223. *Nitration in Sulphuric Acid. Part V. Nitration of 2 : 4-Dinitrotoluene in a Two-phase System.*

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The results of a series of experiments on the rate of nitration of dinitrotoluene in a two-phase system under various conditions are discussed in the light of the study of nitration in homogeneous sulphuric acid solution (Part IV, this vol. p. 474), but a complete analysis of the results is not possible owing to the lack of data concerning the concentrations in the two phases.

The rate of nitration for any one concentration of nitric acid is approximately proportional to the molar excess of sulphuric acid over water present.

Owing to the higher proportion of nitric acid and lower proportion of sulphuric acid present in comparison with the experiments in homogeneous solution, and also to solubility effects, there is no optimum composition of the acid mixture giving a maximum rate of nitration such as occurs with 92% sulphuric acid in homogeneous nitration. Consistently with this the influence of added bisulphates and nitrous acid is in all cases to depress the rate of reaction.

Part IV (*loc. cit.*) of this series described a study of the kinetics of nitration of 2 : 4-dinitrotoluene in homogeneous solution in sulphuric acid, with small concentrations of nitric acid and nitro-compound. The influence of water upon the rate of nitration was shown to be due to the production of bisulphate ion (equation 1), which exerts a dual influence, assisting nitration by increasing the proton-accepting quality of the medium and hindering nitration by its effect upon the extent to which nitric acid is converted into the nitronium ion NO_2^+ (equation 2). This ion is the effective nitrating agent (Part I, *J.*, 1946, 869).

$$H_2O + H_2SO_4 \longrightarrow OH_3^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$HNO_3 + 2H_2SO_4 \rightleftharpoons NO_2^+ + OH_3^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (2)$$

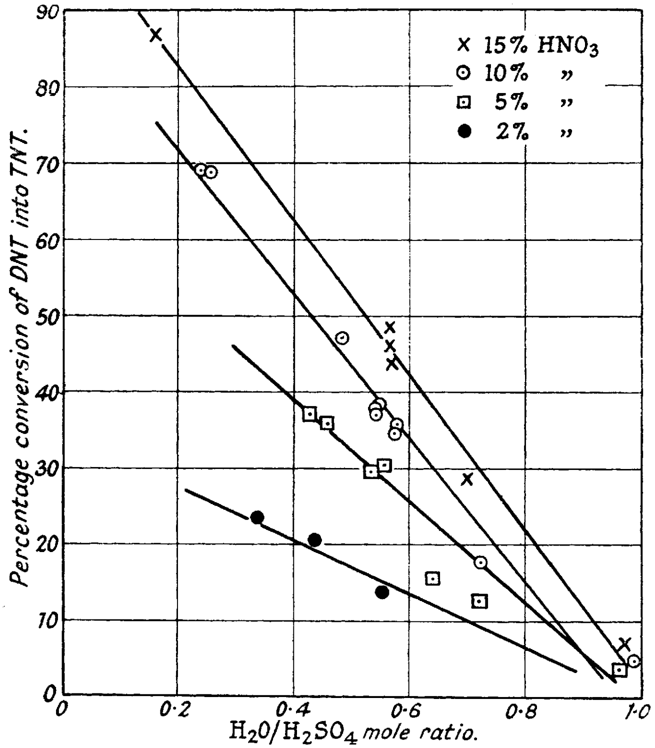
In actual practice, however, the conversion of dinitrotoluene (DNT) into trinitrotoluene (TNT), whether on the laboratory or on the industrial scale, is carried out with larger proportions of nitric acid and with sufficient organic material to produce a two-phase system. In this paper we present the results of laboratory experiments on the two-phase nitration of DNT, designed to show whether the influence of water upon the rate of nitration in a two-phase system is consistent with the conclusions derived from the experiments with homogeneous systems, and, in particular, to ascertain whether added bisulphate ion influences the rate of the two-phase nitration in a predictable manner. The results here described will be confined to those of importance for these two purposes: a more extensive account of the two-phase experiments, with full experimental details, will be published elsewhere.

