Oxidation of Pyridine with Potassium Peroxydisulphate. The Role of Pyridine Cation-radicals as Primary Intermediates

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Detailed results of a study of kinetics, products, and some intermediates (e.s.r. spectroscopy) for reactions of pyridine with peroxydisulphate ion in aqueous media are presented. In neutral solution reaction rates are dependent on the first power of peroxydisulphate ion concentration and on the half power of pyridine concentration. Pyridylpyridinium ions are the major products with isomeric bipyridyls minor products. However, yields of the latter compounds increase rapidly (at the expense of pyridylpyridinium ions) with increasing initial pH of the reaction mixtures. Spin-trapping experiments indicate that pyridine cation-radicals and 2-pyridyl radicals are reaction intermediates. A chain reaction mechanism, involving initial electron transfer from pyridine, satisfactorily accounts for all the experimental observations. The effect of added base is thought to arise from either a competing deprotonation of pyridine cation-radical to pyridyl radicals, or stabilisation of intermediate radical ions produced by attack of sulphate anion-radical on the pyridine nitrogen atom.

HOMOLYTIC and heterolytic mechanisms can be sustained for oxidations by peroxydisulphate ($S_2O_8^{2-}$) ion since the peroxide linkage, as well as undergoing simple homolytic cleavage, is readily attacked by many nucleophilic and electron transfer reagents.[1-3] Reactions are markedly influenced by simple variation of temperature, pH, light, and the presence of electron donors. Oxidation of alcohols,[4] glycols,[5] amides,[6] aliphatic amines,[7] and carboxylic acids[8] as well as phenol[9] and other aromatic coupling reactions[10] proceed *via* homolytic mechanisms whilst the Elbs oxidation of phenols[11] and the oxidation of aromatic amines[12] are considered to follow heterolytic routes. Peroxydisulphate is also used in free radical emulsion polymerization.[13] However, in very few cases is the mechanism clearly established; the homolytic reactions are generally slow but are greatly accelerated by the presence of catalytic amounts of metal ions of low valency, particularly silver(I). In these cases the higher oxidation states of silver play a major role with reactions being essentially due to interaction of the organic substrate (*e.g.* carboxylic acids,[8a,14] aliphatic

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[9] (*a*) R. G. R. Bacon, R. Grime, and D. J. Munro, *J. Chem. Soc.*, 1954, 2275; (*b*) R. G. R. Bacon and D. J. Munro, *ibid.*, 1960, 1339.

[10] R. G. R. Bacon and J. R. Doggart, *J. Chem. Soc.*, 1960, 1332.

[11] E. J. Behrman, *J. Amer. Chem. Soc.*, 1963, **85**, 3478.

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amine,[7b,15] glycols [5d]) with the intermediate Ag^{II} or Ag^{III} species formed. Even the widely assumed mechanism for alcohol oxidation by $S_2O_8^{2-}$ did not explain our recent findings [16] that alkoxyl radicals are important intermediates during such processes. These observations led to a conclusion that the sulphate radical-anion $SO_4^{-\cdot}$ behaves as a one-electron oxidant, a view substantiated by recent product analyses of the peroxydisulphate oxidation of some *N*-methylbiphenyl-2-carboxamides,[17] and by revealing, flow-e.s.r. studies by Norman and his co-workers of the behaviour of $SO_4^{-\cdot}$ with a range of organic substrates.[18]

With these mechanistic considerations in mind, and with a view to extending the synthetic utility of peroxydisulphate, the reaction between potassium peroxydisulphate and pyridine was investigated. Pyridine has no readily abstractable hydrogen, and a homolytic reaction between these reagents might seem improbable and although one report states that reaction does not occur [19] another, using a great excess of persulphate, reports degradation to ammonia.[20] However an interesting report [21] describes a low-yield industrial scale preparation of 2,2′-bipyridyl (2%) and 2,2′,2″-terpyridyl by heating peroxydisulphate ion, pyridine, and sodium carbonate at 90°. Similar observations of bipyridyl production were also noted when pyridine was employed as a co-solvent during the persulphate decarboxylation of benzoic acid.[8d] This report led us to the early work of Baumgarten (overlooked in recent reviews of peroxydisulphate chemistry [1,2]) who isolated pyridylpyridinium salts after refluxing solutions of peroxydisulphate and pyridine for 2—3 h.[22,23]

RESULTS AND DISCUSSION

Kinetic Studies.—Basic kinetic information was sought by following the loss of persulphate in aqueous solutions of pyridine, most runs being performed at 50°. Initially colourless solutions became yellow and then dark red as the reaction proceeded to complete loss of persulphate. Disappearance of persulphate followed a linear first-order dependence for only *ca.* 30% reaction at which point the rate slowed, although still appearing to follow first-order kinetics (Figure 1). Addition of small amounts of acid accelerated the reaction whereas added base slowed the decomposition of persulphate ion. There was no marked salt effect on adding a two-fold excess (over $K_2S_2O_8$) of potassium sulphate and the presence of oxygen (air-saturated solutions) did not, within experimental error, retard the overall reaction. Although the change in rate noted after *ca.* 30% reaction still requires adequate explanation it is probably due to a buffering effect of the product pyridylpyridinium ions.

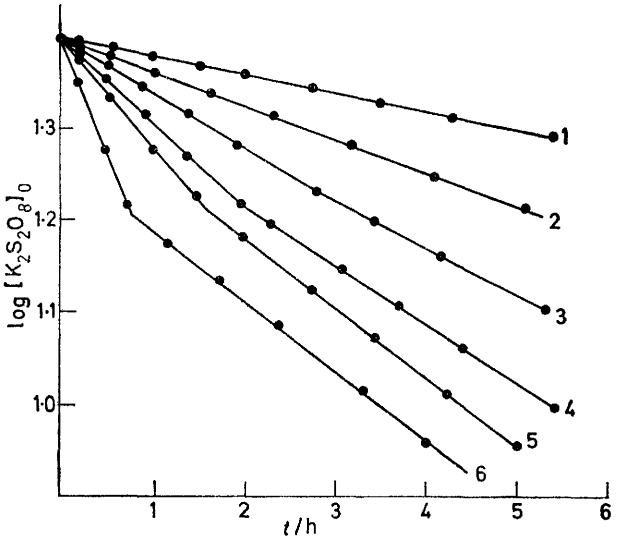

FIGURE 1 Typical kinetic plots for oxidation of pyridine (0·66M) by peroxydisulphate ion (0·05M) in water at 50·0°: 1, containing 2 × 10^{-2}M-KOH; 2, containing 1 × 10^{-2}M-K_2CO_3; 3, containing 2 × 10^{-3}M-K_2CO_5; 4, standard kinetic plot; 5, containing 1 × 10^{-2}M-$KHSO_4$; 6, containing 1 × 10^{-2}M-H_2SO_4. All solutions were saturated with nitrogen

