at 25°, *but the organically bound halogen is less than the theoretical* due to the concurrent cleavage of halogen acid with the production of dehydrocholestanol which cannot add halogen and the formation of cholestenone which does not readily add halogen. Other substances of similar nature may be involved.

5. At 25°, cholesterol undergoes substitution and addition when carbon tetrachloride is the solvent for both the sterol and the halogen reagent.
6. At 0°, with carbon tetrachloride as the sole solvent, cholesterol undergoes addition only and the iodine numbers are the theoretical.
7. Besides dibromocholesterol, cholestenone, dehydrocholestanone-7-ol-4, and probably some dibromocholestenone, other products are formed by the action of the Hanus reagent upon cholesterol. The nature of these substances is not known, excepting that some one or more do give the Lifschütz test for "oxycholesterol."

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The Halochromism of Ketones in Acids

BY LEIGH C. ANDERSON

Benzophenone, xanthone and many other ketones which are colorless in the pure state give colored solutions when dissolved in sulfuric acid or perchloric acid, a phenomenon which has been designated as halochromism. Many hypotheses, including the quinonoid theory, the oxonium theory, the theory of the "coördinately unsaturated central carbon atom," ionization, etc., have been proposed in order to account for the production of the color of these solutions. The arguments which have been used as evidence in favor of each of these theories have usually been dependent upon the color of the solution rather than upon absorption spectra, and as a result many contradictory conclusions have been drawn. Quantitative absorption spectra data from solutions of ketones in sulfuric acid or perchloric acid support the contention that the colored solute which is present in such solutions is produced through the reactivity of the carbonyl group of the ketone. In addition, the data also indicate that quinoidation is, in some instances, a concurrent phenomenon, particularly in those cases where the carbonyl group may become a part of a quinonoid ring.

The absorption curves (Figs. 1 and 2) for ether solutions of benzoquinone, anthraquinone, benzophenone and xanthone[1] disclose absorption bands at frequencies between 2900 and 3300 mm.$^{-1}$ (about 3000 Å.). This is the region in which absorption bands are found in curves for solutions

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(1) The apparatus and the methods used for obtaining the quantitative absorption spectra have been described by Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928); Anderson, *ibid.*, **51**, 1889 (1929).

in hexane and in ether of all the simple ketones and aldehydes, so far as these absorption spectra have been published. It has been stated by Henri[2] that these bands are characteristic of the carbonyl group. A comparison of the absorption curves of sulfuric or perchloric acid solutions[3]

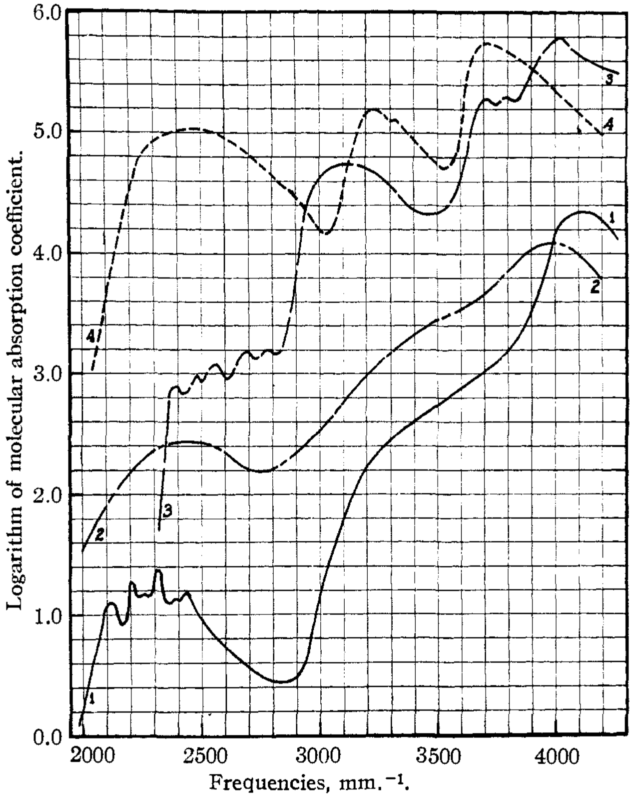

Fig. 1.—1, Benzoquinone in ether; 2, benzoquinone in perchloric acid; 3, anthraquinone in ether; 4, anthraquinone in sulfuric acid.

