A Reinterpretation of the Zeroth-order Kinetics for Nitration in Acetic Anhydride

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The nitration of benzene, toluene, *m*-xylene, and mesitylene in acetic anhydride has been studied using high concentrations of the aromatic compound. Previous observations that the order with respect to the aromatic compound decreases from 1 to 0 as the concentration of the aromatic compound is increased are confirmed. However this change in order is shown to arise mainly from a medium effect, not from the rate-determining formation of the electrophile. Similar medium effects are reported for the addition of inert aromatic compounds to the reaction mixture. This reinterpretation of the zeroth-order kinetic form imposes severe restrictions on the mechanism of formation of the electrophile.

THE nitration of aromatic compounds by nitric acid in acetic acid or nitromethane was shown by Ingold and his co-workers [1] to give rise to the limiting kinetic forms given in equations (1) and (2), where the value of n

$$\text{Rate} = k[\text{ArH}][\text{HNO}_3]^n \qquad (1)$$

$$\text{Rate} = k'[\text{HNO}_3]^n \qquad (2)$$

depends on the concentration of nitric acid and is not necessarily the same for the two equations. The first kinetic form was considered to derive from a rate-determining reaction between the aromatic compound and the nitrating agent. The second kinetic form (observed with more reactive aromatic compounds) was considered to be derived from the rate-determining formation of the nitrating agent. These equations will be referred to as the first-order and zeroth-order kinetic forms.

Nitration by nitric acid in acetic anhydride differs from that in nitromethane or acetic acid because the nitric acid is not present as such but mainly as acetyl nitrate [equation (3)]. However, the reaction rate can still be described in terms of equations (1) and (2) if the

$$\text{HNO}_3 + \text{Ac}_2\text{O} \rightleftharpoons \text{AcONO}_2 + \text{HOAc} \qquad (3)$$

concentration term involving nitric acid is taken to refer to the stoicheiometric concentration.

For nitration in acetic anhydride, the first kinetic form was observed by Cohen and Wibaut [2] in a study of the nitration of benzene and toluene. Evidence for the second kinetic form has been obtained more recently by Fischer, Read, and Vaughan [3] in a study of the nitration of *o*- and *m*-xylene. Fischer and his co-workers considered the second kinetic form to be derived from the rate-determining formation of the nitrating agent. This interpretation of the zeroth order with respect to the aromatic compound has been accepted by later workers [4,5] but there has been less agreement on the identity of the nitrating agent involved.†

The original evidence [3] for the zeroth-order kinetic form [equation (2)] was that the rate coefficient (k') for

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† Certain complications arising from the concurrent acetoxylation led Fischer *et al.* to propose [3] a nitrating agent which could also act as an acetoxylating agent. However, the acetoxylation is now known [6] to be an addition–elimination reaction and so this part of their argument is no longer relevant.

[1] (*a*) C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' Cornell University Press, 2nd edn., 1969, ch. 6; (*b*) J. G. Hoggett, R. B. Moodie, J. R. Penton, and K. Schofield, 'Nitration and Aromatic Reactivity,' Cambridge, 1971, ch. 3.

[2] F. H. Cohen and J. W. Wibaut, *Rec. Trav. chim.*, 1935, **54**, 409.

[3] A. Fischer, A. J. Reed, and J. Vaughan, *J. Chem. Soc.*, 1964, 3691.

[4] J. H. Ridd in 'Studies on Chemical Structure and Reactivity,' ed. J. H. Ridd, Methuen, London, 1966, ch. 7.

[5] S. R. Hartshorn, J. G. Hoggett, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2461.

[6] D. J. Blackstock, A. Fischer, K. E. Richards, J. Vaughan, and G. J. Wright, *Chem. Comm.*, 1970, 641; D. J. Blackstock, J. R. Cretney, A. Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Letters*, 1970, 2793.

the nitration of *o*-xylene was little changed when the concentration of the aromatic compound was changed by a factor of *ca.* 5. The value of k' was also almost the same for *o*- and for *m*-xylene. In a later study, Moodie, Schofield, and their co-workers[5] showed that the nitration of mesitylene and anisole also obeyed equation (2) to a fair approximation and that, under similar conditions, the zeroth-order rate coefficient was similar to that obtained for the xylenes. Thus the nitration of these reactive substrates in acetic anhydride appears to show the typical zeroth-order characteristics observed in the other organic solvents in that the reaction rate is independent of the nature and concentration of the aromatic substrate.

