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SUBSTITUENT EFFECTS OF PHOSPHORUS AND ARSENIC CONTAINING GROUPS IN AROMATIC SUBSTITUTION—I

NITRATION OF BENZENEPHOSPHONIC ACID, BENZENEARSONIC ACID AND RELATED COMPOUNDS

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Abstract—The reactivities of benzenephosphonic acid (I), benzenearsonic acid (II) and some related compounds have been determined for nitration in aqueous sulphuric acid. All compounds, except triphenylphosphine oxide V are nitrated as protonated species. The difference in reactivities of "onium" and "quasionium" derivatives, and of phosphorus and arsenic analogues are discussed in terms of the p_π—d_π interactions of oxygen and the positively charged central atom.

INTRODUCTION

THE TOTAL SUBSTITUENT effect of a group containing a tetravalent phosphorus or arsenic atom will depend on its detailed structure, since that structure will determine the resultant polar effect, as well as the possiblity of mesomeric interactions of the vacant d orbitals of the heteroatom with the aromatic ring. Moreover, in such systems the phosphorus or arsenic can bear, in extreme cases, a unit positive charge, ("onium" or "quasionium" ions), or a fractional charge, the magnitude of which will depend on the nature of the groups bound to the central atom.

The substituent effects of the classical "onium" group YMe_3^+ ($Y = P$, As) on the reactivity of the aromatic ring in electrophilic substitution has been quantitatively studied for nitration,[1] positive bromination[2] and protodesilylation.[3] In all cases, in agreement with the differences in electronegativity and polarizability of Y, lower deactivation has been observed for the arsonium pole; depending on the selectivity of the reaction, the reactivity of $PhAsMe_3^+$ compared to that of $PhPMe_3^+$ ranged from 8·1 (nitration) to 2·0 (*m*-protodesilylation).

Quantitative data on the substituent effects of the groups derived from the oxy-acids of phosphorus or arsenic are much more limited. The principal examples of this class are the phosphonic and arsonic groups YO_3H_2, the net substituent effect of which will result from the nature of the mutual interactions between the atom Y and the oxygen atoms. In addition, for this type of substituent it is necessary to take into account, under conditions of suitable acidity, the possibility of protonation of the Y=O oxygen, which converts the substituent into the "quasionium" group $Y(OH)_3^+$ and therefore enables the aromatic compound $PhYO_3H_2$ to also react as a conjugate acid. The only reaction for which the quantitative estimate of the influence of the phosphonic group (and the related groups containing phosphorus) on the reactivity of the aromatic ring in electrophilic substitution has been achieved, is protodesilylation, extensively studied by Eaborn *et al.*[4] Their results made it possible to compare the effects of phosphonic and trimethylphosphonium groups in desilylation, and since it has been proved that the phosphoryl group is, under the reaction conditions, fully protonated, the comparison actually concerned the phosphonium PMe_3^+ and "quasiphosphonium" $P(OH)_3^+$ substituents. Relative reactivities (reactivity of $PhSiMe_3 = 1$) are shown in Table 1.

TABLE 1. CLEAVAGE OF $X\text{-}C_6H_4SiMe_3$ IN SULPHURIC ACID–ACETIC ACID–WATER[4]

Group X	PMe_3^+	$P(OH)_3^+$
$k_{rel} \times 10^4$		
m	2·9	9·5
p	0·8	2·1

A *ca.* three-fold increase in reactivity for the protonated phosphonic group probably results from the fact that p_π—d_π bonding between the oxygen and phosphorus atoms in $P(OH)_3^+$ slightly outweighs the $-I$ effect of the OH groups.

Nitration of benzenephosphonic acid has been studied only as far as the isomer distribution is concerned. Freedman and Doak found,[5] as was expected, that the phosphonic group is *meta*-directing; however, when nitrated by fuming HNO_3, $PhPO_3H_2$ also yields 13% of *ortho*-product, but no *para*-isomer. The *meta*/*ortho* directing influence in nitration has been also observed for diethylbenzenephosphonate.[6]

The substituent effect of the arsonic group is almost unknown; it was however noted long ago[7] that nitration of benzenearsonic acid is much more difficult than nitration of the phosphonic analogue. This observation has been confirmed by Freedman and Doak[8] who found that benzenearsonic acid can be nitrated only under very drastic conditions, yielding 83% of the *m*-nitro product, together with 1·6% of the isolated *ortho* isomer. The remarkably low reactivity of $PhAsO_3H_2$, contradictory to the electronegativity order of phosphorus–arsenic was explained by the assumption that the arsonic compound reacts as its conjugate acid $PhAs(OH)_3^+$, whereas the phosphonic acid is nitrated in its unprotonated form.

