94. *Nitration in Sulphuric Acid. Part IV. Kinetics of the Nitration of 2 : 4-Dinitrotoluene.*

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Velocities of nitration of 2 : 4-dinitrotoluene have been measured in media varying from 87·4% aqueous sulphuric acid to oleum containing 29·1% of free sulphur trioxide and at temperatures from 60° to 120°. The effects of varying initial concentrations, of variation of the composition of the medium and of additions of potassium bisulphate and nitrosyl bisulphate have been studied in detail.

In any one experiment it is confirmed that the bimolecular coefficient remains constant. The accompanying oxidation reaction is shown to be a simultaneous side reaction of the same order.

The process is regarded as involving attack by the NO_2^+ ion and a proton acceptor simultaneously, the actual proton-accepting species being HSO_4^-, H_2SO_4, and $HS_2O_7^-$. A general equation is developed in the form

$$d[TNT]/dt = \{k[HSO_4^-] + k'[H_2SO_4] + k''[HS_2O_7^-]\}[DNT][HNO_3]Q$$

where k, k', and k'' are coefficients relating to the action of the three proton-acceptors, respectively, and $Q = [NO_2^+]/[HNO_3]$ and is calculable from the ionic equilibria in solution. This is valid at a given temperature for all variations of medium. The constants of this equation have been determined for the temperature 89·9° and it is shown that the experimental results are adequately reproduced by it; in particular, the composition of the medium giving a maximum velocity of nitration is calculated in good agreement with that observed, namely, 92% H_2SO_4.

The constants of the Arrhenius equation have been calculated for the reaction.

In Part I of this series (Bennett, Brand, and Williams, *J.*, 1946, 869) evidence has been presented in support of the view that nitric acid dissolved in sulphuric acid is largely present as the NO_2^+ ion, and that this is the active nitrating agent in such mixtures.

The hypothesis of nitration by the NO_2^+ ion is thus particularly applicable to nitration in sulphuric acid solutions, and conveniently measurable velocities of nitration in such media are found only for aromatic substances such as nitrobenzene and dinitrotoluene containing deactivating substituents. The speed of nitration of benzene or of aromatic substances, such as phenol, containing activating substituents is too great in sulphuric acid for measurement. The nitration of compounds of the latter type has been studied in other solvents, but a comparison of the mechanisms of nitration for the same compound in solvents of different character presents difficulties.

Nitration in sulphuric acid is both faster and simpler than in other media for which quantitative data are available (perchloric acid as a medium is a probable exception, cf. Robinson, *J.*, 1941, 238). In other solvents, the rate of nitration is generally a complicated function of the reactant concentrations, which often appear raised to high powers in the kinetic equations; nitration is subject to positive or negative catalysis by nitrous acid; and the symptoms suggest that chain reactions may be involved, propagated, possibly, by free radicals. Examples are furnished by the nitration of benzene, toluene, ethylbenzene, and monohalogenobenzenes in nitromethane (Benford and Ingold, *J.*, 1938, 929), by the nitration of benzene in acetic anhydride (Cohen and Wibaut, *Rec. Trav. chim.*, 1935, **54**, 409), by the nitration of various aromatic compounds in nitrobenzene (Giersbach and Kessler, *Z. physikal. Chem.*, 1888, **2**, 676; Tronov and Ber, *J. Russ. Phys. Chem. Soc*, 1930, **62**, 2337), and, notably, by the nitration of phenol in water and in organic solvents (*e.g.*, Martinsen, *Z. physikal. Chem.*, 1904, **50**, 385; Arnall, *J.*, 1923, **123**, 3111; Klemenc and Schöller, *Z. anorg. Chem.*, 1924, **141**, 231; Kartashev, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 2129; Veibel, *Z. physikal. Chem.*, 1930, *B*, **10**, 22; *Ber.*, 1930, **63**, 1557, 1582, 2074). In sulphuric acid–water media, the speed of nitration is greatly affected by the proportion of water present; and Martinsen (*loc. cit.*; *ibid.*, 1907, **59**, 605) found that nitration of a number of substituted benzenes in homogeneous solution is fastest in a slightly aqueous sulphuric acid (*ca.* 90% H_2SO_4 at 25° whatever the substance nitrated), becoming slower both in anhydrous sulphuric acid (or oleum) and in media with a higher water content than the optimum. Martinsen's discovery has since been confirmed for the nitration of substituted xylenes (Klemenc and Scholler, *loc. cit.*), of anthraquinone (Lauer and Oda, *J. pr. Chem.*, 1936, **144**, 176) and substituted anthraquinones (Oda and Ueda, *Bull. Inst. Phys. Chem. Res. Japan*, 1941, **20**, 335; *A.*, 1942, II, 58), and of naphthalenesulphonic acids (Lantz, *Bull. Soc. chim.*, 1939, **6**, 280, 289, 302). But in a sulphuric acid medium of given water content, there has been general agreement that nitration is a second-order reaction, not catalytically affected by the presence of nitrous acid or of phosphoric oxide.

The rapidity and kinetic simplicity of nitrations in sulphuric acid, compared with other media, are consistent with the view that nitration in sulphuric acid is ionic; and we have identified the NO_2^+ ion as the active nitrating agent in mixed acids, but the assumption of an ionic nitrating agent does not, by itself, explain why 90% sulphuric acid is an optimum medium. It has been suggested (Lauer and Oda; Lantz; *locc. cit.*) that a nitric acid cation is responsible for nitration in anhydrous sulphuric acid only and that the $NO_2{\cdot}OH$ molecule is the nitrating agent in more aqueous media. This view is not tenable for the nitration of such substances as dinitrotoluene because the reaction is negligibly slow in the medium (having a molar ratio $H_2O/H_2SO_4 = 1$) in which the concentration of molecular nitric acid, $NO_2{\cdot}OH$, is greatest, as Hetherington and Masson have convincingly proved for the nitration of nitrobenzene in two-phase systems (*J.*, 1933, 105). Assuming that the NO_2^+ ion is the most active nitrating agent in all media in which nitration has a measurable speed for substances of this type, an alternative explanation for the optimum medium at 90% H_2SO_4 can be found if it is recalled that nitration requires, not only the attachment of the cation to the benzene nucleus, but also the removal of a proton, provided that it be assumed that the speed of nitration depends upon both factors (cf. Robinson, " Outline of an Electrochemical Theory of the Course of Organic Reactions," Institute of Chemistry, 1932; *J.*, 1941, 238; we are indebted to Sir Robert Robinson, P.R.S., who personally suggested to us in 1942 that the composition of the medium in which the velocity of nitration is a maximum might represent a balance between the acid function of the solvent and its basic function as a proton-acceptor). The most obvious proton-acceptor in a sulphuric acid–water mixture (in which the molar ratio $H_2O/H_2SO_4 < 1$) is the bisulphate ion, though the sulphuric acid molecule is probably also effective to a lesser degree. Increase in the water content of the medium (causing increased bisulphate-ion concentration) increases the facility with which a proton can be removed from the organic compound; but it also reduces the concentration of the NO_2^+ ion, the active nitrating agent. A balance of these two effects leads to the observation of a maximum rate of nitration in a slightly aqueous medium. This theory is formulated quantitatively in a later section of this paper. Its immediate consequences are: (*a*) addition of bisulphate ion—as metallic salt, as nitrosyl bisulphate (nitrous acid), or in any other form—should accelerate nitration in a medium containing more sulphuric acid, and retard it in media containing more water, than the optimum composition; (*b*) since nitric acid forms bisulphate ion when it is dissolved in concentrated sulphuric acid, the bimolecular velocity coefficients recorded for individual nitrations should rise with increasing initial nitric acid concentration in media on the acid side of the optimum and should fall with increasing nitric acid in media on the water side of the optimum. Lauer and Oda (*loc. cit.*) have observed that metallic nitrates nitrate anthraquinone more rapidly than does nitric acid in sulphuric acid media; Westheimer and Kharasch also give evidence of these effects (*J. Amer. Chem. Soc.*, 1946, **68**, 1871). Existing data, however, cover too narrow a range of conditions to be conclusive. In order to test the theory of nitration by an ion, we have therefore investigated the kinetics of nitration over as wide a range of conditions as possible. The anticipated effects have been observed with the four compounds so far examined. The present paper deals with 2 : 4-dinitrotoluene; other substances will be considered in later papers.

The Nitration of 2 : 4-*Dinitrotoluene*.—The nitration of 2 : 4-dinitrotoluene (referred to hereafter as DNT) to 2 : 4 : 6-trinitrotoluene (TNT) is accompanied by oxidation processes, which have been investigated by A. Carruthers and L. A. Wiseman. We are indebted to them for permission to refer to some of their unpublished results. They find that the main detectable products of the oxidation reactions are nitrous acid and equal volumes of carbon monoxide and carbon dioxide. The gases are formed by oxidation of DNT, which suffers complete nuclear disruption, so that the loss of one molecule of DNT gives rise to the production of many molecules of nitrous acid. In preparative nitration, some 3% of DNT is oxidised at 90°. Our experiments have been conducted on homogeneous solutions, composed of small concentrations of DNT and nitric acid (0·05—0·8M) in media containing varying proportions of sulphuric acid and water. The sulphuric acid and water components of the nitrating acid are then present in large excess and can be regarded as forming a constant medium for the nitration. For example, in an experiment in 95·7% sulphuric acid, the initial composition of the system was as follows:

DNT:	0·04 mole	HNO_3:	0·02 mole (0·7% by weight of nitrating acid)
H_2SO_4:	1·8 mole	H_2O:	0·44 mole

The amounts of water and nitrous acid formed during nitration are too small to affect the composition of the system and the rate of nitration appreciably, especially as attention is confined to the early stages of nitration (generally up to not more than 30% conversion of DNT).

Under these conditions, at 90°, some 40% of the total nitric acid consumed appears as nitrous acid, but the amount of DNT consumed in oxidation is negligibly small compared with that consumed in nitration, provided that DNT is initially present in excess over nitric acid. This has been proved by direct analyses of the mixed nitro-compounds isolated from the reaction mixture (by a determination of the density at 90° and by reference to a density–composition curve) and by comparing the extent of conversion of DNT into TNT so deduced with that deduced from acid analyses. The results of these experiments are shown in Table XI and are discussed in the Experimental section. So long as the proportion of DNT oxidised is small, acid analyses will suffice to separate the nitration reaction from the oxidation; and the rate of nitration may be determined in the following way.

