496. *Kinetics and Mechanism of Aromatic Nitration. Part V. Nitration by Acyl Nitrates, particularly by Benzoyl Nitrate.*

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The nitration of benzene by benzoyl nitrate in carbon tetrachloride has been kinetically examined. With the benzene in constant excess, the reaction was approximately of first order. The rate was found to vary with the sample of benzoyl nitrate. Preparations of benzoyl nitrate always contain benzoic anhydride. It was shown that added benzoic anhydride depressed the rate of nitration of benzene by a given sample of benzoyl nitrate. This suggested that benzoyl nitrate might be exerting its nitrating action through a small stationary concentration of dinitrogen pentoxide, formed, along with benzoic anhydride, in the rapidly established equilibrium,

$$2BzO{\cdot}NO_2 \rightleftharpoons N_2O_5 + Bz_2O.$$

Confirmation was secured by examining the effect of benzoic anhydride on the nitrating properties of dinitrogen pentoxide. The latter in carbon tetrachloride nitrated benzene instantly under the conditions of this work. But the addition of excess of commercial benzoic anhydride at once reduced the nitrating power of the dinitrogen pentoxide to approximate equivalence with that of benzoyl nitrate. Commercial benzoic anhydride contains benzoic acid. Pure benzoic anhydride did not act on dinitrogen pentoxide in carbon tetrachloride in the way described; but it did so, if some benzoic acid also was introduced. Thus, a rapid establishment of the above-written equilibrium requires the presence of acid.

Consistently, it was shown that, with a fixed concentration of benzoic acid, the rate of nitration of benzene by dinitrogen pentoxide and excess of benzoic anhydride was decreased by increasing the excess of the latter; and that, with fixed concentrations of benzoic anhydride, the rate of nitration was decreased by increasing the concentration of benzoic acid. From this it is concluded that the above anhydride–anhydride equilibrium, catalysed by acid, arises by combination (addition) of the two anhydride–acid equilibria,

$$N_2O_5 + BzOH \rightleftharpoons BzNO_3 + HNO_3$$
$$Bz_2O + HNO_3 \rightleftharpoons BzNO_3 + BzOH$$

No evidence could be secured that benzoyl nitrate directly attacks the aromatic molecule: its nitrating action seems to be exerted entirely through dinitrogen pentoxide. Experiments by Cohen and Wibaut make a like conclusion probable for the acetyl nitrate, presumed to be present in solutions of nitric acid in excess of acetic anhydride.

(1) *Objects and Background.*

(1.1) *Related Work on the Kinetics of Nitration.*—In Part I (*J.*, 1938, 929) the principles were mentioned by which one might set down a series of actual or possible nitrating agents in the theoretically expected order of diminishing reactivity, *e.g.*,

$$NO_2^+,\ NO_2{\cdot}OH_2^+,\ NO_2{\cdot}O{\cdot}NO_2,\ NO_2{\cdot}OBz,\ NO_2{\cdot}OH.$$

In Parts II, III, and IV (preceding papers), this series has been examined to the following extent: nitration by the nitronium ion has been established; the nitric acidium ion has been shown to dissociate into, and nitrate through, the nitronium ion, but nitration also by the nitric acidium ion itself has been made plausible; and again, the dinitrogen pentoxide molecule has been shown to dissociate into, and nitrate through, the nitronium ion, although nitration also by the undissociated molecule has been realised.

These studies led to a consideration of the fourth member of the above series, in principle a mixed anhydride of nitric acid and a weaker acid, the example being benzoyl nitrate. Expecting this to be a nitrating agent of low efficiency, one might have expected even greater difficulty than before in suppressing nitration through more active nitrating agents formed by its decomposition, and hence greater difficulty in establishing nitration by the original undecomposed molecule. This has been our experience. The decompositions of benzoyl nitrate to more active nitrating agents are on the whole more prominent, and more complicated, than are those of the nitrating agents treated in the preceding studies. Because of this, the nature of the decomposition through which benzoyl nitrate acts as a nitrating agent has been established only in a qualitative way. It is not possible to assert, as a result of the present work, that benzoyl nitrate cannot directly engage in nitration, but no evidence of any such behaviour has been found.