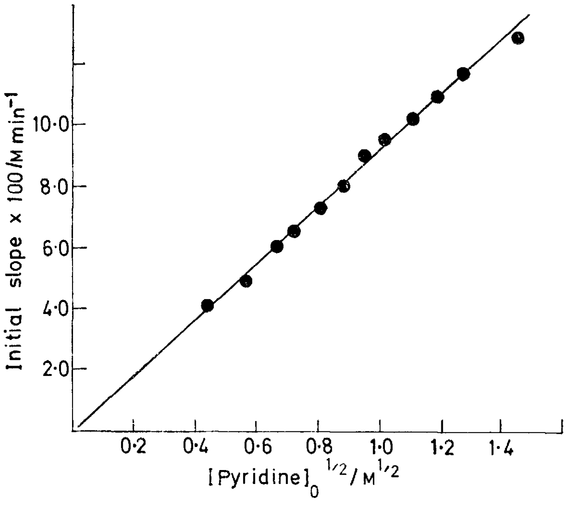

FIGURE 2 Oxidation of pyridine by potassium peroxydisulphate (0·050M) in water at 50·0°. Variation of the initial rate against the square root of the pyridine concentration

Using the method of initial rates the rate of persulphate disappearance at 50° was first order in persulphate and half order in pyridine (Figures 2 and 3). Plots of log initial rate against log concentrations yielded lines of slopes 0·87 and 0·53 respectively. Also the gradients of the 'slow' part of the persulphate decomposition

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[18] (*a*) R. O. C. Norman, P. M. Storey, and P. R. West, *J. Chem. Soc.* (*B*), 1970, 1087; (*b*) R. O. C. Norman and P. M. Storey, *ibid.*, p. 1099; (*c*) B. C. Gilbert, P. Larkin, and R. O. C. Norman, *J.C.S. Perkin II*, 1972, 1272.

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[22] (*a*) P. Baumgarten and E. Dammann, *Ber.*, 1933, **66**, 1633; (*b*) P. Baumgarten, *ibid.*, 1936, **69**, 1938.

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(which is also linear, see line 4 in Figure 1) were linearly proportional to the square root of the initial pyridine concentration.

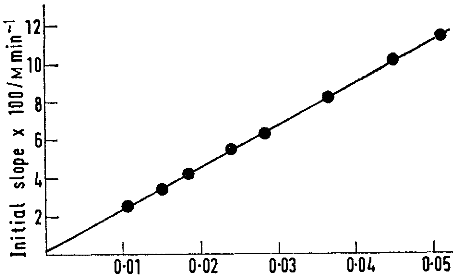
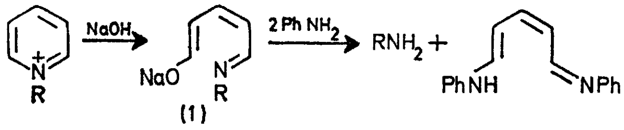


FIGURE 3 Oxidation of pyridine (0·66M) by potassium peroxydisulphate in water at 50·0°. Variation of the initial rate against the peroxydisulphate concentration

Product Studies.—For product studies the concentrations of persulphate and pyridine were increased from those used in the kinetic runs, higher temperatures were generally employed, and all reactions were taken to complete loss of persulphate. Typically the initially colourless aqueous solution of $K_2S_2O_8$ (0·1M) and pyridine (1·0M) became deep red after 4 h at 90°. Ether extraction yielded a pale yellow solution containing (g.l.c. analysis) small amounts of bipyridyl isomers, specifically 2,2′-, 2,3′-, 2,4′-, and 4,4′-bipyridyl. Yields of bipyridyls formed, as well as relative yields of isomers are shown in Tables 1 and 2.

The dark red aqueous solution remaining after ether extraction was concentrated and treated as described in the Experimental section to give an organic salt isolated as either a tetrafluoroborate or a perchlorate and crystallised from absolute ethanol. High yields of these salts were obtained. Spectroscopic analysis, m.p.s, and microanalyses of the isolated organic salts were consistent with pyridylpyridinium salts of the type originally isolated by Baumgarten.[22] Further identification was achieved on carrying out the Zincke degradation reaction (1).[24-27]



(1)

Applying the Zincke reaction to the isolated organic salts yielded only 2-aminopyridine (g.l.c. analysis), indicating a 2-pyridylpyridinium salt. However, on carrying out the degradation sequence with the crude aqueous extract from a persulphate–pyridine reaction, all three aminopyridines were produced in molar ratios 90 : 9 : 1 for the 2-, 3-, and 4-isomers respectively.

Effect of pH.—For the reaction carried out at about neutral pH the main products are pyridylpyridinium salts (with the 2-isomer predominating) and bipyridyls are obtained in only small amounts. A major point of

TABLE 1

Reactions of potassium peroxydisulphate with pyridine in aqueous solution

Run	$[K_2S_2O_8]_0$/M	[Pyridine]$_0$/M	[Additive]$_0$/M	T/°C(t/h)	Initial pH	Yield of pyridyl-pyridinium salt (%) [a]	Yield of bipyridyls (%) [a,c]
1	0·10	1·0	None	90 (4)	Neutral	>80	5 [d]
2	0·20	2·0	None	90 (4)	Neutral	>80	5
3	0·20	0·20	None	90 (4)	Neutral	20	2
4	0·10	1·0	H_2SO_4, 0·8	90 (4)	2	90	2
5	0·10	1·0	K_2CO_3, 0·1	90 (4)	9	30	8
6	0·10	1·0	KOH, 0·4	90 (4)	13	N.d.	20
7	0·10	1·0	KOH, 1·0	90 (4)	14	N.d.	30
8	0·10	1·0	KOH, 2·0	90 (4)	14	N.d. (20)[b]	40
9	0·10	1·0	$AgNO_3$, 0·01 +KOH, 1·0	R.t. (2) [e]	Alkaline	N.d. (15)	25
10	0·10	4·0	$AgNO_3$, 0·01 +KOH, 1·0	R.t. (2)	Alkaline	N.d. (15)	25
11	0·10	0·10	$AgNO_3$, 0·01 +KOH, 1·0	R.t. (2)	Alkaline	N.d.	15
12	0·10	1·0	$AgNO_3$, 0·10 +KOH, 1·0	R.t. (2)	Alkaline	N.d.	25
13		1·0	AgO, 0·20 +KOH, 1·0	40 (4)	Alkaline		0
14	0·10	1·0	$AgNO_3$, 0·01 $+H_2SO_4$, 0·5	R.t. (5)	Acidic	>80	1
15	0·21	2·0	$FeSO_4$, 0·185 $+H_2SO_4$, 0·8	R.t. (4)	Acidic	>80	~1
16	0·10	1·0	$CuSO_4$, 0·035 +KOH, 1·1	R.t. (4)	Alkaline		~0
17		2·0	$FeSO_4$, 0·37 $+H_2O_2$, 0·44 $+H_2SO_4$, 0·8	R.t. (4)	Acidic	20	~1

[a] Based on $K_2S_2O_8$ + 2 Pyridine $\longrightarrow$ Pyridylpyridinium salt + Bipyridyl. [b] N.d. = yields not determined; the number in parentheses refers to the amount of 2-aminopyridine obtained in the ether extract resulting from Zincke degradation. [c] Ether extracts were made from aqueous solutions which were at least at pH 7. See also footnote *b* of Table 2′ [d] The yield of bipyridyl was little different when a solvent system of MeCN–H_2O (8 : 1 v/v) was used. [e] R.t. = room temperature.

