+0.82° (c 6.8, CHCl$_3$). (Found: C 74.93; H 13.15. Calc. for C$_{17}$H$_{36}$O$_2$: C 74.94; H 13.32). The constitution was confirmed by IR- and PMR-spectroscopy.

(−)-1-p-Toluenesulfonyloxy-3-hydroxyheptadecane (VI). (+)-1,3-Dihydroxyheptadecane (V) (0.0013 mol) was tosylated in dry pyridine at *ca.* −17° using 0.0015 mol of *p*-toluenesulfonyl chloride. The reaction mixture was kept at −17° for 3 1/2 h and then placed in a refrigerator (5°) for 21 h. The reaction was followed by TLC (silica gel GF$_{254}$ (Merck)) with benzene-ethyl acetate (17+3) as the eluent. During 1 h and with stirring the reaction mixture was added to 170 ml of ice-cooled water. Upon addition of 100 ml of hydrochloric acid (4 N) the mixture was extracted with chloroform. The filtered and dried extract was evaporated and the residue chromatographed on 75 g of silica gel using benzene-ethyl acetate mixtures as the eluents. Obtained were 289 mg of (−)-1-*p*-toluenesulfonyloxy-3-hydroxyheptadecane (VI), m.p. 58.0−59.0° (petroleum ether); $[\alpha]_D^{20.1}$ −4.9° (c 2.8, CHCl$_3$). (Found: C 67.60; H 10.04. Calc. for C$_{24}$H$_{42}$O$_4$S: C 67.54; H 9.92). The IR-spectrum exhibited the absorption bands expected for (VI).

(+)-3-Hydroxyheptadecane (VII). (−)-1-*p*-Toluenesulfonyloxy-3-hydroxyheptadecane (VI) (250 mg) was hydrogenolysed with lithium aluminium hydride (255 mg) according to Zorbach *et al.*[8] Excess lithium aluminium hydride was destroyed as described above for (+)-1,3-dihydroxyheptadecane. The ether layer, however, was washed with a saturated solution of sodium hydrogen carbonate, dried and evaporated. Chrystallization from methanol-water yielded 123 mg of (+)-3-hydroxyheptadecane (VII), m.p. 54.0−55.0°; $[\alpha]_D^{18.1}$ +5.8° (c 1.4, CHCl$_3$). (Found: C 79.83; H 14.19. Calc. for C$_{17}$H$_{36}$O: C 79.61; H 14.15). The IR-spectrum was identical with that of (−)-3-hydroxyheptadecane (II).

1. Takahashi, M., Isoi, K., Kimura, Y. and Yoshikura, M. *J. Pharm. Soc. Japan* **84** (1964) 752.
2. Bohlmann, F., Niedballa, U. and Rode, K.-M. *Chem. Ber.* **99** (1966) 3552.
3. Takahashi, M. and Yoshikura, M. *J. Pharm. Soc. Japan* **86** (1966) 1051, 1053.
4. Bohlmann, F., Niedballa, U. and Schneider, J. *Chem. Ber.* **98** (1965) 3010.
5. Serck-Hanssen, K. *Arkiv Kemi* **10** (1956) 135.
6. Bohlmann, F., Arndt, C., Bornowski, H. and Kleine, K.-M. *Chem. Ber.* **94** (1961) 958.
7. Breusch, F. L. and Baykut, F. *Chem. Ber.* **86** (1953) 684.
8. Zorbach, W. W. and Tio, C. O. *J. Org. Chem.* **26** (1961) 3543.

ESR Evidence for O$_2^-$ as a Long-Lived Transient in Irradiated Oxygenated Alkaline Aqueous Solutions

ROBERT NILSSON,* FRANCIS M. PICK, ROBERT C. BRAY and MARTIN FIELDEN

Chester Beatty Research Institute and Department of Physics, Institute of Cancer Research, Royal Cancer Hospital, London and Sutton, Surrey, England

It is well known that long-lived UV absorbing transients are formed during irradiation of oxygenated aqueous solutions.[1-4] Czapski and Dorfman concluded[3] that O$_2^-$ decays rapidly at all pH values but that unidentified long-lived species are formed at high pH. Among the hypothetical intermediates suggested by these authors[3] were the diamagnetic species O$_2^{2-}$, O$_4^{2-}$, and HO$_5^{3-}$ as well as the paramagnetic HO$_3^{2-}$. In establishing the nature of the light absorbing transient formed in alkaline solutions the use of ESR would then seem rational.

