495. *Kinetics and Mechanism of Aromatic Nitration. Part IV. Nitration by Dinitrogen Pentoxide in Aprotic Solvents.*

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The kinetics have been studied of the nitration of a number of halogen- and carbalkoxyl-substituted benzenes by dinitrogen pentoxide in aprotic solvents such as carbon tetrachloride. The kinetics are complicated; but analysis shows that there is a simple limiting kinetic form, which is distinguished as the uncatalysed reaction, and that upon this may be superposed small, medium, or large amounts of one or more of a family of reactions, all catalysed by nitric acid. On this account, the total reaction may be appreciably, or even strongly, autocatalysed by the formed nitric acid. The uncatalysed reaction can be approximately isolated; it is a second-order process obeying the rate law $v_0 \propto [ArH][N_2O_5]$. Its rate has a normal temperature coefficient. Its rate is increased in more polar solvents, but the effect is small. On the other hand, the reaction shows a large positive salt effect, ionic nitrates behaving in this respect no differently from salts of other anions (contrast results given in Parts II and III); but the salts appreciably disturb the kinetic form of the reaction. The catalysed reactions have lower temperature coefficients than the uncatalysed, and depend on higher powers of the nitric acid concentration than the first power. Consequently the catalysed reactions, including the autocatalytic effects, are made prominent by the use of low temperatures, and of high concentrations of initially introduced, or of formed, nitric acid. By using conditions which admit the catalysis only in a mild form, a single reaction of the catalytic family is developed. Its rate is proportional to the square of the nitric acid concentration, $v_2 \propto [ArH][N_2O_5][HNO_3]^2$. But the more strongly developed forms of catalysis and autocatalysis involve rates, or partial rates, depending at least on the cube of the nitric acid concentration, $v_3 \propto [ArH][N_2O_5][HNO_3]^3$, and probably on higher powers.

The uncatalysed reaction is interpreted as a nitrating attack on the aromatic molecule by the covalent dinitrogen pentoxide molecule. This agrees with the kinetic form of the reaction, with the absence of retardation by ionic nitrates, and with the small solvent effect on rate. Observations on products are consistent with the view that a reagent other than the nitronium ion is at work. The strong positive salt effect is attributed to the effect of ions in promoting the ionisation of dinitrogen pentoxide, and therefore in leading to more rapid nitration by nitronium ion, with disturbance to the kinetic form of the reaction.

The nitric-acid-catalysed reactions are interpreted as nitronium ion reactions, arising from the ionising action of nitric acid on dinitrogen pentoxide. The smallest number of nitric acid molecules which could be effective for ionising a molecule of dinitrogen pentoxide is considered to be 2; but higher numbers, 3 and 4 particularly, are likely to be utilised when available. Each ionised solvate produces a form of nitronium ion, and each contributes a nitrating reaction to the family of catalysed nitrations. The conclusion that the nitronium ion is at work is supported by the observation that the ratio in which chloronitrobenzenes are formed by the strongly catalysed (but not by the uncatalysed) nitration of chlorobenzene by dinitrogen pentoxide, is substantially the same as the ratio in which they are formed in the nitration of chlorobenzene by nitric acid.

(1) *Object and Background.*

(1.1) *Aim of this Work.*—The suggestions were made in Part I (Benford and Ingold, *J.*, 1938, 955) that a molecule $X{\cdot}NO_2$ will be capable of acting as a nitrating agent if X attracts electrons sufficiently strongly, and that the nitrating efficiency of such a molecule will largely be determined by the electron-attracting power of X. The most efficient nitrating agent arises when X attracts the shared electrons so strongly that it carries them away, so that one is left with the free nitronium ion. By covalently combining the nitronium ion with bases of successively increasing strength, a series may be constructed of real or possible nitrating agents, which should have progressively diminishing efficiencies, *e.g.*,

$$\overset{+}{N}O_2,\ H_2\overset{+}{O}{\cdot}NO_2,\ O_2N{\cdot}O{\cdot}NO_2,\ Ph{\cdot}CO{\cdot}O{\cdot}NO_2,\ HO{\cdot}NO_2.$$

In Part II (*J.*, 1950, 2400) nitration by the nitronium ion was established, and its mechanism was determined. In Part III (*J.*, 1950, 2441) an investigation directed to the study of nitration by the nitric acidium ion was described. It is interesting to see how far along the above series nitration can be realised; and therefore, in this paper, we describe a study of nitration by dinitrogen pentoxide. Nitration with the molecular form of this reagent is realised; but, as we shall find, the details are complicated owing to the great facility with which covalent dinitrogen pentoxide breaks down into its ions.

(1.2) *Previous Work on Nitration by Dinitrogen Pentoxide.*—Considering how often it has been suggested that the nitrating action of nitric acid, or that of mixtures of nitric and sulphuric acids, is due to dinitrogen pentoxide, the amount of exact information in the literature concerning the nitrating properties of dinitrogen pentoxide is remarkably slight. Lothar Meyer states (*Ber.*, 1889, **22**, 23) that Giersbach used it below 55° in the conversion of benzene into dinitrobenzene. Bamberger (*Ber.*, 1894, **27**, 584) and Hoff (*Annalen*, 1900, **311**, 92) studied the action of dinitrogen pentoxide on aromatic amines, which they found to be converted into *N*- and *C*-nitro-derivatives and a number of other products. Haines and Adkins record (*J. Amer. Chem. Soc.*, 1925, **47**, 1419) that benzene, toluene, and bromobenzene were very rapidly nitrated by dinitrogen pentoxide in carbon tetrachloride:

$$N_2O_5 + ArH = Ar\cdot NO_2 + HNO_3,$$

but that nitrobenzene was not thus nitrated, although it was nitrated in a violent reaction with solid dinitrogen pentoxide. Spreckels (*Ber.*, 1919, **52**, 315) used a solution of dinitrogen pentoxide in carbon tetrachloride in order to effect a smooth mononitration of benzotrichloride, without hydrolytic loss of chlorine, for the purpose of a quantitative study of the orientation of nitration; and Cooper and Ingold (*J.*, 1927, 836) employed the same reagent, with the same object, in the example of the nitration of benzoyl chloride.

Klemenc and Schöller's investigation of nitration by dinitrogen pentoxide should be mentioned (*Z. anorg. Chem.*, 1924, **141**, 231), though, as regards the nitration mechanism which is involved, it is more closely connected with Part II than with this paper. They showed that a given amount of dinitrogen pentoxide, dissolved in sulphuric acid, acted like twice as many molecules of nitric acid, dissolved in the same solvent, with respect to the rate at which *m*-xylene-4 : 6-disulphonic acid is nitrated in such solutions. We now understand that this is because the solvent converts both solutes quantitatively into nitronium ion, two such ions being formed from each molecule of dinitrogen pentoxide, but only one from each molecule of nitric acid (cf. *J.*, 1950, papers nos. 499, 506, 508).

(2) *Qualitative Description of the Kinetics of Aromatic Nitration by Dinitrogen Pentoxide in Aprotic Solvents.*

(2.1) *Conditions and Methods of Kinetic Investigation.*—The kinetics of nitration of a number of benzene derivatives by means of dinitrogen pentoxide in various aprotic solvents have been studied, to a small extent by methods of chemical analysis, but mainly by the use of the dilatometer.

The high rates of nitration placed certain practical limitations on the aromatic compounds used, on the solvents, and on the temperatures. The following aromatic compounds were employed: Fluoro-, chloro-, and bromo-benzene; *o*-, *m*-, and *p*-dichlorobenzene; *p*-chlorobromobenzene; *p*-dibromobenzene; 1 : 2 : 4-trichlorobenzene; methyl, ethyl, and *tert.*-butyl benzoate; ethyl *p*-toluate; ethyl *m*-chlorobenzoate; ethyl phthalate. They all contain deactivating halogen or carbalkoxyl substituents, up to a maximum of three of the former or two of the latter. The relative deactivating effects of these substituents can be judged from the results of Bird, Ingold, and Smith's experiments by the competition method on the relative rates of nitration of certain monosubstituted benzenes (*J.*, 1938, 905, 918). In round figures, they found that a single fluorine or iodine substituent reduced nitration rate by a factor of about 6, a single chlorine or bromine substituent by a factor of about 30, and a single carbethoxyl group by a factor of about 300.

The following solvents were employed: Nitromethane, acetonitrile, chloroform, carbon tetrachloride. In addition, a series of mixtures of nitromethane and carbon tetrachloride were employed in the following proportions by volume: $MeNO_2 : CCl_4 = 1 : 9,\ 3 : 7,\ 5 : 5,\ 7 : 3,\ 9 : 1$. For brevity, these mixtures will be termed 1 : 9-NMCT, etc. Carbon tetrachloride was found to be the slowest of the pure solvents. The addition of 10% of nitromethane considerably improved the solubilities of some of the reactants, without increasing the reaction rates unduly. A considerable proportion of the kinetic work was accordingly carried out either in carbon tetrachloride, or in the 1 : 9-NMCT mixture.

