three well-known isomeric trinitrotoluenes are formed by the nitration of toluene, that is, 2:4:6-, 2:3:4-, and 3:4:6-trinitrotoluenes.

Reference Curves.—As a first step, the binary fusion curves for the three isomeric trinitrotoluenes, 2:4:6-, 2:3:4-, and 3:4:6-, were mapped and the ternary fusion diagram for the three isomerides was produced.

The results are shown in Table XIII and Fig. 6.

TABLE XIII.

Trinitrotoluene.			Crystallisation point.
2 : 4 : 6- (α -).	2 : 3 : 4- (β -).	3 : 4 : 6- (γ -).	
100			80.8°
80	20		74.2
59	41		67.3 eutectic.
40	60		82.6
20	80		96.8
	100		109.5
80		20	69
70		30	59 eutectic.
60		40	59.5
52		48	60 eutectic.
40		60	72.8
20		80	94.2
		100	101.5
	80	20	96.2
	60	40	82.7
	47.5	52.5	73.5 eutectic.
	40	60	74.3
	37	63	73.5 eutectic.
	20	80	78.5

The ternary fusion diagram was completed from data furnished by mixtures of all three isomerides. The ternary eutectic was found to have a crystallisation point of 44.4° and the composition 43.5 per cent. of 2 : 4 : 6-, 20 per cent. of 2 : 3 : 4-, and 36.5 per cent. of 3 : 4 : 6-trinitrotoluene.

The product of trinitration of *m*-nitrotoluene had a crystallisation point of 73.8°, and on addition to 2 : 4 : 6-trinitrotoluene gave a fusion curve with a minimum at 38.4° corresponding with the composition 44.5 per cent. of 2 : 4 : 6-trinitrotoluene. As this minimum was 6° lower than the ternary eutectic for 2 : 4 : 6- 2 : 3 : 4-, and 3 : 4 : 6-trinitrotoluenes, it was taken as an indication of the presence of another isomeride in the product of nitration of *m*-nitrotoluene.

Before further quantitative work could be done, it was necessary to investigate the preparation and properties of the rarer dinitrotoluenes and the trinitrotoluenes derivable from them. This work was undertaken by Brady, Drew, and others (T., 1920, 117, 876, 1137). Ultimately Drew succeeded in isolating 2 : 3 : 6-trinitrotoluene as a product of the nitration of 2 : 3-dinitrotoluene and 2 : 5-dinitrotoluene.

A comparison of the thermal analysis of the products of nitration with the fusion curves of 2 : 3 : 4- and 2 : 3 : 6-trinitrotoluenes and 2 : 3 : 6- and 3 : 4 : 6-trinitrotoluenes indicated that 2 : 3-dinitrotoluene gave 16 per cent. of 2 : 3 : 6-trinitrotoluene, and 2 : 5-dinitrotoluene 13 per cent. Brady (private communication) has

found that the nitration of 3 : 4-dinitrotoluene yields 83 parts of 3 : 4 : 6- and 17 parts of 2 : 3 : 4-trinitrotoluene in the product.

From the above results the proportions of the isomeric trinitrotoluenes obtained on nitration of *m*-nitrotoluene are derivable from the composition of the product of dinitration of *m*-nitrotoluene.

		Trinitrotoluene.		
		3 : 4 : 6-	2 : 3 : 4-	2 : 3 : 6-
Thus 55 parts of 3 : 4-dinitrotoluene give		45.7	9.3	
„ 25 „ „ 2 : 3-	„ „		21	4
„ 20 „ „ 2 : 5-	„ „	17.4		2.6
Hence <i>m</i> -nitrotoluene gives		63.1	30.3	6.6

The crystallisation point of a mixture of this composition agrees well with that of the direct nitration product of *m*-nitrotoluene, 73.8°.

Under usual conditions of nitration, the nitro-derivatives obtained at each stage from toluene may therefore be summarised as follows :

Mononitrotoluenes.			Dinitrotoluenes.			Trinitrotoluenes.		
ortho-	62	per cent.	2 : 4-	74.8	per cent.	2 : 4 : 6-	95.5	per cent.
para-	33.5	„ „	2 : 6-	20.7	„ „	3 : 4 : 6-	2.9	„ „
meta-	4.5	„ „	3 : 4-	2.5	„ „	2 : 3 : 4-	1.3	„ „
			2 : 3-	1.1	„ „	2 : 3 : 6-	0.3	„ „
			2 : 5-	0.9	„ „			

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