Nitration of DNT takes place, at a fixed temperature (generally 90°), in homogeneous solution in sulphuric acid mixed with a known proportion of water or sulphur trioxide. Samples of reaction mixtures are withdrawn at known time intervals, in pipettes calibrated for the prevailing conditions. Alternate samples are analysed for nitric acid, by electrometric titration with standard ferrous sulphate solution, and for nitrous acid, by oxidation with standard chloramine-T or ceric sulphate solutions. These results give (*a*) the total amount of nitric acid consumed in both nitration and oxidation, and (*b*) the amount of nitric acid consumed in oxidation alone. The amount of nitric acid consumed in nitration can therefore be deduced. This quantity is equated to the amount of TNT formed, a procedure which is justified by the results of Table XI. The velocity coefficient for nitration is derived by taking rates of nitration at known times directly from a curve drawn to represent the increase of TNT concentration with time, and substituting in the differential equation (1). The curves for a pair

$$\mathrm{d[TNT]}/\mathrm{d}t = k_2\mathrm{[DNT][HNO_3]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

of duplicate experiments are shown in Fig. 1. The derived velocity coefficients for one of them are given below.

Experiment 205.

Medium, 98·7% H_2SO_4. Temp., 89·9°. Initial concn.: DNT = 0·4007M, HNO_3 = 0·2004M

Time (mins.).	Reaction, %.	DNT converted, %.	[TNT]/[HNO_2].	$k_2 \times 1000$.
10	5·8	1·8	1·5	9·4
20	11·6	3·6	1·6	10·4
30	17·2	5·4	1·6	10·8
40	22·5	7·0	1·6	10·7
50	27·5	8·5	1·6	11·3
60	32·1	9·9	1·6	10·4
70	36·5	11·2	1·6	10·8
80	40·5	12·4	1·6	10·7
90	44·3	13·5	1·6	10·9
100	47·7	14·5	1·6	10·9
110	50·8	15·4	1·5	10·5
120	53·7	16·2	1·5	10·0

In this, as in other experiments, the velocity coefficient remains constant during the course of nitration. In a given medium, therefore, and for fixed values of the initial concentrations, the rate of nitration is determined by equation (1). This result is in agreement with the findings of previous workers.

The reason for calculating nitration velocity coefficients from the differential form of equation (1) is that the integrated form cannot be used without making assumptions about the mechanism of the oxidation processes, since nitric acid is used up in oxidation without appreciable consumption of DNT. By making appropriate assumptions, an integrated form may be applied in the following manner.

The Oxidation Reactions.—The chemical facts of oxidation, outlined on p. 475, and the kinetic conclusions about oxidation which may be inferred from the experimental results, are met by the supposition that a few molecules of DNT ultimately break up completely into fragments, which then react independently with nitric acid to form carbon monoxide, carbon dioxide, and nitrous acid. The kinetics require that the preliminary breakdown of DNT molecules should be the rate-determining step in this process. The mechanism may be treated formally in the following way.

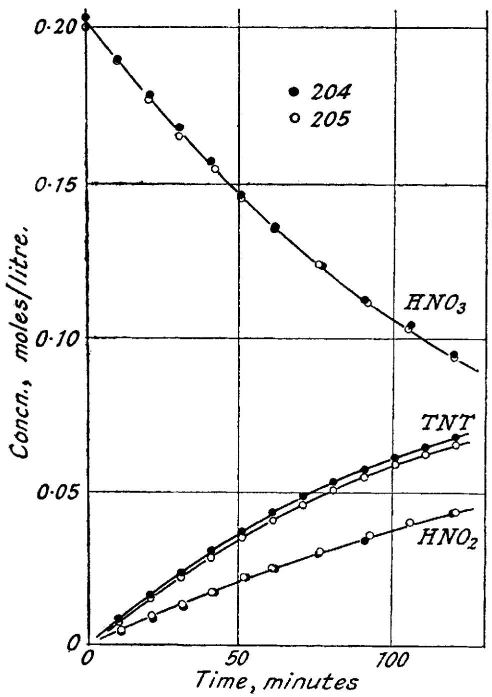
Consider two simultaneous reactions :

(*a*) Nitration : $\text{DNT} + \text{HNO}_3 \longrightarrow \text{TNT} + \text{H}_2\text{O}$

(*b*) Breakdown of DNT : $\text{DNT} + \text{HNO}_3 \longrightarrow \text{X}_1 + \text{X}_2 + \ldots + \text{X}_i + \ldots\ldots + \text{X}_n + \text{etc.}$

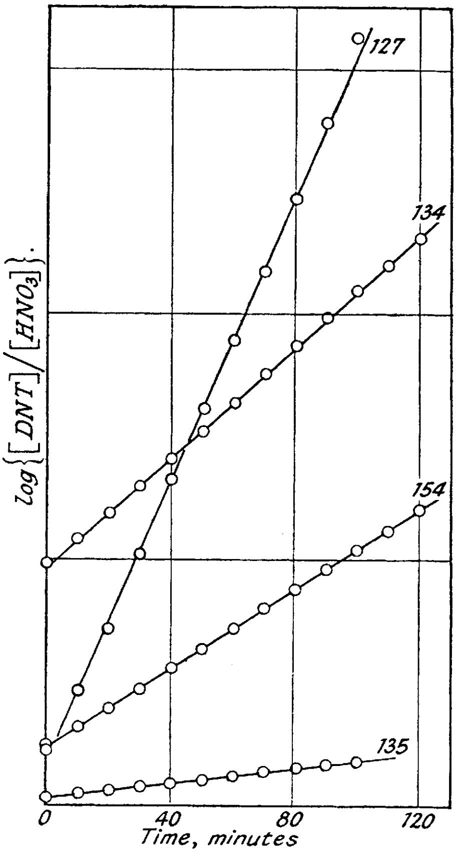
where the X_i are short-lived intermediate fragments, possibly free radicals.

FIG. 1.



Duplicate nitration curves.

FIG. 2.



Let the velocity coefficients of reactions (*a*) and (*b*) be k_a and k_b respectively. The intermediates X_i react with nitric acid in a series of parallel, independent reactions, typified by equation (i).

$$[\text{X}_i] + \text{HNO}_3 \longrightarrow \text{HNO}_2 + \text{etc.} \quad \text{Velocity coeff.} : k_i \quad . \quad . \quad . \quad . \quad \text{i)}$$

Applying the condition $d[\text{X}_i]/dt = 0$, we find :

$$[\text{X}_i] = (k_b/k_i)[\text{DNT}]$$

and

$$d[\text{HNO}_2]/dt = [\text{HNO}_3]\sum_{1}^{n} k_i[\text{X}_i] = nk_b[\text{DNT}][\text{HNO}_3]$$

so that

$$\frac{d[\text{TNT}]/dt}{d[\text{HNO}_2]/dt} = \frac{k_a}{nk_b} = \text{Const.}$$

Integrating, with the condition $[\text{TNT}] = 0 = [\text{HNO}_2]$ when $t = 0$,

$$[\text{TNT}]/[\text{HNO}_2] = k_a/nk_b = \text{Const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This conclusion is in accord with experiment.* The ratio $[\text{TNT}]/[\text{HNO}_2]$ remains constant

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* If nitrous acid is taken to be formed in reaction (*b*), as well as in (i), n in equation (2) becomes $n + 1$. The argument is unaffected.

during nitration or drifts with time only over a small range; and its mean value in a given nitration is insensitive to any change of experimental conditions other than temperature (see Tables II—IV, etc.). The experimental constancy of the ratio [TNT]/[HNO_2] seems sufficiently exact to warrant the inference that Wegscheider's test (*Z. physikal. Chem.*, 1899, **30**, 593) for simultaneous side reactions is approximately fulfilled, which implies that the rate-determining steps in oxidation and nitration of DNT are *simultaneous side reactions of the same order.* Thus the rate of formation of nitrous acid must depend on the DNT concentration, even though the amount of DNT consumed by oxidation is small compared with the amount of nitrous acid formed. The formation of nitrous acid must therefore involve consecutive steps.

The experimentally verified conclusion of equation (2) is satisfied by the following empirical formulation : Let initial concentrations of DNT and HNO_3 be a and b, respectively. Let concentrations of TNT and HNO_2 formed at time t be x and y, respectively.

$$\text{Put } x/y = s \text{ and } (s + 1)/s = r$$

Then
$$y = x/s \text{ and } [\text{DNT}]/[\text{HNO}_3] = (a - x)/(b - rx)$$
$$dx/dt = k_a(a - x)(b - x - y) \text{ and } dy/dt = nk_b(a - x)(b - x - y)$$

and
$$r \,.\, dx/dt = (k_a + nk_b)(a - x)(b - rx)$$

which gives, on integration

$$(k_a + nk_b)t = \frac{2{\cdot}3r}{ar - b} \log_{10} \left\{\frac{b}{a} \cdot \frac{a - x}{b - rx}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

It follows that the plot of $\log_{10}$ [DNT]/[HNO_3] against t should be a straight line of slope l, where

$$k_a = (k_a + nk_b)/r = l \times 2{\cdot}3/(ar - b)$$

This conclusion is verified experimentally. Fig. 2 shows that $\log_{10}$ [DNT]/[HNO_3] is a linear function of time for a number of nitrations. This means, *as an empirical result,* that the rate of reaction is expressed by an integrated bimolecular equation; and the test represented by Fig. 2 has a wider implication than the test based on constancy of the bimolecular nitration velocity coefficient (Expt. 205 above). It means that the rate of consumption of DNT and HNO_3 in both oxidation and nitration follows a bimolecular course, since it is the quotient of total concentrations of DNT and nitric acid which is used in the plot. If the particular oxidation mechanism postulated has any approach to reality, then the velocity coefficient k_a for nitration, derived from the slope l should be identical with k_2, the nitration velocity coefficient calculated from the differential equation (1) as described on p. 476.

A comparison of k_2 (from the *differential* equation 1) with k_a (from the *integrated* equation 3) is made in Table I.

TABLE I.

Comparison of k_2 *with* k_a.

Expt. No.	Medium : % H_2SO_4.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	10^3k_a.	10^3k_2.
154	89·5	0·3984	0·1992	17·3	17·0
134	95·1	0·4008	0·1014	18·4	17·2
126	95·1	0·4011	0·2019	19·2	18·3
137	95·1	0·4002	0·3013	20·3	18·8
130	95·1	0·1000	0·2019	17·2 *	13·8
127	95·1	0·8017	0·2062	23·6	21·5
103	100	0·6014	0·1991	9·5	8·7

* Value unreliable, because $ar \sim b$.

In general, k_a is some 5—10% higher than k_2 as given in Tables II—IV, etc. The discordance is not surprising. The highly formalised mechanism outlined above cannot be exactly true. Experimentally, also, the ratio s (*i.e.*, [TNT]/[HNO_2]) is not very accurately determined. The object of this discussion is merely to define a *type* of mechanism which shall be consistent with the observed products and kinetics of the reaction. For these reasons, velocity coefficients for nitration have always been calculated directly from the differential equation (1), as described on p. 476. The coefficients calculated in this way give a more direct measure of the speed of nitration and do not involve the ratio [TNT]/[HNO_2].

