Kinetics of Nitration of Aromatic Hydrocarbons in Purified Acetic Anhydride; Identification of the Electrophile

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For nitric acid concentrations less than 0.9 mol dm^{-3}, the rate of nitration in acetic anhydride and the order with respect to nitric acid are sensitive to the prior treatment of the solvent. The conductivity of the solutions suggests that this effect derives from the presence of trace impurities in the reagent grade solvent, and that these on protonation give rise to nitrate ions. Rates of nitration in the purified solvent are particularly sensitive to added nitrate ions and water but are almost unchanged by added acetic acid. A new mechanistic criterion based on the true rate constant for the reaction of the electrophile with the aromatic compound indicates that reaction occurs through the nitronium ion.

THE fact that some rates of nitration in acetic anhydride depend on the prior treatment of the solvent was reported briefly in a recent publication.[1] Thus, when AnalaR acetic anhydride is purified by treatment with sodium followed by distillation, the rate of nitration of toluene is increased and the order with respect to nitric acid is decreased. This effect was unexpected since the rate of nitration of benzene in acetic anhydride purified

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[1] N. C. Marziano, J. H. Rees, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 600.

in this way has been stated to be essentially the same as that in the unpurified solvent (A.C.S. reagent grade).[2] As a result of that report, most recent studies of nitration in acetic anhydride have been carried out in the AnalaR solvent.

The rates of nitration in the purified solvent are not necessarily to be preferred, because of the possibility that the treatment with sodium introduces a catalytic impurity. The reason for this difference has therefore been investigated. The results for the nitration of toluene in these solvents are given in Table 1 and plotted in Figure 1. These reactions were carried out with a large excess of nitric acid and the results are consequently expressed in terms of the pseudo-first-order rate coefficient (k_1). The results with the unpurified solvent are typical of those obtained with several batches of reagent grade acetic anhydride and accord well with those in the literature[3] when allowance is made for small differences in the acetic acid content (see below). The results with the purified solvent were obtained immediately after distillation of the solvent: they show that purification increases the rate of nitration of toluene by a factor of *ca.* 3 when $[HNO_3] = 0.3$ mol dm^{-3} and changes the slope of the rate profile from 3.3 to 2.1. A slightly lower reaction rate and some scatter are obtained when the purified solvent is kept for a few days before use.

TABLE 1

First-order rate coefficients for the nitration of toluene at 25 °C with an excess of nitric acid in AnalaR and in purified[a] acetic anhydride

Solvent	10^3[PhMe]/ mol dm^{-3}	[HNO_3]/ mol dm^{-3}	10^4k_1/s^{-1}
AnalaR Ac_2O	0.378	0.382	5.02
([HOAc] 0.04 mol dm^{-3})	2.25	0.465	9.17
	3.36	0.631	27.9
Purified Ac_2O	2.16	0.202	3.83
([HOAc] 0.02 mol dm^{-3})	2.09	0.212	4.32
	2.16	0.227	5.02
	2.09	0.251	6.52
	2.01	0.281	7.54
	2.09	0.341	11.3
	2.10	0.398	14.4
	2.87	0.447	21.7

[a] Purified by treatment with sodium followed by distillation immediately before use.

Other methods used for the purification of acetic anhydride have included fractionation under reduced pressure[4] and treatment with potassium carbonate followed by fractionation under reduced pressure.[5] The rate of nitration of toluene in samples of acetic anhydride purified in these ways has been studied;[6] the rate coefficients obtained correspond to points between the lines in Figure 1. By careful fractionation of acetic anhydride, it is possible to obtain essentially the same results as those reported for the purified solvent in Table 1. However, these methods of purification cannot be made to produce rate coefficients corresponding to points above the upper line in Figure 1. This suggests that the kinetic results in Figure 1 truly reflect the purification of the solvent, not the introduction of a catalytic impurity.

It is known that AnalaR acetic anhydride contains appreciable amounts of acetic acid, but the only kinetic consequence of this is a catalytic effect when the initial concentration of nitric acid is low.[3] The rate increase produced by purification cannot therefore be ascribed to removal of the acetic acid. From g.l.c. studies (see Experimental section) we have detected also some formic acid and traces of acetyl chloride, but it is difficult to see how these impurities can explain the results in Figure 1.