However, in several respects, the zeroth-order reactions in acetic anhydride are less well defined than those in other solvents. This is partly because the concentration of the aromatic compound required to attain the zeroth-order form is much greater in acetic anhydride than in other solvents. This factor and certain difficulties over side reactions with the solvent have led investigators to look mainly at initial rates instead of full kinetic runs. The value of k' [equation (2)] has also been found to depend to some extent on the nature and concentration of the aromatic substrate. Thus, with [ArH] = *ca.* 0·5M, the zeroth-order rate with *m*-xylene is 46% greater than that with *o*-xylene.[3] The zeroth-order rate of nitration of anisole is increased by more than a factor of 2 when the substrate concentration increases from 0·1 to 1·0M.[5] Such deviations from true zeroth-order kinetics have led previous workers to suggest that the kinetic equation should contain a second term derived from a different reaction path[3] or that the value of the zeroth-order rate coefficient (k') is subject to a medium effect.[5]

We do not disagree with the observations of previous workers but from a further examination of the transitional region between equations (1) and (2) have been led to doubt whether this nitration reaction gives rise to a conventional zeroth-order kinetic form involving the rate-determining formation of the electrophile.

Transition between the First-order and Zeroth-order Equations.—Initial rates of reaction (v_0) for a range of substrates under a range of conditions are listed in Table 1. To facilitate comparison with previous work,[5] these measurements have been made using AnalaR acetic anhydride.

In considering the variation of the initial rate with the concentration of the aromatic compound, it is important to keep other concentration terms constant. The relevant sets of results in Table 1 have therefore, where necessary, been corrected to refer to a constant concentration of nitric acid, using the appropriate value for the order with respect to this species (see later). The resulting initial rates have been plotted logarithmically as a function of the concentration of the aromatic compound (Figure 1). A unit slope in this Figure corresponds to the first-order kinetic form [equation (1)], and a zero slope to the zeroth-order kinetic form [equation (2)].

TABLE 1

Initial rates of nitration (v_0) for the transitional region between first-order and zeroth-order kinetics with respect to the aromatic compound. Solvent AnalaR acetic anhydride ([HOAc] = 0·04M) at 25°

Compound	[ArH]/ mol l^{-1}	[HNO$_3$]/ mol l^{-1}	$10^6 v_0$/mol l^{-1} s^{-1}	
			obs.	corr.*
Mesitylene (I)	0·017	0·0367	0·397	0·354
	0·028	0·0333	0·514	0·580
	0·034	0·0388	0·804	0·628
	0·068	0·0364	1·14	1·03
	0·068	0·0331	0·934	1·06
	0·100	0·0384	1·82	1·46
	0·21	0·0355	1·79	1·79
	0·39	0·0380	2·49	2·04
	0·63	0·0339	1·82	1·97
	1·15	0·0270	1·19	2·22
m-Xylene (II)	0·12	0·0755	2·96	2·16
	0·24	0·0660	2·96	2·96
	0·46	0·0624	4·06	4·66
	0·74	0·0657	5·09	5·09
Toluene (III)	0·065	0·111	0·767	
	0·139	0·110	1·43	
	0·274	0·107	2·50	
	0·532	0·104	3·25	
	0·855	0·104	3·15	
	0·855	0·103	2·94	
	1·88	0·107	4·57	
Benzene (IVa)	0·328	0·368	7·91	
	0·328	0·371	7·48	
	0·637	0·370	13·0	
	1·02	0·369	18·2	
	2·27	0·376	17·4	
Benzene (IVb)	0·328	0·273	2·31	
	0·637	0·266	3·13	
	1·02	0·273	3·56	
	2·27	0·269	3·79	

* Corrected to refer to a constant concentration of nitric acid. For mesitylene, this concentration is 0·035M; for *m* xylene 0·066M.