Temperatures were in the range −25° to +25°. The former limit is close to the freezing points of carbon tetrachloride and nitromethane, and is also near the lowest temperatures at which our thermostatic equipment would work with the high precision necessary for dilatometry.

For the determination of kinetic form, Ostwald's isolation method was always employed, either the aromatic compound or the dinitrogen pentoxide being kept in constant excess over the other reactant. Most of the runs were conducted with the aromatic compound in excess, so that the dependence of the rate on the concentration of dinitrogen pentoxide was under observation in each experiment. The dependence of the rate on the concentration of the aromatic compound was given, in the first place, by comparisons between different runs with different constant concentrations of aromatic compound. For some aromatic compounds the dependence of the rate on the concentration of aromatic compound was additionally determined by following runs in which the dinitrogen pentoxide was taken in constant excess.

(2.2) *General Kinetic Forms of Nitration.*—From the results of dilatometric runs made with the aromatic compound in excess, more than 500 reaction–time curves have been drawn. Amongst them, three broad classes can be recognised, *viz.*, (1) approximately exponential curves, (2) curves which run nearly linearly for much of their length, and (3) curves having pronounced sigmoid forms. Examples are shown in Figs. 1—3.

This classification might suggest that, when the aromatic compound is in constant concentration, we have a first-order reaction, a zeroth-order reaction, and an autocatalytic reaction, separately, or in superposition. However, a careful study of the curves shows that the whole series can be more simply and consistently regarded as a single family formed by the mixing of a non-catalysed first-order reaction with an autocatalytic reaction. Almost every gradation between the exponential and linear, and between the linear and sigmoid, forms is represented amongst the results, and none of the linear curves is more exactly linear than could correspond to superposed exponential and sigmoid forms.

This view is strengthened by consideration of the corresponding logarithmic plots, such as are illustrated in Figs. 4—6. The reactions which we have termed exponential give logarithmic plots which are accurately linear, not over the whole reaction, but only over a large proportion, say 80—90%, of it; and when an appreciable deviation from linearity does set in, its direction always corresponds to a reaction rate rising above the experimental rate in the latter part of the reaction. The nearly linear reactions give logarithmic plots to which just the same description applies, except that the deviation from linearity is larger, and sets in earlier, *e.g.*, after 50—70% of reaction. Finally, the sigmoid reactions give logarithmic plots which are again similar, except that the deviation is larger still, and sets in earlier still, *e.g.*, after 20—40% of reaction. Thus the exponential reaction appears as an approach to a limiting non-catalysed reaction, on which, in practice, small, moderate, or large amounts of the autocatalytic reaction are superposed.

The non-catalytic reaction is favoured relatively to the autocatalytic reaction by an increase of temperature, and by a reduction in the initial concentration of dinitrogen pentoxide. But there is no single, absolute requirement, either with respect to a minimum of temperature or to a maximum of dinitrogen pentoxide concentration; and one can often realise all the main kinetic types by changing only one of these variables, provided the other is not too extreme. The most nearly exponential reactions have been observed at temperatures above +10°, with initial concentrations of dinitrogen pentoxide below 0·1M.; but reactions of a more or less exponential kind have been found at temperatures as low as −10°, with dinitrogen pentoxide concentrations below 0·05M. Low temperatures, and high initial concentrations of dinitrogen pentoxide (the aromatic compound being still in constant excess), favour the autocatalytic reaction. No clear solvent effect on kinetic form has emerged, but most of the work has been done either in carbon tetrachloride or in 1 : 9-NMCT, and it is possible that these two solvents are too similar easily to reveal such an effect. The introduction, or the accidental inclusion along with the dinitrogen pentoxide, of a small amount of nitric acid greatly enhances the autocatalytic process [cf. Section (4.2)].

About 60 dilatometric runs have been carried out with dinitrogen pentoxide in constant excess, the time-variable concentration now being that of the aromatic compound. This study has been confined to the compounds, fluorobenzene, chlorobenzene, and *m*-dichlorobenzene, and to the single solvent, carbon tetrachloride. However, even within this more limited range of observation, a completely corresponding set of kinetic phenomena appear. We find reaction–time curves which are nearly exponential, others which for a large part of their length are

FIGS. 1—6.

Illustrating kinetic types of aromatic nitration by dinitrogen pentoxide, the aromatic compound being in constant excess.

FIG. 1.

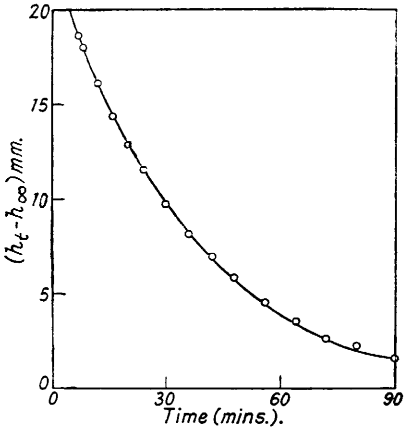


FIG. 2.

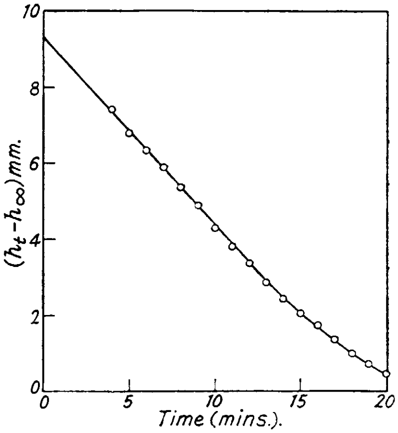


FIG. 3.

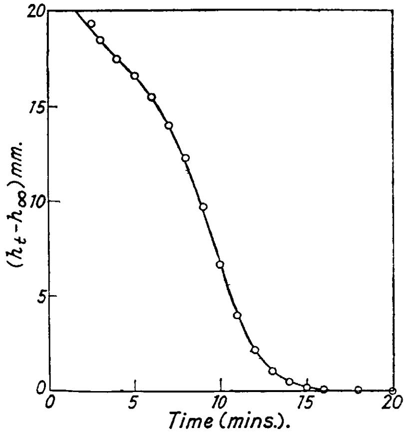


FIG. 4.

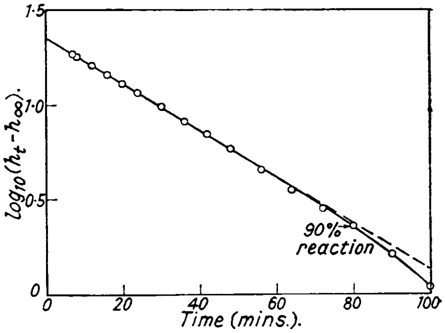


FIG. 5.

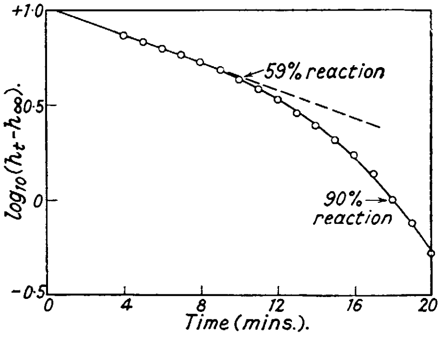
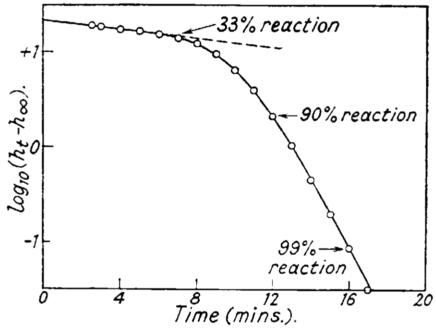


FIG. 6.



FIGS. 1 and 4.—" *Exponential* " *reaction, illustrated by Run* 414. *Nitration of* p-$C_6H_4Cl_2$, *initially* 0·745M., by N_2O_5, *initially* 0·0378M., *in* CCl_4 *at* 14·99°.

FIGS. 2 and 5.—" *Linear* " *reaction, illustrated by Run* 318. *Nitration of* C_6H_5Cl, *initially* 1·215M., *by* N_2O_5, *initially* 0·0711M., *in* CCl_4 *at* —10·00°.