Referring to the last member of the series of nitrating agents written above, we may recall that nitration by nitric acid proceeds, as far as is known (cf. Parts I—III), entirely through either the nitronium ion or the nitric acidium ion. No evidence has been encountered that the nitric acid molecule *per se* can directly engage in nitration. This paper therefore completes the present phase of our study of the above series by the method of reaction kinetics.

(1.2) *Previous Work on Nitration by Acyl Nitrates.*—Lachowicz observed (*Ber.*, 1884, **17**, 1281) that, when benzoyl chloride is heated with silver nitrate, benzoic anhydride is formed together with oxides of nitrogen. Francis reinvestigated this reaction at lower temperatures with a view to isolating intermediates (*J.*, 1906, **89**, 1; *Ber.*, 1906, **39**, 3798). He obtained a yellow oil, which he regarded as benzoyl nitrate, formed in the first of the following series of reactions, which proceed further at higher temperatures :

$$\begin{aligned} \mathrm{BzCl} + \mathrm{AgNO_3} &= \mathrm{BzNO_3} + \mathrm{AgCl} \\ 2\mathrm{BzNO_3} &= \mathrm{Bz_2O} + \mathrm{N_2O_5} \\ 2\mathrm{N_2O_5} &= 2\mathrm{N_2O_4} + \mathrm{O_2} \end{aligned}$$

The analytical data for the yellow oil did not agree with the formula of benzoyl nitrate, but it was suggested that this was due to the presence of benzoic anhydride—a plausible interpretation in view of the ready decomposition of the oil, the known production of benzoic anhydride, and the volatility of oxides of nitrogen.

Francis showed that his benzoyl nitrate could be used to nitrate aromatic compounds in aprotic solvents such as carbon tetrachloride. He investigated particularly benzenoid hydrocarbons and phenol derivatives. Further work on hydrocarbons has been reported by Willstätter and Kubli (*Ber.*, 1909, **42**, 4151), and on phenols and phenol ethers by Oxford (*J.*, 1926, 2004) and by Griffiths, Walkey, and Watson (*J.*, 1934, 631). The last-named investigators made the important observation that the ratio *ortho/para* in which isomerides are formed in the mononitration of anisole by benzoyl nitrate is much higher than that in which they are produced in nitration either by mixed nitric and sulphuric acids, or by nitric acid alone, or by nitric acid in acetic acid, *i.e.*, by reagents which are now known (cf. Part II) to react through the nitronium ion.

The use, for aromatic nitration, of solutions of nitric acid in excess of acetic anhydride was introduced by Orton (*J.*, 1902, **81**, 806). Pictet and Khotinsky reported the isolation of acetyl nitrate from solutions of dinitrogen pentoxide in acetic anhydride (*Compt. rend.*, 1907, **144**, 210; *Ber.*, 1907, **40**, 1163). Its nitrating properties resembled those of Orton's solutions, and also those of Francis's benzoyl nitrate. It gave high *ortho/para* ratios for the nitration of several monosubstituted benzenes. This has been confirmed in a quantitative investigation by Holleman, Hartogs, and van der Linden (*Ber.*, 1911, **44**, 717) on the nitration of acetanilide with Orton's mixture, and in one by Griffiths, Walkey, and Watson (*loc. cit.*) on the nitration of anisole with this reagent, which they found to behave quite similarly to benzoyl nitrate, and very differently from the group of reagents now recognised as reacting through the nitronium ion.

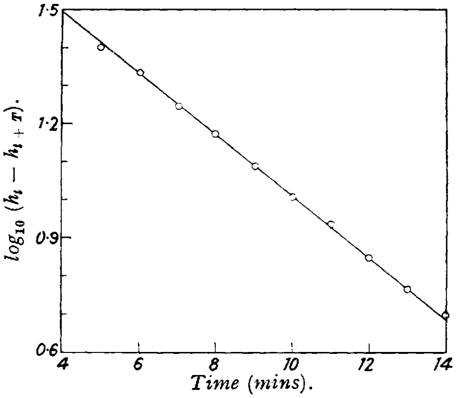
In the present observations on the kinetics of nitration, we have used benzoyl nitrate, rather than acetyl nitrate, because of the tendency of the latter to explode during isolation. Reference will be made later (Section 3.2) to the kinetic study, reported by Cohen and Wibaut (*Rec. Trav. chim.*, 1935, **54**, 409), of nitration with Orton's mixture.

