Summary

Tensimetric measurements of the system thorium bromide and ammonia, in mm. of mercury at 0° and at pressures up to 1190 mm. indicate that the equilibrium $ThBr_4 \cdot 20NH_3 \rightleftarrows ThBr_4 \cdot 14NH_3 + 6NH_3$, exists and that the pressure of the higher ammine is 1180 mm. The decomposition pressure of $ThBr_4 \cdot 14NH_3$ is 268 mm. and that of $ThBr_4 \cdot 10NH_3$ is 22 mm. At 25° the decomposition pressure of $ThBr_4 \cdot 10NH_3$ is 184 mm.

CAMBRIDGE, MASS. RECEIVED MARCH 25, 1935

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Halochromism of Ketones. II[1]

BY LEIGH C. ANDERSON AND C. M. GOODING

Absorption spectra data which have been reported from this Laboratory[2] show that although benzophenone dissolves in ether to give colorless and in sulfuric acid to give colored solutions, the same absorption bands are obtained in each case. The band associated with the carbonyl group was found to be much more intense in the acid solution and the yellow color of the solution was caused by the widening of the base of this band until it extended into the visible region. Since the carbonyl band was intensified and no new bands appeared, we concluded that the colored solute had been produced through the reactivity of the carbonyl group. The fact that the same bands appear in both the colorless and colored solutions is evidence that this is a case of true halochromism as originally defined by Baeyer.[3] This paper presents additional data which constitute conclusive evidence: first, that in the ketones we have studied the reactivity of the carbonyl group alone is responsible for the color in those cases where we find true halochromism; second, that the addition compounds produced with reagents like sulfuric acid and stannic chloride in the presence of hydrogen chloride do not involve the loss of the carbonyl group by addition to the carbonyl double bond; third, that some ketones give a colored solution in sulfuric acid and in addition to the enhancement of the carbonyl band, new bands are produced which we believe to be due to quinoidation, thereby showing two effects which can contribute to the formation of color. In the case of the ketone chlorides, the absorption spectra of their colored solutions with stannic chloride or sulfuric acid are entirely different from those of the corresponding ethylene dichloride solutions. We believe that the color in these solutions is due to quinoidation and not to halochromism. These cases will be discussed later in the paper.

Comparisons of the absorption spectra of sulfuric acid solutions of 4-phenyl- and 4,4′-diphenylbenzophenone with corresponding ethylene dichloride solutions show that these are cases of true halochromism (Figs. 1 and 2). Solutions of these compounds, as well as benzophenone (Fig. 3), in mixtures of ethylene dichloride and stannic chloride give absorption curves which are very similar to those obtained for the corresponding ketone in sulfuric acid. The principal differences noted are that with stannic chloride the band having a maximum in the carbonyl region is displaced toward longer wave lengths (Table I) and is not quite as intense. In these cases, therefore, true halochromism is produced by either stannic chloride or sulfuric acid.

In all ketones that have been studied the absorption spectra of their colored solutions, whether the color is caused by sulfuric acid or stannic chloride, show marked enhancement of the absorption band which occurs in the carbonyl region of the spectrum and a shift of this band toward longer wave lengths. In order to see whether these changes were due to the rearrangement of an aromatic ring with formation of a new chromophore as, for example, the quinonoid nucleus, solutions of a number of aliphatic ketones were separately prepared in ethylene dichloride and sulfuric acid and the absorption spectra determined. The data show that the absorption

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[1] The material in this paper comprises a portion of a thesis presented by C. M. Gooding to the Graduate School of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Philosophy, 1934.

[2] Anderson, THIS JOURNAL, **55**, 2094 (1933).

[3] In the discussion that follows we shall define as examples of true halochromism those solutions where the absorption spectra show that the color is produced through enhancement of the carbonyl absorption band without the production of new bands.

TABLE I

TABLE OF MAXIMA OF ABSORPTION BANDS

The data are arranged as follows after each solute: first, solvent and second, the maxima found, with each maximum, followed in parentheses by the corresponding logarithm of the molecular absorption coefficient.

Acetone: H_2O, 3740 (1.25); H_2SO_4, 3500 (1.95).

3-Hexanone: $C_2H_4Cl_2$, 3510 (1.30); H_2SO_4, 3300 (2.30).

Cyclohexanone: $C_2H_4Cl_2$, 3410 (1.25); H_2SO_4, 3090 (1.95).

Dicyclohexyl ketone: $C_2H_4Cl_2$, 3360 (1.55).

Cyclohexyl phenyl ketone: $C_2H_4Cl_2$, 3060 (1.95), 3450 (2.80), 3580 (3.00); H_2SO_4, 3150 (3.50), 3290 (4.40).

Benzophenone: $C_2H_4Cl_2$ HCl, 3010 (2.40); H_2SO_4, 2910 (4.45), 3420 (4.00).

Benzophenone dichloride: $CHCl_3$ $SnCl_4$, 2140 (1.35).

p-Phenylbenzophenone: $C_2H_4Cl_2$ HCl, 2950 (2.70); H_2SO_4, 2610 (4.60), 3420 (4.40); $C_2H_4Cl_2$ HCl $SnCl_4$, 2390 (4.35), 3160 (4.15); $CHCl_3$ $SbCl_5$, 2530 (4.20).

p,p'-Diphenylbenzophenone: $C_2H_4Cl_2$, 2950 (2.80), 3330 (4.75); H_2SO_4, 2410 (4.80), 2790 (4.35); $C_2H_4Cl_2$ HCl $SnCl_4$, 2170 (4.65), 2570 (4.30).

p,p'-Diphenylbenzophenone dichloride: $CHCl_3$, 3720 (4.65); $CHCl_3$ $SnCl_4$, 1640.

