# 177. *Influence of Directing Groups on Nuclear Reactivity in Oriented Aromatic Substitutions. Part V. A Dilatometric Investigation of the Kinetics of Aromatic Nitration especially in Nitromethane Solution.*

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By the use of tapless dilatometers, a general survey has been made of the kinetics of aromatic nitration in various solvents, in which the rates vary over a wide range; and also a detailed study of nitration in nitromethane, a solvent giving intermediate rates. Nitric acid was always employed in large, effectively constant, excess. Benzene and several derivatives were investigated.

The nitration of benzene was a reaction of order zero. It was retarded by nitrous acid according to the law $k_0 = 1/(a + b\sqrt{n})$, where $n$ is the concentration of nitrous acid. The parameters $a$ and $b$ were determined as power functions of the nitric acid concentration, $N$, and exponential functions of the temperature, $\theta$.

The nitrations of toluene and of ethylbenzene were also reactions of order zero, with absolute rates always equal to each other and to the rate of nitration of benzene for the same $n$, $N$, and $\theta$.

For the halogenobenzenes the rates were smaller than for benzene and its homologues in two degrees, a lower degree for fluoro- and iodo-benzene, and a higher degree for chloro- and bromo-benzene (H > F, I > Cl,Br). The effective reaction order was greater than zero in two degrees, with the same distribution of the compounds (0 = H < F, I < Cl,Br). The effective reaction order always increased as the reaction proceeded, approaching, in the cases of chloro- and bromo-benzene very closely approaching, unity towards the end of a run. The variations of rate with $n$ and $N$ were qualitatively similar to those observed with benzene.

All these facts can be explained by, and indeed seem to necessitate, the chain-reaction mechanism formulated on p. 954.

It is suggested that the efficiency of nitrating agents $X\cdot NO_2$ increases with the electron-affinity of X.

## (Sections 1—4). METHODS AND SURVEY OF SOLVENTS.

### (1) *Relation of the Present to Previous Work.*

(a) *Objects of the Investigation.*—The present work had two objects The first was to develop a convenient general method for studying the kinetics of the nitration of aromatic substances, the methods hitherto described leaving much to be desired. This problem was solved by the elaboration of a dilatometric method capable of wide application.

The second was to find the kinetic laws governing the nitration of benzene and of some of its simpler derivatives under the same experimental conditions: it is remarkable that the kinetics of the nitration of benzene have never yet been elucidated under any conditions. This aim has been fulfilled to the following extent. The dilatometric method was first employed in a brief survey of nitration in various solvents; nitromethane was then chosen as a solvent suitable for further investigation. For this solvent, the nitration of benzene was studied in detail; the kinetic laws were established, and the mechanism of the reaction was elucidated. It proved to be a chain reaction, and we are able to specify in considerable detail the modes of origin, propagation, and extinction of the chains. The nitration of certain benzene derivatives was then examined; for toluene and ethylbenzene the kinetic laws were exactly established, just as for benzene, whilst for the four halogenobenzenes they were qualitatively elucidated. The mechanism, which had been established for the nitration of benzene, was shown to be general amongst these derivatives.

Corresponding to these two objects, we give two brief historical sketches, the subjects treated not having previously been summarised in the literature.

(b) *Previous Work on Dilatometry in Reaction Kinetics.*—Dilatometry was first shown to be applicable to the study of reaction kinetics by Knöfler (Diss., Erlangen, 1888). The form of dilatometer used by him, and by the majority of subsequent investigators (Koelichen, *Z. physikal. Chem.*, 1900, **3**, 489; Galeotti, *ibid.*, 1911, **76**, 105; 1912, **89**, 241; Wright, P., 1913, **29**, 280; Aberlof, *J. Amer. Chem. Soc.*, 1926, **48**, 3048; 1927, **49**, 2957; Murphy, *ibid.*, 1931, **53**, 978; Brönsted *et al.*, *ibid.*, 1927, **49**, 2562; 1929, **51**, 431; 1930, **52**, 1394; *Trans. Faraday Soc.*, 1929, **25**, 59; Sreenivasaya and Sastri, *Biochem. J.*, 1929, **23**, 975; Rona and Lemmer, *Biochem. Z.*, 1931, **235**, 214; Hoather and Goodeve, *Trans. Faraday Soc.*, 1934, **30**, 626), consisted essentially of a bulb with a capillary tube at the top, and a tap at the bottom for filling. This tap has been a frequent source of trouble, since its unprotected presence restricts dilatometry to liquids which do not attack or dissolve tap-grease: a minute leak is sufficient to upset the readings. The difficulty is the same if a ground stopper is used in place of the tap (Duane, *Amer. J. Sci.*, 1901, **11**, 349; Palomaa and Salomon, *Ber.*, 1934, **67**, 424), and a rubber stopper (Riiber, *Ber.*, 1922, **55**, 3132) seems hardly a satisfactory substitute. Two methods have been tried for overcoming this difficulty. One makes the apparatus more complicated by retaining the tap and adding an arrangement to protect it. This was done by Brönsted (*loc. cit.*), who incorporated a device for letting in mercury above the tap, and by Palomaa and Salomon (*loc. cit.*), who similarly protected their stopper. However the protection thus given is not quite complete, and the applicability of the instrument remains limited: one must still consider the properties of the tap and the grease when planning experiments over a temperature range, and one must also exclude liquids which attack mercury (*e.g.*, nitric acid and halogens). The second method seeks to simplify the apparatus by abolishing the tap; and this is obviously the correct method, since it eliminates the leakage error completely, and widens the scope of the instrument to all liquid-phase reactions, and all temperatures, for which glass is not attacked. It has been applied by van 't Hoff (*Sitzungsber.*, 1910, **34**, 963) and by Benrath (*Z. anorg. Chem.*, 1926, **151**, 53). Van 't Hoff stoppered the capillary tube, evacuated the bulb through another tube, which he sealed, and then filled the dilatometer by removing the stopper under the surface of the experimental liquid. Benrath replaced the capillary tube by a tube so wide that the bulb could be filled through it. The former method is accurate but inconvenient and the latter convenient but inaccurate; we think we have advanced the technique by using tapless dilatometers which are both accurate and convenient.

The dilatometric method has not been used to the extent merited by its intrinsic scope and convenience, probably because of the restrictions imposed by taps and stoppers. The chief reactions hitherto studied are the aldol addition (Koelichen, Aberlof, Murphy; also Bell, J., 1937, 1637), keto-enol change (Wislicenus, *Chem. Z.*, 1904, 646; Göz, *Chem. Ztg.*, 1910, **33**, 1325), the mutarotation of sugars (Riiber, Brönsted), the reversible dimerisation of dihydroxyacetone (Bell and Baughan, J., 1937, 1947), hydrolysis of acetals (Brönsted, Palomaa and Salomon), hydrolysis of sucrose (Duane, Galeotti, Wright), the reversible hydrolysis of carboxylic esters (Galeotti, Benrath), the oxidation of sulphurous acid (Hoather and Goodeve), and various types of enzyme action (van 't Hoff, Galeotti, Sreenivasaya and Sestri, and Rona and Lemmer).

(c) *Previous Work on the Kinetics of Aromatic Nitration.*—The earliest recorded experiments on this subject are those of Spinola (*Annalen*, 1884, **224**, 283), who examined the nitration of benzene and some of its simpler derivatives with various amounts of nitric acid at various temperatures. No solvent was used, and hence the reaction mixtures were heterogeneous; no rate constants were obtained. The nitration of benzene in homogeneous conditions with nitrobenzene as the solvent was examined by Giersbach and Kessler (*Z. physikal. Chem.*, 1888, **2**, 676), and by Brauer (Diss., Heidelberg, 1899). Their main result was that the reaction started very rapidly and ended very slowly, so that all ordinary rate coefficients, even third-order ones, decreased with time. The principal cause of this is undoubtedly the formed water, which ionises some of the unused nitric acid, so that it cannot enter into reaction. Holleman and de Bruyn (*Rec. Trav. chim.*, 1900, **19**, 79) nitrated nitrobenzene in a large excess of the same substance, but obtained no recognisable reaction order.

The first to obtain velocity constants in the nitration of aromatic substances was Martinsen (*Z. physikal. Chem.*, 1904, **50**, 385; 1907, **59**, 605), who operated with nitric acid in sulphuric acid. Under these conditions the nitration of benzene was too rapid to be investigated, but that of nitrobenzene proved to be a straightforward second-order reaction. The same result was obtained for the nitration of a number of other compounds, such as 2 : 4-dinitrotoluene and the three nitrobenzoic acids; and it was again obtained much later by Klemenc and Schöller (*Z. anorg. Chem.*, 1924, **141**, 231) for the nitration of yet other compounds, such as 2 : 4-dinitro-*m*-xylene and the chloronitrobenzenes. The last-named authors made the significant observation that, in absolute sulphuric acid, dinitrogen pentoxide, if reckoned in the kinetic equation as $\frac{1}{2}(N_2O_5)$, gave the same second-order rate constants as nitric acid. This is further discussed in Section 10.

The rate of nitration of benzene and other compounds by means of nitric acid in acetic anhydride was first studied by Wibaut (*Rec. Trav. chim.*, 1915, **34**, 241), who obtained unsatisfactory evidence of a second-order law. Continuing the work, Cohen (*Proc. Acad. Sci. Amsterdam*, 1928, **31**, 692) showed that no such law obtained, that the nitration of benzene was catalysed by nitrous acid and was autocatalytic, and that side reactions proceeded by which the nitrating agent disappeared through interaction with the solvent. These results are confirmed in the latest work by Cohen and Wibaut (*Rec. Trav. chim.*, 1935, **54**, 409), in which the aromatic nitration was followed separately from the solvent reaction, and was concluded to be of the first order with respect to the benzene and of the third order with respect to nitric acid and nitrous acid collectively.

The nitration of phenol by nitric acid in water was first examined by Martinsen (*loc. cit.*), who showed that the reaction was autocatalysed by the nitrous acid produced. The same result was obtained by Klemenc (*Monatsh.*, 1914, **36**, 85; Klemenc and Ekl, *ibid.*, 1918, **39**, 641; Klemenc and Schöller, *loc. cit.*) with ether as solvent, and by Arnall (J., 1923, **123**, 3111) with alcohol. Klemenc and Ekl observed that the reaction in ether became very slow or stopped when the nitric acid was in excess of the phenol, a result which seemed contrary to the law of mass action, but can be explained by the formation of an unreactive oxonium salt. Klemenc and Schöller found that in the complete absence of nitrous acid nitration does not proceed; for water as solvent they gave the formula, rate $\propto [HNO_3]^{3 \cdot 2}[HNO_2]^{0 \cdot 3}$, and for ether, rate $\propto [HNO_3]^{2 \cdot 5}[HNO_2]^{0 \cdot 5}$.

Competitive nitration was unsuccessfully tried by Wibaut (*loc. cit.*). The only other published investigations along these lines are those of the present series (J., 1927, 2918; 1931, 1959; and the two preceding papers).

### (2) *Dilatometric Methods.*

Most previous workers have established directly or indirectly that the distance, $l$, travelled by the meniscus of a dilatometer is accurately proportional to the amount by which the reaction under investigation has progressed. We have shown that the same is true for the nitrations quantitatively studied, all of which were accompanied by contractions. The formula for the concentration of reactants at time, $t$, is thus $(l_\infty - l_t)D/R$. Here $D$, the fractional volume change per unit length travelled by the meniscus, is a constant of the dilatometer, and $R$, the fractional volume change per g.-mol. of reaction, is a constant for the reaction; $D$ was determined experimentally for each dilatometer, and $R$ for each reaction (Sections 2, b and 5, a).

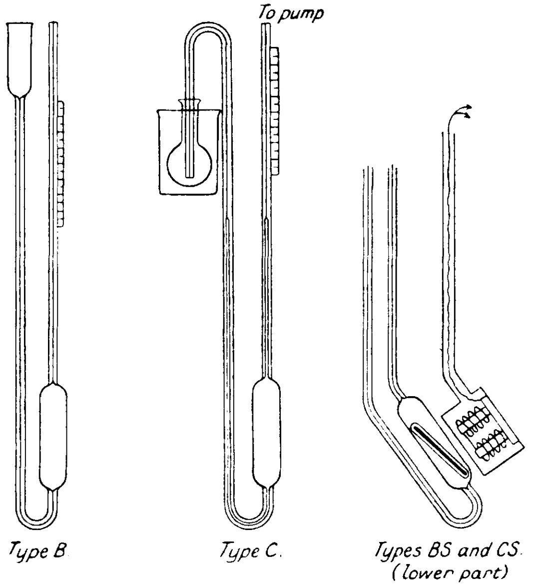
Preliminary experiments were carried out with dilatometers of a conventional design (type A) involving a tap, but consistent results could not thus be obtained. The recorded experiments were performed with tapless dilatometers (Section 2, a). Thermostats of considerable precision were necessary for use both above and below the room temperature (Section 2, c).

(a) *Design of Dilatometers.*—The principal designs are shown in Fig. 1. Instruments of type B were used for nitrations in which the concentration of aromatic compounds was in the range 0·1—0·5M. The bulb (10 c.c.) was made long and narrow in order to secure rapid heat exchange between the contents and the thermostat. The two limbs were of the same capillary tubing of bore 0·08 cm. Filling was accomplished through the funnel. Optical aid was provided by which the scale could be read to 0·01 cm.

