Cation-Radicals: Formation of Methoxy-Radicals by Photochemical and Thermal Oxidation of Methanol

By A. LEDWITH,* P. J. RUSSELL, and L. H. SUTCLIFFE

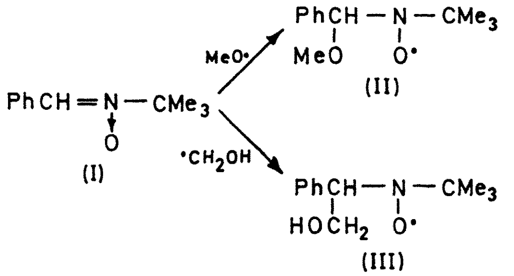
(*Donnan Laboratories, University of Liverpool, Liverpool* L69 3BX)

Summary Spin-trapping experiments with the nitrone, *N*-benzylidene-t-butylamine *N*-oxide (I) and 2-methyl-2-nitrosopropane (IV) have demonstrated that methoxy-radicals are important intermediates in photochemical oxidations of methanol by paraquat dichloride, uranyl nitrate, potassium peroxydisulphate, and lead tetra-acetate; in the γ-radiolysis of methanol; and in thermal oxidation by potassium peroxydisulphate.

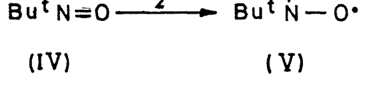
OXIDATION by hydrogen abstraction of primary and secondary alcohols occurs mainly at α-C–H rather than O–H linkages on account of the lower activation energy in the former case. Cleavage of the C-H bond is also the most likely mechanism for the photochemically induced oxidation of alcohols. Recently, however, we suggested[1] that photochemical oxidation of methanol by 1,1′-dimethyl-4,4′-bipyridylium (paraquat, PQ^{2+}) dichloride involves primary electron transfer from methanol to the photoexcited oxidant resulting in formation of methoxy-radicals rather than the more usual hydroxymethyl-radicals (equation 1). Formation of methoxy-radical from the methanol cation radical has also been inferred from studies of the pulse radiolysis of methanol.[2,3]

$$PQ^{2+} \xrightarrow{h\nu} (PQ^{2+})^{*} \xrightarrow{MeOH} [PQ^{+\cdot}, Me\overset{\cdot+}{O}H] \xrightarrow{MeOH}$$

$$PQ^{+\cdot} + MeO\cdot + Me\overset{+}{O}H_2 \qquad (1)$$



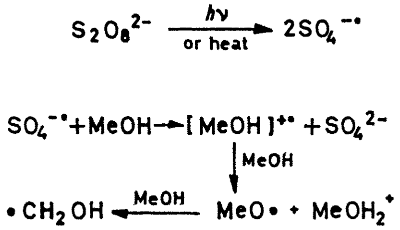
(2)



(3)

Methoxy- and hydroxymethyl-radicals should be distinguishable by the spin-trapping technique which allows short-lived free radicals to be detected and identified in reacting systems.[4] We report details of such a study with the radical scavenger (spin trap) *N*-benzylidene-t-butylamine *N*-oxide[5] (I), and confirm that methoxy-radicals are important intermediates in the oxidation of methanol by a wide range of photochemical oxidants, by γ-radiolysis, and by thermal oxidation with peroxydisulphate ion.

In situ u.v. irradiation of an e.s.r. spectrometer cavity containing methanolic solutions of paraquat dichloride, uranyl nitrate, lead tetra-acetate, and potassium peroxydisulphate, in the presence of the nitrone (I), gave rise to very similar e.s.r. spectra. These consisted of a 1 : 1 : 1 triplet of closely spaced but sharply resolved doublets [subsequently assigned to nitroxide radical (II) (equation 2)] resulting from nitrogen and β-hydrogen couplings (see Table). Similar irradiation of corresponding methanolic solutions of di-t-butyl peroxide, hydrogen peroxide, and 2,3,5,6-tetrachloronitrobenzene, containing (I), also produced a triplet of doublets but the hyperfine splittings and line widths are significantly greater (Table). These spectra are assigned to the nitroxide radical (III) since it is reasonable to assume that photolysis of peroxides in methanol will lead ultimately to hydroxymethyl-radicals *via* hydrogen abstraction, and there is independent evidence[6] to support such a mechanism for the photochemical oxidation of alcohols by 2,3,5,6-tetrachloronitrobenzene.