The conductivity of these solutions provides further evidence on the impurities present; relevant results are given in Table 2. The conductivity of the unpurified acetic anhydride is greater than can be explained by the concentrations of the impurities mentioned above and corresponds to the presence of an ionised salt such as lithium nitrate at a concentration of *ca.* 10^{-5} mol dm^{-3}. This conductivity presumably derives from the ionised sulphates and phosphates introduced during the manufacture of the anhydride. The maximum concentrations of these ions have been given as 0.000 5% for each (Carlo Erba) or 0.000 5% for sulphate only (Merck): this corresponds to a concentration of 5×10^{-5} mol dm^{-3} of sulphate ions. When the acetic anhydride is distilled, the conductivity of the distillate is very low (after the first 50 ml have been rejected), but the conductivity of the residue steadily increases.

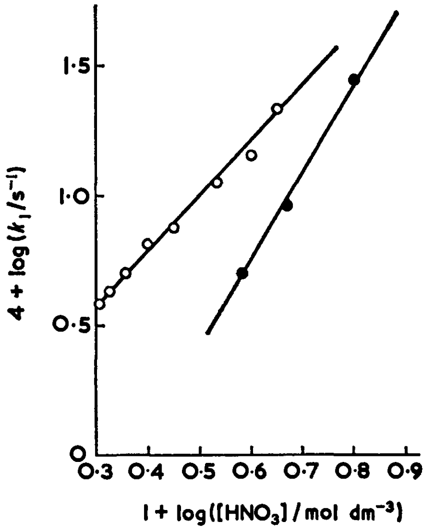

FIGURE 1 Variation of the first-order rate coefficients for the nitration of toluene with the concentration of nitric acid: (○) purified Ac_2O; (●) AnalaR Ac_2O

When nitric acid is added to acetic anhydride, the

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[2] M. A. Paul, *J. Amer. Chem. Soc.*, 1958, **80**, 5329.

[3] S. R. Hartshorn, R. B. Moodie, and K. Schofield, *J. Chem. Soc.* (*B*), 1971, 1256.

[4] A. Fischer, A. J. Read, and J. Vaughan, *J. Chem. Soc.*, 1964, 3691.

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

[6] J. H. Rees, Ph.D. Thesis, University of London, 1973.

conductivity is initially high but it falls over *ca.* 30 min as the nitric acid is converted, almost completely,[5] into acetyl nitrate ($HNO_3 + Ac_2O \longrightarrow AcONO_2 + HOAc$). Shortly after, the conductivity rises again (Figure 2), presumably because of side reactions leading to tetranitromethane.[4] The minimum value of the conductivity is very low: thus, the conductivity of a 0.192M-solution of nitric acid in purified acetic anhydride is about that expected for a 10^{-5}M-solution of lithium nitrate. The difference in the conductivities of the purified and unpurified solvents remains in the presence of nitric acid (Table 2), but the sulphate and phosphate ions should then be partly protonated with the consequent formation of nitrate ions. In this connection, it is significant that the addition of as little as 2.5×10^{-5}M-lithium nitrate to the reaction mixtures in the purified solvent reduces the reaction rate to about that observed in the unpurified solvent and makes a corresponding change in the rate profile (Table 3 and Figure 3). We suggest therefore that the kinetic consequences of solvent purification are derived mainly from the extra concentration of nitrate ions generated in the unpurified solvent by protonation of the impurities. It is reasonable that the retardation produced by a given concentration of added nitrate ions should be less when the concentration of nitric acid is high because of the increased concentration of nitrate ions produced by protonation of the solvent and acetic acid.

TABLE 2

Conductivities (κ) of solutions in purified [a] and unpurified [b] acetic anhydride at 25 °C

Solvent	$[HNO_3]$/mol dm^{-3}	[HOAc]/mol dm^{-3}	$[HCO_2H]$/mol dm^{-3}	[AcCl]/mol dm^{-3}	$10^5\kappa$/S m^{-1}
Unpurified					4.0—4.5 [c]
	0.191				7.0—11.6 [d,e]
Purified					0.0 [f]
	0.192				4.6 [e]
		0.05	0.075		1.2
				0.029	1.6
			$10^3[H_2O]$/mol dm^{-3}	$10^3[LiNO_3]$/mol dm^{-3}	
Purified	0.188		1.1		7.3 [e]
	0.188			0.406	238.4 [e]
	0.198			1.16	523.3 [e]
	0.196			2.96	947.8 [e]

[a] See footnote *a*, Table 1. [b] Carlo Erba, grade RPE. [c] Range of values from 5 bottles. [d] Range of values from 4 bottles. [e] Minimum value taken after *ca.* 30 min: see text and Figure 2. [f] The reported value is 5×10^{-7} S m^{-1} but this is below the sensitivity of the apparatus used here (R. T. Myers, *J. Phys. Chem.*, 1965, **69**, 700).