The more sensitive instruments of type C were employed for more dilute solutions than those mentioned above. The lower part of each limb was made from wide capillary tubing, but the upper 15 cm. of each was made from the same length of capillary tubing of bore about 0·04 cm. Filling was accomplished by the aid of a small flask surrounded by liquid from the thermostat; one limb of the dilatometer dipped into this flask, whilst a vacuum pump was applied to the other.

A small modification, type BG, of the B-form of dilatometer was used in the longer experiments with more concentrated solutions, in order to eliminate the appreciable effect of evaporation on the behaviour of the meniscus. The funnel, instead of being sealed on, was fitted with a ground joint. The funnel being detached, both capillary tubes terminated in male ground joints, and could thus be closed with ground caps, which were removed during reading.

FIG. 1.



Another modification, types BS and CS, permitted the stirring of the contents of these dilatometers. The bulb was inclined with its axis making an angle of 25° with the vertical direction, and 2″ of 1/8″ round malleable iron rod, enclosed in a pyrex glass tube, was included in the bulb when the instrument was being made. This stirring rod was actuated by an electromagnet, fed with interrupted direct current. The magnet was soldered into a brass case for immersion in the thermostat alongside the dilatometer, the electric leads passing out through a brass tube. The interrupter was of a simple brush-and-sector design, the sector-wheel being driven by a variable-speed motor. With this arrangement the speed of stirring could be varied between 25 and 250 strokes per minute.

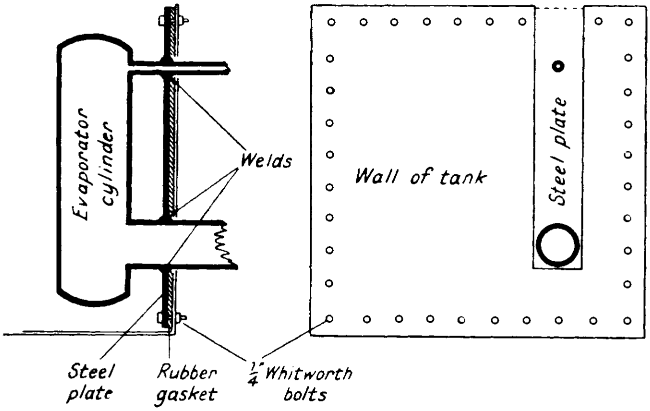
(b) *Calibration of Dilatometers.*—The capillaries were calibrated by a method depending on the thermal expansion of a liquid. In almost every case, the corrections for variations of bore proved negligible, and it was in practice unnecessary to read more than one limb of the instrument : in other words, the dilatometer constant was the same for all parts of the single scale.

The dilatometer constants were determined by observation of the thermal expansion of conductivity water in an adjustable precision thermostat, a Beckmann thermometer being used for the measurement of temperature differences. Correction was made for the thermal expansion of the glass. The temperature correction for the dilatometer constant, calculated from the coefficient of expansion of the glass, was negligible.

(c) *Design of Thermostats.*—From the coefficient of expansion of nitromethane, the principal solvent used in the rate experiments, it was calculated that, for the most sensitive dilatometers, a temperature variation of 0·002° corresponded to a just perceptible displacement, 0·01 cm., of the meniscus. Temperature control was secured by means of two 20-gallon thermostats, one designed for use above the room temperature (25—80°), the other for use below (15° to −10°). The former, built according to known principles, restricted temperature variation to less than 0·001°. The thermostat for low temperatures incorporated an adjustable permanent cooling unit, together with the usual low-powered intermittent heater. The cooling device was an " Electrolux, Type 100 " unit, which has a heat abstracting power of $10^5$ cals./hour when working at its maximum input power of 300 watts. This type of refrigerator is very suitable for the purpose, because its rate of heat absorption depends only on the readily controlled input power to the heating element, provided that the flow of water through the condenser coils is above a necessary minimum.

The evaporator cylinder (cooling element) of the refrigerator unit was fitted into the cubical, copper tank of the thermostat as shown in Fig. 2. The tubes connecting the evaporator cylinder to the main body of the apparatus had been welded by the manufacturers through an 18″ square steel plate. A slot was cut in one wall of the tank to accommodate these tubes, and the steel plate was bolted inside the wall, with an intervening rubber gasket, so that the evaporator cylinder was inside the tank and the rest of the refrigerator outside. The body of the refrigerator was bracketed to a heavy wooden base on which was built a platform to take the weight of the thermostat tank. This was set on a 2″ insulwood base, covered with a 2″ insulwood lid in two sections, and encased at the sides with 3½″ of insulwood and cork shavings. An efficient stirring system was installed, which consisted of a central shaft, with a propeller near the bottom and a turbine-fan near the top, together with a counter-shaft, run by a belt just below the lid, and operating a propeller in the corner shielded from the central stirrer by the evaporator cylinder. The liquid used to fill the tank was a mixture of water, ethylene glycol, and ethyl alcohol, which had a low viscosity and froze at −12°. The temperature variation in this thermostat did not exceed 0·002°.

FIG. 2.



### (3) *Analytical Methods.*

Two analytical methods, *viz.*, the estimation of nitrous acid and of aromatic nitroxyl, were employed to supplement the purely dilatometric measurements. Nitrous acid was estimated in each kinetic experiment. Aromatic nitroxyl was only occasionally measured, in order to provide an independent check on dilatometric determinations of the reaction constant, *R* (Section 2). We have made what appears to be a useful improvement in the Griess–Ilosvay method of estimating nitrous acid.

(a) *Colorimetric Estimation of Nitrous Acid.*—As nitrous acid has definite influence on the kinetics of the nitrations studied, it was important to be able to estimate it in the reaction mixtures, *i.e.*, in the presence of large amounts of nitric acid and traces of various organic solvents and aromatic nitro-compounds. Only small quantities of solution being available, the methods of estimation were necessarily colorimetric.

The usual method for the colorimetric estimation of nitrous acid is the Griess–Ilosvay method (Lunge and Lwoff, *Z. angew. Chem.*, 1898, **7**, 348) : an acetic acid solution of sulphanilic acid and α-naphthylamine produces by diazotisation and coupling the red colours to be compared, when it is treated, on the one hand, with the sample, and, on the other, with standard nitrite in sulphuric acid, both solutions being buffered with sodium acetate. This method could not be used for the nitration mixtures because these and the standard gave qualitatively different colours. They could be made comparable by omitting the sulphuric acid from the standard and the sodium acetate from both solutions, but the colours of the unbuffered solutions were unreliable, and the standard quantitatively unstable. Alternatively, the colours could be made qualitatively similar by adding sulphuric acid to the test solution, but the depth of colour was then not directly proportional to the nitrous acid concentration.

Zambelli has outlined a colorimetric method for the estimation of nitrous acid in water (J., 1887, **52**, 523) : the nitrous acid is made to diazotise sulphanilic acid in acid solution, and the product is coupled with phenol or α-naphthol in ammoniacal solution. The following adaptation of this method gave results, where it was applicable, correct to 5%. A standard solution of sodium nitrite in 90% aqueous sulphuric acid was prepared which contained $10^{-6}$ g. of nitrogen per c.c.; 1% aqueous solutions of sulphuric acid and of α-naphthol were also made. The suitably diluted sample (1 c.c.), the sulphanilic acid solution (1 c.c.), aqueous sulphuric acid (1 c.c.), and water (10 c.c.) were mixed in a standard flask (25 c.c.), and after 10 minutes the α-naphthol solution (1 c.c.) was added, and the mixture made up to the mark with concentrated (*d* 0·880) aqueous ammonia. The standard nitrite solution (1 c.c.) was treated similarly to the sample, and the next day the colours were compared in a Klett colorimeter. This method was used in connexion with nitrations in which acetic anhydride was the solvent, but it could not be employed when the solvent was nitromethane because this produced a colour with ammonia.

For this reason a modification of the Griess–Ilosvay method was developed, which can be employed in the presence of nitromethane, and this proved extremely satisfactory. The main principle of the modification is to produce a colour from nitrous acid in acetic acid under fixed conditions, and to compare this with a standard solution of a stable dye of the same quality of colour, the dye solution having previously been matched against the colour produced from a solution of known nitrous acid content under the aforesaid fixed conditions. The details are as follows.

The reagent was prepared from sulphanilic acid and α-naphthylamine as recommended by Lunge and Lwoff (*loc. cit.*), and kept in full sealed tubes wrapped in black paper. The permanent colour standard was prepared by dissolving " SS-magenta (acid) " (from the British Drug Houses Ltd.) (0·2 g.) in water (2 l.) with a sufficient addition of hydrochloric acid, and diluting the solution 40-fold; it was kept in a well-stoppered bottle wrapped in black paper. A nitrite solution, the strongest of the series required, was prepared by dissolving 0·493 g. of sodium nitrite in 1 l. of water, sterilised by the addition of 5 c.c. of chloroform. This solution contained $10^{-3}$ g. of nitrogen per c.c., and portions of it were diluted to make other solutions of various smaller concentrations.

In order to standardise the dye solution, one of these nitrous acid solutions (1 c.c.), water (10 c.c.), the reagent solution (1 c.c.), and glacial acetic acid (5 c.c.) were successively introduced into a standard flask (25 c.c.), and the mixture was made up to the mark with water. After 25 minutes at room temperature, the colour was compared with that of the dye in a Klett colorimeter, and the ratio " nitrite colour "/" dye colour " was obtained. This was repeated for the whole range of nitrite concentrations, and the following results were obtained :

| | | | | | | |
|---|---|---|---|---|---|---|
| N as $HNO_2$ per c.c. ($10^{-6}$ g.) | 10·0 | 6·0 | 5·0 | 4·0 | 3·5 | 3·0 |
| Nitrite colour/dye colour | 7·47 | 4·50 | 3·85 | 3·05 | 2·75 | 2·34 |
| N as $HNO_2$ per c.c. ($10^{-6}$ g.) | 2·50 | 2·00 | 1·75 | 1·50 | 1·25 | 1·00 |
| Nitrite colour/dye colour | 2·06 | 1·59 | 1·43 | 1·23 | 0·89 | 0·71 |

From these figures a graph was constructed, which was not quite a straight line.

In order to carry out an estimation of nitrous acid, an experiment exactly like that just described is carried out (with the same pipettes, etc.), except that 1 c.c. of the suitably diluted sample is used in place of the 1 c.c. of a solution of known nitrous acid content. The colour ratio in conjunction with the graph determines the concentration of nitrous acid in the sample.

With this method the maximum error was 4%, and we observed no interference from the organic materials contained in the samples.

(b) *Preparation of Nitric Acid free from Nitrous Acid.*—Here and elsewhere in this paper the term nitrous acid is taken to include any substances, such as certain oxides of nitrogen, which with water produce nitrous acid. On account of the effect of such substances on the kinetics of nitration it was important to have available nitric acid containing as little of them as possible. To this end, Kahlbaum's absolute nitric acid was twice distilled from admixture with 2 vols. of sulphuric acid, at 18 mm. in an all-glass still, the receiver of which was cooled in solid carbon dioxide. The crystalline product from the first distillation melted to a very pale yellow liquid, which was 99·9% acid, and contained about 0·2% of nitrous acid. The crystals from the second distillation melted to a colourless liquid which was absolute acid, and contained only a very small trace of nitrous acid. Such acid was either used at once, or stored for at most a few days in sealed tubes, which were wrapped in black paper and kept in a refrigerator at −5° In order to avoid the small amount of decomposition arising from the heat of dilution which is liberated when the absolute acid is mixed with organic solvents, the nitric acid was weighed in solid state, and the solvent, cooled to just above its m. p., was poured on the crystals with shaking and in subdued light.

(c) *Estimation of Nitration Products.*—This type of auxiliary estimation was employed in order to prove that the cessation of a contraction as observed in a dilatometer corresponded to the completion of nitration, *i.e.*, that the total contraction corresponded to the introduction of one nitro-group per molecule nitrated. The interpretation of the dilatometry was checked in this way only for the nitrations in nitromethane, and in this case the aromatic nitro-compound was separated quantitatively from the solvent, and estimated by reduction with titanous chloride, exactly as described in the two preceding papers.

### (4) *Survey of the Properties of Solvents.*

The solvents examined may be divided into three groups which we term for convenience "slow," "intermediate," and "fast" solvents, the designations having reference to the rate of nitration of benzene. The classification is discussed in Section 10.

The progress of nitration was estimated partly dilatometrically, partly by titanometric determination of the aromatic nitro-compound, and partly by alkalimetric measurement of the nitric acid, these methods giving good agreement where they were used in order to check each other.

(a) *Slow Solvents.*—The examples examined were dioxan, acetic acid, and acetonitrile. In these solvents the nitration of benzene, and even of toluene, was very slow at temperatures of about 20—30°, even when the proportion and concentration of nitric acid were high. For example, 0·6% of nitration was found after a 1M-benzene solution in a mixture of equal weights of nitric acid and dioxan had been kept at 20·5° for 25 minutes. Only benzene derivatives with strongly activating groups, *e.g.*, anisole, were nitrated at readily observable rates with nitric acid in these solvents : dilatometric studies of such reactions will be reported later.