Xanthone: $C_2H_4Cl_2$ HCl, 2930 (3.90), 3060 (3.90), 3500 (3.75), 3620 (3.55), 3830 (4.15); H_2SO_4, 2460 (3.75), 2550 (3.88), 2990 (4.60), 3730 (3.90), 3980 (4.85); $C_2H_4Cl_2$ HCl $SnCl_4$, 2380 (3.75), 2520 (3.60), 2950 (4.45).

Phenyl ether: $C_2H_4Cl_2$, 3580 (3.30), 3660 (3.40), 3770 (3.20), 3900 (3.15).

Dibenzodioxin: $C_2H_4Cl_2$, 2970 (1.10), 3450 (3.60); H_2SO_4, 1460 (decomposition) (2.65), 3300 (3.75); $C_2H_4Cl_2$ $SnCl_4$, 2800 (1.80).

Fluorenone: $C_2H_4Cl_2$ HCl, 2500 (2.45), 2630 (2.55), 2760 (2.45), 3050 (3.25), 3220 (3.40), 3370 (3.70), 3510 (3.40), 3850 (5.05); H_2SO_4, 1850 (2.30), 2450 (4.20), 2580 (4.15), 2940 (3.35), 3000 (3.25), 3390 (3.95), 3750 (4.80); $C_2H_4Cl_2$ HCl $SnCl_4$, 2490 (3.05), 2750 (3.45), 2910 (3.50), 3190 (3.55).

Fluorenone dichloride: $CHCl_3$, 3400 (3.90), 3540 (4.00), 3670 (3.95); $CHCl_3$ $SnCl_4$, 2080 (1.20), 2250 (1.15), 2400 (1.25).

curves for aliphatic ketones undergo the same changes (Fig. 4) as do those for the aromatic ketones. This similarity obviously excludes the possibility of attributing the origin of the light

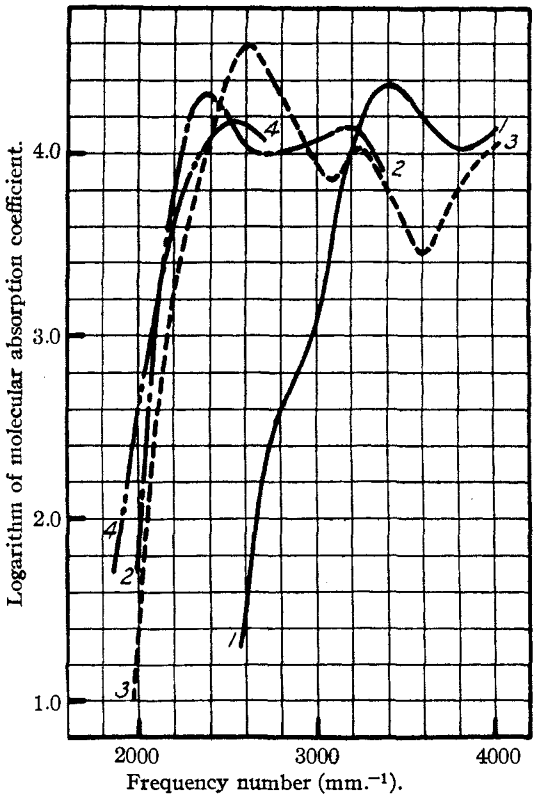


Fig. 1.—*p*-Phenylbenzophenone: 1, $C_2H_4Cl_2$ and $C_2H_4Cl_2$ + HCl; 2, $SnCl_4$ in $C_2H_4Cl_2$ + HCl; 3, H_2SO_4; 4, $SbCl_5$ in $CHCl_3$.

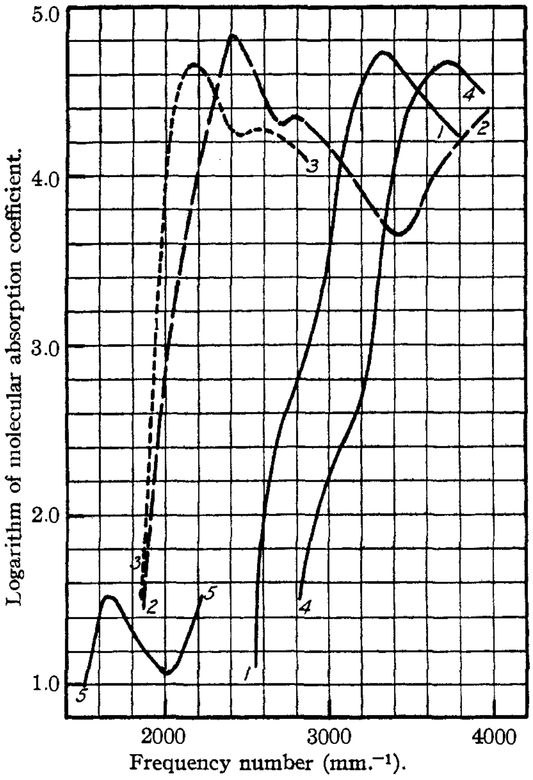


Fig. 2.—*p,p'*-Diphenylbenzophenone: 1, $C_2H_4Cl_2$; 2, H_2SO_4; 3, $SnCl_4$ in $C_2H_4Cl_2$ and HCl. *p,p'*-Diphenylbenzophenone chloride: 4, $CHCl_3$; 5, $SnCl_4$ in $CHCl_3$ (qualitative).

absorption in the visible region to absorption by the aromatic nuclei. The only difference observed between sulfuric acid solutions of the aliphatic and aromatic ketones is that with the former a slightly greater displacement toward the longer wave lengths occurs (Table I).

