

THE PHOTOLYSIS OF CHLORANIL IN ALCOHOLS

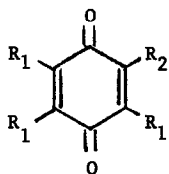
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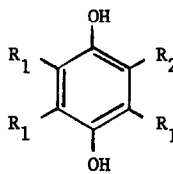
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It has been reported (without yields) that the sunlight photolysis of chloranil 1 in absolute ethanol produces tetrachlorohydroquinone 2 and trichlorohydroxy-p-benzoquinone 3.¹ This



- 1) $R_1=R_2=Cl$
- 3) $R_1=Cl; R_2=OH$
- 4) $R_1=R_2=H$
- 6) $R_1=H; R_2=OH$



- 2) $R_1=R_2=Cl$
- 5) $R_1=R_2=H$

finding was of interest to us in the context of our studies on dipolar state intermediates in dienones.² However, the term "absolute" is a relative one when applied to ethanol since sufficient water is present for direct displacement on the quinone nucleus in a non-photochemical process. In addition, chloranil normally contains trichlorohydroxy-p-benzoquinone as an impurity (approximately 0.25%).³ Hence, we undertook to verify the photochemical displacement of chlorine by hydroxyl and to elucidate the mechanism of this process.

Photolysis of chloranil (0.00203 M in absolute ethanol) with sunlight (Southern California) produces the tetrachlorohydroquinone and the trichlorohydroxyquinone in 68% and 28% yields, respectively. The same reaction was observed in methanol solvent, albeit in lower yield (13% for hydroxyquinone). Hydroquinone formation is straightforward, since ethanol is a good solvent for photoreduction; however, the displacement of chlorine by hydroxyl is unusual.

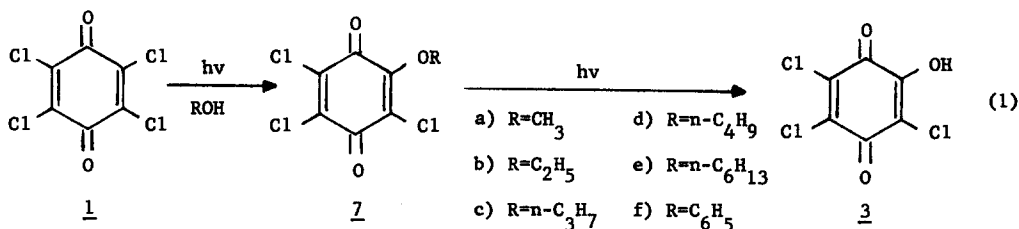
We first considered the possibility that water (approximately 0.5% in absolute ethanol) was involved in the production of the hydroxyquinone 3. Several workers⁴ have observed the formation of hydroquinone 5 and 2-hydroxy-p-benzoquinone 6 from the photolysis of p-benzoquinone 4 in aqueous solution. The suggested mechanism involves abstraction of a hydrogen atom from a water molecule. We do not believe this mechanism to be operative in the genesis of trichloro-

hydroxyquinone for three reasons: 1) from consideration of bond strengths, the abstraction of hydrogen atoms should be much more efficient from ethanol (O-C-H) than from water (O-H)⁵; 2) statistically, abstraction from ethanol is greatly favored (in absolute ethanol, by at least 200 to 1); 3) a hydrogen abstraction mechanism would not yield the alkoxyquinone intermediate 7 (see below).

In order to determine the effect of water, chloranil was photolyzed in 95% ethanol (5% water), absolute ethanol (0.5% water), and "super dry" ethanol (0.05% water).⁶ Quantum and overall chemical yields were determined for hydroxyquinone formation (see Table).⁷ For each 10-fold decrease in water concentration (95% ethanol to absolute to "super dry"), the quantum yields decreased by a factor of approximately 2, but percentage yields remained nearly constant.

The variation in quantum yields may be due to the fact that ethanol and water have approximately the same nucleophilicity, whereas that of aqueous ethanol appears to be higher.⁸ Since the nucleophilicities of ethanol, methanol, and water are comparable, preferential attack by water in ethanol at levels less than 5% is unlikely. The total insensitivity of the chemical yield to water content suggests, although it does not prove, that water is unnecessary for the reaction.

