

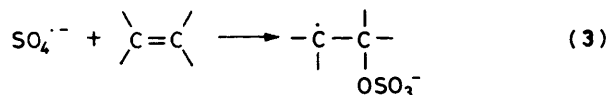
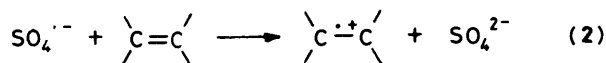
The Role of Copper(II) Salts in the Oxidation of Aryl-substituted Alkenes by Peroxydisulphate Anion

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The effect of copper(II) ions on the oxidation, in acetic acid, of aryl-substituted alkenes by peroxydisulphate anion has been investigated. In the presence of the metal ions an electron-transfer process operates akin to that identified in the oxidation of alkenes by other one-electron oxidants. It is suggested that the electron-transfer agent is copper(III) and that the resultant alkene radical-cation is converted into hydroxy acetates in good yield. $S_2O_8^{2-}$ alone decomposes more slowly to $SO_4^{\cdot-}$ which undergoes radical addition to the alkene leading ultimately to diacetates. The presence of sodium acetate in the system reduces considerably the conversion of alkene as a result, it is suggested, of competitive oxidation of the acetate anion.

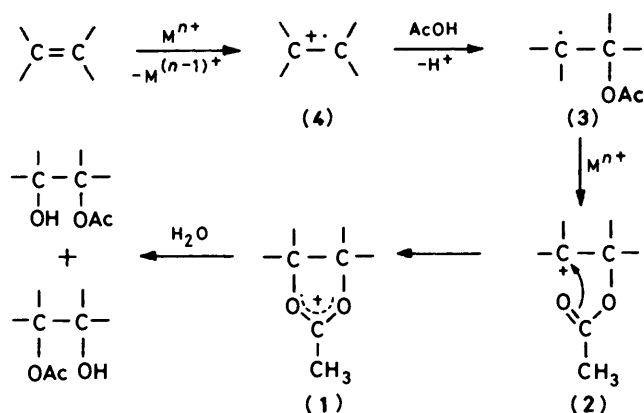
Recent work has demonstrated that peroxydisulphate anion will, in the presence of transition-metal salts as catalysts, oxidise alkenes readily.¹⁻³ When acetic acid is employed as the solvent a single major product can be obtained,^{1,2} but in aqueous media complex mixtures may result.^{1,3} The generally accepted mechanism of such oxidations¹⁻⁴ is that the transition-metal salt accelerates the decomposition of the peroxydisulphate anion and that the resultant radical anion then effects electron-transfer on the alkene [equations (1) and (2)].



However, e.s.r. spectroscopic studies in which the sulphate radical anion is generated from $S_2O_8^{2-}$, either photochemically or by reaction with titanium(III), have failed to provide any evidence for the direct formation of an alkene radical-cation.^{5,6} Instead, the observations are consistent with the radical anion adding to the alkene in the manner expected of a simple radical [equation (3)]. In this paper we present evidence which goes some way to resolving this contradiction between results obtained from product studies and those derived from spectroscopic observations.

Results and Discussions

In a recent paper we demonstrated that a number of one-electron metal oxidants were capable of effecting electron transfer from an alkene and thus generating the alkene radical-cation.⁷ In acetic acid the typical reaction of these species, at least when formed from aryl-substituted alkenes, is nucleophilic attack by the carboxylic acid solvent leading, ultimately, to a mixture of hydroxy acetates (Scheme 1). The good yields of these adducts in acetic acid which contains only adventitious water⁷⁻⁹ (typically no more than 1 mol %) is attributable to the high reactivity of the C-2 position in the acetoxonium ion (1) towards ring cleavage by water.^{10,11} Other nucleophiles react more slowly and effect ring opening *via* substitution at C-3 or C-4. The formation of hydroxy acetates under these conditions



Scheme 1.

is therefore convincing evidence for the intermediacy of (1) and for the formation of its precursor, the acetoxy-substituted carbonium ion (2) (or an incipient version of this ion). We believe further that, since acetoxy radicals have far too short a lifetime¹² for their effective trapping by an alkene to give the substituted radical (3) directly, the presence of hydroxy acetates in the products of reaction of one-electron oxidants with alkenes in acetic acid is good evidence for the generation of the radical-cation (4).