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[24] Th. Zincke, *Annalen*, 1903, **330**, 361.

[25] W. Konig, *J. prakt. Chem.*, 1904, **69**, 105.

[26] F. Krohnke, *Angew. Chem. Internat. Edn.*, 1963, **2**, 380.

[27] H. J. Shine, J. J. Silber, R. J. Bussey, and T. Okuyama, *J. Org. Chem.*, 1972, **37**, 2691.

interest was the origin of the two types of product which may have arisen from the partitioning of a common intermediate or be the consequence of two independent reactions. Accordingly the variation of products with initial pH of the reaction was investigated.* The immediate observation with regard to bipyridyl production was that it rapidly increased with increasing initial pH of the reaction mixture (Table 1); correspondingly yields decreased when reaction took place in the presence of acid. With constant starting concentrations of reactants, maximum bipyridyl production was obtained in the presence of high base concentration. Relative yields and isomer distribution are shown in Tables 1 and 2.

TABLE 2

Relative yields of bipyridyl isomers produced during some of the runs quoted in Table 1

Run no.[a]	[Additive]$_0$/M	Initial pH	Relative yields of bipyridyl isomers[b] 2,2′	2,3′ + 2,4′	4,4′
1	None	Neutral	2·0	1·0	0·1
4	H_2SO_4, 0·8	2	2·2	1·0	0·1
5	K_2CO_3, 0·1	9	1·9	1·0	0·1
6	KOH, 0·4	13	1·6	1·0	0·2
8	KOH, 2·0	14	1·4	1·0	0·4
9	$AgNO_3$, 0·01 + KOH, 1·0	14	1·5	1·0	0·2

[a] For all reactions $[K_2S_2O_8]_0$ = 0·10M; [Pyridine]$_0$ = 1·0M. Reaction conditions are given in Table 1. [b] Total yields are given in Table 1. All solutions were extracted with ether at pH 7—7·5. From controls it was found that the overall yield of bipyridyl, extracted from an aqueous solution, increased with increasing pH (between 6 and 11); however the relative amounts of each isomer extracted remained the same.

The situation regarding pyridylpyridinium salt formation is not as straightforward. Almost quantitative yields were obtained when the persulphate–pyridine reactions were carried out in neutral or acidic conditions and, since acid increases the rate of reaction (see Figure 1), its presence is an advantage for pyridinium salt formation. However as mentioned above the pyridinium salt is unstable to hydroxide ion, being cleaved to the salt (1) which slowly liberates aminopyridine on heating. In the presence of sodium carbonate (0·1M) substantial amounts of the pyridylpyridinium salt were still formed but were not detected when equivalent amounts of sodium hydroxide were used as base. Instead, in the latter case, the ether extract contained a moderate yield of 2-aminopyridine as well as the isomeric bipyridyls.

Effect of Metal Ions.—With reference to other persulphate oxidations it was appropriate to test the effect of added metal ions, in particular silver(I), which are known to be highly efficient activators in homolytic reactions of the persulphate ion. In this particular study there were a number of constrictions regarding choice of metal ions since in neutral solution silver(II),[14,28] iron(II),[29] and copper(I) [30] ions are highly efficient coordinating centres to heterocycles such as pyridine and 2,2′-bipyridyl. However silver(I) ions can be used in alkaline solution as they are still able to induce persulphate decomposition whilst complexes with heterocycles are unstable and liberate the free ligand.[28] Thus the system $S_2O_8^{2-}$–Ag^I–OH^-–pyridine in water offered a convenient, room temperature route to bipyridyls and this was found to be the case as indicated by the data in Tables 1 and 2, runs 9—12. These show that the reaction is of the same type as the uncatalysed process and although the overall yields of bipyridyls are somewhat lower than for the corresponding uncatalysed reaction, the isomer ratios are essentially the same.

Substitution of silver(II) oxide for the $S_2O_8^{2-}$–Ag^I couple failed to give the bipyridyl products anticipated if intermediate silver(II) ion was the crucial reagent during the silver(I) catalysed decomposition of the alkaline persulphate solution. Also no increase in bipyridyl yield occurred when one equivalent, rather than a catalytic amount of silver nitrate was employed; furthermore no increase in bipyridyl yield was apparent on carrying out the silver catalysed reaction at 90°.

The use of iron(II) or copper(II) ions in place of silver(I) ions did not yield bipyridyls when stirred with basic solutions of persulphate and pyridine at room temperature. Ferrous ions were however, effective activators in the production of the pyridylpyridinium salt. Thus addition of ferrous sulphate to a stirred neutral or acidic solution of potassium persulphate at room temperature gave a high yield of 2-pyridylpyridinium salt. Similarly in acid or neutral solution the salt is formed during the room temperature decomposition of $S_2O_8^{2-}$ by a *catalytic* amount of silver nitrate.

Thus whenever the persulphate molecule is cleaved, either thermally or by electron transfer from a metal ion, pyridine is oxidised to pyridylpyridinium ions and bipyridyls. The metal ion promoted reactions provide a convenient, room temperature alternative to the thermal reaction especially in the case of silver(I), when only a trace amount is required.

E.s.r. Spin-trapping Studies.—Previous successful utilisation of nitrones and nitroso-compounds, in conjunction with e.s.r. spectroscopy,[16] to identify radical intermediates (spin trapping [31]) during oxidative processes encouraged us to apply the technique to this particular reaction. Kinetic experiments established qualitatively that radical traps retarded the reaction between persulphate ions and pyridine in aqueous

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* Generally in peroxydisulphate oxidations the pH of the medium decreases as reaction proceeds owing to liberation of hydrogen sulphate ion. In the absence of added acid or base the initial pH of the peroxydisulphate–pyridine solutions were between 7 and 8 and final pH values were between 6 and 7. Thus in these cases the reaction occurs under essentially neutral conditions.

[28] G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, 1930, 2594.

[29] E. Konig, *Co-ordination Chem. Rev.*, 1968, **3**, 471.

[30] A. H. Lewin, R. J. Michl, P. Ganis, and U. Lepore, *J.C.S. Chem. Comm.*, 1972, 661.