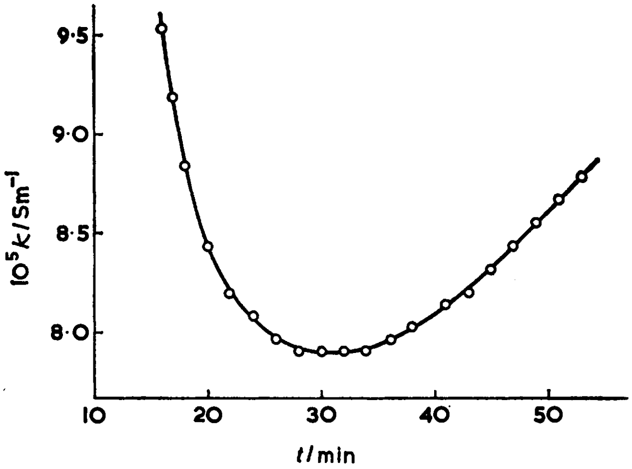

FIGURE 2 Variation with time of the conductivity of a solution of nitric acid (0.191 mol dm^{-3}) in AnalaR acetic anhydride

The results in Figure 3 show also that the catalytic effect of acetic acid is slight on reactions in the purified solvent. The rate of nitration in the purified solvent is however very sensitive to small quantities of added water, *ca.* 4×10^{-4} mol dm^{-3} being sufficient to produce the characteristics of reaction in the unpurified solvent (Table 3 and Figure 3). Partial protonation of the water is the most likely explanation of this, for the reaction of acetic anhydride with small quantities of water is very slow.[7] The sensitivity of the rate of nitration to added water probably explains the slight decrease in reaction rates observed when a given batch of the purified solvent is used over a period of several days. Reaction rates in the unpurified solvent are less sensitive to added water and nitrate ions.

Results for the nitration of benzene and other substrates in the purified solvent are collected in Table 4 and plotted in Figure 4 together with the results of Hartshorn, Moodie, and Schofield [3] for the nitration of benzene in the reagent grade solvent. The results for benzene show that purification of the solvent has a negligible effect when the concentration of nitric acid exceeds 0.9 mol dm^{-3}. The slopes of the plots for toluene in Figure 1 accord with this conclusion. This explains Paul's comment [2] that the purified and unpurified solvents give essentially the same results, for his work was almost entirely limited to concentrations of nitric acid greater than 0.8 mol dm^{-3}.

The slopes of the rate profiles for the nitration of the several aromatic compounds in the purified solvent are parallel and relative reactivities can therefore be calculated. The results are compared in Table 5 with those

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[7] T. Oshima and T. Iwai, *Nippon Kagaku Zasshi*, 1968, **89**, 1036.

reported[8] for nitration in the AnalaR solvent. The differences between the two sets of figures do not arise from any difference in the experimental technique; for our relative reactivities obtained using AnalaR acetic anhydride agree closely with those in the literature. Our results on *m*-xylene, mesitylene, and anisole were carried out a few days after purification of the solvent and so these relative reactivities have been calculated from a further group of kinetic studies on the nitration of benzene under the same conditions.

TABLE 3

First-order rate coefficients for the nitration of toluene at 25 °C in purified acetic anhydride[a] in the presence of added solutes

10^3[ArH]/mol dm^{-3}	[HNO_3]/mol dm^{-3}	10^5[$LiNO_3$]/mol dm^{-3}	10^4k_1/s^{-1}
2.13	0.506	2.55	17.3
2.21	0.457		12.1
1.86	0.431		10.4
2.21	0.376		6.04
1.86	0.352		4.71
1.96	0.313		3.84
1.96	0.275		2.40
2.13	0.261		1.60
		10^4[H_2O][b]/mol dm^{-3}	
2.27	0.353	3.80	5.52
2.18	0.405		8.23
2.18	0.445		11.5
2.18	0.469		14.2
2.18	0.527		20.4
		[HOAc]/mol dm^{-3}	
2.18	0.334	1.00	14.4
1.95	0.363		19.0
1.95	0.401		21.7
1.95	0.430		25.9

[a] See footnote *a*, Table 1. [b] Added to the solvent immediately before the nitration reaction.