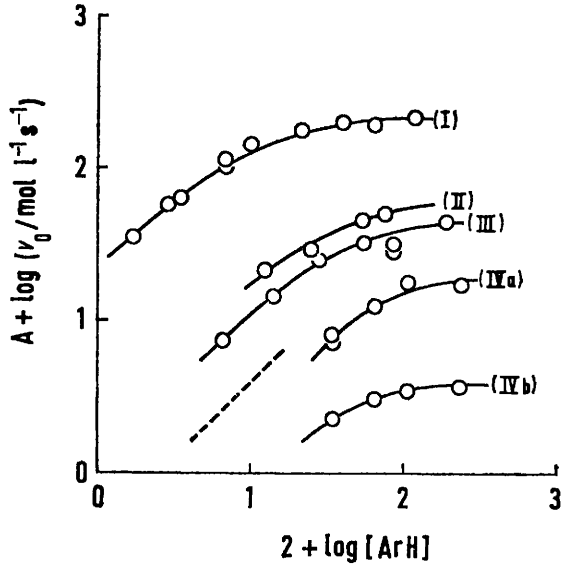

FIGURE 1 The variation of the initial rate of nitration (v_0) of benzene and several alkylbenzenes with the concentration of the aromatic compound. The numbers (I)—(IV) refer to the numbered sets of runs in Table 1. Values of the constant A have been chosen to prevent overlapping of the curves and are as follows: (I) 8; (II), (III) 7; (IVa, b) 6. The broken line has a slope of unity

The results illustrate the expected transition between first-order and approximate or complete zeroth-order kinetics for all the aromatic compounds studied. However, in two important respects, the complete set of results is inconsistent with the conventional interpretation in terms of a transition between the rate-determining formation of the electrophile and the rate-determining reaction of the electrophile with the aromatic compound.

On the conventional interpretation, the rate of formation of the electrophile (E) is given by the term[*] k'[nitric acid]^n in equation (2). This electrophile is then considered to be partitioned between the back reaction

$$\text{Reactants} \xleftarrow[k_{-1}]{X} \text{E} \xrightarrow[k_1]{\text{ArH}} \text{Products}$$

SCHEME

with some species (X) (see Scheme) and the forward reaction with the aromatic compound. The full kinetic form is then as shown in equation (4).

$$\text{Rate} = k'k_1[\text{ArH}][\text{nitric acid}]^n/(k_{-1}[\text{X}] + k_1[\text{ArH}]) \quad (4)$$

At a constant concentration of nitric acid, the form of the plot of log (initial rate) *vs.* log [ArH] predicted by this equation is similar to that shown in Figure 2 and the zeroth-order region is attained when $k_1[\text{ArH}] \gg k_{-1}[\text{X}]$. Hence, for a series of aromatic compounds, the concentrations required to attain the zeroth-order region should be inversely proportional to the values of k_1. This rate coefficient also determines the relative reactivity of aromatic compounds under first-order conditions, for when $k_{-1}[\text{X}] \gg k_1[\text{ArH}]$ we have equation (5). Hence,

$$\text{Rate} = k'k_1[\text{ArH}][\text{nitric acid}]^n/k_{-1}[\text{X}] \quad (5)$$

on the conventional interpretation, the concentrations of aromatic compounds required to attain the zeroth-order region should be inversely proportional to the reactivities of the aromatic compounds in the first-order region.

The plots in Figure 1 deviate markedly from this prediction. Thus, in AnalaR acetic anhydride, mesitylene is more reactive than benzene by a factor of *ca.* 5000, but the lateral displacement of the curves in Figure 2 is less than 1 log unit.[†] A similar argument could be put forward on the basis of the curves for mesitylene and toluene.

TABLE 2

Variation of the initial rate of nitration (v_0) under ' zeroth-order conditions ' with the concentration of nitric acid. Solvent as for Table 1

Compound	[ArH]/mol l^{-1}	[HNO$_3$]/mol l^{-1}	$10^6 v_0$/mol l^{-1} s^{-1}
Mesitylene	0·21	0·0330	1·58
		0·0355	1·79
		0·0695	8·96
		0·0694	9·11
m-Xylene	0·24	0·0354	0·803
		0·0533	1·78
		0·0660	2·96
		0·0692	3·28
		0·0774	4·77
Toluene	0·86	0·0651	0·782
		0·0901	1·94
		0·104	3·15
		0·131	7·57
Benzene	1·02	0·176	0·755
		0·214	1·36
		0·273	3·56
		0·369	18·2

TABLE 3

Comparison of relative reactivities under first-order and ' zeroth-order ' conditions

	Relative reactivity	
Compound	First-order *	Zeroth-order
Benzene	1	1
Toluene	50	19
m-Xylene	870	118
Mesitylene	5000	212

* S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2447.

