714. *Kinetics of Acetoxylation and Nitration of* o-*Xylene: A Rate-determining Protonation.*

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In the reaction between *o*-xylene and nitric acid–acetic anhydride mixtures, the acetoxylation : nitration rate ratio is constant under a variety of conditions when the individual rates change by factors of up to 330. The total rate (acetoxylation plus nitration) is independent of *o*-xylene concentration and is only slightly increased when *m*-xylene is used as substrate. The rate ratio of acetoxylation : nitration, however, changes from 43 : 57 for *o*-xylene to 4 : 96 for *m*-xylene. Sulphuric acid exerts marked catalytic effect on both reactions. These results are explained in terms of a rate-determining formation of a single reactive species—protonated acetyl nitrate. The kinetic effects of added sulphuric acid, acetic acid, and lithium nitrate are consistent qualitatively with the suggested mechanism.

WHEN *o*-xylene is treated with nitric acid in acetic anhydride, in addition to the expected 3- and 4-nitro-xylenes, 3,4-dimethylphenyl acetate is formed and is the major product.[1] Other hydrocarbons also give rise to acetoxy-products when they react with nitric acid in acetic anhydride, and it has been suggested [1] that the acetoxylating species is protonated acetyl nitrate, $Ac \cdot \overset{+}{O}H \cdot NO_2$. We now report a kinetic study of the concurrent acetoxylation and nitration reactions of *o*- and of *m*-xylene. The results establish that the same reactive species is responsible for both acetoxylation and nitration of these substrates, namely protonated acetyl nitrate.

EXPERIMENTAL

Acetic anhydride (Riedel–de Haën reagent grade) was fractionated under reduced pressure and then had b. p. 60°/55 mm. Acetic acid (AnalaR) was fractionated and had b. p. 118·5°. *o*-Xylene (British Drug Houses Ltd.) was 99·5% pure by gas chromatography. *m*-Xylene was purified by preparative gas chromatography (Bechman Megachrom). An analytical chromatogram of the purified product indicated complete removal of isomeric hydrocarbons. 3-Nitro-*o*-xylene was purified by preparative gas chromatography. 4-Nitro-*o*-xylene (m. p. 27°) was recrystallised (×3) from ethanol. 3,4-Dimethylphenol (m. p. 64°) was recrystallised (×3) from light petroleum (b. p. 40—60°)–carbon tetrachloride.

Nitric acid was prepared by distilling a mixture of fuming nitric acid (1 vol.) and concentrated sulphuric acid (2 vol.) at 25—30°. The acid was collected in a cold trap (−78°) and could be stored as the solid for several weeks without becoming discoloured. Analysis gave the acid content as 99·8 ± 0·3%. Application of the Griess–Ilosvay test [2] showed that the freshly-prepared acid contained less than 5×10^{-3} mole-% of nitrous acid, while a sample after 6 weeks storage contained less than 0·1 mole-% nitrous acid.

Kinetics.—A known excess of hydrocarbon was added to a freshly-prepared ($\gg$30 min. old) solution of nitric acid in acetic anhydride at 25·0°. Samples (5 ml.) were withdrawn from the mixture at suitable intervals and shaken with 2N-sodium hydroxide solution (100 ml.) in a separatory funnel. The nitro-compounds and unchanged hydrocarbon were extracted from the alkaline phenoxide solution with carbon tetrachloride (3 × 5 ml.) and the combined extracts were diluted to a known volume with methanol or (better) propan-2-ol. The alkaline solution was centrifuged and the concentration of phenoxide was determined by ultraviolet (u.v.) spectrophotometry. The concentration of the nitro-compounds in the alcohol solution was similarly determined; the parent hydrocarbon did not absorb significantly at the chosen wavelength (300 mμ). Suitable tests showed that the phenyl acetate was completely hydrolysed, that the nitro-compounds were completely extracted from the alkaline solution, and that the phenol was not extracted with the nitro-compounds from the alkaline solution.

[1] Fischer, Packer, Vaughan, and Wright, *Proc. Chem. Soc.*, 1961, 369; *J.*, 1964, preceding Paper.
[2] Lunge and Lwoff, *Z. angew. Chem.*, 1898, **7**, 348; Benford and Ingold, *J.*, 1938, 929.

Kinetic measurements were, in general, restricted to initial rates (up to 25% reaction). At first we were uncertain as to the importance of the side-reaction between nitric acid and acetic anhydride, forming (ultimately) tetranitromethane. Moreover, it is likely that nitrous acid (which is produced in the acetoxylation reaction) exerts an anticatalytic effect on the reaction (cf. ref. 3). Kinetic deviations arising from these two sources would be expected to be more marked at greater extents of reaction. Some runs were followed to *ca.* 70% reaction and these did show curvature (decreasing rate).

There are conflicting reports on the rate of the side-reaction between nitric acid and acetic anhydride. Cohen and Wibaut [4] directly measured the rate of this reaction. Their results, for 0·7M-acid, imply that the reaction is autocatalytic. The nitric acid concentration decreases only slightly over the first 3 hr., after which a more rapid reaction with a half-life of *ca.* 24 hr. occurs. On the other hand Paul,[5] on the basis of the curvature in his rate plots for the nitration of benzene in acetic acid–nitric acid (0·4—2·0M), claimed that the side-reaction has a half-life of *ca.* 1 hr. In order to investigate this point a set of reactions with *o*-xylene was carried out, using the same stock nitric acid (0·05M), which was maintained at 25·0°. Reactions were started 20, 45, 76, and 105 min., respectively, after the stock solution was prepared. These four reactions had identical rates within experimental error, *i.e.*, no decomposition detected, for 0·05M nitric acid, in 105 min. Furthermore, when nitric acid (0·05M) more than 24 hr. old reacted with *o*-xylene, the nitroxylenes and dimethylphenyl acetate accounted for more than 78% of the initial nitric acid. These results, which imply that the half-life of 0·05M nitric acid is at least 48 hr., are in better agreement with Cohen and Wibaut's directly measured rates than with Paul's more arbitrary values. Clearly the side-reaction of nitric acid with solvent is not a major complication in the kinetics of nitration of xylenes.