Unfortunately this test cannot be applied to the work described in the three principal papers on the reactions of alkenes with $S_2O_8^{2-}$ in acetic acid. In two cases^{1,3} significant quantities of water were employed as co-solvent, presumably in order to increase the solubility of the peroxydisulphate salt. Any hydroxy acetates formed under these conditions might result from direct nucleophilic attack by water on the carbon atoms of the double bond after these have been rendered electron-deficient by the oxidant or from partial hydrolysis of a diacetate during the course of the reaction. Even so, in few of the alkene oxidations reported in these papers have hydroxy acetates appeared amongst the products. Stilbene gives such a compound in substantial yield whilst styrene produces a limited amount.³ Cyclohexene too can give significant quantities of hydroxy acetate but only in the absence of copper(II) salts and when large quantities of water ($H_2O-AcOH > 1:1$) are present.¹ When the metal ions are added, allylic oxidation is the major reaction route. In the third investigation,² acetic anhydride was included in the system in order to ensure that conditions were anhydrous.

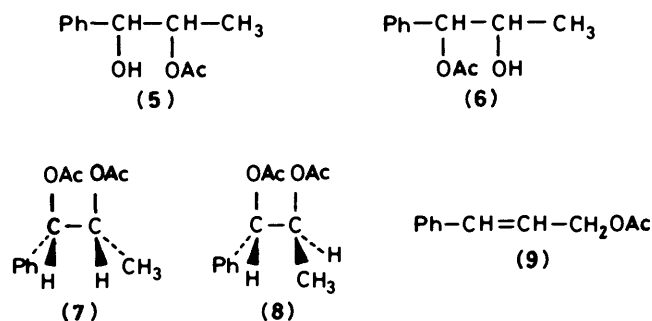
Table 1. Products from the oxidation of 1-phenylpropene by potassium peroxydisulphate in acetic acid at reflux temperature (reaction time 4 h)

Experiment	Oxidant	Products (%)						
		PhCH=CHMe	(5) + (6)	(7)	(8)	(9) ^a	PhCH ₂ COMe + PhCOCH ₂ Me	PhCHO
1	Cu ^{II} + S ₂ O ₈ ²⁻	10	56	9.0	5.6	4.4	1.4	5.0
2	S ₂ O ₈ ²⁻	24	1.6	32	11		7.1	7.0
3	Cu ^{III} biuret complex	26	5.5	4.4	4.0			3.5
4	Cu ^{II} + S ₂ O ₈ ²⁻ + biuret	35	21	6.5	4.3	2.0	<1.0	4.7
5	Cu ^{II} + S ₂ O ₈ ²⁻ ^b	8.0	54	4.3	4.6	1.0	8.8	6.3
6	Cu ^{II} + S ₂ O ₈ ²⁻ ^c	33	36	4.7	2.4	2.8	<1.0	4.4
7	S ₂ O ₈ ²⁻ ^c	75	1.2	<1.0	<1.0		<1.0	5.2

^a Incomplete resolution from compound (7) on g.c.; yields quoted are approximate. ^b Walling's conditions used (ref. 3): acetic acid (5 parts) containing water (1 part) as solvent; (NH₄)₂S₂O₈ as oxidant. ^c 0.25 Equiv. of sodium acetate added.

In the present study we employed glacial acetic acid as the solvent and 1-phenylpropene as the alkene. This substrate was chosen for several reasons. Its ionisation potential is sufficiently low for radical-cations to be generated readily should electron-transfer be a significant mode of reaction under the conditions used; there is the possibility for allylic substitution should this process be favoured relative to reaction at the double bond; and, finally, as this alkene has been the subject of earlier investigations most of the expected products were available to us.^{7,10} Experiments demonstrated that, when the acetic acid was refluxed alone in the apparatus for a short period, the chemical shift of the hydroxyl proton changed from δ 11.70 to δ 11.42, implying the absorption of ca. 3 mmol of water, enough to give some 60% conversion of an alkene to hydroxy acetates should the species (1) be formed.

