

Polyene Oxidation: The Oxidation of Squalene with Singlet Oxygen

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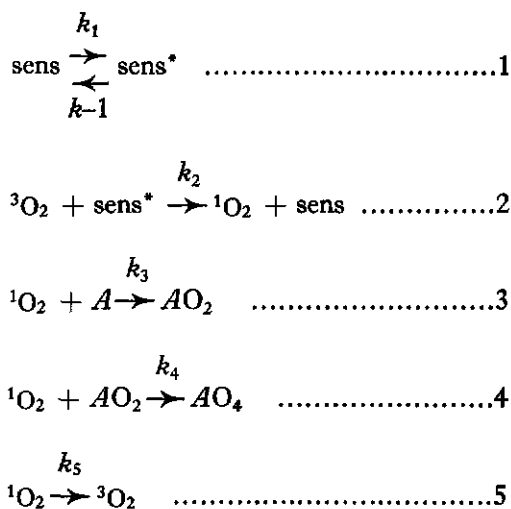
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The reactivity (β) of squalene with singlet oxygen in dichloromethane has been determined as 0.02. Using an estimate for the singlet oxygen life time (τ) in dichloromethane, the absolute rate constant for the reaction is found to be of the order 8×10^5 mole⁻¹ litre sec⁻¹ at 35°C.

Free-radical oxidation and autoxidation of rubber and rubber-like substances have been extensively studied, mainly through model systems (BATEMAN, 1954). Squalene has proved to be a useful model because the double bond arrangement in it best approximates the situation found in rubber (HOLLAND AND HUGHES, 1949). Hydroperoxides are the initial products in radical oxidation and in oxidation by singlet oxygen in one of its recognised modes of reaction with olefinic systems (BARTLET *et al.*, 1970; SAM, 1972). These hydroperoxides subsequently participate in further oxidation and enhance the overall rate of reaction. Squalene also reacts with singlet oxygen produced by decomposition of the triphenylphosphite-ozone adduct and from dye-sensitised photochemical formation (KAPLAN AND KELLEHER, 1972). The products were established to be hydroperoxides isolated as mono-alcohol mixtures after reduction with triphenylphosphine. These mono-alcohols were themselves reactive towards singlet oxygen. This is not unexpected as squalene bears six trisubstituted double bonds suitable for reaction.

The reaction of an olefin (*A*) with singlet oxygen produced during a dye-sensitised photochemical reaction in solution can be considered as proceeding formally by the following steps (STEVENS, 1973):



Step 1 represents the excitation of the sensitiser upon irradiation. In *Step 2* the excited sensitiser converts a ground state triplet oxygen molecule (${}^3\text{O}_2$) into singlet oxygen (${}^1\text{O}_2$) which subsequently reacts

with the olefin A or with product if liable or alternatively the singlet oxygen is quenched by solvent molecules. In *Step 5* the quenching rate (k_5) is related to the half-life (τ) of the singlet oxygen in that solvent ($k_5 = 1/\tau$).

No direct evidence exists for the participation of a discrete singlet oxygen intermediate as proposed in the reaction scheme. However, product analyses have shown that dye-sensitised photo-oxidation of olefins is indistinguishable from oxidation with electrically or chemically generated singlet oxygen (FOOTE, 1968). This supports the assumption of the intermediacy of a singlet oxygen moiety in photo-oxidation in solution.

Assuming steady state concentration for the reactive species, sens^* and $^1\text{O}_2$, the singlet oxygen concentration can be obtained from the expression

$$(^1\text{O}_2) = \frac{k_2(^3\text{O}_2)k_1(\text{sens})}{k_{-1} + k_2(^3\text{O}_2)} \times \frac{1}{k_3(A) + k_4(\text{AO}_2) + k_5} \quad \dots\dots\dots(1)$$

