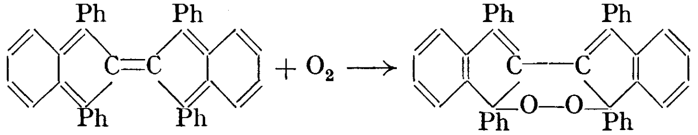
233. *The Photo-oxidation of Rubrene.*

By Edmund J. Bowen and Fred Steadman.

The red hydrocarbon rubrene, $C_{42}H_{28}$, first prepared by Moureu, Dufraisse, and Dean (*Compt. rend.*, 1926, **182**, 1440), forms a peroxide when its solution containing dissolved oxygen is exposed to visible light. No oxidation takes place in the dark. The reaction is probably



The peroxide is stable in solution, and is colourless, so the progress of the oxidation can be followed by colorimetric estimation of the dissolved rubrene.

The molecular weight of the peroxide (cryoscopic in benzene) is 561 (calc. for $C_{42}H_{28}O_2$: 564).

Experimental.

Preparation of Rubrene.—*ααγ-Triphenylpropargyl alcohol.* 4·8 G. of magnesium were allowed to react with 23 g. of ethyl bromide in ether, and 20 g. of phenylacetylene, diluted with ether, were added. After boiling under reflux for 30 minutes, the solution was added in small portions to an ethereal solution of 35 g. of benzophenone cooled in ice. The mixture was again boiled under reflux for 1 hour, cooled, and poured on ice, and 13 g. of sulphuric acid were slowly added. The ethereal layer was washed, dried with sodium sulphate, and the ether distilled off, leaving a brown oil which deposited crystals of the carbinol on standing. This was recrystallised from ligroin and benzene; m. p. 78—80° (yield, 20%).

Conversion of the carbinol into the chloride. 9 G. of the carbinol and 40 c.c. of dry light petroleum (b. p. 40—60°), in a vessel fitted with a thermometer and a stirrer, were cooled to 4° and 1·4 g. of phosphorus trichloride, dissolved in 10 c.c. of light petroleum, were added drop by drop. The solid was filtered off, washed with sodium bicarbonate solution, and then with water, and dried over sulphuric acid in a vacuum. The chloride melted at 60—62° (yield, 70%). When purified by solution in ether, addition of alcohol, and crystallisation in a vacuum, it had m. p. 67—71°. This purification was wasteful, however, and was found unnecessary.

Rubrene. 2 G. of the chloride together with a trace (2%) of quinoline were heated in an oil-bath at 120° in a test-tube evacuated by a water-pump. After 2 hours, evolution of hydrogen chloride had ceased, and crude rubrene remained. The solid was washed with ether and dissolved in benzene, high-boiling ligroin added, and most of the benzene evaporated off in a vacuum. The red crystals deposited were recrystallised in this way several times (daylight being excluded), the yield of purified rubrene being about 35%. The substance melted quite sharply at about 330° on the surface of molten lead.

Insolation.—The light source was a Hanovia mercury-vapour lamp, the light being condensed and rendered monochromatic with the filters already described (Bowen, J., **1932**, 2236). The rubrene solutions were exposed in parallel-walled quartz cells holding 2—30 c.c., according to the concentration of the solutions. Through the rubrene solutions, oxygen (or air, or oxygen–nitrogen mixtures) was bubbled from a fine jet so that the solution was kept saturated (as shown by the constancy of the reaction rate with the rate of flow of gas). For the colorimetric estimation of the variations of the concentration of the rubrene solutions after exposure, a spectrophotometer was not available. It was found, however, that the extinction coefficients of the solutions varied rapidly enough with wave-length in the yellow region of the spectrum to make measurements of concentration possible from the position of the "edge" of the absorption band as seen in a visual spectrometer.

Exposures were made at the ordinary temperature and at three wave-lengths, **5460**, **4360**, and **3666** Å.; the light absorption of the rubrene solutions was complete down to concentrations of $M/1000$; below this concentration, absorptions were measured with a Pulfrich colorimeter.

The numbers of quanta absorbed in the reactions were estimated by separate exposures using Leighton and Forbes's uranyl sulphate–oxalic acid method (*J. Amer. Chem. Soc.*, **1930**, **52**, 3139). As this method is inapplicable to the green line **5460** Å., determinations for this line were made by comparison of its intensity with that of the **4360** Å. line by means of a thermopile.

The following is a summary of the results (all rubrene concentrations are given in g.-mols./100 l.).