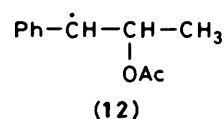
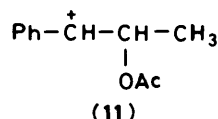
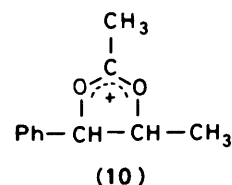
The results from a series of oxidations of 1-phenylpropene with S₂O₈²⁻ in acetic acid are set out in Table 1. When copper(II) acetate was included in the system the maximum conversion was achieved in 4 h and, besides some unchanged alkene, six major products were formed: the hydroxy acetates (5) and (6)*, the diacetates (7) and (8), benzaldehyde, and cinnamyl acetate (9). The production of compounds (5) and (6) in more than 50% yield when so little water is present can only mean that acetoxonium ions have been formed in the system and, as we argued earlier, that alkene radical-cations have been generated. It is likely that most, if not all, the diacetates produced in this reaction are formed through esterification of (5) and (6).



* Each hydroxy acetate presumably is present as a pair of diastereoisomers. A single peak corresponding to hydroxy acetate was obtained by g.c. and the yields of the individual components have not been established. Experience with closely related systems^{10,13} has shown that such regioisomers are in rapid dynamic equilibrium, presumably *via* the acetoxonium ion.

Doubling the reaction time resulted in a much increased yield of (7) and (8) with a corresponding reduction in that of the hydroxy acetates.

In contrast, when the copper(II) salt was omitted, other conditions being maintained constant, only a small quantity of the hydroxy acetates was produced. A substantial amount of alkene remained unconverted, confirming that the presence of copper(II) does indeed accelerate the process, and larger amounts of benzaldehyde were formed. Most significantly, from the point of view of this study, considerable quantities of diacetates were found amongst the products. The formation of substantial yields of hydroxy acetates in the reactions of alkenes with the anhydrous oxidants lead(IV) acetate¹⁰ and cobalt(III) acetate⁷⁻⁹ under similar conditions, coupled with the results of the n.m.r. experiment described above, confirm that sufficient water should be present to hydrolyse any acetoxonium ion (10) to (5) and (6). Since a check showed that the rate of esterification of (5) and (6) is not affected by copper(II) ions, we conclude that the intermediate (10) and hence the carbonium ion (11) are not



formed to a significant extent from peroxydisulphate alone.

It has been argued² that the difference between reactions of S₂O₈²⁻ in the presence and the absence of copper(II) salts stems from the metal ions oxidising simple carbon-centred radicals, whereas peroxydisulphate anion is unable to bring about such transformations. We can find no experimental evidence for this last claim. Indeed, data from spectroscopic studies suggest that S₂O₈²⁻ can oxidise radicals as unactivated as CH₃,¹⁴ let alone the benzylic radicals which might be formed in the reactions of 1-phenylpropene. It would thus seem unlikely that the radical (12) is present in the system and, given the ready nucleophilic attack by acetic acid on a radical-cation,⁷ that peroxydisulphate, by itself, can generate this species from 1-phenylpropene.

Since copper(II) acetate alone is unable to oxidise 1-

phenylpropene some other intermediate must be formed in the $\text{Cu(II)}\text{-S}_2\text{O}_8^{2-}$ system which is capable of effecting electron transfer. The most likely candidate is a copper(III) species. This oxidation state of copper is normally difficult to isolate but it can be stabilised by a range of ligands, *e.g.* peptides, periodate, and biuret.^{15,16} Indeed, complexes with this last ligand have been shown to oxidise a variety of organic substrates to give products which could be derived from radical-cations, though yields tend to be low.¹⁷ Amongst these substrates was cyclohexene which gave, under conditions very similar to those employed in peroxydisulphate oxidations, cyclohexenyl acetate, the same product as obtained with this last reagent in the presence of copper(II).¹

