caproic and nonylic acids, phenol, *p*-toluidine, resorcinol, thymol, camphor and sodium chloride.

2. When a bubble passes through a solution of a simple substance, it carries with it from 2 to 8 times as much of the solute as is predicted by the Gibbs adsorption theorem either in its exact or in its approximate form. The amounts carried are from 2 to 4 times that which can be accommodated in a monomolecular film of closely packed, vertically oriented molecules.

These findings fully substantiate those of McBain and Davies and support the views of McBain and of Hardy as to the constitution of surfaces of ordinary solutions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND OF STANFORD UNIVERSITY]

THE PHOTOCHEMICAL DECOMPOSITION OF BENZOQUINONE IN WATER AND IN ALCOHOL

BY PHILIP ALBERT LEIGHTON AND GEORGE SHANNON FORBES

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Parabenzoquinone, stable in the solid phase, can be photolyzed in alcohol or water solutions. In alcohol the products are acetaldehyde, hydroquinone and a third more complex product.[1] In water hydroquinone and a larger amount of the complex product are formed. Hartley and Leonard[2] found for the complex product approximately the formula of a dimer.

A similar photochemical decomposition of quinone in ether, glycerin, benzaldehyde, acetaldehyde, toluene, carbon tetrachloride and other solvents has been reported.[3]

Hartley and Little[4] made a qualitative study of the quinone photolysis, and a number of measurements of the absorption spectra of quinone solutions have been made[5,2] chiefly with reference to theories of the structure of the quinone "chromophore."

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[1] Ciamician and Silber, *Ber.*, **19**, 2899 (1886); **34**, 1530 (1901).

[2] Hartley and Leonard, *J. Chem. Soc.*, **95**, 34 (1909).

[3] Ciamician and Silber, *Ber.*, **35**, 1080 (1902); **36**, 1575, 4128 (1903); Klinger and Standke, *ibid.*, **24**, 1340 (1891); Klinger, *ibid.*, **19**, 1864 (1886); **24**, 1340 (1891); Klinger and Kolvenbach, *ibid.*, **31**, 1214 (1898).

[4] Hartley and Little, *Proc. Chem. Soc.*, **27**, 137 (1911); *J. Chem. Soc.*, **99**, 1079 (1911).

[5] Hartley, Dobbie and Lander, "British Association Report," **1902**, p. 107; Hartley, *J. Chem. Soc.*, **95**, 52 (1909); Baly and Stewart, *ibid.*, **89**, 506 (1906); Purvis, *ibid.*, **123**, 1841 (1923); Klingstedt, *Compt. rend.*, **176**, **1550** (1923); Lifschitz and collaborators, *Rec. trav. chim.*, **43**, 269, 403, 654 (1924); *Z. Physik*, **38**, 61 (1926); Light, *Z. physik. Chem.*, **122**, 414 (1926); Marchlewskii and Moroz, *Bull. soc. chim.*, **35**, 473 (1924).

The absorption spectrum of quinone between 2000 and 6000 Å. consists of three bands or regions, which Light, from an analysis of the vapor spectrum, holds to be due to different electronic states of excitation.

Lifschitz, from a study of the effect of substitution on the absorption spectrum, attributes the visible band to electrons belonging to the central carbon atoms in the conjugated quinone ring, and the first ultraviolet band to electrons belonging to the oxygen atoms.

We have carried out a critical quantitative study of this photolysis, varying wave length and the several concentrations. A second paper will deal with the effect of temperature and of various substituents.

The light source was a quartz mercury vapor arc designed to combine as fully as possible the long life of large diameter arcs with the high intensity of the constricted arc.[6] The legs of an inverted U, 6 mm. in internal diameter, dipped into mercury reservoirs left open to the atmosphere. A 5-cm. capillary, nearly filled with an iron wire, attached to each arm of the U rendered oscillation negligible. The electrodes were water cooled, and by adjusting the relative heights of water and electrode surface, mercury transfer was neutralized. Running on 3 amperes at 12 volts per cm. the radiation flux could be kept constant within 1% by taking readings once an hour.