Despite its advantages for identification of radicals, ESR has not generally been applied in such work, largely because of its low time resolution. This drawback may be overcome by trapping the radicals at low temperatures. The "rapid-freezing"

* Permanent address: Avdelningen för Strålningsbiologi, Biokemiska Institutionen, Stockholms Universitet, Box 6409, S-113 82 Stockholm, Sweden.

technique [5,6] consisting of squirting aqueous solutions *via* a fine jet into a cold immiscible liquid, has been useful for trapping moderately unstable species for ESR study in biochemical work. Using this method, evidence for enzymic reduction of O_2 to O_2^- has recently been presented.[7,8] We have now combined pulse radiolysis and rapid-freezing ESR technique and obtained clear evidence for the presence of a paramagnetic species, identical with O_2^-, in oxygenated alkaline solutions several hundred milliseconds after irradiation. Czapski and Dorfman [3] also discussed the possibility of the paramagnetic intermediate HO_3^{2-} being involved. In view of the characteristics of the ESR signal obtained, *e.g.* the absence of proton splitting, this alternative could be excluded.[7] Our results have provided confirmation for the identification [7] of this same radical generated enzymically and support for the conclusion [7] that the long-lived "alkaline stabilized form of O_2^-",[2,3] is in fact O_2^- itself. The belief [3] that O_2^- disappears rapidly by reaction with itself needs to be revised.

Irradiation of solutions by 4 MeV electrons was carried out at about 20°C while they were flowing through a polyethene tube at a rate of 0.42 ml/sec from a hydraulically driven syringe system. A single pulse dose of $1-6$ Krad was given. After passing through an appropriate dead space, solutions were squirted into isopentane at $-140°$ to obtain samples [5] for low temperature ESR measurement. In some cases a mixing chamber was inserted into the system [5] so that additions could be made to the solutions following irradiation but before freezing.

The ESR spectrum of a typical sample is presented in Fig. 1. It shows $g \perp 2.00$ with $g \parallel 2.08$ to 2.09 and integration indicated a concentration in the region of 10^{-5} M. The signal is indistinguishable from those previously attributed to O_2^- obtained in enzymic reduction of oxygen,[7,8] during reaction between H_2O_2 and periodate ions,[7] and in reactions between trapped electrons (generated with sodium and ice) and oxygen.[9] The interval between irradiation and freezing (260 msec) was sufficiently long for the more labile intermediates such as $OH(O^-)$ and O_3^- to disappear and it might have been expected [3] that O_2^- would also have disappeared. Experiments with the conventional optical detection system of the pulse radiolysis apparatus showed that the long-lived absorption at 250 nm was produced under
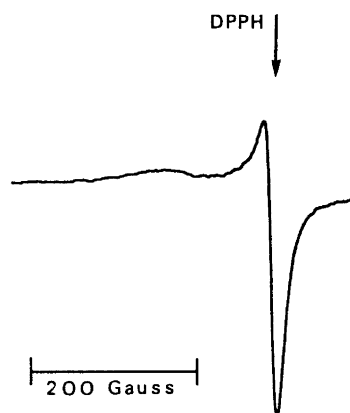
Fig. 1. ESR spectrum recorded at about 100°K of an oxygen-saturated aqueous solution of approx. 10^{-3} M $Ba(OH)_2$ irradiated at about 20°C with 4 MeV electrons, then frozen 260 msec after irradiation.

the same conditions and that it had a pH dependent first order decay as previously described.[2,3] Thus at the time of freezing the only species detectible optically was that with an absorption peak at 250 nm. Nevertheless, we found, in confirmation that at least the precursor of the species observed was O_2^-, that no signal was obtained when the solution was saturated with N_2 in place of O_2 nor, as anticipated,[1] was a significant signal found using oxygen saturated sodium carbonate buffer (pH 11). Tetranitromethane, $C(NO_2)_4$, reacts rapidly with one-electron reducing agents, including both the solvated electron and O_2^- (Ref. 10). When an oxygen saturated NaOH solution was reacted for 16 or 90 msec with tetranitromethane in a two syringe system, mixing taking place 230 msec after irradiation, O_2^- signals were completely absent.