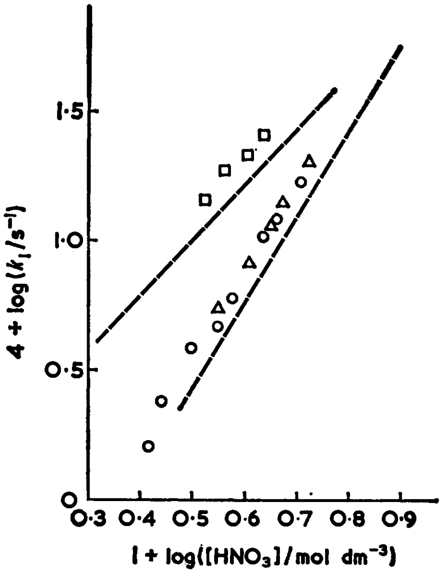

FIGURE 3 Effect of added solutes on the first-order rate coefficients for the nitration of toluene in purified acetic anhydride (the broken lines are in the positions of the full lines in Figure 1) (○) $LiNO_3$ 2.55 × 10^{-5} mol dm^{-3}; (△) H_2O 3.8 × 10^{-4} mol dm^{-3}; (□) HOAc 1 mol dm^{-3}

TABLE 4

First-order rate coefficients for the nitration of aromatic compounds in purified acetic anhydride[a] at 25 °C

Substrate	10^3[ArH]/mol dm^{-3}	[HNO_3]/mol dm^{-3}	10^4k_1/s^{-1}
Benzene	28.0	0.258	0.192
	13.9	0.324	0.292
	13.8	0.436	0.575
	7.07	0.574	0.997
	7.07	0.727	1.60
	6.35	0.865	2.33
	6.76	1.25	4.36
	4.51	1.72	10.0
	7.89	1.89	11.6
m-Xylene	1.06	0.219	16.6
	2.18	0.278	30.5
	1.10	0.324	36.6
	0.935	0.378	70.2
	2.18	0.391	71.2
Mesitylene	0.954	0.164	28.8
	5.97	0.178	34.8
	0.473	0.180	37.1
	0.954	0.208	48.4
	2.06	0.220	59.4
	1.43	0.239	61.7
	0.954	0.266	82.9
Anisole	8.69	0.226	60.3
	0.610	0.229	56.9
	0.306	0.235	66.8
	0.306	0.294	109
	0.184	0.344	140

[a] Purified by treatment with sodium followed by distillation.

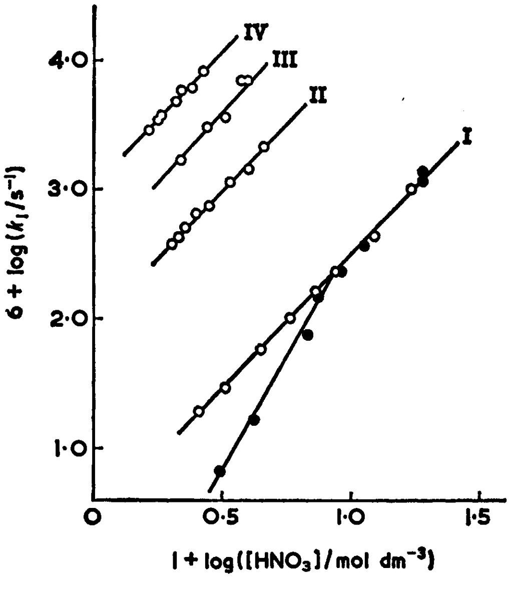

FIGURE 4 First-order rate coefficients for the nitration of aromatic hydrocarbons in purified and AnalaR acetic anhydride (I) benzene, (II) toluene, (III) *m*-xylene, (IV) mesitylene; (○) purified Ac_2O; (●) AnalaR Ac_2O (ref. 8)

Implications concerning the Reaction Mechanism.— The above results suggest that acetic anhydride is a somewhat unsuitable solvent for mechanistic studies of aromatic nitration. The marked kinetic effect of trace impurities; the sensitivity of the reaction rate to traces of moisture; and the variation of the conductivity of

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

the nitric acid–acetic anhydride system with time are all undesirable complications. Fortunately there remains one simple argument which provides a clear indication of the nature of the electrophile.