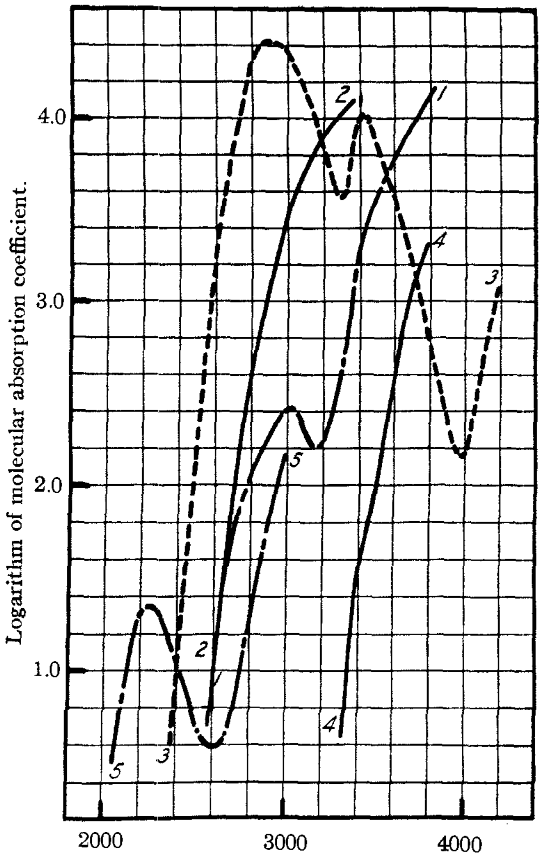


Fig. 3.—Benzophenone: 1, $C_2H_4Cl_2$ and $C_2H_4Cl_2$ + HCl; 2, $SnCl_4$ in $C_2H_4Cl_2$ + HCl; 3, H_2SO_4. Benzophenone chloride: 4, ether; 5, $SnCl_4$ in $CHCl_3$.

The absorption spectrum of cyclohexyl phenyl ketone when compared with those for dicyclohexyl ketone and benzophenone furnished a transitional example between the strictly aliphatic and the entirely aromatic series (Fig. 5). Dicyclohexyl ketone was found to conform to the behavior of the other aliphatic ketones, although its curve in sulfuric acid must be considered only qualitative, since decomposition which was found to take place in this solvent resulted, after a number of days, in absorption even in the visible region. The curves for cyclohexyl phenyl ketone in ethylene dichloride show the appearance of a second band at 3515 mm.$^{-1}$. Other investigators[4] have found a similar second absorption band in the same region for ketones like acetophenone and benzyl phenyl ketone which have the carbonyl group attached to both an aliphatic and an aromatic group.

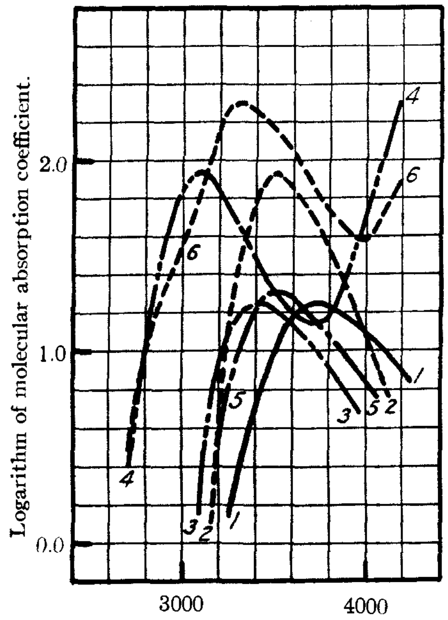
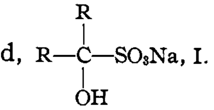


Fig. 4.—Acetone in 1, H_2O; 2, H_2SO_4: 3-Hexanone in 3, $C_2H_4Cl_2$; 4, H_2SO_4. Cyclohexanone in 5, $C_2H_4Cl_2$; 6, H_2SO_4.

A necessary prelude to the rearrangement of a phenyl group to a quinonoid structure is the breaking of the carbonyl double bond. It is possible to show that this does not occur in the colored solutions of the ketones we have studied. Acetone and cyclohexanone react with sodium bisulfite to form addition products. Raschig and Prahl[5] assign structure I to compounds thus produced,



$$\begin{array}{c} \text{R} \\ | \\ \text{R—C—SO}_3\text{Na} \\ | \\ \text{OH} \end{array}, \text{ I.}$$

We have made spectroscopic investigations of solutions containing the above aliphatic ketones and sodium bisulfite. The reaction, admittedly far from complete, progressed to such an extent that the material present in the ketone form was reduced below the concentration required to produce selective absorption and the carbonyl band disappeared from the curve. Biquard[6] has experienced similar results with phenylacetaldehyde in presence of sodium bisulfite and anhydrous hydrocyanic acid (Formulas II and III).

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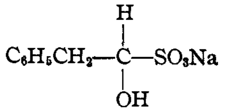
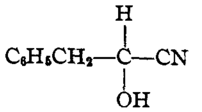
(4) Henri, "Études de Photochemie," Gauthier-Villars et Cie, Paris, France, 1919, p. 417; Ley and Manecke, *Ber.*, **56**, 778 (1923).

(5) Raschig and Prahl, *Ann.*, **448**, 265 (1926).

(6) Biquard, *Ann. chim.*, **20**, 112 (1933).