The constancy of rates of the successive runs, mentioned above, illustrates a second point, *viz.*, that formation of acetyl nitrate from nitric acid and acetic anhydride (see below) is rapid at 25°. This was confirmed by direct measurement of the optical density (290 mμ) of a solution of nitric acid (0·06M) in acetic anhydride. The density became constant in 10 min., 95% of the estimated increase occurring in 5 min.

Extinction Coefficients.—Alkaline 3,4-dimethylphenoxide solutions became increasingly yellow as the reaction proceeded. The ultraviolet spectra of such solutions indicated the presence of a material causing considerable background absorption at 295 mμ. The colour did not arise from absorption by nitrophenoxide (from nitrophenyl acetates) as no appropriate peaks were found. Because of the background absorption, the extinction coefficient of 3,4-dimethyl-phenoxide ($\varepsilon = 2753$ at 295 mμ) could not be used in the analyses.

The ratio of 4-nitro-*o*-xylene : 3-nitro-*o*-xylene was 2·0 : 1 (determined by gas chromatography and corrected for the slightly different thermal conductivity of the isomers). From the measured extinction coefficients at 300 mμ (4-nitro-*o*-xylene 4858, and 3-nitro-*o*-xylene 1339, in propan-2-ol), the extinction coefficient of the mixture was calculated (3673 l. mole^{-1} cm.$^{-1}$; for methanol solutions 4034 l. mole^{-1} cm.$^{-1}$). For a series of reactions of *o*-xylene with nitric acid (0·01—0·05M) in acetic anhydride containing 2·2M-acetic acid, it was shown by spectrophotometry that at complete reaction the concentration of the nitro-isomers was 57% of the initial nitric-acid concentration. On the assumption that the rest of the nitric acid was consumed in the formation of the 3,4-dimethylphenyl acetate, and knowing the optical densities of the phenoxide solutions at complete reaction, the apparent extinction coefficient for the phenoxide was calculated (4912 l. mole^{-1} cm.$^{-1}$) and used in analyses of the phenoxide solutions obtained in the kinetic runs. The ratio (43 : 57) of the phenoxide : nitro-isomers, determined by spectrophotometry, is in agreement with the value [1] determined by gas chromatography.*

Solutions of the phenoxide obtained from the *m*-xylene reaction mixtures were colourless and displayed no general absorption. The extinction coefficient of 2,4-dimethylphenol in alkali ($\varepsilon = 3158$ at 296 mμ) [6] was therefore adopted. The extinction coefficient for the mixture of

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* The exact agreement is fortuitous. The ratio of 4-nitro- to 3-nitro-*o*-xylene determined earlier [1] (2·2 : 1) is somewhat higher than that now reported (2·0 : 1). Use of the higher value would lead to a greater extinction coefficient of the mixture of nitro-isomers and a slightly larger value for the phenoxide : nitro-isomer ratio (44 : 56).

³ de la Mare and Ridd, " Aromatic Substitution," Butterworths Publs., London, 1959, p. 73.
⁴ Cohen and Wibaut, *Rec. Trav. chim.*, 1935, **54**, 409.
⁵ Paul, *J. Amer. Chem. Soc.*, 1958, **80**, 5329.
⁶ Herington and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 138.

nitro-m-xylene-isomers ($\varepsilon = 3206$ at 300 mμ) was obtained from the optical density of the nitro-xylene extract at complete reaction; allowance was made for the small amount of nitic acid used up in the acetoxylation reaction (3·5%).

RESULTS

Table 1 shows a typical run in detail. Table 2 shows a selection of the rate data obtained for o-xylene. The third-order rate constants (k) were calculated on the assumption that the

TABLE 1.

Concurrent acetoxylation and nitration of o-xylene in acetic anhydride containing added acetic acid.*

t (min.)	D_A	m	$F(m)$	D_N	A/N
3	0·176	0·032	1·035	0·202	0·72
6	0·327	0·059	1·067	0·364	0·74
9	0·468	0·084	1·098	0·534	0·72
12	0·587	0·106	1·126	0·654	0·74
15	0·695	0·125	1·152	—	—
18	0·800	0·144	1·180	—	—
4 days	0·703	—	—	0·497	0·70
	($f_A = 120$)			($f_N = 200$)	

* $[HNO_3] = 0.0528$M; $[o\text{-xylene}] = 0.321$M; $[AcOH] = 0.343$M; ε_A (phenoxide solution) = 4912; ε_N (nitroxylene solution) = 4034; f_A (dilution factor for phenoxide solution) = 20; f_N (nitroxylene solution) = 20; D_A is the optical density (1-cm. cells) of the alkaline phenoxide solution (obtained by hydrolysis of the phenyl acetate) corrected for a slight blank of 0·022; D_N is the optical density of the ntroxylene mixture in methanol corrected for the blank of 0·011; m, the mole fraction of nitric acid consumed, was obtained by dividing the acetate concentration by 0·429, the mean value of $A/(A + N)$; A/N is the ratio of phenyl acetate : nitroxylenes; $F(m) = 1/(1 - m) + 0.08\,m$, a simplified form of the rate equation (13). The rate constant (7·4 × 10⁻³ l.² mole⁻² sec.⁻¹) was obtained from the slope of the plot of $F(m)$ vs. t.