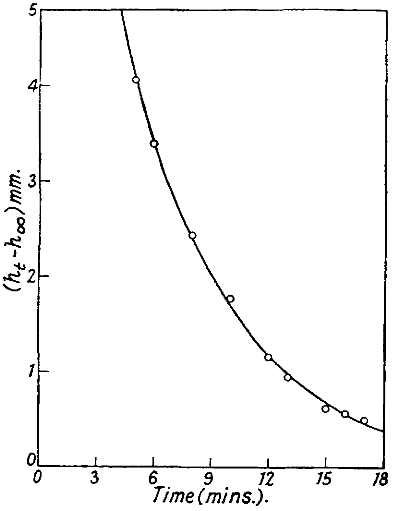
FIGS. 3 and 6.—" *Sigmoid* " *reaction, illustrated by Run* 447. *Nitration of* C_6H_5Cl, *initially* 1·037M., *by* N_2O_5, *initially* 0·1212M., *in* 1 : 9-NMCT *at* —9·77°.

nearly linear, and yet others which are markedly sigmoid. The exponential and sigmoid types are illustrated in Figs. 7 and 8. A careful study of all the curves shows that, as before, we are dealing with a limiting non-catalytic reaction, upon which varying amounts of an autocatalytic reaction are superposed.

The main circumstances favouring the non-catalysed reaction, as against the autocatalytic reaction, are, as before, a sufficiently high temperature, and a sufficiently low initial concentration of that reactant which is in deficit—in the present case, the aromatic compound. But again, neither requirement, considered separately, is absolute: rather accurately exponential reactions have been observed at −5° with initial concentrations of aromatic compound up to 0·05M.; and approximately exponential reactions have been followed at temperatures as low as −25°, although with considerably smaller initial concentrations of aromatic compound, *e.g.*, 0·01M. In general, a low temperature, and a high initial concentration of aromatic compound (the dinitrogen pentoxide remaining in constant excess), favour the autocatalytic reaction, which is also greatly strengthened if small amounts of nitric acid are introduced into the reaction system [cf. Section (4.2)].

FIG. 7. FIG. 8.

Illustrating kinetic types of nitration by dinitrogen pentoxide when the dinitrogen pentoxide is kept in constant excess.



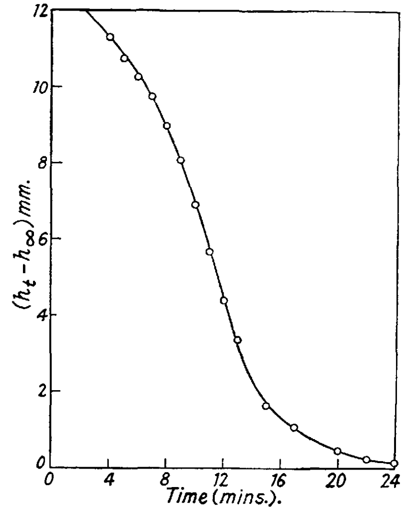


FIG. 7.—" *Exponential*" *reaction illustrated by Run* 685: *Nitration of* C_6H_5F, *initially* 0·011M., *by* N_2O_5, *initially* 0·402M., *in* CCl_4 *at* −24·55°.

FIG. 8.—" *Sigmoid*" *reaction, illustrated by Run* 684: *Nitration of* C_6H_5F, *initially* 0·030M., *by* N_2O_5, *initially* 0·402M., *in* CCl_4 *at* −24·55°.

(3) *Observations on the Limiting Non-catalytic Reaction.*

(3.1) *Molecularity of the Reaction.*—The observations that nitration follows an approximately exponential law when either the aromatic compound is in large excess over the dinitrogen pentoxide, or the latter is in large excess over the former, can evidently be correlated by the assumption that the limiting reaction is bimolecular, the rate equation being

$$\text{Rate} = k_2[\text{ArH}][N_2O_5]$$

This can be confirmed. From any one experiment with one reactant, say, the aromatic compound, in large excess, an approximate first-order rate constant can be derived. If a block of such experiments be conducted with different concentrations of aromatic compound (always in large excess over the dinitrogen pentoxide), all other conditions being the same, then the deduced first-order rate constants should be proportional to the concentrations of aromatic compound; and therefore, the second-order rate constants, obtained by dividing the first-order constants by the concentrations of aromatic compound, should not vary. How far this is true can be seen from Table I.

TABLE I.

First-order rate constants (k_1 *in* $sec.^{-1}$) *and second-order rate constants* (k_2 *in* $sec.^{-1}$ *g.-mol.*$^{-1}$ *l.*) *for exponential-type nitrations with dinitrogen pentoxide, the aromatic compound being in excess.*

No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.	No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.
Temperature 10·06° :											
				ArH = p-$C_6H_4Cl_2$.							
253	CCl_4	0·573	0·0514	1·82	3·18	260	1 : 9-NMCT	1·278	0·0405	8·52	6·67
255	,,	0·821	0·0514	2·51	3·06	266	,,	1·331	0·0552	8·50	6·39
257	1 : 9-NMCT	0·576	0·0466	4·63	8·04	265	,,	1·782	0·0552	10·31	5·79
256	,,	0·824	0·0466	5·94	7·21	262	3 : 7-NMCT	0·639	0·0385	9·57	14·98
267	,,	0·880	0·0552	6·40	7·27	263	,,	0·967	0·0385	11·97	12·38
261	,,	0·952	0·0405	7·14	7·50	264	,,	1·298	0·0385	13·96	10·78
Temperature 14·99° :											
272	CCl_4	0·696	0·0445	3·53	5·07	390	CCl_4	1·181	0·0610	6·29	5·33
389	,,	0·854	0·0610	4·51	5·28	400	,,	1·558	0·0424	8·60	5·52
403	,,	0·867	0·0424	4·97	5·74	388	,,	1·940	0·0610	10·29	5·30
273	,,	1·042	0·0391	5·65	5·42						
				ArH = p-C_6H_4ClBr.							
412	,,	0·535	0·0378	2·70	5·21	405	CCl_4	0·973	0·0424	5·70	5·86
411	,,	0·688	0·0378	3·75	5·45	404	,,	1·201	0·0424	6·38	5·31
				ArH = p-$C_6H_4Br_2$.							
413	,,	0·446	0·0378	2·36	5·29	414	CCl_4	0·745	0·0378	4·53	6·08
				ArH = o-$C_6H_4Cl_2$.							
420	,,	0·611	0·0427	5·04	8·25	423	CCl_4	1·106	0·0427	8·88	8·03
421	,,	0·880	0·0427	7·21	8·19	422	,,	1·420	0·0427	10·95	7·71
				ArH = m-$C_6H_4Cl_2$.							
418	,,	0·658	0·0669	8·20	12·46	415	CCl_4	1·069	0·0557	12·91	12·08
419	,,	0·889	0·0669	10·68	12·01	416	,,	1·342	0·0557	16·08	11·98
				ArH = $C_6H_5{\cdot}CO_2Me$.							
429	,,	0·643	0·0434	10·51	16·34	431	CCl_4	1·211	0·0434	17·21	14·21
430	,,	0·833	0·0434	12·75	15·30	432	,,	1·499	0·0434	20·31	13·43
				ArH = $C_6H_5{\cdot}CO_2Et$.							
192	,,	0·546	0·0410	10·21	18·70	196	CCl_4	0·871	0·0329	14·52	16·67
195	,,	0·578	0·0329	10·54	18·24	383	,,	1·076	0·0529	16·28	15·31
384	,,	0·692	0·0529	12·23	17·67	194	,,	1·093	0·0410	17·39	15·91
386	,,	0·802	0·0529	12·62	16·98	385	,,	1·354	0·0529	19·51	14·41
				ArH = $C_6H_5{\cdot}CO_2Bu^t$.							
433	,,	0·566	0·0434	14·40	25·44	441	CCl_4	0·902	0·0571	19·98	22·15
439	,,	0·734	0·0571	17·44	23·76	440	,,	1·069	0·0571	22·10	20·67
				ArH = p-$C_6H_4Me{\cdot}CO_2Me$.							
444	,,	0·556	0·0313	10·35	18·61	443	CCl_4	0·887	0·0571	16·02	18·06
198	,,	0·643	0·0329	11·97	18·61	445	,,	1·127	0·0313	17·76	15·76
442	,,	0·658	0·0571	13·07	19·86						
				ArH = m-$C_6H_4Cl{\cdot}CO_2Et$.							
451	,,	0·616	0·0650	5·43	8·81	450	CCl_4	1·170	0·0650	9·71	8·30
446	,,	0·903	0·0437	7·77	8·60	452	,,	1·190	0·0650	10·38	8·72
				ArH = p-$C_6H_4Cl_2$.							
434	1 : 9-NMCT	0·627	0·0479	8·55	13·64	437	1 : 9-NMCT	0·998	0·0479	12·94	12·97
436	,,	0·813	0·0479	11·11	13·66	435	,,	1·285	0·0479	15·13	11·77
				ArH = 1 : 2 : 4-$C_6H_3Cl_3$.							
392	,,	0·553	0·0487	3·77	6·82	396	1 : 9-NMCT	0·912	0·0487	5·65	6·10
393	,,	0·696	0·0487	4·31	6·19	395	,,	1·056	0·0487	6·29	5·96
397	,,	0·796	0·0487	4·81	6·04	394	,,	1·201	0·0487	6·96	5·80
Temperature 20·00° :											
				ArH = p-$C_6H_4Cl_2$.							
379	CCl_4	0·480	0·0443	4·94	10·29	382	CCl_4	1·080	0·0443	9·97	9·23
380	,,	0·680	0·0443	6·59	9·69	381	,,	1·785	0·0443	16·35	9·16
351	1 : 9-NMCT	0·501	0·0481	12·31	24·58	353	1 : 9-NMCT	1·026	0·0481	23·96	25·35
352	,,	0·633	0·0481	15·76	24·90						

TABLE I.—(*continued*).