This approach is based on a comparison of the relative rates of nitration in purified acetic anhydride with those of Moodie, Schofield, and their co-workers[8] for nitration in acetic acid. If the actual electrophile is written as X then a rate coefficient (k_2) for the reaction of this species with the aromatic compound can be defined by equation (1). In this equation, k_1 refers to the observed first-order rate coefficient for the reaction of the aromatic compound with an excess of nitric acid.

TABLE 5

Relative rates of nitration in acetic acid and in purified[a] and unpurified acetic anhydride

	Relative rate		
Substrate	Purified Ac_2O	Unpurified Ac_2O	HOAc
Benzene	1	1	1
Toluene	34	50 ± 6[b]	23[b]
m-Xylene	220 ± 20	870[b]	136[b]
Mesitylene	650 ± 50	5 000[b]	355[b]
Anisole	650 ± 50	1 500[c]	

[a] Purified by treatment with sodium followed by distillation: $[AcOH] < 0.05$M. [b] S. R. Hartshorn, R. B. Moodie, K. Schofield, and M. J. Thompson, *J. Chem. Soc.* (*B*), 1971, 2447. [c] S. R. Hartshorn, personal communication.

$$\text{rate} = k_1[\text{ArH}] = k_2[\text{ArH}][\text{X}] \qquad (1)$$

From the arguments of Moodie, Schofield, and their co-workers,[8] it appears that mesitylene reacts with the electrophile on encounter in both solvents and so, for this substrate, the values of k_2 can be estimated from the viscosities of the two media using the equation[9] $k_2 = 8RT/3000\eta$. The corresponding values (which we write as k_2^{M}) are as follows at 25 °C: $k_2^{\text{M}}(Ac_2O) = 7.7 \times 10^9$; $k_2^{\text{M}}(\text{HOAc}) = 5.7 \times 10^9$ dm^3 mol^{-1} s^{-1}. Now, if we make the reasonable assumption that the nitrations of toluene and mesitylene involve the same electrophile then for the first-order and second-order rate coefficients of toluene (superscript T) we can write equation (2). It follows that the values of k_2^{T} can be calculated from the relative reactivities in Table 5 and the values of k_2^{M}. The results are: $k_2^{\text{T}}(Ac_2O) = 4.0 \times 10^8$; $k_2^{\text{T}}(\text{HOAc}) = 3.6 \times 10^8$ dm^3 mol^{-1} s^{-1}. The rate of nitration of toluene is below the encounter rate by more than a factor of 10 and so the reactivity of the electrophile must be important in determining the second-order rate coefficient. It would be a curious coincidence if there were two nitrating agents which happened to have the same rate coefficient for reaction with toluene. The similarity in the values of k_2^{T} in Ac_2O and HOAc indicates therefore that both reactions involve the same nitrating agent and, from previous experiments in the acetic acid solvent,[8] this appears to be the nitronium ion. The closeness of these values is greater than would be expected in view of the approximations involved and the possible medium effects. This similarity is dependent on the use of the purified solvent: the reagent grade solvent appears to give rise to a more discriminating electrophile (Table 5) for reasons which are not yet clear.

$$k_1^{\text{T}}/k_1^{\text{M}} = k_2^{\text{T}}/k_2^{\text{M}} \qquad (2)$$

The suggestion that the nitronium ion might be the nitrating agent for solutions of nitric acid in acetic anhydride has not always been accepted in the past, in part because the reactivity of toluene relative to benzene ($k_1^{\text{T}}/k_1^{\text{B}}$) has seemed unusually high. However for nitronium ion reactions, the value of $k_1^{\text{T}}/k_1^{\text{B}}$ in a given solvent appears to be influenced by the nearness of these reaction rates to the limiting encounter rate.[8] Recent comparisons of nitration and bromination together with studies of deviations from the additivity principle[10] have suggested that, in the absence of diffusion control, the value of $k_1^{\text{T}}/k_1^{\text{B}}$ for nitronium ion reactions could be as high as 79. The value now reported for reaction in the purified solvent (34) is less than that obtained previously and well within the acceptable range.