TABLE 2.

Concurrent acetoxylation and nitration of o-xylene.

Run no.	$10^2[HNO_3]$ (M)	[o-Xylene] (M)	(AcOH] (M)	10^6 rate (mole l.⁻¹ sec.⁻¹)	$10^3 k$ (l.² mole⁻² sec.⁻¹)	A/N
1	7·16	0·346	—	5·34	14·5	—
2	7·12	0·344	—	5·44	15·1	0·71
3	6·18	0·310	—	3·33	14·1	—
4	5·96	0·337	—	3·06	14·5	0·71
5	5·55	0·286	—	2·18	12·7	0·69
6	5·36	0·303	—	2·18	14·1	—
7	3·93	0·323	—	0·91	15·0	—
8	2·12	0·393	—	0·117	12·3	—
9	2·07	0·486	—	0·106	12·0	0·73
10	4·60	0·029	—	0·82	8·4	—
17	4·50	0·114	0·369	5·9	7·0	—
18	4·28	0·504	0·351	5·3	7·4	—
22	4·99	0·310	2·20	35·1	6·5	0·73
23	3·98	0·308	2·21	18·2	5·2	0·71
24	3·37	0·373	2·19	14·9	6·0	0·74
25	3·00	0·306	2·21	10·7	5·4	0·73
26	2·58	0·293	2·21	8·9	6·1	0·74
27	· 2·00	0·304	2·21	4·6	5·2	0·73
28	1·00	0·302	2·21	0·82	3·7	0·73
34	4·14	0·306	3·04	29·6	5·9	0·75

				$10^6[H_2SO_4]$ (M)			
36	3·93	0·323	—	9·9	1·76	28·9	0·71
41	3·91	0·319	—	45·1	15·8	264	0·73

				$10^4[LiNO_3]$ (M)			
47	10·60	0·558	0·788	21·1	4·10	0·41	0·73
48	6·64	0·682	0·298	8·4	1·43	0·89	0·72
49	6·66	0·559	0·260	5·8	0·99	0·68	—
50	7·05	0·110	0·273	6·2	0·54	0·32	—

rates are of zeroth order with respect to *o*-xylene and either (i) of third order in nitric acid in the absence of added acetic acid or (ii) of second order in nitric acid and first order in (added acetic acid + nitric acid). " Rate constants " so calculated for reactions in which sulphuric acid or lithium nitrate were added are not, of course, true rate constants. Such " rate constants," when compared with those obtained in the absence of these additions, provide a measure of the effect of the additive on the rate.

Relevant rate data obtained for *m*-xylene are shown in Table 3. The third-order rate constants were evaluated on the assumption that the rates are of zeroth order in *m*-xylene, second order in nitric acid, and first order in (added acetic + nitric acid).

TABLE 3.

Concurrent acetoxylation and nitration of *m*-xylene.

Run no.	$10^2[HNO_3]$ (M)	[*m*-Xylene] (M)	[AcOH]	10^6 rate (mole l.$^{-1}$ sec.$^{-1}$)	10^3k (l.^{2} mole^{-2} sec.$^{-1}$)	A/N
51	4·50	0·111	0·369	6·58	7·9	0·034
52	4·26	0·528	0·349	7·68	10·8	0·023
53	4·46	0·563	0·348	8·16	10·5	0·029
54	4·72	0·120	0·368	7·59	8·2	0·038

Runs 17 and 18, in which the nitric acid and acetic acid concentrations are maintained constant while the *o*-xylene concentration is varied, indicate that the reaction is of zeroth order with respect to *o*-xylene. Several other runs carried out with varied xylene concentration, constant nitric acid concentration, and in the absence of added acetic acid, gave a constant rate. Moreover, the ratio of acetate : nitroxylenes (A/N) was constant (0·71) throughout each of these runs and from one run to another, demonstrating that the nitration and acetoxylation reactions are each of zeroth order with respect to *o*-xylene. In the course of the measurements, many
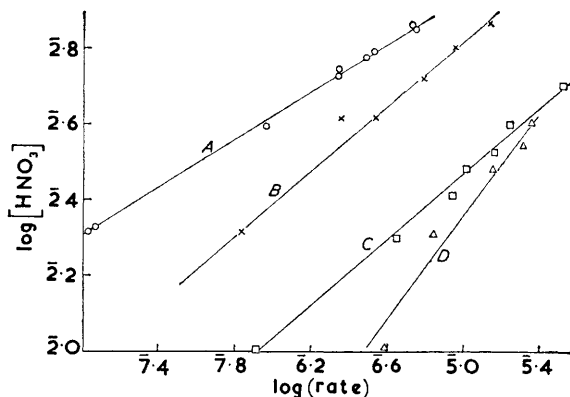

FIG. 1. Order plots for reaction of *o*-xylene with varied concentrations of nitric acid in acetic anhydride. *A*, no additive; *B*, [AcOH] = 0·34M; *C*, [AcOH] = 2·2M; *D*, [H₂SO₄] = 3·5 × 10⁻⁵M. In *B*, *C*, and *D* log (rate increase) is plotted.

runs were carried out in which the xylene concentration, as well as the concentration of other reactants was varied (*e.g.*, runs 4 and 9). Rate constants and A/N ratios evaluated from such runs, assuming that the rate was independent of xylene concentration, showed only random variation with xylene concentration. The low rate constant for run 10 may possibly be attributed to the intrusion of an *o*-xylene rate-dependence at the low concentration used.