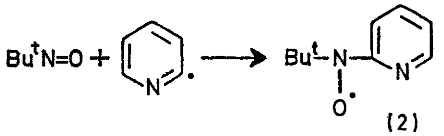
[31] For reviews to 1970 see (*a*) M. J. Perkins, ' Essays on Free-radical Chemistry,' *Chem. Soc. Special Publ.*, 1970, No. 24, ch. 5; (*b*) E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; (*c*) C. Lagercrantz, *J. Phys. Chem.*, 1971, **75**, 3466.

solution at 50°, suggesting the involvement of intermediate radicals. During the spin trapping experiments both 2-methyl-2-nitrosopropane and benzylidene-t butylamine *N*-oxide were employed and, as found in other studies,[16] different yet complementary results were obtained from each radical scavenger.

When the thermal reaction between aqueous potassium persulphate and pyridine was carried out in the presence of a small amount of 2-methyl-2-nitrosopropane in the cavity of an e.s.r. spectrometer a weak but definite signal of 2-pyridyl t-butyl nitroxide (2) was observed indicating trapping of 2-pyridyl radicals. Identification of the nitroxide (2), and hence the 2-pyridyl radical was made from previous work[32] in which the three isomeric pyridyl radicals were independently generated (in the presence of 2-methyl-2-nitrosopropane) from a number of different sources.*

Spin-trapping experiments using benzylidene-t-butylamine *N*-oxide (3) were also carried out as (3) is a highly efficient scavenger of radical intermediates which add on to the carbon atom forming very stable nitroxide adducts of the type (4).

After carrying out the thermal or silver(I) ion induced decomposition of potassium peroxydisulphate in an aqueous pyridine solution of nitrone (3) e.s.r. analysis revealed an intense spectrum consisting of a 1 : 1 : 1 triplet of 1 : 2 : 2 : 1 quartets (*g* 2·006). Control experiments (see Experimental section) indicated that the signal only appeared when sulphate radical-anions ($SO_4^{\cdot-}$) were generated in the presence of pyridine.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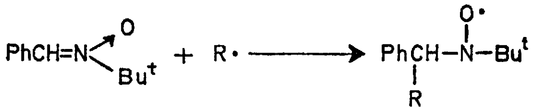
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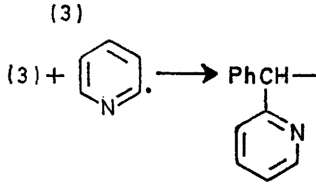
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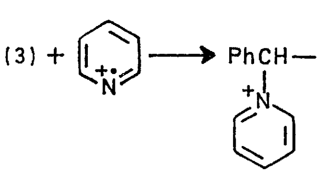
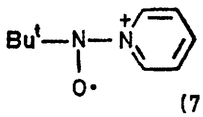

(5)

(6)

The particular signal observed is very unusual in that most nitroxides resulting from reaction (3) display a triplet of doublets due to the nitroxide nitrogen and β-hydrogen in the adduct nitroxide (4). Very rarely is there any contribution to the hyperfine structure from the attached radical. Independent addition of 2-pyridyl radicals (generated by the method of ref. 32) to the nitrone gives nitroxide (5) which, as expected, does display a triplet of doublets (a_N 1·42, a_H 0·22 mT). However the triplet of quartets is consistent with a nitroxide having structure (6) and from the mechanism of the reaction elucidated below its formation is consistent with the trapping of a pyridine cation-radical [reaction (5)].

Thus the 1 : 1 : 1 triplet of 1 : 2 : 2 : 1 quartets is analysed in terms of a nitroxide nitrogen triplet (a_N 1·37 mT) and an identical coupling of 0·29 mT for both the β-hydrogen and the pyridine nitrogen nuclei. Nitroxide (6) would certainly be expected to be reasonably stable unlike the highly unstable adduct nitroxide (7) which would be produced by analogous trapping of pyridine cation-radicals by 2-methyl-2-nitrosopropane.


(7)

Addition of nitrogen cation-radicals to an unsaturated carbon atom [equation (5)] finds precedence in the studies of Neale[33] and Minisci[34] who have both established that such species are rapidly trapped by a variety of substituted olefins forming 1 : 1 adducts in good yields.

Mechanism of Reaction.—Mechanistically the reaction between persulphate and pyridine presents a number of novel and challenging considerations. Foremost was to decide whether the reaction proceeds homolytically or heterolytically and whether the initial step is nucleophilic attack of pyridine on persulphate or the breakdown of the peroxide linkage with subsequent reaction by the sulphate radical-anion. As two major types of product are formed the possible operation of two independent mechanisms was also considered. Furthermore nucleophilic attack by pyridine on the peroxide linkage could occur by two modes, reactions (6) and (7). Both types of attack are considered

$$C_5H_5N + S_2O_8^{2-} \longrightarrow C_5H_5\overset{+}{N}\text{-}OSO_3^{-} + SO_4^{2-} \qquad (6)$$

$$C_5H_5N + S_2O_8^{2-} \longrightarrow (C_5H_5N\text{-}OSO_3^{-})\cdot + SO_4^{\cdot-} \qquad (7)$$

unlikely because of the following experimental observations: (a) no reaction occurs between purified reagents at room temperature; (b) traces of silver(I) ions cause a rapid reaction at room temperature; (c) use of undistilled water led to erratic kinetics; and (d) with pure reagents the reaction rate (loss of persulphate)

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* These include the oxidation of hydrazines, *N'*-2-pyridylbenzohydrazide, and 2-pyridyl-hydrazine and the reaction between 2-aminopyridine and pentyl nitrite in benzene.

[32] T. W. Bentley, J. A. John, R. A. W. Johnstone, P. J. Russell, and L. H. Sutcliffe, *J.C.S. Perkin II*, 1973, 1039.

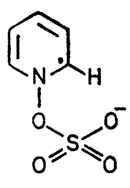
[33] R. S. Neale, *J. Org. Chem.*, 1967, **32**, 3263, 3273; *Synthesis*, 1971, 1.

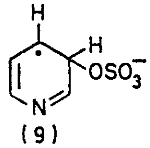
[34] F. Minisci, R. Galli, and M. Cecere, *Tetrahedron Letters*, 1966, 3163; F. Minisci, *Synthesis*, 1973, 1.

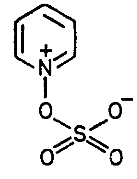
is not first order in both reagents, as is almost invariably the case with known nucleophilic reactions at peroxide linkages.[35b]

Experimental observations are however, consistent with initial breakdown of the persulphate molecule into sulphate radical anions ($SO_4^{\cdot-}$) which subsequently attack the pyridine nucleus.

The precise nature of this attack may be speculated on in a manner which finds analogy in the considerations outlined by Norman and his co-workers in analysing e.s.r. spectra observed for the interaction of the $SO_4^{\cdot-}$ with some aromatic substrates.[18a] Of the three main possibilities direct hydrogen atom abstraction from the pyridine ring seems unlikely and would not in any case explain the observed products. Direct electron abstraction (*cf.* the mechanism proposed for alcohol oxidation [16]) is however, a very likely pathway particularly in view of the two available non-bonded electrons on the ring nitrogen atom. The third possibility is an addition–elimination sequence involving formation of adduct radicals (8) or (9). Sulphate radical anion has marked electrophilic character [18a] and would consequently have a preference for either the nitrogen or the β-carbon atom of the pyridine ring (the positions of highest electron density). Formation of the adduct (8) is thus easily visualised and its geometrical and pyridinyl radical character give it added stability; furthermore complexes of the type (10) have been reported and whilst both pyridyl radicals and pyridine radical-cations can be formed from the same intermediate [equation (9)], formation of a pyridyl radical by the direct electron-abstraction route [equation (8)] must arise by subsequent deprotonation or further reaction of the cation-radical.

