Kinetics and Mechanisms of Oxidations with Nitrous Acid. Part 1. Substituted Benzyl Alcohols and Benzyl Methyl Ether in Aqueous Sulphuric Acid

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The kinetics and products of oxidation of several substituted benzyl alcohols and of benzyl methyl ether, by nitrous acid in aqueous sulphuric acid (30—50%) at 25 °C, have been investigated. Conversion into substituted benzaldehyde, when nitrous acid is taken in excess, is quantitative. Stoicheiometry, kinetic form, kinetic and product hydrogen isotope effects, and the dependence of rate coefficients on acidity, support a mechanism in which there is rate-determining abstraction by the nitrosonium ion of a hydride ion, either in one step or by electron transfer followed by hydrogen-atom abstraction, from the α-carbon atom of the alcohol or ether. The fate of the HNO so formed depends upon the presence or absence of oxygen.

The title reaction [equation (1)] is of interest (*a*) as a potentially convenient method of oxidising alcohols to aldehydes, (*b*) because of its possible relevance to the formation of aldehyde side products during the nitration of methylbenzenes,[1] and (*c*) in the treatment of 'spent acids'.[2]

$$RCH_2OH \xrightarrow{HNO_2} RCHO \qquad (1)$$

There are many reactions in which nitrous acid, or species derived from it, react oxidatively. A variety of mechanisms have been postulated. The oxidative dealkylation of tertiary amines by nitrous acid is thought to proceed *via* pre-equilibrium complexation of NO^+ on nitrogen followed by *syn*-elimination of HNO.[3] Nitrosonium salts are useful oxidants, and mechanisms suggested include one-electron transfer[4] and hydride abstraction,[5] the latter most notably in the present context from benzyl alcohols.[6]

Also relevant are reactions in which nitric acid is the oxidant, but nitrous acid is a necessary promoter. A variety of substrates,[7] including benzyl ethers[8] and alcohols,[9] have been oxidised in this way.

It has been shown that benzyl alcohols may be oxidised to benzaldehydes by nitrous acid in acidic solution, in the absence of nitric acid.[10] In the only reported investigation of the mechanism of this reaction,[11] the important observations were made that the addition of nitric acid has no effect upon the rate, that the rate profile of log(second-order rate constant) against acidity shows a maximum at about 60% H_2SO_4, that at this acidity the relative reactivities of four *p*-X-benzyl alcohols are (X =) Me > H > Cl > NO_2, and that benzyl methyl ether reacts at a rate similar to that of benzyl alcohol.

We have undertaken a detailed investigation of the mechanism of this reaction, and in this paper report on the kinetic form, stoicheiometry, the dependence of rate constant upon acidity, the effects of substituents, and the effects of isotopic substitution of the α-hydrogen atoms of the benzyl alcohol.

Results and Discussion

Kinetics and Stoicheiometry.—In the range of acidity represented by 30—50% H_2SO_4, and with nitrous acid present in at least twenty-fold excess over the benzyl alcohol, the reactions of all the substrates studied here were found to proceed much more quickly than the decomposition of nitrous acid, except in the case of benzyl methyl ether at the lowest acidity used. With this exception, reactions were kinetically, accurately first-order. First-order rate coefficients k_1 were proportional to the concentrations of nitrous acid. Second-order rate coefficients k_2, obtained by dividing k_1 by the stoicheiometric concentration of nitrous acid, are in Table 1.

After ten half-lives for the first-order reaction with an excess of nitrous acid, there was quantitative conversion of the alcohol into the aldehyde as shown by u.v. spectrometry. In some cases, measurements of yield were also made by g.l.c.; the results are in Table 2. It has been reported[11] that when the alcohol is taken in excess, yields of the aldehyde based on nitrous acid can exceed 100%, and the conclusion was drawn that there may be some oxidation, probably by dissolved oxygen, of the reduced nitrogen species back to nitrous acid. Our studies support that conclusion. We found that when nitrous acid reacted with the alcohol in excess, the yield based on nitrous acid (and measured after twelve half-lives as estimated from the rate-coefficient established in the absence of oxygen) was 430% (air-saturated solutions) or 570% (oxygen-saturated solutions). If oxygen was excluded, however, the yield was only a little over 50% (Table 2).