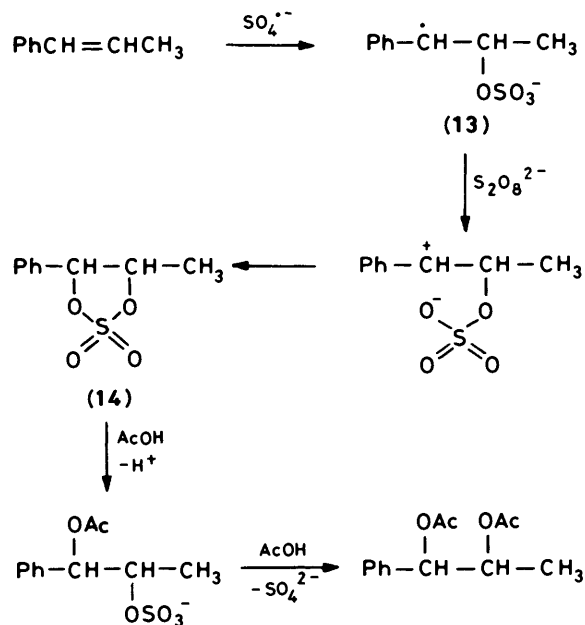
We accordingly attempted to oxidise 1-phenylpropene with copper(III)-bisbiuret complex. Reaction in acetic acid was virtually non-existent but the addition of a small amount of trifluoroacetic acid¹⁷ did lead to reaction (experiment 3), the same products being formed in low yield as result from $\text{Cu}^{\text{II}}\text{-S}_2\text{O}_8^{2-}$ oxidations. As expected of an electron-transfer process under these conditions, hydroxy acetates are the major product. The low overall yield appears to be associated with the presence of the biuret ligand since the addition of biuret to a copper(II)-peroxydisulphate oxidation leads to a very substantial reduction in the conversion of 1-phenylpropene (experiment 4). Copper(III) then must join the growing list of one-electron oxidants capable of effecting electron transfer from alkenes of sufficiently low ionisation potential.

The question remains as to the means by which $\text{S}_2\text{O}_8^{2-}$ itself, or more likely $\text{SO}_4^{\cdot-}$ derived from this anion, brings about oxidation of 1-phenylpropene if it is not by electron transfer. Studies employing *e.s.r.* spectroscopy suggest that, at least with simple alkenes, the preferred mode of reaction is by addition of $\text{SO}_4^{\cdot-}$ to a double bond,^{5,18} a high degree of regioselectivity being observed in the reaction. In some instances radicals apparently derived from alkene radical-cations are found, but only when the substrate possesses substituents capable of stabilising strongly an electron-deficient carbon centre.^{5,19} Even in these circumstances it is possible that the radical-cation is not formed by direct electron-transfer but results instead from decomposition of an initial adduct.

Given the low concentrations of radicals which can be detected by the technique, caution needs to be employed when extending *e.s.r.* results to those derived from product studies. Nevertheless the proven ability of $\text{SO}_4^{\cdot-}$ to form radical adducts with alkenes does suggest a means by which diacetates, but not hydroxy acetates, might be formed when copper(II) is absent from the system (Scheme 2). Oxidation of the adduct radical (13) could lead to a cyclic sulphate ester (14), solvolysis of which provides a route to diacetates without the need to invoke an intermediate acetoxonium ion. Such 1,3,2-dioxathiolane dioxides are particularly susceptible to nucleophilic ring opening in an $\text{S}_{\text{N}}2$ manner.²⁰

A significant product of oxidation of 1-phenylpropene both with and without added copper(II) is benzaldehyde. A ready explanation for the formation of this compound is available for those cases in which compounds (5) and (6) are formed. The reaction of alcohols with $\text{SO}_4^{\cdot-}$ results in the production of carbonyl compounds, often with cleavage of a carbon-carbon bond.²¹ For instance, substantial yields of benzaldehyde are obtained on oxidation of 1-phenylethanol and 2-methyl-1-phenylpropan-1-ol: the alcohol (5) would be expected to behave in a similar manner. However in the absence of any significant quantity of hydroxy acetate there is no obvious route by which benzaldehyde can be produced unless it be *via* further reaction of the dioxathiolane (14).

Cinnamyl acetate (9) is obtained when copper(II) is included in the system, though not in its absence. This corroborates the earlier report¹ that the inclusion of the metal ion encourages



Scheme 2.

allylic acetoxylation. However the results in Table 1 suggest that, in contrast to the reaction with simple alkenes, this process is not the predominant one with 1-phenylpropene.