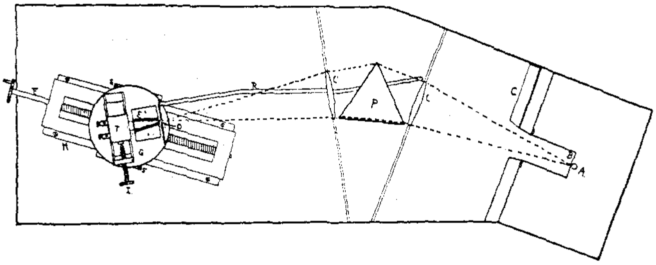

Fig. 1.—The monochromator.

The monochromator, illustrated by Fig. 1, included a fused quartz prism, P, 9.5 cm. along the base and 6.4 cm. high, and two fused quartz lenses, 6.4 cm. in diameter and 25 cm. in focus for λ3030 Å. The lamp A and collimating slit (1.2 by 30 mm.) were fixed with relation to the prism and lenses. The exit slit D (1 by 21.5 mm.) together with trapezoidal cell E and thermopile T were mounted on the table G which could be moved along the focal plane by the screw F and was kept perpendicular to the light beam by the pivoted rod R.

The energy fluxes normally obtained at the exit slit as it was moved along the focal plane were of the following order

Wave length, mm..........	1014	577	435	406	366	313	302	280	270	254
Intensity in ergs./sec. mm.^{2}..	325	910	490	360	900	610	420	100	150	99

The thermopile, constructed by one of us, was of bismuth–silver, with 20 couples. The galvanometer, of sensitivity 14.6 mm. per microvolt, was mounted on a heavy Julius suspension. An energy flux of 1.00 erg./sec. mm.^{2} produced a deflection of 1.5 cm. on a scale 5 meters distant. Shunt and series combinations were necessary for many readings. The thermopile was calibrated with two standard carbon lamps

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[6] Forbes and Harrison, *J. Opt. Soc. Am.*, **11**, 99 (1925); THIS JOURNAL, **47**, 2449 (1925).

C39 and C40 certified by the Bureau of Standards. Experiments showed that the deflection obtained was not linearly proportional to the energy flux, and that it varied with the position of the mirror (that is, the portion of the scale covered). Accordingly, the galvanometer was adjusted so that the low or zero point of the swing always fell at or near the same point on the scale, and the calibration was extended to cover all possible deflections.[7] Three to five readings, using the ballistic method, were taken and averaged for each measurement.

The height of the focal plane slit, D, and the volume of liquid in the cell were so adjusted that the emergent beam as it fell on the thermopile was exactly the height of the sensitive column. Then by moving the thermopile across the beam by means of the screw I, taking readings at 2 mm. intervals, the entire beam was covered and the energy integrated as twice the sum of these readings ($2\Sigma B$) after the method of Villars devised in this Laboratory.[8] These values agreed to within 0.5% with those obtained by taking readings every mm. This method assumes that the thermopile itself integrates correctly the energy falling on it from top to bottom. The thermopile could be substituted for the cell when desired, in order to measure the relative incident intensity. By repeating this process at suitable intervals during an experiment, the integrals of the energy, incident and absorbed, could be built up.

Several absorption cells, differing in depth and volume, were used. They were covered to prevent evaporation, and so that oxygen could be excluded when desired.

In this reaction the photosensitive substance, quinone, is used up in known amount, with the formation of absorbing products. In addition, the solvent itself may absorb. The method devised takes account of these features.

The decomposition of quinone was followed by iodimetry. The calculation of the light absorbed by the undecomposed quinone was complicated through absorption by the solvent and also by the increase in strongly absorbing reaction products.

Ethyl alcohol was purified by the following steps: (1) allowed to stand over calcium oxide, then distilled; (2) 25 cc. of 12 N sulfuric acid added per liter of alcohol, the mixture refluxed several hours, then distilled; (3) 20 g. of potassium hydroxide and 10 g. of silver nitrate added per liter of alcohol, the mixture refluxed and distilled; (4) dried a second time over calcium oxide, this time being filtered before distillation. A one-centimeter layer of this alcohol transmitted 88% of λ2700.

Alcohol purified by addition of iodine[9] was found to fluoresce visibly in the shorter ultraviolet, so this method was not used.

The quinone used was purified by three successive sublimations, using the lowest possible temperature. Quinone was determined by the method of Valeur,[10] that is, adding an excess of hydriodic acid at 0° and titrating the liberated iodine with thiosulfate, using starch indicator, and excluding oxygen by bubbling carbon dioxide or nitrogen through the flask.