Taken together these results suggest that the rate-determining step involves one molecule of nitrous acid or a species derived from it and leads to the aldehyde and a reduced nitrogen species. The latter reacts in a fast step with a second molecule of nitrous acid. The reduced nitrogen species is most probably HNO, which is known† to react with HNO_2 (in acid solution and in the absence of oxygen) to give two molecules of NO. Oxygen, if present, alters the stoicheiometry because it reacts with NO and/or HNO, regenerating HNO_2. (It is also possible that HNO_3, formed together with HNO_2 from the reaction of NO with O_2, reacts with HNO to give HNO_2.) An outline of the mechanism (in the absence of oxygen) is given as equations (2) and (3).

$$HNO_2 + XC_6H_4CH_2OH \xrightarrow{slow} XC_6H_4CHO + HNO \qquad (2)$$

$$HNO_2 + HNO \xrightarrow{fast} 2NO \qquad (3)$$

There are two indications that step (3) is not sufficiently fast, relative to step (2), for the proper application of the steady-state approximation to HNO. If it were, the yield based on nitrous acid when benzyl alcohol is taken in excess in the absence of oxygen would be 50%, whereas it is slightly greater (Table 2). Also, equations (4) and (5) would follow, permitting calculation of the second-order rate coefficient, k_2, from the observed first-order rate coefficient, k_1, under conditions where the concen-

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† The mechanism of this step is probably complex.[12]

Table 1. Observed second-order rate coefficients for the oxidation of substituted benzyl alcohols and benzyl methyl ether by nitrous acid at 25.0 (±0.1) °C

H_2SO_4(%)	10^5[substrate][a] mol dm^{-3}	$10^5[HNO_2]$[b] mol dm^{-3}	k_2[c] mol^{-1} dm^3 s^{-1}
p-Methoxybenzyl alcohol			
30.1	5.28	107	0.124
30.1	5.28	214	0.124
30.1	5.28	428	0.131
35.0	5.28	107	0.443
35.0	5.28	214	0.429
35.0	5.28	428	0.439
39.8	5.28	107	1.49
39.8	5.28	214	1.52
p-Methylbenzyl alcohol			
30.1	3.98	318	0.0567
35.0	3.98	159	0.157
35.0	3.98	318	0.160
39.8	3.98	159	0.560
45.4	3.98	79.7	2.86
m-Methylbenzyl alcohol			
39.8	4.02	159	0.309
Benzyl alcohol			
35.0	7.81	318	0.0642
39.8	7.81	318	0.218
45.4	7.81	159	1.06
45.4	79.5	7.98	0.64[d]
45.4	159	7.98	0.66[d]
45.4	7.98	159	1.36[e,f]
45.4	7.98	159	1.36[e,g]
45.4	7.98	159	1.44[e,h]
p-Fluorobenzyl alcohol			
39.8	8.20	318	0.198
m-Fluorobenzyl alcohol			
39.8	8.09	318	0.0619
m-Bromobenzyl alcohol			
39.9	8.37	318	0.0528
Benzyl methyl ether			
39.9	7.85	320	0.0137[i]
45.4	7.85	320	0.0965
49.8	7.85	160	0.502
49.8	7.85	320	0.499
p-Methoxy[α,α-$^2H_2$]benzyl alcohol			
35.0	5.28	214	0.143
39.9	5.28	214	0.530
[α,α-$^2H_2$]benzyl alcohol			
39.9	8.05	318	0.0684

[a] Initial concentration of substituted benzyl alcohol or benzyl methyl ether. [b] Initial stoicheiometric concentration of nitrous acid, added as sodium nitrite. [c] Observed second-order rate coefficient obtained by dividing the observed first-order rate coefficient by the initial stoicheiometric concentration of nitrous acid, unless otherwise noted. [d] Runs conducted in the absence of oxygen. The observed second-order rate coefficient was calculated by using equation (5). [e] In the presence of a stoicheiometric concentration (x) of nitric acid. [f] $x = 0.110$ mol dm^{-3}. [g] $x = 0.126$ mol dm^{-3}. [h] $x = 0.208$ mol dm^{-3}. [i] From initial rate measurements.

tration of substrate considerably exceeds that of nitrous acid, and in the absence of oxygen. Values of k_2 obtained in this way

$$-d[HNO_2]/dt = 2k_2[\text{substrate}][HNO_2] \qquad (4)$$

$$k_1 = 2k_2[\text{substrate}] \qquad (5)$$

(see the fourth and fifth entries under benzyl alcohol in Table 1) are not in agreement with the value obtained when nitrous acid was the reagent in excess (preceding entry).

The following discussion relates only to experiments where nitrous acid was taken in excess, and the fate of HNO is not relevant.