Runs 1—9 show the variation in reaction rate produced by variation in nitric acid concentration in the absence of added acetic acid. Fig. 1(A) expresses this dependence of rate on concentration in the form of a log–log plot. The slope of this plot (3·16) is not significantly different from 3·0. The reaction, in the absence of added acetic acid, is therefore of third order with respect to nitric acid. The ratio A/N is again constant (0·71) within each run and from run to run.

Runs 22—28 show the effect of variation in the nitric acid concentration on the rate, where a constant amount of acetic acid (2·2M) is added. The increase in rate over that observed in the absence of added acetic acid may be calculated by subtracting the rate interpolated from Fig. 1(A). Thus for run 22, the corresponding rate in the absence of added acetic acid, interpolated from Fig. 1(A) for 0·0499M-nitric acid, is 1·7 × 10⁻⁶ mole l.$^{-1}$ sec.$^{-1}$. The rate

increase is therefore 33.4×10^{-6} mole l.$^{-1}$ sec.$^{-1}$. The relationship between the rate increase and the nitric acid concentration is depicted in Fig. 1(C). The slope of the log–log plot is 2·31. Another set of runs was carried out at varied nitric acid concentration and at a fixed acetic acid concentration of 0·34M. The plot of log(rate increase) against log[HNO$_3$] is shown in Fig. 1(B). The slope of this plot is 2·34. Runs were also carried out at fixed nitric acid concentration (0·04M) and varied acetic acid concentrations. The plot of log(rate increase) against log[AcOH] is given in Fig. 2(B). The slope (0·91) is not significantly different from 1·0. Addition of acetic acid results in a marked increase in the reaction rate. Thus in run 34 the 3·0M acetic acid accelerates the rate by a factor of 30. The A/N ratio was measured for more than twenty of the runs in which acetic acid was added. The individual A/N values showed only random variations throughout each run, and the mean values, which ranged from 0·70 to 0·76, showed only random variation from run to run, about the overall mean of 0·73. Rate constants of runs 1—9 are substantially greater than those of runs 17—36, probably because of catalysis by a trace of acetic acid in the acetic anhydride (see below).

Several runs were measured in which sulphuric acid was added. Runs 36 and 41 are typical and illustrate the marked catalytic effect of very small concentrations of sulphuric acid. In run 41, addition of 4.45×10^{-5}M-sulphuric acid increased the rate by a factor of 19. Fig.
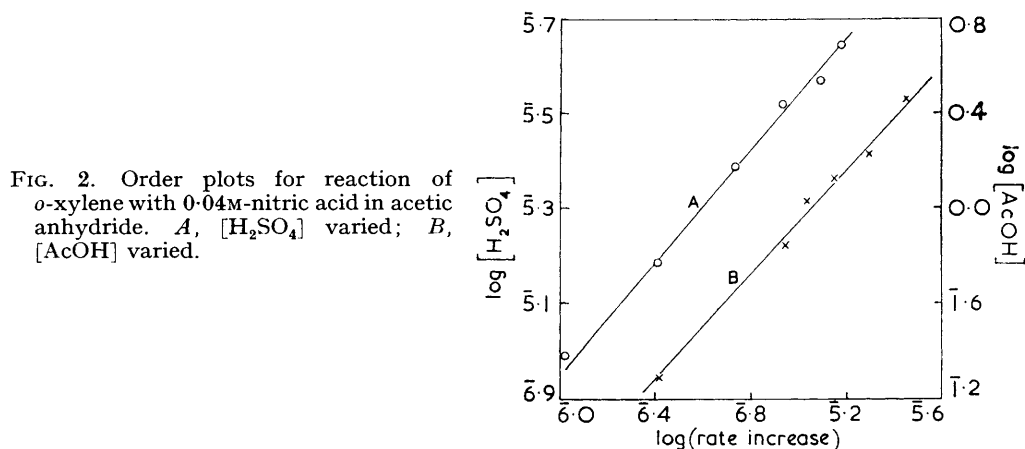

Fig. 2. Order plots for reaction of o-xylene with 0·04M-nitric acid in acetic anhydride. A, [H$_2$SO$_4$] varied; B, [AcOH] varied.

1(D) shows the relationship between the increase in rate and the concentration of nitric acid when a constant amount of sulphuric acid (3.5×10^{-5}M) is added. The slope of the log–log plot is 1·46. Fig. 2(A) is a log–log plot showing the dependence of the rate increase on the sulphuric acid concentration when the nitric acid concentration is maintained constant (0·039M). The slope of this graph is 1·70. In Fig. 1(D) there is a marked scatter of the points about the best straight line. The greater deviations in rates measured in the presence of sulphuric acid may perhaps be due to the marked effect that small variable amounts of basic impurities would have at the very low sulphuric acid concentrations employed (7×10^{-6}—45×10^{-6}M). For ten of the runs carried out with added sulphuric acid, A/N values were measured. The A/N values were constant throughout each run and from run to run. Mean values ranged from 0·68 to 0·74, with an overall mean of 0·71.

Runs 47—50 were carried out in the presence of lithium nitrate. (Lithium carbonate was dissolved in acetic acid and added to the solution of nitric acid in acetic anhydride.) The anti-catalytic effect of the nitrate is very marked; in run 50 addition of 6×10^{-4}M-lithium nitrate reduced the rate by 95%. Runs 49 and 50 also indicate that in the presence of lithium nitrate the rate is no longer independent of the xylene concentration. Constancy of the A/N ratio (0·72) is, however, preserved.