No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.	No.	Solvent.	$[ArH]_0$.	$[N_2O_5]_0$.	10^4k_1.	10^4k_2.
Temperature 20·00° :											
				ArH = 1 : 2 : 4-$C_6H_3Cl_3$.							
343	,,	0·708	0·0486	8·74	12·34	340	1 : 9-NMCT	1·149	0·0431	11·44	9·96
342	,,	0·825	0·0431	9·14	10·67	368	,,	1·250	0·0342	12·98	10·04
				ArH = o-$C_6H_4(CO_2Et)_2$.							
346	,,	0·589	0·0586	8·26	14·02	349	1 : 9-NMCT	0·896	0·0481	12·45	13·90
347	,,	0·742	0·0486	10·61	14·30	350	,,	1·202	0·0481	15·74	13·09
				ArH = p-$C_6H_4Cl_2$.							
289	3 : 7-NMCT	0·708	0·0618	30·8	43·5	310	3 : 7-NMCT	0·785	0·1042	32·6	41·6
				ArH = 1 : 2 : 4-$C_6H_3Cl_3$.							
315	,,	0·569	0·0698	11·82	20·77	311	3 : 7-NMCT	1·168	0·0367	19·24	16·47
312	,,	0·775	0·0367	14·91	19·24	314	,,	1·190	0·0367	19·46	16·35
316	,,	0·869	0·0698	16·35	18·79						

It appears from the data that, as the initial concentration of aromatic compound is increased, the first-order rate constant always increases to a comparable extent, whilst the second-order constant either remains constant or changes (usually falls) only slightly; a fall of the order of 10%, while the concentration of aromatic compound is being increased 100%, is not uncommon. We should not expect exact constancy in the second-order constant for several reasons: the reactions, or most of them, are not quite kinetically pure; the excess of aromatic compound is not an infinite excess; and the proportion in which the aromatic compound is present is sufficient to render it an important constituent of the medium. It seems that the second-order constant shows a greater tendency to drop, with increasing concentration of the aromatic compound, when the nitrations are conducted in mixed nitromethane–carbon tetrachloride solvents than when they are carried out in pure carbon tetrachloride. As an example, the figures for the nitration of p-dichlorobenzene in 1 : 9-NMCT at 10° may be compared with those applying to the nitration of the same compound in carbon tetrachloride at 15°. The difference can be understood on the basis, which will be illustrated below, that nitromethane is a substantially faster solvent than carbon tetrachloride for these nitrations. Probably the aromatic halogen compounds belong to the class of somewhat slow solvents, and are much more nearly comparable, as solvents, to carbon tetrachloride than to nitromethane. Thus, in the presence of nitromethane, they will act as diluents towards the latter, diminishing its accelerative effect; and hence they will reduce bimoleuclar reaction rates much more than if the solvent were only carbon tetrachloride. Aromatic compounds which do not contain halogen, in particular, the alkyl benzoates and methyl p-toluate, appear to be even slower, as solvents, than carbon tetrachloride; for even in this solvent, as well as in the mixed solvents, their presence in considerable concentration reduces the bimolecular reaction rates. On the whole, then, the bimolecular nature of the limiting reaction seems confirmed by these comparisons.

(3.2) *Solvent Effect on the Bimolecular Reaction Rate.*—The effect of the solvent on the rates of the bimolecular reaction is illustrated by the second-order rate constants assembled in Table II. Owing to the effect of the aromatic compounds in acting as rate-reducing components of the more polar media, we ought to compare rate constants which have been extrapolated to zero concentration of the aromatic compound. This has been done for the halogen compounds, the necessary data being available. It could not be done for the two esters for lack of suitable data; and for these esters, therefore, the comparison of solvents has been made for finite, but fixed, concentrations of aromatic compound.

These figures show that polar solvents accelerate bimolecular nitration by dinitrogen pentoxide. But the acceleration is very moderate, a factor of the order of 6 apparently sufficing to cover the whole range from non-dipolar carbon tetrachloride to highly polar nitromethane. By way of contrast, the solvent effect on nitrations by nitric acid in organic solvents may be recalled (Part II, *J.*, 1950, 2400): alike for the zeroth-order and the first-order reactions, as observed in the presence of a constant excess of nitric acid, factors of the order of 40 separate the rates in acetic acid from those in nitromethane; and we would certainly expect very much larger factors between corresponding rates in carbon tetrachloride, if they could be measured, and the rates in nitromethane.

(3.3) *Salt Effects on Reaction Rate.*—Added salts, nitrates as well as other salts, have a strong accelerative effect on bimolecular nitration rates in NMCT solvents. This is illustrated in Table III.

TABLE II.

Effect of solvent on second-order rate constants (10^4k_2 *with* k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *of bimolecular nitration by dinitrogen pentoxide.*

ArH :	p-$C_6H_4Cl_2$.			*as*-$C_6H_3Cl_3$.	Ph·CO_2Et.	o-$C_6H_4(CO_2Et)_2$.
$[ArH]_0$:	zero	zero	zero	zero	0·5M.	0·8M.
Temp. :	10°	15°	20°	20°	20°	20°
Solvent.						
CCl_4	—	5·45	8·85	—	32 [1]	—
$CHCl_3$	—	—	—	—	44·1	—
1 : 9-NMCT	9·04	16·5	26·5	12·33	—	14·1
3 : 7-NMCT	18·5	—	—	24·73	—	—
5 : 5-NMCT	—	—	—	27·6 [2]	—	20·2
7 : 3-NMCT	—	—	—	—	—	22·7
9 : 1-NMCT	—	—	—	—	—	27·0
MeCN	—	—	—	—	—	29 [3]
$MeNO_2$	—	—	—	—	—	30·7

[1] Calculated as 1·7 times the value at 15°. [2] Extrapolation based on two runs only.
[3] Value at $[ArH]_0$ = 1·1M.

TABLE III.

Effect of added salts on second-order rate constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *of bimolecular nitration of* p-*dichlorobenzene in a nitromethane–carbon tetrachloride solvent.*

($[ArH]_0$ ~0·8M., $[N_2O_5]_0$ ~0·05M., Solvent 1 : 9-NMCT, throughout.)

No.	[Salt.]	10^4k_2.	No.	[Salt.]	10^4k_2.	No.	[Salt.]	10^4k_2.
(*Salt :* Tetraethylammonium picrate. *Temp. :* 10·03°.)			(*Salt :* Tetraethylammonium hydrogen sulphate. *Temp. :* 20·00°.)			(*Salt :* Tetraethylammonium nitrate. *Temp. :* 24·80°.)		
536	0	7·99	631	0	24·4	735	0	33·9
541	0·0018	12·51	633	0·00046	32·6	755	0·00045	37·5
539	0·0025	22·79	634	0·00093	38·7	756	0·00060	44·8
540	0·0040	30·56	637	0·0012	43·1			

Little can be said concerning the quantitative aspect of the effect, partly because one is limited to very small salt concentrations by the low solubilities of the salts, and partly because the salts appreciably disturb the kinetic form of the reaction, thereby divesting the rate constants of an exact significance. The disturbance can be described qualitatively by stating that the accelerative effect of a salt in any one experiment is less near the end of the run than near the beginning.