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(2) Henri, "Études de Photochemie," Gauthier-Villars et Cie., Paris, France, 1919, p. 64.

(3) Benzoquinone decomposes almost immediately when dissolved in sulfuric acid even when the acid has been diluted with dimethyl sulfate. A perchloric acid solution of benzoquinone is fairly stable in an atmosphere of carbon dioxide. It has been reported [Hofmann, Metzler and Lecher, *Ber.*, **43**, 178 (1910)] that anthraquinone does not form a compound with perchloric acid even in the presence of water-free solvents. We have found that it is insoluble in 70% perchloric acid but dissolves in a mixture of 70% perchloric acid and anhydrous magnesium perchlorate to produce an intense yellow colored solution similar to that which is obtained with 95% sulfuric acid. The carbonyl and quinonoid bands are increased in intensity in the perchlorate solution as compared to the ether solution and approach the height of the corresponding bands that were found in the sulfuric acid solution. In the case of benzophenone and xanthone the curves for the perchloric and sulfuric acid solutions for each are practically identical and, therefore, the curve for only one acid solution is being presented in this paper. References to previous work on the absorption of these compounds can be found in Volume 5 of the "International Critical Tables." The frequencies of maximum absorption which we have found for xanthone sulfate are in excellent agreement with those which have been reported by Gibbs, Johnson and Hughes [THIS JOURNAL, **52**, 4900 (1930)].

of the ketones listed by us above, with those for the corresponding ether solutions, shows that the absorption in the carbonyl region is markedly greater in the acid solutions. This change in absorption cannot be accounted for by assuming that the absorption as a whole has been increased, since the acid solutions, which possess considerably greater absorption in the carbonyl region than the corresponding ether solutions, possess sometimes more and sometimes much less absorption in the regions of shorter wave lengths than do the corresponding ether solutions. The fact that a common effect is being produced in the carbonyl region only leads one to believe that the carbonyl group in each of these cases is directly involved in the formation of the product which is responsible for the color in the acid solutions.

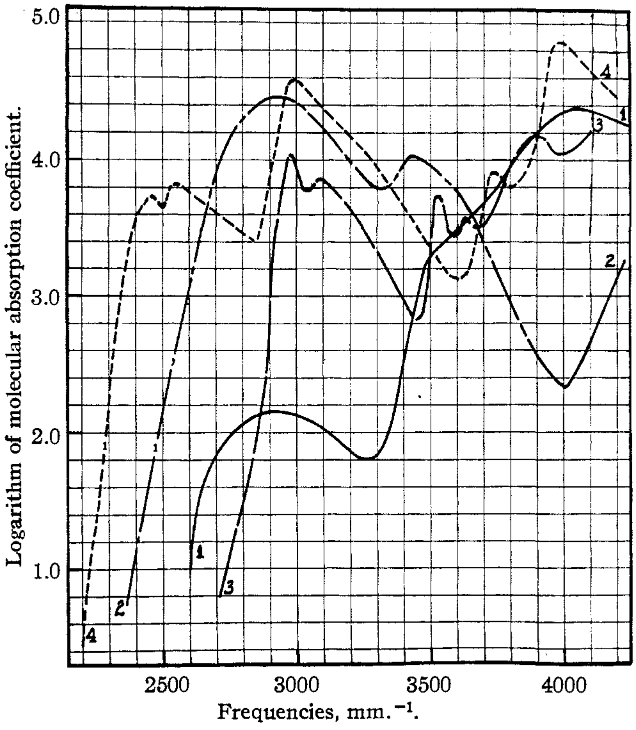

Fig. 2.—1, Benzophenone in ether; 2, benzophenone in sulfuric acid; 3, xanthone in ether; 4, xanthone in sulfuric acid.

Anthraquinone may be written as quinonoid (I) or benzenoid (II) in structure. The absorption curve for its ether solution shows the same type of narrow band absorption in the violet and near ultraviolet region[4] of the spectrum that we find in benzoquinone. A broad band which is much enhanced in the sulfuric acid solution is also found in the carbonyl

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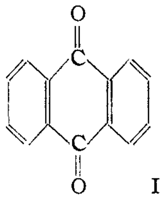
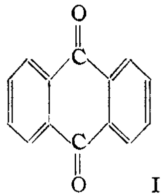
[4] For the purpose of description, the bands in this region are being called quinonoid bands.