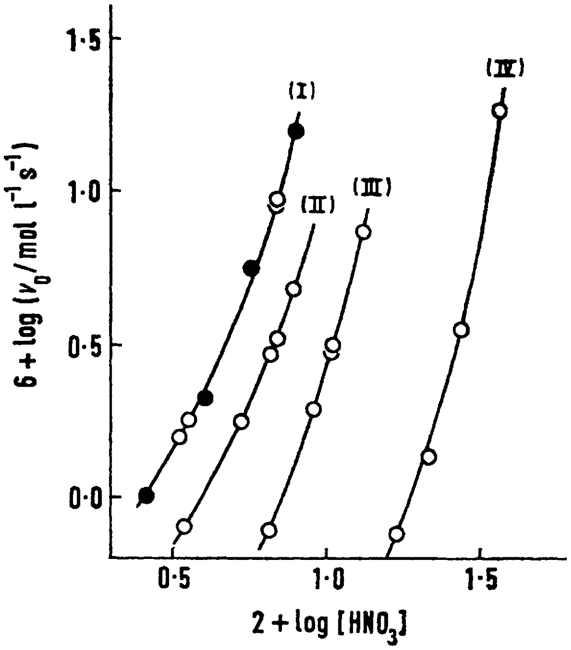

FIGURE 2 The variation of the initial rate of nitration (v_0) under zeroth-order conditions with the concentration of nitric acid. Open circles correspond to the results in Table 2 and dots to the results of Moodie, Schofield, and their co-workers (ref. 5). The numbering of the compounds is shown in Table 1

The other difficulty in fitting these results to the conventional interpretation (Scheme) comes from the zeroth-order rates observed with different substrates. On the conventional interpretation, the initial rate of reaction under zeroth-order conditions should depend on the concentration of the nitric acid but not on the nature of the aromatic compound. Initial rates of reaction for concentrations of aromatic compounds giving approximately zeroth-order kinetics are listed in Table 2 for various concentrations of nitric acid. The logarithmic plot of these results in Figure 2 shows that the results for each aromatic compound define a separate line. At a given concentration of nitric acid these lines are approxi-

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[*] Nitric acid is written out in full here to show that the stoicheiometric concentration not the molecular concentration is implied.

[†] This argument overlooks the fact that the plots for mesitylene and benzene refer to different concentrations of nitric acid. However, the two plots for benzene suggest that the position of the curve on the concentration axis is insensitive to the concentration of nitric acid.

mately parallel, permitting the calculation of relative reactivities under ' zeroth-order conditions '. The relative reactivities are compared with those obtained under first-order conditions in Table 3.

On the conventional interpretation of the zeroth-order kinetics, some dependence of these initial rates on the nature of the aromatic compound might be expected because the concentrations listed in Table 2 do not all correspond exactly to horizontal parts of the plots in Figure 1. However, the deviations which could arise in this way should not be more than a factor of 2. The observed dependence on the nature of the aromatic compound is much greater than could arise in this way and rules out the conventional interpretation of the zeroth-order region.

Before considering other interpretations, two minor matters related to the above results require mention. We find the slope of the plots in Figure 2 to be *ca.* 3, in agreement with previous workers.[5] However, there is evidence for a systematic curvature increasing with the concentration of nitric acid so that the plot for mesitylene has a slope of *ca.* 2·4 and that for benzene increases from 3 to more than 4. In correcting certain results for mesitylene and *m*-xylene to a constant concentration of nitric acid (Table 1) the order with respect to nitric acid has been taken as 2·4. Our results for mesitylene accord well with those obtained by Moodie, Schofield, and their co-workers [5] using [ArH] = 0·8M (Figure 2).

All the above results refer to work carried out with AnalaR acetic anhydride, but some parts of the work have been repeated using acetic anhydride purified by treatment with sodium. Purification of the solvent causes some changes in the reaction rate * but the results show the same characteristics (Table 4). The variation of the initial rate of nitration of *m*-xylene with the concentration of *m*-xylene provides a hint that it may be easier to attain the zeroth-order region in the purified solvent.