Method of Experiment.—In each nitration chosen quantities of reagents were vigorously stirred together at a specified temperature (usually 100°) for a certain time (usually 60 mins.), the reaction was stopped by pouring into water, and the composition of the organic products found, after washing and drying, by measurement of density with a pyknometer and by reference to a density–composition curve. The material subjected to nitration was usually a 50% dinitrotoluene–trinitrotoluene mixture in order to make the experiment similar in conditions to those found in one of the vessels of a nitrating plant where nitration is proceeding vigorously.

To determine strictly comparable rates of reaction would require the measurement of instantaneous initial velocities of the process, but the experimental errors would be large for short times of reaction so that a compromise was necessary and the nitrations were continued for times sufficient to give changes large enough for accurate determination. A consideration of the various experimental errors shows that an observed change of 1% in the proportion of TNT present may be regarded as significant, but the corresponding calculated percentage conversion will be of the order of 2%.

Sulphuric Acid–Water Ratio.—The criteria we have used in examining the process are the H_2O/H_2SO_4 and the HNO_3/DNT molar ratios. Fig. 1 summarises the results obtained at 100° with widely varying H_2O/H_2SO_4 ratios for four different values of the HNO_3/DNT ratio, and shows clearly that nitration becomes negligible when the water/sulphuric acid ratio approaches unity. This is reminiscent of the nitration threshold found by Hetherington and Masson (*J.*, 1933, 105) for the nitration of nitrobenzene at 35°, but the latter substance has a much higher speed of nitration and, in presence of large amounts of nitric acid, its nitration continued to points somewhat beyond the 1 : 1 ratio of water to sulphuric acid. The results of our velocity measurements for the nitration of dinitrotoluene in homogeneous solution show values falling towards zero in the region of a H_2O/H_2SO_4 mole ratio of 0·87, and although this agrees approximately with the indications of Fig. 1 there appears to be a small but real discrepancy since appreciable nitration was found in two-phase experiments for acids of ratio 1·0. The explanation of this may lie in the slight change of composition of the acid mixture in consequence of the partition of water and acids between the two phases. Complete data on this point are not available, but some unpublished experiments by Mr. S. E. Napier, made to study the compositions of the two phases in such nitrations, showed that the aqueous acid present in the organic phase, amounting to 5—10% of that phase, always showed a H_2O/H_2SO_4 ratio much higher than that of the acid phase in equilibrium with it. This must result in the effective H_2O/H_2SO_4 molar ratio in two-phase nitrations being somewhat lower than that of the acid mixture as prepared and analysed before the experiment, and may well account for the discrepancy observed.

FIG. 1.



Extent of nitration in 1 *hour at* 100° *of* 50% DNT *in* TNT *mixture with* 2·43 *wts. of mixed acids of various compositions.*

Fig. 1 shows that rates of nitration for each concentration of nitric acid fall in an approximately linear manner towards the point when $H_2O/H_2SO_4 = 1$, and this means that the rates are nearly proportional to $1 - H_2O/H_2SO_4$ or $(H_2SO_4 - H_2O)/H_2SO_4$, *i.e.*, nearly proportional to the fraction of sulphuric acid which is in molar excess of the water present. This is consistent with our view that nitration must depend on there being a molecular excess of sulphuric acid over the water present in the nitrating mixture, because the reaction (1) is complete, and it is only the excess of sulphuric acid which converts nitric acid into the active nitrating species NO_2^+ on which the reaction depends.

A detailed analysis of the results of these two-phase experiments in terms of the velocities of reaction determined in homogeneous sulphuric acid solution is, however, not at present possible because the available data as to the exact compositions of the two phases are far too fragmentary.