$C_6H_5CH_2-\underset{OH}{\overset{H}{C}}-SO_3Na$ II



$C_6H_5CH_2-\underset{OH}{\overset{H}{C}}-CN$ III

The fact, then, that the carbonyl band is not diminished and on the contrary is found to be very greatly enhanced on solution of our ketones in sulfuric acid indicates that the carbonyl group is not removed in the manner indicated in Equation 1.

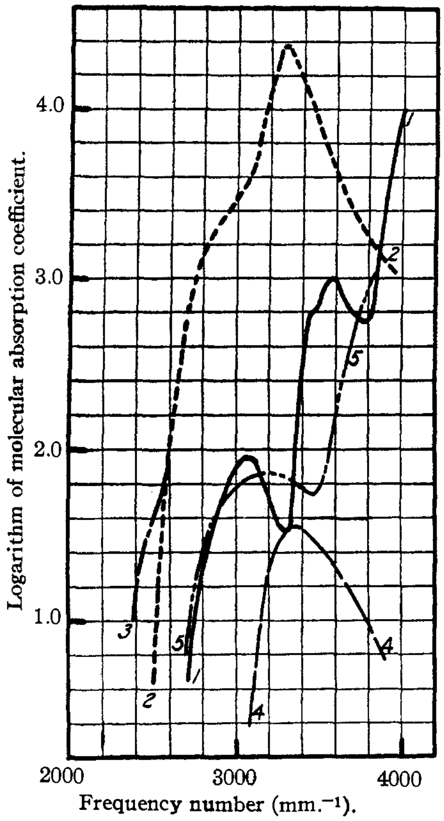
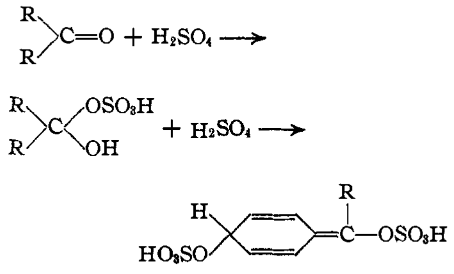


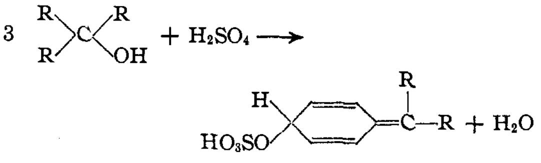
Fig. 5.—Cyclohexyl phenyl ketone: 1, in $C_2H_4Cl_2$; 2, H_2SO_4; 3, H_2SO_4 (after standing). Dicyclohexyl ketone: 4, $C_2H_4Cl_2$; 5, H_2SO_4 (after 20 hours).

Eqs. 1 and 2

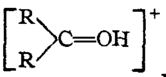


Division of the carbonyl double bond would lead to the formation of an hydroxyl group and the resulting compound might be expected to show (Equation 2) at least a tendency toward the same behavior as is observed with the aromatic triaryl carbinols (Equation 3).

Eq. 3

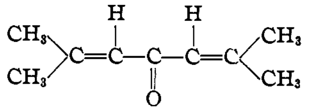


Upon addition of a color producing agent, triaryl carbinols are known to give rise to entirely new absorption bands where none previously existed.[7] This is not the case for simple aromatic ketones since no new bands appear and, on this basis also, one concludes that the carbonyl double bond is still present in the colored solutions. On the basis of the foregoing observations, the structure indicated in Formula IV does not appear unreasonable for the halochromic aromatic ketones of the benzophenone type.[8]



$\left[{R \atop R}\!>\!C=OH\right]^+ OSO_3H^-$ IV

Other investigators have found that sulfuric acid solutions of unsaturated ketones of the type of dibenzalacetone give rise to entirely different light absorption from that of the saturated aliphatic and aromatic types of ketones. Several authors[9] have pointed out the similarity existing between the colored solutions of unsaturated ketones and aromatic carbinols. It is interesting to note in the literature that phorone (V)[10] when dissolved in sulfuric acid shows only simple enhancement of the carbonyl band. This seems to indicate that the presence of double bonds is not the only factor involved in the absorption changes noted



${CH_3 \atop CH_3}\!>\!C=\overset{H}{C}-\underset{\underset{O}{\|}}{C}-\overset{H}{C}=C\!<\!{CH_3 \atop CH_3}$ V

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[7] Anderson, THIS JOURNAL, 52, 4567 (1930); Schoepfle and Ryan, *ibid.*, 54, 3687 (1932).

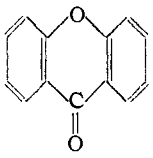
[8] A formula which differs from this one by having a single bond between the C and O has been suggested and discussed by other writers, including, for example, Dilthey (*J. prakt. Chem.*, [2] 109, 303 (1925)) and Wizinger (*Z. angew. Chem.* 40, 939 (1927)). In the structure as we picture it, the double bond is present as in the simple ketones and if, in the simple ketones, there is "polar activation" of the carbonyl bond as ascribed by Lowry (*J. Chem. Soc.*, 123, 822 (1923); 620 (1926)) and conversion of the non-polar into a semi-polar double bond: $>C=O \rightleftharpoons >C^{+}-O^{-}$, we suggest that true halochromism involves a shift of this equilibrium toward the right (see also, Watson, Nathan and Lourie, *J. Chem. Physics*, 3, 170 (1935)). The hydrogen ion is probably linked to the carbonyl oxygen in the same manner as it is linked to the oxygen of water in the hydronium ion $[H_2OH]^+$ and to N in the ammonium ion $[H_3NH]^+$.

[9] Baker, *J. Chem. Soc.*, 91, 1491 (1907); Lifschitz and Lourie, *Z. wiss. Phot.*, 16, 269 (1917); Kehrmann and Effront, *Ber.*, 54, 417 (1921); Hantzsch, *ibid.*, 55, 954 (1922); Kauffmann, *ibid.*, 55, 1967 (1922).