TABLE 4

Initial rates of nitration at 25° in acetic anhydride purified by treatment with sodium

Compound	[ArH]/ mol l^{-1}	[HNO$_3$]/ mol l^{-1}	$10^6 v_0$/mol l^{-1} s^{-1} obs.	$10^6 v_0$/mol l^{-1} s^{-1} corr.*
Mesitylene	0·21	0·0341	1·73	
		0·0378	2·23	
		0·0656	7·16	
		0·0673	8·40	
m-Xylene	0·24	0·0290	0·582	
		0·0337	0·802	
		0·0653	4·09	
		0·0667	4·48	
	0·012	0·0403	0·124	0·0884
	0·029	0·0347	0·186	0·190
	0·082	0·0295	0·279	0·421
	0·12	0·0397	0·851	0·629
	0·24	0·0337	0·802	0·879
	0·46	0·0313	0·643	0·841
	0·74	0·0302	0·630	0·898

* Corrected to refer to [HNO$_3$] = 0·035M using *n* [equation (2)] = 2·4.

Evidence for a Medium Effect.—The curvature of the plots in Figure 1 could be explained if high concentrations of aromatic compounds decrease the rate of nitration by a medium effect. The apparent zeroth-order region would then arise from the superposition of this medium effect on the normal first-order kinetic form. The difference between the zeroth-order rates given by different aromatic compounds could then be understood.

This hypothesis has been tested by determining the effect of inert aromatic compounds on the rate of nitration of mesitylene. The results for the addition of 1,2,4-trichlorobenzene and of 1,4-dichlorobenzene are in Table 5. The figures in the final column show that these two additives cause similar and significant medium effects, and that the medium effects in the purified and AnalaR solvents are also similar.

TABLE 5

Effect of inert aromatic compounds (*p*-dichlorobenzene and 1,2,4-trichlorobenzene) on the first-order rate coefficients (*k*) for the nitration of mesitylene with an excess of nitric acid at 25°. Solvent AnalaR acetic anhydride ([HOAc] = 0·04M) except where indicated

		Additive		10^3k/s^{-1}		
10^3[mesitylene]/ mol l^{-1}	[HNO$_3$]/ mol l^{-1}	compound	conc./ M	with add.	without add.	*f* *
1·91	0·154	$C_6H_4Cl_2$	0·085	1·54	2·45	0·63
	0·148		0·248	1·32	2·30	0·57
	0·156		0·597	1·16	2·60	0·45
1·96	0·184		0·663	2·12	4·30	0·49
	0·174		1·06	1·05	3·60	0·29
1·91	0·217		0·286	3·63 †	5·4 †	0·63
	0·174		0·414	1·78 †	3·3 †	0·54
	0·199		0·594	2·43 †	4·5 †	0·54
	0·216		1·02	1·41 †	5·5 †	0·27
1·91	0·213	$C_6H_3Cl_3$	0·08	3·87	6·6	0·59
	0·233		0·24	3·34	7·6	0·44
	0·233		0·48	2·83	7·6	0·37

* Factor by which the additive changes the first-order rate coefficient. † Carried out in sodium-purified acetic anhydride.

As a crude first approximation, these medium effects have been used as a model for the medium effects of the reactive aromatic compounds studied. The plots for mesitylene and toluene in Figure 1 have been corrected on this basis to show the form that they would have were the medium effect absent. The results (Figure 3) show that the corrected plot for mesitylene retains some curvature but that the corrected plot for toluene is almost linear. The corrected plot for mesitylene is based on the medium effect of 1,2,4-trichlorobenzene and that for toluene on the medium effect of 1,4-dichlorobenzene: the conclusions would however be the same were these assignments reversed.

The curvature of the plots for benzene and toluene in Figure 1 can now be ascribed with some confidence to the medium effects of these compounds. The same explanation can be applied to the plot for mesitylene if the medium effect of mesitylene is considered to be greater than those of the other compounds. Alternatively, it is possible to ascribe the residual curvature of the plot for mesitylene to a partial transition towards a conventional zeroth-order process.

In distinguishing between these possibilities, it is

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* The reasons for this are discussed in ref. 7.