The quinone solution to be studied was made up fresh at the start of each experiment, and equal portions were pipetted into two similar cells, one of which was kept in the dark and the other exposed. At first the solution was stirred occasionally with a fine quartz rod during exposure. Later a mechanically driven stirrer was introduced, and all solutions were kept in an atmosphere of nitrogen at all times.

Integrations of emergent energy, $2\Sigma B$, and the corresponding relative incident intensity, ΣF, were made during each experiment on (a) cell plus water, (b) cell plus solvent, (c) cell plus solution before exposure and (d) cell plus solution after exposure.

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[7] G. S. Forbes, *J. Phys. Chem.*, **32**, 481 (1928).

[8] Villars, THIS JOURNAL, **49**, 330 (1927).

[9] Henri and Castille, *Bull. soc. chim. biol.*, **6**, 299 (1924).

[10] Valeur, *Ann. Chem.*, **21**, 470 (1900).

Also, F readings were made at intervals during the exposure. The time which the solution was exposed in obtaining the energy readings was added to the time of the main exposure. The variation in intensity across the beam as well as from front to back of the cell makes necessary the unreserved assumption of the reciprocity law.

The corrections for reflection by the quartz faces were applied as in the work of Villars,[8] taking account both of the change in n with wave length and of the small deviation from normal incidence of the edges of the beam.

If we let $\Sigma F_{H_2O}/\Sigma B_{H_2O} = K$, it can be shown readily that the reflection correction cancels out and for any absorbing solution the fraction of the light transmitted, compared with the transmission of pure water as 1.00, is

$$L = \frac{\Sigma B_{\text{soln.}}}{\Sigma F_{\text{soln.}}} \times K \qquad (1)$$

From the laws of Lambert and Beer it can be shown[11] that

$$Q = (1 - L)\frac{\log L - \log I}{\log L} \qquad (2)$$

and

$$Q' = (1 - L')\frac{y(\log L - \log I)}{\log L'} \qquad (3)$$

where Q and Q' are the calculated fraction of light absorbed by the quinone only, before and after the reaction, respectively; L and L' are as defined above for the solution before and after the reaction, respectively. As several different cells were used, these values cannot be compared without additional data not included here. I is the light transmitted by pure solvent compared with that transmitted by water as 1; y is the fraction of the original quinone remaining after the exposure.

Lacking a mathematical integration which would give the fraction, Q_m, of the total incident energy of the exposure which was absorbed by the quinone alone, we found by experiment that

$$Q_m = \sqrt{QQ'} \qquad (4)$$

very nearly. The total incident energy in ergs incident on the solution during the entire exposure is given by

$$E_{\text{total}} = \frac{2(\Sigma F_{\text{av}} S)}{(1 - r)K} \qquad (5)$$

where ΣF_{av} is the average between each two successive F readings taken during exposure; S is the exposure in seconds between those same two readings; r is the fraction of the incident light reflected by a quartz wall (both faces).

In calculating ergs absorbed by the quinone from this, a small correction is made for the light reflected back into the solution from the rear face. The mean fraction so reflected is given nearly enough by 0.056 × $(L + L')/2$.

[11] Luther and Weigert, *Z. physik. Chem.*, **53**, 408 (1905).

Assuming that the same fraction, Q_m, is absorbed as was absorbed in its first passage through the solution, we obtain

$$\text{Total ergs absorbed by quinone alone} = E_{\text{total}}\, Q_m\, [1 + 0.028(L + L')] \qquad (6)$$

From this the photochemical efficiency

$$\Phi = \frac{\text{Molecules reduced}}{\text{Quanta absorbed}} = \frac{Nh\nu\ Vx}{1000Q_m\ [1 + 0.028\ (L + L')]E_{\text{total}}} \qquad (7)$$

where V is volume of reaction mixture in cc., and x is molal concentration of quinone disappearing during exposure. Now setting A equal to the original molal concentration of quinone, i = absorption coefficient of solvent, q = absorption coefficient of quinone, p = absorption coefficient of products (all absorption coefficients given are exponents of the base ten), d = length of path of light beam in cell, in cm., and $E_{\text{total}} = E_0S$, where E_0 is incident intensity in ergs/sec. Equations 1–7 give the following general equation for Φ.

$$\Phi = \frac{Nh\nu\ Vx}{1000E_0Sq\sqrt{\dfrac{(1 - 10^{-(jc + qA)d})\ (1 - 10^{-(ic + q(A-x) + px)d})\ (A - x)A}{[ic + qA]\ [ic + q(A - x) + px]}}}$$

