The red sulfide is readily soluble in solutions of alkali hydroxides or sulfides, forming deep red solutions, from which the addition of alcohol causes the separation of red, viscous liquids. The sulfide is slowly oxidized in air at 350°, and rapidly at higher temperatures, forming GeO_2 and SO_2. When heated to about 150° in hydrogen chloride, germanium chloroform and hydrogen sulfide are formed. Chlorine attacks the sulfide at room temperature forming $GeCl_4$ and chlorides of sulfur.

Crystalline Germanium Monosulfide.—When red, amorphous germanium monosulfide is held at 450° in an atmosphere of nitrogen, it changes in a few hours to the black crystalline form described by Dennis and Joseph.[6] The substance is slowly oxidized by an ammoniacal solution of hydrogen peroxide and also by chlorine water or potassium permanganate. It begins to sublime in nitrogen at 430°, and melts at 625°. Its specific gravity is d_4^{20} 3.78.

Summary

This article describes the preparation and properties of hydrous and anhydrous germanium monoxide, and of amorphous and crystalline germanium monosulfide.

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THE EFFECTS OF SUBSTITUENTS ON QUANTUM EFFICIENCY IN THE QUINONE-ALCOHOL REACTION

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The average of over twenty determinations[1] of quantum efficiency for the photochemical reaction between benzoquinone and ethyl alcohol in the wave length region λ4350–2537 Å. yields the figure 0.502. In other words, for every quinone molecule decomposed, two quanta are absorbed. The nearness of this ratio to one-half immediately raises interest as to its source.

Weigert and Brodmann[2] explained a quantum efficiency of one-half in the nitrobenzaldehyde photolysis as due to the different possible orientations of the absorbing molecules with respect to the electric vector of the incident light, by which statistically only one-half of the absorbed light could be effective in producing activation and subsequent chemical change.

By assuming a superoxide structure for quinone, the same explanation can be applied to the observed quantum efficiency in the quinone reaction. However, as was pointed out, the results can also be explained by assuming that every absorbed quantum is effective in producing activation, and that a 50% efficient secondary reaction is responsible for the observed yields.

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[1] Leighton and Forbes, THIS JOURNAL, **51**, 3549 (1929).

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

Changes in quinone concentration throw no light on this question, the alcohol being present in such excess that the reaction is pseudomonomolecular, and the quantum efficiency hence independent of concentration within measurable limits. Very low concentrations of alcohol and quinone in a neutral solvent might be used to gain evidence on this point, but a simpler method offers itself in the possibility of substituting heavy groups in the quinone molecule. If the quantum efficiency of one-half is inherent in the process of absorption and activation of molecules of the nitrobenzaldehyde and quinone type, substituents should not affect it; but if a secondary reaction, involving collisions with a low probability of effectiveness, is responsible, substituents should offer a steric hindrance to the reaction, with a resultant change in quantum yield.

We have investigated, therefore, the effects of substitution in a series of chloro and aliphatic substituted quinones.

Apparatus and Materials

The monochromator described earlier was used,[1] with the addition between the front slit and the collimating lens of a quartz–water cell to cut down infra-red radiation. In this cell could be placed Corning glass filter combinations, which were used to increase the purity of those mercury arc lines lying in the visible region. For example, the separation of λ5460 from λ5770, imperfect with the monochromator alone or with filters alone, is almost complete with the combination of monochromator and filters.

The experimental procedure and method of calculation employed were the same as described.[1] Some trouble was experienced with the analysis in the case of the alkyl substituted quinones, but this was overcome by using more concentrated hydrogen iodide solutions and by titrating dark and exposed samples simultaneously.

Monochloroquinone was prepared by the oxidation of monochlorohydroquinone with dichromic acid.[3]

Dichloroquinone was prepared by the oxidation of symmetrical trichlorophenol with chromic acid.[4]

Toluquinone was prepared by oxidizing *o*-toluidine with manganese dioxide under steam distillation.[5]

Chloranil and thymoquinone were obtained commercially. All the quinones were carefully purified by successive sublimation before use.

Experimental

Measurements of the amount of quinone disappearing during the exposure and of the number of ergs of monochromatic energy absorbed by the quinone itself were used in calculating quantum efficiencies. All experi-

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[3] Den Hollander, *Rec. trav. chim.*, **39**, 481 (1920); Clark, *Am. Chem. J.*, **14**, 571 (1892).

[4] Kehrmann and Tiesler, *J. prakt. Chem.*, [2] **40**, 481 (1889).