Solutions in Benzene Saturated with Oxygen at 1 *Atm.*

(a) *Variation with light intensity.*

Rubrene concn.	2·0	2·0	0·1	0·1
Light intensity	100	27	100	27
Rate/light intensity	26	27	16·3	15·5

The rate is directly proportional to the light intensity.

(b) *Variation with wave-length.*

		3660	4360	5460
Wave-length, Å.		3660	4360	5460
Quantum efficiency	Rubrene concn. 2·0	0·92	0·95	0·91
	„ „ 0·96	0·97	1·08	1·00

The quantum efficiency is independent of wave-length between these limits.

(c) *Variation with rubrene and oxygen concentration.*

Partial press. of O (atm.) in equilibrium with solutions.

Quantum efficiency.

Rubrene concn.	1·0.		0·2.		0·1.		0·02.	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
2·0	1·04 0·92	0·98	0·95	0·90				
1·53	—	—	1·0	0·87				
1·30	1·0	0·97	1·0	0·86	—	—	0·4	0·38
1·20	1·01	0·96	—	—				
0·85	—	—	0·76	0·80				
0·70	1·0	0·94	0·70	0·77	0·55	0·62	0·4	0·25
0·65	1·09 0·87	0·94	0·70	0·76				
0·32	0·95 0·83	0·88	0·5	0·6				
0·25	0·90	0·85	0·34	0·54				
0·10	0·75 0·71	0·70	—	—				
0·02	0·37	0·32	0·12	0·09				
0·01	0·22	0·19	0·09	0·05				

The points in the fig. show the measured quantum efficiencies of oxidation plotted against the rubrene concentrations.

It seems clear from the results that (*a*) the oxidation is not a chain reaction; (*b*) collisions between normal and excited rubrene molecules do not result in deactivation, since at a rubrene concentration of $2\cdot0 \times 10^{-2}M$ in benzene saturated with oxygen in equilibrium with the air ($1\cdot5 \times 10^{-3}M$-oxygen; Fischer and Pfleiderer, *Z. anorg. Chem.*, **1922**, **124**, 61), the number of collisions of an excited rubrene molecule with normal rubrene molecules is 3×10^9 per sec., while the number of collisions with oxygen molecules is $4\cdot6 \times 10^8$ per sec. (calculated from the gas-collision formulæ; see Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford, **1933**, p. 17), the quantum efficiency, however, being unity.

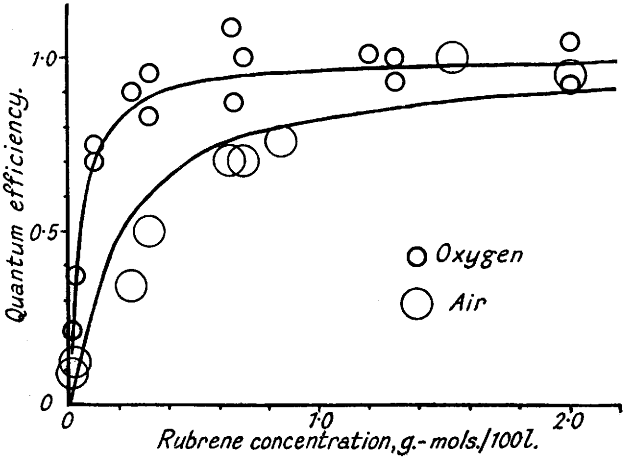
If the concentration range examined had not been below 0·01M, it might have been concluded that the photo-oxidation was simply $R + h\nu \longrightarrow R'$; $R' + O_2 \longrightarrow RO_2$. This, however, does not account for the falling off of quantum efficiency below this concentration. The results are most simply interpreted by the following mechanism :

$$R + h\nu \longrightarrow R' \xrightarrow{k_1} \text{deactivated (by collision with solvent molecules or by fluorescence)}$$

$$R' + O_2 + R \xrightarrow{k_2} RO_2 + R$$

$$\begin{aligned} \text{Rate of formation of } R' &= \text{quanta absorbed per second} \\ &= \text{rate of disappearance of } R' \\ &= k_1[R'] + k_2[R'][R][O_2] \\ \text{Rate of formation of } RO_2 &= k_2[R'][R][O_2] \\ \text{whence, quantum efficiency} &= [R][O_2]/\{k_1/k_2 + [R][O_2]\} \end{aligned}$$

The curves in the fig. are plotted for this equation, k_1/k_2 being taken as 3×10^{-6}, and in the " calculated " columns of the foregoing table are given the quantum efficiencies calculated from this equation. The agreement is within the accuracy of the measurements, which was limited by the method of estimation employed.