This paper, the first of the studies on the substituent effects of groups containing phosphorus or arsenic in aromatic substitution, is concerned with nitration of benzenephosphonic acid, benzenearsonic acid and related systems.

RESULTS AND DISCUSSION

First it is necessary to estimate the relative reactivities of substrates and to establish whether the free "bases" or their conjugate acids undergo nitration. The second-order rate coefficients for the nitration of benzenephosphonic (I), benzenearsonic (II), benzenephosphonous (III), and diphenylphosphinic (IV) acids and of triphenylphosphine oxide (V) are summarized in Table 2.

The results from Table 2 together with those for nitration of the phenyltrimethylammonium ion[9] are plotted logarithmically in Fig. 1.

The first obvious conclusion is that benzenearsonic acid is much less reactive than the phosphonic acid. Since the linear sections of these two plots are satisfactorily parallel, a direct comparison of reactivities is possible and gives the relative reactivity $k_{AsO_3H_2}/k_{PO_3H_2}$ *ca.* 6 × 10^{-4}.

Table 2. Rate coefficients for nitration in aqueous sulphuric acid at 25·0°

Substrate % H_2SO_4	10^2 k_2 (l.mole^{-1} sec^{-1}) $PhPO_3H_2$ I	 $PhAsO_3H_2$ II	 $PhPO_2H_2$ III	 PhP(O)(OH)Ph IV	 $PhP(O)Ph_2$ (V)
72·1					0·103
72·3	0·00215				
75·0	0·0175				
75·2					0·450
76·3				0·0370	
77·3	0·0625				
77·8					1·50
78·2					1·84
78·5				0·285	
78·8	0·276		0·0715		
79·8				0·715	
80·7	2·02		0·492		8·19
81·5				2·22	
82·7	12·7		3·20		
83·1					19·56
83·5		0·00167			
83·7				15·9	25·18
85·1				47·2	
86·1		0·0290			
86·6	50·9				
87·7					38·96
89·7					26·41
92·8		0·0689			
93·0	112·0				
97·2		0·0227			

A useful criterion which can be employed in judging whether the aromatic compound is nitrated as a base B or conjugate acid BH^+, is the value of the slope for the plot: log k_2 vs. acidity of the medium. For the nitration of the "classical" onium salts, where the formation of conjugate acids is not possible, the following values for the slopes have been found: 0·38 for $PhNMe_3^+$,[9] 0·40 for $PhSbMe_3^+$ [1] and 0·41 for $PhCH_2NMe_3^+$.[11] Accordingly it has been proved that such compounds as aniline (slope 0·38)[12] or benzamide (slope 0·35)[13] are nitrated in H_2SO_4aq exclusively as protonated species; for the nitration proceeding through free bases much lower slope values were found, *e.g.* 0·23 for *p*-nitroaniline[14] and 0·26 for diphenylsulphoxide.[15] Schofield *et al.* showed[16] that in 81–85% H_2SO_4 chinoline N-oxide is nitrated at positions 5 and 8 as a conjugate acid (slope 0·37), but at position 4 as a free base (slope 0·2).

The values of the slopes obtained for compounds I–V (calculated by the least-squares method) are as follows: for I, 0·37; for II, 0·37; for III, 0·39; for IV, 0·35; and for V, 0·22. These values prove that for a given acidity range, compounds I–IV react as conjugate acids; the abnormal relative reactivity $k_{AsO_3H_2}/k_{PO_3H_2}$ cannot therefore be determined by the protonation equilibrium. Since the plots for compounds I–IV and for the phenyltrimethylammonium ion are parallel to a good approximation, and since the reactivity of the latter related to benzene is known,[11] the k_{rel} values for I–IV can be given by a single set of logarithms of rate coefficients. For triphenylphosphine oxide (V) the relative reactivity appears to be a function of acidity; for the purpose of comparison we have taken the values of rate constants obtained at high acidities.