(b) *Intermediate Solvents.*—We found two solvents of this type, *viz.*, nitromethane and acetic anhydride.

With benzene and nitric acid, both in about 1M-concentration in nitromethane, nitration proceeded slowly at 30° and rapidly at 60°. Even at the latter temperature, however, the reaction stopped when about half the benzene had been nitrated : no velocity constants could be obtained, and all the usual types of "constant" diminished as reaction progressed. This is what Griersbach and others observed for nitration in nitrobenzene (Section 1, c), and we explain it as already mentioned, *viz.*, by assuming that the water formed ionises the nitric acid and thus puts it out of action. Therefore, in the nitromethane experiments described in the following sections, we always employed a large excess of nitric acid, thus avoiding this disturbance. The usual orders of magnitude of the initial concentrations were 0·1M for the substance nitrated and 5M for the nitric acid. Under these conditions, benzene was nitrated, rather rapidly at room temperature, but at rates convenient for measurement at lower temperatures, *e.g.*, 0°. The solvent itself was not attacked by nitric acid, as was proved by keeping the materials together at 60° for one week in one of the sensitive dilatometers : the movement of the meniscus could not be read.

These observations directed our choice of nitromethane as the first solvent for detailed study.

It is well known that a solution of nitric acid in acetic anhydride contains an active nitrating agent, generally considered to be acetyl nitrate. We carried out a number of dilatometric experiments on nitration in an acetic anhydride solvent, but this was before Cohen and Wibaut's paper appeared (Section 1, c), and before our investigation (Part III, this vol., p. 905) into the by-products of nitration in acetic anhydride had been completed. We found dilatometrically, as Cohen and Wibaut did by analysis, that, in the nitration of benzene in acetic anhydride, the nitrating agent attacks the solvent as well as the benzene. After examining the dependence of the rates on nitrous acid and other factors, we came to the conclusion that the wanted and the unwanted reactions together formed a system too complicated for study by our method.

(c) *Fast Solvent.*—Sulphuric acid is a fast solvent. It is much too fast to permit the kinetic study of the nitration of benzene itself, or of any benzene derivatives except those containing strongly deactivating groups, such as nitroxyl. For such derivatives, however, the dilatometric method can be employed, and it is hoped later to report kinetic studies with this solvent.

## (Sections 5—8) KINETICS OF NITRATION IN NITROMETHANE SOLUTION.

### (5) *Kinetics of the Nitration of Benzene.*

For the reasons explained in Section 4, b we used always a very large excess of nitric acid, the active mass of which was therefore constant. The method of conducting the experiments was simply to mix two solutions, one of benzene in nitromethane and the other of nitric acid in nitromethane (Section 3, b), these solutions having previously been brought to the temperature of the thermostat; and then to introduce the mixture into the dilatometer already set up in the thermostat, and take a set of readings.

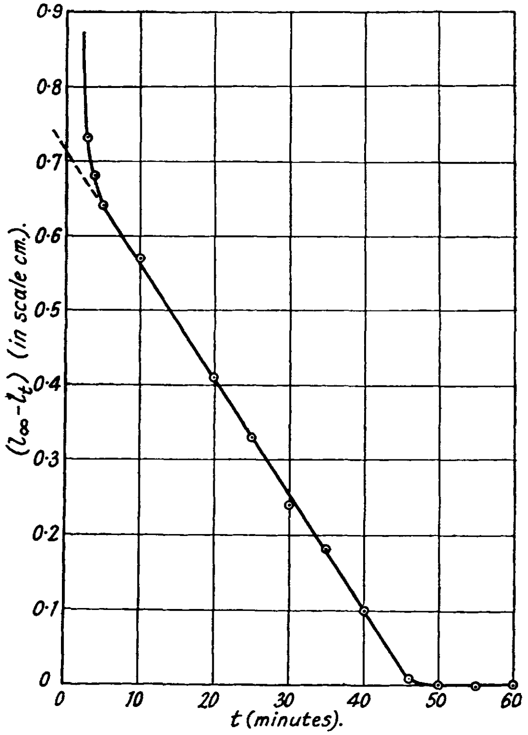
(a) *General Form of the Results.*—For all the experiments with benzene the curves expressing the dependence of the dilatometer reading on time had the form illustrated in Graph I (Fig. 3), which is the record of an experiment carried out at 0° in dilatometer B4. The unit of the ordinates, $l_\infty - l_t$, is 1 cm. of the scale of B4. The abscissæ are reckoned from the moment of mixing of the two solutions. No reading could be taken before 2 mins., which is but little longer than the time required to fill the dilatometer. After 50 mins. (in other experiments other periods, none less than 30 mins.) the readings remained constant indefinitely. The curves all fall sharply for 3 or 4 minutes, then exactly linearly for 30 minutes or longer, and then they suddenly become horizontal. We shall discuss in turn (i) the initial sharp fall, (ii) the total extent of fall, and (iii) the slope of the steady fall.

(i) We interpret this as a temperature disturbance, first because we expect one, and secondly because we have supporting evidence. Nitric acid has a positive heat of dilution with nitromethane, and hence, although the nitric acid and benzene solutions have the thermostat temperature before mixing, they must be warmer immediately after mixing. Furthermore, the mixed solutions must be warmed further during the filling of the dilatometer by passage through those parts of it which project outside the thermostat. Hence we expect an initial disturbance due to the cooling of the solution in the dilatometer to the thermostat temperature. Evidence that this is the cause of the initial sharp contraction is given in Section 5, b. Therefore in considering the progress of nitration we disregard the initial contraction, and treat the graph representing the volume change due to nitration as a straight line throughout its length. The straight part of each time graph was produced back as shown in Fig. 3, the intercept on the axis of ordinates being taken as corresponding to the volume of the solution at zero time and at thermostat temperature.

(ii) The total fall in $l_\infty - l_t$, counting from the extrapolated value for $t = 0$, was multiplied by the dilatometer constant ($D = 0{\cdot}00129$ for B4) and thus converted into a fractional contraction. In Table I, fractional contractions (col. 3) are compared with initial benzene concentrations (col. 2). Col. 4 contains the fractional contractions per unit molar initial concentration of benzene ($R$), and it will be seen that these values are substantially constant. (These experiments were done in ice-water. The low-temperature thermostat, which was built soon afterwards, gave a great improvement in accuracy.) The constancy shows that the total contraction, reckoned as described, corresponds to the introduction of a constant number of nitroxyl groups per benzene molecule. The following experiments show that this number is one.

An experiment of the same type was carried out except that nitrobenzene was used in place of benzene. After 4 hours in the dilatometer at 0° there was still no contraction that could be read on the scale. This shows that dinitration could not have participated in the experiments with benzene, none of which lasted as long as 4 hours at 0°.

FIG. 3.



*Graph I.*

*General Form of Results (as shown by Expt.* 191).

A more direct confirmation was obtained by keeping a benzene reaction mixture in the thermostat at 0° for a somewhat longer time than a similar mixture in a dilatometer would have needed to cease contracting, and then estimating the aromatic nitroxyl by reduction with titanous chloride (Section 3, c). The number of nitroxyl groups per benzene molecule was estimated as 1·003, *i.e.*, unity to within the error of measurement.

(iii) The rectilinear character of those parts of the graphs which represent nitration shows that the nitration is a reaction of order zero with respect to the substance nitrated. The gradients of the graphs (cm. min.$^{-1}$) can be converted into zero-order rate constants, $k_0$ (sec.$^{-1}$ g.-mol. l.$^{-1}$), by multiplication by $D/60R$. These rate constants were at first not reproducible and seemed to bear no relation to the initial concentration of nitric acid; but they became reproducible when the same specimen of nitric acid was used in the same concentration. This is illustrated in the last three cols. of Table I: after seven experiments with various samples of nitric acid, two pairs were carried out, one pair with the same sample of freshly distilled acid, and the other with the same sample of Kahlbaum's acid. Since the main difference between these two types of acid is that the former contains little, and the latter much, real or potential nitrous acid (lower oxides of nitrogen), it appears that such substances are anticatalytic.

TABLE I.

| Expt. No. | Benzene concn. (M). | Fractional contrn. | Contrn. per g.-mol. $C_6H_6$. | Nitric acid. | | $10^5 k_0$. |
|---|---|---|---|---|---|---|
| | | | | Sample.* | Concn. (M). | |
| 62 | 0·563 | 0·00798 | 0·0139 | — | 6·14 | 6·04 |
| 63 | 0·390 | 0·00534 | 0·0137 | — | 6·20 | 7·86 |
| 64 | 0·303 | 0·00406 | 0·0134 | — | 6·55 | 7·07 |
| 65 | 0·198 | 0·00268 | 0·0135 | — | 6·55 | 8·61 |
| 71 | 0·290 | 0·00369 | 0·0127 | — | 6·27 | 6·07 |
| 73 | 0·443 | 0·00566 | 0·0128 | — | 7·00 | 11·19 |
| 79 | 0·299 | 0·00406 | 0·0136 | — | 6·11 | 6·53 |
| 98 | 0·414 | 0·00558 | 0·0135 | D | 6·30 | 11·92 |
| 99 | 0·414 | 0·00524 | 0·0127 | K | 6·30 | 4·21 |
| 100 | 0·414 | 0·00567 | 0·0137 | D | 6·30 | 11·16 |
| 101 | 0·414 | 0·00535 | 0·0129 | K | 6·30 | 4·32 |

Mean reaction constant ($\bar{R}$) = 0·0133.

* D = Sample of distilled acid. K = Sample of Kahlbaum's acid (undistilled).

(b) *Test for Rate-controlling Physical Process.*—It was necessary to determine whether the zero-order rates were determined by a rate of transport. This was investigated as follows. The same reaction mixture was simultaneously introduced into two dilatometers, one of which was furnished with stirring gear (Section 2, a). They were set side by side in the thermostat, and, while the mixture in one was stirred, the contraction in each was observed. The results were as follows.

For the first 4 minutes from the time of making the mixture, the behaviour observed in the two dilatometers differed widely: the unstirred solution showed the usual sharp initial contraction, but the stirred mixture did not. This confirms our view (Section 5, a) that the sharp initial contraction is a thermal effect: by stirring we bring the reaction mixture into temperature equilibrium with the thermostat before the first reading can be taken, and thus the whole of the observed contraction is linear.

For the remainder of the period of contraction, this process followed the same linear course in both dilatometers; also it proceeded at the same rate and ceased at the same moment in the stirred and unstirred solutions. This shows that the observed rate is not conditioned by a rate of transport, if we except heat transport during the first few minutes.

(c) *Test for Rate-controlling Heterogeneous Reaction.*—Next it was necessary to test for a surface reaction, and to this end a dilatometer (B 16) was prepared which had its internal glass surface artificially increased by the inclusion of glass powder. The glass particles had been graded and some of them measured: from the measurements it was computed that the internal surface area was 12·5 times that of a similar dilatometer having no glass powder. The same reaction mixture was introduced into the empty and into the glass-filled dilatometer, which were set side by side in the thermostat. In both, the contractions followed the same linear course, proceeded at the same rate, and terminated at the same moment. This was found true for the whole range of rates encountered in the subsequent investigation (Sections 5, d and 5, e). It follows that the zero-order rates are not controlled by a surface reaction.

(d) *Effect of "Nitrous Acid."*—References to the amount or concentration of nitrous acid will be understood to refer to the nitrous acid equivalent of those substances which yield nitrous acid on dilution of the reaction mixtures with water.

(i) *Method of experiment.* In this group of experiments the nitric acid concentration and temperature were kept constant, the former being 5M and the latter 0°. Since it had been established that the rates are independent of the benzene concentration, this concentration was not accurately standardised; it was always about 0·1M. The nitrous acid concentration was varied. A 5M-solution of vacuum-distilled nitric acid in nitromethane was made up, with the precautions against decomposition mentioned in Section 3, b. A similar solution was made from nitric acid rich in nitrous acid. By mixing these solutions in various proportions it was possible to obtain solutions containing the same concentration of nitric acid but different amounts of nitrous acid. To each solution (15 c.c.) the benzene was added (5 drops), and part was introduced into a dilatometer, whilst another part was diluted with water (50—500 vols.) to give a solution suitable for the estimation of nitrous acid (Section 3, a).

