Oxidation by Photochemically Produced Singlet States of Oxygen

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THERE is now considerable evidence that many photo-oxidations involve the low-lying singlet states of oxygen ($^1\Delta_g$ and $^1\Sigma_g^+$) as intermediates.[1] Similar reactions have been carried out using singlet oxygen produced either chemically or in an electric discharge.[1] I describe here oxidations caused by direct photochemical excitation of oxygen at high pressures dissolved in an inert organic solvent.

The Figure (a) shows the absorption spectrum (470—1300 nm.) of oxygen at 2000 lb./sq. in. pressure dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane (a good and safe solvent for oxygen under pressure.) Measurable absorption leading to the $^1\Delta_g$ and $^1\Sigma_g^+$ states, and also to the "double" states $(^1\Delta_g)_2$ and $(^1\Delta_g{}^1\Sigma_g^+)$ is observed. By a fortunate coincidence the normal wavelength of a He–Ne laser, 632·8 nm., almost exactly coincides with that of the $(^1\Delta_g)_2 \leftarrow (^3\Sigma_g^-)_2$ transition. Irradiation with a He–Ne laser of a cell containing oxygen at 2000 lb./sq. in. dissolved in a dilute solution of 9,10-dimethylanthracene in 1,1,2-trichloro-1,2,2-trifluoroethane gave 9,10-dimethylanthracene peroxide. No detectable reaction occurred in the dark. For a $1{\cdot}8 \times 10^{-4}$M-solution the quantum yield (calculated from the rate of disappearance of the 9,10-dimethylanthracene) was *ca.* 0·13, and for a $4{\cdot}4 \times 10^{-5}$M-solution *ca.* $0{\cdot}04_9$.† For a 9×10^{-6}M-solution of the very reactive compound 1,3-diphenylisobenzofuran under similar conditions, the quantum yield was *ca.* $0{\cdot}6_5$. The Figure (b) shows the relative rates of photo-oxidation of a 4×10^{-5}M-solution of 9,10-dimethylanthracene saturated

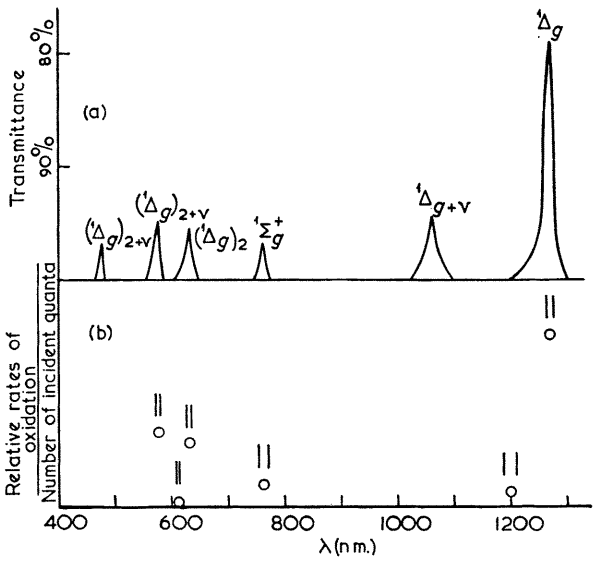

FIGURE. (a) *The absorption spectrum of oxygen at* 2000 *lb./sq. in. dissolved in* 1,1,2-*trichloro*-1,2,2-*trifluoroethane.*

(b) *The relative rates of photo-oxidation of a* 4×10^{-5}M-*solution of* 9,10-*dimethylanthracene saturated with oxygen at* 2000 *lb./sq. in., divided by the number of quanta incident upon the cell. The vertical lines indicate the approximate widths at half-intensity of the interference filters used.*

† The oxygen-induced singlet–triplet bands[2] of 9,10-dimethylanthracene will also lie in this region, but for the very dilute solutions studied will be very weak.

with oxygen at 2000 lb./sq. in., with approximately monochromatic radiation of various wavelengths. It is clear that photochemical excitation of the single $^1\Delta_g$ and $^1\Sigma_g^+$ states can also cause oxidation of the organic substrate. This technique for studying oxidation by singlet states of oxygen has the advantage of high selectivity.

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[1] C. S. Foote, *Accounts Chem. Res.*, 1968, **1**, 104.
[2] D. F. Evans, *J. Chem. Soc.*, 1957, 1351.