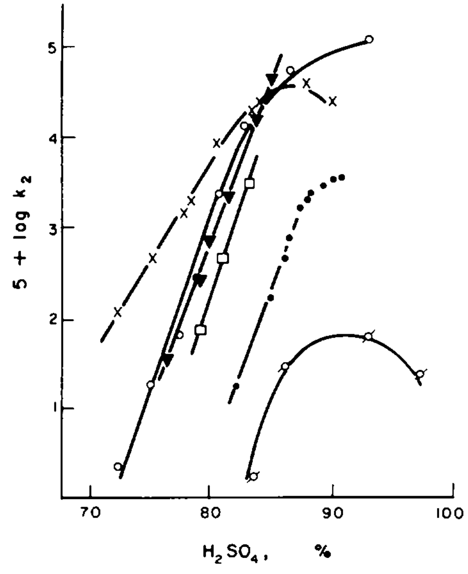

FIG 1. Variation of rate coefficients (l. mole^{-1} sec^{-1}) with acidity for nitration in sulphuric acid; ⌀, $PhAsO_3H_2$; ●, $PhNMe_3^+$ (ref. 9); □, $PhPO_2H_2$; ▼, Ph_2PO_2H; ○, $PhPO_3H_2$; ×, Ph_3PO.

Additional support for the nitration of benzenephosphonic acid through the protonated species comes from the medium effect on the relative reactivity. If I reacts in H_2SO_4 aq as $PhP(OH)_3^+$, so, in an aprotic solvent its reactivity, involving nitration of free base, should be considerably increased. Using the method of competitive nitration, we have estimated the reactivity of I related to bromobenzene and to ethyl benzoate (and therefore indirectly to benzene) for the nitration by acetyl nitrate in acetic anhydride. These values, together with those obtained for compounds I–V in aq H_2SO_4, and for some compounds described elsewhere, are collected in Table 3.

The replacement of H_2SO_4 by Ac_2O in the nitration of I lowers the deactivation of the ring by a factor of at least 200. Although Bott *et al.*[4] postulated that protonation of the P=O group increases the deactivating effect of the $P(O)Ph_2$ substituent in

TABLE 3. RELATIVE REACTIVITIES IN NITRATION (25·0°)

	Substrate	Medium	Relative reactivity (Benzene = 1)
1	$Ph{-}PO_3H_2$	aq. H_2SO_4	$1{\cdot}1 \times 10^{-5}$
		Ac_2O	$2{\cdot}8 \times 10^{-3a}$ $3{\cdot}0 \times 10^{-3b}$
2	$Ph\text{-}AsO_3H_2$	aq. H_2SO_4	$6{\cdot}7 \times 10^{-9}$
3	$Ph\text{-}PO_2H_2$	aq. H_2SO_4	$0{\cdot}2 \times 10^{-5}$
4	$Ph\text{-}P(O)(OH)Ph$	aq. H_2SO_4	$0{\cdot}4 \times 10^{-5c}$
5	$Ph\text{-}P(O)Ph_2$	aq. H_2SO_4	$0{\cdot}3 \times 10^{-5c}$
6	$Ph\text{-}PPh_3^+$	aq. H_2SO_4	$1 \times 10^{-7c,d}$
7	$Ph\text{-}PMe_3^+$	aq. H_2SO_4	$1{\cdot}6 \times 10^{-7e}$
8	$Ph\text{-}AsMe_3^+$	aq. H_2SO_4	13×10^{-7e}

[a] from competition with $PhCO_2Et$
[b] from competition with PhBr
[c] calculated for single phenyl ring
[d] taken from Ref. 17
[e] taken from Ref. 1.

protodesilylation less than 100-fold; the factor of *ca.* 260 obtained by us for benzenephosphonic acid seems quite reasonable considering the higher selectivity of nitration (ρ values for protodesilylation and nitration are $-4{\cdot}6$[18] and $-6{\cdot}0$,[19] respectively). Schindlbauer[20] estimated the Hammett constant for the unprotonated *m*-$P(O)(OEt)_2$ groups, as $\sigma_m = 0{\cdot}23$. Using the equation

$$\log f_m = \rho\sigma_m$$

and taking the reaction constant for nitration by $AcONO_2$ in Ac_2O as $\rho = -6{\cdot}91$,[21] it can be calculated that $f_m^{P(O)(OEt)_2} = 25{\cdot}7 \times 10^{-3}$. From the value of the relative reactivity for I in Ac_2O (Table 3) and from the content of *m*-isomer in nitration as 82% (below), we obtain the *meta* partial rate factor for the unprotonated PO_3H_2 group as $f_m^{PO_3H_2} = 7{\cdot}4 \times 10^{-3}$. This value is in good agreement with that calculated, particularly because the correction due to the difference of the polar effects of the acidic and ester phosphonic groups should reduce the observed difference.