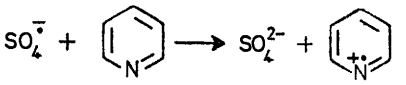

(8)

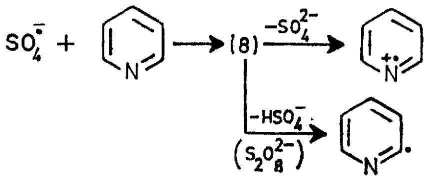

(9)

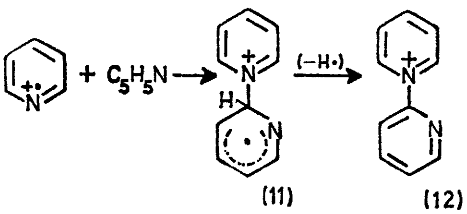

(10)

On the basis of the present experimental evidence it is not possible to discriminate between these two reaction paths.

The radical trapping results with 2-methyl-2-nitrosopropane and nitrone (3) are consistent with a high yield of pyridine cation-radicals and a relatively much lower (about two orders of magnitude *) yield of 2-pyridyl radicals. No direct evidence has been obtained for a pyridinyl radical of the type (8) or (9).


(8)


(9)


(11) (12)

(10)

Rapid interaction of pyridine and the pyridine cation-radical, followed by subsequent oxidation, readily explains the formation of pyridylpyridinium ions [equation (10)]. Nucleophilic capture of cation radicals is a well established reaction,[35] having first gained consideration from anodic oxidation studies where cation-radical intermediates are now, in the majority of cases, thought to be the primary intermediates [36] and is the basis of the e.c.e. mechanism (electron transfer oxidation of aromatic substrate to cation-radical followed by chemical attack of cation-radical by unoxidised nucleophile and further electron transfer oxidation of the cation-radical–nucleophile adduct). Direct examples of cation-radical capture by pyridine are known,[35c,37] and unequivocal evidence for this type of process has been presented;[38] the whole concept of nucleophilic capture of aromatic cation-radicals has also been discussed and extended.[39] Furthermore recent work reported by Shine and his co-workers [40] indicates that reaction of pyridine with the cation-radicals of perylene, thianthrene, and phenothiazine is extremely fast ($>10^7$ l mol^{-1} s^{-1}) although the precise mechanism of interaction is still to be established. Thus considering first oxidation of pyridine by $S_2O_8^{2-}$ in neutral solution where the major products are 2-pyridylpyridinium ions, the experimental data are consistent with the chain reaction of Scheme 1. Applying stationary state kinetics the rate of reaction is given

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* This assumes that the two nitroxides (2) and (6) have comparable stability; both are relatively stable at room temperature.

[35] (*a*) K. Nyberg, *Acta Chem. Scand.*, 1971, **25**, 3770; (*b*) 1973, **27**, 503; (*c*) V. D. Parker and L. Eberson, *J. Amer. Chem. Soc.*, 1970, **92**, 7488; (*d*) V. D. Parker, *Acta Chem. Scand.*, 1970, **24**, 2757, 2775, 3151, 3162, 3171; (*e*) V. D. Parker and L. Eberson, *Tetrahedron Letters*, 1969, 2839, 2843; (*f*) R. O. C. Norman, C. B. Thomas, and J. S. Wilson, *J.C.S. Perkin I*, 1973, 325.

[36] M. E. Peover and B. S. White, *J. Electroanalyt. Chem.*, 1967, **13**, 93; J. Phelps, K. S. V. Santhanam, and A. J. Bard, *J. Amer. Chem. Soc.*, 1967, **89**, 1752; L. S. Marcoux, J. M. Fritsch, and R. Adams, *ibid.*, p. 5766.

[37] (*a*) H. Lund, *Acta Chem. Scand.*, 1957, **11**, 1323; (*b*) V. D. Parker, *Chem. Comm.*, 1969, 973; (*c*) M. Sainsbury, *J. Chem. Soc.* (*C*), 1971, 2888.

[38] G. Manning, V. D. Parker, and R. N. Adams, *J. Amer. Chem. Soc.*, 1969, **91**, 4584.

[39] (*a*) R. N. Adams, *Accounts Chem. Res.*, 1969, **2**, 175; (*b*) L. Eberson and K. Nyberg, *ibid.*, 1973, **6**, 106.

[40] C. V. Ristagno and H. J. Shine, *J. Org. Chem.*, 1971, **36**, 4050.

by equation (11) where $k_4k_5[PyPy^{+\cdot}]^2/k_1k_2 + k_5[PyPy^{+\cdot}]/k_2 - [Pyridine] = 0$. Solving for $[PyPy^{+\cdot}]$ and bearing in mind that k_1 is of the order of 10^{-4} s^{-1} and k_2 is (by analogy with the rate constant for the attack of $SO_4^{\cdot-}$ on benzene[42]) of the order of 10^8 l mol^{-1} s^{-1} gives equation (12) which is in agreement with the kinetic results reported above.

$$S_2O_8^{2-} \xrightarrow{k_1} 2SO_4^{\cdot-}$$

$$SO_4^{\cdot-} + Py \xrightarrow{k_2} SO_4^{2-} + Py^{+\cdot}$$

$$Py^{+\cdot} + Py \xrightarrow{k_3} PyPy^{+\cdot}$$

$$PyPy^{+\cdot} + S_2O_8^{2-} \xrightarrow{k_4} PyPy^{+} + SO_4^{\cdot-} + HSO_4^{-}\,^{*}$$

$$PyPy^{+\cdot} + SO_4^{\cdot-} \xrightarrow{k_5} PyPy^{+} + HSO_4^{-}$$

SCHEME 1 Py = Pyridine, $Py^{+\cdot}$ = pyridine cation-radical $PyPy^{+\cdot}$ = (11), $PyPy^{+}$ = (12)

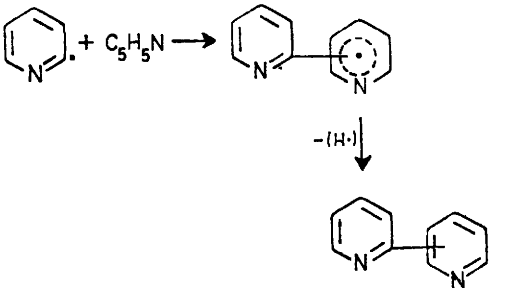
* This step bears a close resemblance to the key step of the induced decomposition of decanoyl peroxide during the homolytic alkylation of protonated quinoline.[41]

$$-d[S_2O_8^{2-}]/dt = k_1k_2[S_2O_8^{2-}][Pyridine]/k_5[PyPy^{+\cdot}] \quad (11)$$

$$-d[S_2O_8^{2-}]/dt = (k_1k_2k_4)^{\frac{1}{2}}[S_2O_8^{2-}][Pyridine]^{\frac{1}{2}}/k_5^{\frac{1}{2}} \quad (12)$$

