171. *The Effect of Temperature on the Proportions of Isomers formed in the Mononitration of Toluene.*

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Toluene has been nitrated with mixtures of nitric and sulphuric acids at various temperatures from − 30° to 60°. The proportion of *m*-nitrotoluene formed in each instance has been calculated from the setting point of the derived TNT. The results afford evidence that in applying the Arrhenius equation $k = nAe^{-E/RT}$ to the mononitration of toluene, $A_o = 2{\cdot}90\,A_m$, $A_p = 2{\cdot}70\,A_m$, $E_m - E_o = 917$ and $E_m - E_p = 1103$ cal. deg.$^{-1}$ mol.$^{-1}$.

THE manufacture of trinitrotoluene is complicated by the undesirable formation of *m*-nitrotoluene in the mononitration stage. Several workers have published data on the proportions of isomers formed in the mononitration of toluene at various temperatures and in several media. Their results, for percentage *m*-nitrotoluene, are collected in Table I. Generally the proportions of isomers were determined by thermal analysis, but Ingold *et al.* (*loc. cit.*) also determined the meta-content by solubility measurements on the derived nitrobenzoic acids.

TABLE I.

			C.				
Temp.	A.	B.	*a.*	*b.*	*c.*	D.	E.
−30°	2·7	3·5	—	—	—	—	—
0	3·1	3·9	2·5	4·5	3·3	3·7	—
20	—	—	4·3	4·5	3·9	—	4·1
30	3·2	4·4	—	—	—	4·4	—
40	—	—	—	4·2	—	—	—
50	—	—	—	4·3	—	—	—
60	4·0	5·1	—	—	—	—	—

A. Van den Arend, *Rec. Trav. chim.*, 1909, **28**, 408. Nitration in 85% HNO_3.
B. Holleman, Vermeulen, and de Mooy, *ibid.*, 1914, **33**, 1. Recalculation of results of Van den Arend.
C. Gibson, Duckham, and Fairbairn, *J.*, 1922, **121**, 270. Nitration in :

(*a*) 94% HNO_3;
(*b*) Mixed acid containing 58·7% H_2SO_4, 23·8% HNO_3, 17·5% H_2O;
(*c*) Mixed acid containing 64·4% H_2SO_4, 13·7% HNO_3, 21·9% H_2O.

D. Ingold, Lapworth, Rothstein, and Ward, *J.*, 1931, 1959. Nitration in acetic anhydride and in nitromethane.
E. de Beule, *Bull. Soc. chim. Belg.*, 1933, **42**, 27. Nitration in HNO_3 and mixed acid.

The figures recorded in Table I show rather wide variations and, in particular, they indicate that change in meta-nitration with temperature is much less for nitration in mixed acid than in other media. Because of its technical importance, nitration in mixed acid has been reinvestigated, using a new method of analysis which is simpler and considered to be less liable to error than thermal analysis.

2 : 4-Dinitrotoluene, *p*-nitrotoluene, and known mixtures of *m*- and *p*-nitrotoluene were trinitrated by the standard method described in the experimental part, and the setting points of the products were determined. The results are recorded in Table II, the setting points being corrected. Setting points have been calculated from the equation :

TABLE II.

	2 : 4-DNT.	Mixtures of *m*- and *p*-nitrotoluene.				
Concn. of *m*-nitrotoluene (%) ...	—	0	2·11	3·22	4·58	5·75
Setting point of TNT, found	80·80°	80·78°	79·87°	79·26°	78·70°	78·13°
,, ,, ,, , calc.	—	80·80°	79·82°	79·30°	78·67°	78·13°

$$\text{Setting point} = 80{\cdot}80 - 0{\cdot}465\ (\text{concn. of } m\text{-nitrotoluene}) \quad . \quad . \quad . \quad . \quad (1)$$

which was derived from the data by the method of least differences. That trinitration in these experiments was substantially complete is shown by the close agreement between the setting points of products derived from *p*-nitrotoluene and 2 : 4-dinitrotoluene with that recorded by Rintoul (*J. Soc. Chem. Ind.*, 1915, **34**, 60).

Toluene was nitrated at various temperatures with 1·2 mols. of nitric acid in the form of a mixed acid. The nitrotoluenes, after removal of unchanged toluene, were trinitrated by the standard method. The setting points of the trinitrotoluenes were determined and the proportions of *m*-nitrotoluene in the original nitrotoluenes were calculated from equation (1). The results, collected in Table III, show that the proportion of *m*-nitrotoluene changes almost linearly with temperature and there is no evidence that the rate of change is less for mixed acid nitrations than for nitrations in other media.

TABLE III.