The reactivities of compounds I–V in aq H_2SO_4 need some further comment. Compounds IV and V can be considered as derived from benzenephosphonic acid (I) by subsequent replacement of OH groups of the substituent by phenyl groups. This change is followed by a decrease in the value of the slopes (0·37, 0·35 and 0·22, respectively), pointing out that in the case of triphenylphosphine oxide the nitration through the free base cannot be neglected. This decrease of the basicity can result from steric hindrance to solvation of the positively charged substituent by the highly polar solvent. The value of k_{rel} for V (Table 3) has been therefore taken from the region of high acidity, where nitration predominantly involves the protonated form.*

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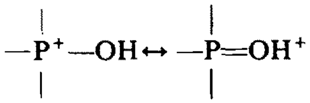
[*] Bott *et al.*[4] estimated for the triphenylphosphine oxide the value of $pK_a = -3{\cdot}65$; assuming that the compound behaves as a Hammett's base, it follows that at 83% H_2SO_4 only *ca.* 0·02% of substrate is present as free base.

Table 3 shows that for phosphorus derivatives exchange of Me groups by Ph groups (compounds 6 and 7, Table 3) does not modify the reactivity of the ring, but the introduction of a P═O group (the formation of a $-\overset{|}{\underset{|}{P}}-OH^+$) significantly increases reactivity; this increase, related to the effect of the trimethylphosphonium substituent varys from 12 to 70 for the compounds studied. The opposite effect is observed for the arsonic compound; the change from an $AsMe_3^+$ to an $As(OH)_3^+$ substituent drastically lowers the reactivity of the ring by a factor of *ca.* 200.

It seems logical that the reduction of the deactivating influence of the substituent that follows the change $-\overset{|}{\underset{|}{P}}{}^+-C \rightarrow -\overset{|}{\underset{|}{P}}{}^+-OH$ results from a strong mesomeric interaction between the "onium" phosphorus and oxygen atoms, indicating the importance of resonance structures like VIa:



$$-\overset{|}{\underset{|}{P}}{}^+-OH \leftrightarrow -\overset{|}{\underset{|}{P}}=OH^+$$

VI VIa

Analogical order of reactivities has been reported for protodesilylation;[4] the stronger effect observed by us for nitration is most likely a result of the higher selectivity of the latter type of substitution.

Our results show that this $p_\pi - d_\pi$ interaction in a system $-\overset{|}{\underset{|}{Y}}{}^+-OH$ is not important in the case of arsonic compounds. This can be due to the lower electronegativity of arsenic or to the more diffuse character of the 4d orbitals, but the reason may also involve the essential difference in Y—O bond lengths (As—OH in II is 1·65–1·75 Å;[22] P—OH in $(PhCH_2O)_2P(O)-OH$ is 1·56 Å[23]), together with a negligible difference in the lengths of the C—Y bonds (which allows in both cases atom Y to interact mesomerically with the aromatic ring). In the $As(OH)_3^+$ group, instead of mesomeric reduction of deactivation, three hydroxyl groups contribute through their $-I$ effect to the total electron-withdrawing influence of the substituent, markedly increasing deactivation, relative to that of the trimethylarsonium pole.

It seems worthwhile to note that the $PO_2H_3^+$ group deactivates the ring more than the $PO_3H_3^+$ (factor of *ca.* 5) and more than the $P(OH)_2Ph^+$ (factor of *ca.* 2) groups, giving the deactivating order $P^+-H > P^+-Ph > P^+-OH$. Rakshys *et al.*[24] found the mesomeric electron-attracting power of this series, as demonstrated by the ^{19}F NMR shielding parameters, to be $P^+-OH > P^+-H > P^+-Ph$.