Kinetics of acetoxylation and nitration of *m*-xylene were investigated in much less detail. The major interest was the comparative rates of reaction of o-xylene and *m*-xylene. Runs on each substrate were carried out under closely similar conditions. Thus in runs 51 and 52, the same stock solution of nitric acid in acetic anhydride was used as for runs 17 and 18. It is to be noted that, although the reaction rates of o-xylene and *m*-xylene are closely similar, *m*-xylene

does react slightly faster, particularly at the higher substrate concentrations. This difference need not be significant, since the experimental errors involved in comparing two runs with different substrates are greater than those with one. However, the increase in rate in going from 0·1 to 0·5M-*m*-xylene, though small, is significant. Thus the rate of " acetoxylation plus nitration " of *m*-xylene is not quite independent of the concentration of the *m*-xylene. It is also to be noted that values of the ratio *A*/*N* are slightly, but consistently, higher at the lower *m*-xylene concentrations. In this connection it should be re-emphasised that runs were carried out in pairs under closely similar conditions, 51 and 52 being one pair, 53 and 54 another and so on. The difference in the *A*/*N* ratio between, *e.g.*, runs 51 and 52, is therefore of more moment than the difference between runs 52 and 53.

DISCUSSION

The Reactive Species.—The most significant feature of the kinetic results obtained for the reaction of *o*-xylene with nitric acid in acetic anhydride is that the ratio of the yield of 3,4-dimethylphenyl acetate to that of 3- plus 4-nitro-*o*-xylene is constant (0·72) throughout each reaction and from one reaction to another, under all the conditions investigated. Thus the rate of acetoxylation to nitration is invariant when the individual rates change by factors of up to 330 (between runs 9 and 22). We conclude that either the same reactive species is responsible for both acetoxylation and nitration or that the separate acetoxylating and nitrating species must have a common precursor. This single reactive species, or pre-cursor to separate species, must effectively contain both an acetoxy- and a nitro-group, and acetyl nitrate is the most obvious species.

From vapour-pressure measurements on the nitric acid–acetic anhydride systems, Vandoni and Viala [7] inferred that for solutions in which the mole-fraction of (stoicheio-metric) nitric acid was less than 0·5, most of the nitric acid is converted into acetyl nitrate according to the equilibrium

$$Ac_2O + HNO_3 \rightleftharpoons AcO \cdot NO_2 + AcOH \tag{1}$$

and that at higher mole-fractions of nitric acid appreciable amounts of dinitrogen pentoxide are formed, according to the equilibrium

$$Ac_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2AcOH \tag{2}$$

Considerable evidence from Raman spectra,[8] viscosity, density, and refractive-index measurements,[9] other vapour-pressure measurements,[10] and i.r. spectra [11] supports Vandoni and Viala's conclusions. Further evidence that the equilibrium constant of equation (1) is large is provided by the work of Bordwell and Garbisch [12] on the recovery of nitric acid (precipitated as urea nitrate) from solutions of nitric acid in acetic anhydride. If the solutions were prepared at −10°, at which temperature no acetyl nitrate was formed in the time allowed, recovery of the nitric acid was quantitative. If the solutions were prepared at ambient temperature and then cooled to −10°, only one-third of the nitric acid could be recovered, the other two-thirds presumably being converted into acetyl nitrate.*

However, since nitric acid in excess of acetic anhydride exists almost entirely as acetyl nitrate, the latter cannot be the reactive species because the rates of both acetoxylation and nitration are of zeroth order in *o*-xylene and of third order in nitric acid. If acetyl

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* We have calculated the equilibrium constant for equation (1) from these data. On the assumption that all the water in the concentrated nitric acid reacts rapidly with the acetic anhydride to form acetic acid (which represses the formation of acetyl nitrate) the value of 1·7 is obtained. On the other hand, if it is assumed that none of this water reacts with the acetic anhydride in the time allowed, a *K* value of 0·21 is derived. Even if the smaller value is correct, over 95% of the nitric acid in a 0·1M-solution in acetic anhydride is present as acetyl nitrate.

[7] Vandoni and Viala, *Mem. Services chim. État*, 1945, **32**, 80.
[8] Chedin and Feneant, *Compt. rend.*, 1949, **229**, 115.
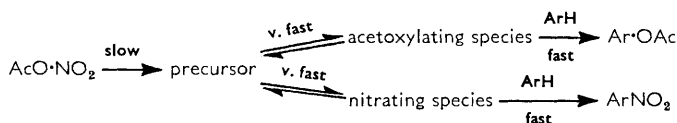[9] Mal' Kova, *Zhur. obshchei Khim.*, 1954, **24**, 1157.
[10] Lloyd and Wyatt, *J.*, 1957, 4268.
[11] Marcus and Frescoe, *J. Chem. Phys.*, 1957, **27**, 564.
[12] Bordwell and Garbisch, *J. Amer. Chem. Soc.*, 1960, **82**, 3588.

nitrate were the active entity, rates would be first order in both *o*-xylene and nitric acid. It would appear, therefore, that acetyl nitrate is the precursor of the reactive species which must be formed in, or subsequent to, the rate-determining step. In view of the enormous accelerating effect resulting from the addition of minute amounts of sulphuric acid, the reactive species must be protonated, or formed from a protonated precursor, or formed in a protonation reaction. In any event, an essential step would seem to involve reaction between acetyl nitrate and acid.