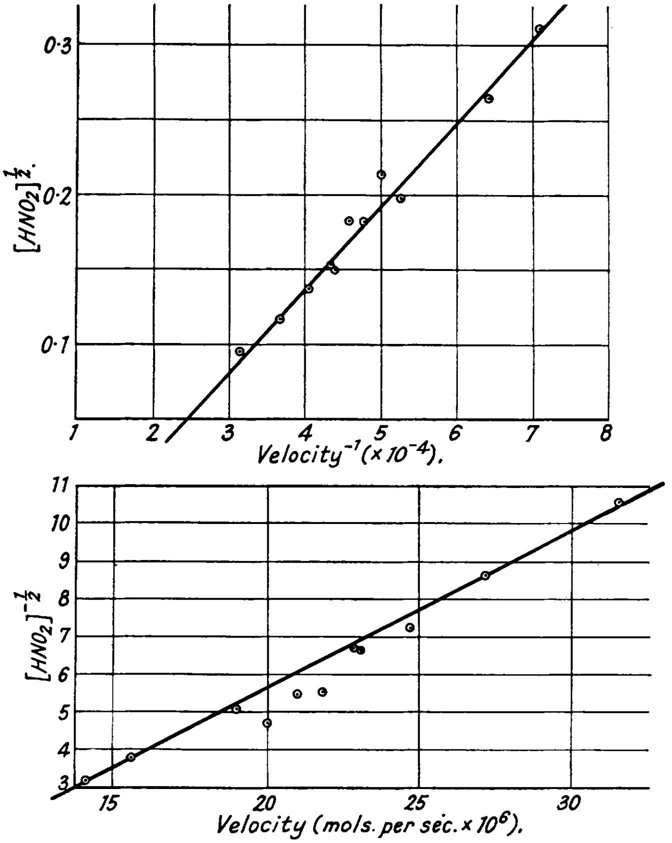
(ii) *Constancy of nitrous acid.* In four experiments the nitrous acid was estimated at the beginning and also at the end of the contraction period. The results were as follows :

| | | | | |
|---|---|---|---|---|
| Initial $[HNO_2]$ (M) | 0·0861 | 0·0760 | 0·0545 | 0·0211 |
| Final $[HNO_2]$ (M) | 0·0832 | 0·0768 | 0·0563 | 0·0214 |

The agreement of the initial and the final concentration in each experiment being within the error of the determination (Section 3, a), it follows that nitrous acid is not appreciably consumed or produced during nitration. Having established this, we subsequently measured only initial nitrous acid concentrations.

FIG. 4.

*Graph II.*



*Graph III.*

(iii) *Functional connexion with rate.* Eleven further experiments (a " block ") were carried out with nitrous acid concentrations ranging from less than 0·01M to 0·1M. The zero-order rate constants are given in Table II (Expts. 188—199; $[HNO_3]$ = 5M). By an examination of these figures, two simple relationships can be suggested between the nitrous acid concentration and the rate of reaction :

(α) The square root of the nitrous acid concentration is a linear function of the reciprocal velocity, as shown in Graph II (Fig. 4) : $1/k = a + b[HNO_2]^{1/2}$.

(β) The reciprocal square root of the nitrous acid concentration is a linear function of the velocity, as shown in Graph III (Fig. 4) : $k = a' + b'/[HNO_2]^{1/2}$.

These relations are, of course, not equivalent. The former seems slightly preferable on experimental grounds (see graphs), and we can interpret it theoretically (Section 9, a).

(e) *Effect of Nitric Acid.*—Several blocks of experiments were carried out, each quite similar to the block of eleven just described. The temperature was 0° throughout. In each block the nitric acid concentration was kept constant, and the rate of nitration was traced as a function of the nitrous acid concentration. From one block to the next the nitric acid concentration was changed in steps of ½M over the range 3M to 7M. Beyond these limits the rates were of inconvenient orders of magnitude, and the accuracy correspondingly diminished. The rate constants (sec.$^{-1}$ g.-mol. l.$^{-1}$) are given in Table II.

TABLE II.

*Zero-order Rate Constants for the Nitration of Benzene at 0°.*

| Expt. No. | $[HNO_2]$, (M). | $10^6k_0$. |
|---|---|---|
| $[HNO_3]$ = 7·0M. | | |
| 294 | 0·0083 | 184·2 |
| 296 | 0·0321 | 98·5 |
| 297 | 0·0516 | 88·0 |
| 299 | 0·113 | 71·9 |
| 298 | 0·125 | 65·7 |
| 295 | 0·150 | 58·1 |
| $[HNO_3]$ = 6·5M. | | |
| 288 | 0·0073 | 103·0 |
| 290 | 0·0212 | 77·0 |
| 291 | 0·0373 | 64·3 |
| 293 | 0·0822 | 51·3 |
| 292 | 0·119 | 44·6 |
| 289 | 0·133 | 42·3 |
| $[HNO_3]$ = 6·0M. | | |
| 236 | 0·0226 | 55·5 |
| 235 | 0·0472 | 46·8 |
| 237 | 0·0564 | 42·5 |
| 234 | 0·0674 | 38·2 |
| 232 | 0·104 | 33·5 |
| 231 | 0·118 | 31·2 |
| $[HNO_3]$ = 5·5M. | | |
| 239 | 0·0138 | 35·8 |
| 240 | 0·0513 | 26·2 |
| 241 | 0·0715 | 24·3 |
| 245 | 0·0860 | 24·2 |
| 242 | 0·0788 | 23·0 |
| 244 | 0·101 | 22·3 |
| 243 | 0·128 | 20·5 |
| $[HNO_3]$ = 5·0M. | | |
| 188 | 0·0089 | 32·8 |
| 190 | 0·0134 | 27·2 |
| 191 | 0·0189 | 24·7 |
| 193 | 0·0225 | 22·9 |
| 192 | 0·0228 | 23·0 |
| 199 | 0·0330 | 21·8 |
| 197 | 0·0331 | 21·0 |
| 198 | 0·0392 | 19·0 |
| 196 | 0·0455 | 20·0 |
| 195 | 0·0702 | 15·6 |
| 194 | 0·0984 | 14·1 |
| $[HNO_3]$ = 4·5M. | | |
| 262 | 0·0062 | 13·3 |
| 258 | 0·0081 | 16·1 |
| 259 | 0·0089 | 13·3 |
| 264 | 0·0089 | 13·2 |
| 265 | 0·0116 | 12·3 |
| 261 | 0·0139 | 13·3 |
| 267 | 0·0258 | 10·7 |
| 268 | 0·0402 | 9·60 |
| 266 | 0·0883 | 8·01 |
| 260 | 0·0896 | 7·88 |
| 263 | 0·0947 | 7·43 |
| $[HNO_3]$ = 4·0M. | | |
| 270 | 0·0056 | 8·45 |
| 271 | 0·0115 | 7·35 |
| 272 | 0·0190 | 6·63 |
| 273 | 0·0356 | 6·05 |
| 269 | 0·0764 | 4·63 |
| $[HNO_3]$ = 3·5M. | | |
| 274 | 0·0041 | 4·73 |
| 276 | 0·0093 | 4·13 |
| 277 | 0·0140 | 3·86 |
| 278 | 0·0335 | 3·32 |
| 279 | 0·0799 | 3·02 |
| 275 | 0·0803 | 2·70 |
| $[HNO_3]$ = 3·0M. | | |
| 283 | 0·0046 | 3·52 |
| 286 | 0·0347 | 1·99 |
| 282 | 0·0575 | 1·64 |

Each block of experiments obeyed the relationship $k_0^{-1} = a + b\,[HNO_2]^{1/2}$, but the parameters *a* and *b* varied from one block to another. The graphs (IV and V) from which *a* and *b* were computed as functions of the nitric acid concentration are shown in Figs. 5 and 6. The values thus obtained are in Table III.

TABLE III.

*Parameters of the Equation* $k_0^{-1} = a + b[HNO_2]^{1/2}$.

| $[HNO_3]$ | 7·0 | 6·5 | 6·0 | 5·5 | 5·0 | 4·5 | 4·0 | 3·5 | 3·0 |
|---|---|---|---|---|---|---|---|---|---|
| $10^{-4}\,a$ | 0·35 | 0·56 | 0·74 | 1·74 | 1·74 | 5·0 | 8·3 | 17·2 | 15·7 |
| $10^{-4}\,b$ | 3·30 | 4·85 | 7·03 | 8·80 | 17·3 | 27·0 | 47·5 | 70·0 | 188·5 |

The dependence of the parameters *a* and *b* on the nitric acid concentration (represented by *N*) is shown in graphs VI and VII (Fig. 7). It will be seen that the plot of $1/a$ against $N^6(27 - N)$, and the plot of $1/b$ against $N^5(27 - N)$, are both straight lines which pass through the origins of the co-ordinates.

The whole set of results can thus be represented by the equations

$$k_0^{-1} = a + bn^{1/2} \qquad (1)$$

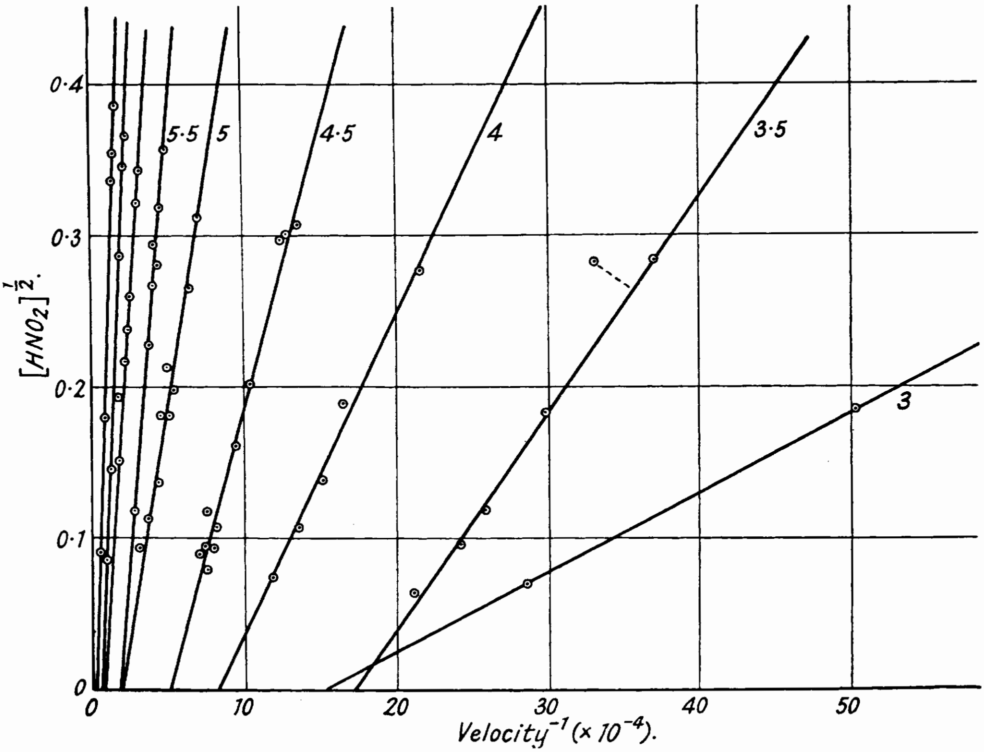
$$a = AN^{-6}(27 - N)^{-1} \qquad (2)$$

$$b = BN^{-5}(27 - N)^{-1} \qquad (3)$$

where *n* denotes the nitrous acid concentration. Equation (1) has theoretical significance, but, owing to the large concentrations of nitric acid, equations (2) and (3) cannot be other than semi-empirical functions of concentration; the quantity 27 — *N* represents the concentration of the solvent. The constants *A* and *B* depend only on temperature, and for 0° the values are

$$A = 8{\cdot}4 \times 10^9 \qquad B = 11{\cdot}3 \times 10^9$$

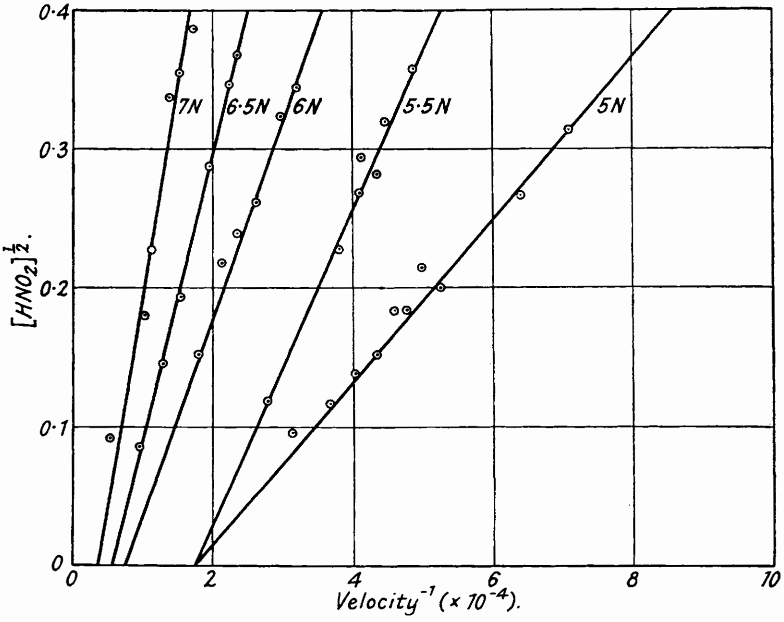
FIG. 5.



*Graph IV.*

*Blocks of Nitrations in* 7N- *to* 3N-$HNO_3$ *solution—in steps of* 0·5N *from left to right.*

FIG. 6.