Kinetic Hydrogen Isotope Effect.—Rate coefficients k_2 for reaction of 4-X-benzyl alcohol and 4-X-[α,α-$^2H_2$]benzyl alcohol (X = H or MeO) are in Table 1. The value of k_2^H/k_2^D [the kinetic hydrogen isotope effect (k.h.i.e.)] (Table 3) is close to 3. This demonstrates that the α-hydrogen atom is removed in the rate-determining step or (in view of the fact that 3 is a relatively low value for a primary k.h.i.e.) in a step which is partially rate-determining. If the latter possibility were correct, the product hydrogen isotope effect (p.h.i.e.) would be expected to be considerably greater than the k.h.i.e. The p.h.i.e. was measured as the ratio of the yield of [α-^2H]benzaldehyde to that of benzaldehyde from the oxidation of [α-^2H]benzyl alcohol, and found to be 2.5 (±0.5) (Table 4). This is smaller than the k.h.i.e. of 3.2 (±0.1) (Table 3), and the difference, though barely outside experimental error, can readily be accounted for in terms of secondary isotope effects which work in opposite directions in the k.h.i.e. and p.h.i.e. experiments. It is clear that the step in which the α-hydrogen atom is lost is fully rate-determining. Both the magnitude of the k.h.i.e.[13] and its insensitivity to substituent change[14] (Table 3) are consistent with hydride transfer.

Acidity Dependence of k_2.—Figure 1 shows that *p*-X-benzyl alcohols (X = MeO, Me, or H) provide straight-line plots of log k_2 against ($-H_0$), with slopes of 1.47, 1.52, and 1.56, respectively. The plots are almost parallel, which makes it unlikely that there is significant protonation of the alcohols in this range of acidity. The steepness of the plots cannot be attributed to the need for ionisation of the alcohol to the carbocation, because the alcohols exchange their oxygen more

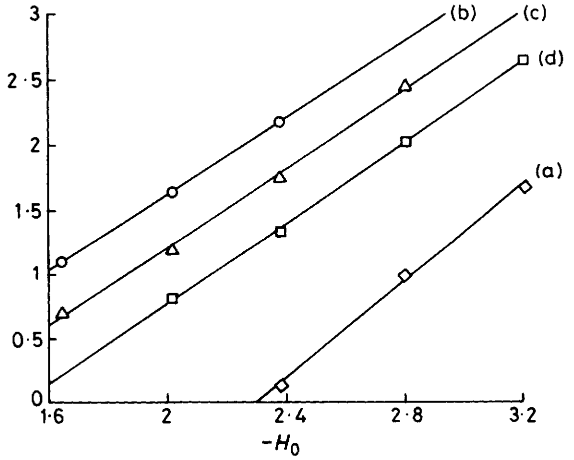


Figure 1. Dependence upon the Hammett acidity function (H_0) of the logarithm of the second-order rate coefficient for oxidation by nitrous acid in aqeuous sulphuric acid at 25 °C of (a) benzyl methyl ether, and of *p*-X-benzyl alcohols [(b) X = MeO; (c) X = Me; (d) X = H]

Table 2. Yields of aldehyde from the oxidation of *p*-X-benzyl alcohol with nitrous acid

X	H_2SO_4(%)	10^5[substrate][a] mol dm^{-3}	10^5[HNO_2][b] mol dm^{-3}	Yield[c] (%)
MeO	39.9	8.0	160	100, 98
Me	39.9	8.0	320	103
H	45.4	8.0	160	103, 101, 104, 100
	45.4	160	8.0	65,[d] 56,[d] 56[d]
	45.4	160	8.0	430, 430
	45.4	160	8.0	570[e]

[a] Initial concentration of *p*-X-benzyl alcohol. [b] Initial stoicheiometric concentration of nitrous acid, added as sodium nitrite. [c] Yields based on the initial concentration of *p*-X-benzyl alcohol or of nitrous acid, whichever was present in least amount. Where more than one experiment was performed, individual results are listed. Solutions were saturated with air unless otherwise noted. [d] Runs conducted in the absence of oxygen. [e] Solutions saturated with oxygen at a pressure of 1 atm.