The results we have obtained are not notably at variance with those reported by Citterio *et al.*² given that those workers included acetic anhydride in the solvent. However, they do differ so markedly from those cited by Walling *et al.*,³ using only slightly different conditions, that we repeated that reaction. We obtained (experiment 5) a product distribution very similar to that in experiment 1. A *g.c.* peak with a retention time corresponding to benzyl methyl ketone, the major product reported by Walling, was shown by mass spectrometry to be a composite of that compound (ions of *m/z* 92, 91, and 65) and propiophenone (ions of *m/z* 105 and 77). The combined yield of the two compounds was less than 10%.

One notable feature of Table 1 is the effect of sodium acetate upon the reaction. Both with and without copper(II) ions present the addition of this salt in less than equivalent quantity reduces considerably the extent of conversion of the alkene (compare experiment 6 with experiment 1 and experiment 7 with experiment 2). A carboxylate anion is oxidised by $\text{SO}_4^{\cdot-}$ much more rapidly than is the corresponding acid.²² The lower yields of products may well, therefore, reflect the ability of acetate anion to compete with an alkene for peroxydisulphate anion. This would be particularly true of reactions not involving copper(II) salts, since these are significantly slower. In a number of studies alkali-metal acetates have been added in substantial quantities to peroxydisulphate oxidation systems.¹⁻³ They certainly speed up the rate of decomposition of the oxidant but their presence could well prove deleterious to the oxidation of the substrate under investigation.

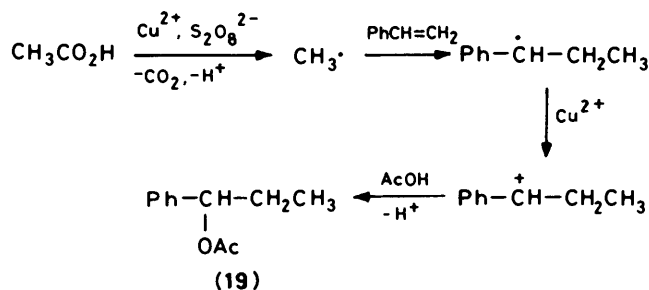
A similar sensitivity to the presence of copper(II) acetate is shown in the oxidation of styrene (Table 2). With the metal salt added, conversion to the hydroxy acetates (15) and (16) results but, with the copper(II) absent, a mediocre yield of diacetate (17) is obtained and no hydroxy acetate could be detected. Of the other compounds identified, benzaldehyde and phenylacetaldehyde mirror analogous materials obtained from 1-phenylpropene, whilst 1-phenylethyl acetate (18) presumably results from addition of acetic acid to the alkene, the greater yield in experiment 7 reflecting the substantially slower oxidation in the

Table 2. Products from the oxidation of styrene by potassium peroxydisulphate in acetic acid at reflux temperature (reaction time 4 h)

Experiment	Oxidant	Products (%)							
		PhCH=CH ₂	(15) + (16)	(17)	(18)	(19)	PhCHO	PhCH ₂ CHO	Dimeric products
8	Cu ^{II} + S ₂ O ₈ ²⁻	29	35	13	0.2	0.5	2.0	trace	ca. 8
9	S ₂ O ₈ ²⁻	12		16	8.4		0.7	2.6	ca. 3
10	Cu ^{II} + S ₂ O ₈ ^{2-a}	1.3	25	1.8			4.2		

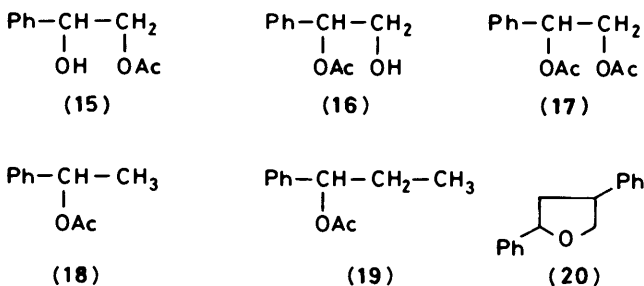
^a Walling's conditions used (ref. 3): acetic acid (5 parts) containing water (1 part) as solvent; (NH₄)₂S₂O₈ as oxidant.