Whilst formation of pyridylpyridinium ions may be understood on the basis of the above mechanism, the isomer distribution obtained, namely 90 : 9 : 1 for the 2-, 3-, and 4-pyridylpyridinium ions, has not been accounted for. Pyridine cation-radical has not yet been observed directly by e.s.r. spectroscopy but loss of an electron from the nitrogen lone-pair orbital seems more probable than loss of an electron from the π-system,[43] although ionisation potentials from photoelectron spectra are not conclusive.[44] Nucleophilic attack occurs preferentially at the 2-position in pyridine and even more so in pyridinium ions so it is to be expected that the 2-isomer is formed in the greatest amount. The order of the relative reactivities in fact corresponds to the relative magnitude of the calculated free valencies[45] of the pyridine cation-radical.

As depicted in Scheme 1 the proposed mechanism is also compatible with formation of the minor product bipyridyl when reaction occurs in neutral or acid solution (Table 1). 2-Pyridyl radicals, formed either by breakdown of the radical adduct (8) or by loss of proton from the pyridine cation radical[46] would undergo homolytic substitution into the pyridine nucleus giving, after oxidation, 2,2′-, 2,3′-, and 2,4′-bipyridyls [reaction (13)]. The ratio of 2,2′-bipyridyl to the sum of 2,3′- and 2,4′-bipyridyls is 2 : 1 and is to be compared with the corresponding values of *ca.* 1 : 1 for phenylation of pyridine[47] and *ca.* 2 : 1 for the homolytic substitution of 3-pyridyl radicals into pyridine.[48] Only a trace of 4,4′-bipyridyl is observed under these conditions compared to the significant amount formed in alkaline solution (see Table 1).



(13)

2,2′-,2,3′- and 2,4′- bipyridyls.

As shown above hydroxide ion has a pronounced effect on the reaction. Peroxydisulphate ion decomposition is much slower and any pyridylpyridinium ions formed are immediately cleaved under the prevailing conditions. The decrease of such products and a corresponding large increase in the yield of bipyridyls indicates a change in reaction pathway. Initially it was considered that sulphate radical-anions were reacting with hydroxide ion to produce hydroxyl radicals which were responsible for the increase in bipyridyl formation. This conclusion was not substantiated by the finding that similar amounts of bipyridyls were formed when either the Fe^{2+}–$S_2O_8^{2-}$ or Fe^{2+}–H_2O_2 couples were used to oxidise aqueous solutions of pyridine under moderately acidic conditions.† The importance of reaction (14) was also

$$SO_4^{\cdot-} + \overset{-}{O}H \xrightarrow{k_{14}} SO_4^{2-} + OH \qquad (14)$$

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† Reactions with the Fe^{2+}–H_2O_2 couple with organic substrates were originally investigated by Merz and Waters[49] and recently they have received further attention from Walling and his co-workers.[50] In the original work[49] pyridine was actually one of the substrates studied although no products were isolated. On addition of reagents with vigorous stirring at room temperature a dark blue solution is produced. Ether extraction yielded a little bipyridyl although, as in the case of the Fe^{2+}–$S_2O_8^{2-}$ reaction with pyridine, the 2,2′-isomer was not all extracted due to co-ordination with Fe^{II}. On treating the aqueous extract as for the isolation of pyridylpyridinium ions, a moderate amount of the 2,2′-isomer was isolated (see Experimental section). The dark blue colour indicated other products were also produced which have not been identified. In an analogous reaction using quinoline as substrate Breslow and Lukens identified a small yield of 3-hydroxyquinoline;[51] the aqueous extract which may have contained a quinolylquinolinium salt was not analysed.

[41] F. Minisci, A. Selva, O. Porta, P. Barilli, and G. P. Gardini, *Tetrahedron*, 1972, **28**, 2415.

[42] W. Roebke, M. Renz, and A. Henglein, *Internat. J. Radiation Phys. Chem.*, 1969, **1**, 39.

[43] H. J. Bower, J. A. McRae, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1968, 2696.

[44] C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, 1972, **94**, 1466.

[45] R. Bhattachavya and S. Basu, *J. Chem. Phys.*, 1962, **59**, 125.

[46] *Cf.* M. Masui and H. Ohmori, *J.C.S. Perkin II*, 1973, 1112.

[47] R. A. Abramovitch and J. G. Saha, *J. Chem. Soc.*, 1964, 2175; D. H. Hey, C. J. M. Stirling, and G. H. Williams, *J. Chem. Soc.*, 1955, 3963; J. M. Bonnier and J. Court, *Compt. rend.*, 1967, **265C**, 133.

[48] R. L. Frank and J. V. Crawford, *Bull. Soc. chim. France*, 1958, 419.

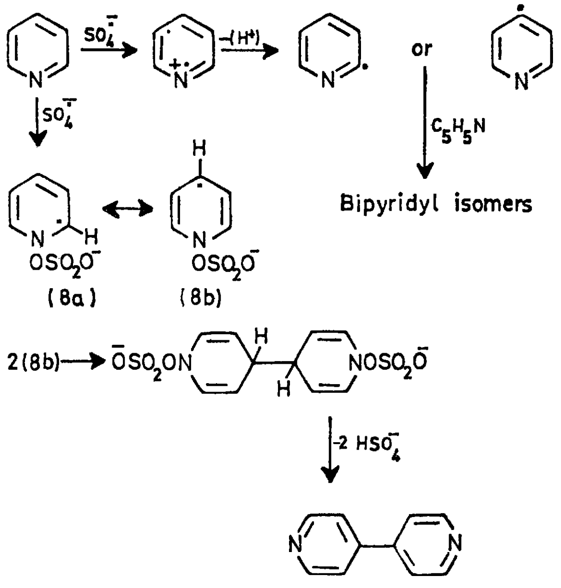
[49] J. H. Merz and W. A. Waters, *J. Chem. Soc.*, 1949, 515; *Discuss. Faraday Soc.*, 1947, No. 2, 179; see also C. Neuberg, *Biochem. Z.*, 1909, **20**, 526.

[50] C. Walling and S. Kato, *J. Amer. Chem. Soc.*, 1971, **93**, 4275; C. Walling and G. M. El-Taliawi, *ibid.*, 1973, **95**, 844, 848; see also D. L. Ingles, *Austral. J. Chem.*, 1973, **26**, 1021.

[51] R. Breslow and L. N. Lukens, *J. Biol. Chem.*, 1960, **235**, 292.