If this mechanism is correct, molecules capable of deactivating excited rubrene molecules should exert an inhibitory action by raising k_1 to $[k_1 + k_3$ (inhibitor concentration)].

Table I gives some measurements on solutions of rubrene in different solvents saturated with oxygen at 1 atm., γ being the quantum efficiency.

TABLE I.

Wave-length : 5460 Å.

Solvent.	Rubrene concn.	γ.	Solvent.	Rubrene concn.	γ.
Benzene	1·30	1·0	100 G.-mols. of C_6H_6 + x g.-mols. of x.		
Carbon disulphide	0·74	0·64			
Anisole	0·37	0·53			
Benzaldehyde	0·45	0·38	3 *o*-Nitrophenol	0·8	0·007
Nitrobenzene	0·38	0·006	10 Phenol	0·9	0·82
Aniline	0·34	0·001	Resorcinol (saturated)	1·07	0·88
Quinoline	0·41	0·002	10 Iodobenzene	0·8	0·85
			10 *p*-Toluonitrile	0·8	0·91
			10 Nitromethane	0·7	1·0

It is clear that certain substances exert a marked inhibitory effect, whereas others, *e.g.*, benzaldehyde or phenol, which might be expected to inhibit, hardly do so at all. The rates are very slow in nitrobenzene, quinoline, and aniline, and further experiments, given in Table II, show the effect of addition of these substances to benzene solutions of rubrene.

TABLE II.

Wave-length = 5460 Å.; rubrene concn. = $1·0 \times 10^{-2}$ g.-mol./l.

Solvent : 100 g.-mols. benzene + x g.-mols. inhibitor (saturated with oxygen at 1 atm.).

Inhibitor.	x.	γ, obs.	γ, calc.	Inhibitor.	x.	γ, obs.	γ, calc.
Aniline	1	0·85	0·76	Nitrobenzene	2	0·33	0·33
	2	0·65	0·62		4	0·12	0·19
	3	0·58	0·53		6	0·11	0·14
	4	0·46	0·46	Quinoline	2	0·94	0·87
	10	0·20	0·25		5	0·76	0·76
					10	0·48	0·63

Solvent : 100 g.-mols. benzene + 5 g.-mols. aniline (saturated with oxygen at 1 atm.).

Rubrene concn.	γ, obs.	γ, calc.
1·41	0·50	0·51
0·68	0·31	0·34

The values of γ, calc. in Table II, are obtained from the formula $\gamma = [R][O_2]/\{3 \times 10^{-6} + k_3[I] + [R][O_2]\}$ where [I] is the inhibitor concentration; the specific inhibiting powers (k_3) of nitrobenzene, aniline, and quinoline being $6·0 \times 10^{-4}$, $1·66 \times 10^{-4}$, and $0·27 \times 10^{-4}$ respectively

The above conclusions about the course of the reaction, and also the nature of the molecules which inhibit it, show that the mechanism of inhibition is not, as is often the case in the inhibition of chain oxidations, an oxidation of the inhibiting molecule (cf. Bäckström and Alyea, *J. Amer. Chem. Soc.*, 1929, **51**, 90). Neither can the inhibition be ascribed to compound formation between rubrene and the inhibitor, for the absorption spectra of benzene solutions of rubrene are not appreciably changed by addition of the inhibitor. If the inhibiting action is a specific deactivating effect, it would be expected that the strong fluorescence of rubrene in benzene solution would be destroyed by inhibiting substances. Actually, it was observed that, although very small additions of nitrobenzene and of *o*-nitrophenol destroyed the fluorescence of solutions of rubrene in benzene, yet aniline and quinoline had little or no effect, solutions of rubrene in these liquids fluorescing as brightly as solutions in benzene. Since nitrobenzene and organic bases are powerful inhibitors and phenol is not, it seems possible that a molecule is an inhibitor if it is a " proton acceptor," *i.e.*, the activated rubrene molecule is capable of prototropic change (resulting in deactivation) on collision with such molecules, in the same way as the (unexcited) molecule of nitroamine behaves (cf. Bronsted and Pedersen, *Z. physikal. Chem.*, 1924, **108**, 185). It is hoped that further experiments along these lines may throw light on the chemical nature of the activated, as distinct from the normal, rubrene molecule.

SUMMARY.

1. The photochemical oxidation of rubrene by dissolved oxygen in benzene solution has been shown to depend on a termolecular collision between an activated and a normal rubrene molecule and an oxygen molecule.

2. The reaction is inhibited by certain substances in a manner which suggests that the deactivation is of the nature of a protropic change of the excited molecule.

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[*Received, June 4th*, 1934.]