Results.—The results of all velocity measurements are collected in Tables II—V, VIII, and IX. For all experiments, concentrations are expressed in moles/litre and time is in minutes.

TABLE II.

Influence of medium on rate of nitration (Temp. 89·9°).

Medium.							
Wt. % of H_2SO_4.	Acid No.	$\frac{H_2O}{H_2SO_4}$.	Expt. No.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	$\frac{[TNT]}{[HNO_2]}$.	10^3k_2.
100	16	0	Table III : 99, 100, 101, 208			1·6	7·4
99·3	6	0·039	15	0·398	0·193	1·5	8·5
99·2	15	0·046	Table IV : 80, 86			1·4	8·6
98·7	34	0·075	204	0·4000	0·2032	1·8	10·8
98·7	34	0·075	205	0·4007	0·2004	1·6	10·6
97·8	32	0·120	200	0·4005	0·2016	1·7	11·0
97·8	32	0·120	201	0·4001	0·2006	1·6	10·8
97·7	35	0·128	206	0·4005	0·2005	1·5	12·3
97·7	35	0·128	207	0·4004	0·2016	1·7	12·5
96·5	33	0·197	202	0·4000	0·2000	1·8	15·0
96·5	33	0·197	203	0·4005	0·2007	1·6	14·4
95·1	20	0·285	Table III : 125, 126, 145			1·5	18·8
95·0	21	0·277	Table III : 146, 152			1·5	19·2
94·7	C	0·305	120	0·4001	0·1932	1·6	19·5
94·7	C	0·305	121	0·4005	0·2007	1·6	19·7
93·8	D	0·360	113	0·4000	0·1961	1·5	21·5
93·0	D	0·410	115	0·4010	0·2161	1·8	22·5
92·6	B	0·435	109	0·4013	0·2000	1·5	23·5
92·5	D	0·442	117	0·4010	0·2133	1·9	23·5
92·3	C	0·454	122	0·4008	0·1939	1·6	23·8
92·0	B	0·470	110	0·4012	0·2008	1·5	24·1
91·9	D	0·480	114	0·4006	0·2001	1·6	24·3
91·9	D	0·480	119	0·4012	0·2041	1·8	23·2
91·7	A14	0·495	76	0·4012	0·1960	1·9	23·6
91·7	A14	0·495	94	0·4012	0·2034	1·7	22·9
91·4	D	0·512	116	0·4019	0·1963	1·8	22·2
91·0	D	0·538	118	0·4012	0·2003	1·9	20·5
91·0	C	0·538	123	0·4004	0·2004	1·8	21·4
89·5	22	0·636	154	0·3984	0·1992	1·8	17·0
89·5	40	0·636	242	0·4004	0·2008	1·7	16·7
89·3	12	0·653	88	0·4010	0·2061	2·0	16·2
89·3	10	0·655	Table IV : 49, 51			1·8	16·0
87·6	43	0·770	287	0·3990	0·2000	1·6	6·9
87·6	43	0·770	290	0·4000	0·2002	1·3	6·3
87·4	11	0·788	53	0·4012	0·1909	1·5	7·2
87·4	11	0·788	55	0·4009	0·1920	1·5	6·7

Note.—In order to determine a number of points in the region of the maximum, an acid of known composition, differing slightly from that of the optimum acid, was taken as standard; and known weights of water were introduced in individual nitrations. The various series of acid compositions obtained in this way are those indicated by letters in Table II.

For a given temperature, the results may be summarised as follows :

Influence of medium composition. With fixed initial concentrations of the reactants (0·4M-DNT and 0·2M-HNO_3) the rates of nitration have been measured in media ranging in composition from 87·4% sulphuric acid (with water) to 29·1% sulphur trioxide in sulphuric acid (see Tables II and VIII). The nitration velocity coefficient has a maximum value in a medium composed of 92% sulphuric acid and 8% water (compare Fig. 3). This composition is frequently referred to below as the " optimum composition ".

Influence of reactant and bisulphate concentrations (Tables III—V). The observed facts are :

(1) *In media containing more sulphuric acid than the optimum composition.* The bimolecular velocity coefficient k_2 *rises* (*a*) with rising initial concentration of nitric acid (for a fixed initial concentration of DNT), (*b*) with rising initial concentration of DNT (for a fixed initial concentration of nitric acid), (*c*) with rising concentration of bisulphate, added either as potassium bisulphate or as nitrosyl bisulphate (for fixed initial concentrations of both reactants). The conclusions (*a*) and (*b*) hold also for an oleum medium (Table VIII).

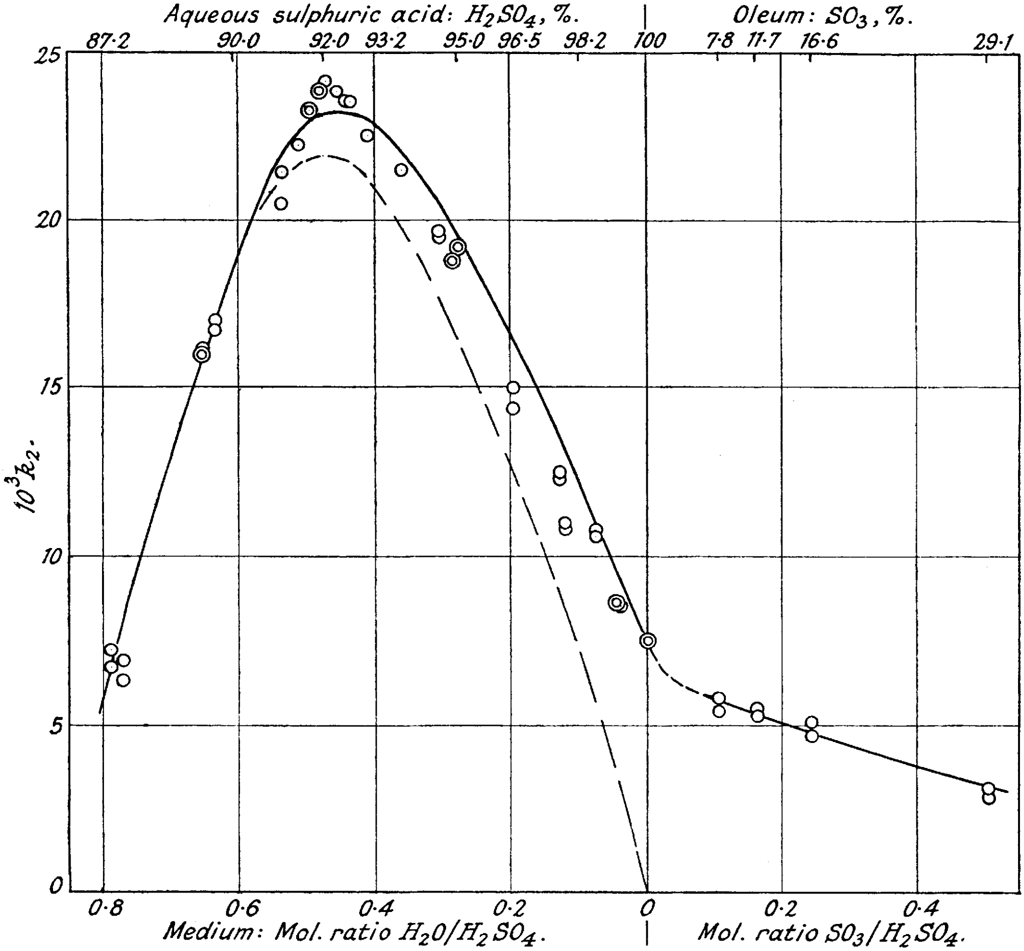
(2) *In media containing less sulphuric acid than the optimum composition.* The bimolecular

velocity coefficient k_2 *falls* (*a*) with rising initial concentration of nitric acid, (*b*) with rising initial concentration of DNT, (*c*) with rising concentration of added bisulphate.

In each instance, the relation between k_2 and reactant concentration is approximately linear over the range examined (Figs. 4 and 5).

It follows that the nitration of DNT to TNT is not really a second-order reaction, despite the constancy of k_2 observed in individual nitrations. Nevertheless, we have not tried to derive

FIG. 3.



Influence of medium upon rate of nitration at initial concns.: DNT = 0·4M, HNO$_3$ = 0·2M.

○ *Experimental points.* —— *Calculated curve of equation*

- - - 1*st approximation.*

$$10^3k_2 = \frac{3{\cdot}3[HSO_4^-] + 0{\cdot}37[H_2SO_4]}{1 + \frac{[OH_3^+]}{33{\cdot}6}\left\{\frac{[HSO_4^-]}{[H_2SO_4]}\right\}^2} + 0{\cdot}56[HS_2O_7^-]$$

the formal order of reaction from the variation of nitration speed with initial concentrations of reactants, for the following reasons:

(1) The dependence of k_2 on initial concentration, though linear, is not a proportionality. Consequently, no integral order could represent the reaction.

(2) The sign of the variation of k_2 with initial concentration of either reactant is inverted when the medium composition is varied so as to pass through its optimum value. Any "order" deduced by formal methods would thus be different for media on either side of the optimum.

Variations of k_2 with initial nitric acid concentration and with added bisulphate concentration, of opposite sign in media on either side of the optimum composition, are required by the theory of nitration put forward below (compare p. 487). But the closely similar variation of k_2 with initial DNT concentration is unexpected and is not accounted for by the theory in its present form. The point is discussed further in a later section. Provisionally, the discussion which follows must be held to refer to a fixed initial concentration of DNT; and the experiments quoted in support of the postulated mechanism are all for 0·4M initial DNT.

TABLE III.

Variation of initial nitric acid concentration (Temp. 89·9°).