In the shorter wave lengths water itself becomes an appreciable absorbent.[12] This affects both absorption coefficients and absolute energy measurements. The absorption coefficients of quinone for those wave lengths were so much greater than those of water that the correction was inappreciable, but the absolute energy measurements, being taken as the light *transmitted* by pure water, were in error by the amount which the water absorbed. Accordingly, E_{total} was multiplied by the following factors, calculated from Kreusler's data

λ	1.06-cm. cell	3.27-cm. cell
2537	1.029	1.093
2700	1.025	1.078

Any hydroquinone formed by the reaction combines with more quinone to form quinhydrone. The method of calculating classes absorption by quinhydrone with that of the products and disregards the possible removal of quinone as quinhydrone. Assuming that quinone so removed is rendered completely inactive, that all the quinone reduced goes to form hydroquinone, and using the dissociation constant of Luther and Leubner[13] for quinhydrone, it is found that the calculated values for quantum efficiency would be from 1 to 5% too low, depending on the amount of quinone reduced.

We constructed a quartz spectrograph of 60 cm. focal length, and obtained upon each plate used spectrograms of the light transmitted by our absorption cells with and without solute. The characteristic curve of

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[12] Kreusler, *Ann. Physik*, **6**, 421 (1901).

[13] Luther and Leubner, *J. prakt. Chem.*, **85**, 314 (1922).

each of these plates was derived from additional spectrograms made upon it with calibrated blackened wire screens in constant irregular motion. The plates were measured up by using a photometer similar to one described by Harrison but constructed by us. We are grateful for valuable suggestions offered by Professor Harrison during the measurements. Absorption coefficients were in good agreement. The absorption coefficients of potassium nitrate solutions measured on our monochromator agreed within experimental errors with those obtained by von Halban and Ebert,[14] thus checking our procedure.

Experimental Results

1. **Preliminary.**—The velocity of the dark reaction is indicated by Table I. In alcohol solution, λ3660 is much more strongly absorbed by the products than any other wave length. Addition of 5% hydroquinone actually decreased the absorption of λ3660 by about 2%, so the increase cannot be due to quinhydrone formation.

TABLE I

DARK REACTION

	Relative oxidizing power				Light absorbed, %		
Time, min.	In alcohol		In water	Time, min.	In alcohol		In water
	25°	0°	25°		λ4350	λ3660	λ3660
0	100	100	100	0	85	42	42
30	94	100	100	10	85	56	42
60	90	100	100	30	85.5	90	42
120	82	99	100	60	87	98	42
1440	..	..	100.5	120	88	100	42
			...	1500	97	...	50

TABLE II

TEMPERATURE COEFFICIENT OF DARK REACTION

	Period 20–30°
Calcd. from slope of dx/dt curve	2.8
Calcd. from k for 1st order reaction	3.0
Calcd. from k for 2nd order reaction	2.9

Measurements of the dark reaction velocity were also made at 20 and 30°, and the temperature coefficient of the velocity calculated (Table II). Assuming $\Delta k_{10^\circ} = 2.9$ for the interval 20–30°, the corresponding activation energy (using Arrhenius' equation) is 18,750 cal. This does not correspond to any of the vibrational periods in the band spectrum as analyzed by Light.[5]

The effects of dissolved substances on the reaction velocity are summarized in Table III. Oxygen retards the light reaction rate slightly in water, more in alcohol. Acids greatly retard the light reaction in water, but accelerate it slightly in alcohol. The dark reaction is much accelerated in alkaline solutions, but the light reaction is retarded.

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[14] Von Halban and Ebert, *Z. physik. Chem.*, **112**, 331 (1924).

TABLE III

EFFECT OF DISSOLVED SUBSTANCES

Dissolved substance	Percentage decomposed, time constant Water in light	Alcohol In light	In dark	Difference
None (N_2)	27.0	29	0.8	28
Satd. O_2	24.5	17	.6	16
0.012 *M* H_2SO_4	13.0	31	.0	31
.012 *M* H_3PO_4	..	32	.5	32
.012 *M* HCl	2.0	38	4.0	34
.012 *M* NaCl	8.0	..	..	..
.012 *M* Na_2SO_4	21.0	..	..	..
.012 *M* $NaC_2H_3O_2$	..	38	11.0	27
.012 *M* NaOH	..	81	70	11

As the products of the dark reaction absorb much of the light, it may be that the actual light reaction is not affected by alkali.