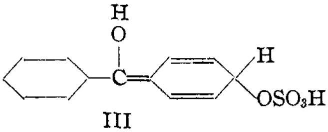
I



II

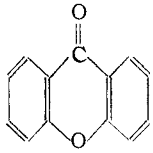
region. The use of the acid as a solvent in place of ether also produces a very obvious change in the intensity of absorption in the quinonoid region at the edge of the visible. These changes are analogous in every way to the effects that are obtained with ether and perchloric acid solutions of benzoquinone. It is apparent, therefore, that the same type of structure must be assigned to each of these two compounds and that at least part of the anthraquinone that is in solution must be assigned the quinonoid structure.

Benzophenone forms halochromic compounds which can be pictured as quinonoid (III) but thus far no evidence has been obtained to substantiate such an hypothesis. Ether solutions of benzophenone show the presence of a band in the carbonyl region and the intensity of this band is very much enhanced on solution of this compound in sulfuric or perchloric acid. There is no indication in either ether or acid solution of any absorption band in the quinonoid region. The color of such solutions is due only to the enhancement of the carbonyl band and consequent shift of the base of this band into the visible region.

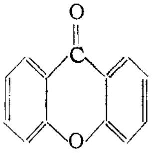


III

Xanthone, like anthraquinone, may be represented structurally as either quinonoid (IV) or benzenoid (V). The absorption curve for its



IV



V

ether solution shows two bands close together in the carbonyl region. The curves for the acid solutions differ from that of the ether solution in two notable respects: first, the carbonyl band is enhanced without material change in position and, second, two bands which almost merge into one large one have developed in the edge of the visible where benzoquinone and anthraquinone have bands. These results indicate that a change has taken place on solution of xanthone in sulfuric or perchloric acid which did not take place in the case of benzophenone. The shape of the curve obtained from the acid solutions approaches that of anthraquinone.

The data discussed above constitute evidence that anthraquinone exists, at least partially, in a quinonoid state in ether solution; that xanthone exists entirely in a benzenoid state in ether solution and that both of these compounds exist, at least partially, in a quinonoid state in sulfuric or perchloric acid solutions. The data also indicate that benzophenone does not possess a quinonoid structure in either sulfuric or perchloric acid solutions.

Summary

Curves are presented for the quantitative absorption spectra for solutions of each of the following compounds: anthraquinone, benzophenone, and xanthone in ether and in sulfuric acid, respectively, and for ether and perchloric acid solutions of benzoquinone. The curves indicate that the colored solute which is produced when ketones are dissolved in sulfuric or perchloric acid is produced through the reactivity of the carbonyl group of the ketone. They show, furthermore, that in some instances quinoidation may also be responsible for the color.

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The Dissociation into Free Radicals of Di-tert-butyltetradiphenylethane

BY JAMES B. CONANT AND RAYMOND F. SCHULTZ

In recent years it has become evident that a branched alkyl group is effective in promoting the dissociation of a highly substituted ethane. Thus, dicyclohexyltetraphenylethane[1] and di-*tert*-butyltetraphenylethane[2] contain a very reactive carbon to carbon linkage and in the case of the latter substance clear evidence of its dissociation into a free radical can be obtained. The free radical is formed in appreciable quantities only above about 50° and at these temperatures quickly disproportionates; for this reason no molecular weight determinations could be made and it was necessary to rely on color changes and chemical reactions. In the dixanthyl series, the free radicals with a branched alkyl group on the central carbon atom are much more stable and less associated. Relatively stable solutions of cyclohexylxanthyl, *sec*-butylxanthyl and isopropylxanthyl have been prepared. The solutions of these free radicals[3] are highly colored and absorb oxygen very rapidly. Unfortunately all attempts to obtain a crystalline form of the associated free radical (the dialkyl-dixanthyl) failed. It was, therefore, impossible to carry out molecular weight determinations in this case also.

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(1) Ziegler and Schnell, *Ann.*, **437**, 237 (1924).

(2) Conant and Bigelow, THIS JOURNAL, **50**, 2041 (1928).

(3) Conant, Small and Sloan, *ibid.*, **48**, 1743 (1926).