Temperature of mononitration	−30°	0°	30°	60°
Setting point of TNT	79·42°	79·09°	78·76°	78·52°
Concn. of *m*-nitrotoluene (%)	2·97	3·68	4·39	4·90

DISCUSSION.

Bradfield and Jones (*J.*, 1928, 1006) calculated, for several substitutions, the proportions of isomers formed at one temperature from the experimentally determined proportions at a second temperature by means of the Arrhenius equation, $k = nAe^{-E/\boldsymbol{R}T}$, in which, for each isomer, k is the rate of formation, n is the number of equivalent substitution positions, A is a temperature-independent factor, E is the energy of activation, and T is the absolute temperature. They obtained fair agreement with experiment on the assumption that A was the same for each isomer formed in a particular reaction. The close agreement, for the proportion of *m*-nitrotoluene formed at 0° and 30°, between our results and those of Ingold *et al.*, determined by entirely different techniques, is strong evidence for the essential reliability of the experimental data. The values for *m*-nitrotoluene, calculated for other temperatures by the method of Bradfield and Jones from the data of Ingold *et al.* at 30°, are given in the left side of Table IV. They show increasing divergence from our experimental values as the temperatures depart from 30°. As these deviations are considerable and show a systematic trend they cannot be attributed to experimental error.

Better agreement between calculated and experimental results can be obtained only by assuming that the temperature-independent factors are different for the three isomers. Appropriate values for these factors can be calculated from the proportions of isomers at two temperatures, thus :

$$\text{Let } k_o = 2A_oe^{-E_o/\boldsymbol{R}T};\ k_m = 2A_me^{-E_m/\boldsymbol{R}T};\ k_p = A_pe^{-E_p/\boldsymbol{R}T}$$

$$\text{Then } k_o/k_m = (A_o/A_m)e^{(E_m - E_o)/\boldsymbol{R}T}$$

If r_1 and r_2 are the ratios of *o*- to *m*-nitrotoluene formed at two temperatures T_1 and T_2, then

$$2{\cdot}303\,\{\log_{10}r_1 - \log_{10}(A_o/A_m)\} = (E_m - E_o)/\boldsymbol{R}T_1 \quad . \quad . \quad . \quad . \quad (2)$$

$$\text{and } 2{\cdot}303\,\{\log_{10}r_2 - \log_{10}(A_o/A_m)\} = (E_m - E_o)/\boldsymbol{R}T_2$$

Dividing and transposing we obtain

$$\log_{10}(A_o/A_m) = (T_2\log_{10}r_2 - T_1\log_{10}r_1)/(T_2 - T_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Similarly, if s_1 and s_2 are the ratios of *p*- to *m*-nitrotoluene at T_1 and T_2,

$$\log_{10}(A_p/2A_m) = (T_2\log_{10}s_2 - T_1\log_{10}s_1)/(T_2 - T_1) \quad . \quad . \quad . \quad . \quad . \quad (4)$$

By substituting in equations (3) and (4) the ratios of isomers given by Ingold *et al.* for 0° and 30° it was found that

$$A_o = 2{\cdot}90A_m \text{ and } A_p = 2{\cdot}70A_m,$$

and by further calculation the proportions of isomers formed at − 30° and 60°, shown in the right side of Table IV, were obtained. It is evident that much better agreement with experiment is given by the new equations.

TABLE IV.

	$A_o = A_m = A_p$.			$A_o = 2{\cdot}90A_m;\ A_p = 2{\cdot}70A_m$.		
Temp.	*o* (%).	*m* (%).	*p* (%).	*o* (%).	*m* (%).	*p* (%).
−30°	58·33	2·32	39·35	57·55	2·98	39·47
0	58·49	3·31	38·20	(58·10)	(3·70)	(38·20)
30	(58·45)	(4·40)	(37·15)	(58·45)	(4·40)	(37·15)
60	58·21	5·54	36·25	58·66	5·07	36·27

The numbers in parentheses are the experimental values on which the calculations are based.

The values of A_o and A_p are nearly equal and only small changes in the proportions of *o*- and *p*-nitrotoluene, but none in the proportions of *m*-nitrotoluene, are caused by adopting the mean value, 2·80, for both. There does not, however, appear to be any reason why, in the general case, A_o should be equal to A_p and so the separate values have been used in the calculations of Table IV.

From equation (2) and the corresponding equation for the ratio of *p*- to *m*-nitrotoluene we have obtained the following values, in cal. deg.$^{-1}$ mol.$^{-1}$, for activation energy differences :

$$E_m - E_o = 917 \qquad E_m - E_p = 1103$$

EXPERIMENTAL.