(2) *Kinetic Observations.*

(2.1) *Nitration by Benzoyl Nitrate.*—As heretofore, the dilatometric method of following the kinetics of nitration was adopted. Chemical analysis was employed as a check. Carbon tetrachloride was used as solvent throughout the work. It was found that benzene could be nitrated, at temperatures near 20°, by means of benzoyl nitrate in carbon tetrachloride at rates convenient for dilatometric observation; and accordingly, benzene was taken as the substance to be nitrated in most of the experiments of the present series.

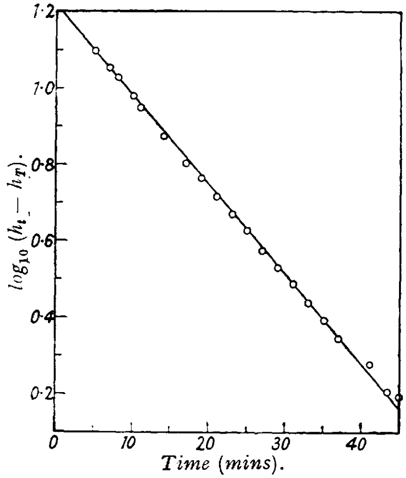
A number of samples of benzoyl nitrate were prepared by Francis's method. Kinetic experiments on the nitration of benzene in constant excess with this reagent in carbon tetrachloride at 20° indicated a reaction of approximately first order with respect to the nitrating agent. This is illustrated by the linearity of the logarithmic plot in Fig. 1. However, the first-order rate constants varied from run to run, as is illustrated in Table I, in a manner which suggested that some impurity, present in different proportions in the different samples of benzoyl nitrate, was affecting the rate of nitration. Since the work of Lachowicz and of Francis shows that benzoic anhydride is a decomposition product of benzoyl nitrate, and is normally present in preparations of the latter, the effect on nitration rate of added benzoic anhydride was tested. Table II shows the results obtained in a pair of runs, which were made with the same sample of benzoyl nitrate, all conditions being the same, except that, in one of the runs, some benzoic anhydride was introduced. These and similar experiments established that added benzoic anhydride depresses the rate of nitration of benzene by benzoyl nitrate.

FIG. 1.



Nitration of benzene in constant excess by benzoyl nitrate, prepared by Francis's method, in carbon tetrachloride at 20°. *Kinetics illustrated by Run No.* 16. *Plot covers* 85% *of reaction.*

FIG. 2.



Nitration of benzene in constant excess by a mixture of dinitrogen pentoxide, benzoic anhydride, and benzoic acid, in carbon tetrachloride at 20°. *Run No.* 150. *Plot covers* 90% *of reaction.*

TABLE I.

Some first-order rate constants (k_1 *in sec.*$^{-1}$) *for the nitration of benzene in excess by benzoyl nitrate in carbon tetrachloride at* 19·90°.

(Initially, $[C_6H_6] = 4{\cdot}47$M.; $[BzNO_3] = 0{\cdot}030$M.)

Run No.	8	10	11	14	15	16
10^4k_1	29·1	39·4	38·4	32·0	28·4	30·3

TABLE II.

Illustrating the effect of benzoic anhydride on the first-order rate constant (k_1 *in sec.*$^{-1}$) *of nitration of benzene in excess by benzoyl nitrate in carbon tetrachloride at* 20·00°.

(Initially, $[C_6H_6] = 2{\cdot}36$M.; $[BzNO_3] = 0{\cdot}030$M.)

Run No.	Added $[Bz_2O]$.	10^4k_1.	Run No.	Added $[Bz_2O.]$	10^4k_1.
251	—	44·0	252	0·035	20·0

These results suggested that benzoyl nitrate might be exerting its property of nitration through a small stationary concentration of the presumably more reactive entity, dinitrogen pentoxide, formed, along with benzoic anhydride, in the following rapidly reversible process :

$$2BzO{\cdot}NO_2 \rightleftharpoons Bz_2O + N_2O_5 \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

Accordingly the series of experiments next to be described was directed towards the building-up of a nitrating agent equivalent to benzoyl nitrate from the components benzoic anhydride and dinitrogen pentoxide.

