180. *The Function of Sulphuric Acid in Nitration.*

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Most of the work now reported formed part of a more extended investigation, conducted some years ago, to determine the optimal conditions for efficient trinitration of toluene, but Hetherington and Masson's results (J., 1933, 105) have suggested a new aspect of it. These authors found that, for the mononitration of nitrobenzene and nitrotoluene within the limits of temperature and of molar concentration of sulphuric acid under which their experiments were conducted, " if there is at least enough sulphuric acid present to form the monohydrate H_2SO_4,H_2O with the water initially present *plus* the water formed chemically, the nitric acid is all available for this nitration," and that " temperature within our limits appears to play only a minor part in determining how far the reaction goes."

Trinitration, however, requires different temperatures and different concentrations of sulphuric acid from dinitration, and it by no means follows that the system represented by H_2SO_4-HNO_3-H_2O has the same constituent composition under both conditions. It would seem that, other things being equal, it is the composition of this acid system that is the main factor in determining the course and end-point of the nitration. The results herein stated (Fig. 1), which concern the trinitration of toluene, show that up to a point, approximately represented by 95° and an excess of 4 mols. of H_2SO_4 beyond that required for monohydrate formation, the constituent components of the acid system, as indicated by the nitration products, remain the same, and the conclusions of Hetherington and Masson (*loc. cit.*) concerning the effect of sulphuric acid hold good. Within approximately these limits, at any given time the velocity of the reaction and, consequently, the percentage nitration, is a relatively simple function of the molar excess of sulphuric acid present, the action of the excess of acid being sufficiently explained by its effect on the miscibility of the dinitro-compound with the acid phase (Fig. 2).

FIG. 1.

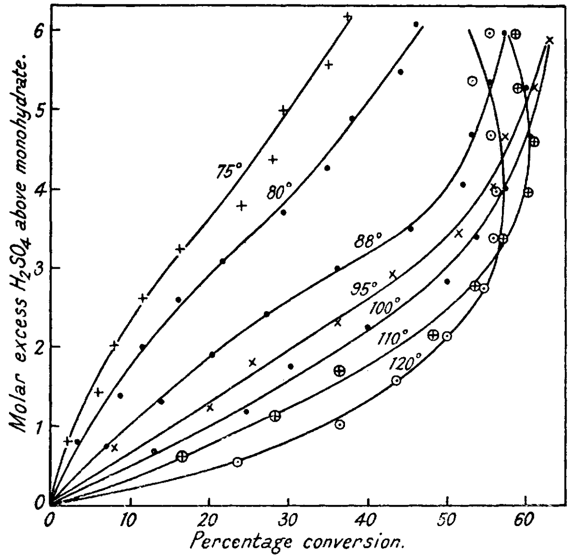
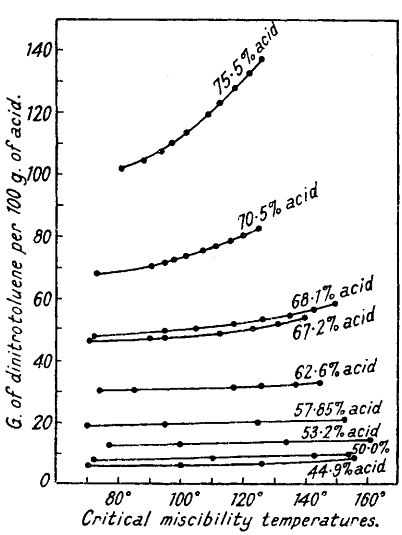


FIG. 2.



Beyond these limits, the constituent composition of the nitrating acid appears to be different. Increase of temperature and of concentration of sulphuric acid progressively diminish the amount of nitric acid available for nitration as determined from the yield of nitro-compound. This effect is being investigated further, but quantitative balance-sheets constructed for a number of preliminary trinitrations show that the diminishing yields are not due to losses consequent on fuming, or on such side reactions as are customarily associated with nitration under these conditions. For instance, a typical experiment at 105°, in which the molar concentrations of the original components were represented by the ratios D.N.T. : HNO_3 : H_2O : H_2SO_4 = 1·0 : 1·83 : 3·60 : 8·0, revealed that, when after 5 hours the reaction had come to a virtual standstill, 9·25% of the dinitrotoluene remained unchanged although the spent acid contained 30·0% of the original nitric acid.

EXPERIMENTAL.