[10] Baly, Collie and Watson, *J. Chem. Soc.*, 95, 144 (1909) Scheibe, *Ber.*, 58, 594 (1925).

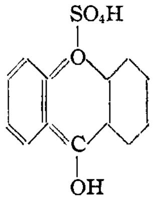
for dibenzalacetone and that the presence of phenyl groups is also required.

Xanthone contains a carbonyl group of which the carbon atom is a part of a six-membered ring containing oxygen. Anderson[11] has found that a solution of xanthone in sulfuric acid shows enhancement of the carbonyl group in harmony with the results obtained for the ketones previously discussed. However, it also possesses a new band appearing in the visible region and this new band was attributed to a stabilization of the quinone structure for xanthone (VI). We have now found that stannic chloride in ethylene chloride brings about an identical change (Fig. 6). Even dry hydrogen chloride is capable of this stabilization to a small extent. This reactivity with hydrogen chloride is not found in the other ketones studied and is presumed to be a result of the influence of the ortho bridge oxygen upon the 9-carbon of xanthone.

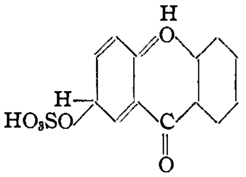


VI

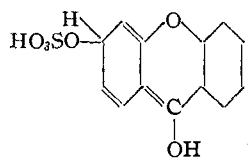
It was deemed advisable to investigate the absorption spectra of sulfuric acid solutions of aromatic ethers in connection with possible oxonium formation at the ether oxygen of xanthone, Formulas VII and VIII, a mechanism which several workers have preferred instead of quinoidation (Formulas IX and XI), especially in relation to the constitution of the salts of pyrone and its derivatives.



VII (Oxonium, *o*-quinonoid)



VIII (Oxonium, *p*-quinonoid)



IX (Quinonoid, no carbonyl)

Pfeiffer's[12] work has shown that only one oxygen in xanthone takes part in addition reactions with color producing agents and that xanthone conforms exactly to the molecular ratios found between a large number of other ketones not possessing an additional oxygen atom and the acids or metal halides, and he concludes that, in xanthone, the carbonyl oxygen is the reactive one.

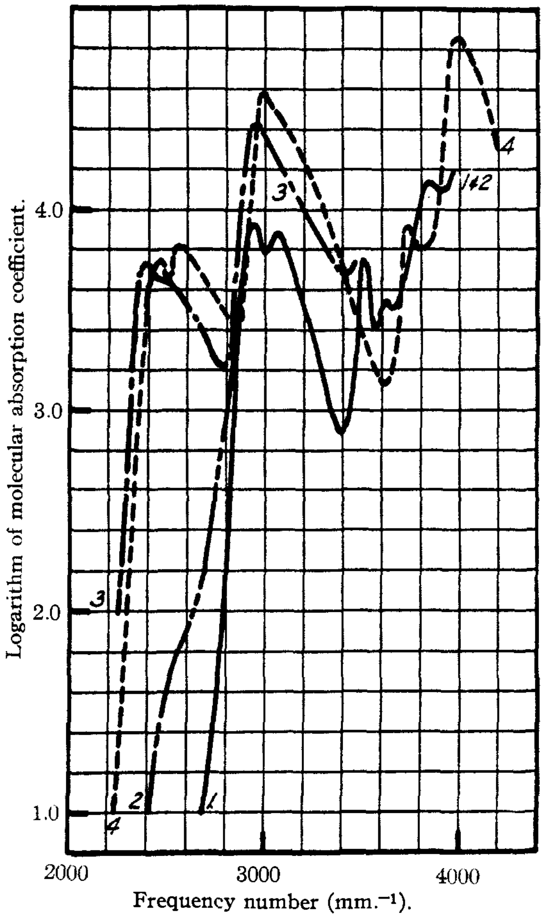
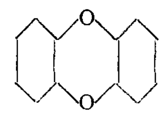


Fig. 6.—Xanthone: 1, $C_2H_4Cl_2$; 2, $C_2H_4Cl_2$ + HCl; 3, $SnCl_4$ in $C_2H_4Cl_2$ + HCl; 4, H_2SO_4.

The absorption curves for diphenyl ether in ethylene dichloride and in sulfuric acid are given in Fig. 7. In sulfuric acid solution the group of narrow bands becomes one broad band and there is a slight displacement of the absorption toward the longer wave lengths; the latter change is not unusual, as is to be noted in our work with the ketones. No new bands appear in the sulfuric acid solution which could account for the bands formed near the visible region in the xanthone absorption spectra.

The report that dibenzodioxin, X, dissolves in concentrated sulfuric acid to produce an intensely blue colored solution is of interest, especially as regards xanthone. The position of an absorption band for this solu-

X



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[11] Anderson, THIS JOURNAL, **55**, 2094 (1933).

[12] Pfeiffer, "Organische Molekulverbindungen," Stuttgart, Germany, 1922, p. 66.

tion was determined by Moir.[13] He states that the temperatures were too low and the observations made too quickly for sulfonation to have taken place. In our experiments it was difficult to wet the perfectly colorless crystals of dibenzodioxin with sulfuric acid and thirty-six hours did not suffice to dissolve 20 mg. in 25 cc. of acid in a closed flask on a shaking machine. However, when 2 g. was vigorously stirred with 100 cc. of acid in air, complete solution was accomplished in seven hours. Using these solutions, we were able to check the one absorption maximum in the visible region of the spectrum recorded by Moir (Fig. 8). When the solutions were poured into twice their volumes of water at a temperature not exceeding 30°, no dibenzodioxin was recovered although it is very insoluble. It appears that solution must have taken place as a result of sulfonation or oxidation. In justification of this conclusion it may be noted that the corresponding monosulfur, selenium, and tellurium cyclic compounds have been shown by Drew[14] to dissolve in sulfuric acid with formation of oxidation products accompanied by pronounced color changes. It seems obvious, therefore, that the appearance of color upon dissolving dibenzodioxin in sulfuric acid is not related to the question of the color of corresponding solutions of xanthone.