Since the dye concentration is constant, Equation (1) can be re-expressed as follows when the oxygen concentration is kept constant by ensuring saturation in the solvent:

$$(^1\text{O}_2) = \frac{z}{k_3(A) + k_4(\text{AO}_2) + k_5} \quad \dots\dots\dots(2)$$

where z summarises the oxygen and dye concentration variables. The rate expression for the disappearance of olefin A is now,

$$-\frac{d(A)}{dt} = \frac{k_3 Z(A)}{k_3(A) + k_4(\text{AO}_2) + k_5} \quad \dots\dots\dots(3)$$

which is convertible to

$$-\frac{1}{d(A)/dt} = \frac{1}{Z} + \left\{ \frac{\alpha(\text{AO}_2) + \beta}{Z} \right\} \frac{1}{(A)} \quad (4)$$

where $\alpha = k_4/k_3$ representing the relative reactivity rate of olefin A and its first formed

product AO_2 and $\beta = k_5/k_3$ is the reactivity of olefin A in the solvent (FOOTE, 1968).

If it is assumed that $\alpha \ll 1^a$, then at early stages of the reaction when the concentration of the product AO_2 is low, Equation (4) can be simplified to:

$$-\frac{1}{d(A)/dt} = \frac{1}{Z} + \frac{\beta}{Z} \frac{1}{(A)} \quad \dots\dots\dots(5)$$

β is then obtained as the ratio of the gradient and intercept of the plot of $-\frac{1}{d(A)/dt}$ against

$1/(A)$. Normally, the rate, $-\frac{1}{d(A)/dt}$ can be obtained directly from measurements of the quantum yields (STEVENS, 1973) but in the absence of the necessary equipment it is possible to obtain this required rate by a numerical analysis of the concentration-time relationship for the olefin A . This relationship can be expressed as a binomial equation:

$$\text{Concentration} = at^2 - bt + C_0 \quad \dots\dots\dots(6)$$

where C_0 is the initial concentration, a and b are constants peculiar to each experimental set of data and t is the time. The rate of reaction then is obtained by differentiation as:

$$\frac{dc}{dt} = 2at - b \quad \dots\dots\dots(7)$$

Thus it is possible to calculate $-\frac{1/d(A)}{dt}$ and plot this against $1/(A)$ when (A) is either the observed concentration or the smoothened value obtained from Equation (6).

EXPERIMENTAL

Runs were generally made by first saturating a solution of squalene of final concentrations

^aThis value for squalene is indicated by the oxidation studies of KAPLAN AND KELLEHER (1972).

of ca. 0.02 to 0.03M and triphenyl phosphine oxide (0.01 to 0.03M final concentrations) in dichloromethane with oxygen in the dark (Figure 1). A solution of methylene blue (ca. 4–8 mg) in dichloromethane (ca. 20 ml) was then added. Final volumes of the solutions varied between 100–140 millilitres. After addition of the dye solution, the annular fluorescent light sources (total rated power of 120 W) were switched on. Aliquots were withdrawn at regular intervals for gas chromatography.

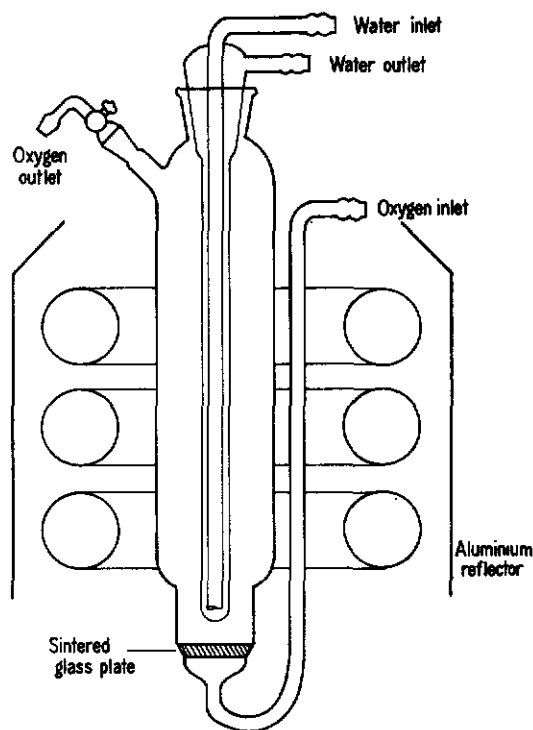


Figure 1. Apparatus for singlet oxygen reactions. The three annular fluorescent lamps shown in cross-section are Mashushita (National) 40W Daylight tubes.

