Cation Radicals: Scavenging of t-Butoxy-radicals by Electron Transfer from Paraquat (*NN*-Dimethyl-4,4′-bipyridylium) Cation Radical

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Summary t-Butoxy radicals generated by photolysis of di-t-butyl peroxide, or thermolysis of di-t-butyl hyponitrite, are quantitatively reduced to t-butoxide ion by electron transfer from paraquat cation radical; the reaction affords a novel and convenient method of studying rates of homolytic fission in organic molecules.

PREVIOUSLY we have proposed[1] a mechanism for the photochemical oxidation of alcohols by paraquat dichloride (and other photo-oxidants[2]) in which the primary step is electron transfer from alcohol to excited photo-oxidant. A necessary consequence of the proposed mechanism is that tertiary-alkoxy-radicals should be efficiently reduced to tertiary-alkoxide ion by the paraquat cation radical ($PQ^{+\cdot}$) and this has now been confirmed experimentally. Solutions of the intensely coloured paraquat cation radical in H_2O–Bu^tOH mixtures are completely decolourised when allowed to react with t-butoxy-radicals generated by photolysis of dissolved di-t-butyl peroxide, or thermolysis of di-t-butyl hyponitrite.[3]

The u.v.–visible absorption spectrum[4] of $PQ^{+\cdot}$ has a 'window' at *ca.* 310—350 nm convenient for photodecomposition of di-t-butyl peroxide; control experiments showed that the latter does not react thermally with $PQ^{+\cdot}$ at room temperature, and that no reaction occurs on selective photoexcitation of the cation radical in H_2O–Bu^tOH solvent systems. In contrast, photolysis (250 W medium pressure mercury lamp) of solutions of $Bu^tO{\cdot}OBu^t$ and $PQ^{+\cdot}$ in 1 : 1 H_2O–Bu^tOH using an interference filter to isolate the 313 nm line, or with unfiltered light, resulted in steady decay of the blue colour due to $PQ^{+\cdot}$. Reaction rates ($-\mathrm{d}[PQ^{+\cdot}]/\mathrm{d}t$) were monitored spectrophotometrically and were found to be first order in $[Bu^tO{\cdot}OBu^t]$, and essentially independent of $[PQ^{+\cdot}]$, temperature (below 60°), and solvent composition. The photochemical reaction necessitated comparatively long reaction times to build up sufficient alkalinity in the systems for quantitative assay, and, since paraquat is slowly degraded in alkaline solutions,[5] it was not possible to establish a correlation between the amounts of paraquat cation radical consumed and Bu^tO^- produced. Consequently di-t-butyl hyponitrite was used as a more convenient source of t-butoxy-radicals.

TABLE

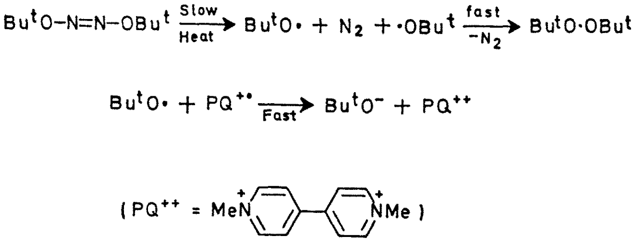
Reactions of paraquat cation radical[a] *with di-t-butyl hyponitrite in* 1 : 1 v/v H_2O-Bu^tOH

$10^3[PQ^{\dot{+}}]_0$/M	$10^3[Bu^tO{\cdot}N_2{\cdot}OBu^t]_0$/M	Temp. t/°C	$-d[PQ^{\dot{+}}]/dt$ (10^{-5}M min^{-1})
0·288	2·017	65	3·40
1·067	2·017	65	3·48
1·400	2·017	65	3·50
1·091	0·489	65	1·09
0·833	0·767	65	1·52
0·617	1·137	65	2·34
1·233	2·017	65	3·49
1·633	3·020	65	4·94
0·813	1·023	50	0·37
0·983	2·156	50	0·80
0·725	3·020	50	1·26

[a] Paraquat cation radical was generated by controlled reduction of paraquat dichloride with zinc powder in a conventional high vacuum apparatus, and determined spectrophotometrically by measuring optical density at 600 nm ($\epsilon_{600} = 1{\cdot}2 \times 10^4$M^{-1} cm^{-1}).

Thermal decomposition of di-t-butyl hyponitrite in 1 : 1 v/v H_2O–Bu^tOH containing $PQ^{\dot{+}}$ was monitored spectrophotometrically, at two temperatures, and the rate data obtained are shown in the Table. For the concentration ranges employed, reaction rates ($-d[PQ^{\dot{+}}]/dt$) were independent of $[PQ^{\dot{+}}]$ and essentially first order in $[Bu^tO{\cdot}N_2{\cdot}OBu^t]$. Measured in this way, the first-order rate coefficient for homolysis of di-t-butyl hyponitrite at 65° ($3{\cdot}5 \pm 0{\cdot}2 \times 10^{-4}$ s^{-1}) is in good agreement with values extrapolated from data of Traylor and Keifer[3] ($3{\cdot}7 \times 10^{-4}$ s^{-1}) in iso-octane, and Neuman and Bussey[6] ($3{\cdot}6 \times 10^{-4}$ s^{-1}) in n-octane, the latter values being obtained by quite different techniques. The kinetic data are best interpreted by reactions as in the Scheme in which t-butoxy-radicals are scavenged by electron transfer from paraquat cation radical.

In agreement with this reaction scheme, titration of product reaction mixtures with dilute acid established that 1 mol. equiv. of Bu^tO^- ion was produced for each mol. equiv. of cation radical consumed. Representative experimental results at 50° were (a) in 1 : 1 H_2O–Bu^tOH with $[Bu^tO{\cdot}N_2{\cdot}OBu^t] = 10^{-2}$M, a solution having initial $[PQ^{\dot{+}}] = 4{\cdot}2 \times 10^{-3}$M yielded, after complete decolouration, a solution containing $4{\cdot}1 \times 10^{-3}$M base, and (b) in 1 : 6 H_2O–Bu^tOH with $[Bu^tO{\cdot}N_2{\cdot}OBu^t] = 5 \times 10^{-2}$M, a solution having initial $[PQ^{\dot{+}}] = 1{\cdot}2 \times 10^{-3}$M similarly yielded a solution containing $1{\cdot}3 \times 10^{-3}$M base. It follows that, in H_2O–Bu^tOH solvent systems, t-butoxy-radical must possess oxidising power in excess of that of paraquat, for which[7] $E_0 = -$ 446 mV in water, and may, therefore, function as a primary one-electron oxidant in reactions presently interpreted in other ways.



SCHEME

The intense colours, high stability, and varied redox potentials[7] of cation radicals from bipyridylium salts suggest convenient reagents for the characterisation of the redox behaviour of organic radicals and detailed studies now in progress indicate that this type of scavenging, by electron transfer, may be used to determine the rates of homolysis of various labile molecules.

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