Knowles *et al.*[7] attempted to reconcile their conclusion, now confirmed more directly, that O_2^- has a relatively long life-time in alkaline media, with the earlier data by Czapski and Dorfman.[3] They proposed that O_2^- decomposes *via* reversible equilibrium with a dimer, this requiring a proton for breakdown to O_2 and the hydrogen peroxide anion. This scheme would explain the rapid second order decay at neutrality and slower, pH dependent, decay in alkali. Further work on the mechanism is, however, clearly required.

1. Adams, G. E., Boag, J. W. and Michael, B. D. *Proc. Roy. Soc.* **A 289** (1966) 321.
2. Fielden, E. M. *Ph. D., Thesis,* Manchester 1964.
3. Czapski, G. and Dorfman, L. M. *J. Phys. Chem.* **68** (1964) 1169.
4. Felix, W. D., Gall, B. H. and Dorfman, L. M. *J. Phys. Chem.* **71** (1967) 384.
5. Bray, R. C. *Biochem. J.* **81** (1961) 189; Bray, R. C. and Pettersson, R. *Biochem. J.* **81** (1961) 194.
6. Bray, R. C. In Chance, B., Eisenhardt, R. H., Gibson, Q. H. and Lonberg-Holm, K. K. *Rapid Mixing and Sampling Techniques in Biochemistry,* Academic, New York 1964, p. 195.
7. Knowles, P. F., Gibson, J. F., Pick, F. M. and Bray, R. C. *Biochem. J.* **111** (1969) 53.
8. Nilsson, R., Pick, F. M. and Bray, R. C. *Biochim. Biophys. Acta* **192** (1969) 145.
9. Bennett, J. E., Mile, B. and Thomas, A. *Trans. Faraday Soc.* **64** (1968) 3200.
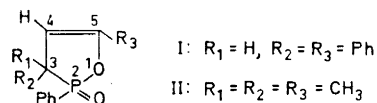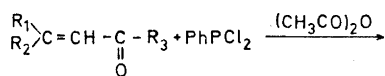10. Rabani, J., Mulac, W. A. and Matheson, M. S. *J. Phys. Chem.* **69** (1965) 53.

NMR and Kinetic Studies of Some Oxaphospholene Derivatives

KNUT BERGESEN

Chemical Institute, University of Bergen, Bergen, Norway

Some years ago the syntheses of 2-oxo-2,3,5-triphenyl-1,2-oxaphospholene (I) and 2-oxo-2-phenyl-3,3,5-trimethyl-1,2-oxaphospholene (II) were reported.[1] The compounds were prepared from phenylphosphine dichloride, acetic anhydride, and the unsaturated ketones benzalacetophenone and mesityloxide, respectively.

$$\begin{array}{c} R_1 \\ R_2 \end{array} C = CH - \underset{\underset{O}{\|}}{C} - R_3 + PhPCl_2 \xrightarrow{(CH_3CO)_2O}$$

I: $R_1 = H$, $R_2 = R_3 = Ph$

II: $R_1 = R_2 = R_3 = CH_3$

The NMR spectrum of the olefinic proton in position 4 in compound I occurs as two doublets ($\delta = 4.72$) due to the coupling to the phosphorus atom and the proton in position 3 (Table 1). The same magnitude of the phosphorus coupling is also found in compound II, but the doublet is further splitted into two quartets (Fig. 1), due to
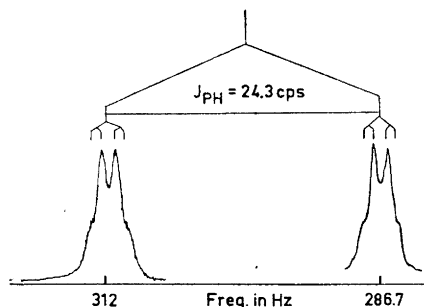
$J_{PH} = 24.3$ cps

312   Freq. in Hz   286.7

Fig. 1. Spectrum at 60 Mc of the olefinic proton in II in $CDCl_3$ with TMS as internal standard.

the coupling of the olefinic proton to the protons of the methyl group in position 5. This was confirmed by irradiation of the