Recent work[7] with 2-methyl-2-nitrosobutan-3-one as spin trap has shown unambiguously that alkoxy-radicals are produced on photo-oxidation of alcohols by lead tetra-acetate. Thus, the radical (II) would be expected from methanol in the presence of (I),† confirming that methoxy-radicals are important intermediates in similar photo-oxidations with paraquat dichloride, uranyl nitrate, and potassium peroxydisulphate. Additional evidence was obtained from the e.s.r. spectra of radicals produced by γ-radiolysis (^{137}Cs) of liquid methanol containing (I). Again a triplet of sharply defined doublets was observed, identical to those assigned to the radical (II) (Table), and confirming that methoxy-radicals result from fragmentation of the methanol cation radical.[2,3] It should be noted that the radical (III) is responsible for the major signal produced during unfiltered u.v. irradiation of the nitrone (I) itself in methanol, confirming that photo-excited (I) is able to abstract hydrogen from donor solvents;[4] no signal is observed when the light is filtered (Table).

---

† Only a very weak signal was observed before irradiation. Control experiments with sodium acetate in methanol produced no signal.[8]

Thermal decomposition (*ca.* 55°) of potassium peroxydisulphate in the presence of (I) also gave rise to (II). However, detailed studies of the thermolysis have established that lowering of the concentration of nitrone (I) results in an e.s.r. spectrum identical to that assigned to nitroxide (III). Control experiments have shown that the spin adduct is not the result of the trapping of $SO_4^{-\cdot}$ radical anions, although in the absence of oxidisable substrate this intermediate does give rise to weak signals with the nitrone (*cf.* addition of $SO_4^{-\cdot}$ to aci-anions of nitroalkanes[9]).

TABLE

Oxidation of methanol in the presence of N-*benzylidene-t-butylamine* N-*oxide*[a] (I)

	Oxidant[a]	Nitroxide radical splittings[b] a_N	$a_{\beta H}$	Radical type
Photochemical oxidation[c]	Paraquat dichloride	1·437	0·286	(II)
	Paraquat dichloride[d]	1·452	0·298	(II)
	$Pb(OAc)_4$	1·442	0·287	(II)
	$UO_2(NO_3)_2$	1·435	0·288	(II)
	$UO_2(NO_3)_2$[d]	1·459	0·296	(II)
	$K_2S_2O_8$[d]	1·449	0·295	(II)
	$Bu^tO{\cdot}OBu^t$	1·531	0·373	(III)
	HO·OH	1·541	0·373	(III)
	2,3,5,6-Tetrachloronitrobenzene	1·535	0·373	(III)
Thermal oxidation[e]	$K_2S_2O_8$[d,f]	1·450	0·294	(II)
	$K_2S_2O_8$[d,g]	1·536	0·376	(III)
γ-Radiolysis[h] of liquid methanol		1·439	0·288	(II)

[a] [I] = 0·08—0·12M; [oxidant] = 0·01—0·1M.

[b] In mT. Each coupling constant is an average of at least twenty measurements and the e.s.d. is typically ±0·005 and ±0·002 mT for a_N and $a_{\beta H}$ respectively.

[c] Photolysis of degassed solutions by 250 W medium-pressure mercury lamp through a filter solution containing 0·5M nitrone (I) in methanol.

[d] Solvent 9 : 1 v/v MeOH–H_2O.

[e] At *ca.* 55° but spectra recorded at room temperature.

[f] [I] = 0·3M.

[g] [I] = 0·01M.

[h] 100 Ci ^{137}Cs source: irradiation in unsealed vessels.