(3.4) *Effect of Added Nitric Acid on the Bimolecular Reaction Rate.*—Added nitric acid accelerates nitration by dinitrogen pentoxide. In some cases, particularly at the lower temperatures, the effect is very strong, and involves a pronounced change of kinetic form ; for not only is there catalysis, but also the autocatalysis is notably increased. At higher temperatures, the whole accelerative effect is weaker, though it is still considerable ; but the induced autocatalysis is much weaker, so that substantial increases of rate can be realised without serious complication to the kinetic form of the reaction. We illustrate this weaker and simpler type of effect in Table IV, for the nitration of p-dichlorobenzene in carbon tetrachloride at 20° ; similar results have been obtained for the nitration of 1 : 2 : 4-trichlorobenzene in carbon tetrachloride at 25°.

TABLE IV.

Effect of added nitric acid on second-order rate constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *of bimolecular nitration of* p-*dichlorobenzene in carbon tetrachloride at* 20·03°.

($[ArH]_0$ ~0·6M., $[N_2O_5]_0$ ~0·04M., throughout.)

Run no.	$[HNO_3]_0$.	10^4k_2.	$11 + 80c^2$.	Run no.	$[HNO_3]_0$.	10^4k_2.	$11 + 80c^2$.
624	0	10·1	11·0	628	0·174	33·1	35·5
625	0·071	16·1	15·0	629	0·181	37·5	37·2
626	0·080	16·6	16·1	630	0·251	61·1	61·5

The experimental rate constants in Table IV agree fairly well with the requirements of the equation $10^4k_2 = 11 + 80c^2$, where $c = [HNO_3]_0$. The catalysed reaction is thus of approximately second order with respect to the nitric acid catalyst, over this range of conditions.

(3.5) *Effect of Temperature on the Bimolecular Reaction Rate.*—This has not been studied over a sufficient range of temperature, with any one aromatic compound and solvent, to allow good Arrhenius parameters to be given. It can, however, be computed from the measured rates that the activation energies of the bimolecular reactions of *p*-dichlorobenzene in carbon tetrachloride and in 1 : 9-NMCT, and of 1 : 2 : 4-trichlorobenzene in the latter solvent, are close to 17 kcals., whilst the corresponding non-exponential factors of the Arrhenius equation have values in the neighbourhood of 10^{10} sec.$^{-1}$ g.-mol.$^{-1}$ l.

(3.6) *Effect of Aromatic Substituents on the Bimolecular Reaction Rate.*—Some rate constants for the bimolecular nitration by dinitrogen pentoxide of different aromatic compounds, in the same solvent at the same temperature, are collected in Table V. The values given have been extrapolated, where necessary, in order to eliminate the medium effect of the aromatic compound itself.

TABLE V.

Comparable second-order rate constants (k_2 *in sec.*$^{-1}$ *g.-mol.*$^{-1}$ *l.*) *for the bimolecular nitration of aromatic compounds by dinitrogen pentoxide.*

(Values correspond to $[ArH]_0 = 0$. Solvent CCl_4, temp. 15°, throughout.)

ArH.	10^4k_2.	ArH.	10^4k_2.	ArH.	10^4k_2.	ArH.	10^4k_2.
p-$C_6H_4Cl_2$	5·4	*o*-$C_6H_4Cl_2$	8·5	$C_6H_5{\cdot}CO_2Me$...	18·2	*p*-$Me{\cdot}C_6H_4{\cdot}CO_2Me$	21·8
p-C_6H_4ClBr ...	5·5	*m*-$C_6H_4Cl_2$.........	12·1	$C_6H_5{\cdot}CO_2Et$ ...	21·7	*m*-$Cl{\cdot}C_6H_4{\cdot}CO_2Et$	8·7
p-$C_6H_4Br_2$	5·7	1 : 2 : 4-$C_6H_3Cl_3$	2·5[1]	$C_6H_5{\cdot}CO_2Bu^t$	30·2	*o*-$C_6H_4(CO_2Et)_2$ ...	3·0[2]

[1] From observation in 1 : 9-NMCT at 15°, by division by 3·0 (cf. Table II). [2] From observation in 1 : 9-NMCT at 20°, allowing a factor 1·7 for the temperature difference (cf. Table I).

The only monosubstituted benzenes in the list are the benzoic esters. As to these, the illustrated accelerating effect of homology in the alkyl group is theoretically consistent with the known effect of homology in reducing the proportion in which *m*-nitration takes place (cf. Ingold, *Rec. Trav. chim.*, 1929, **48**, 801).

The figures for the di- and tri-substituted benzenes show that the methyl substituent is slightly activating, that the halogens deactivate moderately, chlorine and bromine behaving very similarly, and that carbalkoxyl groups deactivate more strongly. All this is qualitatively consistent with theory, and with the results derived for monosubstituted benzenes by the competition method (cf. Bird, Ingold, and Smith, *locc. cit.*); but the differences now obtained for the polysubstituted compounds are of distinctly smaller magnitude than those given by the competition method for the monosubstituted benzenes.

Of the three dichlorobenzenes, the *m*-compound is the least deactivated. This is intelligible, because halogens deactivate *m*-positions more strongly than they do *o*- and *p*-positions (*locc. cit.*); and *m*-dichlorobenzene is the only isomeride having positions available for substitution which are *not meta* with respect to any chlorine atom. Steric hindrance may exert a special effect in reducing the rate for *p*-dichlorobenzene, substitution in which is necessarily *ortho* with respect to one chlorine atom.

(4) *Observations on the Autocatalytic Reaction.*

(4.1) *Influence of Solvent, Temperature, and Concentration.*—It has not been found possible to represent the rates of the autocatalysed reactions by any single, chemically significant equation; and therefore our diagnostic material concerning this reaction consists essentially of its qualitative features, which, fortunately, are quite striking. Some features of the autocatalytic reaction have been described and illustrated already (Section 2.2); we shall here summarise them, and then add to them.

No major effect on the intensity of autocatalysis appears to result from a change of solvent from carbon tetrachloride to the mixed solvent 1 : 9-NMCT.

A reduction in the temperature of nitration has a notable effect in advancing the onset, and increasing the intensity, of autocatalytic acceleration, though a temperature lower than some fixed limit seems not to be a definite requirement for such acceleration if other conditions are favourable.

An increase in the concentration of whichever reactant is in deficit, whether it be the aromatic compound or the dinitrogen pentoxide—in other words, an increase in the concentration in which reaction products can be formed—leads to a similar advancement and intensification of the autocatalysis.

Nitric acid must be a product of nitration by dinitrogen pentoxide. It has been shown in Section 3.4 that the limiting bimolecular reaction is considerably accelerated by added nitric acid. Evidently the production of nitric acid by nitration might account for the autocatalysis.

(4.2) *Effect of Added Nitric Acid on the Autocatalysis.*—It has been observed that initially added nitric acid not only accelerates nitration from the outset, but also increases the autocatalysis of the reaction. When the reaction observed in the absence of added nitric acid follows a course which is very close to that of the limiting bimolecular reaction, then the effect of added acid on the autocatalysis is not very noticeable. Advantage was taken of this for the purpose of studying the simple catalysis by nitric acid of the bimolecular reaction, as described in Section 2.4. However, the effect of added nitric acid on autocatalysis is very striking, when the reaction in the absence of nitric acid shows an appreciable (but still not large) departure from the strict bimolecular form—for instance, if it gives a reaction–time curve of shape intermediate between what we have termed the " exponential " and " linear " forms, one reactant being in constant excess. In such a case, added nitric acid may not only increase the rate from the commencement; it may also lead to the development of an actual acceleration during an intermediate period of the run, so that the reaction–time curve now assumes a sigmoid form.

This effect is illustrated in Fig. 9, in which two reaction–time curves are shown. The runs represented by these curves were strictly comparable as to initial conditions, except that a small amount of nitric acid was added to one of them. The slower of the two is the control, the rate of which drops continuously as reaction proceeds. The other reaction (the one affected by the added nitric acid) is not only generally faster, but also exhibits a rising rate during a considerable part of its course.

FIG. 9.

Effect of added nitric acid.

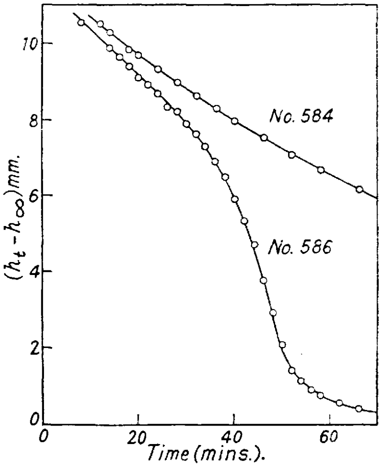


FIG. 10.

Effect of added sulphuric acid.