[7] J. H. Rees, Ph.D. Thesis, London, 1973.

helpful to reconsider the relative reactivities under first-order and zeroth-order conditions. The results in Table **3** show that the relative reactivity of toluene to benzene is less under zeroth-order than under first-order conditions. This cannot be explained as a partial transition to a conventional zeroth-order reaction because *m*-xylene and mesitylene react much more rapidly than toluene. It follows that the medium effect of toluene must be greater than that of benzene. It is reasonable therefore that the medium effects of *m*-xylene and mesitylene should be greater than that of toluene.

The foregoing work thus removes all compelling evidence of a conventional zeroth-order process in these nitration reactions. The previous work can be understood in terms of the medium effects produced by these high concentrations of aromatic compounds. It is difficult to show that no transition towards a conventional zeroth-order process occurs with high concentrations of mesitylene but the plots in Figure 3 show that, when allowance is made for the medium effect, little progress has been made towards such a zeroth-order form even with 0·5M-mesitylene. At this concentration, at least half and probably most of the electrophile is still undergoing the back reaction with X (see Scheme).

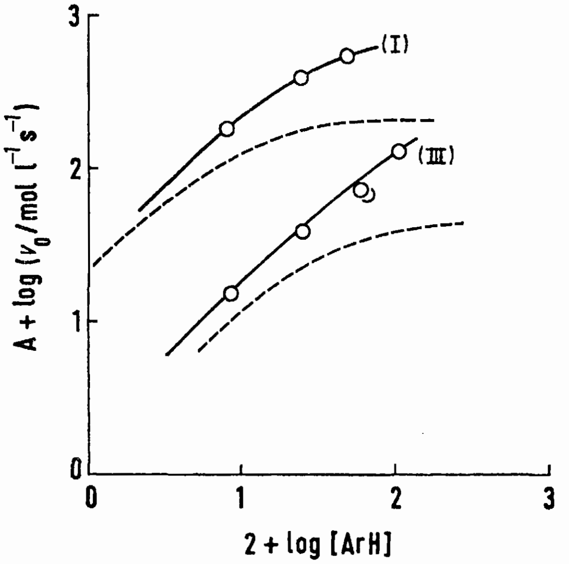

FIGURE 3 Plots of the initial rate of nitration (v_0) against the concentration of the aromatic compound after correction for the medium effect of the aromatic compound (see text). The broken lines show the uncorrected plots; (I) mesitylene, (III) toluene

The foregoing arguments have ignored one possible kinetic criterion for distinguishing between the conventional and new interpretations of the zeroth-order region. On the conventional interpretation the reactions should be zeroth-order with respect to the aromatic compound throughout a single kinetic run. On the interpretation involving medium effects the reactions should be first-order with respect to the aromatic compound throughout a single kinetic run, although this first-order form would be distorted if the medium effects of the aromatic compound and its nitro-derivative were unequal.

Little work has been reported on the kinetic form throughout the major part of a kinetic run for reaction in the zeroth-order region but deviations from the zeroth-order form have been observed [3] and attributed to side reactions. We have carried out a number of kinetic runs on nitration of mesitylene and *m*-xylene in the zeroth-order region to about 80% reaction and have obtained results consistent with a unit order with respect to the aromatic compound. Unfortunately the high concentration of the aromatic compound required for reaction in the zeroth-order region precludes the use of a large excess of nitric acid and this factor, together with the high order with respect to nitric acid, causes the kinetic form during a run to be largely determined by the change in the concentration of nitric acid. These experiments proved therefore less conclusive than those outlined above.

Implications concerning the Reaction Mechanism.—Earlier studies have shown that the nitrating agent under these conditions is a positive ion and most recent authors [4,5,8] have considered this to be the nitronium ion (possibly solvated by nitric or acetic acid). The present work provides some evidence on the mechanism of formation of the electrophile through the identity of the species X (Scheme) which competes with the aromatic compound for the electrophile. In the past, this has been taken as the nitrate ion [3,5] because the addition of an ionised nitrate to the reaction under zeroth-order conditions increases the order with respect to the aromatic compound. However this argument is based on the old interpretation of the zeroth-order kinetics and is therefore no longer compelling. In addition there is now good evidence against the identification of X as the nitrate ion.