(2.2) *Nitration by Mixtures of Dinitrogen Pentoxide, Benzoic Anhydride, and Benzoic Acid.*—The above hypothesis of the nitrating action of benzoyl nitrate requires the following statements to be true under the experimental conditions : (*a*) dinitrogen pentoxide must be an intrinsically more active nitrating agent than benzoyl nitrate; (*b*) the equilibrium between the three anhydrides must lie towards the left in the reaction as written above, *i.e.*, an excess of benzoic anhydride, added to dinitrogen pentoxide, must destroy nearly the whole of the latter ; and (*c*) the rate at which this reaction proceeds to equilibrium must be greater than the rate at which the aromatic compound is nitrated.

Condition (*a*) is satisfied. This becomes obvious when we compare the kinetic runs reported in this paper with those in the preceding paper. Most of the runs with benzoyl nitrate as the nitrating agent have been carried out with benzene as the substance nitrated, the solvent being carbon tetrachloride, and the temperature 20°. But benzene is nitrated by dinitrogen pentoxide in carbon tetrachloride much too rapidly to allow the kinetics to be followed even at the freezing-point of the solvent. In order to obtain measurable rates at 20° with dinitrogen pentoxide as the nitrating agent, it is necessary to employ much less reactive aromatic compounds, such as *p*-dichlorobenzene or ethyl benzoate, which have specific nitration rates some hundreds of times smaller than that of benzene. This is a measure of the intrinsically greater reactivity of dinitrogen pentoxide than of benzoyl nitrate as nitrating agent.

Conditions (*b*) and (*c*) were together shown to be fulfilled by following kinetically the nitration of benzene in carbon tetrachloride at 20° with mixtures of dinitrogen pentoxide and (commercial) benzoic anhydride as nitrating agent. The benzene, instead of being nitrated by the dinitrogen pentoxide within a few seconds, as it would have been in the absence of the benzoic anhydride, was nitrated by mixtures containing a small excess of benzoic anhydride at rates comparable to those obtained by the use of Francis's benzoyl nitrate as the nitrating agent. This shows that the benzoic anhydride must have destroyed most of the dinitrogen pentoxide, giving a material similar in nitrating properties to benzoyl nitrate; and it shows that this must have happened at a rate considerably greater than the rate at which the resulting material nitrated the benzene. The benzene being in constant excess, the kinetic form of these runs again indicated a reaction of approximately first order with respect to the nitrating agent.

In these experiments, which were intended to be of a preliminary nature, the dinitrogen pentoxide was carefully prepared according to our usual routine; but the benzoic anhydride was the commercial material, and it contained free benzoic acid. When the runs were repeated with our own benzoic anhydride, which was free from benzoic acid, different results were obtained. The benzoic anhydride did not now depress initial rates of nitration by dinitrogen pentoxide, and, in particular, did not reduce the rate of nitration of benzene to a measurable order of magnitude. Indeed, the dinitrogen pentoxide even began to nitrate the benzoic anhydride, much as it would have nitrated a benzoic ester, had one been present, according to the experiments described in the preceding paper.

The runs were therefore again repeated, but with the addition of benzoic acid, as well as of pure benzoic anhydride. The nitrating power of the dinitrogen pentoxide was once more greatly reduced by the added substances. In the presence of a reactive aromatic compound, such as benzene, very little nitration either of benzoic acid or of benzoic anhydride took place. Instead, the benzene was nitrated at rates comparable to those which had been obtained either with benzoyl nitrate as the nitrating agent, or by the use of mixtures of dinitrogen pentoxide with commercial benzoic anhydride. Again, with the benzene in constant excess, the kinetics indicated a reaction of approximately first order with respect to the nitrating agent, as is illustrated by the logarithmic plot in Fig. 2.

TABLE III.