Table 3. Kinetic hydrogen isotope effect, $k_2{}^H/k_2{}^D$, for the oxidation of 4-X-benzyl alcohol and 4-X-[α,α-$^2H_2$]benzyl alcohol by an excess of nitrous acid at 25.0 (±0.1) °C

X	H_2SO_4(%)	$k_2{}^H/k_2{}^D$
MeO	35.0	3.0
MeO	39.8	2.9
H	39.9	3.2

slowly[15] than they undergo oxidation by nitrous acid. It seems more likely that these slopes, and that for benzyl methyl ether which is steeper still [$d(\log k_2)/d(-H_0) = 1.90$; $d(\log k_2)/d(-H_R) = 0.88$ (ref. 16*a*) or 0.77 (ref. 16*b*)], reflect the need for pre-equilibrium ionisation of nitrous acid to nitrosonium ion [equation (6)].

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \qquad (6)$$

Quantitative appraisal of the acidity dependence of k_2 by any current method[16] is hampered by lack of information about equilibrium (6) in aqueous sulphuric acid. The data available are sparse[17] and do not relate to 25 °C. We hope to re-investigate the equilibrium, but for the present note that the slopes (Figure 1) are not inconsistent with a transition state consisting of aromatic substrate and nitrosonium ion. The difference in slope between the alcohols on the one hand and the ether on the other (Figure 1) is most readily accounted for if in the transition state the alcoholic proton is hydrogen bonded to water. This would be the case if the alcohol oxygen bore a partial positive charge, as it would in a transition state resembling the carbocation in Scheme 2.

Substituent Effects on k_2.—These are illustrated in Figure 2. The plots of log k_2 against σ and σ^+ are not straight, but the plot against [$\sigma + r(\sigma^+ - \sigma)$] (Yukawa–Tsuno method) gives a good straight line if $r = 0.4$, and the slope, ρ, is −1.7 (correlation coefficient 0.999). This demonstrates that in the transition state there is development of positive charge on the α-carbon atom, and that to some extent this is delocalisable into $+M$[18] *para*-substituents.

Possible Mechanisms.—The simplest mechanism consistent with all these observations is one in which nitrosonium ion abstracts hydride ion from the α-carbon atom of the alcohol or ether in the rate-determining step (Scheme 1). The transition state of Scheme 1 has developing carbocation character (Scheme 2). It would therefore be expected that the value of *r* in the Yukawa–Tsuno equation would be greater than zero (because the available resonance structures include one in which a $+M$ *p*-substituent bears the positive charge) and less than unity (because, unlike the developing carbocation in the

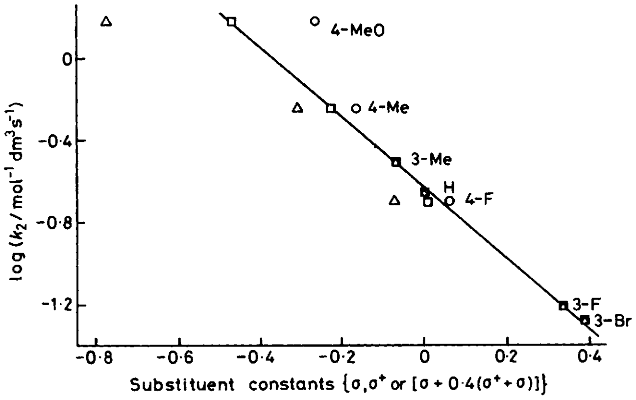
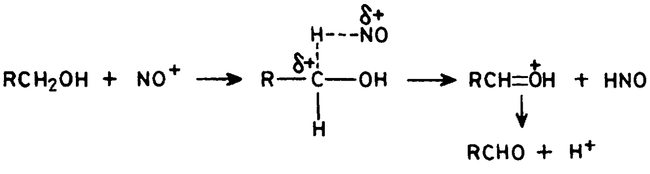
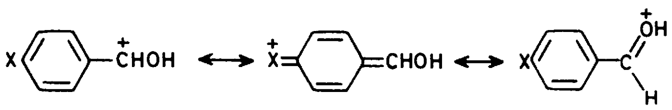


Figure 2. The dependence upon the substituent constants σ^+ (triangles), σ (circles), and [$\sigma + 0.4\ (\sigma^+ - \sigma)$] (squares) of the logarithm of the second-order rate coefficient for oxidation of substituted benzyl alcohols by nitrous acid in 39.8% H_2SO_4 at 25 °C



Scheme 1.