The data in Table IV indicate that quinone is the absorbent sensitive to light, and that the alcohol and the reaction products are "dark" absorbents; also that the reaction proceeds at a constant rate with respect to time.

TABLE IV

EXPERIMENTAL DATA

	Time, min.	Quinone concn., *N*	Alcohol, %	Percentage reduced by light
Quinone concn. changed	10	0.251	50	2.1
	10	.100	50	7.2
	10	.020	50	15
	10	.004	50	28
Alcohol concn. changed	10	.016	3.3	26
	10	.016	16.5	27
	10	.016	33	29
	10	.016	50	27
	10	.016	65	25
	10	.016	80	23
	10	.016	98	21
Time changed	5	.005	50	2.1
	10	.005	50	4.2
	15	.005	50	6.2
	20	.005	50	8
	25	.005	50	11
	30	.005	50	13
	35	.005	50	15

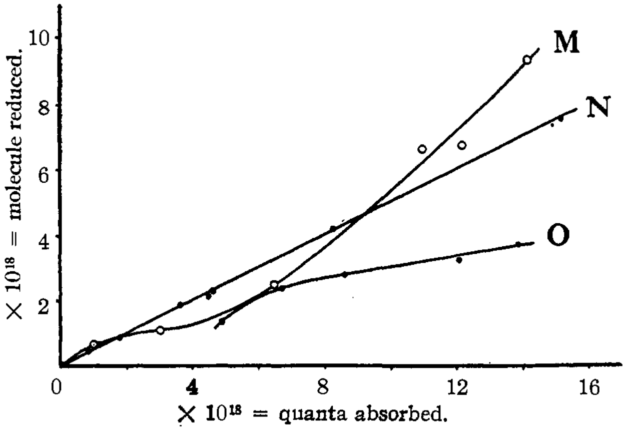
2. **Quantitative Measurements in Pure Water.**—See Table V and Graph 1. The presence of an induction period is indicated by Graph 1. The slope of the curves at any point represents the quantum efficiency, Φ, at that point. Removal of oxygen increases the reaction rate evenly over the entire range. One run only at 17° and one at 19°, compared with analogous runs at 25°, show a temperature coefficient of $\Delta k_{10^\circ} = 1.03 \pm 0.08$. This point is being further investigated.

Table V

Results in Pure Water (at 25° except as Noted)

λ	Quinone concn.	Reduced, %	L	L'	Q_m	Molecules reduced $\times 10^{-18}$	Quanta absorbed $\times 10^{-18}$	Φ
4350	0.010	7.5	0.218	0.042	0.578	2.34	6.7	0.35
	.005	8.65	.495	.136	.374	1.35	4.9	.27
	.005	17.4	.500	.027	.281	2.72	8.6	.31
	.005	23.4	.500	.007	.224	3.65	13.9	.26
	.005	20.5	.500	.007	.226	3.20	12.1	.26
3660	.010	6.1	.460	.078	.375	1.93	3.5	.56
	.010	9.0	.416	.058	.405	2.84	5.0	.56
	.010	5.5	.452	.098	.402	1.71	3.9	.44
	.010	4.5	.500	.168	.392	1.42	3.2	.43
	.010	7.5	.470	.150	.404	2.28	3.3	.69
	.010	8.6	.448	.017	.312	2.70	8.1	.33
	.010	15.9	.460	.00025	.180	5.21	12.2	.43
	.010	25.2	.460	0	.125	7.85	15.4	.51
	.005	8.0	.664	.246	.260	1.25	2.3	.54
	.0025	9.6	.774	.541	.200	0.750	1.4	.55
	.0025	12.2	.812	.473	.156	.925	1.2	.77
	.0010	7.9	.911	.765	.0822	.246	0.44	.56
2700	.0010	10.0	.0239	.0091	.833	.308	0.57	.54
2537	.0050	4.3	...	..	.97	.67	1.22	.55
	.0025	0.85	...	..	.99	.066	0.10	.66
	.0025	1.4	...	..	.99	.109	0.30	.36
	.0025	3.15	...	..	.975	.245	0.65	.38
	.0025	8.5	...	..	.94	.663	1.10	.61
	.0025	12.0	...	..	.92	.93	1.42	.66
	.0010	9.4	...	..	.94	.30	0.49	.61

In one experiment the exposure was allowed to proceed long enough to have received the full effect of the inhibition, then interrupted for fifteen



M, Water, λ2537; N, alcohol; O, water, λ4350.