The arguments in this paper show that much of the electrophile undergoes the back reaction with X even in the presence of 0·5M-mesitylene. Since the reaction with mesitylene occurs on encounter,[9] the back reaction with X must occur at or near the encounter rate and the concentration of X, if a neutral species, must be $\geqslant$0·5M. If X were a negative ion, a lower concentration of X could be equally effective. A calculation using Debye's method [10] and treating the electrophile and X as spherical ions with a distance of 2·7 Å between the centres on encounter suggests that in acetic anhydride (dielectric constant 21) the encounter rate between opposite charged univalent ions is enhanced electrostatically by a factor of *ca.* 10. Thus, if X were a negative ion, the concentration required to compete effectively with mesitylene would be $>$0·05M.

This calculation rules out the identification of X as the nitrate ion. It is difficult to estimate the exact concentration of nitrate ions in the solutions used, but the

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[8] J. M. A. Baas and B. M. W. Wepster, *Rec. Trav. chim.*, 1972, **91**, 831.

[9] S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, **2447**.

[10] P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265.

fact [5] that added sodium nitrate (1×10^{-4}M) reduces the rate of nitration of mesitylene (10^{-3}—10^{-4}M) with *ca.* 0·2M-nitric acid by more than a factor of 2 implies that this nitrating medium contains $<10^{-4}$M nitrate ion. Thus the concentration of nitrate ions is too low to compete effectively with the aromatic compound by a factor of >500.

The foregoing argument on the identity of X rules out not only the nitrate ion but also all species derived from the added nitric acid. This arises because the runs with *ca.* 0·5M-mesitylene were carried out with *ca.* 0·03M-nitric acid. No neutral species derived from the nitric acid and not associated with the electrophile should be able to compete effectively with a reaction on encounter between the electrophile and 0·5M-mesitylene. No negative ion, other than the nitrate ion, need be considered.

Thus if $AcONO_2H^+$ were the electrophile, it could not be formed predominantly by the protonation of $AcONO_2$ by either HNO_3 or H_2OAc^+ for, by the principle of microscopic reversibility, such reactions would be equivalent to the identification of X as the nitrate ion or acetic acid, respectively. The protonation of $AcONO_2$ by Ac_2OH^+ would be a possible route to the electrophile for the back reaction would then be with the solvent. Correspondingly, if $NO_2^+(HOAc)$ were the electrophile, it could not be formed by the reaction of N_2O_5 with HOAc but it could be formed by the heterolysis of $AcONO_2H^+$ [equation (7)]; the back reaction is then with a species retained in the solvation shell.

$$AcONO_2H^+ \rightleftharpoons NO_2^+(HOAc) \qquad (7)$$

The consideration of encounter rates therefore places severe restrictions on the way in which the electrophile can be formed but does not provide a clear identification of this species.

EXPERIMENTAL

Materials.—Benzene and toluene were AnalaR reagents and were distilled before use; *m*-xylene and mesitylene were laboratory reagents and the first was purified by distillation. Nitric acid was obtained by vacuum distillation from a 1 : 2 (v/v) mixture of fuming nitric acid and 98% sulphuric acid. The white solid obtained was stored at −80° and used within 1 week. AnalaR acetic anhydride was either used as such or was purified by leaving over sodium wire for 4—12 days. The solvent was then distilled under reduced pressure using a short Dufton column. The analyses for acetic acid in acetic anhydride were performed by an n.m.r. method.[5] For the experiments with inert additives, the *p*-dichlorobenzene was recrystallised from ethanol [m.p. 51·5—52·5° (lit.,[11] 51—52°)] and the 1,2,4-trichlorobenzene was distilled before use.

Kinetic Methods.—The runs were followed in the usual way [5] by observing the change in the optical density of the reactant solution using an absorption cell maintained at a constant temperature in a Unicam SP 500 spectrophotometer. Most runs were followed for less than 5% reaction and the initial reaction rate was calculated on the basis of data at the following wavelengths (extinction coefficients in parentheses): benzene 350 nm (163); toluene 340 nm (381); *m*-xylene 345 nm (619): mesitylene 335 nm (587). Other details were as described elsewhere.[5,7]

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[11] R. G. Coombes, D. H. G. Crout, J. G. Hoggett, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1970, 347.