Materials.—" Nitration " toluene (National Benzole Specification No. 7, 1938) was distilled through a short column. The middle fraction, having $d^{15.5^\circ}_{15.5^\circ}$ 0·8710, n^{20° 1·4963, was used. Commercial *m*-nitrotoluene was purified by fractional freezing until the maximum setting point, 16·0° (corr.), was reached. Commercial *p*-nitrotoluene and 2 : 4-dinitrotoluene were recrystallised from alcohol until the setting points remained unchanged at 51·6° (corr.) and 69·8° (corr.).

A stock of mononitration mixed acid was made from sulphuric acid (*d* 1·84, 18·8 kg.), nitric acid (*d* 1·42, 1·1 kg.), liquid nitrogen tetroxide (0·9 kg.), and water (4·7 kg.). Analysis of the mixture gave 71·4% H_2SO_4, 5·35% HNO_3, 1·75% HNO_2, and 21·5% H_2O. Nitrous acid was added because it catalyses the nitration and prevents undue temperature fluctuations in the early stages. Dinitration and trinitration acids were made up as required for each nitation from concentrated sulphuric and nitric acids and 20% oleum that had been titrated.

Mononitration.—The all-glass apparatus was a 2-l., 3-necked, bolt-head flask fitted with paddle stirrer, reflux condenser, dropping funnel, and thermometer, the last two reaching to near the bottom. The flask was immersed in a suitable cooling bath : solid carbon dioxide and trichloroethylene for — 30° and 0°, ice-water for 30°, and water at the ordinary temperature for 60°. Mixed acid (2300 g.) was placed in the nitrator and cooled to just below the reaction temperature, and toluene (150 g.) was run in, fairly rapidly at first till the intended temperature was reached and then more slowly to keep the temperature constant. After the initial warming up, the maximum variation in temperature was ± 1°. The addition of toluene took about 30 minutes, and the reaction was continued for a further 75 minutes except for the — 30° nitration which was run for a total time of 4·5 hours. During the later stages of the reaction the bath temperature was raised gradually to keep the reaction temperature constant until, finally, outside and inside temperatures were almost equal. The reaction mixture was poured into ice-water (4 kg.), the aqueous layer was removed, and more water was added followed by ether until the organic layer was the lighter. The ethereal layer was washed with water till acid-free and dried (Na_2SO_4), and the ether was distilled off. Traces of ether and any un-nitrated toluene were removed by passing a current of air through the residue heated to 100° under reduced pressure. The nitrotoluenes were tested colorimetrically for toluene by shaking with an equal volume of a solution of sodium nitrite (2·5 g.) in 88% sulphuric acid (100 c.c.). Absence of a red colour indicates less than 0·2% of toluene (Dr. J. K. N. Jones, private communication).

Dinitration.—The apparatus was similar to that used for mononitration, except that the flask was of 1 l. capacity. It was immersed in a stirred oil-bath provided with means for heating and cooling. Mononitrotoluene (50 g.) was dissolved in 90% sulphuric acid (120 g.) in the nitrator at 50°. Mixed acid (125 g.), containing 70·0% of sulphuric acid, 21·5% of nitric acid, and 8·5% of water, was added cautiously from the dropping funnel. As soon as reaction had started the bath was cooled to about 30° and the rate of addition controlled so that all the mixed acid was added at about 50° in 30 minutes. The mixture was then rapidly heated to 70° and this temperature maintained for 1·5 hours. The product was washed thrice at 100°, each time by stirring vigorously for 15 minutes with an equal volume of water, allowing to settle for 5 minutes, and separating the aqueous layer. Solid which separated from the washings on cooling was collected and added to the main product, and the whole was dried at 100° for 3 hours.

Trinitration.—The same apparatus was used as for dinitration. The whole of the dinitration product (or 65 g. in the case of 2 : 4-dinitrotoluene) was dissolved in 100% sulphuric acid (220 g.) in the nitrator at 100°, the oil-bath was cooled to about 97°, and the addition of mixed acid (125 g.), containing 60% of sulphuric acid, 40% of nitric acid, and 0% of water, was started. Reaction did not begin immediately, and the addition of mixed acid was stopped after a few g. had been added until there was a noticeable rise in temperature. The bath was then cooled to about 80° and the rate of addition controlled to keep the temperature at 100°. The addition was complete in 30 to 45 minutes. Towards the end of the addition of mixed acid the bath temperature was gradually raised so that it was 95° at the end of the addition, and it was further raised to about 98° during the additional reaction time of 3·5 hours. Finally, the reaction mixture was poured on ice and kept overnight, and the solid was then collected. The trinitrotoluene was washed with water at 100°, in the same manner as the dinitrotoluene, till the acidity of the last wash, titrated to phenolphthalien, was equivalent to not more than 0·002 g. of sulphuric acid. The washed trinitrotoluene was dried for 6 hours at 100° and its setting point determined. The observed value was corrected for exposed stem.

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