(1) 50 G. of pure 2 : 4-dinitrotoluene with 200 g. of sulphuric acid of the required concentration, in long-necked flasks loosely closed with glass wool, immersed in a large bath, were

nitrated with 13·5 c.c. (20 g.) of 96% HNO_3, the latter being added slowly in successive quantities of 2·7, 5·4, and 5·4 c.c. and the whole operation occupying 25 minutes. The flasks then remained in the bath for a further 20 minutes, being thoroughly agitated at 5-minute intervals. The products were poured into 2 l. of cold water, kept over-night, filtered off, washed thoroughly with 2 l. of running water at 95° under standardised conditions, dried at 110° for 5 hours, and their specific gravities determined in a 10-c.c. pyknometer after being kept at 90° for 15 minutes. Their composition was determined by comparison with a large-scale specific-gravity curve constructed from synthetic mixtures of pure 2 : 4-dinitro- and 2 : 4 : 6-trinitro-toluene at 90°. The isomeric trinitrotoluenes do not differ materially in specific gravity; consequently, their presence does not vitiate this determination.

A large-scale setting-point curve of these synthetic mixtures was also constructed for comparison; it shows a well-marked compound of approximately 3 mols. dinitrotoluene with 2 mols. trinitrotoluene of f. p. 45·9°, with eutectics of either constituent of f. p.'s 45·3° and 45·4° containing 37·0% and 47·5% respectively of trinitrotoluene. Guia (*Ber.*, 1914, **47**, 1718) found indications of such a compound on the m.-p. curve of these two substances, but the maximum on the curve between the two eutectics, recorded as 44·55° and 45·1° respectively, was too small to be determined. The specific-gravity curve shows a maximum deviation of 0·7% from the normal in the portion corresponding approximately to that of compound formation as indicated on the f.-p. curve.

The loss due to the method of isolation was small, not exceeding 2% of the original material.

Nitrations of 2 : 4-*dinitrotoluene.* (Initial molar proportions of the nitration mixture were D.N.T. : HNO_3 : H_2O : H_2SO_4 = 1·195 : 1·0 : *x* : *y*.)

Mols.		Temp.	75°.	80°.	88°.	95°.	100°.	110°.	120°.
x.	*y*.	Excess H_2SO_4.	Nitration, %.						
7·8	8·63	0·83	2·2	3·5	7·5	8·0	13·2	16·4	23·6
7·25	8·74	1·49	6·0	8·8	14·0	20·0	24·8	28·4	36·4
6·71	8·84	2·13	8·0	11·4	20·4	26·0	30·2	36·8	43·6
6·18	8·94	2·76	11·6	16·0	27·2	36·4	40·0	48·4	50·0
5·61	9·04	3·43	16·0	21·6	36·4	43·0	50·0	53·6	54·0
5·07	9·14	4·07	24·2	29·6	45·6	51·6	53·6	56·4	55·8
4·52	9·24	4·72	28·0	34·8	52·2	56·2	57·2	60·0	56·4
3·98	9·34	5·36	29·2	38·0	53·2	57·2	61·2	60·8	55·3
3·43	9·44	6·01	34·8	44·0	55·6	61·0	58·6	58·8	53·0
2·88	9·54	6·66	37·2	46·0	57·2	62·8	62·8	58·4	55·3

The import of these figures is clearly shown by plotting curves for percentage nitration against the molar excess of sulphuric acid beyond that required for monohydrate formation, adjustment having been made for the water formed by the nitration reaction (Fig. 1).

(2) The miscibility curves for the system D.N.T.–H_2SO_4–H_2O (Fig. 2) were constructed from the critical miscibility temperatures determined for a large number of synthetic mixtures of known composition. The method is accurate and rapid; the end-points are sharply defined and are the same whether observed on heating or on cooling. Concentrations of acid are expressed in molar percentages.

SUMMARY.

The conclusions of Hetherington and Masson (J., 1933, 105) concerning the effect of sulphuric acid on the mononitration of nitrobenzene and nitrotoluene are extended to the nitration of 2 : 4-dinitrotoluene. Up to a point, approximately represented by 95° and an excess of 4 mols. sulphuric acid beyond that required to form the monohydrate H_2SO_4,H_2O, the action of the excess of sulphuric acid is sufficiently explained by its promoting the miscibility of the components. Beyond this point, increase of temperature and increase of sulphuric acid concentration progressively diminish the amount of nitric acid available for nitration, as indicated by the yield of trinitro-compound. The investigation is being continued.

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