*Graph V.*

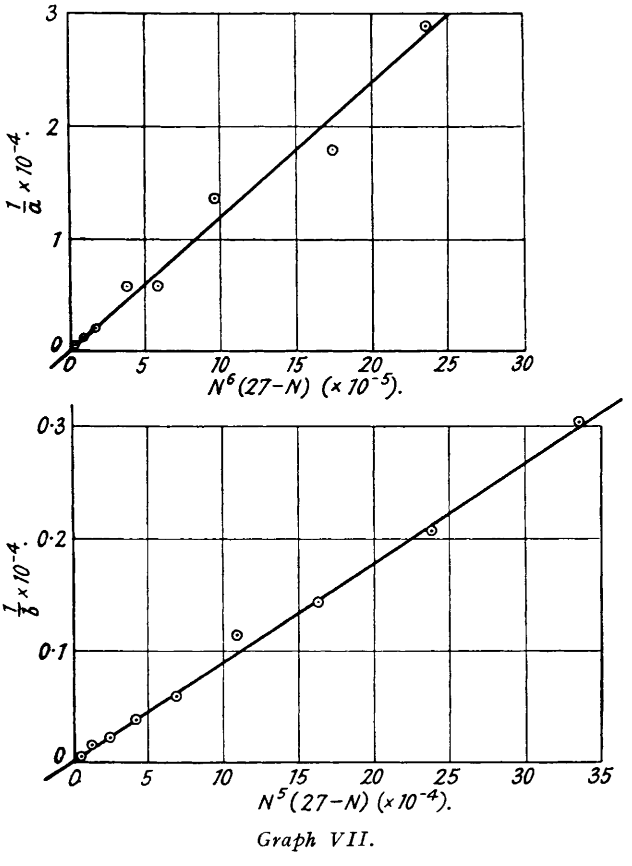
*Block of Nitrations in* 7N- *to* 5N-$HNO_3$ *solution.* (*Five times scale of IV.*)

(f) *Effect of Temperature.*—This has not been fully investigated, because we cannot, as is obvious from the reaction order, deduce the activation energy for any reaction directly affecting the aromatic compound.

Experiments at temperatures other than 0° were carried out for two nitric acid concentrations, $N = 3{\cdot}0$ and $5{\cdot}0$ M; the former concentration was investigated at 20° and the latter at —10° and 10°. As before, several blocks of experiments each corresponding to a particular temperature and nitric acid concentration were carried out, and within each block the nitrous acid concentration was varied. The whole series of experiments gave rectilinear reaction-time curves, and all the blocks of experiments gave straight-line curves when the reciprocals of the zero-order rate constants were plotted against the square roots of the nitrous acid concentrations. The whole set of results can thus be summarised in terms of the dependence of the parameters $a$ and $b$ of equation (1) on temperature and nitric acid concentration. This is done in Table IV. From these results we can deduce the factors by which $a$ and $b$ decrease for a rise of temperature of 10°, at temperatures not too far removed from 0° : these factors are given in the last line but one in the table. Since, both for $a$ and for $b$, the temperature factors are substantially independent of the nitric acid concentration, their mean values, given in the last line of the table, may be accepted as the factors by which the constants $A$ and $B$ of equations (2) and (3) respectively become decreased for a rise of 10° in temperature. Putting the same statement into a logarithmic form, we can set up equations (4) and (5) which, with (1), (2), and (3), compactly

FIG. 7.

*Graph VI.*



*Graph VII.*

express the kinetics of the reaction over the range of variables investigated ($\theta$, —10° to +20°; $N$, 3·0—7·0M; $n$, 0·005—0·15M; $[C_6H_6]$, $<$0·01 to 0·5M):

$$\log_{10} A = 9{\cdot}924 - 0{\cdot}0415\theta \qquad . \quad . \quad . \quad . \quad (4)$$

$$\log_{10} B = 10{\cdot}053 - 0{\cdot}0544\theta \qquad . \quad . \quad . \quad . \quad (5)$$

TABLE IV.

*Temperature Variation of Parameters of Equations* (1), (2), *and* (3).

| | $N$ = 3·0M. | | $N$ = 5·0M. | |
|---|---|---|---|---|
| Temp. | $10^{-4}a$. | $10^{-4}b$. | $10^{-4}a$. | $10^{-4}b$. |
| —10° | — | — | — | 5·70 |
| 0 | 15·7 | 189 | 1·52 | 1·80 |
| +10 | — | — | 0·60 | 0·48 |
| +20 | 2·15 | 15·2 | — | — |
| Factors by which $a$ and $b$ fall for 10° rise of temperature | 2·7 | 3·5 | 2·5 | 3·5 |
| Factors by which $A$ and $B$ fall for 10° rise of temperature | $A$, 2·6 | | $B$, 3·5 | |

Let us assume that $A$ and $B$ each satisfy an equation of the Arrhenius type: $A = B_A e^{-E_A/RT}$ and $B = B_B e^{-E_B/RT}$. We can then estimate $E_A$ and $E_B$:

$$E_A = -15 \text{ kilocals.}; \; E_B = -19 \text{ kilocals.}$$

The significance of $E_A$ and $E_B$ is considered in Section 9, a.

### (6) *Kinetics of Nitration of Toluene and Ethylbenzene.*

We shall summarise these experiments very briefly, because it will appear that all the results for toluene and ethylbenzene can be reduced to one simple statement. As before, we employed temperatures in the neighbourhood of 0° and solutions containing large, time-invariant concentrations of nitric acid.

(a) *General Form of the Results.*—The contraction–time curves for toluene and ethylbenzene were of exactly the same form as those previously obtained for benzene (see Section 5, a). This was true over the range of variables considered in the case of benzene.

(b) *The Absolute Rates.*—Since the rates of nitration of benzene, toluene, and ethylbenzene are independent of the concentration of hydrocarbon, we should expect them to be independent of which hydrocarbon is being nitrated. This deduction was tested in experiments of which the following is typical.

A solution of nitric acid (4·00M) in nitromethane, known as to its content of nitrous acid (0·0731M), was divided into three portions, which were treated severally with benzene, toluene, and ethylbenzene in quantities sufficient to make solutions about 0·1—0·2M with respect to the hydrocarbons. Using C-type dilatometers, the contractions were followed at 0°, and the zero-order rate constants calculated as usual. The rates ($\times 10^5$) were: benzene, 527; toluene, 530; ethylbenzene, 532 sec.$^{-1}$ g.-mol. l.$^{-1}$; that is, they were equal to within the error of observation. This result was generalised by means of similar experiments for other nitric and nitrous acid concentrations and temperatures within the range of variation already illustrated.

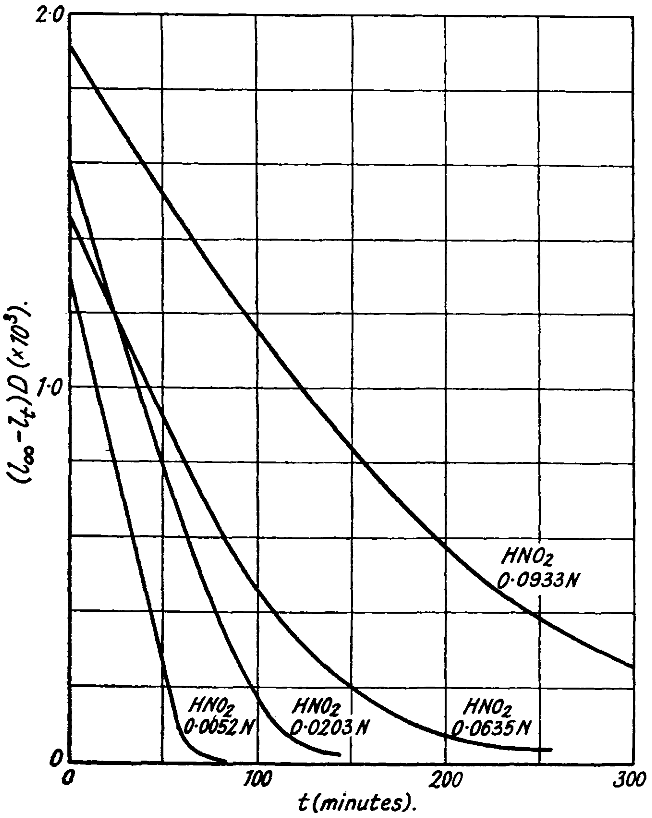
Therefore, the zero-order rates of nitration of toluene and ethylbenzene are quantitatively defined by the equations (1—5) already given for the rate of nitration of benzene.

### (7) *Kinetics of the Nitration of Fluoro-, Chloro-, Bromo-, and Iodo-benzene* (*Qualitative Features*).

Unlike the nitration of benzene and its monoalkyl derivatives, nitration of the monohalogeno-derivatives of benzene followed no simple order. For this reason, we are unable, on the basis of the relatively few experiments so far performed, to give exact mathematical expression to the results. We shall therefore illustrate the latter by means of typical curves, and generalise only with respect to qualitative features. It is probable that with the help of many more experiments (several hundreds) we could set down the rate equations complete with their numerical parameters, as has been done for the simpler kinetics of the hydrocarbons; this follows because even the qualitative features, as elucidated in the present work on the halogeno-compounds, are sufficiently significant in relation to the results for hydrocarbons to indicate the general form which the rate laws must assume (cf. Section 9, c).

As before we have worked with large, time-invariant concentrations of nitric acid, which were changed from one block of experiments to another, and with concentrations of nitrous acid which were varied within each block. All the experiments of this series were, however, done at 0°.

Fig. 8.



*Graph VIII.*

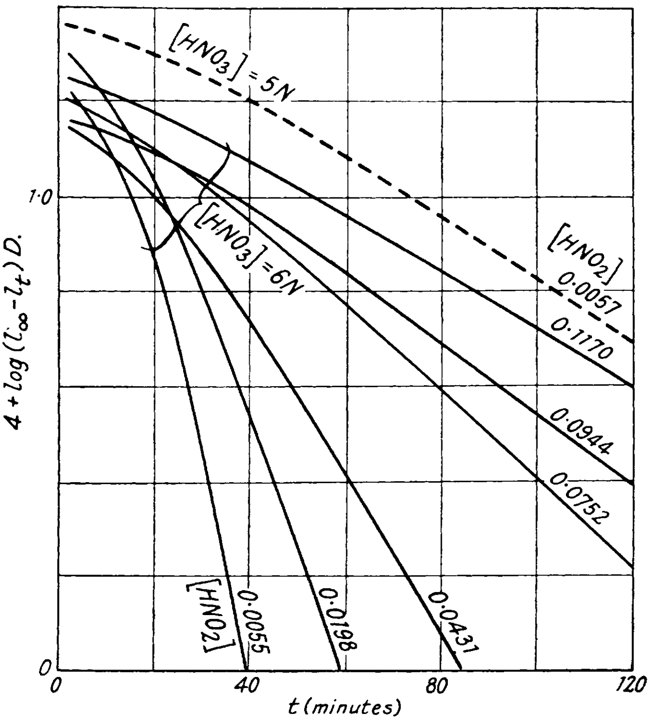
*Nitration of Fluorobenzene in* 5N-*Nitric Acid at* 0°.

(a) *General Comparison with Benzene.*—There were two qualitative differences between the behaviour of the halogenobenzenes, on the one hand, and benzene, toluene, and ethylbenzene, on the other. The first was that the volume changes observed with the halogenobenzenes were all considerably slower than with the hydrocarbons under the same conditions. Unlike the hydrocarbons, the halogenobenzenes showed individual differences, but the above statement is true of all of them. The point is illustrated in Fig. 10, in which the reaction-time curves of the four halogenobenzenes are compared with one another and with curves for benzene, for the same temperature and nitric and nitrous acid concentrations.

The second difference was that the volume-time graphs for the halogenobenzenes, instead of being rectilinear as for the hydrocarbons, were markedly curved, being convex to the time axis. This is illustrated in Figs. 8 and 10 (lower part), and it means that the rate of reaction has some dependence on the concentration of the substance which is being nitrated. The rate, being sensitive to the concentration, must be sensitive also to the chemical nature of the substance nitrated, and hence it is consistent that the halogenobenzenes do not all behave alike, as the hydrocarbons do.

There were also two qualitative similarities between the behaviour of the halogenobenzenes and that of the hydrocarbons. One was that nitrous acid was an anticatalyst, with the same order of rate-diminishing power for the halogenobenzenes as for the hydrocarbons. This is illustrated by the four curves in Fig. 8, which relates to the nitration of fluorobenzene at 0° in a 5M-nitric acid solution containing various proportions of nitrous acid. It will be appreciated that no special significance attaches to the crossing of curves such as those shown in Figs. 8, 9, and 10 : each graph starts from a point determined by the amount of the aromatic substance taken for nitration, and hence a curve for a faster reaction with more material may cut one representing a slower reaction with less. The important point is that the slopes of the graphs in Fig. 8 diminish with increasing concentration of nitrous acid, provided we compare slopes at corresponding stages of contraction. The same point is illustrated by the full-lines curves of Fig. 9, which relates to the nitration of chlorobenzene at 0° in 6M-nitric acid solutions containing various concentrations of nitrous acid : the method of plotting is different, but the relative rates can be assessed by an analogous comparison of slopes.

FIG. 9.