Graph 1.—Comparison of reaction rate in water and alcohol.

hours and continued. The result was exactly the same as obtained with an uninterrupted exposure, showing that the cause of the inhibition is something inherent in the solution.

3. **Quantitative Measurements in 50% Ethyl Alcohol.**—Shown in Table VI. As indicated by Graph 1, the induction period found with water has disappeared. For all runs made in air the quantum efficiency decreases as the percentage of quinone reduced increases, and it becomes necessary to extrapolate back to zero reduction to get a true value of Φ. When oxygen was excluded, Φ was within limits of error independent of the amount reduced. The efficiency is also independent, within the range measured, of the original quinone concentration, and for wave lengths from 4350 to 2537 Å., independent of the wave length. Over this region Φ (extrapolated back to zero reaction for those experiments in air) averages, within limits of error, very close to 0.50. A definite threshold region is indicated by the decrease in efficiency above 4350 Å.

TABLE VI

RESULTS IN 50% ETHYL ALCOHOL (AT 25°)

λ	Quinone concn.	Reduced, %	L	L'	Q_m	Molecules reduced	Quanta absorbed $\times 10^{-18}$	Atm.	Φ
5770	0.010	2.4	0.528	0.561	0.401	8.6×10^{17}	19.0	Air	0.045
5460	.010	7.2	.385	.363	.598	1.36×10^{18}	6.93	N_2	.20
4350	.010	10.8	.149	.095	.734	3.37×10^{18}	6.94	Air	.49
	.010	16.2	.145	.033	.612	5.05×10^{18}	14.8	Air	.34
	.010	28.7	.145	.028	.558	8.95×10^{18}	29.7	Air	.30
	.005	14.0	.277	.170	.599	2.18×10^{18}	4.84	Air	.45
	.005	18.6	.420	.325	.496	2.90×10^{18}	6.11	Air	.48
	.005	20.5	.477	.413	.464	3.92×10^{18}	7.68	N_2	.51
	.005	29.0	.200	.144	.698	4.53×10^{18}	9.30	Air	.49
	.025	12.1	.598	.566	.354	0.94×10^{18}	1.85	Air	.51
	.025	21.1	.618	.542	.312	1.65×10^{18}	3.64	Air	.45
	.025	43.5	.594	.448	.273	3.39×10^{18}	10.66	Air	.37
	.001	8.0	.762	.774	.170	0.188×10^{18}	0.386	Air	.49
	.001	9.4	.799	.765	.168	0.293×10^{18}	0.651	Air	.45
3130	.005	6.5	.0151	.0125	.932	0.985×10^{18}	1.97	N_2	.50
	.005	8.1	...	...	.92	0.75×10^{18}	1.53	Air	.49
	.005	27.6	.0172	.0077	.77	4.18×10^{18}	8.68	N_2	.48
	.0025	15.2	.0038	.00175	.84	1.35×10^{18}	3.5	Air	.39
3020	.010	8.0	.00072	.00018	.86	3.1×10^{18}	6.5	Air	.48
	.005	3.0	.0010	.0004	.91	0.54×10^{18}	1.4	Air	.39
2700	.010	3.7	.0034	.0020	.90	1.4×10^{18}	2.35	Air	.60
2537	.005	4.3	...	...	.98	0.77×10^{18}	1.40	N_2	.55

4. **Quantitative Measurements in Absolute Ethyl Alcohol.**—Shown in Table VII. All were made in an atmosphere of nitrogen. As with 50% alcohol, the quantum efficiency is independent of wave length below λ4350 Å. The average for this region is 0.49. It drops off in λ5460, exactly as in 50% alcohol. The probable error of a single determination is ±0.05.