A remarkable regularity was observed in the course of some experiments carried out by Messrs. J. C. Dine and D. Fysh directed to answering the practical question "what is the necessary composition of mixed acid to give a specified extent of nitration?" It was found that for various concentrations of nitric acid (of 5% and upward when working at 100°) the required rate of nitration was obtained when the water mole-fraction had a certain value. Moreover, this was found to hold at three different temperatures, a necessary minimum concentration of nitric acid and a prescribed water mole-fraction being specified for each temperature.

A partial explanation of this result is again suggested by our theory when the concentrations of nitronium ion present in these acid mixtures are considered. Calculation from the ionic equilibria, using the constants determined in our study of kinetics in homogeneous sulphuric acid solution (Part IV, *loc. cit.*), shows that the acids giving the required rate of nitration have approximately constant concentrations of NO_2^+ ion. The data for six such acids found to give a prescribed rate of 16·5% conversion of DNT in 30 minutes at 100° are shown in the table above. The experimental measurements of Chédin (*Mem. des Services chimiques de l'Etat*, 1944, **31**, 113), interpreted according to our views, give results of the same order and equally consistent except for acid No. 6. Such acids might be expected to have equal nitrating powers. This leaves out of account, however, the two-phase nature of the system, and the fact that the concentrations in the acid phase, where nitration takes place, must differ slightly from those in the nitrating acid selected.

Composition of nitrating acids giving a specified rate of nitration at 100°.

	Wt., %.			Mole-fractions.			
Acid No.	H_2SO_4.	HNO_3.	H_2O.	H_2SO_4.	HNO_3.	H_2O.	Calculated moles of NO_2^+/l.
1	75·0	15·0	10·0	0·489	0·152	0·359	0·60
2	80·6	9·85	9·6	0·543	0·103	0·354	0·72
3	85·4	5·06	9·5	0·590	0·054	0·356	0·62
4	87·3	3·94	8·8	0·618	0·043	0·338	0·64
5	87·5	3·71	8·75	0·621	0·041	0·338	0·61
6	93·6	2·0	4·4	0·776	0·026	0·198	0·58

When a wide range of nitration data are re-examined in relation to the water mole-fraction in the acid used it appears from Fig. 2, in which the extent of nitration is plotted against the water mole-fraction, that with acids of 5% nitric acid and upwards the rate of nitration varies in a linear manner with varying water mole-fraction, independently of wide variations in the concentration of nitric acid present.

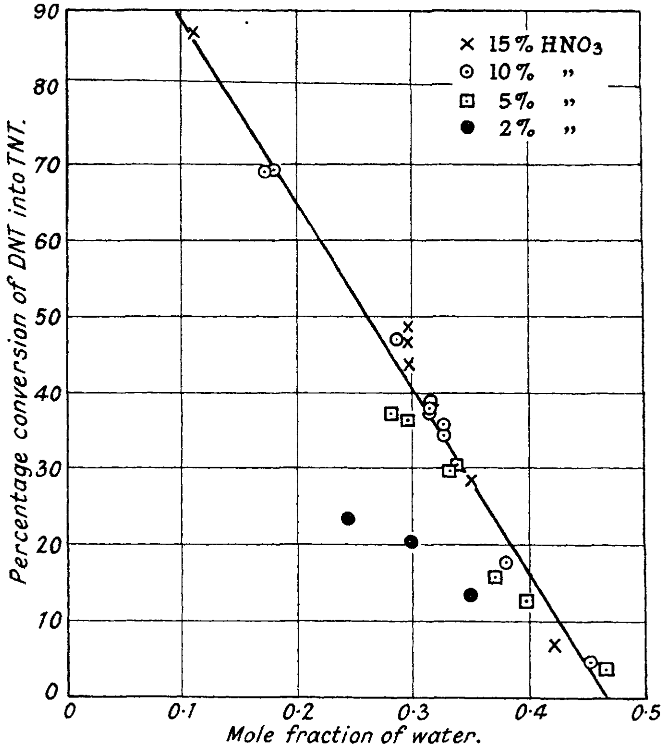
It may be pointed out that acids of the same water mole-fraction are acids of nearly equal water/sulphuric acid ratios since the mole-fraction of sulphuric acid in them does not vary much. In fact, if the nitric acid present is increased while the water mole-fraction is kept constant, a slightly lower H_2O/H_2SO_4 ratio must result and the relationship shown in Fig. 2 may arise from a compensation in the ionisation equilibrium between a somewhat diminished proportion of free sulphuric acid and the increased amount of nitric acid present.