Effect of benzoic anhydride on the first-order rate constant (k_1 *in* $sec.^{-1}$) *of nitration of benzene in excess by dinitrogen pentoxide in carbon tetrachloride at* 20·00° *in the presence of a fixed amount of benzoic acid.*

(Initially, $[C_6H_6]$ = 2·36M.; [BzOH] = 0·0633M.)

Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	10^4k_1.	Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	10^4k_1.
145	0·0305	0·0346	21·1	150	0·0265	0·1025	9·12
153	0·0341	0·0417	14·0	156	0·0341	0·1435	9·35
148	0·0214	0·0696	10·23	152	0·0265	0·1721	7·30
154	0·0341	0·0753	12·45	151	0·0265	0·2050	6·15
155	0·0341	0·0753	12·20				

Experiments were carried out in order to ascertain the effect of the addition of different initial amounts of benzoic anhydride, and of benzoic acid, on the rate of nitration of benzene by dinitrogen pentoxide. The results of one such series of experiments are reported in Table III. Here the concentrations of benzene and of benzoic acid were kept constant, and that of the dinitrogen pentoxide was given certain fixed values, whilst the concentration of the benzoic anhydride was varied from run to run. Some sets of runs of a different kind are reported in Table IV. In these, the concentrations of benzene and benzoic anhydride were fixed, whilst the concentrations of dinitrogen pentoxide and of benzoic acid were varied.

TABLE IV.

Effect of benzoic acid on the first-order rate constants (k_1 in sec.$^{-1}$) of nitration of benzene in excess by dinitrogen pentoxide in carbon tetrachloride at 20·00° *in the presence of fixed amounts of benzoic anhydride.*

(Initially, $[C_6H_6] = 2{\cdot}36$M.)

Run No.	Initial $[N_2O_5]$.	Initial $[Bz_2O]$.	Initial [BzOH].	10^4k_1.
145	0·0305	0·0346	0·0633	21·1
146	0·0242	,,	0·1267	10·7
149	0·0265	0·0696	0·0254	18·6
148	0·0214	,,	0·0633	10·65
158	0·0354	0·1025	0·0252	18·05
150	0·0265	,,	0·0633	9·12
157	0·0354	,,	0·1267	7·74

The figures in Tables III and IV are not suitable for quantitative treatment, because some of the initial concentrations have no simple significance for the whole kinetic runs, to which the quoted rate constants apply. However, it is obvious from Table III that, with fixed concentrations of benzene and of benzoic acid, the rate of nitration diminishes with increasing concentration of benzoic anhydride. It can be shown by means of a graphical representation of the figures that, for a fixed initial concentration of dinitrogen pentoxide, the reciprocal of the first-order rate constant increases approximately linearly with increasing concentration of benzoic anhydride. It also appears that, for a fixed concentration of benzoic anhydride, the rate constant increases with the initial concentration of dinitrogen pentoxide. All this is true for a fixed concentration of benzoic acid. The figures in Table IV show that, for fixed concentrations of benzene and benzoic anhydride, the rate of nitration diminishes with increasing concentration of benzoic acid.

(3) *Discussion.*

(3.1) *Mechanisms of Nitration by Benzoyl Nitrate.*—It has been shown in Section 2 that the rate of nitration of benzene by benzoyl nitrate, prepared by Francis's method, is depressed by added benzoic anhydride. It has also been shown that rates of nitration by benzoyl nitrate can be simulated by employing, as the nitrating agent, mixtures of dinitrogen pentoxide and benzoic anhydride, provided that they contain some free benzoic acid. Finally, it has been established that the first-order rate constants for the nitration of benzene in constant excess by mixtures of dinitrogen pentoxide, benzoic anhydride, and benzoic acid, increase with the concentration of dinitrogen pentoxide, when the concentrations of benzoic anhydride and of benzoic acid are constant, and decrease with increasing concentration of either benzoic anhydride or benzoic acid when the other concentrations are fixed.

Nearly all these effects are qualitatively interpreted by the hypothesis that benzoyl nitrate exerts its nitrating power through the nitrating action of a small concentration of dinitrogen pentoxide, which is formed along with benzoic anhydride in the reversible reaction (1) (p. 2469). It appears that this reaction attains equilibrium only slowly in the absence of acids, but that it runs rapidly to equilibrium under the catalytic influence of benzoic acid, which is usually present in the systems now considered, unless special measures are taken to secure its exclusion.