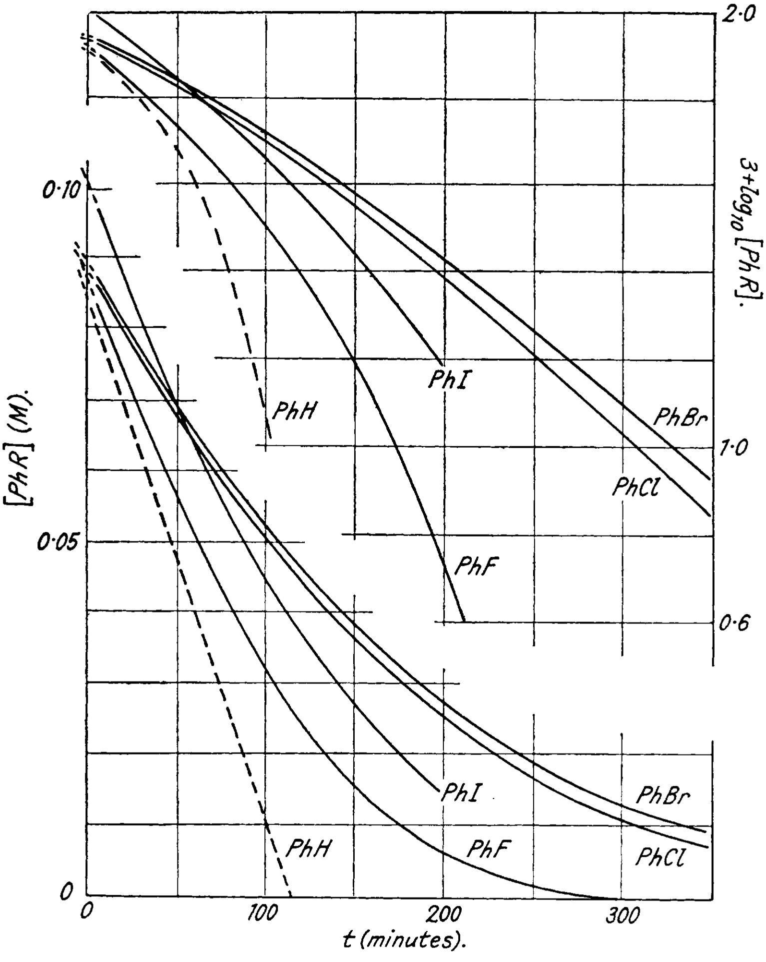
*Graph IX.*

*Nitration of chlorobenzene at* 0°.

The second point of similarity relates to the effect of the concentration of nitric acid on the speed. As for the hydrocarbons, so also for the halogeno-compounds, the speed increases very rapidly with increase in the nitric acid concentration within the investigated range. In Fig. 9, along with the curves for the block of experiments on the nitration of chlorobenzene at 0° in 6M-nitric acid, we include the curve for one experiment of a similar block in 5M-nitric acid. This curve (broken line) may be compared with the lowest curve in the same diagram, since the nitrous acid concentrations for the two are practically the same. The large difference of slope is due to the moderate difference of nitric acid concentration

(b) *Form of the Volume–time Curves.*—The convexity of these curves to the time axis may be expressed formally by the statement that the effective reaction order with respect to the aromatic substance is greater than zero. The effective reaction order is smallest in the examples of fluoro- and iodo-benzene. In the contraction–time curves for these compounds, *e.g.*, those reproduced in Fig. 8, one can see distinct vestiges of the rectilinear law which obtains for benzene itself.

FIG. 10.



*Graph X.*

*Comparative nitrations of benzene and the halogenobenzenes.*

The effective reaction order is greatest for chloro- and bromo-benzene, but even for these substances it is not as great as unity. This is illustrated in Fig. 9, where, instead of plotting the contraction $[(l_\infty - l_t)D]$ itself, we have plotted its logarithm, against the time. If the reaction order with respect to the chlorobenzene were unity, these curves would be straight lines : their concavity to the time axis shows that the effective reaction order is less than unity.

Further inspection of Fig. 8 shows that the effective reaction order is far from being constant throughout a single experiment : the volume–time graphs are considerably less curved at the beginning than in the later stages of contraction. This means that the rate of nitration becomes more and more dependent on the substance nitrated the less there is of it. The same thing is shown in another way in Fig. 9, from which it can be seen that the logarithmic curves are rather strongly bent initially, and become more nearly straight towards the end of reaction. This signifies that the effective reaction order, although well below unity at the commencement of reaction, rises towards unity as nitration proceeds. Further illustrations will be seen in the curves of Fig. 10.*

(c) *Comparison of Rates for the Four Halogenobenzenes.*—Comparison can be effected by interpolation to identical conditions but the direct method, previously used for benzene, toluene, and ethylbenzene, has also been employed. The following is an example.

A solution of nitric acid (5·00M) in nitromethane, known as to its content of nitrous acid (0·115M), was divided into five portions, which were severally treated with benzene and with fluoro-, chloro-, bromo-, and iodo-benzene, in quantities sufficient to form solutions approximately 0·1M with respect to the several aromatic compounds. C-Type dilatometers being used, the contractions were followed at 0°. The results are shown graphically in Fig. 10.

Similar experiments were carried out with other concentrations of nitric and nitrous acids. Although the absolute rates changed very greatly with changes in the concentration of these reagents, the following comparative statements hold true for all experiments. (1) The compounds fall into three groups with regard to rate of nitration: fluoro- and iodo-benzene nitrate at nearly the same rate, which is smaller than the rate for benzene; and chloro- and bromo-benzene also nitrate at about the same rate, which is smaller than for the other compounds: $PhH > PhF, PhI > PhCl, PhBr$. The slight distinction between chloro- and bromo-benzene is in the direction $PhCl > PhBr$.† (2) The compounds divide themselves into the same three groups with respect to the dependence of the reaction rate on the concentration of the substance nitrated. With benzene there is no dependence. With fluoro- and iodo-benzene there is a small dependence in the initial stages, rising to a considerable dependence in the later stages, of reaction. With chloro- and bromo-benzene there is considerable dependence in the initial stages, and this rises nearly to proportionality as reaction proceeds.

It will be observed that there is a general antiparallelism between the rate of nitration of the aromatic substance under given conditions and the dependence of the rate on the concentration of the aromatic substance; and, when, as in benzene and the alkylbenzenes, the rate has reached a value which apparently cannot be exceeded, its dependence on the concentration has vanished.

### (8) *The Colour accompanying Nitration.*

The production of red colours in the course of the nitration of aromatic substances by means of nitric acid in nitromethane (and in acetonitrile) was first reported in Part II (J., 1931, 1966). These colours arise whilst nitration is actually in progress; they fade as the reaction comes to a natural end, but can be destroyed at any moment by the addition of water (which also stops nitration). On account of their apparent connexion with the nitration process, we have investigated these colours both qualitatively and colorimetrically.

(a) *Observations on the Colours arising in Nitration.*—The colours initially produced by adding equivalent quantities of different aromatic compounds to equal portions of the same solution of nitric acid in nitromethane at the same temperature differ considerably. The rule is that, *ceteris paribus*, the more intense colours are given by those aromatic compounds that are more reactive in electrophilic substitution; *e.g.*, the compounds that would have the higher rates of nitration as determined in competitive experiments. Thus colour intensity increases in the series $PhCl < PhH < PhMe < p\text{-}Me_2C_6H_4$; and, although the colours are similar enough in quality to be matched in a colorimeter, the direct visual impression given by solutions of comparable concentration may range in such a series from pale yellow in chlorobenzene, through orange-red and blood-red, almost to black in *p*-xylene.

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* The crystallisation of *p*-iodonitrobenzene occasionally interfered with the investigation of the latter part of the reaction of iodobenzene.

† These results are consistent with the competition investigation of Part IV, where the rate series $PhF \gg PhCl > PhBr \ll PhI$ was found (preceding paper).

The colours initially produced by adding different quantities of the same aromatic compound, *e.g.*, benzene, to equal portions of the same solution of nitric acid in nitromethane at the same temperature are more intense the greater the quantity of the aromatic compound. As the colours at once begin to fade, no attempt was made to establish the relation between initial colour and initial concentration quantitatively. The rate of fading was, however, measured colorimetrically in the case of benzene, the method being to match the fading solution against diminishing lengths of a column of alcoholic iodine. The colour intensity was found to fall linearly with time to within the accuracy of the measurements; and the time required for the total fall was equivalent to the time required to complete nitration. Since we know from the work described in Section 5 that the concentration of benzene falls linearly with time during nitration, the conclusion must be drawn that the colour intensity is directly proportional to the benzene concentration in any given nitration solution at constant temperature.

The addition of equal quantities of the same aromatic compound, *e.g.*, benzene, to equal amounts of solutions in nitromethane containing identical concentrations of nitric acid but varying concentrations of real or potential nitrous acid, at the same temperature, produced initial colours increasing in intensity as the nitrous acid concentration increased. The addition of urea inhibited the formation of colours.

The addition of equal amounts of benzene to equal portions of the same solution of nitric acid (containing nitrous acid) in nitromethane at different temperatures produced initial colours having greater intensity the lower the temperature.

(b) *Production of the Colours by Various Reagents.*—The colours produced in the experiments mentioned below, which were carried out with benzene, could be visually matched against the colours arising in nitration solutions.

A number of observations were made with oxides of nitrogen. When nitric oxide was passed through a nitration solution the depth of colour at first increased, but the nitric acid was decomposed, nitrogen peroxide being formed. This experiment was then varied by omitting various substances or replacing them with others. When the nitric acid was omitted there was no colour; but when, in place of nitric acid, a little sulphuric acid or phosphoric oxide was added the usual colour was generated, in the former case homogeneously and in the latter on the surface of the oxide. The omission of nitromethane made no difference to any of these observations. When the benzene was omitted no colour was formed in any circumstances. When all these experiments, except those involving nitric acid, were repeated using dinitrogen trioxide, and again using nitrogen dioxide, in place of nitric oxide, the results were exactly the same.

(c) *Relation of Colour to Nitration Kinetics.*—The above observations establish that a coloured complex is formed from benzene and a lower oxide of nitrogen in the presence of an anhydrous condensing agent such as sulphuric or nitric acid or phosphoric oxide; and, furthermore, that the complex is in mobile equilibrium with its factors; and that it is on the low-energy side of a mobile equilibrium.

The same observations also establish that the formation of the coloured complex plays no essential rôle in the mechanism that determines the reaction kinetics. This follows because the colour intensity is proportional to the benzene concentration, whilst the nitration rate is independent of this concentration, wherefore the colour intensity can have no connexion with the rate. It is nevertheless true that real or potential nitrous acid is concerned both in the formation of the colour and in the determination of the rate. We conclude that the coloured substance is produced in such small quantity that the consumption of nitrous acid in its formation is negligible : were this not so, the liberation of nitrous acid due to the progressive reversal of complex formation as colour fades in the course of nitration would, by reason of the anticatalytic effect of nitrous acid, give rise to a progressively growing deceleration of the reaction; whereas, in fact, the velocity remains constant. This holds for benzene, toluene, and ethylbenzene, although it may not hold for hydrocarbons, such as *p*-xylene, which give considerably more intense colours and non-linear reaction-time curves. We do not further discuss such cases in this paper, as much more detailed investigation of them seems to be required.

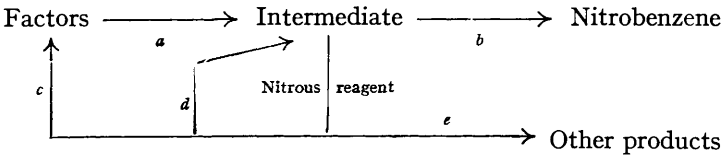
## (Sections 9 and 10) DISCUSSION.

### (9) *Mechanism of Nitration in Nitromethane Solution.*

(a) *Nitration of Benzene.*—The principal facts to be explained are as follows (Section 5). With nitric acid in large and substantially constant concentration, the reaction is of order zero. Nitrous acid, or, more accurately, some substance which in the water-diluted solution is estimated as nitrous acid, decelerates reaction according to the law, $k_0 = 1/(a + b\sqrt{n})$, where $k_0$ is the measured rate constant and $n$ the equivalent nitrous acid concentration. Nitrous acid does this without appreciably changing its own concentration in the course of reaction, and without disturbing the zero-order law. The reaction is strongly accelerated by increasing the nitric acid concentration, but this involves no disturbance either to the zero-order time law, or to the form of the nitrous acid rate law; indeed, the acceleration is the joint result of comparable decreases of the nitrous-acid-dependent and nitrous-acid-independent parts of the reciprocal rate. The reaction is accelerated by rise of the temperature, and this acceleration also arises from comparable changes in the two parts of the reciprocal rate.