[5] Clark, *Am. Chem. J.*, **14**, 565 (1892).

ments were performed at 25°. Solutions were 0.005 *M* in absolute alcohol except that for chloranil an 0.0025 *M* solution was used. The solutions were kept under pure nitrogen at all times.

Alcoholic quinone solutions, especially those of the chloro-substituted quinones, decompose slowly in the dark, the average amount of decomposition being shown in Table I.

TABLE I

DARK REACTION (25°)

	Time, sec.	% Decomposed	Time, sec.	% Decomposed
Monochloroquinone	5660	1.0	10036	2.0
			15310	3.0
Dichloroquinone	4992	1.5	1926	1.0
Chloranil	6105	2.5		

The rate of the dark reaction apparently increases with amount of chlorine substitution.

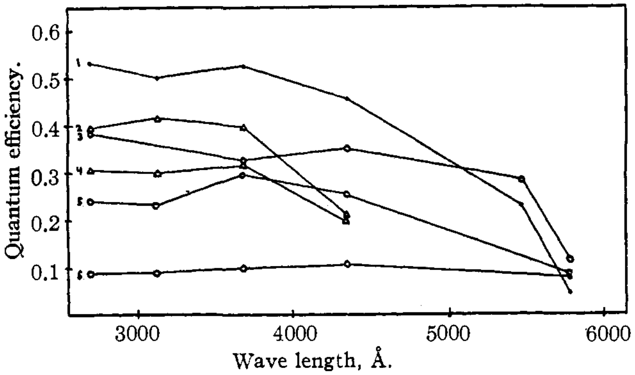

Fig. 1.—Relation between quantum efficiency and wave length. Circles represent chloroquinones; triangles, alkylquinones. 1, Benzoquinone; 2, toluquinone; 3, monochloroquinone; 4, thymoquinone; 5, dichloroquinone; 6, tetrachloroquinone.

Error from the dark reaction was avoided by always pipetting equal portions of solution into two similar cells, one being kept in the dark while the other was exposed, and both being analyzed simultaneously. Light reaction was then taken as the difference between dark reaction and total reaction.

In Table II, Q_m represents the fraction of the total incident energy of the entire exposure which was absorbed by the quinone alone,[1] and Φ represents the quantum efficiency, molecules/quanta. The individual values of Φ possess, in general, a probable error of ±10 to 15%.

Discussion

The quantum efficiencies are summarized in Table III, and compared on Graph 1.

Three points are to be observed. (1) For each quinone there is a region in which the efficiency of the reaction is, within limits of error, independent of the wave length. At longer wave lengths, however, for every quinone except chloranil there is a region in which the efficiency drops off rapidly. In other words, every quinone shows a threshold region below which the quantum efficiency is independent of wave length.

(2) This threshold region varies from one quinone to another—moving toward longer wave lengths with increasing chlorine substitution and toward shorter wave lengths with alkyl substitution. The oxidation potentials of the quinones are shifted in a similar manner, as shown by the following comparison.

Quinone	Oxidation potential[6]	Approximate threshold region, Å.
Thymoquinone	0.5875	λ4000–4350
Toluquinone	.6454	4000–4350
Benzoquinone	.6990	4350–5000
Monochloroquinone	.7125	*circa* 5000
Dichloroquinone	.7220	*circa* 5000
Tetrachloroquinone	...	5770

TABLE II

(a) MONOCHLOROQUINONE, $C_6H_3ClO_2$

λ	% Reduced	Q_m	Quanta absorbed	Molecules reduced	Φ
5770	3.70	0.016	4.88×10^{18}	5.61×10^{17}	0.115
5460	0.90	.042	4.80×10^{17}	1.36×10^{17}	.284
4350	6.6	.168	3.05×10^{18}	1.07×10^{18}	.350
3660	14.4	.564	7.03×10^{18}	2.33×10^{18}	.326
2700	13.8	1.0	5.80×10^{18}	2.27×10^{18}	.385

(b) DICHLOROQUINONE, $C_6H_2Cl_2O_2$

λ	% Reduced	Q_m	Quanta absorbed	Molecules reduced	Φ
5770	2.0	0.060	3.54×10^{18}	3.03×10^{17}	0.086
4350	14.2	.611	5.74×10^{18}	1.45×10^{18}	.253
3660	10.5	.729	5.35×10^{18}	1.59×10^{18}	.297
3130	13.5	.783	9.24×10^{18}	2.19×10^{18}	.234
2700	19.3	.905	6.07×10^{18}	1.46×10^{18}	.241