Medium.							
Wt. % H_2SO_4.	Acid No.	$\frac{H_2O}{H_2SO_4}$	Expt. No.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	$\frac{[TNT]}{[HNO_2]}$.	10^3k_2.
100	16	0	102	0·2006	0·1996	1·4	6·9
	,,	,,	97	0·2008	0·3859	1·6	8·0
	,,	,,	100	0·4014	0·1990	1·6	7·5
	,,	,,	99	0·4010	0·1984	1·6	7·1
	,,	,,	101	0·4022	0·1989	1·7	7·5
	31	0	208	0·3956	0·1994	1·6	7·4
	36	0	220	0·3998	0·2010	1·5	7·6
	16	0	95	0·4002	0·3883	1·4	8·2
	,,	,,	106	0·4011	0·8201	1·3	10·5
	,,	,,	104	0·6015	0·1991	1·7	8·5
	,,	,,	103	0·6014	0·1991	1·6	8·6
	,,	,,	98	0·5999	0·3865	1·9	10·6
	,,	,,	105	0·6024	0·8331	1·3	12·1
99·2	7	0·0395	35	0·198	0·0528	1·6	8·1
	6	0·039	21	0·195	0·0984	1·6	7·8
	6	,,	18	0·198	0·196	1·4	7·8
	6	,,	5	0·197	0·196	1·2	7·9
	6	,,	10	0·190	0·187	1·5	8·5
	6	,,	20	0·182	0·384	1·6	9·0
95·7	8	0·246	42	0·211	0·117	1·4	14·5
	8	,,	38	0·189	0·421	1·6	14·3
	8	,,	40	0·195	0·915	1·4	17·8
	28	,,	181	0·4001	0·6068	1·6	19·5
	28	0·243	182	0·4002	0·6038	1·1	19·9
	28	,,	183	0·4000	0·6040	1·9	19·8
95·1	20	0·285	131	0·4004	0·1015	1·4	17·2
	20	,,	134	0·4008	0·1014	1·6	17·2
	39	0·283	233	0·3989	0·2027	1·3	18·2
	20	0·285	125	0·4002	0·2082	1·4	18·6
	20	,,	126	0·4011	0·2019	1·5	18·3
	20	,,	145	0·4014	0·2038	1·6	19·4
	21	0·277	146	0·4009	0·2038	1·5	18·9
	21	,,	152	0·4008	0·2058	1·4	19·4
	20	0·285	137	0·4002	0·3013	1·5	18·8
	20	,,	132	0·4000	0·3999	1·5	18·4
	20	,,	133	0·4008	0·4116	1·5	18·2
	20	,,	139	0·4000	0·4026	1·5	19·8
	20	,,	143	0·4017	0·4156	1·5	20·1
	21	0·277	147	0·4008	0·4044	1·5	19·8
	20	0·285	136	0·4004	0·5125	1·5	19·6
	20		138	0·4011	0·5005	1·5	20·0
	20	,,	135	0·4008	0·6145	1·5	20·3
	20	,,	144	0·4006	0·5951	1·5	20·7
	21	0·277	148	0·4012	0·6160	1·6	20·7
	21	,,	153	0·4007	0·6031	1·45	19·7
89·5	22	0·636	160	0·4007	0·1008	1·8	18·2
	,,	,,	154	0·3984	0·1992	1·8	17·0
	,,	,,	159	0·4006	0·4002	1·7	15·6
	,,	,,	163	0·4001	0·4012	2·0	16·9
	,,	,,	162	0·4002	0·4964	1·8	16·0
	,,	,,	161	0·3997	0·5937	2·0	15·9

TABLE IV.

Variation of initial DNT *concentration* (Temp. 89·9°).

Medium.							
Wt. % H_2SO_4.	Acid No.	$\frac{H_2O}{H_2SO_4}$.	Expt. No.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	$\frac{[TNT]}{[HNO_2]}$.	10^3k_2.
100	16	0	107	0·1003	0·1986	1·3	6·0
	,,	—	102	0·2006	0·1996	1·4	6·9
	,,	Table III, Average		0·400	0·199	1·6	7·4
	,,	Table III, Average		0·601	0·199	1·6	8·6
	,,	,,	97	0·2008	0·3859	1·6	8·0
	,,	,,	95	0·4002	0·3883	1·4	8·2
	,,	,,	98	0·5999	0·3865	1·9	10·6
	,,	,,	106	0·4011	0·8201	1·3	10·5
	,,	,,	105	0·6024	0·8331	1·3	12·1
99·2	6	0·039	19	0·102	0·197	1·4	7·4
	6	Table III, Average		0·195	0·193	1·4	8·0
	6	,,	15	0·398	0·193	1·5	8·5
	15	0·046	80	0·4011	0·2018	1·7	9·0
	15	,,	86	0·4011	0·1964	1·1	8·2
	6	0·039	17	0·525	0·190	1·4	9·1
	6	,,	4	0·302	0·315	1·4	9·3
95·7	8	0·246	44	0·100	0·186	1·6	14·1
	,,	,,	47	0·103	0·191	1·4	13·3
	,,	,,	43	0·385	0·207	1·6	14·9
	,,	,,	39	0·321	0·311	1·6	17·4
95·1	20	0·285	130	0·1000	0·2019	1·3	13·8
	20	,,	129	0·2003	0·2102	1·3	15·2
	20/21	Table III, Average		0·401	0·205	1·5	18·9
	20	0·285	128	0·6040	0·2079	1·5	19·5
	20	,,	127	0·8017	0·2062	1·5	21·5
89·5	22	0·636	157	0·1000	0·2005	2·0	19·8
	,,	,,	156	0·2503	0·1998	1·6	17·4
	,,	,,	154	0·3984	0·1992	1·8	17·0
	,,	,,	155	0·5977	0·2006	2·0	16·0
	,,	,,	158	0·8017	0·1987	1·7	14·3
89·3	10	0·655	52	0·200	0·186	1·6	16·5
	5	,,	12	0·200	0·223	1·8	16·6
	10	0·655	51	0·402	0·179	1·7	15·5
	10	,,	49	0·398	0·186	1·9	16·5
	12	0·653	88	0·4010	0·2061	2·0	16·2

TABLE V.

Influence of added bisulphates (Temp. 89·9°).

				Added material.			
Medium.	Expt. No.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	Subst.	Mols./l.	$\frac{[TNT]}{[HNO_2]}$.	10^3k_2.
99·3% H_2SO_4	Mean from Table IV			—	—	1·4	8·6
	28	0·400	0·199	$KHSO_4$	0·300	1·3	9·3
	32	0·401	0·187	$KHSO_4$	0·604	1·4	10·5
	11	0·199	0·191	$KHSO_4$	0·972	1·3	10·6
	34	0·401	0·0563	$KHSO_4$	1·000	1·55	11·1
	30	0·401	0·195	$KHSO_4$	1·002	1·2	11·4
	31	0·395	0·176	$KHSO_4$	1·476	1·4	14·0
	46	0·396	0·202	$NO{\cdot}HSO_4$	0·13	1·3	8·8
	45	0·408	0·177	$NO{\cdot}HSO_4$	0·16	1·2	9·0
	48	0·401	0·198	$NO{\cdot}HSO_4$	0·34	(1·6)	9·9
89·3% H_2SO_4	Mean from Table IV			—	—	1·9	16·1
	89	0·401	0·215	$KHSO_4$	0·195	2·0	12·2
	72	0·396	0·195	$KHSO_4$	0·196	1·35	11·9
	70	0·401	0·206	$KHSO_4$	0·513	1·7	10·5
	90	0·401	0·207	$KHSO_4$	0·605	1·6	9·0
	74	0·401	0·197	$KHSO_4$	1·00	1·7	7·2
	68	0·403	0·204	$NO{\cdot}HSO_4$	0·191	1·8	14·6
	50	0·403	0·173	$NO{\cdot}HSO_4$	0·20	(2·0)	14·3
	91	0·401	0·200	$NO{\cdot}HSO_4$	0·215	1·7	14·2
	92	0·401	0·209	$NO{\cdot}HSO_4$	0·333	1·8	11·6
	69	0·401	0·202	$NO{\cdot}HSO_4$	0·377	1·7	10·8

DISCUSSION OF RESULTS.

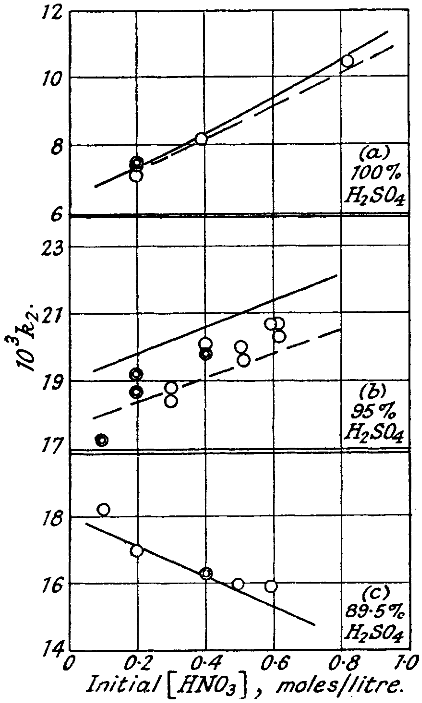
We take the nitrating agent to be the NO_2^+ ion in all sulphuric acid media—from oleum to the equimolecular mixture of sulphuric acid and water, in which the NO_2^+ concentration falls virtually to zero (Bennett, Brand, and Williams, *loc. cit.*) and the nitration of DNT ceases (Table II, Fig. 3). In sulphuric acid–water media, the concentration of NO_2^+ ion is governed by the equilibria (4) and (5). The vapour pressure of water over sulphuric acid–water mixtures

$$NO_2{\cdot}OH + 2H_2SO_4 \rightleftharpoons NO_2^+ + OH_3^+ + 2HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$H_2O + H_2SO_4 \rightleftharpoons OH_3^+ + HSO_4^- \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

is exceedingly small if the water content is less than 14·5 wt.% (Daudt, *Z. physikal. Chem.*, 1923, **106**, 255), which justifies the assumption that equilibrium (5) lies virtually completely to the right in all mixtures in which sulphuric acid is present in molecular excess over water. In the following it is assumed that water is always completely converted into oxonium and bisulphate ions.

FIG. 4.

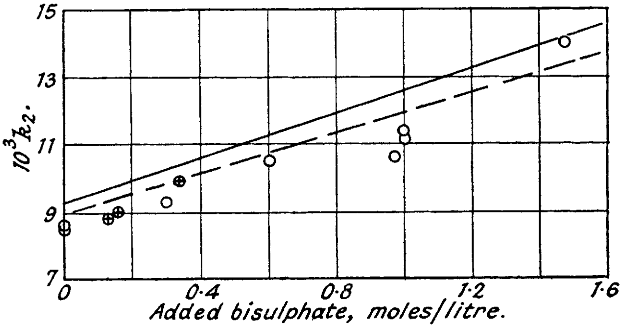


Variation of k_2 *with initial concentration of nitric acid. Lines calculated, points experimental.*

Full lines : $10^3\,k = 3{\cdot}3$.
Broken lines : $10^3\,k = 3{\cdot}0$.

It is assumed further that the completion of nitration requires, not only the attachment of the NO_2^+ ion to the nucleus, but also the removal of a proton from the nucleus by a specific proton-acceptor, so that both acidic and basic functions of the medium are involved. We suppose, therefore, that the rate of nitration is governed by the frequency of suitable collisions between a DNT molecule, a NO_2^+ ion, and a proton-acceptor molecule. In sulphuric acid–water media, the most efficient proton-acceptor is probably the bisulphate ion; but this cannot be the sole available proton-acceptor, because the nitration velocity coefficient in 100% sulphuric acid has a value almost one-third as great as the maximum value in 92% sulphuric acid. The most probable additional proton-acceptor is the sulphuric acid molecule. That this molecule can accept protons is proved by its self-ionisation (Hantzsch, *Ber.*, 1925, **58**, 941; Hammett and Deyrup, *J. Amer. Chem. Soc.*, **1933**, **55**, 1900); and a possible mechanism for its action in nitration might be :

FIG. 5.



