association reaction (eq 11) is apparently the reason for

$$2MV^{+}\cdot \rightleftarrows (MV)_2^{2+} \qquad (11)$$

the absorbance shift, and it appears that $(MV)_2^{2+}$ reacts more rapidly with H_2O_2 than does the monomeric $MV^{+}\cdot$. Unfortunately, further study of this fast rate must await resolution of another problem with solutions having higher radical concentrations.

(2) When the concentrations of $MV^{+}\cdot$ and of added salt are raised, insoluble dark-colored materials were formed in most reactions. Precipitation is often very slow, and the darkness of these concentrated solutions so obscures the process of deposition that one may be unaware of the presence of a suspended solid. This can, of course, seriously interfere with rate measurements at high concentrations. We plan to investigate the nature of these interesting solids.

Many bipyridylium salts are efficient herbicides. The formation of radical cations, persistent and stable in the absence of air, is a prerequisite for this activity. In addition, the parent cations must have a reduction potential comparable to those electron acceptors natural to the photosynthetic assembly plus a certain size and shape.[26-28]

The rate constants obtained in aqueous solution are not necessarily the same as those which may obtain in chloroplast assemblies. We have found that the rate constant for H_2O_2 and $MV^{+}\cdot$ is significantly lower in pure methanol than in water or aqueous methanol, and the reaction of O_2 with $MV^{+}\cdot$ has a solvent-dependent rate.[10] Further the reaction of MV^{2+} with a solvated electron has a rate which changes with micelle concentration in an aqueous solution containing sodium dodecyl sulfate.[29] It seems certain that extrapolating rates from aqueous in vitro studies to real photosynthetic systems is not a reliable procedure.

Nevertheless, the fact that H_2O_2 reacts with $MV^{+}\cdot$ and $DQ^{+}\cdot$ by eight powers of ten more slowly than O_2 and $O_2^{-}\cdot$ react suggests that a buildup of hydrogen peroxide is an important possibility in chloroplasts containing the herbicidal dications under light, particularly since the catalase in plant cells is believed to be located at sites spacially separated from the chloroplast stack.[30] Thus H_2O_2 may indeed be able to oxidize plant tissue and thereby cause plant death.

Finally, the rate of reaction of H_2O_2 and $MV^{+}\cdot$ is sufficiently slow so that deviations from the usual 4:1 stoichiometry for $MV^{+}\cdot/O_2$ in the oxygen analysis techniques are to be expected under some conditions.

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Registry No. $MV^{+}\cdot$, 25239-55-8; $DQ^{+}\cdot$, 59079-66-2; H_2O_2, 7722-84-1; $H_2P_2O_8^{2-}$, 20824-76-4; $HP_2O_8^{3-}$, 56795-74-5; $P_2O_8^{4-}$, 15538-83-7.

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Photooxidation of Alcohols by Ferric Ion

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Near-UV photolysis (through Pyrex) of 0.15 M solutions of $Fe(ClO_4)_3$ in a series of primary alcohols, RCH_2OH, leads to a variety of products, RCHO, CH_2O, RH, RR, RCH_2OR, alkenes, and tetrahydrofurans. Both the products and the variation in their distribution with structure are consistent with the initial production of alkoxy radicals from the alcohols. Photolysis rates parallel the importance of a charge-transfer band in the near UV, implying that it is involved in the primary photochemical process.