Acetoxylating entities which might be formed from acetyl nitrate by reaction with acid are protonated acetyl nitrate and acetoxonium ion. Nitrating species which might be formed similarly are protonated acetyl nitrate, nitronium ion, nitric acid, nitric acidium ion, and dinitrogen pentoxide. Now, one of the following statements must be correct in order to accommodate the observations that the acetoxylation : nitration rate ratio is dependent upon the nature of the hydrocarbon substrate (0·72 for *o*-xylene but 0·04 for *m*-xylene) but independent of the concentration of a particular substrate. Either (i) the acetoxylating and nitrating species are one, and this is formed in, or subsequently to, the rate-determining step, or (ii) a common precursor * formed in, or subsequently to, the rate-determining step gives rise to separate acetoxylating and nitrating species which are involved in a very fast equilibrium according to the scheme below.

$$AcO \cdot NO_2 \xrightarrow{\text{slow}} \text{precursor} \underset{\text{v. fast}}{\overset{\text{v. fast}}{\rightleftharpoons}} \begin{array}{c} \text{acetoxylating species} \xrightarrow[\text{fast}]{\text{ArH}} Ar \cdot OAc \\ \text{nitrating species} \xrightarrow[\text{fast}]{\text{ArH}} ArNO_2 \end{array}$$

As to statement (i), if the acetoxylating and nitrating species are different, and the one is not formed from the other, then, since acetoxylation and nitration are of zeroth order in substrate, the formation of either species must be rate-determining and the rate ratio will be invariant with change of the substrate. If one species is formed from the other, then the rate ratio should depend upon the concentration of the hydrocarbon substrate, since there is competition between fission of the intermediate species and its bimolecular reaction with substrate. Statement (ii) is subject to the restrictions that acetic acid cannot be formed together with the nitrating species, and nitrous acid cannot be formed together with the acetoxylating species, for otherwise the ratio of the equilibrium concentrations of acetoxylating and nitrating species would change, both in the course of a run (when the acetic acid and nitrous acid concentrations increase) and when acetic acid is added. Such a change would lead to a change in the rate ratio. Since there are no obvious entities which satisfy these restrictions and fit into the reaction scheme above, statement (ii) is not considered further.

Since the rate ratio is independent of the *o*-xylene concentration, and since *m*-xylene has a rate ratio different from that of *o*-xylene, we conclude that the acetoxylating species *is* the nitrating species and that this is *one* of the three possible protonated acetyl nitrates. Of the nitrating and acetoxylating species cited above, only protonated acetyl nitrate can *both* acetoxylate and nitrate.

Evidence from the m-*Xylene Reaction.*—It is essential to the above argument that *m*-xylene and *o*-xylene react at the same total rate, since the formation of the single reactive species is rate-determining. In fact *m*-xylene reacts slightly faster than *o*-xylene, and the reaction is not quite of zeroth order in *m*-xylene. These related observations may be explained as follows.

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* Though the assumption that the common precursor contains both an acetyl group and a nitro-group is not necessary, it is difficult to envisage a common precursor which does not contain the potential acetyl and nitro-groups and yet can generate the separate active acetoxylating and nitrating entities by reaction with other species in the solution. Further, the acetoxylating and nitrating species must be in very fast equilibrium, and the concentrations of these species (but not the position of equilibrium) must be affected by change in concentration of nitric acid and by addition of acetic acid, sulphuric acid, or lithium nitrate.

As the reactivity of the substrate is increased it is to be expected that the slow, rate-determining, formation of the reactive intermediate will eventually be short-circuited, and the substrate will then react with some less reactive (but more rapidly formed) species in a rate-determining bimolecular reaction. It is suggested that intrusion of this process is just beginning with *m*-xylene. It is further suggested that this new reaction leads to nitro-product only. No acetoxy-products have been detected in the nitration of highly-activated substrates.[13] The apparent rate constant of nitration of *m*-xylene, k'_N, may be written in the form

$$k'_N = k_N + k''_N[\text{ArH}] \tag{3}$$

where k_N is the rate constant for nitration by protonated acetyl nitrate and k''_N is the " rate constant " for nitration of *m*-xylene by the second nitrating species in 0·045M-nitric acid. Pairs of values of $k'_N[= kN(A + N)]$ and [ArH] obtained from the data in Table 3 were substituted into equation (3). Solution of the resulting two pairs of simultaneous equations led to the k''_N values $7\cdot0 \times 10^{-3}$ and $5\cdot2 \times 10^{-3}$ l.^{3} mole^{-3} sec.$^{-1}$ from runs **51** and **52**, and **53** and **54**, respectively. The corrected total rate constants (acetoxylation plus nitration) obtained by subtracting $k''_N[\text{ArH}]$ from the k values of Table 3 are shown in Table 4. The mean value, $6\cdot1 \times 10^{-3}$ l.^{3} mole^{-3} sec.$^{-1}$, was used for k''_N. Also shown in Table 4 are corrected A/N ratios, *i.e.*, k_A/k_N values.
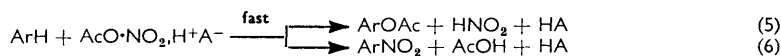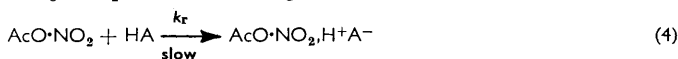
TABLE 4.

Concurrent acetoxylation and nitration of *m*-xylene by protonated acetyl nitrate.

Run no.	10^3k (corrected)	A/N (corrected)
51	7·3	0·039
52	7·6	0·034
53	7·1	0·045
54	7·5	0·044

It is to be noted that there is now excellent agreement between the corrected k values of Table 4 and those for *o*-xylene measured under closely similar conditions (runs **17** and **18** in Table 2). Furthermore, there is now only random variation of A/N with change in *m*-xylene concentration.