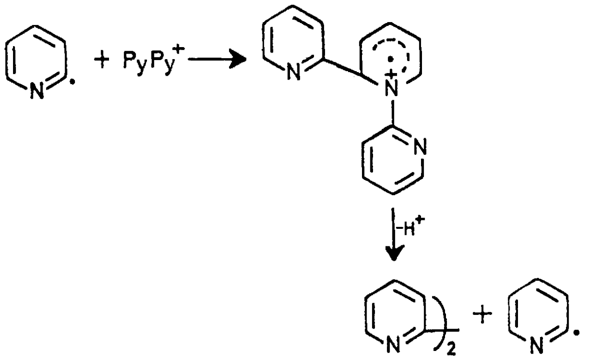
diminished by comparing reported rate constants from pulse radiolysis [42] and flash photolysis [52] measurements indicating a value of 7×10^8 l mol^{-1} s^{-1} for attack of $SO_4^{-\cdot}$ on benzene, an order of magnitude higher than that of k_{14} 5×10^7 l mol^{-1} s^{-1}. No value exists for reaction with pyridine but it is reasonable to expect a value at least as large as that for benzene. Norman and his co-workers also conclude that the sulphate radical-anion is formed in basic solution.[18a]

From the above evidence it appears that the sulphate radical-anion is the reactive species in both acidic and basic solution. Using the mechanism already advanced for neutral and acidic solution (Scheme 1), two possible explanations for the change in product distribution are apparent. First the pyridine cation-radical deprotonates [46] prior to nucleophilic capture by pyridine so that pyridyl radicals are rapidly formed and bipyridyls subsequently produced by homolytic substitution processes. The second plausible route to bipyridyls is through dimerization of the pyridinyl adduct radicals (8) now stabilised in alkali solution.* The latter mechanism is consistent with formation of significant amounts of 4,4′-bipyridyl and also with the marked decrease in rate of persulphate decomposition when basic conditions are employed (Scheme 2). Pyridinyl radicals have a great tendency to dimerise and they do so predominantly in the 4-position,[53] possibly accounting for the observed increase in the yield of 4,4′-bipyridyl relative to the 2,2′-isomer when reaction occurs in alkaline conditions.



SCHEME 2

It is possible that the small yields of bipyridyl isomers formed in neutral solution might be due to subsequent reactions of the pyridylpyridinium ions [reaction (15)]. To test this possibility,† both phenyl radicals (from PhN=NCPh$_3$) and 2-pyridyl radicals (from the silver oxide oxidation of 2-hydrazinopyridine in acetonitrile) were generated in the presence of 4-pyridylpyridinium chloride. However g.l.c. analysis of the ether-extracted reaction mixture showed no support for reaction (15) and the very small amount of bipyridyl formed in the latter case was produced by coupling of pyridyl radicals from the hydrazine oxidation. Zinc reduction of 4-pyridylpyridinium chloride solutions also failed to yield any bipyridyl products. It seems reasonable to conclude therefore that formation of bipyridyls, even in neutral solutions, occurs *via* the reactions indicated in Scheme 2.



(15)

EXPERIMENTAL

AnalaR potassium peroxydisulphate was used as received after checking its purity by iodometric titration against standard thiosulphate solution. AnalaR pyridine was distilled and kept in the dark saturated with nitrogen. Water was distilled. ^{1}H N.m.r. spectra were measured at 60 MHz for solutions in D$_2$O and i.r. spectra were recorded for Nujol mulls. G.l.c. analyses were carried out on Pye instruments; the main columns used were (i) a 1·6 m glass column of 3% O.V.1 and (ii) a 0·5 m glass column containing 28% Pennwalt 223 coated with 4% KOH. The latter column gave well resolved, symmetrical peaks with nitrogen heterocycles including the isomeric bipyridyls. However neither column could separate 2,4′-, 2,3′-, and 4,4′-bipyridyl and reaction mixtures were also analysed by Dr. G. J. Moore of I.C.I. Mond Division, on a 1·0 m glass column packed with 10% sodium dodecyl benzenesulphonate on Celite which separated all bipyridyl isomers except the 2,4′- and 2,3′-isomers. Quantitative analyses were carried out using the internal standard procedure (see below). Radical trapping using 2-methyl-2-nitrosopropane and nitrone (3) in conjunction with e.s.r. spectroscopy was carried out as previously described.[16] Control experiments

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* By analogy with the observations of Norman and his co-workers [18a] on the interaction of $SO_4^{-\cdot}$ with benzene, breakdown of the adduct radical (8a) requires acid catalysis; kinetic results (Figure 1) are consistent with such an effect.

† This mechanism has been advanced (J. G. Carey, personal communication) as a possible route for bipyridyl production from 4-pyridylpyridinium chloride when the latter is heated above 180° in the presence of an excess of pyridine.

[52] E. Hayon, A. Treinin, and J. Wilf, *J. Amer. Chem. Soc.*, 1972, **94**, 47; I. Kraljic, *Internat. J. Radiation Phys. Chem.*, 1970, **2**, 59.

[53] (*a*) J. Chaudhuri, S. Kume, J. Jagur-Grodzinski, and M. Szwarc, *J. Amer. Chem. Soc.*, 1968, **90**, 6421; (*b*) C. D. Schmulbach, C. C. Hinkley, and D. Wasmund, *ibid.*, p. 6600; (*c*) V. Kalyanarman, C. N. R. Rao, and M. V. George, *J. Chem. Soc.* (*B*), 1971, 2406.

were performed with both radical traps and no signals were obtained when either persulphate or pyridine was excluded. In experiments with the nitrone no signals were produced when aqueous solutions of pyridine, containing the nitrone, were left to stand in the presence of air, or were shaken up with silver oxide.

Kinetic Runs.—Unless the presence of air was desired all reactant solutions used in kinetic experiments were purged with nitrogen for 1 h prior to mixing. Fresh solutions of persulphate were made up daily. Stock solutions (2M) of pyridine in distilled water were kept under nitrogen and stored in the dark. Thus separate aqueous solutions of $K_2S_2O_8$ and pyridine, with or without additives, were nitrogen flushed, thermally equilibrated in a water-bath, and rapidly mixed. Persulphate disappearance was monitored by removal of 5 ml portions and estimation of the unchanged persulphate by addition of an excess of acidified ferrous ammonium sulphate and back titration with standard $KMnO_4$ solution. The iodometric method [54] could not be used due to complexation of liberated iodine with unchanged pyridine.[55] Kinetic curves were generally reproducible to within 5% but were markedly affected by traces of metal ions and non-distilled water. For solutions *ca.* 0·5M in $K_2S_2O_8$ and 0·5M in pyridine at 50° the pH of the solution decreases from 7—8 to 6—7 during the course of three half-lives of persulphate decomposition.