absence of copper(II). Of some note, despite the small yield, is the presence in experiment 6 of compound (19). The most likely route by which this could arise is *via* the trapping by the alkene of methyl radicals (Scheme 3) [*c.f.* the oxidation of aryl-



Scheme 3.

substituted alkenes by lead(IV)^{10,23}] implying that the presence of these radicals cannot be excluded from copper(II)-peroxydisulphate oxidations. They might be involved in allylic acetoxylation. Once again (experiment 10), using Walling's conditions, we were unable to obtain his product distribution.³



In two experiments employing styrene as the substrate, several products with long retention times on gas chromatography were also observed. Whilst these were not identified unambiguously, g.c.—m.s. suggested them to involve the combination of two molecules of styrene. One was a hydrocarbon of composition C₁₆H₁₄ and may be 1,3-diphenylbutadiene (intense ions of *m/z* 206, 204, 203, and 202 together with doubly-charged ions of *m/z* 102, 101.5, and 101). But the principal dimeric product contained oxygen. Major ions of *m/z* 224, 194, and 193 would be compatible with the structure (20) and the ¹H n.m.r. spectrum of a sample isolated by preparative g.c. is consistent with its being a mixture of the two diastereoisomers of this formula. The likelihood, given the high temperatures employed and the relatively long reaction times, is that these dimeric products result from thermal dimerisation. Certainly polymeric material was also present. However, the possibility is not excluded that they could stem from attack on a

second molecule of styrene by an electron-deficient intermediate generated from that alkene in the normal course of oxidation.

Experimental

The analytical procedures employed in this study and most of the authentic materials have been described previously.^{7,10,23} Styrene and (*E*)-1-phenylpropene (Aldrich) were commercial samples redistilled under reduced pressure before use.

Copper(III)-Biuret Complex.—Biuret (2.2 g), copper(II) sulphate pentahydrate (2.5 g), and potassium hydroxide (3.0 g) were dissolved in water (25 cm³). Potassium peroxydisulphate (2.7 g) was added to the solution until no more precipitate formed, the solid was filtered off, washed with warm water, and dried *in vacuo* (2.7 g, 87%). The i.r. spectrum of the solid showed absorptions typical of potassium bis(biuretato)cuprate(III) at 1 695 and 1 590 cm⁻¹.¹⁶

Oxidations with S₂O₈²⁻.—A typical oxidation was carried out as follows: 1-Phenylpropene (1.2 g), potassium peroxydisulphate (2.7 g), and copper(II) acetate monohydrate (2.0 g) were heated together in acetic acid (20 cm³) at reflux temperature for 4 h. The mixture was cooled, filtered, the precipitate washed twice with a little acetic acid, and the combined filtrate poured into water (*ca.* 100 cm³). The aqueous mixture was extracted with ether and the combined extracts washed with sodium carbonate solution and water and then dried (MgSO₄). After removal of the solvent the residue was analysed by combined g.c.—mass spectrometry, the products being identified by comparison of their spectra and retention times with those of authentic compounds. In the oxidations employing styrene, dimeric products were present and were separated by gas chromatography: two of these were tentatively identified as 1,3-diphenylbuta-1,3-diene and 2,4-diphenyltetrahydrofuran from their mass spectra: *m/z* 206 (36%, M⁺⁺), 204 (100, M - H₂), 203 (69, M - H₂ - H), 202 (57, M - 2H₂), 102 [11, (M - H₂)²⁺], 101.5 [9, (M - H₂ - H)²⁺], 101 [34, (M - 2H₂)²⁺], and 91 (21, C₇H₇⁺); and *m/z* 224 (59%, M⁺), 194 (100, M - CH₂O), 193 (66, M - CH₂O - H), 179 (30, M - CH₂O - Me), 133 (37, M - PhCH₂·), 117 (61, C₉H₉⁺), 105 (52, C₈H₉⁺), and 91 (39, C₇H₇⁺), respectively.

Oxidation with Copper(III)-Biuret Complex.—A mixture of 1-phenylpropene (0.6 g) and potassium bis(biuretato)cuprate(III) (1.93 g) in acetic acid (10 cm³) containing trifluoroacetic acid (3 cm³) were heated together at reflux temperature for 4 h. The reaction system was worked up and analysed as above.

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