The photooxidation of organic substrates by aqueous ferric ion with concomitant reduction of the iron has been studied intermittently for over 30 years.[1] For uncomplexed Fe^{3+}, data are consistent with the formation of hydroxyl radicals, e.g., eq 1, and their subsequent reactions.

$$Fe^{3+}\,(H_2O) \overset{h\nu}{\rightleftharpoons} Fe^{2+} + H^{+} + \cdot OH \qquad (1)$$

In the absence of organic substrates O_2 is evolved, but quantum yields are very low due to the reversibility of eq 1. In the presence of organic substrates, hydroxyl radicals are scavanged, and primary quantum yields of the order of 0.065 have been reported.[2] The oxidation products reported for such photooxidations are typical of hydroxyl radical reactions. Aromatics undergo ring hydroxylation or side-chain oxidation, and alcohols are oxidized to carbonyl compounds.[3] In cases where the substrate complexes with Fe^{3+}, photooxidation may occur at longer wavelengths, and it appears that the photoexcited state

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Table I. Product Yields (%) from Fe^{3+}-Alcohol Photooxidations

alcohol	system[a]	RCHO	THF	CH_2O	total %	other[b]
1-propanol	A	78.3 ± 3.1		9.05 ± 0.75	87.0 ± 2.8	RH, RR, ethylene
	B	59.0		7.7	73.3	ether, 13.2
1-butanol	A	79.2 ± 1.9	0.6 ± 0.3	8.8 ± 0.9	89.6 ± 2.6	RH, 7.3 ± 1.6; RR, tr; propylene, tr
	B	52.5 ± 0.8	1.0	9.1 ± 1.7	68.3 ± 1.7	ether, 12.9 ± 1.3
1-pentanol	A	71.2 ± 5.7	5.4 ± 0.3	8.3 ± 1.1	84.9 ± 4.5	RH, 7.1 ± 0.3; RR, tr; propane, tr
	B	38.7 ± 8.6	3.4 ± 0.4	9.3 ± 1.9	60.2 ± 10.2	ether, 17.7 ± 0.3; RH, tr; butene, tr
4-methyl-1-pentanol	A	50.6 ± 0.6	17.1 ± 1.2	11.8 ± 0.6	79.5 ± 1.9	RH, 1.9 ± 0.5
	B	22.2	17.9	11.1	60.1	ether, 17.7
4-phenyl-1-butanol	A	*c*	28.9 ± 1.3	11.4		RH, 10.9 ± 2.3 (allylbenzene, indan, 0)
	B	*c*	30.7	12.1		ether, 24.9; RH, 1.4; allylbenzene, 3.3
2-methyl-1-butanol	A	34.9 ± 7.1	~0	37.8 ± 1.1	79.6 ± 6.1	RH, 11; RR, 5.6; ether, 7.7; 1-butene, 3.0; 2-butenes, 3.3
	B	7.46	~0	29.3	41.7	1-butene, 7.7; 2-butenes, 2.7; ether, 0
2,2-dimethyl-1-butanol	A	8.9 ± 3.6		44.1 ± 0.5	85.4 ± 2.7	RH, 0.6 ± 0.6; ether, 60.3 ± 1.0; 2-methylbutenes

[a] A: 0.15 M $Fe(ClO_4)_3$. B: 0.015 M $Cu(ClO_4)_2 \cdot 6H_2O$ added. [b] R's correspond to R in RCH_2OH, ether = $ROCH_2R$, THF is the corresponding tetrahydrofuran. [c] Not determined because of GC instability of the corresponding acetal.

may collapse directly to Fe^{2+} and radical products derived from the substrate.[1]

Rather less is known about photolyses conducted in nonaqueous media. Neat alcohols undergo oxidation to the corresponding carbonyl compounds.[4] A plausible hypothesis here is that, by analogy to reaction 1, alkoxy radicals are generated in the primary photochemical reaction, and the best supporting evidence is Groves' observation that 2-cyclohexylethanol yields some perhydrobenzofuran (see below).[5] Measurements of ESR spectra obtained by irradiating frozen alcohol glasses containing Fe^{3+} sometimes indicate β-scission reactions typical of alkoxy radicals, both 2-butanol and 2-methyl-2-butanol giving ethyl radicals,[6] but other studies have given less clear-cut results.[7]

Because of our interest in metal ion and alkoxy radical reactions, we have investigated in detail the products obtained in the Fe^{3+} photooxidation of a series of primary alcohols, either neat or in acetonitrile solution. Although we observe complex mixtures of products, our results are consistent with the assumption that alkoxy radicals are indeed the primary photoproduct. They also provide new data on dark reactions between carbon radicals and Fe^{3+} and Cu^{2+} ions in alcoholic media.