Another difficulty with the interpretation in terms of the nitronium ion is that the reaction in acetic acid gives zeroth-order kinetics[11] when [toluene] >0.04 mol dm^{-3} whereas the reaction in acetic anhydride[1] is still giving essentially first-order kinetics when [toluene] = 1.8 mol dm^{-3}. It is obvious that the back reactions of the electrophile with the solvent or non-aromatic solutes compete with the nitration reaction much more successfully in acetic anhydride than in acetic acid. It may be significant that, in the acetic acid solvent, the nitric acid is still present as such whereas, in the acetic anhydride solvent, the nitric acid is effectively converted into acetyl nitrate. The greater acidity of the acetic acid medium could lead to a reduced nucleophilicity of the oxygen atoms as a result of hydrogen bonding. As outlined previously[1] the absence of a zeroth-order rate for nitration in acetic anhydride places certain restrictions on the way that the nitronium ion is formed.

We have not attempted to deduce the reaction mechanism from the detailed kinetic form because it is likely that the ions NO_2^+ and NO_3^- are solvated by other solutes (HNO_3 or HOAc) and the relationship between mechanism and kinetic form is very sensitive to the assumptions made concerning solvation.[5] Thus, in presenting the case for reaction through the nitronium ion, we do not wish to exclude such solvated nitronium ions. The main point is that the reactivity and discrimination of the electrophile suggest reaction by the nitronium ion.

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[9] E. A. Moelwyn-Hughes, 'The Kinetics of Reactions in Solution,' 2nd edn., Oxford University Press, London, 1947, ch. 8.

[10] R. Danieli, A. Ricci, H. M. Gilow, and J. H. Ridd, *J.C.S. Perkin II*, 1974, 1477.

[11] E. D. Hughes, C. K. Ingold, and R. I. Reed, *J. Chem. Soc.*, 1950, 2400.

EXPERIMENTAL

The reactants benzene, toluene, *m*-xylene, mesitylene, and nitric acid were as described previously. Anisole was used as the laboratory reagent and was purified by distillation. Acetic anhydride (AnalaR or Carlo Erba) was either used as such or purified by treatment with sodium followed by distillation.[1] Except where indicated, the purified material was used immediately after distillation. Acetic acid was of reagent grade.

The analyses for acetic acid in acetic anhydride were performed by n.m.r. spectroscopy.[5] The g.l.c. analyses of acetic anhydride were carried out on a Hewlett–Packard 5700A instrument (6 ft 10% polyphenyl ether on H.P. Chromosorb AW DMCS column at 80—90 °C). The concentration of formic acid detected was typically *ca.* 0.06 mol dm^{-3} and experiments at different temperatures showed that this was not produced by decomposition of the acetic anhydride. The conductivity measurements were carried out by using a Halosis type SA instrument with stainless steel electrodes.

Kinetics.—The nitrating solutions were prepared by adding acetic anhydride at 0 °C to a known weight of nitric acid. The solution was then brought to 25 °C and to a known volume. The solution was allowed to remain at 25 °C for *ca.* 20 min and then reaction was started by addition (by Hamilton microlitre syringe) of a small volume of a solution of the aromatic compound in acetic anhydride. For the nitrations of toluene, *m*-xylene, mesitylene, and anisole the reactions were followed as described previously from the change in the u.v. spectra of the solutions using the listed wavelengths and extinction coefficients.[1,6] The nitration of benzene was followed from the optical density at 268 nm of quenched samples,[2] taking the molar extinction coefficient of the product as 7 620. Product studies on the nitration of mesitylene and benzene show that the reactions go effectively to completion.[6] Kinetic runs in the presence of lithium nitrate were carried out by dissolving this salt in the nitric acid before addition of the acetic anhydride. Kinetic runs in the presence of water were carried out by adding the acetic anhydride to a known weight of water, bringing this solution to 25 °C, and then adding a portion to the solution of nitric acid in acetic anhydride before addition of the aromatic compound. Experiments in which the solution of water in acetic anhydride was kept for periods of up to 1 h before addition to the reaction mixture gave essentially the same results, supporting the very slow reaction of water with acetic anhydride in acetic anhydride as solvent.

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