The Mechanism and its Kinetic Implications.—(*a*) *General.* On the assumption that the reactive species is protonated acetyl nitrate, formed in a slow step, the overall mechanism can be written as

$$\text{HNO}_3 + \text{Ac}_2\text{O} \rightleftharpoons \text{AcO·NO}_2 + \text{AcOH} \tag{1}$$

$$\text{AcO·NO}_2 + \text{HA} \xrightarrow[\text{slow}]{k_r} \text{AcO·NO}_2,\text{H}^+\text{A}^- \tag{4}$$

$$\text{ArH} + \text{AcO·NO}_2,\text{H}^+\text{A}^- \xrightarrow{\text{fast}} \begin{array}{l} \text{ArOAc} + \text{HNO}_2 + \text{HA} \quad (5)\\ \text{ArNO}_2 + \text{AcOH} + \text{HA} \quad (6) \end{array}$$

For the overall reaction between acetyl nitrate and *o*-xylene,

$$\text{AcO·NO}_2 + \text{ArH} \longrightarrow 0\cdot43 \text{ ArOAc} + 0\cdot57 \text{ ArNO}_2 + 0\cdot43 \text{ HNO}_2 + 0\cdot57 \text{ AcOH} \tag{7}$$

The above mechanism leads to several kinetic predictions which are derived as follows. The total rate of acetoxylation plus nitration is the rate of reaction (4).

$$\text{d}x/\text{d}t = k_r[\text{AcO·NO}_2][\text{HA}] \tag{8}$$

For reactions without added strong acid, free nitric acid acts as the catalytic acid (HA). Therefore, from (1) and (8)

$$\text{d}x/\text{d}t = (k_r/K[\text{Ac}_2\text{O}])[\text{AcO·NO}_2]^2[\text{AcOH}] \tag{9}$$

In general $[\text{AcO·NO}_2] = X - x$, where X is the initial concentration of nitric acid and

[13] Dewar, Mole, and Warford, *J.*, 1956, 3581; Dewar and Urch, *J.*, 1958, 3079.

x is its decrease in time t. Furthermore, for reactions in purified (free of acetic acid) acetic anhydride $[AcOH] = X + 0.57x$. Making these substitutions and writing $k = k_r/(K[Ac_2O])$, equation (9) becomes

$$\mathrm{d}x/\mathrm{d}t = k(X - x)^2(X + 0.57x) \qquad (10)$$

Integration of (10) and substitution of $mX = x$ leads to the rate law:

$$1/(1 - m) + 0.36[\ln(1 + 0.57m) - \ln(1 - m)] = 1.57X^2kt + 1 \qquad (11)$$

Equation (10) predicts correctly that the initial rates, in pure acetic anhydride, should be of third order with respect to nitric acid. The rate constants listed in Table 2 were calculated from the rates on the assumption of a third order nitric acid dependence. Considering the fifty-fold range of rates encompassed by runs 1—9, the rate constants are satisfactorily consistent with a mean of 13.8×10^{-3} $1.^2$ mole^{-2} sec.$^{-1}$. However, the rate constant of run 10 is significantly lower than the other values in this set. It is possible that, at the low xylene concentration employed in run 10, the rates of the aromatic substitution steps are no longer faster than the rate of protonation of the acetyl nitrate.

(b) *Addition of acetic acid.* For reactions carried out in acetic anhydride containing added acetic acid of concentration C, equation (10) is replaced by

$$\mathrm{d}x/\mathrm{d}t = k(X - x)^2(X + C + 0.57x) \qquad (12)$$

The rate equation becomes $[S = X/(X + C)]$

$$\frac{1}{1 - m} + \frac{0.57S}{1 + 0.57S} \ln \frac{1 + 0.57Sm}{1 - m} = (1 + 0.57S)X(X + C)kt + 1 \qquad (13)$$

Comparison of equations (10) and (12) indicates that the increase in the initial rate, resulting from addition of the acetic acid, is kX^2C. The agreement between prediction and observation is less satisfactory in this case, as the observed order of the rate increase, with respect to nitric acid, is 2.34. However, as predicted, qualitatively, the order is markedly lower than the 3.16 found for runs without added acetic acid. Furthermore, the order with respect to acetic acid (0.91) agrees with the predicted value of 1.0, within experimental error, and the agreement would be even better if account could be taken of the effect of the small amount of acetic-acid impurity no doubt remaining in the purified acetic anhydride.*

The rate constants listed in Table 2 for runs 17—34 were obtained on the assumption that the rates are of second order with respect to nitric acid and of first order with respect to (total) acetic acid. The values are satisfactorily consistent (mean 6.4) but are substantially lower than those obtained in the absence of acetic acid (runs 1—10). We attribute at least part of this discrepancy to acetic acid remaining in the " acetic-acid free " acetic anhydride. Thus, for example, if the acetic anhydride contained 0.3% of acetic acid then the true rate constant for run 6 would be 7.3×10^{-3} and not 14.1×10^{-3} as recorded in Table 2.