Product Analyses.—Reaction between potassium persulphate and pyridine in neutral solution. Potassium peroxydisulphate (2·70 g, 10^{-2} mol) was dissolved in distilled water (90 ml) and pyridine (8 ml, 10^{-1} mol) added. The homogeneous solution was heated to 90° with stirring for 4 h during which time all the persulphate decomposed and the solution became dark red. The pH of the final solution was adjusted to 7 before ether extraction (3 × 100 ml). The ether extracts were combined, washed with water, and concentrated. Analysis by g.l.c. revealed the presence of bipyridyl isomers (Table 1) identification of which was made by comparison of retention times and peak enhancement with mixed injections using the three columns described above.

The separated, dark red, aqueous extract was concentrated by boiling to *ca.* 20 ml and cooled with refrigeration during which solidification took place. After dissolving in acetone, an excess of either sodium tetrafluoroborate or sodium perchlorate was added and, following vigorous shaking, the orange solution was allowed to settle before filtration and evaporation. This process was repeated with a further batch of acetone, then methanol, and finally dry absolute ethanol. On removal of the excess of inorganic salts the crude yellow-orange solid was crystallised from dry absolute ethanol. With both the perchlorate and tetrafluoroborate ions double salts were obtained and m.p.s of the perchlorates varied somewhat owing to slight differences in the constitution of the salt. Both were light brown. For the tetrafluoroborate salt 3·0 g was isolated (85%), m.p. 165—168° (Found: C, 34·45; H, 2·8; B, 6·45; F, 43·95; N, 7·95; Na, 5·8. Calc. for $C_{10}H_9B_2F_8N_2Na$: C, 34·0; H, 2·6; B, 6·1; F, 43·0; N, 7·9; Na, 6·5%), τ 0·8 (t), 1·1 (t), and 1·5 (t). For the perchlorate salt two forms of the double salt were encountered. The first had m.p. 255—260° (Found: C, 33·6; H, 3·2; Cl, 19·65; N, 7·65; O, 35·5. Calc. for $C_{10}H_{10}Cl_2N_2O_8$: C, 33·6; H, 2·8; Cl, 19·8; N, 7·8; O, 35·8%). The second salt had m.p. 300—301° and analysis indicated a mixture of the double salts $C_{10}H_{10}Cl_2N_2O_8$ and $C_{10}H_9Cl_2N_2NaO_8$. N.m.r. spectra of the two perchlorate salts were identical with that of the fluoroborate salt. Also allowing for differences in the anions the i.r. spectra of all three salts were identical.

Attempts to isolate the pyridylpyridinium salt as the iodode (by addition of sodium iodide) were not satisfactory owing to difficulties in isolation.

Reaction in acid. Reaction between $K_2S_2O_8$ and pyridine in the presence of added acid ($KHSO_4$ or H_2SO_4) in the same manner as method (i) produced a light orange solution which, however, turned dark red on neutralization to pH 7 at the end of the reaction. Products were the same as obtained in neutral solution (Table 1).

Reaction in base. In the presence of potassium carbonate both bipyridyls and pyridylpyridinium salts were obtained (Table 1). When the reaction was carried out in the presence of 1M-KOH however, persulphate disappearance was considerably slower with an orange solution being finally obtained. As expected no pyridylpyridinium ions were apparent at the end of the reaction. Ether extracts were almost colourless and g.l.c. revealed good yields of bipyridyl isomers as well as a peak corresponding to a moderate yield of 2-aminopyridine.

Estimation of yields of bipyridyl isomers. This was carried out by adding 10·0 ml of a 2·5 × 10^{-2}M-biphenyl solution in ether to the first ether extract of the reaction mixture. The combined ether extracts were concentrated to 50 ml. Previous calibrations of known bipyridyl concentrations against 5·0 × 10^{-3}M-biphenyl solution enabled quantitative analyses to be made.

Reaction in the presence of metal ions. The required amounts of $K_2S_2O_8$, pyridine, and other additives (*e.g.* H_2SO_4 or KOH) were dissolved in distilled water and the particular metal salt ($AgNO_3$, $FeSO_4,7H_2O$ *etc.*) added with vigorous stirring. Estimation of products was as before.

Zincke degradation of the pyridylpyridinium salts. To a solution of a pyridylpyridinium perchlorate (2·6 g) in water an excess of sodium hydroxide was added. Aniline hydrochloride (2·0 g) was added and the solution darkened as gentle heat was applied. Gradual acidification with dilute HCl precipitated a black solid and after standing for a short time the solution was made slightly alkaline and extracted with ether. The combined ether extracts were washed and concentrated. Analysis by g.l.c. indicated the presence of an aminopyridine as well as some unchanged aniline which served as a useful internal marker for the identification and estimation of isomeric aminopyridines. G.l.c. comparisons and co-injections with authentic samples of the three aminopyridines also confirmed their presence.

On carrying out the same procedure with commercial 4-pyridylpyridinium chloride a quantitative amount of 4-aminopyridine was obtained.

To check for the formation of other pyridylpyridinium isomers, the dark red aqueous extract from a repeat of the $C_5H_5N-S_2O_8^{2-}$ reaction in neutral solution was, in a similar way, subjected to the Zincke degradation. G.l.c. analysis of the ether extract revealed the presence of all three aminopyridines in the molar ratio of *ca.* 90 : 9 : 1 2- : 3- : 4-aminopyridine respectively, indicating that whilst the 2-pyridylpyridinium salt is the (as expected) major

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[54] T. L. Allen, *J. Amer. Chem. Soc.*, 1951, **73**, 3589.

[55] C. Reid and R. S. Mulliken, *J. Amer. Chem. Soc.*, 1954, **76**, 3869.

isomer, the 3- and 4-isomers are also produced albeit in low yield.

Reaction of iron(II) *sulphate and hydrogen peroxide.* To $FeSO_4,7H_2O$ (10·25 g, $3·7 \times 10^{-2}$ mol) in water (100 ml) and concentrated H_2SO_4 (4·5 ml), pyridine (16 ml, 0·2 mol) was added and the mixture stirred whilst 30% (100 volume) AnalaR hydrogen peroxide (5 ml, $\sim 4·4 \times 10^{-2}$ mol) was added. The solution turned dark blue and was stirred for 4 h at room temperature. Work-up as before was carried out and both bipyridyl isomers (in the ether extract) and 2-pyridylpyridinium perchlorate (in the aqueous extract) were isolated. The recrystallised salt gave identical i.r. and n.m.r spectra to those of the 2-pyridylpyridinium perchlorates although it appeared slightly darker in colour and had m.p. 280—281° (Found: C, 33·65; H, 3·1; Cl, 19·7; N, 7·68; O, 35·55. Calc. for $C_{10}H_{10}Cl_2N_2O_8$: C, 33·6; H, 2·8; Cl, 19·8; N, 7·8; O, 35·8%).

Reaction of 4-pyridylpyridinium chloride with radical initiators. A suitable quantity (2×10^{-2} mol) of the chloride salt was dissolved in acetonitrile. The radical initiator $PhN{=}NCPh_3$ or a mixture of 2-hydrazinopyridine and silver oxide was added slowly with stirring. Ether extracts were concentrated and analysed by g.l.c.

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