Acceleration of nitration by added bisulphate in 99·2% H_2SO_4.
Open circles $KHSO_4$; *crossed circles* $NO{\cdot}HSO_4$.
Upper and lower lines calculated for $10^3k = 3{\cdot}3$ *and* $3{\cdot}0$.

$$H^+ + H_2SO_4 \longrightarrow H_3SO_4^+$$

$$H_3SO_4^+ + HSO_4^- \leftrightarrows 2H_2SO_4$$

The chemical equations for the nitration of DNT are (6) and (7) :

$$DNT + NO_2^+ + HSO_4^- \longrightarrow TNT + H_2SO_4 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$DNT + NO_2^+ + H_2SO_4 \longrightarrow TNT + H_3SO_4^+ \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The equation for the rate of nitration takes the form

$$d[TNT]/dt = k[DNT][NO_2^+][HSO_4^-] + k'[DNT][NO_2^+][H_2SO_4] \quad . \quad . \quad . \quad (8)$$

in which the constants k and k' are *independent of medium*.

Equation (8) may be transformed as follows, in order to express the nitration rate in terms of the measurable total concentration of nitric acid. Let [HNO_3] represent the concentration of total nitric acid (all forms) in moles/litre, and let the molar concentrations of other species at equilibrium be [$NO_2{\cdot}OH$] for undissociated nitric acid, [H_2SO_4] for *free* (undissociated) molecular sulphuric acid, and [NO_2^+], [OH_3^+], [HSO_4^-] for the ions. Then the "concentration" equilibrium constant of (4) is

$$K_c = \frac{[NO_2^+][OH_3^+]}{[NO_2{\cdot}OH]} \cdot \left\{\frac{[HSO_4^-]}{[H_2SO_4]}\right\}^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and since [HNO_3] = [NO_2^+] + [$NO_2{\cdot}OH$], the fraction of nitric acid present as NO_2^+ ion given by

$$Q = \frac{[NO_2^+]}{[HNO_3]} = \frac{1}{1 + \dfrac{[OH_3^+]}{K}\dfrac{[HSO_4^-]^2}{[H_2SO_4]^2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and equation (8) may be written in the form

$$d[TNT]/dt = \{k[HSO_4^-] + k'[H_2SO_4]\}[DNT][HNO_3]Q. \quad . \quad . \quad . \quad (11)$$

in which Q is determined by equation (10).

Experimentally, equation (1) holds for a fixed set of initial concentrations in a particular medium. By combination with equation (11),

$$k_2 = \{k[HSO_4^-] + k'[H_2SO_4]\}Q \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Equation (12) should describe the variation of k_2 with change of medium, change of reactant concentration, or any other circumstance except change of temperature.

In certain circumstances, equation (12) may be put in a simpler form. For relatively small concentrations of HSO_4^- ion, $Q \sim 1$, as may be seen in Table VII, which shows that Q is not less than 0·97 even in 95% sulphuric acid, when [HSO_4^-] = 5·2M.

If the water content of the medium is less than 5%, we can therefore write without serious error

$$k_2 = k[HSO_4^-] + k'[H_2SO_4] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

This equation is valid for changes of medium from 0 to 5% of water and may also be applied to changes of bisulphate ion concentration in a given sulphuric acid–water medium, provided that the (fixed) water content be less than 5%. Such changes are brought about by (*a*) variation of initial nitric acid concentration, through the operation of equilibrium (4); (*b*) addition of bisulphate ion as potassium or nitrosyl bisulphate (nitrous acid)—see Table V. Variation (*b*) leaves [H_2SO_4] unaltered, so the change of k_2 caused by addition of bisulphate ion in a medium with less than 5% water content should be given by the equation

$$k_2 = k[HSO_4^-] + \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

The Constants of Equation (11).—These constants must be influenced by kinetic salt effects. However, since the salt effects (discussed further on p. 486) cannot be calculated quantitatively for the prodigious ionic strengths involved (*e.g.*, about 10 in 90% sulphuric acid), and since they cannot be predicted, with certainty, even qualitatively, the only course is to test the form of equation (11) by evaluating its constants provisionally, disregarding salt effects. This may be done, for k and k', by applying equations (13) and (14) to the experimental results for the variation of k_2 (equation 1) with medium, added bisulphate concentration, and initial nitric acid concentration, in solvents containing not more than 5% of water. The values for k and k' are shown in Table VI together with that of a third coefficient k'' concerned with the reaction in oleum, discussed below (p. 487). The agreement in the results derived from independent experimental sources is not unsatisfactory. A further independent estimate for k (and K_c) may be obtained by neglecting the term $k'[H_2SO_4]$ in equation (12), which is much smaller than the term $k[HSO_4^-]$ in all but the least aqueous media (those in which the molar ratio $H_2O/H_2SO_4 < 0{\cdot}2$, see Table VII). This is equivalent to supposing that the bisulphate ion is the only effective proton-acceptor in the more aqueous media. Two sets of experimental results (Table II) are inserted in the modified form of equation (12), Q being given by equation (10), and simultaneous equations are solved for k and K_c. The results, together with others calculated on the same assumption, are given in Table VI as "1st Approx.". The simplifying assumption is seriously inaccurate for the results in this column derived from data II and III.

TABLE VI.

Evaluation of the constants k, k′, *and* k″.

Experimental source.	10^3k.	$10^3k'$.	$10^3k''$.	1st Approx. 10^3k.
I. Accelerating influence of $KHSO_4$ and $NO{\cdot}HSO_4$ in 99·3% H_2SO_4 (Table V, Fig. 5)	3·3	—	—	3·3
II. Accelerating influence of increased initial concentration of HNO_3 :				
(*a*) in 100% H_2SO_4	3·1	0·37	—	2·5
(*b*) in 95% H_2SO_4 .... (Table III, Fig. 4)	3·0	0·33	—	2·3
III. Accelerating influence of water on acid side of optimum medium composition (Table II, Fig. 3)	3·0	0·38	—	2·7
IV. Retarding influence of water on water side of optimum medium composition (Table II, Fig. 3)	—	—	—	3·5
(calculated for media with $H_2O/H_2SO_4 = 0{\cdot}55$ and 0·70)	—	—	—	$K_c = 33$
V. Variation of oleum composition (Table VIII)	—	0·37	0·56	—

Note.—In I and II, *k* has been calculated from the experimental points, and not from the lines drawn in Figs. 4 and 5. The meaning of the lines is explained later.

General Application of the Theoretical Equation.—In order to apply equation (12) to the whole of the results, its constants are derived in the following way : (1) A representative value of *k* is taken from Table VI. (2) Using this value of *k*, the value of *k′* is calculated from the experimental results for 100% sulphuric acid medium by means of equation (13). (3) The equilibrium constant K_c of the nitric acid equilibrium (4) has been evaluated by inserting the values of *k* and *k′* in equation (12) with (10) and then applying the equation to experimental points on the water side of the optimum medium composition, with the following results :

Medium, H_2O/H_2SO_4.	k_2, exptl.	K_c, calc.
0·80	6·1	35·8
0·70	13·0	33·7
0·55	21·0	31·4

The following have been taken as representative values :

$$k = 3{\cdot}3 \times 10^{-3};\ k' = 0{\cdot}37 \times 10^{-3};\ K_c = 33{\cdot}6.$$

For some preliminary calculations we derived a rough value of 30—42 for the constant of equilibrium (4) from Chédin's estimates (*Ann. Chim.*, 1937, **8**, 243) of the intensities of the Raman line Δν 1400 cm.$^{-1}$ (cf. Part I, *loc. cit.*) in sulphuric acid–nitric acid–water mixtures.

I. *Medium Effect.*—The application of equation (12) to the calculation of k_2 in different media is shown in Table VII. The required concentrations of the various molecular species furnished by the medium are calculated on the assumption that water is, in all circumstances, *completely* converted into oxonium and bisulphate ions. The figures in Table VII have also the limitation that they hold only for the conditions DNT = 0·4M and HNO_3 = 0·2M. Allowance is made for the bisulphate-ion concentration contributed by the nitric acid (equilibrium 4). To compute correctly the amount of sulphuric acid furnished by the medium, allowance must also be made for the volume taken up by DNT (Table XII) and a further small correction is applied for " volume " occupied by nitric acid. This last correction becomes appreciable when larger concentrations of nitric acid are involved (see Experimental section).

From the value of *Q* as a function of medium composition in Table VII it may be appreciated that the rise in k_2 with increasing water content in media on the acid side of the optimum is due to the increased concentration of HSO_4^- (acting as proton-acceptor) by the operation of equation (5), because the extent of ionisation of nitric acid falls relatively slowly in this region; whilst the fall in k_2 in media on the water side of the optimum is caused by the rapid fall in the extent of nitronium-ion formation as governed by equation (4) when H_2O/H_2SO_4 exceeds 0·5. For this reason, the constant *k* is best evaluated from data falling on the " acid limb " and K_c from data on the " water limb ".

The columns headed " $3{\cdot}3[HSO_4^-]$ " and " $0{\cdot}37[H_2SO_4]$ " in Table VII represent the relative contributions to nitration speed due to proton-acceptance by bisulphate ions and sulphuric acid molecules respectively. Their sum, multiplied by *Q*, gives the final value of k_2, calc. The calculated curve for the variation of nitration velocity coefficient with medium com-

TABLE VII.

Calculation of influence of medium upon nitration rate.

Medium.								
$\frac{H_2O}{H_2SO_4}$.	H_2SO_4, Wt. %.	$[OH_3^+]$, M.	$[HSO_4^-]$, M.	$[H_2SO_4]$, M.	Q, $\frac{[NO_2^+]}{[HNO_3]}$.	$3{\cdot}3[HSO_4^-]$.	$0{\cdot}37[H_2SO_4]$.	10^3k_2, calc.
0	100	0·2	0·4	16·42	1	1·32	6·08	7·40
0·075	98·70	1·44	1·64	15·00	1	5·41	5·55	10·96
0·1	98·20	1·86	2·06	14·50	0·999	6·80	5·36	12·15
0·128	97·70	2·32	2·52	13·96	0·998	8·32	5·17	13·46
0·2	96·46	3·45	3·65	12·61	0·992	12·05	4·66	16·57
0·3	94·78	4·98	5·18	10·76	0·967	17·09	3·98	20·37
0·4	93·16	6·43	6·62	9·02	0·907	21·83	3·34	22·82
0·45	92·37	7·14	7·31	8·18	0·855	24·12	3·03	23·21
0·475	91·98	7·48	7·65	7·74	0·821	25·24	2·87	23·09
0·55	90·82	8·47	8·61	6·53	0·695	28·40	2·42	21·43
0·65	89·30	9·77	9·87	4·95	0·464	32·58	1·83	15·96
0·7	88·61	10·30	10·34	4·32	0·363	34·11	1·60	12·96
0·8	87·19	11·50	11·53	2·81	0·147	38·03	1·04	5·76

position is shown as the full line in Fig. 3, where it is compared with the experimental results from Table II.