(c) *Addition of sulphuric acid.* Sulphuric acid reacts with acetic anhydride to form acetylsulphuric acid.[14]

$$Ac_2O + H_2SO_4 \rightleftharpoons AcOH + AcO \cdot SO_2 \cdot OH \qquad (14)$$
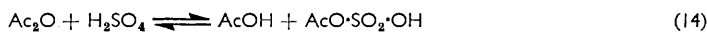
We therefore write the rate of acetoxylation plus nitration as

$$\mathrm{d}x/\mathrm{d}t = k[AcO \cdot NO_2][HNO_3] + k^\dagger[AcO \cdot NO_2][H_2SO_4] + k^\ddagger[AcON_2][AcO \cdot SO_2 \cdot OH] \qquad (15)$$

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* Equation (9) predicts that the rate should be inversely dependent upon the acetic anhydride concentration. In runs carried out with varied acetic acid concentrations, the acetic anhydride concentration changes from 10·2M (no added acid) to 8·4M (in 3M-acetic acid). However, to the extent that the acetic anhydride concentration is changed, the nature of the solvent must also be altered, thus introducing a further unpredictable rate effect. In view of this and of the fact that the correction is too small to affect the conclusions drawn above, no such correction was made.

[14] Russell and Cameron, *J. Amer. Chem. Soc.*, 1938, **60**, 1345.

Under our conditions, the nitric acid concentration greatly exceeds that of the sulphuric acid; hence [AcOH] = [AcO·NO$_2$]. The increased rate on addition of sulphuric acid is thus predicted to be of first order in sulphuric acid, and of between zeroth and second order in nitric acid (in the absence of added acetic acid), depending upon the position of equilibrium of equation (14) and the relative catalytic powers of sulphuric acid and acetyl sulphuric acid. The observed order with respect to sulphuric acid is 1·70. It is possible that the acetic anhydride contains trace " basic " impurities (*ca.* 5 × 10^{-5} mole-% would suffice) which neutralise a larger proportion of the sulphuric acid at the lower concentrations and consequently cause the apparent order to be greater than unity. Because of the scatter of points in the order plot we attach no particular significance to the precise value of the observed order with respect to nitric acid (1·46), other than that it is inconsistent with a small value for the equilibrium constant of equation (14) and with acetyl sulphuric acid as the active catalytic species.* Furthermore, the value of the order is significantly less than that obtained when acetic acid is added (2·31) or when only nitric acid is added (3·16) in at least qualitative accord with the proposed mechanism.

Addition of lithium nitrate. Nitrate ion should compete with aromatic substrate for protonated acetyl nitrate. It is indeed likely that nitrate ion can destroy the protonated acetyl nitrate, not only by simple proton abstraction:

$$\text{AcO·NO}_2\text{,H}^+\text{A}^- + \text{M}^+\text{NO}_3^- \longrightarrow \text{AcO·NO}_2 + \text{HNO}_3 + \text{M}^+\text{A}^-$$
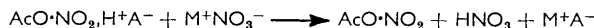
but also by formation of nitrogen pentoxide:

$$\text{AcO·NO}_2\text{,H}^+\text{A}^- + \text{M}^+\text{NO}_3^- \longrightarrow \text{AcOH} + \text{N}_2\text{O}_5 + \text{M}^+\text{A}^-$$
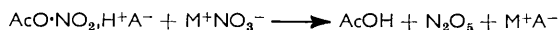
Furthermore, increase in concentration of the aromatic substrate should be accompanied by increase in effectiveness of the substrate as a competitor for the protonated acetyl nitrate. As a consequence, the zeroth-order rate dependence should not be preserved in the presence of added nitrate. Both these predictions were realised. Thus in run 50, addition of 6 × 10^{-4}M-lithium nitrate leads to a " rate constant " only one-twentieth of that observed in the absence of added nitrate, while from runs 49 and 50 it is seen that the rate is halved when the xylene concentration is reduced to a fifth, the concentrations of nitric acid, acetic acid, and lithium nitrate being about the same in both runs.

Structure of the Reactive Species.—Finally, the position of protonation in the reactive species should be considered. In acetyl nitrate, protonation should occur more readily at the carbonylic oxygen than at the nitro-group (pK values for dissociation of the conjugate acids of benzoic acid and nitrobenzene are −7·3 [16] and −11·4,[17] respectively). Protonation of the central oxygen should be even more difficult, since it is flanked by two powerful −*I*–*M* groups. Now, it is more likely that acetoxylation occurs by an S_N2 attack of the substrate at the central oxygen atom rather than by a S_N2' attack at the carbonylic oxygen atom, since the former atom should be a far more powerful electrophilic centre. Furthermore, attack at the more hindered central oxygen atom would account more easily for the greater steric hindrance to acetoxylation than to nitration.[1] We can only speculate as to which of the protonated acetyl nitrates is the effective one, but the following points appear to be relevant. Of the three protonation reactions mentioned above, that at the carbonylic oxygen is the most unlikely to be sufficiently slow to be rate-determining and by the same token would generate the least active acetoxylating species. Conversely, protonation at the central oxygen would generate the most active acetoxylating species and such reaction is also the most likely to be sufficiently slow to be rate-determining. However, if the effective protonation did occur at the central oxygen atom then the faster protonation at the nitro-group would seem to generate a more reactive nitrating species and it would be

* According to Jeffery and Satchell [15] the equilibrium constant for equation (14) is 10.

[15] Jeffery and Satchell, *J.*, 1962, 1887.
[16] Brand, Horning, and Thornley, *J.*, 1952, 1374.
[17] Paul and Long, *Chem. Rev.*, 1957, **57**, 1.

expected that nitration would then occur preferentially through this species, in disagreement with the conclusion from the experimental results that acetoxylation and nitration involve the same reactive intermediate. Protonation at the nitro-group would most easily account for the greater selectivity of acetoxylation compared with nitration. This protonated intermediate would carry a formal positive charge on the nitrogen atom but no formal charge on the central oxygen, and it might be argued that such a species would therefore be more active but less selective in nitration than in acetoxylation.[1]

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