If, on the other hand, we consider the trend of the results of two-phase nitrations in acids of diminishing water content, we find that the nitration rates (using nitrating acids containing 5 or 10% HNO_3) increase steadily as the mole-fraction of water is reduced to zero and show no sign of a maximum for a nitrating acid composed of nitric acid and any aqueous sulphuric acid, comparable with the sharp maximum in homogeneous solutions at 92% H_2SO_4(H_2O/H_2SO_4 molar ratio = 0·48). There are two reasons which may account for this difference :

(*a*) In two-phase experiments with dinitrotoluene the nitration takes place in the acid phase. Nitration in the organic phase is negligible, as shown by Mr. W. W. Jones and Mr. A. E. Flood (unpublished observations; compare Hetherington and Masson, *loc. cit.*, who state that no nitration occurs in the nitrobenzene phase, and Lewis and Suen, *Ind. Eng. Chem.*, 1940, **32**, 1095, who found the rate of nitration of benzene to be 5—10 times as fast in the acid phase as in the organic phase). The solubility of dinitrotoluene in the acid phase increases with diminishing water content, and this must at least tend to move the optimum composition for nitration in the direction of acids of lower water content (compare D. I. James, *J.*, **1935**, 785).

(*b*) The occurrence of a medium giving a maximum rate for homogeneous nitration depends on the existence of a range of nitrating acids in which an increase in water content accelerates nitration, and this is due to the nearly complete conversion of water and nitric acid into ionic forms by the sulphuric acid in this range. The rising proportion of water therefore increases the concentration of HSO_4^- ion in this region much faster than it diminishes that of the NO_2^+ ion. This can only occur, however, when sulphuric acid is present in sufficient molecular excess over both water and nitric acid. In a typical two-phase experiment the nitrating acid was of composition 84·4% H_2SO_4, 9·9% HNO_3, 5·7% H_2O (nitric acid in 93·7% sulphuric acid) and the actual quantities in reaction were : dinitrotoluene 0·0384, sulphuric acid 0·293, nitric acid 0·0538, water 0·108 mole. In this mixture sulphuric acid is in 1·8-fold excess over the nitric acid plus water, as compared with a 4-fold excess in our homogeneous nitration in 96% sulphuric acid. It is readily shown by calculation of the ionic equilibria in these mixtures (discussed in Parts I and IV of this series) that with 5 or 10% of nitric acid present the conversion of the nitric acid into the cationic form NO_2^+ does not approach completeness with any sulphuric acid–water mixture. An examination of the curves from the observations of Chédin (*loc. cit.*) also leads to the same conclusion.

FIG. 2.



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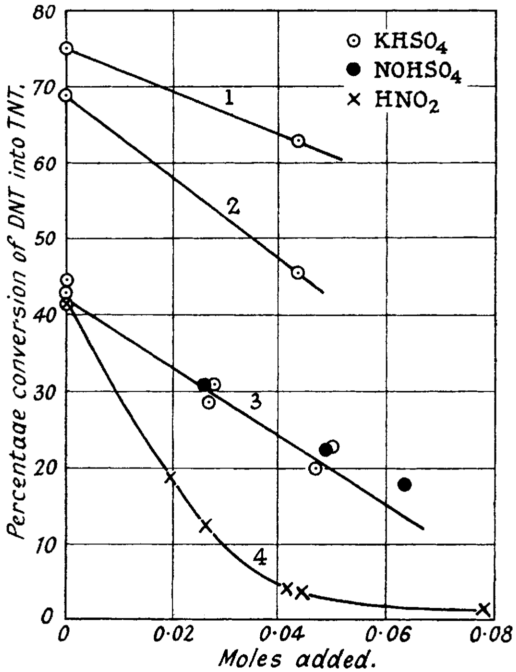
This view is supported by the effect produced on the rate of nitration by the addition of bisulphates.