The *meta* directing influence of the substituents of the $-\overset{|}{\underset{|}{Y}}=O$ type is well known;[5,6,8] nitration of butyldiphenyl-[25] and triphenylphosphine[26] oxides has been discussed in terms of exclusive formation of the *meta*-isomer. We have estimated the product composition for the nitration of benzenephosphonic and benzenearsonic acids. For the former, TLC analysis carried out in presence of three isomeric mononitrobenzene-phosphonic acids showed the formation (besides the *meta*-isomer) of significant amounts of the *ortho*-nitro compound, but the *para*-isomer has not been detected. The *meta*/*ortho* ratio was determined from the UV absorption spectrum of the nitration mixture, using the spectrophotometric characteristics of the synthetic mononitroderivatives. The calculation gave 82% of *meta*- and 18% of *ortho* isomers, virtually in agreement with Freedman and Doak,[5] showing however even higher *ortho*-nitration. The artificial mixture of *meta*- and *ortho*-derivatives of I, in identical proportion to that calculated, gave an absorption curve coinciding with the curve of the reaction product (Fig. 2).

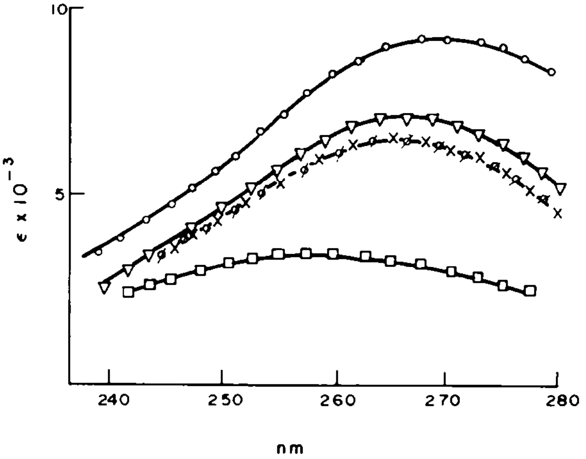


Fig 2. UV absorption spectra of □, o-$NO_2C_6H_4PO_3H_2$; ∇, m-$NO_2C_6H_4PO_3H_2$; ○, p-$NO_2C_6H_4PO_3H_2$; ×, nitration product; ∅, mixture of 82% of m-$NO_2C_6H_4PO_3H_2$ and 18% of o-$NO_2C_6H_4PO_3H_2$.

Analysis of the product obtained in nitration by acetyl nitrate in Ac_2O showed that a change of medium practically does not alter product composition; we assumed therefore the *meta*/*ortho* ratio to be the same as for the reaction in H_2SO_4. Chromatographic analysis of the product obtained by nitration of benzenearsonic acid showed the considerable amounts of *para* isomer, but no *ortho*-nitro compound. Spectrophotometric analysis gave the isomer composition as 83% of *meta*- and 17% of *para*-derivative; the content of the main product agrees very well with the value reported.[8] The corresponding absorption spectra, including that of the model mixture are shown in Fig. 3.

Isomer distribution, together with the relative reactivities data, made it possible to calculate for I and II (reacting as conjugate acids) the partial rate factors for nitration. These values, compared with those for the trimethylphosphonium and arsonium positive poles are collected in Table 4.

Replacement of the arsonium pole $AsMe_3^+$ by the "quasiarsonium" $As(OH)_3^+$ is followed by a marked change of substituent effect, but mainly in terms of the intermolecular selectivity. Analogical structural modifications of phosphorus derivatives

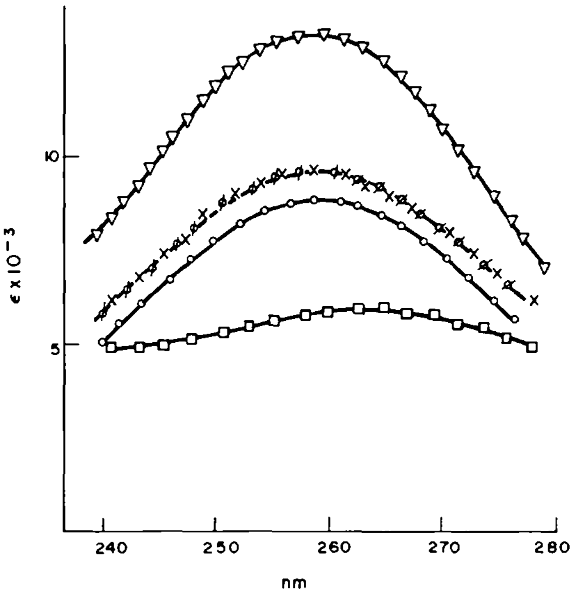


FIG 3. UV absorption spectra of □, o-$NO_2C_6H_4AsO_3H_2$; ○, m-$NO_2C_6H_4AsO_3H_2$; ▽, p-$NO_2C_6H_4AsO_3H_2$; ×, nitration product; ∅, mixture of 83% of m-$NO_2C_6H_4AsO_3H_2$ and 17% of p-$NO_2C_6H_4AsO_3H_2$.

change both inter- and intramolecular selectivity. Although it is known that the $\frac{1}{2}o/p$ ratio for nitration of some derivatives of benzene (e.g. for nitrobenzene[27]) is much higher than unity, explanation of the drastic switch to the *meta/ortho* orientation in the benzenephosphonic acid is difficult without the assumption of some specific interactions between the nitrating species and the phosphonic group.