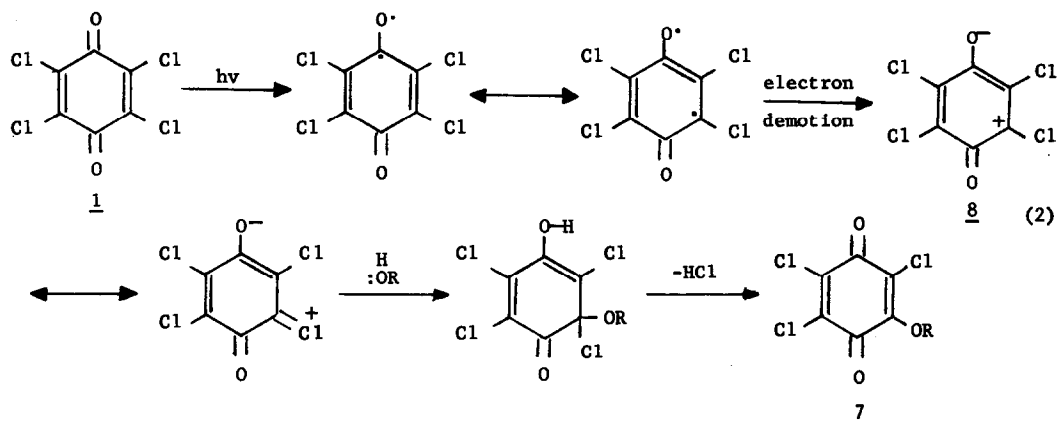
On the basis of the foregoing, we feel that a mechanism based on involvement of alcohol solvent is demanded. If so, the simplest explanation of our data is that the vinyl ether 7 is formed as an intermediate in the photolysis of chloranil in alcoholic solvents, and is converted to hydroxyquinone in a second photochemical step (eqn. 1). As a test of this hypothesis the



quinones 7 a-e were synthesized and irradiated in absolute ethanol, benzene,¹² and hexane.¹² Every quinone was converted to trichlorohydroxyquinone in each solvent in yields varying from 70% (ethanol) to 15% (hexane).

The postulated vinyl ether intermediates 7a and 7b were detected by gas chromatographic analysis of reaction mixtures from interrupted photolyses of chloranil in methanol and ethanol.¹³ We estimate that 30% of the photolysis follows this route by dividing the overall yield by the

yield of the second step. In agreement with this conclusion, we find that when chloranil is photolyzed in the presence of phenol, the trichlorophenoxyquinone 7f is isolated in the anticipated yield (30%). The phenoxyquinone is reasonably stable to photolysis, thus permitting its isolation in a yield close to that of its formation. Alkoxyquinone 7 may arise as follows:



Dipolar species 8 has analogy in the literature^{2,14} and is converted to ether 7 following nucleophilic attack by solvent. The postulated zwitterion is an allylic carbonium ion and will be further stabilized by resonance contributions from chlorine, which is known to display an exalted electron donation effect when directly attached to a positive center.¹⁵

The conversion of the alkoxyquinone to hydroxyquinone is under investigation.¹⁶

Table

	<u>Solvent</u>	Φ	<u>%</u>
Yields of trichlorohydroxyquinone formation in the photolysis of chloranil in various solvents.	95% ethanol	0,022	18
	absolute ethanol	0,0092	25
	"super dry" ethanol	0,0064	16
	methanol	0,0024	13

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7. All quantum yields and percent yields were determined in sealed tubes using solutions deoxygenated by nitrogen bubbling. Photolyses were carried out on a merry-go-round apparatus equipped with high pressure Hg lamp (Hanovia L679A), CuSO_4 filter solution, and CS 7-83 glass filters to isolate 3660 Å light. The santonin-lumisantonin actinometer was employed. Trichlorohydroxy-p-benzoquinone yields were measured with a Cary Model 14 spectrophotometer. The anion of the quinone is the only known component of the system having absorption at 5500 Å.
8. The assumption is basic to the treatment of Winstein, et.al,⁹ and to that of the Swain group.¹⁰ Results from the latter workers¹⁰ appear to confirm these expectations with the qualification that methanol appears to be somewhat more nucleophilic than water or ethanol. On the other hand, water is more nucleophilic than methanol for the specific reaction of displacement at Pt(II).¹¹
9. S. Winstein, E. Grunwald, and H. W. Jones, ibid., 73, 2700 (1951).
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12. To remove moisture, the benzene and hexane were distilled from calcium hydride and stored over molecular sieve 3A.
13. Trichloromethoxyquinone 7a was also detected by glc in a (dark) control reaction of chloranil and methanol. However, the quantity of 7a produced in the photolysis as an intermediate was more than 6 times that in the control.
14. H. E. Zimmerman and J. S. Swenton, J. Am. Chem. Soc., 86, 1436 (1964); H. W. Moore and K. Folkers, Ann. Chem., 684, 212 (1965).
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16. Evidence already in hand suggests this process begins with a photofragmentation to alkyl radical and quinone moiety.