Gas chromatography was carried out on a Varian 1700 Aerograph instrument fitted with thermal conductivity detectors using a 3 ft 5% S.E. 30 column operating at 285°C

with helium as carrier. Under these conditions triphenylphosphine oxide, the internal standard, preceded squalene. Calibrations indicated that the relative concentrations of internal standard and squalene were proportional to the ratio of the peak heights.

RESULTS AND DISCUSSION

Squalene was subjected to dye-sensitised photo-oxidation in dichloromethane using methylene blue as the dye. The reaction mixture also contained an internal standard, triphenylphosphine oxide. Squalene concentration during irradiation in the apparatus shown in Figure 1 was monitored by gas chromatography.

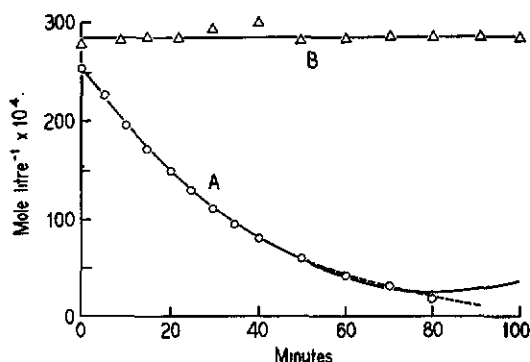


Figure 2. Typical curve (A) of squalene concentration as a function of time during reaction with singlet oxygen. Inconsistency in the computed least-square curve (bold) at advanced reaction stages (> 80%) is indicated on comparison with the experimental curve (broken line). Curve B is the control obtained in the absence of methylene blue.

The plot of concentration versus time is shown as Curve A in Figure 2 for one such run at 35°C. The curve fitting was done using a polynomial regression programme on a Hewlett-Packard Desk Calculator Model 9830A. The curve, as expected, is parabolic and does not represent the concentration-

time relation beyond a certain region since it is strictly a numerical solution. *Curve B* is the plot obtained from a run under identical conditions but without sensitizer. The control establishes the involvement of singlet oxygen.

Curve A at the early stages of the reaction where Equation (5) is expected to hold must represent the concentration-time relation. The constants a and b of Equation (6) are obtained from the polynomial regression programme. The rate of reaction at any time (t) is therefore given by Equation (7). The plots of the reciprocal of this calculated rate against the reciprocal of the observed concentration for three runs are shown in Figure 3. Similar plots using smoothed

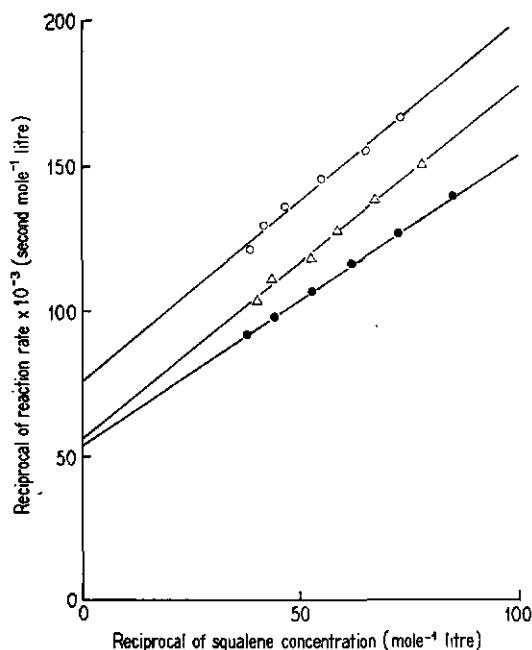


Figure 3. Plots of the reciprocal of the derived reaction rate against the reciprocal of the experimental concentrations for three separate runs. The slopes are equal to β .