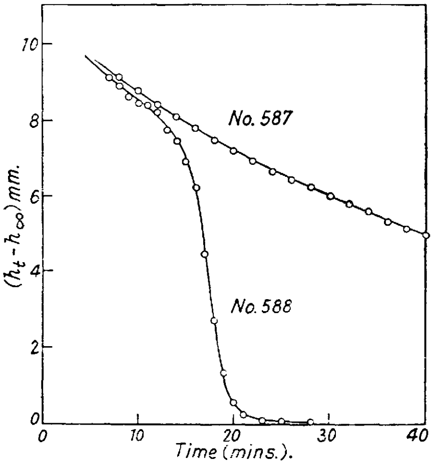


FIG. 9.—*Nitration of* C_6H_5Cl, *initially* 1·375M., *by* N_2O_5, *initially* 0·049M., *in* CCl_4 *at* −10·35°. *Run* 584. *No initial* HNO_3. *Run* 586. *Initially added* HNO_3 = 0·021M.

FIG. 10.—*Nitration of* C_6H_5Cl, *initially* 1·375M., *by* N_2O_5, *initially* 0·045M., *in* CCl_4 *at* −10·35°. *Run* 587. *No initial* H_2SO_4. *Run* 588. *Initially added* H_2SO_4 = 0·0019M.

Assuming the autocatalysis to be due to formed nitric acid, these results mean that, the higher the instantaneous concentration of nitric acid, the more sensitive is the rate to a given increment of produced nitric acid. In other words, the dependence of the rate on nitric acid must involve a higher power of concentration than the first. Even a second-power dependence is found to be insufficient to account for the magnitude of some of the effects observed (cf. Section 5).

(4.3) *Effect of Added Sulphuric Acid on the Autocatalysis.*—Qualitatively similar results have been obtained by the initial addition of sulphuric acid. Again the strongest effects on the autocatalysis arise in nitrations which, in the absence of added acid, show an appreciable (but still only a small) departure from the limiting bimolecular form. Sulphuric acid is more potent than nitric acid for the intensification of the autocatalysis.

An illustration is given in Fig. 10. Again the reaction in which no sulphuric acid is added initially, that represented by the upper curve, becomes progressively slower throughout its course (only part of which is shown in the diagram), whilst a reaction carried out under identical conditions, except that a small amount of sulphuric acid was added initially, develops, as the lower curve illustrates, a powerful autocatalytic acceleration.

Since the action of sulphuric acid on an excess of dinitrogen pentoxide must obviously give rise to nitric acid, the effects of the two acids in promoting the autocatalysis of nitration by dinitrogen pentoxide are evidently closely connected.

(5) *Discussion of the Mechanisms of Nitration.*

(5.1) *A Mathematical Model illustrating the Kinetic Forms of Nitration.*—Consider the consequences of supposing that the rate of nitration, v, of ArH by N_2O_5 is expressed by the equation

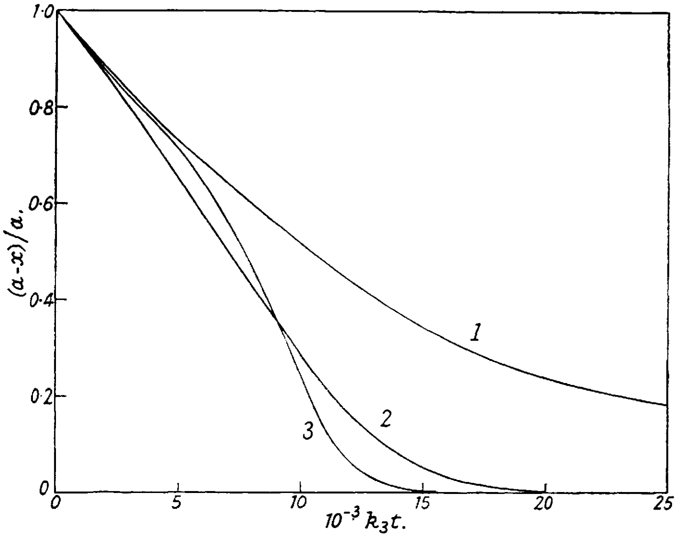
$$v = k_0(a - x) + k_3(a - x)(b + x)^3$$

where a = initial $[N_2O_5]$, if ArH is in constant excess, or
= initial [ArH], if N_2O_5 is in constant excess,
b = initial $[HNO_3]$, and
x = formed $[HNO_3]$ = formed $[ArNO_2]$.

This equation assumes the total reaction to be the sum of an uncatalysed part and a catalysed part. The uncatalysed reaction has been shown (Section 2.2 and 3.1) to be bimolecular: accordingly its rate must be of first-order form, as the equation represents it, if, in accordance with the conditions of our measurements, one reactant is taken to be in constant excess. The catalysed reaction is assumed to be of the same molecularity with respect to the reactants, and therefore, under the conditions of the measurements, to be of the first order with respect to either reactant. The catalysed reaction is assumed to depend also on the third power of the concentration of nitric acid. We shall not now attempt to justify the use of the third power in the present illustration; but it will be suggested in Section 5.2 that this power lies within the range of a series of powers which are thought to be in general simultaneously operative.

FIG. 11.

Graphs of the rate equation.



(1) : $a = 0{\cdot}04, b = 0{\cdot}00, k = 0{\cdot}04$. (2) : $a = 0{\cdot}04, b = 0{\cdot}04, k = 0{\cdot}04$. (3) : $a = 0{\cdot}10, b = 0{\cdot}00, k = 0{\cdot}04$.

The integrated form of the equation is

$$k_3t = \frac{1}{(a+b)^3 + k^3} \cdot \ln\frac{a}{a-x} + \frac{1}{3k^2(a+b+k)} \cdot \ln\frac{k+b+x}{k+b} + \frac{2k-(a+b)}{6k^2\{(a+b)^2 - k(a+b) + k^2\}} \cdot \ln\frac{(x+b)^2 - k(x+b) + k^2}{b^2 - kb + k^2} + \frac{(a+b)}{\sqrt{3}k^2\{(a+b)^2 - k(a+b) + k^2\}} \cdot \left\{\tan^{-1}\frac{2(x+b)-k}{\sqrt{3}k} - \tan^{-1}\frac{2b-k}{\sqrt{3}k}\right\}$$

where $k = (k_0/k_3)^{1/3}$. Some graphs of this equation are shown in Fig. 11. It is immediately apparent that graphs 1, 2, and 3 are qualitatively similar to the experimental curves shown in Figs. 1, 2, and 3, and in some of the other figures in this paper. In particular, we find that, when a is low and b is zero, curves are obtained, which may be of approximately exponential form, and in any case represent a velocity continuously diminishing with time (graph 1). When a is higher, and b is still zero, curves of greater slope are obtained, which may run nearly linearly for a large part of their length. When a is higher still, with b still zero, the curves assume a sigmoid form, representing an autocatalytic acceleration at some time after the commencement of reaction (graph 3). We observe a similar series of changes when, starting again from the case in which a is low and b is zero, a is kept constant and b is given a succession of increasing finite values : the curves again pass through a nearly linear form (graph 2), and finally become sigmoid.

Evidently two of the factors which have been found to control the incidence of autocatalytic acceleration are directly reproduced in this model, *viz.*, the intensification of autocatalysis on increasing the initial concentration of whichever reactant is in deficit, and its intensification by the initial introduction of nitric acid. As to the third factor, *viz.*, temperature, we may, quite generally, expect the fourth-order reaction to be less important at higher temperatures, as it would have a lower entropy and energy of activation than the first-order reaction.

We have investigated the effect of assuming catalysis by nitric acid according to other powers of its concentration than the third. The assumption of a first-power, or of a second-power, catalysis leads to curves which show some flattening relatively to the non-catalytic curve, but which do not assume a markedly sigmoid form. On the other hand, as one might expect, the use of the fourth power of the nitric acid concentration produces sigmoid curves which are more sharply inflected than that illustrated.

(5.2) *Chemical Interpretation of the Kinetics of the Catalysed Reaction.*—Let us introduce the hypothesis, at first in a general form, that nitric acid catalyses nitration by dinitrogen pentoxide by combining with it to form aggregates, which may be of various sizes :

$$N_2O_5 + nHNO_3 \rightleftharpoons N_2O_5,nHNO_3, \text{ where } n = 1, 2, 3, \ldots$$

This equation is intended to indicate only the composition, and not the chemical nature, of the aggregates. Each aggregate is assumed to be capable of participating in nitration. For conditions in which one reactant, let us say, the aromatic compound, is in constant excess, the expression for the reaction rate must take such a form as the following, *viz.*,

$$v = \sum_{n=0}^{\infty} k_n[X_n]$$

where $X_n = N_2O_5,nHNO_3$. The uncatalysed portion of the rate is included through the term in $n = 0$. Assuming rapidly attained equilibria, we have

$$[X_n] = K_n[N_2O_5][HNO_3]^n$$

the K_n being equilibrium constants; and therefore the rate equation can be written

$$v = \Sigma k_n K_n(a - x)(b + x)^n$$

Here $K_0 = 1$, and k_0 has values which can readily be determined by experiment. The higher K_n must diminish as n increases beyond a certain point, because the size of the aggregates must be limited for steric and dynamical reasons. We shall show presently that k_n should be expected to increase with n over a certain range. Hence it may well be that, under our conditions, the term $n = 0$, and some intermediate term, such as $n = 3$, for which k_nK_n is maximal, will represent the two most important parts of the rate.