Scheme 2.

$$RCH_2OH + NO^+ \rightleftharpoons RCH_2\overset{+}{\dot{O}}H + NO$$

$$RCH_2\overset{+}{\dot{O}}H + NO \longrightarrow RCH\overset{+}{O}H + HNO$$

$$\downarrow$$

$$RCHO + H^+$$

Scheme 3.

$$RCH_2OH + NO^+ \rightleftharpoons RCH_2\overset{+}{\dot{O}}H + NO$$

$$NO + HNO_3 \rightleftharpoons NO_2 + HNO_2$$

$$RCH_2\overset{+}{\dot{O}}H + NO_2 \longrightarrow RCH\overset{+}{O}H + HNO_2$$

$$\downarrow$$

$$RCHO + H^+$$

Scheme 4.

Table 4. Peak height ratios[a] in the mass spectra of benzaldehyde, [α-^{2}H]benzaldehyde, and the product of oxidation of [α-^{2}H]benzyl alcohol by an excess of nitrous acid in 39.8% H_2SO_4

			Product from [α-^{2}H]benzyl alcohol			
				Calculated for a p.h.i.e.[b] of		
m/*z*	C_6H_5CHO	$C_6H_5C(^2H)O$	Observed	3	2.5	2
107	8	105	75	81	77	72
106	106	8	34	33	36	41
105	(100)	(100)	(100)	(100)	(100)	(100)

[a] Peak heights are relative in each case to the peak with *m*/*z* = 105. [b] Product hydrogen isotope effect; see text.

solvolysis of 1-aryl-1-methylethyl chlorides for which $r = 1$ by definition,[18] there is an alternative important resonance structure in which the oxygen bears the positive charge).

The observed value of r is 0.4, which accords well with these considerations. The fact that the ρ value (-1.70) is numerically less than that observed in 1-aryl-1-methylethyl chloride solvolysis (-4.54)[18] can be explained in a similar way.

The hydride transfer can be considered (as can any hydride transfer) to take place either in one step as shown in Scheme 1 or by pre-equilibrium electron transfer, followed by rate-determining hydrogen-atom abstraction (Scheme 3). This mechanism is equally in accord with the observations, because the transition state is again close to the carbocation in Scheme 2. The mechanism of Scheme 3 suggests an explanation for the close similarity of substituent effects in the present reaction and in the oxidation of benzyl alcohols by nitric acid,[8,9] because in the presence of an excess of nitric acid nitric oxide is reversibly oxidised to nitrogen dioxide.[19] The rate-determining step could then be hydrogen-atom abstraction by nitrogen dioxide (Scheme 4). With the last step rate-determining, the reaction would be zero order in nitrous acid but the presence of nitrous acid would be necessary for reaction to proceed, as was observed.[8,9]

We could find no evidence for the involvement of nitric acid under our conditions, in agreement with previous work.[11] The very modest increase in rate constant in the presence of up to 0.2 mol dm^{-3} nitric acid (Table 1) can be accounted for by the increased acidity arising from the dissociation of nitric acid.[20] The mechanism of Scheme 3 remains a possibility however, and the question of whether the hydride transfer takes place in one step or two remains unresolved.

Experimental

Materials.—Sodium nitrite and sulphuric acid (98%) were AnalaR reagents. Dichloromethane was h.p.l.c. grade reagent. *p*-Methoxybenzyl alcohol, *m*-methylbenzyl alcohol, benzyl alcohol, *p*-fluorobenzyl alcohol, *m*-fluorobenzyl alcohol, *m*-bromobenzyl alcohol, *p*-methoxybenzaldehyde, benzaldehyde, and acetonitrile were distilled before use. *p*-Methylbenzyl alcohol, 1,2,3-trichlorobenzene and 1,2-dichloro-4-nitrobenzene were purified by recrystallisation. Benzyl methyl ether was purified by passage through an activated alumina column.

[α-^{2}H]Benzyl alcohol, [α,α-$^2H_2$]benzyl alcohol and *p*-methoxy[α,α-$^2H_2$]benzyl alcohol were prepared by reduction with lithium aluminium deuteride of benzaldehyde, benzoic acid, and *p*-methoxybenzoic acid, respectively. The deuteriated compounds were purified by distillation. The dueterium incorporation was shown by n.m.r. and mass spectroscopic measurements to be >99%.

Concentrations of aqueous sulphuric acid were determined by measurements of density.