Results

Photooxidations were carried out on solutions of $Fe(ClO_4)_3$ in neat alcohol or alcohol–acetonitrile mixtures in Pyrex vessels in the absence of O_2, using a Hanovia 450-W, lamp. Thus, reaction was due primarily to UV light above 300 nm. In contrast to aqueous solutions which are almost colorless, $Fe(ClO_4)_3$ solutions in alcohols are yellow to orange in color, the consequence of a visible tail to UV absorbance which rises rapidly at shorter wavelengths. In addition, solutions in primary straight-chain alcohols show a charge-transfer band at about 354 nm, essentially independent of chain length. As might be expected for an electron transfer from ligand to iron, this is shifted to shorter wavelengths by electron-withdrawing groups. Thus, for 2,2,2-trichloroethanol the peak is shifted to 345 nm, and for 2,2,2-trifluoroethanol it becomes a shoulder at 295–310 nm. Somewhat more surprisingly, secondary and tertiary alcohols show no charge transfer band and only a smoothly rising absorption. Chain branching on C-2 also affects spectra. With 2-methyl-1-butanol the band becomes merely a shoulder at about 260 nm. A plausible explanation of these differences (which must also apply to the halo alcohols) is steric crowding which increases the separation of the alcohol and iron in the complex, raising the energy required for the charge-transfer process and shifting it to shorter wavelengths[8] where it is largely obscured by other absorptions. In spite of these differences, visual appearance of all alcohol solutions are very similar, and UV absorption is strong enough that essentially all light was absorbed during most of the course of our experiments.

Table II. Photooxidation of 1-Pentanol by Fe^{3+} in Acetonitrile[a]

RCH_2OH:MeCN	RCHO	THF	CH_2O	total %
1:1	54.4	5.2	11.0	70.6
1:3	38.7	9.9	9.6	58.3
1:9	21.0	11.1	7.4	39.5
1:126	3.6	4.1	2.3	10.3

[a] Conditions as in A in Table I.

Although quantum yields were not determined, qualitative observations were consistent with the above and the assumption that absorption in the charge-transfer band is chiefly responsible for the photolyses. In straight-chain primary alcohols, Fe^{3+} was completely reduced in 6–12 h. In 2-methyl-1-butanol the reaction took about 72 h, and in 2,2-dimethyl-1-butanol, 130–160 h. Similarly, in secondary alcohols reduction was very slow, requiring several days, and no change in color at all was observed with tertiary alcohols in our system. Photooxidations were also

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(8) For a similar effect of steric hindrance on charge transfer spectra in alkylmetal–I_2 complexes, cf.: Fukuzumi, S.; Kochi, J. *J. Am. Chem. Soc.* **1980**, *102*, 2141–2152.

Table III. GC Columns, Internal Standards, and Products Analyzed

alcohol	column[a]	standard	products analyzed
1-propanol	10 ft A	benzene	RCHO, RCH_2OR
	6 ft B	3-methylcyclohexanone	H_2CO acetal, RCHO acetal
1-butanol	18 ft A	methyl acetate	RCH_2OR
		3-methylcyclohexanone	H_2CO acetal, RCHO acetal
	6 ft C	*n*-pentane	RH, RR
		methyl acetate	RCHO, THF
1-pentanol	10 ft A	benzene	RCHO, RCH_2OR, 2-methyl-THF, RR
		2,4-dichlorotoluene	H_2CO acetal, RCHO acetal
	6 ft C	*n*-pentane	RH
4-methyl-1-pentanol	10 ft A	benzene	RCHO, RCH_2OR, 2,2-dimethyl-THF, RH
		methyl benzoate	H_2CO acetal, RCHO acetal
4-phenyl-1-butanol	4 ft A	propiophenone	RCHO, 2-phenyl-THF, RH, alkane
	6 ft D	triptycene	H_2CO acetal, RCH_2OR
2-methyl-1-butanol	18 ft A	*n*-pentane	RH, alkenes, RR
		benzene	RCHO, RCH_2OR, 3-methyl-THF
	10 ft A	2,4-dichlorotoluene	H_2CO acetal, RCHO acetal
2,2-dimethyl-1-butanol	10 ft A	benzene	RCHO, RCH_2OR
		2,4-dichlorotoluene	H_2CO acetal, RCHO acetal