This generalised hypothesis evidently interprets, at least as well as the simplified model did, the main kinetic features of nitric acid catalysis, especially the factors which determine the incidence and intensity of autocatalytic acceleration. The effect of temperature may be described more specifically than before : the aggregates will be formed exothermically; and hence, as the temperature is raised, they will be reduced in size, and the larger ones in number; and thus sensitivity to catalysis by nitric acid will be reduced at higher temperatures.

Let us now consider the nature of the aggregates more particularly. We know that dinitrogen pentoxide dissolved in organic solvents, such as carbon tetrachloride and nitromethane, consists entirely of covalent molecules. We also know that, when dissolved in nitric acid, dinitrogen pentoxide consists entirely of nitronium and nitrate ions, which are strongly and exothermically solvated by nitric acid (Ingold and Millen, *J.*, 1950, paper no. 510 ; Gillespie, Hughes, and Ingold, *ibid.*, paper no. 504). Therefore we must expect that, when small amounts of nitric acid are added to a solution of dinitrogen pentoxide in some aprotic solvent, the nitric acid molecules will concentrate towards each molecule of dinitrogen pentoxide, and, when present in sufficient amount to solvate ions and thus to liberate energy, will bring about ionisation of the dinitrogen pentoxide, and perhaps dissociation of the ions.

The smallest number of nitric acid molecules that can readily be pictured as effective for the ionisation of a molecule of dinitrogen pentoxide is 2, *i.e.*, one molecule to take care of each ion. Thus it is reasonable to suppose that the limit of weak catalysis by nitric acid might be represented by the term $n = 2$. The weak catalysis observed at higher temperatures does in fact operate according to a quadratic law, as has been illustrated in Section 3.4.

The solvation number of dinitrogen pentoxide dissolved in pure nitric acid has been found to be 4, two nitric acid molecules being combined with each of the two ions (Gillespie, Hughes, and Ingold, *loc. cit.*). This solvation number is likely to depend in part on the exothermicity of transfer of a nitric acid molecule from the nitric acid medium to the ions. The exothermicity of a transfer of nitric acid from a largely aprotic medium to the ions might well be greater. Hence the conclusion is, not that $n = 4$ necessarily represents a maximum for aggregate formation from an ample supply of nitric acid, but that n can rise at least as high as 4 in aprotic solvents under suitable conditions. Thus we believe that the kinetic terms corresponding to $n = 2$, 3, and 4 at least can be effective, though which of them will be dominating will depend on the circumstances.

The ionic dissociation is doubtless endothermic, and hence we must expect that increased exothermic solvation of the ions by nitric acid will increase the dissociation. Thus the larger the value of n, the more will the nitronium ion behave like a " free " ion, *i.e.*, one liberated from the influence of a neutralising anion. This is the basis of our view (cf. Section 1.1) that the rate constant k_n of nitration by X_n will increase with n over the range of effective values of n.

To summarise, we find that all the main kinetic features of the catalysis by nitric acid, and of the autocatalysis, of nitration by dinitrogen pentoxide can be interpreted on the basis that the nitric acid molecule exerts its catalytic effect by aggregating around the originally covalent dinitrogen pentoxide molecules, thereby causing ionisation and ionic dissociation. The nitrating entity in the catalysed nitration is thus the nitronium ion, which is progressively freed by the solvating nitric acid from the influence of anions. Nitration by the nitronium ion involves, as was shown in Part II (*J.*, 1950, 2400), the slow addition of the nitronium ion to the aromatic molecule, with the formation of a complex cation, which rapidly ejects a proton. In the present case, the proton must eventually combine with a nitrate ion. The steps may be formulated as follows :

$$\begin{aligned}
NO_2{\cdot}O{\cdot}NO_2 + (x + y)HNO_3 &\overset{\text{fast}}{\rightleftharpoons} \overset{-}{N}O_2(xHNO_3) + \overset{-}{N}O_3(yHNO_3) \\
ArH + \overset{+}{N}O_2(xHNO_3) &\xrightarrow{\text{slow}} \overset{+}{A}rH(NO_2) + xHNO_3 \\
\overset{+}{A}rH(NO_2) &\xrightarrow{\text{fast}} ArNO_2 + \overset{+}{H} \\
\overset{+}{H} + \overset{-}{N}O_3(yHNO_3) &\xrightarrow{\text{fast}} (y + 1)HNO_3
\end{aligned}$$

Catalysis by sulphuric acid is attributed to the direct formation of nitronium ions, and, simultaneously, of nitric acid molecules; and, in minor degree, to the replacement of nitrate ions by the less nucleophilic hydrogen sulphate ions.

(5.3) *Nature of the Nitrating Agent in the Uncatalysed Reaction.*—The above analysis of the mechanism of the catalysed reaction involves the conclusion that the nitrating entity in the uncatalysed reaction is the covalent dinitrogen pentoxide molecule. Several independent indications confirm this conclusion.

Suppose that we did not accept it. Then we might try to account for the kinetic order of the uncatalysed reaction on the basis that, in aprotic solvents, there is a rapidly attained equilibrium between covalent dinitrogen pentoxide and its ions, and that the nitronium ion, in small stationary concentration, effects the nitration. Any such equilibrium proportion of nitronium ions, and of nitrate ions, would have to be assumed to be very small, since in fact it is beyond the limits of detection by ordinary physical means. It follows that the rate of the uncatalysed reaction must be very strongly depressed by small amounts of added nitrate ions (cf. Part II, *J.*, 1950, 2400). This is not according to the evidence: it was shown in Section 3.3 that tetraethylammonium nitrate (like tetraethylammonium picrate and the hydrogen sulphate) accelerates the uncatalysed reaction.

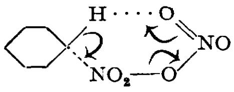
The further point arises that, with all three salts, the acceleration is very large, the amount of salt needed to double the reaction rate in 1 : 9-NMCT being in each case of the order of M/1000. We explain this effect as a kind of catalysis, which depends, like catalysis by nitric acid, on the great ease with which covalent dinitrogen pentoxide molecules will split into ions in a suitable environment. We assume that, in this case, ionisation of the dinitrogen pentoxide is promoted by association with the ions of the added salt. That pre-formed ions do promote the ionisation of dinitrogen pentoxide molecules is suggested by the circumstance that each such molecule splits into ions as it adds itself to the ionic lattice of a crystal of dinitrogen pentoxide (Ingold, Millen, and Poole, *Nature*, 1946, **158**, 480; Millen, *J.*, 1950, paper no. 509), which is growing, either in the vapour, or in a solution containing, as solute, only the molecular form of the substance.

Again, the solvent effect on the bimolecular reaction rate indicates that this reaction occurs between the aromatic compound and the non-ionised dinitrogen pentoxide molecule. It was shown in Section 3.2 that polar solvents increase nitration rate, but do so only slightly, a factor of the order of 6 covering the whole range of investigated solvents from carbon tetrachloride to nitromethane. Since the initial materials are indubitably neutral molecules, this small solvent effect makes it certain that the products formed immediately on completion of the rate-determining stage are neutral molecules, and not ions. Therefore the entity which attacks the aromatic molecule must be the dinitrogen pentoxide molecule, and not the nitronium ion. The observed small solvent effect is consistent with the idea of a transition state which, though neutral as a whole, is dipolar, and because of its polarity is somewhat more solvated than are the original reactants.

Summarising, we conclude that the uncatalysed nitration of aromatic compounds by dinitrogen pentoxide in aprotic solvents is a single-stage bimolecular process, involving direct attack by the non-ionised dinitrogen pentoxide molecule :

$$\mathrm{ArH} + \mathrm{NO_2{\cdot}O{\cdot}NO_2} \longrightarrow \mathrm{ArNO_2} + \mathrm{HNO_3}$$

Speculatively, one may suggest a cyclic form (inset) for the transition complex.