Effect of Bisulphates and Nitrous Acid.—In Part IV it was shown that the effect of bisulphate ions in homogeneous nitrations was to accelerate the reaction in the region between the optimum concentration and 100% sulphuric acid but to retard it in acid–water mixtures of less than 92% sulphuric acid. According to our view, the two-phase nitrating mixtures are all effectively analogous to the latter range of media for homogenous nitration, and this requires that bisulphates should always retard the two-phase process. This question has been examined experimentally, for two-phase nitrations with a mixed acid containing 10% of nitric acid, by observing the effect of adding (*a*) potassium bisulphate, (*b*) nitrosyl bisulphate, and (*c*) nitrous acid. The last of these reacts reversibly according to the equation $HNO_2 + 2H_2SO_4 \rightleftharpoons NO^+ + H_3O^+ + 2HSO_4^-$, so that one mole of nitrous acid produces two moles of bisulphate ion and one mole of oxonium ion all capable of affecting the nitric acid ionisation equilibrium.

FIG. 3.



Effects of added substances on extent of nitration at 100°.

Curve 1. 89·1% H_2SO_4 : H_2O/H_2SO_4 = 0·072. *Nitration for* 30 *mins.*
2. 86·2% H_2SO_4 : H_2O/H_2SO_4 = 0·245. *Nitration for* 60 *mins.* } HNO_3 = 9·8%.
3 *and* 4. 81·8% H_2SO_4 : H_2O/H_2SO_4 = 0·563. *Nitration for* 60 *mins.*

The results of these experiments are shown in Fig. 3. A retardation of the reaction is apparent in all cases. The large retarding effect of bisulphate, shown in the upper two curves, is specially noteworthy since the H_2O/H_2SO_4 ratios for these acids were 0·072 and 0·245, corresponding to points well on the acid side of the optimum velocity point in homogeneous nitrations (H_2O/H_2SO_4 = 0·48). This confirms the supposition made above [p. 1188, (*b*)] that, in two-phase nitration, the proportion of nitric acid present is usually too high for its conversion into nitronium ion to be nearly complete.

In this connection it is noteworthy that the nitration of benzoic acid and other substances by means of potassium nitrate and concentrated sulphuric acid (Houben, " Methoden der Organischen Chemie ", 3rd edn., 1941, iv, 195) involves essentially homogeneous conditions and that here the reaction is facilitated by the potassium bisulphate formed in solution.

The effects of potassium and nitrosyl bisulphate are not quite equivalent, but the discrepancy is accounted for when allowance is made for the incompleteness of the ionisation reaction of nitrous acid : the substance is 90% ionised in such solutions according to the estimate of Hantzsch and Berger (*Z. anorg. Chem.*, 1930, **190**, 321).

The effect of nitrous acid in depressing the speed of nitration is seen to be more than twice that of potassium bisulphate, as was to be expected, but here again the result is modified by the reversal of the ionisation equilibrium.

The influence of nitrous acid upon two-phase nitration has made itself felt in another way. If the initial nitrating agent contains too high a proportion of water, nitration stops before the whole of the available reacting material has been consumed. Such an effect, which is similar to the nitration threshold of Hetherington and Masson for nitrobenzene (compare p. 1186), is a natural consequence of the accumulation of water liberated during nitration with a consequent increase of the H_2O/H_2SO_4 ratio to a point where the speed of nitration becomes negligible. But the arrest in the nitration of DNT actually occurs at an earlier stage, because the oxidation processes accompanying the nitration (see Part IV, *loc. cit.*) produce nitrous acid, the retarding action of which is added to that of the water in bringing the reaction to a standstill.

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