Table VII

Results in 100% Ethyl Alcohol (at 23° except as Noted)

Quinone concn., 0.005 *M*. Oxygen excluded

λ	Reduced, %	*L*	*L'*	Q_m	Molecules reduced $\times 10^{-18}$	Quanta absorbed $\times 10^{-18}$	Φ
5460	6.5	0.377	0.330	0.598	1.24	5.40	0.230
4350	4.6	.552	.483	.438	0.879	1.88	.467
	11.6	.593	.541	.446	2.22	4.98	.446
3660	2.4	.845	.709	.152	0.458	0.842	.544
	11.2	.790	.429	.178	2.15	4.21	.510
3130	9.6	.0031	.0017	.904	1.83	3.65	.502
2700	4.6	.0085	.00735	.930	0.879	1.85	.475
	21.6	.00848	.00370	.793	4.13	8.29	.598

Discussion

The reaction in water differs from the reaction in alcohol. In water, at the start, when the inhibitive effect is a maximum, light produces little reduction of the quinone, yet the absorption coefficient of the solution increases sharply, showing that some change, not detectable by our method of analysis, is occurring.[2] The increase in absorption during the induction may be due to formation of the dimer postulated by Hartley and Leonard.[2]

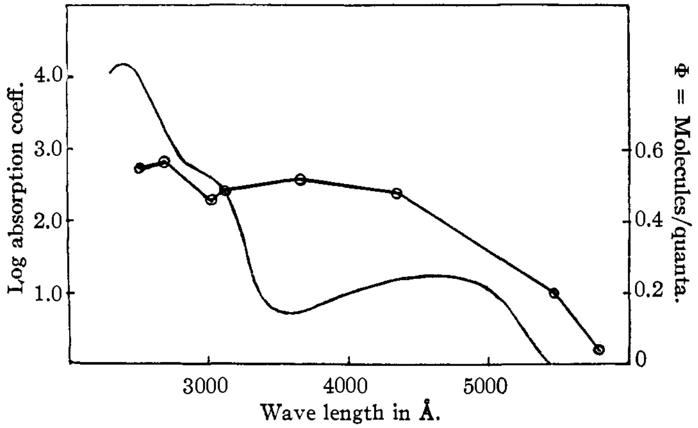
Beyond the induction period, the efficiency, as indicated by the slopes in Graph 1, becomes constant at about 0.16 for λ4350 and 0.9 for λ3660 and 2537. This indicates either a change in efficiency with wave length or else a threshold between λ3660 and 4350. In alcohol solutions the threshold is definitely between λ4350 and 5460, that is, it is displaced toward longer wave lengths by addition of alcohol.

In this regard, Light,[5] in the vapor spectrum, observed a disappearance of fine structure at about λ3100, which is in the second absorption band (attributed to oxygen electrons). According to the ideas developed by Henri this indicates a predissociation or activation which in the presence of a suitable acceptor can produce photochemical reaction. In both water and alcohol solutions, the point at which the molecule becomes sufficiently activated to react is displaced toward longer wave lengths, in fact, into the first absorption band. Light's measurements indicate an incipient disappearance of fine structure at about λ4500 in the first absorption band, which apparently corresponds with the photochemical threshold in alcohol solutions.

It becomes of interest to compare the photochemical efficiency at different wave lengths with the absorption spectrum in absolute alcohol,[5] (Graph 2). The threshold is clearly inside the first absorption band. The efficiency reaches its constant value (within limits of error) at λ4350 *and remains at this value into and clear through the second absorption band.*

These two bands probably represent absorption in two parts of the molecule, certainly two different electronic excited states, yet the quantum efficiency of the reaction produced is the same throughout.

The value of 0.5 for the efficiency recalls Weigert's[15] explanation of the same yield for nitrobenzaldehyde as due to the necessity for a proper orientation of the molecule with respect to the incident light before an effective absorption is produced. This explanation can be applied to quinone if one assumes the superoxide formula.



Graph 2.

However, the results can be explained equally well by assuming that every absorbed quantum is effective in producing activation, and that a 50% efficient secondary reaction is responsible for the observed yields. The quantum efficiencies in water solution, and the effect of dissolved substances on reaction rate, favor this latter explanation.

Summary

The photochemical decomposition of benzoquinone in water and alcohol solutions has been quantitatively investigated.

The reaction in water, as measured by amount of quinone reduced, shows an induction period, which disappears in alcohol solutions.

Evidence is shown of a threshold in the first absorption band, lying toward longer wave lengths in alcohol, toward shorter in water. Inside the threshold the photochemical efficiency is independent of wave length throughout the remainder of the first and the whole of the second absorption bands.

In alcohol the efficiency is independent of quinone concentration, and averages 0.5 at 25°. The temperature coefficient, Δk_{10°, is near unity for the reaction in water.

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[15] Weigert and Brodmann, *Trans. Faraday Soc.*, **21**, 453 (1925).