One other point may be mentioned, even though it has yet been studied only in a preliminary way. It has been noticed that the proportions in which mononitro-isomerides are formed in the nitration of an aromatic compound by the nitric-acid-catalysed reaction of dinitrogen pentoxide, and by the non-catalysed reaction of this nitrating agent, are in some cases very different. Thus, in the catalysed nitration of chlorobenzene by dinitrogen pentoxide, the proportion in which *p*-chloronitrobenzene is formed is practically the same as that in which Holleman found this isomeride in the product of the nitration of chlorobenzene by nitric acid; whereas, in the non-catalysed nitration of chlorobenzene by dinitrogen pentoxide, the proportion of formed *p*-chloronitrobenzene is distinctly smaller. This is consistent with our conclusion that different nitrating agents are operative in the two types of nitration. It is satisfactory that the orientational data for the catalysed nitration agree with data for nitration in nitric acid; for it is certain that in this medium the nitrating entity is the nitronium ion (Part II, *J.*, 1950, 2400).

(6) *Experimental Methods.*

(6.1) *Materials.*—The required aromatic compounds, organic solvents, and tetraethylammonium salts were prepared or purified by standard methods. The mixed NMCT-solvents were prepared by making 99·96 c.c. of nitromethane up to 1000·0 c.c. at 20·0° with carbon tetrachloride, 29·94 and 49·98 c.c. of nitromethane each up to 100·0 c.c. at 20·0° with carbon tetrachloride, and 29·70 and 9·97 c.c. of carbon tetrachloride each up to 100·0 c.c. at 20·0° with nitromethane. Nitric acid was purified as described in Part II.

Dinitrogen pentoxide was prepared in all-glass apparatus by the dehydration of nitric acid with phosphoric oxide, followed by sublimation on to phosphoric oxide, and resublimation, in a stream of ozonised oxygen. The method and apparatus were similar in principle to those of Russ and Pokorny (*Monatsh.*, 1913, **34**, 1053), Daniels and Bright (*J. Amer. Chem. Soc.*, 1920, **42**, 1133), and Chédin (*Ann. Chim.*, 1937, **8**, 243), but the passage of ozone, along with dinitrogen pentoxide vapour, through drying tubes of commercial phosphoric anhydride, which largely decomposes the ozone (Smith, *J. Amer. Chem. Soc.*, 1925, **47**, 1852), was avoided. A stiff paste of nitric acid and phosphoric oxide, prepared at −30°, was gradually warmed to 33° during the first sublimation in ozonised oxygen, while the dinitrogen pentoxide was collected at −80°. Ground glass joints were sealed with phosphoric acid, except that the joint of the tube in which the product was collected was kept dry. At each end of the gas-train, traps of sulphuric acid and phosphoric oxide excluded moisture, while heated sections of tube prevented the egress of ozone. Prepared samples * of dinitrogen pentoxide were preserved in the dark at −80°.

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* They were crystalline and colourless. We did not obtain dinitrogen pentoxide in the form of a yellow liquid at −40°, as recently described by Angus *et al.* (*Nature*, 1949, **164**, 433).

(6.2) *Dilatometric Methods.*—These were essentially the methods of Benford and Ingold (*J.*, 1938, 929) with the improvements mentioned by Hughes, Ingold, and Reed (*J.*, 1950, 2400). Benford and Ingold's tapless dilatometers of " type C " were employed. Solutions of the aromatic compound, and of the dinitrogen pentoxide, were allowed 8 minutes to approach the temperature of the thermostat, before being mixed and drawn into the dilatometer. The pre-mixing period was standardised, because of the thermal (unimolecular) decomposition of dinitrogen pentoxide : standardisation ensures that, in all experiments carried out at the same temperature, the same small fraction of dinitrogen pentoxide will have decomposed before the beginning of the timed run. The zero of time was taken as the time of mixing. Nitration by dinitrogen pentoxide is accompanied by a contraction. But for 3—7 minutes after mixing, no significant readings could be obtained owing to thermal disturbances.

Graphical methods have been used for evaluating the results. For the investigation of kinetic form, either the variable part of the dilatometric height ($h_t - h_\infty$), or its logarithm, was plotted against the time (t). As mentioned in Section 2.1, reactions of an essentially bimolecular nature were brought to an approximately first-order kinetic form by the use of a large excess of one reactant. For the determination of first-order constants, Guggenheim's method of plotting from paired readings was followed. The derived rate-constants are, in principle, the sums of the rate-constants of all the first-order processes occurring in the dilatometer, *viz.*, the nitration, and the thermal decomposition of dinitrogen pentoxide. In order to isolate the rate constant corresponding to nitration, we should subtract from the over-all first-order constant the rate constant for the decomposition of dinitrogen pentoxide. This correction is just appreciable near the upper end of our range of temperatures, and, when significant, it was always applied. The rate constants for the decomposition of dinitrogen pentoxide were taken from data by Eyring and Daniels (*J. Amer. Chem. Soc.*, 1930, **52**, 1472), values for mixed solvents being computed by interpolation.

(6.2) *Chemical Control of the Dilatometric Runs.*—The methods by which a check was kept on what was being measured in the dilatometric runs were in general as described in Part II (*J.*, 1950, 2400). For present illustration, we shall refer to chemical examinations made of the products of a few completed runs, and then give an example of a run followed chemically throughout.

The product from a dilatometric run of first-order type on *p*-dichlorobenzene, in carbon tetrachloride, with the aromatic compound in excess over the dinitrogen pentoxide, was washed with water, and dried; and the solvent was then evaporated below room temperature under reduced pressure. The nitro-compounds were reduced by means of tin and hydrochloric acid, the tin was removed by hydrogen sulphide, and, after the latter had been boiled off, the solution was made alkaline. The amines were extracted with ether, distilled completely, and analysed (Found : C, 44·9; H, 3·2; N, 8·0; Cl, 43·6. Calc. for $C_6H_3Cl_2{\cdot}NH_2$: C, 44·5; H, 3·1; N, 8·6; Cl, 43·7%).

The product from a dilatometric run of autocatalytic type on chlorobenzene in 1 : 9-NMCT, with the chlorobenzene in excess over the dinitrogen pentoxide, was evaporated below room temperature under reduced pressure, in order to remove the solvent, the nitric acid, and the excess of chlorobenzene. The residual yellow solid was analysed (Found : C, 44·8; H, 2·7; N, 8·6; Cl, 22·5. Calc. for $C_6H_4Cl{\cdot}NO_2$: C, 45·7; H, 2·6; N, 8·9; Cl, 22·5%).

The product of a dilatometric run on chlorobenzene in carbon tetrachloride, with the dinitrogen pentoxide in excess over the chlorobenzene, was worked up in a similar way, and the yellow solid residue was analysed (Found : C, 46·0; H, 2·6; N, 8·8; Cl, 22·0%). This experiment shows that the use of a large excess of dinitrogen pentoxide does not lead to dinitration.

When a run was to be followed throughout by chemical analysis, it was conducted in an all-glass system consisting of a bulb furnished with a narrow delivery tube leading to an automatic pipette. The bulb was immersed in the thermostat, whilst the delivery tube and pipette had jackets through which the thermostat liquid was driven by means of a circulating pump. Samples (6 c.c.) were withdrawn into the pipette by suitable adjustments of the pressure in the apparatus, which was protected at both ends from the incursion of moisture. The samples were delivered into portions of 100 c.c. of acetone, to which 1% of water had been added, in order to secure hydrolysis of unchanged dinitrogen pentoxide. The acid then present was titrated with aqueous sodium hydroxide, lacmoid being the indicator. The end-points were good at first; but they deteriorated as the run proceeded, probably on account of the formation of small amounts of nitrophenolic by-products, which form coloured salts with alkalis. An example of this type of experiment is recorded in Table VI.

TABLE VI.

Illustrating the kinetics of nitration by dinitrogen pentoxide as followed by chemical analysis.

Nitration of *p*-dichlorobenzene by dinitrogen pentoxide in carbon tetrachloride at 14·99°. Initially $[C_6H_4Cl_2]$ = 0·599M., and $[N_2O_5]$ = 0·048M. Samples of 6·0 c.c. titrated with 0·0435N-sodium hydroxide. First-order rate constants, k_1, in sec.$^{-1}$.

Time (sec.).	Titre (c.c.).	10^4k_1.	Time (sec.).	Titre (c.c.).	10^4k_1.
0	13·56	—	2512	11·01	2·79
109	13·37	3·59	3458	10·16	3·28
774	12·76	2·23	5870	9·55	2·74
1404	11·92	2·84	∞	8·55	—

Mean rate constant : $k_1 = 2{\cdot}9 \times 10^{-4}$ sec.$^{-1}$.

A dilatometric experiment under very nearly the same conditions gave the value $k_1 = 3{\cdot}0 \times 10^{-4}$ sec.$^{-1}$.

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