[a] A = 20% Carbowax 20M on Chromasorb W; B = 10% OV-17 on Chromasorb W; C = Porapak N; D = 10% apiezon L.

carried out in the presence of added $Cu(ClO_4)_2{\cdot}6H_2O$. Since Cu^{2+} solutions have little absorption in the near UV and Cu^{2+} had no effect on rate, it was assumed to play no role in the primary photooxidation.

Products of the photooxidations were complex and are listed in Tables I and II. In spite of this complexity, material balances, based on Fe^{3+}, were usually about 80%, indicating that most major products were accounted for. In every case, products fall in three groups: aldehydes corresponding to the alcohol employed (present in large part (50–90%) as the corresponding acetals—the strongly acid nature of our reactions leading to rapid equilibration between aldehyde the acetal), cleavage products consisting of formaldehyde (present as its formal), alkane, alkenes, and ether, RCH_2OR, and substituted tetrahydrofuran. The variation of product distribution with alcohol and reaction conditions is considered below.

Discussion

If the primary process in our photooxidations involves alkoxy radical formation, the above groups of products should be derived from the following reactions (eq 2–9) using *n*-pentanol as a convenient example ($R = n\text{-}C_4H_9$), all of which are well established in alkoxy radical chemistry.[9]

$$RCH_2OH{\cdot}Fe^{3+} \xrightarrow{h\nu} RCH_2O{\cdot} + H^+ + Fe^{2+} \quad (2)$$

$$RCH_2O{\cdot} + RCH_2OH \rightarrow RCH_2OH + R\dot{C}HOH \quad (3)$$

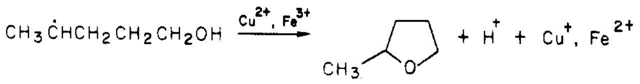
$$R\dot{C}HOH + Fe^{3+}\ (Cu^{2+}) \rightarrow RCHO + H^+ + Fe^{2+}\ (Cu^+) \quad (4)$$

$$RCH_2O{\cdot} \rightarrow R{\cdot} + H_2CO \quad (5)$$

$$R{\cdot} + RCH_2OH \rightarrow RH + R\dot{C}HOH \quad (6)$$

$$R{\cdot} + Cu^{2+}\ (Fe^{3+}) \rightarrow C_4H_8 + ROCH_2R + Cu^+\ (Fe^{2+}) \quad (7)$$

$$RCH_2O{\cdot} \rightarrow CH_3\dot{C}HCH_2CH_2CH_2OH \quad (8)$$



It should be noted that aldehyde is thus not produced from the alcohol originally oxidized, but by radical attack, reactions 3 and 6, on a second alcohol molecule.

Variations in product distribution are entirely consistent with this scheme. The yield of β-scission products increases as the introduction of methyl groups on the β-carbon increases the stability of the resulting radical, going from about 8% for straight chain alcohols to 44% for 2,2-dimethyl-1-butanol. Similarly, the importance of the intramolecular hydrogen-abstraction process (eq 8) increases as the strength of the C–H bond attacked is weakened in the order primary < secondary < tertiary < benzyl. The yields of tetrahydrofurans rise accordingly from about 1% to 30%.