Variation in the concentration of (I) within the range indicated (Table) gave rise to complex e.s.r. spectra as a result of the simultaneous formation of nitroxide radicals (II) and (III). It seems reasonable to conclude therefore that methoxy-radicals [giving (II)] are formed initially during reactions of $SO_4^{-\cdot}$ with methanol, and that isomeric hydroxymethyl radicals [giving (III)] are produced by subsequent hydrogen abstraction. At high concentrations of (I), MeO· radicals formed initially are completely scavenged, whereas at lower concentrations, competitive hydrogen abstraction from methanol yields the thermodynamically more stable isomer, $\cdot CH_2OH$. (The half-life of MeO· has been estimated[2] to be *ca.* 4 μs in pure methanol.)

Additional confirmation of these conclusions was obtained by spin-trapping experiments in similar systems with 2-methyl-2-nitrosopropane (IV).[10] In this case only one type of e.s.r. signal was observed and this has previously been assigned[11] to the hydroxymethyl adduct (V) (equation 3). Alkoxy-radical adducts of nitroso-alkanes are thermally unstable at room temperature[4] and, in this sense, the nitroso-compounds must be regarded as less efficient radical scavengers than the nitrones.

Very similar results have been obtained from preliminary work with other primary and secondary alcohols, although it appears that substituents affect the relative rates of reaction of alkoxy-radicals with the spin-trapping agents and in hydrogen abstraction. It is clear therefore that the present widespread assumption[12] of hydrogen abstraction by $SO_4^{-\cdot}$, as the primary step in oxidation of alcohols by peroxydisulphate ion, must be reconsidered. These findings also cast some doubt on the mechanism proposed for the photo-oxidation of alcohols by uranyl salts[13] and assumptions of hydrogen abstraction mechanisms for other photo-oxidants should be carefully examined.

(*Received, May 24th,* 1971; *Com.* 828.)

[1] A. S. Hopkins, A. Ledwith, and M. F. Stam, *Chem. Comm.*, 1970, 494.

[2] F. S. Dainton, I. V. Janovsky, and G. A. Salmon, *Chem. Comm.*, 1969, 335.

[3] L. M. Dorfman, *Accounts Chem. Res.*, 1970, **3**, 224.

[4] E. G. Janzen, *Accounts Chem. Res.*, 1971, **4**, 31; M. J. Perkins in "Essays on Free-radical Chemistry", *Chem. Soc. Special Publ.*, 24, 1970, ch. 5.

[5] E. G. Janzen and B. J. Blackburn, *J. Amer. Chem. Soc.*, 1969, **91**, 4481.

[6] D. J. Cowley and L. H. Sutcliffe, *J. Chem. Soc.* (*B*), 1970, 569.

[7] S. Forshult, C. Lagercrantz, and K. Torssell, *Acta Chem. Scand.*, 1969, **23**, 522; see also C. Walling and J. Kjellgren, *J. Org. Chem.* 1969, **34**, 1488.

[8] A. R. Forrester and S. P. Hepburn, *J. Chem. Soc.* (*C*), 1971, 701.

[9] D. J. Edge, R. O. C. Norman, and P. M. Storey, *J. Chem. Soc.* (*B*), 1970, 1096.

[10] R. J. Holman and M. J. Perkins, *J. Chem. Soc.* (*C*), 1970, 2195, and references therein.

[11] M. J. Perkins, P. Ward, and A. Horsfield, *J. Chem. Soc.* (*B*), 1970, 395; I. H. Leaver and G. C. Ramsay, *Tetrahedron*, 1969, **25**, 5669.

[12] D. A. House, *Chem. Rev.*, 1962, **62**, 185; J. E. McIsaac and J. O. Edwards, *J. Org. Chem.*, 1969, **34**, 2565; L. Dogliotti and E. Hayon, *J Phys. Chem.*, 1967, **71**, 2511.

[13] S. Sakuraba and R. Matsushima, *Bull. Chem. Soc. Japan*, 1970, **43**, 2359.