The calculated line lies above the experimental points in the most concentrated sulphuric acid media and below them in the region of the optimum medium. Table VI shows that results in concentrated sulphuric acid media are represented better by the value $10^3k = 3{\cdot}0$ than by the value 3·3, used in Table VII and Fig. 3 as giving the best representation of the results as a whole. An alternative curve calculated with the constants $k = 3{\cdot}0 \times 10^{-3}$, $k' = 0{\cdot}38 \times 10^{-3}$, $K_c = 34{\cdot}6$, is in better accord with experiment in concentrated sulphuric acid media, but lies still further below the observed maximum velocity coefficients. It is possible that $10^3k = 3{\cdot}0$ is the better value (see discussion below on kinetic salt effects).

In Fig. 4 (*a*) and (*b*) and in Fig. 5, calculated lines are shown for both values of k. Fig. 5 gives a calculation from equation (14) for the influence of added bisulphate in 99% sulphuric acid, compared with the experimental results of Table V.

The broken curve in Fig. 3 is derived from the " 1st Approx." constants $k = 3{\cdot}5 \times 10^{-3}$, $K_c = 33$, $k' = 0$. This curve must fail on the acid side of the optimum because it is drawn on the assumption that bisulphate ion is the sole proton-acceptor, so that k_2 must fall almost to zero in 100% sulphuric acid. It is included for its significance in showing that from two points on the water side of the optimum (cf. Table VI) constants may be calculated which predict a maximum rate of nitration in a medium of just about the composition actually observed.

Kinetic Salt Effects.—The numerical values deduced for the constants of equation (11) —and of equation (16)—should be regarded as partly empirical. The variation of the experimental velocity coefficient k_2 with medium and with nitric acid concentration has been expressed in terms of invariant coefficients k and k'. But these must be subject to primary kinetic salt effects, which have been disregarded; so that k and k', as calculated above, should not be strictly independent of medium. Since k and k' are evaluated from experiments at relatively low ionic strength (Table VI) and since, also, salt effects must be unusually small in sulphuric acid as solvent (Hammett and Deyrup, *loc. cit.*) the values employed are perhaps not far removed from those which would be appropriate to " zero " ionic strength. The salt effects acting on k and k' in relatively aqueous media cannot be estimated theoretically, even qualitatively, without knowing how the activity coefficients of the various ions and neutral molecules involved in reactions (4) and (5) change at very high ionic strengths. There are experimental indications that k may rise with increasing ionic strength, which may help, if substantiated, to explain why the calculated curve in Fig. 3 lies below the experimental results in the region of the optimum medium.

The concentration of NO_2^+ ion will also be influenced by secondary salt effects, not taken into account by equation (9); but these will only be considerable in media on the aqueous side of the optimum composition, for it is only here that nitric acid behaves as a weak electrolyte. The equilibrium constant K_c is evaluated from experiments in these more aqueous media and should therefore automatically contain some allowance for secondary salt effects.

A further factor which has been left out of account is that collision frequencies of DNT molecules or NO_2^+ ions with sulphuric acid molecules or bisulphate ions may be affected by changes of viscosity in different media.

II. *Concentration Effects.*—Increase of initial nitric acid concentration means that an increased concentration of bisulphate ions is present throughout the nitration. If the medium is one in which increased bisulphate concentration accelerates nitration, then k_2 will rise with increased nitric acid concentration. If bisulphate ion has the opposite effect, then k_2 will fall. In either event, the extent of the variation of k_2 should be given by equation (12). In Fig. 4 the full lines are calculated from equation (12) for three different media, allowance being made for decrease in the amount of sulphuric acid present as the amount of nitric acid is increased. The experimental results are also shown in the diagrams. For 95% sulphuric acid medium with $k = 3{\cdot}3 \times 10^{-3}$ the equation reproduces the gradient of k_2 but gives absolute values which are too high throughout. The broken lines are for $k = 3{\cdot}0 \times 10^{-3}$.

Changes of concentration *during* the nitration reaction do not bring about any appreciable drift of k_2, because the bisulphate ions originally derived from nitric acid are largely replaced by new bisulphate ions derived from the products, nitrous acid and water.

The Influence of Initial DNT *Concentration.*—Equation (12) does not predict any variation of k_2 with initial DNT concentration. In fact, such a variation is observed (Table IV). It is not large, but it is of the same order of magnitude as the variation of k_2 with initial nitric acid concentration; and, like the latter, it is of opposite sign in media on either side of the optimum. For 0·2M initial nitric acid concentration, the variation of k_2 with initial DNT concentration is given empirically by the equations

$$\text{In } 100\%\ H_2SO_4 \text{ medium}: \ 10^3k_2 = 5{\cdot}5 + 5{\cdot}1[\text{DNT}]_{t=0}$$

$$\text{In } 89{\cdot}5\%\ H_2SO_4 \text{ medium}: \ 10^3k_2 = 20{\cdot}6 - 7{\cdot}9[\text{DNT}]_{t=0}$$

No explanation can be given for this variation at present; but we believe it to be connected, in some way, with the oxidation reaction, because this kind of variation is not observed in the nitrations of *p*-chloronitrobenzene and nitrobenzene which are otherwise closely analogous to that of DNT. A qualitatively attractive explanation is that additional bisulphate-ion concentration is formed by ionisation of the fragments X_i of p. 477; but the concentrations of X_i are easily calculated to be insufficient to account for the magnitude of the effect. Change in the amount of sulphuric acid in the reaction mixture with variation of initial DNT concentration (Table XII) is also inadequate as an explanation of the effect. Further experiments are needed.

Nitration in Oleum Media.—Results in oleum media are given in Tables VIII and IX.

TABLE VIII.

Nitrations in oleum media (Temp. 89·9°).

Medium.							
Wt. % free SO_3.	Acid No.	$\frac{SO_3}{H_2SO_4}$.	Expt. No.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	$\frac{[TNT]}{[HNO_2]}$.	10^3k_2.
7·8	23	0·104	173	0·3998	0·2003	1·8	5·8
			174	0·4002	0·2003	1·6	5·4
			176	0·3994	0·8000	1·7	7·9
			175	0·7975	0·2034	2·0	8·4
11·7	26	0·162	177	0·3998	0·1998	1·7	5·5
			178	0·4009	0·1986	1·8	5·3
16·6	25	0·244	171	0·4004	0·2052	2·2	4·7
			172	0·4000	0·2024	2·4	5·1
29·1	27	0·503	179	0·4006	0·1960	(1·3)	(2·8)
			180	0·4001	0·2053	(2·3)	(3·1)

The velocity coefficients in 29·1% oleum are not accurate, owing to analytical difficulties; but the reaction curves showed unmistakably that nitration was slower in 29·1% oleum than in 16·6% oleum. Thus, the rate of nitration is less in oleum media than in 100% sulphuric acid; and decreases with rising proportion of sulphur trioxide in the oleum. This behaviour may be ascribed to the decreasing opportunities for proton-removal in oleum media. For the bipyrosulphate ion, being more weakly basic, will accept a proton less readily than the bisulphate ion; and the concentration of sulphuric acid molecules falls as the sulphur trioxide content of the oleum increases. Pyrosulphuric acid is a stronger acid than sulphuric acid.

Extension of Theory to Oleum Media.—In oleum media the principal proton-acceptors are probably the sulphuric acid molecule and the bipyrosulphate ion; nitration will take place according to equations (7) and (15):

$$\text{DNT} + NO_2^+ + HS_2O_7^- \longrightarrow \text{TNT} + H_2S_2O_7 \quad . \quad . \quad . \quad . \quad (15)$$

The rate of nitration is given by equation (16) :

$$d[TNT]/dt = k'[DNT][NO_2^+][H_2SO_4] + k''[DNT][NO_2^+][HS_2O_7^-] \quad . \quad . \quad . \quad (16)$$

which may be put in the form

$$d[TNT]/dt = \{k'[H_2SO_4] + k''[HS_2O_7^-]\}[DNT][HNO_3]Q$$

where $Q = [NO_2^+]/[HNO_3] = 1$ in oleum.

Hence $$k_2 = k'[H_2SO_4] + k''[HS_2O_7^-] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

To draw up a concentration table for oleum media, analogous to Table VII, it is necessary to make assumptions about the fraction of pyrosulphuric acid which exists as $HS_2O_7^-$ ion in sulphuric acid solution. The identity of the cations existing in such a solution is not certain. We have made the calculation by postulating the equilibrium :

$$H_2SO_4 + H_2S_2O_7 \rightleftharpoons H_3SO_4^+ + HS_2O_7^- \quad . \quad . \quad . \quad . \quad . \quad (18)$$

for the relatively strong oleums in question, and by taking a value of 1 for its equilibrium constant. This figure gives results which are consistent with chemical evidence (Part III, Brand, *J.*, 1946, 880) about the relative strengths of sulphuric and pyrosulphuric acids. It being assumed that nitric acid, in these relatively strong oleums, is completely converted into NO_2^+ ion according to equation (19), the concentrations $[HS_2O_7^-]$ and $[H_2SO_4]$ may be calculated

$$NO_2{\cdot}OH + 2H_2S_2O_7 = NO_2^+ + HS_2O_7^- + 2H_2SO_4 \quad . \quad . \quad . \quad . \quad (19)$$

for different oleums and combined with the experimental values of k_2 from Table VIII to determine the constants of equation (16).

TABLE IX.

Variation of temperature.