Isomer distributions for nitration of compounds III–V have not been studied in detail; we suppose however that the directing properties of the protonated PO_2H_2 and PO_3H_2 groups are very similar. When the reaction mixture resulting from nitration of III in H_2SO_4 was oxidized by $HgCl_2$ (oxidation of PO_2H_2 to PO_3H_2 group[28]), a mixture of mononitroderivatives of I was obtained. The UV spectrum of this mixture was practically identical with that for the nitration product for I; it gives therefore the following values for the partial rate factors for nitration of Ph—$PO_2H_3^+$: $f_o \sim 10^{-6}$; $f_m \sim 5 \times 10^{-6}$.

TABLE 4. PARTIAL RATE FACTORS FOR NITRATION IN AQ. SULPHURIC ACID, 25·0°

Substituent	$f_o \times 10^7$	$f_m \times 10^7$	$f_p \times 10^7$
$P(OH)_3^+$	60	270	—
PMe_3^{+a}	—	2·5	0·1
$As(OH)_3^+$	—	0·17	0·07
$AsMe_3^{+a}$	—	19·4	1·6

[a] taken from Ref. 1.

EXPERIMENTAL

Solvents were purified by conventional methods. M.ps and b.ps are uncorrected. TLC was carried out on standard glass plates covered with Kieselgur G (E. Merck). Samples were analysed as *ca.* 5% solns in MeOH. Solvent system: dioxane–water (9:1). All chromatograms were developed by spraying with weakly alkaline solution of Methyl Red. The following commercial substrates were used. Benzenephosphonic acid (I) (Eastman Chemical), m.p. 161–163°, (lit.[29] m.p. 161–162°); Benzenearsonic acid (II) (Eastman Chemical), m.p. 158–160°, (lit.[30] m.p. 155–158°); Benzenephosphonous acid (III) K & K Lab., Inc.), m.p. 85–87°, (lit.[31] m.p. 85–86°); Triphenylphosphine oxide (V) (Fluka AG), m.p. 157–158°, (lit.[32] m.p. 156°); *m*-Nitrobenzenearsonic acid (Eastman Chemical), m.p. 173–175°, (lit.[8] m.p. 177–180°).

Diphenylphosphinic acid (IV) was obtained as described.[33] M.p. 190–191°, (lit. m.p. 190–192°).

The remaining isomeric mononitroderivatives of I and II were prepared according to reported procedures. The properties of the products are collected in Table 5.

TABLE 5. MONONITRODERIVATIVES OF BENZENEPHOSPHONIC (I-NO_2) AND BENZENEARSONIC (II-NO_2) ACID

Compound	m.p.	(lit. m.p.)	λ_{max} (H_2O) nm	$\varepsilon_{max} \times 10^{-3}$	R_f	Ref.
I-NO_2						
ortho	200–203	(200–201)	262–264	3·3	0·97	34
meta	155–156	(155–156)	266–268	7·1	0·85	5
para	194–195	(197–198)	268–270	9·2	0·51	35
II-NO_2						
ortho	227–230	(225–229)	268–272	5·5	0·90	8
meta	173–175	(177–180)	260	8·3	0·40	8
para	304–306	(298–300)	260	12·9	0·50–0·60	30

Bromobenzene was dried over $MgSO_4$ and distilled through a fractionating column; b.p. 156–157°.

Ethyl benzoate was distilled under reduced pressure; b.p. 115°/30 mmHg; n_D^{20} 1·5060.

Acetic anhydride was distilled through a fractionating column and fraction b.p. 139–141° was collected.

Solutions of sulphuric acid required as reaction media were obtained by diluting AnalaR sulphuric acid (*d* 1·83) and standardized by titration with NaOHaq. AnalaR nitric acid (*d* 1·42) was distilled from an equal volume of conc. H_2SO_4 immediately before use.