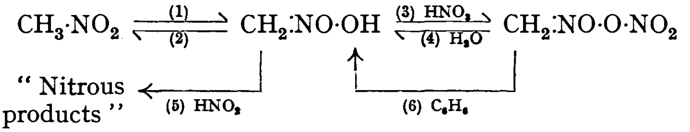
The zero-order time law shows at once that the slowest stage of the complete process does not involve benzene: we have to decide what it does involve. Nitrous acid, and products dependent on it, are excluded by the observation that the time law remains the same at the lowest attainable concentrations of nitrous acid. Responsibility for the time law thus lies between nitric acid and nitromethane. It is unlikely that nitric acid is the sole reagent for the slow process, first, because it is difficult to think of a probable change, and secondly, because in nitrations by means of nitric acid with sulphuric acid as solvent the reaction order with respect to the aromatic compound is not zero but one (Section 1, c): this seems to make the nitromethane at least partly responsible for the time law. The possibilities are that nitromethane is the sole reagent, with nitric acid as a possible catalyst, and that nitromethane and nitric acid interact as direct reagents; we might, for instance, assume $CH_3{\cdot}NO_2 \longrightarrow CH_2{:}NO{\cdot}OH$, or $CH_3{\cdot}NO_2 + HNO_3 \longrightarrow NO_2{\cdot}CH_2{\cdot}NO_2 + H_2O$, or some other kinetically equivalent isomerisation or condensation. Because we cannot explain the part played by nitrous acid without postulating *two* low-concentration intermediates in the nitration, we shall actually use a combination of these ideas.

The reason why one low-concentration intermediate will not explain the facts can be understood without entering into the quantitative details of the nitrous acid effect. Suppose we set up a one-intermediate scheme, *viz.*, the reactions *a* and *b* represented below, *a* being the slow process, involving nitromethane and possibly nitric acid, and *b* the rapid process. We then have to explain the decelerating action of nitrous acid by supposing that it, or something derived from it—we may call this shortly the " nitrous reagent "—reacts with the intermediate. The reaction or chain of reactions thus set up might terminate (*c*) with the factors, (*d*) with the single postulated intermediate, or (*e*) with other substances:



We shall find that there are objections to all these alternatives, though *c* and *d* are at first sight attractive, since they complete cyclic processes whereby the nitrous reagent could be regenerated, thus affording an explanation for the fact that the amount of it which disappears is inappreciable. We exclude alternative *c*, since it would amount to a catalytic shifting of the pseudo-equilibrium between factors and intermediate, and the shift would be in the direction of the factors. It is true that a catalyst may shift an equilibrium if there is sufficient of it; but in our case the direction of the shift is wrong, because, although the concentration of the nitrous reagent may be much larger than that of the intermediate, it must be very small compared with those of the factors. Therefore the nitrous reagent cannot alter the free energy of the latter, and its assumed effect must be envisaged as an increase of the partial molar free energy and fugacity of the intermediate. This implies repulsive forces between the intermediate and the nitrous reagent, and, further, that these entities would, in dilute solution, stay in each other's force-range in the presence of such forces—an absurd conclusion. Alternative *d* can at once be dismissed because, in the steady state, just as many molecules of the intermediate would be regenerated per second as were being destroyed by the nitrous reagent; thus the stationary concentration of intermediate, and the rate of production of nitrobenzene from it, would be unaffected, and the known influence of the nitrous reagent would remain unexplained. Reactions *e* would normally destroy potential nitrous acid, and, since we know that the amount destroyed is small compared with the initial amounts of nitrous acid and of benzene, we have to assume that the consumption of intermediate by route *e* is small relatively to its consumption by route *b*. But that is exactly what we must not assume if reactions *e* are to explain the decelerating effect. The possibility that potential nitrous acid is regenerated by some chain mechanism in reactions *e* is also excluded, because in any case, if we are to explain the anticatalysis, route *e* must absorb intermediate, and therefore, indirectly, factors, in quantity comparable to the quantity of nitrobenzene formed. But we know, from experiments with smaller concentrations of nitric acid than were taken for the kinetic measurements, that the alkalimetrically-measured amounts of nitric acid consumed agree with the titanometrically-determined quantities of nitrobenzene formed, leaving no margin for an appreciable consumption of nitric acid by any route other than nitration.

Because all one-intermediate schemes break down, we postulate two low-concentration intermediates. They are obtained by combining the possibilities already mentioned, *viz.*, the isomerisation of nitromethane and its condensation with nitric acid. We can then associate a nitrous acid reaction of type *e* with an intermediate which does *not* directly produce nitrobenzene : this is essential for the avoiding of the difficulties mentioned. The isomerisation would evidently be the first reaction, and the nitric acid condensation the second, since only the latter could give an active nitrating agent. Further, the isomerisation will certainly be strongly reversible, and the subsequent condensation with nitric acid is sure to be slightly reversed in the presence of the water it produces. Thus the preliminary system consists in reactions (1)—(4), supplemented by a nitrous acid reaction (5), which has to be further considered. In reaction (6) the second intermediate nitrates the benzene, being thereby reconverted into the first :



(Scheme I)

This cyclic linking of the two intermediates, which follows automatically from the rest of the scheme, is also essential to the interpretation of the qualitative observations : unless there were some such regenerative process, we could not explain why an inconsiderable consumption of nitrous acid produces a large effect on the reaction speed. Thus scheme I seems to provide the simplest possible basis for an attempted interpretation. On account of the chosen experimental conditions, we disregard the reactions (reversible proton-transfer) between nitric acid and water; these reactions would, however, play an essential part in the treatment of the more general kinetic problem which arises on removing the restriction that the proportion of nitric acid is large :

$$HNO_3 + H_2O \underset{(8)}{\overset{(7)}{\rightleftharpoons}} NO_3^- + H_3O^+ \qquad (I;\ 7,\ 8)$$

It is convenient to divide the quantitative treatment of the nitrous acid effect into two parts. We first consider why the significant power of the nitrous acid concentration is the square root. This point is dealt with simply by choosing the right form for reaction (5) in scheme I. It is assumed that what is estimated as nitrous acid is present in the nitration solutions almost wholly as a molecule which decomposes rapidly, slightly, and reversibly into two molecules, one of which is the " nitrous reagent." Reasonable details are easily supplied : in the strongly dehydrating conditions of the nitration mixtures, nitrous acid is likely to exist almost wholly as dinitrogen trioxide, and this is known to be dissociated rapidly, slightly, and reversibly into nitric oxide and nitrogen dioxide. The rate of any reaction involving a single molecule of either of the last-named oxides would be some function of the square root of the equivalent nitrous acid concentration :

$$2HNO_2 \rightleftharpoons N_2O_3 + H_2O \qquad N_2O_3 \rightleftharpoons NO + NO_2 \qquad \text{(I; 5)}$$
$$[\text{stoicheiometric } HNO_2] \approx [N_2O_3] = K[NO][NO_2] = K[NO]^2 = K[NO_2]^2$$

As to the mode of action of the " nitrous reagent " we can only surmise. One possibility, mentioned solely as an illustration, is that nitrogen dioxide adds slowly to the unsaturated link in *aci*nitromethane, forming a free radical, which in the oxidising surroundings rapidly loses a hydrogen atom to give dinitromethane.

$$NO_2 + CH_2{:}NO_2H \xrightarrow[\text{(slow)}]{} NO_2{\cdot}CH_2{\cdot}NO_2H \xrightarrow[\text{(fast)}]{} CH_2(NO_2)_2 + H \qquad \text{(I; 5)}$$

The second part of the problem is to explain why the function expressing the dependence of the rate on the square root of the nitrous acid concentration is the reciprocal of a linear function of the latter, *viz.*, $k_0 = 1/(a + bn^{\frac{1}{2}})$. The interpretation of this cannot now be assisted by *ad hoc* choice of the details of reaction, and our only course is to ascertain whether the scheme already developed from other considerations leads to the required relationship.

We consider the steady state of reaction in which the two intermediates have small, and therefore in an absolute sense only slowly varying, concentrations. Let $v_1, v_2, \ldots . v_6$ be the *instantaneous* rates of the reactions (1), (2), . . . (6) of scheme I, $v$ being the measured rate of nitration. The rate of formation of the first intermediate from nitromethane is $v_1$. The fraction of first intermediate which passes into the second intermediate is $f_{\text{I}} = v_3/(v_2 + v_3 + v_5)$, so that the rate of formation of the second intermediate in this direct way is $v_1 f_{\text{I}}$. This follows because the amount of material stored in the form of first intermediate is effectively zero and therefore effectively constant. The fraction of the second intermediate that enters into nitration is $f_{\text{II}} = v_6/(v_4 + v_6)$, so that the rate of nitration by the route specified is $v_1 f_{\text{I}} f_{\text{II}}$. This is true because the storage of material as second intermediate is effectively zero and hence effectively invariant. The rate of regeneration of the first intermediate from second intermediate, formed as described, is $v_1 f_{\text{I}}$, and hence the extra rate of production of second intermediate from material that has gone once round the reaction cycle is $v_1 f_{\text{I}}^2$. The consequential extra rate of nitration will be $v_1 f_{\text{I}}^2 f_{\text{II}}$. Continuing this argument we find :

$$v = v_1(f_{\text{I}} + f_{\text{I}}^2 + f_{\text{I}}^3 + \ldots)f_{\text{II}} = v_1 f_{\text{I}} f_{\text{II}}/(1 - f_{\text{I}}) = v_1 v_3 v_6/(v_2 + v_5)(v_4 + v_6)$$

We know that $v$ is independent of the time. Since $v_4$ will always involve the time owing to the progressive accumulation of water during nitration, the expression on the right cannot be independent of the time unless $v_6 \gg v_4$, in which case it reduces to $v_1 v_3/(v_2 + v_5)$. In order to see if this obviously necessary condition for time-invariance is also sufficient, we replace these instantanious rates by rate constants and appropriate functions of the reagent concentrations: $v_1 = k_1\phi_1(M)\text{F}_1(N)$, $v_2 = k_2M^*\text{F}_2(N)$, $v_3 = k_3M^*\text{F}_3(N)$, $v_5 = k_5M^*n^{\frac{1}{2}}\text{F}_5(N)$. Here $M$ is the concentration of nitromethane, $M^*$ that of *aci*nitromethane (first intermediate), and $N$ and $n$ those of nitric and nitrous acids. Since the concentrations of nitromethane and nitric acid are large, they occur in the equations in the form of functions $\phi_1$, $\text{F}_1$, $\text{F}_2$, $\text{F}_3$, $\text{F}_5$ which cannot be specified : we cannot even assert that $\text{F}_1$ and $\text{F}_2$ are the same, as they would be for thermodynamic reasons if $N$ were considerably smaller than it is. However, the only concentration which can exhibit a considerable *proportional* variation with time is $M^*$, and this disappears from the final equation by cancellation; thus $v$ becomes independent of the time and may be replaced by $k_0$ :

$$k_0 = \frac{k_1\phi_1(M)\text{F}_1(M) \,.\, k_3\text{F}_3(N)}{k_2\text{F}_2(N) + k_5n^{\frac{1}{2}}\text{F}_5(N)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This equation (6) is obviously identical with the empirical equation (1), and thus our reaction scheme gives a satisfactory account of the observed rate laws. The values of $a$ and $b$ are interpreted thus:

$$a = \frac{k_2}{k_1 k_3} \cdot \frac{\mathrm{F}_2(N)}{\phi_1(M) \,.\, \mathrm{F}_1(N) \,.\, \mathrm{F}_3(N)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$b = \frac{k_5}{k_1 k_3} \cdot \frac{\mathrm{F}_5(N)}{\phi_1(M) \,.\, \mathrm{F}_1(N) \,.\, \mathrm{F}_3(N)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

These equations, (7) and (8), have to be compared with equations (2) and (3). Since the proportional variation of $M$ is small in the experiments, $\phi_1(M)$ will be a linear function of $M$, that is, of $27 - N$. Taking $\phi_1$ as proportional to $27 - N$, the theoretical and empirical equations agree if $\mathrm{F}_1\mathrm{F}_3/\mathrm{F}_2 = N^6$ and $\mathrm{F}_1\mathrm{F}_3/\mathrm{F}_5 = N^5$ within the range of variation of $N$. On general grounds we expect $\mathrm{F}_3$ to be particularly sensitive to $N$, and to account to a considerable extent for these high indices.

The temperature-variable parameters $A$ and $B$ are given (except possibly for a constant) by the equations

$$A = k_2/k_1k_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$B = k_5/k_1k_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

Equations (9) and (10) are consistent in form with the empirical equations (4) and (5). This follows because $k_1, k_2, k_3$, and $k_5$ are expected separately to obey the Arrhenius equation; so that $A$ and $B$ will satisfy equations of the same form, and their logarithms will be linear functions of temperature for the short temperature ranges considered. If $E_1$, $E_2$, $E_3$, and $E_5$ are the energies of activation of the four reactions, our results for the temperature-variation of $A$ and $B$ receive the interpretation:

$$E_1 + E_3 - E_2 = 15; \qquad E_1 + E_3 - E_5 = 19 \text{ kilocals.}$$

Since most reactions that go with observable velocities near room temperature have energies of activation of the order of 20 kilocals., it seems consistent that values of this order are interpreted as combinations of three such energies, two with positive signs and one with a negative sign.

(b) *Nitration of Toluene and Ethylbenzene.*—The facts to be explained (Section 6) are that the nitrations of these substances are reactions of order zero, with absolute rates always equal to each other and to the rate for the nitration of benzene under the same conditions with regard to temperature and the concentrations of nitric and nitrous acids.