The fate of the radical, R·, produced in the β-scission process (eq 5) is a bit more complicated. When R· is a primary radical, it is apparently quite inert to oxidation by Fe^{3+} and chiefly attacks another alcohol molecule via eq 6 to give alkane. Small amounts of dimer (e.g., *n*-octane from 1-pentanol) are also formed. If R· is secondary or tertiary, this process is presumably slower, and oxidation by Fe^{3+} becomes easier: less alkane and significant ether, $ROCH_2R$, plus olefin are produced. With the secondary 2-butyl radical slightly less than half of the radicals are oxidized. With the tertiary 2-methyl-2-butyl radical, oxidation is almost complete. In both cases, ether is the major oxidation product. Addition of Cu^{2+}, a more effective and less selective radical oxidant, quite changes this picture. Even with primary R·'s, alkane formation is largely eliminated and ether (together with some olefin) is produced. The portion of aldehyde formed via eq 6 and 4 is concomitantly reduced. The high ratio of ether to olefin formed from primary radicals is of some interest, since this sort of ratio in Cu^{2+} oxidations is known to be strongly solvent dependent. Oxidations in acetic acid or acetonitrile have been shown by Kochi to give chiefly olefin, but in more aqueous solvents alcohols are formed via attack of a nucleophilic water molecule on an intermediate organocopper species.[10] Apparently alcohols behave in the same way as water, suggesting that oxidation of primary radicals by Cu^{2+} may provide a useful ether synthesis in alcoholic media. In the case of the secondary 2-butyl radical from 2-methyl-1-butanol, oxidation by Cu^{2+} is also apparently complete since no alkane was detected, but olefins, rather than ether, are formed.

Table II shows the result of dilution of the Fe^{2+}–1-pentanol system with acetonitrile. Except at the highest dilution, yields of 2-methyltetrahydrofuran and CH_2O show little change, but RCHO yield drops steadily. This

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[9] For reviews of alkoxy radical chemistry, cf.: Walling, C., *Pure Appl. Chem.*, **1967**, *15*, 69–80; Kochi, J. *Free Radicals* **1973**, *2*, Chapter 23.

[10] Kochi, J. *Free Radicals* **1973**, *1*, Chapter 11.

would be expected from the competition between the first-order reactions 5 and 8 and the second-order reactions 3 and 6 and provides further evidence that aldehydes arise from attack on an intermediate radical on a second alcohol molecule. On the other hand, the total yield of all three products drops. Since Fe^{3+} solutions in acetonitrile alone undergo photoreduction at almost the same rates as in the presence of alcohol, it appears that an additional primary photoreaction is occurring involving the acetonitrile, although this was not investigated.

In summary we conclude that the photooxidation of primary alcohols by Fe^{3+} involves excitation of a charge-transfer band and dissociation to alkoxy radicals, which in turn lead to the observed products by a sequence of well-established reactions. It thus parallels closely the photolysis at shorter wavelengths of aquoferric ion in water to yield hydroxyl radicals. What happens in concentrated aqueous systems, where the two paths might compete, has not been investigated, but, in view of the longer wavelength absorption of the alcohol complexes, products might well be wavelength dependent. In this regard, Carey, Cosgrove, and Oliver[11] have concluded that in the Fe^{3+} photooxidation of fairly concentrated solutions of ethylene glycol (0.5–2 M), their results are consistent with two reaction paths. One involves HO· attack on the glycol giving $HOCH_2\dot{C}HOH$ radicals which then undergo acid-catalyzed rearrangement and reduction to acetaldehyde,[12] and the other involves photolysis of a Fe^{3+}· glycol species to generate the alkoxy radical followed by β-scission to yield, eventually, two molecules of formaldehyde.