The observation which this hypothesis does not cover is the decrease of rate of nitration, by fixed concentrations of dinitrogen pentoxide and benzoic anhydride, in the presence of increasing concentrations of benzoic acid. In order to accommodate this finding, we assume that, in addition to the anhydride–anhydride equilibrium (1), an anhydride–acid equilibrium is set up, one form of which is shown in equation (2) :

$$N_2O_5 + BzOH \rightleftharpoons BzNO_3 + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Assuming equilibrium, it makes no difference whether we regard the benzoic acid as directly destroying dinitrogen pentoxide as represented in equation (2), or as acting analogously on benzoyl nitrate, as in equation (3), thereby producing benzoic anhydride, which destroys dinitrogen pentoxide according to equation (1). Thus the alternative form (3) of the anhydride–acid equilibrium,

$$BzO{\cdot}NO_2 + BzOH \rightleftharpoons Bz_2O + HNO_3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is not independent of (2). In other words, the equilibrium conditions for the reactions (1), (2), and (3) are expressible in terms of only two equilibrium constants. Reactions (2) and (3) evidently provide a mechanism for reaction (1), accommodating its acid catalysis. It follows that the presence of benzoic acid will always involve the presence of nitric acid; and that the catalysis of reaction (1), which we have described as catalysis by benzoic acid, must not be regarded as specific to that acid. Such reactions should be subject to a general catalysis by acids.

On the whole, the case for assuming that benzoyl nitrate nitrates by way of dinitrogen pentoxide seems as strong as qualitative evidence can make it.* The preceding paper shows that the dinitrogen pentoxide may nitrate directly, although in some circumstances it will act through the nitronium ion.

(3.2) *Mechanism of Nitration by Acetyl Nitrate and by Solutions of Nitric Acid in Acetic Anhydride.*—No kinetic study has yet been made of aromatic nitration as effected by isolated acetyl nitrate. However, as was noted in Section 1.2, there is a good deal of evidence indicating that the nitrating properties of solutions of nitric acid in acetic anhydride are due to the formation of acetyl nitrate; and Cohen and Wibaut have recorded a study of the kinetics of the nitration of benzene by means of such solutions (*loc. cit.*).

According to our conclusions concerning the mode of nitration by benzoyl nitrate, we should expect nitration by acetyl nitrate, or by a solution of nitric acid in acetic anhydride, to proceed by way of dinitrogen pentoxide, formed in the following system of balanced reactions :

$$HNO_3 + Ac_2O \rightleftharpoons AcOH + AcNO_3$$
$$HNO_3 + AcNO_3 \rightleftharpoons AcOH + N_2O_5$$

and therefore,

$$2AcNO_3 \rightleftharpoons Ac_2O + N_2O_5$$

Cohen and Wibaut's kinetic results for the nitration of benzene by solutions of nitric acid in an acetic anhydride solvent are, as the authors point out, very difficult to interpret, because of the simultaneous occurrence of nitration of the acetic anhydride. Indeed, the conditions for their main series of experiments seem to have been somewhat unhappily chosen. However, the authors have also provided a limited body of data concerning the nitration of benzene by nitric acid, in the presence of acetic anhydride, under conditions in which the disturbance of side-reactions is much less serious, *i.e.*, in carbon tetrachloride as solvent, with the addition of only small amounts of acetic anhydride. The recorded results indicate, as is concluded by the authors, that the rate of nitration is increased by decreasing the concentration of acetic anhydride. The authors interpret this as a solvent effect; but if it should be simply a solvent effect on nitration by nitric acid, or by some entity formed from nitric acid without the direct participation of acetic anhydride, then still greater rates should be obtained if the latter substance is omitted altogether. Apparently Cohen and Wibaut did not test this inference; but we have tested it, although in doing so we had to add a little nitromethane to the carbon tetrachloride solvent, because nitric acid, in the absence of any acetic anhydride, is only slightly soluble in pure carbon tetrachloride. We find that nitric acid, when dissolved in this mixed carbon tetrachloride solvent, at concentrations of the order of those used by Cohen and Wibaut, does not nitrate benzene at 20° to any detectable extent. When a small quantity of acetic anhydride is added, nitration supervenes; but there is an optimum amount of this reagent, and an excess of it tends to suppress nitration.