Kinetics. The nitrations in H_2SO_4aq commenced by addition of a volume of a solution of HNO_3 in H_2SO_4 to a stirred volume of a solution of an equimolar amount of substrate in H_2SO_4 at 25·0°. Aliquot portions were withdrawn at suitable times and quenched in water, and the UV spectrum examined using a Carl Zeiss-Jena VSU-2 spectrophotometer. The concentration of nitrocompounds in the reaction mixture (*x*) was calculated from the equation:

$$x = (y.\mathrm{OD} - \varepsilon_s.a)/(\varepsilon_p - \varepsilon_s)$$

where *y* is dilution factor during quenching, OD is the experimental optical density, ε_s and *a* are the extinction coefficient and initial concentration of the starting material, and ε_p is the experimental extinction coefficient corresponding to 100% reaction. The values of ε_s and ε_p used were as follows: (I), $\varepsilon_p = 6000$, $\varepsilon_s = 500$; (II), $\varepsilon_p = 9000$, $\varepsilon_s = 1000$; (III), $\varepsilon_p = 7000$, $\varepsilon_s = 620$; (IV), $\varepsilon_p = 7100$, $\varepsilon_s = 1200$; (V), $\varepsilon_p = 8550$, $\varepsilon_s = 2150$. With all substrates, the variation of the extent of reaction with time gave good agreement with the usual second-order kinetic equation. A typical run is shown in Table 6.

Competitive nitrations. A solution of acetyl nitrate in acetic anhydride was added to a solution of I and bromobenzene (or ethyl benzoate) in acetic anhydride at 25·0°. The reaction mixture was brought to 10 ml by addition of more solvent and left for a suitable time (~1 hr for bromobenzene and ~20 hr for ethyl benzoate). For the system: I/PhBr, the mixture was diluted 50 times with 3% aq. NaOH, and after de-

TABLE 6. NITRATION OF $PhPO_3H_2$ IN 80·7 SULPHURIC ACID AT 25·0°. INITIAL CONCENTRATION OF I = $[HNO_3] = 1{\cdot}50 \times 10^{-2}$ M

Time (sec.)	1218	1830	2405	3000	3595	4188	4818
OD (263 nm.)	0·624	0·763	0·875	0·948	1·062	1·118	1·155
$10^2 \times$ (M)	0·41	0·53	0·63	0·70	0·80	0·85	0·88
k_2 (l.mole^{-1} sec^{-1})	0·0206	0·0199	0·0201	0·0194	0·0212	0·0208	0·0196

composition of the anhydride the solution was extracted with ether. After further dilution, when necessary, the UV spectra of the aqueous and etheral layers were determined and concentrations of products calculated. For the system: I/$PhCO_2Et$, the mixture was diluted 50 times with water and a products determination was carried out as before. In preliminary experiments involving only one of the aromatic reactants, neither the phosphonic compounds in the etheral, nor the non-phosphorus aromatic derivatives in the aqueous layers, were detected. The ratio of the rate coefficients for the nitration was calculated in the usual way.[11]

Product determination. Nitration of I and II* $3{\cdot}5 \times 10^{-3}$ mole of substrate was dissolved in fuming HNO_3 (*d* 1·5, 2 ml) and the solution kept at room temp for 24 hr. HNO_3 was evaporated under reduced pressure at room temp and the residue dried in vacuum over NaOH. The nitration product (quantitative yield) was the examined chromatographically (TLC) and spectrophotometrically (UV).

Nitrations of benzenephosphonous acid. $1{\cdot}5 \times 10^{-2}$ mole of III was dissolved in conc H_2SO_4 (2·5 ml) and to this solution the nitrating mixture, containing the equimolar amount of HNO_3 was added portionwise with cooling and stirring. The mixture was left overnight at room temp and diluted 10 times with water. The aqueous solution of the required amount of $HgCl_2$ was then added dropwise with stirring, the solution was refluxed for 1 hr and left overnight. The precipitated Hg_2Cl_2 was filtered off, and the filtrate, after further dilution, examined spectrophotometrically.

Nitration of IV *and* V. Substrates were nitrated in the usual way and nitration products were isolated by dilution with water and filtration. The analytical and spectroscopic (IR) data showed the quantitative yields of nitration; the products of any dinitration have not been detected.

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* It was found more convenient to isolate the reaction product when nitrations were carried out in fuming HNO_3. We have found however, that there is no difference in the product composition for nitration in H_2SO_4 and in HNO_3 alone.

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