Kinetics.—For oxidations with an excess of nitrous acid, known quantities of solutions of substituted benzyl alcohol or benzyl methyl ether in acetonitrile (typically 100 µl; 0.02 mol dm^{-3}) and aqueous sodium nitrite (always added last) were transferred by syringe into aqueous sulphuric acid (25.0 cm^3) thermostatically maintained at 25.0 °C. The stoicheiometric concentration of nitrous acid was arranged always to be in at least twenty-fold excess over the concentration of alcohol or ether. A u.v. cell was rinsed and filled with the solution and placed in the thermostatically controlled cell compartment (25.0 ± 0.1 °C) of a Pye-Unicam SP1800 or Perkin-Elmer Lambda 5 spectrophotometer. Absorbance–time measurements were taken directly by a microcomputer. First-order rate coefficents were computed from measurements over 3—6 half-lives by a non-linear least-squares method.

For oxidation with an excess of benzyl alcohol in the absence of oxygen, a solution of benzyl alcohol in acetonitrile (typically 100 µl; 0.4 mol dm^{-3}) was added to aqueous sulphuric acid (25.0 cm^3) in a vessel to which a u.v. cell was attached. Aqueous sodium nitrite solution was transferred by syringe into the U-shaped side arm of the same vessel. The stoicheiometric concentration of nitrous acid was less than one-tenth of the concentration of the alcohol. The solutions were degassed by three cycles of freezing (78 K) the solutions, outgassing ($\leqslant$0.01 mmHg) the vessel, and thawing. The solutions were allowed to equilibrate at 25 °C and mixed, and the resulting reaction mixture was passed into the u.v. cell which was sealed using a tap, detached from the vessel, and placed in the thermostatically controlled cell compartment of a Perkin-Elmer Lambda 5 spectrophotometer. First-order rate coefficients were obtained as already described.

Products.—For the oxidation of benzyl alcohol or *p*-methoxybenzyl alcohol with an excess of nitrous acid, the reaction solution was prepared in the same way as for kinetic studies with an excess of nitrous acid, and the reaction was allowed to continue for at least eight half-lives. The reaction mixture was quenched in cold water, a reference standard was added as a solution in dichloromethane, and the mixture was extracted with dichloromethane (1 × 30 cm^3; 7 × 10 cm^3). The combined extracts were dried ($MgSO_4$), and most of the dichloromethane was removed by careful fractional distillation to leave a concentrated solution (*ca.* 2 cm^3) of products.

Products from the oxidation of benzyl alcohol were analysed with a Pye-Unicam PU 4 500 gas chromatograph [flame-ionisation detector; 102 °C; 2 m PEGA (5%) on Chromosorb W (AN 80—100 mesh); N_2 at 40 cm^3 min^{-1}]. The reference standard used was 1,2,3-trichlorobenzene. Retention times of benzaldehyde, benzyl alcohol, and the reference standard were 330, 1 400, and 680 s, respectively.

Products from the oxidation of *p*-methoxybenzyl alcohol were analysed with a Pye-Unicam G.C.D. gas chromatograph [flame-ionisation detector; 144 °C; 2 m PEGA (5%) on Chromosorb W (AN 80—100 mesh); N_2 at 40 cm^3 min^{-1}]. The reference standard used was 1,2-dichloro-4-nitrobenzene. Retention times of *p*-methoxybenzaldehyde, *p*-methoxybenzyl alcohol, and the reference standard were 360, 830, and 460 s, respectively.

In determining the products of the oxidation of [α,α-$^2H_2$]benzyl alcohol with an excess of nitrous acid (product isotope effect), the experimental procedure was essentially the same except that no reference standard was used and the products were analysed by g.l.c.–mass spectroscopy [V.G. Micromass 16F instrument fitted with a 2 m PEGA (5%) column and S.G.E. splitless injection system].

In order to determine the products of the oxidation of benzyl alcohol with an excess of alcohol, a solution of benzyl alcohol in acetonitrile (100 μl; 0.4 mol dm^{-3}) was added to aqueous sulphuric acid (25.0 cm^3; 45.4%). The solution was thermostatically maintained at 25 (±0.1) °C. Aqueous sodium nitrite (100 μl; 0.02 mol dm^{-3}) was added and reaction was allowed to proceed for 70 min. Quenching of the reaction and analysis of products was carried out as already described.

(1) *Products in absence of oxygen.* The reactant solutions were degassed as already described prior to mixing of reactants.

(2) *Products in unmodified conditions.* Reaction was allowed to proceed under normal atmospheric conditions.

(3) *Products in oxygen-enriched aqueous sulphuric acid.* Oxygen was bubbled through the aqueous sulphuric acid for 90 min prior to the addition of the reactants. The reaction was allowed to proceed under oxygen at a pressure of 1 atm.

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