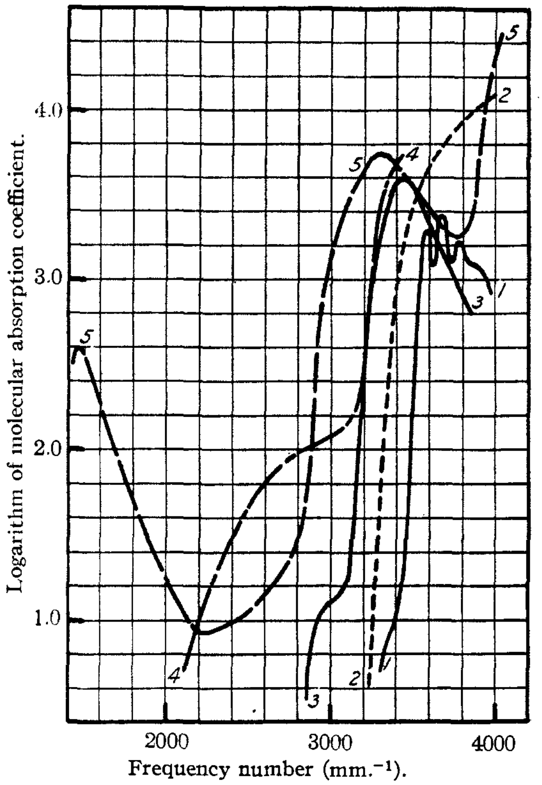


Fig. 7.—Phenyl ether in 1, $C_2H_4Cl_2$; 2, H_2SO_4. Dibenzodioxin in 3, $C_2H_4Cl_2$; 4, $SnCl_4$ in $C_2H_4Cl_2$; 5, H_2SO_4.

The absorption curves for sulfuric acid solutions of fluorenone show changes similar to those noted for xanthone (Fig. 8). They, like xanthone, show normal enhancement of the carbonyl band and, in addition, a new band arising from the stabilization of a quinonoid structure, XI. No ether oxygen is present in fluorenone and yet it exhibits the same type of color formation associated with solutions of xanthone in sulfuric acid. However, in the absence of the bridge oxygen, the carbonyl group resembles that of benzophenone more than that of xanthone in its reaction with stannic chloride in ethylene chloride

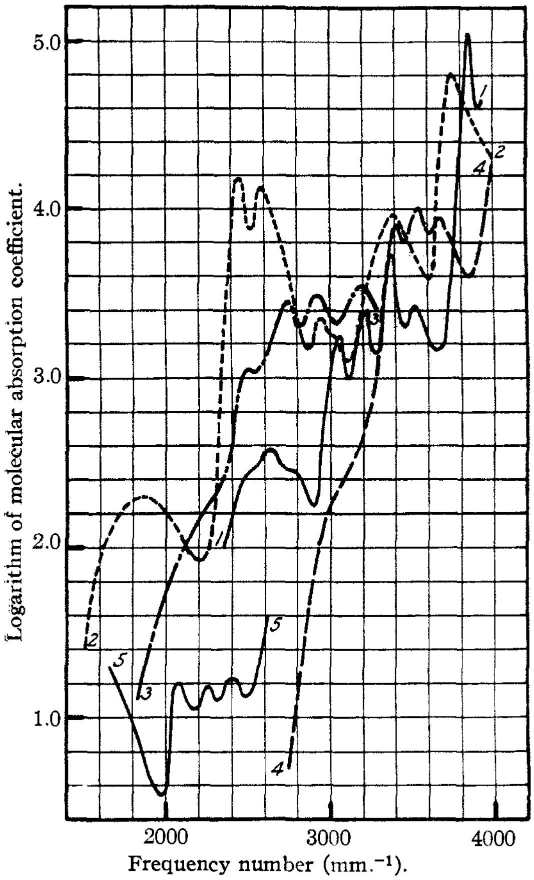
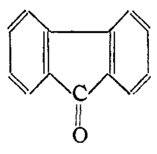


Fig. 8.—Fluorenone: 1, $C_2H_4Cl_2$ and HCl; 2, H_2SO_4; 3, $SnCl_4$ in $C_2H_4Cl_2$ and HCl. Fluorenone chloride: 4, $CHCl_3$; 5, $SnCl_4$ in $CHCl_3$ (qualitative).


XI

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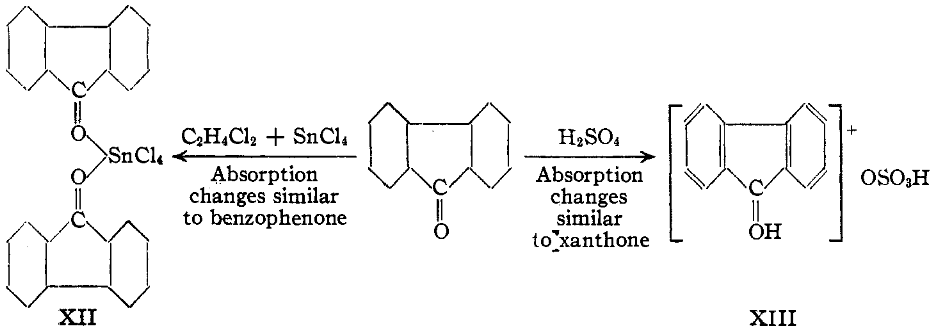
(13) Moir, *Trans. Roy. Soc. S. Africa*, **18**, Pt. 2, 137 (1929).