(c) CHLORANIL, $C_6Cl_4O_2$

λ	% Reduced	Q_m	Quanta absorbed	Molecules reduced	Φ
5770	9.7	0.050	8.94×10^{18}	7.35×10^{17}	0.082
4350	3.6	.488	2.54×10^{18}	2.72×10^{17}	.106
3660	8.8	.676	7.22×10^{18}	7.13×10^{17}	.098
3130	5.4	.831	4.61×10^{18}	4.09×10^{17}	.089
2700	8.0	1.0	7.36×10^{18}	6.48×10^{17}	.088

(d) TOLUQUINONE, $C_6H_3(CH_3)O_2$

λ	% Reduced	Q_m	Quanta absorbed	Molecules reduced	Φ
4350	12.4	0.550	1.26×10^{19}	2.64×10^{18}	0.210
3660	14.4	.650	5.51×10^{18}	2.18×10^{18}	.396
3130	28.3	.870	1.03×10^{19}	4.29×10^{18}	.417
2700	20.6	.872	7.92×10^{18}	3.13×10^{18}	.395

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[6] La Mer and Baker, THIS JOURNAL, **44**, 1960 (1922); Conant and Fieser, *ibid.*, **45**, 2208 (1923).

TABLE II (*Concluded*)

(e) THYMOQUINONE, $C_6H_2(CH_3)(C_3H_7)O_2$

λ	% Reduced	Q_m	Quanta absorbed	Molecules reduced	Φ
4350	19.0	0.680	1.45×10^{19}	2.88×10^{18}	0.198
3660	21.8	.742	1.03×10^{19}	3.30×10^{18}	.320
3130	21.2	.915	1.08×10^{19}	3.21×10^{18}	.300
2700	15.8	.90	7.81×10^{18}	2.39×10^{18}	.307

TABLE III

SUMMARY OF QUANTUM EFFICIENCIES

Quinone	Mol. wt.	Φ at following wave lengths 5770	5460	4350	3660	3130	2700	Mean of quantum efficiency in constant region
Benzo	108	0.045	0.230	0.457	0.527	0.502	0.536	0.505
Tolu	122	..	..	.210	.396	.417	.395	.403
Monochloro	142.5	.115	.284	.350	.326	..	.385	.354
Thymo	164	..	..	.198	.320	.300	.307	.309
Dichloro	177	.086	..	.253	.297	.234	.241	.256
Tetrachloro	246	.082	..	.106	.098	.089	.088	.095

The oxidation potential indicates an increase in the activity of the quinones as one goes from thymoquinone to the chloroquinones. The threshold region, in shifting toward longer wave lengths, indicates for the same progression a decrease in the amount of energy needed to activate the molecule. The two effects are entirely in accord—the more active quinones require less energy for activation.

(3) The value of the quantum efficiency below the threshold (in the region where it is independent of wave length) also varies from one quinone to another. Here, however, the effect appears to be independent of the chemical nature of the substituting groups. *It is a function only of their mass.* This is brought out by comparing the mean quantum efficiency in the constant region with the molecular weight of the quinone (graph 2).[7]

We believe this to be purely a space effect. The effect on the threshold region shows that substitution influences the energy needed to activate the molecule. Once activated, its fate is determined by the probability of a reaction-producing collision with an alcohol molecule. This may be represented by the reaction scheme

$$\text{Quinone} + h\nu \longrightarrow \text{Quinone}' \qquad (1)$$

$$\text{Quinone}' \longrightarrow \text{Quinone} + \text{energy} \qquad (2)$$

$$\text{Quinone}' + \text{alcohol} \longrightarrow \text{Hydroquinone} + \text{aldehyde} \qquad (3)$$

The quantum efficiency then is determined by the relative probabilities of Reactions 2 and 3. The larger and heavier the molecule, the smaller the probability of a suitable collision, or, the smaller the relative proba-

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[7] It is to be noted that the alkyl quinones both deviate from the curve connecting the chloroquinones and benzoquinone. As this deviation lies just on the limits of experimental error, we cannot say that it is real.

bility of Reaction 3 compared with Reaction 2. The chemical nature of the substituting groups is without effect.

On this basis, the nearness of the quantum efficiency to one-half for benzoquinone can only be regarded as fortuitous, and the mechanism proposed by Weigert does not apply. Weight is added to this conclusion by the observation that in acid solutions the reaction rate is increased as much as 20%.