	Medium.							
Temp.	Wt. % H_2SO_4.	Acid No.	$\frac{H_2O}{H_2SO_4}$.	Expt. No.	Initial concn. of DNT, M.	Initial concn. of HNO_3, M.	$\frac{[TNT]}{[HNO_2]}$.	10^3k_2.
80°	100	31	0	209	0·3959	0·1969	1·6	2·84
80	,,	31	,,	210	0·3966	0·2003	1·8	2·78
70	,,	31	,,	211	0·3970	0·2007	3·1	1·13
70	,,	31	,,	212	0·3967	0·2011	2·7	1·13
120	95·0	39	0·283	239	0·4004	0·2011	0·95	251
120	,,	39	,,	240	0·4000	0·2006	0·90	221
110	,,	39	,,	236	0·4000	0·1987	0·94	104
110	,,	39	,,	237	0·3995	0·1994	1·2	104
110	,,	39	,,	238	0·3999	0·2005	1·05	106
100	,,	39	,,	234	0·3994	0·2023	1·1	43·7
100	,,	39	,,	235	0·3994	0·1967	1·1	41·1
80	,,	29	0·287	185	0·4000	0·2004	1·9	7·5
80	,,	29	,,	186	0·3998	0·1957	1·8	8·0
80	,,	29	,,	187	0·4001	0·2002	1·9	7·6
70	,,	29	,,	188	0·4005	0·2013	2·1	2·90
70	,,	29	,,	189	0·4000	0·1998	2·3	2·92
70	,,	29	,,	190	0·6001	0·2013	2·2	3·36
60	,,	29	,,	194	0·3999	0·2011	2·3	1·00
60	,,	29	,,	195	0·4006	0·2041	2·7	1·02
110	89·5	40	0·636	247—250	0·4004	0·2006	1·2	84
100	,,	40	,,	244	0·4004	0·2000	1·4	(35·0)
100	,,	40	,,	245	0·3999	0·2002	1·4	37·3
100	,,	40	,,	246	0·4008	0·1991	1·4	36·9
70	,,	30	0·638	198	0·3987	0·2004	2·5	2·65
70	,,	30	,,	199	0·4004	0·2008	2·4	2·54
80	87·6	43	0·770	289	0·3999	0·2003	1·6	2·9
80	,,	43	,,	291	0·3993	0·2001	1·8	2·6
	Wt. % SO_3	Acid No.	$\frac{SO_3}{H_2SO_4}$.					
80	7·8	23	0·104	192	0·4000	0·1934	1·4	2·06
80	,,	,,	,,	193	0·3999	0·1995	1·8	2·33
70	,,	,,	,,	196	0·3998	0·1995	1·8	0·76
70	,,	,,	,,	197	0·4000	0·2007	2·5	0·84

Solving simultaneous equations for each of the oleum pairs 7·8—16·6% SO_3 and 11·7—29·1% SO_3, we find $10^3k' = 0{\cdot}35$ and 0·39, to be compared with the value 0·37 deduced for aqueous sulphuric acid media (Table VI). Inserting the value 0·37 in equation (16), we find for the four different oleum media: $10^3k'' = 0{\cdot}47$, 0·60, 0·60, 0·55. A theoretical curve to represent the variation of k_2 in different oleum media has been drawn from equation (16) with $k' = 0{\cdot}37 \times 10^{-3}$ and $k'' = 0{\cdot}56 \times 10^{-3}$. The curve is shown in the right-hand portion of Fig. 3.

General Equation.—The foregoing argument thus leads to the general equation

$$d[\mathrm{TNT}]/dt = \{k[\mathrm{HSO_4}^-] + k'[\mathrm{H_2SO_4}] + k''[\mathrm{HS_2O_7}^-]\}[\mathrm{DNT}][\mathrm{HNO_3}]Q$$

which reproduces the velocity observations over the entire range of media studied.

Influence of Temperature.—The variation of k_2 with temperature for several media may be een from Table IX, together with results for 90° from previous tables.

For a given medium, log k_2 falls on a straight line when plotted against $1/T$. Since the rate of nitration is given by the sum of two terms—equations (11) or (16)—deviations from the Arrhenius equation might have been anticipated. However, the temperature range is not great, and since the differences between k, k', and k'' are due only to differences of basic strength between HSO_4^-, H_2SO_4, and $HS_2O_7^-$, their temperature variations may well be similar. From the results for different media, the constants of equation (11) may be calculated roughly for different temperatures. The temperature variation of k_2 is due mainly to changes in the coefficients k and k'. The constants of the Arrhenius equation for different media are shown in Table X.

TABLE X.*

Contants of the equation $k_2 = Ae^{-E/RT}$.

Medium.	E (kg.-cals.).	$A \times 10^{-10}$
7·8% SO_3	24·18	3·3
100% H_2SO_4	23·35	1·4
95·0% H_2SO_4	23·54	4·7
89·5% H_2SO_4	22·58	10·5
87·6% H_2SO_4	22·32	0·71

* In this table, k_2 is calculated in *seconds*$^{-1}$. The significance of the temperature variation of nitration speed will be considered in a later paper, when the results for DNT can be combined with those for other compounds nitrated at much lower temperatures.

EXPERIMENTAL.

Materials.—2 : 4-Dinitrotoluene was prepared by the nitration of *p*-nitrotoluene and recrystallised from alcohol until its setting point was constant. The setting point was taken on 10—15 g. of molten material, allowed to cool slowly in a Thermos jacket, previously warmed to 70°. Pure nitric acid was obtained by distilling a mixture of 70% nitric acid and 98% sulphuric acid, in a volume ratio of approximately 2 : 3, at about 15 mm. pressure. Alkali titration of the distillate gave its purity as 99·97% (mean). It was normally dissolved without delay in sulphuric acid to give 0·0008 mole/g. of nitric acid. Salts: "AnalaR" Potassium sulphate, potassium hydrogen sulphate, and potassium nitrate were employed, dried in the oven before use.

Nitration Media.—Solutions for a nitration experiment were made up in two vessels, one containing a solution of DNT in sulphuric acid medium, the other a solution of nitric acid in medium having the same molecular ratio H_2O/H_2SO_4. The reaction was started by mixing these two solutions. For each medium, therefore, two stock solutions were made up, one being the pure medium, the other a solution of nitric acid in this medium. Both solutions were analysed before use.

(1) Sulphuric acid–water media were made up by weight from 98% sulphuric acid. The nitric acid solution was obtained by adding pure nitric acid to the medium already prepared. All solutions were analysed at least in duplicate. Analyses were made on weighed samples, suitably diluted; *e.g.*

Medium NM/20. By alkali titration: $95{\cdot}0_2$, $94{\cdot}8_7$, $95{\cdot}2_5$%; mol. ratio $H_2O/H_2SO_4 = 0{\cdot}284$.
Corresponding nitric acid solution.
Total acid (against alkali): $0{\cdot}00191_9$, $0{\cdot}00192_2$ equiv./g.
Nitric acid (by ferrous sulphate): $0{\cdot}000842_9$, $0{\cdot}000842_7$ mole/g.
Hence, mol. ratio $H_2O/H_2SO_4 = 0{\cdot}285$.

The strengths of sulphuric acid–water media were sometimes checked by density measurements, a 2-c.c. pyknometer being used at 25°. The method is only satisfactory for acids containing less than 95% sulphuric acid.

(2) 100% Sulphuric acid medium was made up by adjusting a weak oleum to maximum freezing point (Hantzsch, 1907, *loc. cit.*). Alkali titration gave its strength as 99·95% H_2SO_4 (mean). To make the corresponding nitric acid solution, pure nitric acid was added to 100% sulphuric acid. Analysis by alkali and ferrous sulphate gave a water content of −0·003%.

(3) *Oleum media.* Sulphur trioxide was distilled (at *ca.* 45°) from commercial oleum (*ca.* 20% free SO_3) into sulphuric acid, and then redistilled into a second sample of sulphuric acid to form a stock solution (containing up to 40% free SO_3). The stock distillate was diluted with sulphuric acid to

give the required medium composition and analysed for free sulphur trioxide by titrating with water (Brand, *J.*, 1946, 585). A solution of nitric acid in oleum was also made up, to have the same ratio SO_3/H_2SO_4, by adding pure nitric acid to the oleum medium prepared as above. Nitric acid in this solution was estimated by ferrous sulphate titration. The SO_3/H_2SO_4 ratio in the nitric acid solution was checked by water titration, use being made of the fact that one mole of nitric acid, dissolved in oleum, prevents the fuming of 1·5 mole of sulphur trioxide (Brand, Part III, *loc. cit.*).

> Example : Water titration of an oleum medium gave its sulphur trioxide content as 29·1% (mean) and its molar ratio SO_3/H_2SO_4 as 0·503. The corresponding nitric acid solution contained $0{\cdot}000886_2$ mole/g. HNO_3. By water titration, apparent SO_3 content = 0·002110 mole/g. SO_3 equivalent of HNO_3 = 0·001329 mole/g. Therefore, real SO_3 content = 0·003439 mole/g. ; and molar ratio SO_3/H_2SO_4 = 0·504, in agreement with the medium before adding nitric acid.

100% Sulphuric acid and oleum media were stored in a special apparatus, from which they could be drawn into the reaction flasks without coming into contact with moist air.

The compositions of all types of media were frequently tested by re-analysis.

Velocity Measurements.—Temperature was controlled to within ± 0·075° by an electrically operated water thermostat. The water was covered by a layer of paraffin oil. The thermometer was calibrated against the transition temperature of strontium bromide (88·62°; Richards and Yngve, *J. Amer. Chem. Soc.*, 1918, **40**, 89). Most of the reactions took place at 89·9°. At higher temperatures a glycerol thermostat was used.

Start of reaction. Two solutions, one of DNT and one of nitric acid, both in the same medium, were made up to 50 c.c. at thermostat temperature in Pyrex graduated flasks. The reaction vessel was a stoppered glass bottle, large enough to allow rapid mixing of the reactants by shaking. The two reactant solutions were poured successively into the bottle and the latter shaken. Draining errors for equal volumes poured from equal sized vessels are negligible. The starting time of the reaction was taken as 30 secs. after the beginning of pouring the second (nitric acid) solution into the reaction vessel.

In the later experiments, a special apparatus was used to give quick mixing and to eliminate temperature disturbances at the start of a reaction. The whole apparatus was immersed in the thermostat; and the two solutions were admitted simultaneously into the reaction bulb through ground necks, fitted with stoppers.

Extraction of samples. The samples for analysis (5 c.c. for HNO_3; 2 c.c. for HNO_2) were withdrawn in pre-heated pipettes, drained for 15 secs. The pipettes were calibrated for delivery of sulphuric acid medium, levelled to the pipette mark at the reaction temperature. Two methods of calibration were used : (*a*) direct weighing of the sulphuric acid medium delivered, coupled with a measurement of the density of the medium at 90°; (*b*) a more exact reproduction of the conditions prevailing when withdrawing samples from a reaction in progress : a solution of nitric acid of known concentration was made up in sulphuric acid medium at reaction temperature. Samples were extracted and analysed for nitric acid, thus providing a calibration factor for the pipette. For example, at 90° : calibrated by method (*a*), a 2-c.c. and a 5-c.c. pipette delivered 1·996 ± 0·0014 and 5·01 ± 0·0053 c.c. respectively (mean of five determinations for each); calibrated by method (*b*), another pipette delivered 2·013 ± 0·003 c.c. (five determinations).