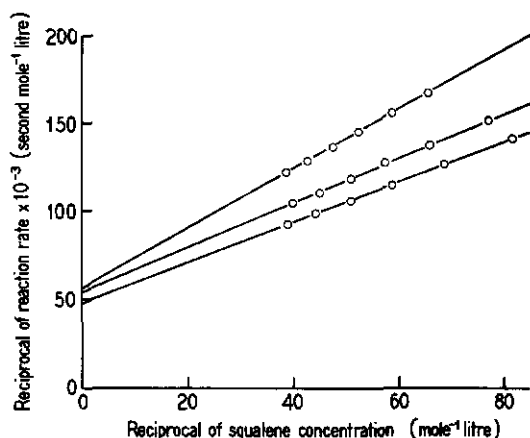


Figure 4. As for Figure 3 but utilising corrected squalene concentrations derived from the least-square curve (Equation 6).

values for the concentrations obtained from Equation (6) are shown in Figure 4. In all cases, the plots have been taken to approximately 50% reaction. The value of β that emerges is 0.02 based on calculated and experimental concentration.

Although the half-life of singlet oxygen in dichloromethane is presently unavailable from literature, it should be of the order of 60 μ sec, the observed life-time of singlet oxygen in chloroform (MERKEL AND KEARNS, 1972). The absolute rate constant (k_3) is therefore of the order 8×10^5 mole⁻¹ litre sec⁻¹. As a comparison, the absolute rate constant for the more reactive tetrasubstituted olefin, tetramethylethylene (TME) is $4 \pm 1 \times 10^7$ mole⁻¹ litre sec⁻¹ (MERKEL AND KEARNS, 1972).

BATEMAN (1954) had noted that the direct reaction between triplet molecular oxygen and an olefin is probably very small ($< 10^{-6}$ mole litre⁻¹ sec⁻¹ for tetralin at 75°C). However, in the presence of sensitizers capable of converting triplet molecular oxygen into singlet oxygen, this direct reaction may be significant and under such circumstances, as observed for squalene, polyene systems may undergo rapid oxidative

changes through a combination of singlet oxygen attack and the subsequent autoxidation induced by hydroperoxides formed. Recently, SATO AND MURAYAMA (1974) have shown that olefins themselves may be capable of participating in the conversion of triplet molecular oxygen to singlet oxygen. They postulate a charge-transfer excitation mechanism to account for the observation of 41% singlet oxygen attack and 59% radical oxidation in (+)-limonene during unsensitised photo-oxidation. The fast reaction between singlet oxygen and the possible role of the polyenes themselves in the formation of singlet oxygen from ground state molecular oxygen suggest that present ideas on environmental oxidative degradation of rubber and rubber-like substances which do not take into account the possible role of singlet oxygen occurring before and during radical oxidation may need revision.

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REFERENCES

- BARTLETT, P.D., MENDENHALL, M.S. AND SCHAAP, A.P. (1970) Competitive modes of reaction of singlet oxygen. *Ann. N.Y. Acad. Sci.*, **171**(Art 1), 79.
- BATEMAN, L. (1954) Olefin oxidation. *Quart. Reviews*, **8**, 147.
- FOOTE, C.S. (1968) Photosensitised oxygenations and the role of singlet oxygen. *Acc. Chem. Res.*, **1**, 104.
- HOLLAND, J.P. AND HUGHES, H. (1949) The primary oxidation products of squalene. *J. Chem. Soc.*, 492.
- KAPLAN, M.L. AND KELLEHER, P.G. (1972) Polydiene oxidations with singlet oxygen. *Rubber Chem. Technol.*, **45**(2), 423.
- MERKEL, P.B. AND KEARNS, D.R. (1971) Direct measurement of the life-time of singlet oxygen in solution. *Chem. Physic letters*, **12**, 120.
- MERKEL, P.B. AND KEARNS, D.R. (1972) Radiationless decay of singlet oxygen in solution: an experimental and theoretical study of electronic-to-vibrational energy. Transfer. *J. Am. Chem. Soc.*, **94**(21), 7244.
- SAM, T.W. (1972) Singlet oxygen. *Proc. Seminar on Current Research Trends in the School of Chemical Sciences, USM and the RRI*, 1973, 12.
- SATO, T. AND MURAYAMA, E. (1974) The unsensitised photo-oxidation of (+)-limonene, 1,2-dimethylcycloheptene and *endo*-dicyclopentadiene. *Bull. Chem. Soc. Jap.*, **47**(3), 715.
- STEVENS, B. (1973) Kinetics of photoperoxidation in solution. *Acc. Chem. Research*, **6**(3), 90.