(14) Drew, *J. Chem. Soc.*, 3054 (1926); *ibid.*, 506 (1928).

solution. The absorption curve in this solvent indicates only slight formation of a quinonoid addition compound. These relations may be illustrated in the following manner

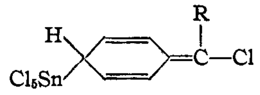


XII XIII

Like benzophenone, its absorption is unaltered by dry hydrogen chloride at room temperature.

Ketone chlorides are capable of undergoing changes in structure under the influence of an agent which produces color, because direct union of the agent with the central carbon atom is possible in absence of the stable double bond found in ketones. It was found that changing from an indifferent solvent like ethylene dichloride to a color-producing solvent like sulfuric acid or ethylene dichloride containing stannic chloride produces changes in the absorption curve of the ketone chloride which are different from those noted in the case of the parent ketone. Intensely colored solutions are obtained which have absorption bands far out in the visible region beyond all limits of absorption by the colorless solutions of the ketone chloride or even the sulfuric acid solutions of the ketone from which it is derived. This same change in the form of the absorption curve always appears when triarylcarbinols and the triarylmethyl halides are similarly treated. As in the case of the latter substances, the appearance of the new bands in the colored solutions of the ketone chlorides suggests that a profound change in structure of the solute has occurred.

Some investigators have attributed these color changes to ionization but Lifschitz and Girbes[15] have pointed out that the cause for the altered light absorption cannot be ionization alone. It appears necessary, therefore, to assume formation of a new chromophore. A convenient and very probable configuration is that of a quinonoid structure for one of the phenyl groups,



XIV

The ease with which the bromine atoms in 4,4'-dibromobenzophenone are replaced by chlorine when the ketone is heated with phosphorus pentachloride indicates that ketone chlorides exist in a quinonoid modification. Also, when *p*-bromobenzoyl chloride is treated with phosphorus pentachloride the bromine is replaced by chlorine.[16] These reactions are unusual for a normal ring-substituted halogen atom while they are in accord with those which might be expected of a halogen attached to the para position in the quinonoid ring.

The intense colors resulting when a ketone chloride is dissolved in sulfuric acid slowly fade as hydrogen chloride is eliminated and after two days the original ketone may be recovered by pouring upon ice.[17] The ketone chloride addition products with stannic chloride were also found to decompose in solution at rates somewhat dependent upon the solvent employed. The curves for benzophenone chloride (Fig. 4) are quantitative. Those for fluorenone chloride and *p,p'*-diphenylbenzophenone dichloride are qualitative, since the solutions were not stable.

Several double compounds were prepared from ketones and mercuric chloride. The absorption curves for their solutions were found to show no noticeable difference from those of the free ketone or quinone, and the results appear to indicate that these double compounds are dissociated in solution. Measurements were made on solutions of the double compounds which were weighed out as such and also upon solutions prepared by addition of the organic component to a solution containing excess of the mercuric chloride. No

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(15) Lifschitz and Girbes, *Ber.*, **61**, 1484 (1928).

(16) Cone and Long, THIS JOURNAL, **28**, 518 (1906); Cone and Robinson, *Ber.*, **40**, 2160 (1907).

(17) Straus and Ecker, *Ber.*, **39**, 3005 (1906).

reduction of mercuric chloride to mercurous chloride was noticed since the solutions remained clear during the course of a determination.

Experimental

Each solvent employed in this work was carefully purified and was optically clear in the spectral region under investigation. We found that saturation of anhydrous ethylene chloride with dry hydrogen chloride gas generated in a special all-glass apparatus previous to the addition of stannic chloride greatly increased the solubility of the stannic chloride double compounds. This procedure also prevented the separation of insoluble stannic chloride hydrates on the faces of the absorption cells due to moisture unavoidably acquired during preparation of the solutions and transference to the absorption cells. The effect of addition of dry hydrogen chloride upon the absorption spectrum of the solute as compared to that in the neutral solvent was determined and no change was observed except in the case of xanthone. The average of five separate titrations indicated the solvent to be 0.2 *N* with respect to hydrochloric acid.

Preparation of Solutes

Acetone.—First converted to bisulfite compound and after conversion back to ketone it was refluxed with and distilled from potassium permanganate. Refluxed with and distilled from calcium oxide; n^{15}_D 1.3621 (literature, n^{15}_D 1.3620).

Cyclohexanone.—Converted to bisulfite compound (three times); dried with calcium chloride, fractionated; b. p. 151–151.8° (739 mm.) (literature, b. p. 155.4° (760)).

3-Hexanone.—From Grignard reaction of $CH_3CH_2CH_2MgBr + CH_3CH_2CN$; ketone fractionated three times, n^{22}_D 1.3997; b. p. 118–119° (747 mm.) (literature, n^{22}_D 1.39899; b. p. 123–123.5° (765)).

Dicyclohexyl Ketone.—Oxidation by dilute chromic acid at 45–50° of dicyclohexylcarbinol which was prepared from cyclohexylmagnesium chloride and ethyl formate; ketone, b. p. 164–165° (33 mm.); n^{14}_D 1.4851 (literature, n^{14}_D 1.484).