Analytical Methods.—1. *For nitrous acid.* Considerable work was done upon methods of estimating nitrous acid. Satisfactory results for the conditions of the nitration experiments were obtained by running 2-c.c. samples either into standard chloramine-T solution, buffered by sodium acetate, or into standard ceric sulphate solution, residual reagent being determined in both methods with potassium iodide and sodium thiosulphate. The chloramine-T method is not accurate for reactions in oleum media; but in other media results from the two methods are concordant.

2. *For nitric acid.* The 5-c.c. sample was run into about 20 c.c. of concentrated sulphuric acid, cooled in ice, and titrated against standard ferrous sulphate solution by the electrometric method of Treadwell and Vontobel (*Helv. Chim. Acta*, 1937, **20**, 573). The ferrous sulphate is dissolved in 30% sulphuric acid.

The proportion of sulphuric acid present must not fall below 75% at the end of the titration. A ferrous sulphate solution gave values 0·4550, 0·4548, and 0·4552 N., when standardised, respectively, against standard potassium nitrate in concentrated sulphuric acid, against aqueous standard potassium nitrate, and against aqueous standard nitric acid, the last two being run into concentrated sulphuric acid for titration. Ferrous sulphate concentrations of 0·1, 0·32, and 0·64 N. were ordinarily used, according to the initial concentration of nitric acid in the reaction mixture. The presence of DNT did not affect the sharpness of the end-point.

Calculation of Results.—The quantities measured during the course of nitration are (*a*) the decrement of nitric acid concentration, and (*b*) the increment of nitrous acid concentration, both at known times. The calculation of the amount of nitric acid consumed in nitration as the difference between the total amount consumed and the amount of nitrous acid formed involves the assumption that no nitric acid is consumed in any other way than in the formation of TNT and nitrous acid. No evidence against this assumption has been obtained except in the most aqueous medium investigated, 87·4% sulphuric acid. Some evolution of nitrous fumes was observed during nitration in this medium, especially in the presence of added nitrosyl bisulphate. In more concentrated sulphuric acid media, fuming is absent, probably owing to the relatively high degree of ionisation of nitric acid to nitronium ion. Equating the amount of nitric acid consumed in nitration (increment in TNT concentration) to the amount of DNT consumed involves the further assumption that the amount of DNT consumed in oxidation is small compared with that consumed in nitration. This assumption has been tested experimentally.

Composition of Nitration Product : Density Method.—In order to determine how accurately the increase in TNT concentration is measured by the observed changes in nitric and nitrous acid concentrations, the composition of the nitration product has been found, in a number of reactions, by an independent method. A sample of reaction mixture (*ca.* 80 c.c.) is drowned in ice-cold water at a known time. The precipitated solid mixture of DNT and TNT is filtered off and freed from acid by repeated washing of the molten material with water. The product is finally dried for not more than 3 hours in the steam-oven, and its density is taken in a 2-c.c. pyknometer at 90°. Its TNT content is deduced from a curve relating the densities of DNT–TNT mixtures at 90° to their composition. One of many checks on the drowning and washing procedure gave the following results :

> 14·002 G. of a mixture of DNT and TNT, containing 50·3% of TNT, density at 90° 1·3783, was melted under 500 c.c. of water containing 34 g. of nitrating acid. The mixture was cooled and filtered, and the solid freed from acid in the usual way. Density of dried product : 1·3875, 1·3778; average 1·3782, corresponding to 50·2% TNT. The recovery of solid was 13·653 g., or 97·5%.

Results of density measurements are given in Table XI. The figures under " % of possible reaction " in this table refer to over-all consumption of whichever reactant is present in defect. Since nitric acid is used up to form both TNT and nitrous acid, DNT can only be considered to be in defect if the initial proportion of nitric acid to DNT is greater than about 1·7 : 1. Only then does " % of possible reaction " become identical with " % Conversion of DNT ". The last two columns of Table XI give comparative results for the extent of conversion of DNT into TNT in homogeneous nitration, as determined by acid analysis and by density. Agreement is satisfactory in Table XI (A), with DNT present in initial molecular excess over nitric acid. Deviations are not large even after more than 90% consumption of nitric acid (Expts. 152, 160). Under these conditions, therefore, it may be assumed that the amount of DNT consumed in oxidation is small and that losses of nitric acid are negligible.

The agreement is sometimes less satisfactory with equivalent initial proportions of DNT and nitric acid; and discrepancies become marked when nitric acid is present in excess [Table XI (B)], particularly when the extent of conversion of DNT exceeds 35%. (It appears, however, that the factor determining the occurrence of discrepancy is excess nitric acid, rather than mere extent of conversion—Expts. 150, 183.) In these circumstances, the conversion deduced from the density of the product is always greater than that found by acid analysis. A discrepancy in this direction could arise from loss of DNT in oxidation, but not from loss of nitric acid. (Loss of nitric acid would result in overestimate of TNT formation by acid analysis.)

Another possibility is that the nitration product, when isolated, contains some substance other than DNT and TNT, *i.e.*, some reaction product with density higher than that of DNT. However, extraction of nitration product with sodium hydrogen carbonate solution after its density had been determined gave a residue whose density was unchanged after being re-washed and dried (Expt. 181). Similar results were obtained with products from oleum media. The molecular ratio of TNT formed to nitrous acid formed (both estimated by acid analysis) appears to be much the same whether DNT or nitric acid is in excess (Tables III and IV).

TABLE XI.

Extent of nitration, estimated by density of product and by acid analysis (Temp. 89·9°).

		Initial concn.		% of possible reaction.	% Conversion of DNT.	
Medium.	Expt. No.	DNT, M.	HNO_3, M.		By density.	By acid analysis.
		(A) With initial excess of DNT.				
Oleum :						
16·7% SO_3	171 *	0·400	0·205	38·2	12·5	12·8
7·8% ,,	173 *	0·400	0·200	47·3	14·5	14·0
Aq. sulphuric acid :						
96% H_2SO_4	43	0·385	0·207	66·2	20·9	20·9
95 ,,	146	0·401	0·204	73·6	22·5	22·0
95 ,,	152	0·401	0·206	96·9	30·2	28·6
95 ,,	185 †	0·400	0·200	72·6	23·4	22·8
95 ,,	189 ‡	0·400	0·200	44·1	14·4	14·8
89·5 ,,	160	0·401	0·101	92·8	13·4	14·4
89·5 ,,	154	0·398	0·199	66·5	21·4	21·0
89·5 ,,	155	0·598	0·201	74·2	15·8	16·2
89·5 ,,	158	0·802	0·199	80·0	11·9	12·5
		(B) Without initial excess of DNT.				
99 ,,	4	0·302	0·315	56·1	32·7	33·1
96 ,,	39	0·321	0·311	49·7	29·2	29·8
95·7 ,,	150	0·398	0·614	22·0	23·8	22·3
95·7 ,,	183	0·400	0·604	22·0	21·5	20·4
95·7 ,,	181	0·400	0·607	59·0	60·1 §	53·5
95 ,,	148	0·401	0·606	60·0	63·2	55·0
95 ,,	144	0·401	0·595	60·9	62·3	53·8
95 ,,	153	0·401	0·603	60·7	60·8	52·4
89·5 ,,	156	0·250	0·200	73·3	38·4	35·5
89·5 ,,	159	0·401	0·400	54·0	36·7	34·5
89·5 ,,	161	0·400	0·594	48·5	49·9	48·5

* HNO_2 by ceric sulphate. † At 80°. ‡ At 70°.

§ After extraction by $NaHCO_3$, 60·2%.

Reproducibility of Results.—Data for a duplicate pair of experiments are shown in Fig. 1. Others may be found in the tables (*e.g.*, Tables VIII and IX). Concordance in the results from the chloramine-T and the ceric sulphate method for estimating nitrous acid is illustrated by Expts. 99, 100, and 101 of Table III. The agreement between results for identical concentrations in independently prepared but matched media may be judged from the tables, by comparing media having approximately the same composition but different "Acid No." (*e.g.*, in Table III, for 100% and 95·1% H_2SO_4; cf. also Fig. 3).

Amounts of Medium in Reaction Mixtures.—For theoretical reasons it is necessary to know, not only the molar concentrations of DNT and nitric acid, but also the molar concentrations of sulphuric acid and water present in all reaction mixtures. Since reaction mixtures are always made up to a definite *volume*, the weight of a given medium present varies for different concentrations of DNT and nitric acid. The correction for volume of DNT is considerable; that for nitric acid is smaller, but is noticeable for the higher nitric acid concentrations. It is not practicable to weigh the complete reaction mixtures, so experiments have been made to furnish corrections applicable for each reactant separately.

1. DNT *Correction.* Flasks of known volume, containing known weights of DNT, were filled to the mark at 90° with sulphuric acid medium and then weighed. The densities of DNT and medium at 90° are known, so the partial volumes of DNT and sulphuric acid medium may be calculated. The results in Table XII show, for two different sulphuric acid media, that the volumes of DNT and media are strictly additive. Thus, the volume of medium (and hence the weight) in a reaction mixture can be calculated for any initial amount of DNT. Volume corrections for other temperatures were estimated, assuming additivity, by applying the interpolation formula given by Schiff (*Annalen*, 1884, **223**, 247) for the density of DNT.

TABLE XII.

Additivity of volumes in DNT–*sulphuric acid mixtures at* 90°.

DNT, mole/l.	Wt. of DNT, g.	Wt. of acid, g.	Partial vol. of DNT, c.c.	Partial vol. of acid, c.c.	Sum of vols., c.c.	Vol. o flask, c.c.
(*a*) For 95·0% sulphuric acid, $d^{90°}$ = 1·768 g./c.c.						
0·0998	0·910	87·304	0·7	49·4	50·1	50·1
0·2008	1·820	85·759	1·4	48·5	49·9	49·9
0·3993	3·651	83·647	2·8	47·3	50·1	50·1
0·602	5·463	80·893	4·2	45·75	49·95	49·9
0·802	7·312	78·734	5·6	44·5	50·1	50·1
1·198	10·924	73·490	8·3	41·6	49·9	49·9
(*b*) For 89·5% sulphuric acid, $d^{90°}$ = 1·743 g./c.c.						
0·1002	0·910	85·672	0·7	49·2	49·9	49·9
0·4000	3·647	82·485	2·8	47·3	50·1	50·1
0·8013	7·277	77·179	5·6	44·3	49·9	49·9

For DNT, $d^{90°}$ = 1·310 g./c.c.

2. *Nitric acid correction.* Although densities are available for nitrating acids, the corrections to be applied were estimated directly by determining the weights of sulphuric acid–water media in 100 c.c. of mixture at 90° for various nitric acid concentrations and for various proportions of sulphuric acid and water. The corrections were less than 1% for 0·2M-HNO_3, rising to about 2% and 3% respectively for 0·8M-HNO_3 in 99% and 89·5% sulphuric acid media.

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