It is known that electron-releasing alkyl groups enhance the reactivity of the benzene ring towards electrophilic reagents. Nitration is an electrophilic substitution, and in Part II (J., 1931, 1959) it was shown that toluene is nitrated about 25 times faster than benzene when the same nitrating agent competes for the two hydrocarbons. Presumably ethylbenzene would be found to nitrate a little faster than toluene in experiments of this type. Now, in experiments by the competitive method, the reactions whose rates are compared are those in which the aromatic compounds are directly concerned; *i.e.*, they are of the type of reaction 6 of scheme I. Therefore, whilst reactions 1—5 of scheme I remain the same, independently of what is being nitrated, reaction 6 will depend on the aromatic compound and will have greater specific rates for toluene and ethylbenzene than for benzene. But we have seen that, so long as $v_6$ is sufficiently larger than $v_4$ to enable the latter to be neglected in comparison, *both* $v_4$ *and* $v_6$ disappear from the rate equation, thus eliminating the dependence of the measured rate both on the substance which is being nitrated and on the time: the rate is determined solely by reactions (1), (2), (3), and (5). It is evident that, if the necessary condition relating to $v_6$ and $v_4$ is fulfilled for benzene, it will be, with a still larger margin, for toluene and ethylbenzene. Hence the measured rate for these substances, as for benzene, will be independent of the time, and also independent of the substance.*

* One sees at once from this example why the competitive method, and not the kinetic method, is the right one for measuring the relative rates of nitration of aromatic compounds (cf. Part III, this vol., p. 907).

(c) *Nitration of the Halogenobenzenes.*—The facts to be explained are as follows (Section 7). For all four halogenobenzenes the measured rates of nitration are smaller than for benzene in two degrees, a lesser degree for fluoro- and iodo-benzene and a greater degree for chloro- and bromo-benzene (H>F,I>Cl,Br). For all four halogenobenzenes the effective reaction order is greater than zero, although for none is it greater than unity; and it is greater than zero in two degrees, a lesser degree for fluoro- and iodo-benzene and a greater degree for chloro- and bromo-benzene ($0 = \text{H} < \text{F,I} < \text{Cl,Br}$). The effective reaction order is not independent of time, but invariably rises during a run; in the case of chloro- and bromo-benzene it closely approaches unity towards the end of a run. As in the case of benzene, nitrous acid decreases the rate, whilst an increased concentration of nitric acid strongly increases the rate.

It is known that the electron-attracting halogen atoms decrease the reactivity of the benzene ring towards electrophilic reagents. In Part IV (preceding paper) it was shown that fluoro- and iodo-benzene are nitrated about 6 times, and chloro- and bromo-benzene about 30 times, slower than benzene when the same nitrating agent competes for halogenobenzenes and for benzene. Since these experiments measure the relative rates of reactions of the type of reaction (6) in scheme I, we have an obvious explanation for the facts noted above: in the nitration of the halogenobenzenes $v_6$ is no longer sufficiently greater than $v_4$ to enable the latter to be neglected. Intuitively one can see that under these conditions the relative reactivities of the halogenobenzenes, that is, their rates in reaction 6, will to some extent be reflected in the measured rates, and that, depending on the degree to which this is so, the effective reaction orders will be greater than zero.

To control intuition, and obtain further details concerning the consequences of the theory, we must examine the generalised rate equation:

$$\begin{aligned} v &= v_1 v_3 v_6/(v_2 + v_5)(v_4 + v_6) \\ &= \frac{k_1\phi_1(M)\mathrm{F}_1(N) \,.\, k_3\mathrm{F}_3(N) \,.\, k_6[\text{Arom.}]\mathrm{F}_6(N)}{\{k_2\mathrm{F}_2(N) + k_5 n^{\frac{1}{2}}\mathrm{F}_5(N)\}\{k_4[\mathrm{H_2O}]\mathrm{F}_4(N) + k_6[\text{Arom.}]\mathrm{F}_6(N)\}} \quad . \quad . \quad (11) \end{aligned}$$

Here Arom. stands for the aromatic compound and $\mathrm{F}_4$ and $\mathrm{F}_6$ are new unknown functions of the nitric acid concentration. (The concentration $M^{**}$ of the second intermediate, like $M^*$, the concentration of the first, disappears by cancellation.) There are three special cases.

The first is the limiting case already considered (and realised), in which $v_6 \gg v_4$ over practically the whole experimental range: $v$ is then independent of time, of [Arom.], and of $k_6$.

The second is an intermediate critical case in which, not merely are $v_6$ and $v_4$ comparable, but, more particularly, $k_4\mathrm{F}_4(N)$ equals $k_6\mathrm{F}_6(N)$ precisely. Since for stoicheiometric reasons $[\text{Arom.}] + [\mathrm{H_2O}]$ is constant, the second factor of the denominator of equation (11) will now be constant, and therefore $v$ will be proportional to [Arom.]; that is, the reaction will be accurately of the first order throughout its course.

The third is the opposite limiting case in which $v_6 \ll v_4$ over practically the whole experimental range: this means that $v$ will be proportional to $[\text{Arom.}]/[\mathrm{H_2O}]$, *i.e.*, to $[\text{Arom.}]/\{[\text{Arom.}]_0 - [\text{Arom.}]\}$, so that the reaction will start relatively extremely rapidly and end relatively very slowly.

Throughout the whole region between the first limiting case and the critical case, the effective reaction order will be between zero and unity; and it will rise during a run, approaching unity asymptotically towards the end of reaction. This can be seen as follows. In the case considered, $k_6\mathrm{F}_6(N)$ is greater, but not enormously greater, than $k_4\mathrm{F}_4(N)$. Expressing these factors as $N_6$ and $N_4$, writing $x$ for [Arom.], and omitting factors which are independent of the time, we find:

$$v \propto \frac{N_6 x}{N_4(x_0 - x) + N_6 x} \propto \frac{N_6}{N_4} \cdot \frac{x}{x_0} \cdot \left[1 + \frac{N_6 - N_4}{N_4} \cdot \frac{x}{x_0}\right]^{-1}$$

This means that, so long as $x/x_0$ is not small, *i.e.*, near the commencement of reaction, $v$ will diminish with time more slowly than $x$ does, so that the *initial* effective reaction order will have some definite value between zero and unity; when, however, $x/x_0$ becomes small, near the end of reaction, $v$ will become asymptotically proportional to $x$, and the effective reaction order will rise asymptotically to unity.

Throughout the whole region between the critical case and the second limiting case, the effective reaction order will be between unity and infinity; and it will fall during a run, approaching unity asymptotically towards the end of reaction. The law of variation of $v$ with time will be that just formulated, with $(N_6 - N_4)/N_4$ now a negative quantity: $v$ will decrease with time more rapidly than $x$ does as long as $x/x_0$ is not small; but when it becomes small, then $v$ will be proportional to $x$.

Now we know that benzene belongs to the first limiting case ($v_6 \gg v_4$). It does this so definitely and accurately (as shown by the absence of curvature near the end of the reaction–time curves) that a reduction in the specific rate of reaction (6) by factors of the order of only 6, or even 30, cannot be expected to displace the example from the first limiting case across the critical case into the region between the latter and the second limiting case. It is therefore satisfactory that in order to account for our results we have to assume that the halogenobenzenes fall in the region between the first limiting case and the critical case: $k_6F_6(N)$ is greater than $k_4F_4(N)$, but not incomparably greater. With this assumption the detailed interpretation follows immediately. In the nitration of fluoro- and iodo-benzene, for which the differences between $k_6F_6(N)$ and $k_4F_4(N)$ are still relatively large, the measured reactions are slower than for benzene, and their effective orders, not much above zero near the commencement of nitration, rise in the direction of unity towards the end. In the nitration of chloro- and bromo-benzene, for which $k_6F_6(N)$ is not much larger than $k_4F_4(N)$, the measured reactions are still slower, and their effective orders, which are considerably above zero at the commencement of nitration, become asymptotically equal to unity near the end.

From the form of equation (11) it is easily seen that nitrous acid must decelerate the measured reaction qualitatively as for the special case governed by equation (6). Except in the unlikely event of $F_6/F_4$ varying as a large negative power of $N$, the measured rate will increase rapidly with the nitric acid concentration in the general case of equation (11), as it has been shown to do in the special case of equation (6). Thus all the qualitative observations are explained.

(d) *Expression of the Mechanism as a Chain Reaction.*—The nature of the process elucidated in the foregoing section is best appreciated by writing it as a chain-reaction. The fundamental chain-mechanism is as follows:

*Chain initiation*:

$$\mathrm{CH_3{\cdot}NO_2 \longrightarrow CH_2{:}NO{\cdot}OH} \text{ (catalysed by } \mathrm{HNO_3})$$

*Chain propagation*:

$$\left\{\begin{array}{l}\mathrm{CH_2{:}NO{\cdot}OH + HNO_3 \longrightarrow CH_2{:}NO{\cdot}ONO_2 + H_2O}\\ \mathrm{CH_2{:}NO{\cdot}ONO_2 + HAr \longrightarrow CH_2{:}NO{\cdot}OH + NO_2{\cdot}Ar}\end{array}\right.$$

*Chain destruction* (*normal*):

$$\mathrm{CH_2{:}NO{\cdot}OH \longrightarrow CH_3{\cdot}NO_2} \text{ (catalysed by } \mathrm{HNO_3})$$

In addition there is a reaction which renders ineffective individual " links " in the " chain " without breaking the chain as a whole; and also a further method of chain destruction:

*Link destruction*:

$$\mathrm{CH_2{:}NO{\cdot}ONO_2 + H_2O \longrightarrow CH_2{:}NO{\cdot}OH + HNO_3}$$

*Chain destruction* (*abnormal*):

$$\left\{\begin{array}{l}\mathrm{2HNO_3 \rightleftharpoons N_2O_3 + H_2O \rightleftharpoons NO + NO_2 + H_2O}\\ \mathrm{CH_2{:}NO{\cdot}OH + NO_2 \longrightarrow CH_2(NO_2)_2 + H}\end{array}\right.$$

(or some other reaction between $\mathrm{CH_2{:}NO{\cdot}OH}$ and NO or $\mathrm{NO_2}$).

### (10) *Nitrating Agents and the Rôle of Solvents in Nitration.*

The unexpected conclusion that nitromethane functions as a convenient nitration solvent simply because its *aci*-form can give rise to a mixed anhydride with nitric acid, suggests a correlation between this and several other conclusions and observations. We have, for example, classified nitration solvents into three groups (Section 4): in most neutral organic solvents, *e.g.*, dioxan or acetonitrile, nitration is very slow; in acetic anhydride and nitromethane it proceeds at a medium rate; in sulphuric acid it is very fast. In sulphuric acid the reaction is bimolecular, the rate being proportional to the stoicheiometric concentration of nitric acid; and the same is true when the nitrating agent is introduced as dinitrogen pentoxide, the kinetic effect of which is the same as that of twice as many molecules of nitric acid (Section 1, c). The fact that the solvents acetonitrile and nitromethane, which for most reactions behave very similarly, are strongly differentiated with respect to nitration is significant in connexion with the conclusion that the *aci*-form of nitromethane plays an essential rôle.

We are familiar with the idea that the efficacy of brominating agents X·Br depends on the affinity of X for the electrons of the X·Br bond, since this determines the affinity of the bromine atom for the aromatic electrons: Cl·Br is a better brominating agent than Br·Br, which is in turn better than OH·Br (Ingold, Smith, and Vass, J., 1927, 1245). It may now be suggested that nitrating agents are always of the form $X{\cdot}NO_2$, their efficacy being determined by the electron-affinity of X, as indicated, for instance, by the acid-strength of X·H. If this is true, the nitric acid molecule itself, $HO{\cdot}NO_2$, *i.e.*, nitric acid in not too concentrated solutions in inert solvents, would be a weak nitrating agent, corresponding to the very weakly acidic character of water, HO·H. In nitromethane and acetic anhydride solutions, the nitric acid becomes acylated, and the product $AcO{\cdot}NO_2$ is a more active nitrating agent, in agreement with the greater acidity of the organic acids AcO·H. In sulphuric acid solution, $SO_4H{\cdot}NO_2$ can be formed (as it surely will be when dinitrogen pentoxide is employed) and this would be a powerful nitrating agent for the reason which makes $SO_4H{\cdot}H$ a very strong acid.

The hydroxonium ion, $H_3O^+$, is to be regarded as an acid, which is not so strong as sulphuric acid, but yet much stronger than acids obeying the dilution law. Therefore $H_2O^+{\cdot}NO_2$ should be a very active nitrating agent. Hantzsch has shown (*Ber.*, 1925, **58**, 941) that in nearly absolute nitric acid protons are transferred from one molecule of nitric acid to another with the production of $NO(OH)_2^+$ and $N(OH)_3^{++}$, the perchlorates of which he and Wolf isolated. He surmised that the second of these might be the nitrating agent of "mixed acid," whilst Brewin and Turner (J., 1928, 334) suggested $N(OH)_4^+$. Our point of view leads us to suppose that the first of Hantzsch's cations, in its tautomeric form $NO_2{\cdot}OH_2$, is the nitrating agent of fuming nitric acid: the other cations have not the right type of structure. In "mixed acid" $NO_2{\cdot}OH_2^+$ and $NO_2{\cdot}SO_4H$ may both occur, and both should be highly active.

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