Experimental Section

Materials. Alcohols and reference compounds for analyses were commercial materials or prepared by standard synthetic methods. All were carefully purified and characterized by IR or NMR spectroscopy. Alcohols were dried by distillation from Na or Mg–I$_2$ under N$_2$. In spite of rigorous purification, some contained traces of aldehyde, and this was corrected for in the subsequent product analysis, using controls prepared from the same alcohol sample and put through the same workup cycle without irradiation. Iron was in the form of anhydrous $Fe(ClO_4)_3$ (G. Frederick Smith Chemical Co., ferric perchlorates, reagent, nonyellow). When copper was added it was in the form of $Cu(ClO_4)_2 \cdot 6H_2O$.

Photolyses were carried out in Pyrex tubes immersed in a water bath at 16 or 21 °C, using a Hanovia 450-W medium-pressure mercury lamp in a quartz immersion well in the bath. Tubes were purged with argon for 30 min in the dark before irradiation. Reaction mixtures were in general 0.15 M in Fe and 0.015 M in Cu (when added). Photolyses were continued until solutions were colorless and tested for complete reduction of Fe^{3+} by testing an aliquot with aqueous ferrocyanide.

Workup and Analysis. When higher boiling components were to be analyzed, iron and copper were removed from reaction mixtures by passage through short alumina columns until the effluent gave negative tests with ferro- and ferricyanide. Low-boiling hydrocarbons were determined on separate samples in tubes sealed with serum caps. After photolyses these were chilled in dry ice, enough alumina was added to absorb metal ions, the tubes were recapped and warmed to room temperature, and samples for analysis were removed by means of a hypodermic syringe.

All analyses were by GC (gas chromatography), using internal standards with response factors calibrated against authentic reference compounds. Products from 1-pentanol, 2-methyl-1-butanol, and 2,2-dimethyl-1-butanol were identified by IR or NMR spectroscopy after isolation by preparative GC. Since all systems gave similar products, others were determined by retention time on one or more columns. Columns and internal standards that were found effective are summarized in Table III.

Yields are summarized in Tables I and II. Where experimental uncertainties are given, they represent the range of two or more independent experiments. In calculating yields, 2 mol of Fe was assumed to be consumed in the formation of RCHO and THF, and 1 mol in the formation of H$_2$CO, and total yield is taken as the sum of these. In cases where significant RCHO is formed via reactions 5 and 6, this gives a slightly high value.

Acknowledgment. Support of this work by a grant from the National Science Foundation and a fellowship to one of us (R.W.R.H.) from the National Research Council of Canada is gratefully acknowledged.

Registry No. 1-Propanol, 71-23-8; 1-butanol, 71-36-3; 1-pentanol, 71-41-0; 4-methyl-1-pentanol, 626-89-1; 4-phenyl-1-butanol, 3360-41-6; 2-methyl-1-butanol, 137-32-6; 2,2-dimethyl-1-butanol, 1185-33-7; Fe^{3+}, 20074-52-6.

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Comparison of the Activity and Lifetime of Raney Nickel and Nickel Boride in the Hydrogenation of Various Functional Groups

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Nickel borides (Ni$_2$B) are prepared by the reduction of a nickel salt with sodium borohydride. These materials have been shown to be active hydrogenation catalysts. The activity and lifetime of a P-1.50 nickel boride catalyst, which is prepared in a 50% water/ethanol solvent, are reported for the hydrogenation of unsaturated carbon and nitrogen bonds and for aldehydes. The data are compared to those obtained for similar reductions which employ Raney nickel as the catalyst. The nickel boride is more active and productive than Raney nickel in the hydrogenation of hexene, cyclohexene, and acrylonitrile. The properties of the two catalysts are similar for the reduction of cinnamaldehyde, 2-ethylhexanal, and benzaldehyde. The data for the reduction of nitrobenzene, adiponitrile, and propionitrile indicate that the nickel boride is more susceptible to nitrogen poisoning than Raney nickel.

The reduction of an inorganic nickel salt with sodium borohydride in solution gives a finely divided black precipitate that contains boron.[1] If the borohydride reduction is performed in aqueous solution, the product is referred

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