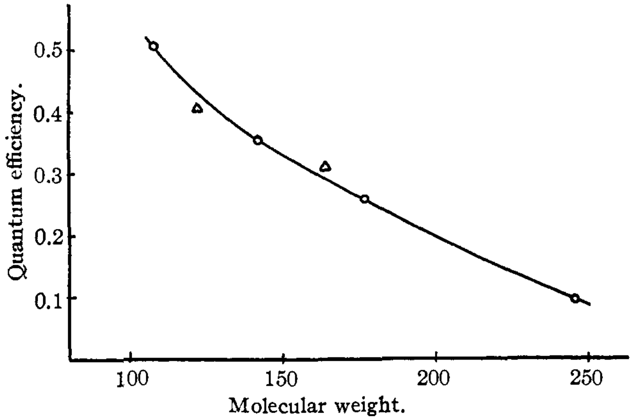

Fig. 2.—Showing relationship between quantum efficiency and the molecular weight of the quinone used. Circles are for chloro-substituted, triangles for alkyl-substituted, quinones.

Further measurements are in progress to determine whether the effects described here apply to other photochemical reactions. If found to be general, we believe these effects will give a valuable insight into the phenomenon of "steric hindrance" in chemical reactions. By the photochemical method of study it might be possible to separate pure space effects from those specific effects arising from the chemical nature of the substituents.

Summary

1. The quantum efficiencies of the photochemical decomposition of five chloro and alkyl substituted quinones in alcoholic solutions have been measured between λ2700 and λ5770 Å.

2. For each quinone, a threshold region, below which the efficiency is independent of the wave length, is observed.

3. Substituents which increase the oxidation potential of the quinone shift the threshold toward longer wave lengths and *vice versa*.

4. Substitution decreases the quantum efficiency as the mass of the molecule is increased, irrespective of the chemical nature of the substituents.

5. The specific effects on the threshold and the general effects on the efficiency are sharply differentiated. The first is ascribed to changes

produced by substitution on the energy of activation of quinone. The second is ascribed to a "steric hindrance" affecting the probability of reaction of the activated molecule.

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THE SENSITIZED PHOTOSYNTHESIS OF CARBON DIOXIDE AT LOW CHLORINE PRESSURES

BY G. K. ROLLEFSON

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In studying the photosynthesis of phosgene, Chapman and Gee[1] found that oxygen had an inhibiting effect on the reaction. Later Bodenstein[2] showed that the concentration of the oxygen did not remain constant during the reaction, but decreased, due to the formation of carbon dioxide. Schumacher,[3] in a more extensive investigation, found that at high oxygen pressures the phosgene formation was so small that it could be neglected for chlorine pressures below 50 mm. In this case the oxygen and carbon monoxide reacted to form carbon dioxide, the rate law being

$$\frac{d(CO_2)}{dt} = kI_{abs.}^{0.71}\ (CO)^{1/2}$$

or for small absorption of light

$$\frac{d(CO_2)}{dt} = kI_0^{0.71}\ (Cl_2)^{0.71}\ (CO)^{1/2}$$

where I_0 is the intensity of the incident light. The exponent, 0.71, for the light absorbed suggests at once that the conditions were probably such that two parallel reactions were involved, one being proportional to the first power of the light absorbed, the other to the square root. A case of this type was shown to exist in the photosynthesis of hydrobromic acid.[4,5] That reaction followed the square root law at high pressures and the first power at low pressures. It seemed not unreasonable to think that in the sensitized formation of carbon dioxide a similar behavior should be found so that at high pressures of chlorine the square root of the light absorbed would appear in the rate law and at low pressures the first power. In both reactions the explanation of this behavior would be the same, *i. e.*, the destruction of the halogen atoms by first order reactions such as collisions with the walls of the reaction vessel or with impurities predominates at low pressures, whereas the recombination in the gas phase is of greater importance at high pressures.

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[1] Chapman and Gee, *J. Chem. Soc.*, **99**, 1726 (1911).

[2] Bodenstein, *Sitzb. preuss. Akad. Wiss.*, **13**, 104 (1926).

[3] Schumacher, *Z. physik. Chem.*, **129**, 241 (1927).

[4] Briers and Chapman, *J. Chem. Soc.*, **130**, 1802 (1928).

[5] Jost and Jung, *Z. physik. Chem.*, **B3**, 83 (1929).