The parallelism between these observations and those relating to the effect of added benzoic anhydride on rate of nitration by benzoyl nitrate is evident. We may reasonably infer, first, that the nitrating power of solutions of nitric acid in acetic anhydride is indeed due to the formation of acetyl nitrate, and secondly, that the nitrate acts by a mechanism similar to that which we have already derived for nitration by benzoyl nitrate, *i.e.*, by way of dinitrogen pentoxide, reversibly formed in the system of equilibria written above.

(4) *Experimental Methods.*

(4.1) *Preparation of Materials.*—Benzoyl nitrate was prepared by Francis's method in an all-glass apparatus. The benzoyl chloride was introduced into the reaction bulb by distillation, together with enough carbon tetrachloride to reduce its freezing point below −15°. The silver nitrate, previously fused, ground, and dried in a vacuum over phosphoric oxide, was added by rotating a side-tube attached by a lubricated ground-glass joint. A vent, through phosphoric oxide, allowed gaseous products, which were formed in only small amount, to pass out of the reaction chamber. After the conclusion of the reaction, which was conducted with continuous stirring below −15°, the solution was passed through a

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* Even with the simplest assumptions, *viz.*, that mixtures of dinitrogen pentoxide, benzoyl nitrate, benzoic anhydride, nitric acid, and benzoic acid, always preserve equilibrium, and that nitration by such mixtures proceeds through molecular dinitrogen pentoxide only, the hypothesis offered in the text leads to an expression for the nitration rate which is algebraically complicated, and involves three disposable constants. For this reason, we have not attempted its quantitative experimental confirmation.

ground-glass filter by inverting the apparatus; and thus the mixture of benzoyl nitrate and carbon tetrachloride was collected. It was stored at about −10°, and diluted for use, as required, with dry carbon tetrachloride.

Benzoic anhydride was prepared as usual from benzoic acid and excess of acetic anhydride. After a preliminary purification by distillation under diminished pressure, the product was washed in ethereal solution with aqueous sodium hydroxide in order to remove all free benzoic acid; and the ether was then dried by means of calcium chloride and a little potassium carbonate, and distilled. The benzoic anhydride thus obtained was finally purified by crystallisation from light petroleum.

Dinitrogen pentoxide was prepared as described in the preceding paper.

(4.2) *Dilatometric Methods.*—The apparatus and method for following the kinetics of nitration by dilatometry were substantially as described in the preceding paper. For the nitrations by benzoyl nitrate, a fixed volume of the stock solution of benzoyl nitrate in carbon tetrachloride was delivered from a pipette into additional carbon tetrachloride, and, after 10 minutes allowed for the mixture to attain the temperature of the thermostat, the benzene, also at thermostat temperature, was added from a pipette, and the dilatometer, already immersed in the thermostat, was filled with the mixture. For the study of the effect of benzoic anhydride on nitration by benzoyl nitrate, the same procedure was used, except that the sample from stock of benzoyl nitrate dissolved in carbon tetrachloride was delivered into a solution of benzoic anhydride in carbon tetrachloride. In the experiments with dinitrogen pentoxide, a measured volume of a solution of this substance in carbon tetrachloride was added to a solution of benzoic anhydride, or of benzoic anhydride and benzoic acid, in carbon tetrachloride, and the whole was allowed 8 minutes to attain the temperature of the thermostat, before the benzene was added and the dilatometer filled.

The course of two dilatometric runs is shown graphically in Figs. 1 and 2 (p. 2469).

(4.3) *Analytical Control.*—Analytical checks on the dilatometric measurements were carried out exactly as described in the preceding paper, and the results were generally similar. Rate constants obtained by following the change of acidity agreed approximately with corresponding rate constants determined dilatometrically, the latter being the more precise.

The authors of this series of papers thank Imperial Chemical Industries Limited, for grants in aid of this work.

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[*Received, December* 17*th*, 1949.]