Cyclohexyl Phenyl Ketone.—(1) Oxidation of carbinol from Grignard reaction of cyclohexyl-MgCl + C_6H_5CHO. (2) Grignard reaction of cyclohexyl-MgCl + C_6H_5CN; m. p. (both samples) 57.5–58.5° (highest value in literature, m. p. 59–60°).

Benzophenone.—Two distillations at 25 mm. pressure, then two crystallizations from ether; m. p. 48°.

***p*-Phenylbenzophenone.**—Friedel–Crafts reaction of benzoyl chloride + biphenyl + $AlCl_3$ in carbon disulfide. Biphenyl removed by steam distillation and petroleum ether extraction. Ketone crystallized from methanol, twice crystallized from ethanol and once from ether; m. p. 102–103° (literature, 102–103°).

***p,p'*-Diphenylbenzophenone.**—Friedel–Crafts reaction of carbonyl chloride + biphenyl + $AlCl_3$ in carbon disulfide. Ketone crystallized twice from toluene, three times from xylene and finally acetic acid; m. p. 233.5–234.5° (literature, highest m. p. 233.4°).

Fluorenone.—Eastman Kodak material crystallized successively from ethanol and ether; m. p. 83.8–84.3° (literature, same).

Xanthone.—Same as fluorenone, m. p. 174°.

Diphenyl Ether.—Three successive fractional crystallizations; b. p. 248.5–249.5° (745.5 mm.), m. p. 28° (literature, b. p. 252° (760), m. p. 26, 27, 29°).

Dibenzodioxin.—Dry distillation of potassium *o*-chlorophenolate. Distillate after washing with dilute alkali was crystallized first from ether and then successively from benzene and twice from ethanol; m. p. 119–120° (literature, same).

Benzophenone Dichloride.—From ketone + PCl_5 at 150°: chloride distilled *in vacuo* three times. The clear, white liquid showed no carbonyl absorption.

Fluorenone Dichloride.—From fluorenone + PCl_5: twice recrystallized from ether; m. p. 102.3–103.3° (literature, highest m. p. 101.5–102.5°). No carbonyl absorption found.

***p,p'*-Diphenylbenzophenone Dichloride.**—Same procedure as for preceding chlorides. Recrystallized three times from ether; m. p. 135.7–137° (literature, same).

Benzophenone $HgCl_2$.—From benzophenone + $HgCl_2$ in (1) ether and (2) alcohol. Products crystallized from ether; m. p. 78–79° with decomposition (literature, highest m. p., 81°). *Anal.* Calcd: Hg, 44.24. Found: Hg, 43.98.

Benzophenone $HgBr_2$.—From alcohol solution containing 1 mole ketone + 2 moles $HgBr_2$. Recrystallized three times from ethanol; m. p. 76° (decomposition). *Anal.* Calcd.: Hg, 36.98. Found: Hg, 37.64.

Fluorenone $HgCl_2$.—From alcohol solutions of ketone and $HgCl_2$; m. p. 158–159°. K. H. Meyer[18] describes a compound, fluorenone $(HgCl_2)_2$, as orange-red needles but no melting point is given. Starting with the proportions of 1 mole of fluorenone to 2 moles of $HgCl_2$ in alcohol solution, $HgCl_2$ was first precipitated followed by the orange-red crystals corresponding to the molecular ratio 1:1. *Anal.* Calcd.: Hg, 44.42; Cl, 15.70. Found: Hg, 44.75; Cl, 15.28.

Xanthone $HgCl_2$.—From either acetic acid or alcohol solutions of xanthone and $HgCl_2$ as colorless needles melting at 229–230° to a light brown liquid. *Anal.* Calcd.: Hg, 42.9. Found: Hg, 42.97, 43.09.

Quinone $HgCl_2$.—From alcohol solutions of quinone and $HgCl_2$; recrystallized orange-red needles from alcohol; m. p. 153–154° (decomposition). *Anal.* Calcd.: Hg, 52.85; Cl, 18.68. Found: Hg, 52.62; Cl, 18.51.

The quantitative absorption spectra and positions of maximum absorption (Table I) were obtained by methods which have been described.[19]

Summary

1. Solutions of the ketones: acetone, 3-hexanone, cyclohexanone, dicyclohexyl ketone, cyclohexyl phenyl ketone, benzophenone, *p*-phenylbenzophenone and *p,p'*-diphenylbenzophenone in sulfuric acid show increased light absorption in the region associated with the carbonyl group. They retain their ketonic structure in these solutions.

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[18] K. H. Meyer, *Ber.*, **43**, 162 (1910).

[19] Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928); Anderson, *ibid.*, **51**, 1889 (1929).

2. In addition to showing the above change, xanthone and fluorenone possess new bands in sulfuric acid solutions which are believed to be associated with the stabilization of the quinonoid structure for these compounds. Solutions of stannic chloride produce the same changes on the absorption spectrum of xanthone that sulfuric acid does.

3. The production of color with xanthone and sulfuric acid or stannic chloride is not due to the ether oxygen.

4. The color of ketone chlorides and sulfuric acid or stannic chloride is of a different nature from that of ketones and resembles that of triarylcarbinols and salts of these carbinols. It is postulated that in such solutions the ketone chlorides exist in a quinonoid modification.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Films Built by Depositing Successive Monomolecular Layers on a Solid Surface

BY KATHARINE B. BLODGETT[1]

A previous paper[2] has described briefly a method of depositing successive monomolecular layers of "stearic acid" on glass. Subsequent experiments,[3] which will be discussed in this paper, have shown that the substance deposited on the glass was calcium stearate and not stearic acid. The layers were deposited one at a time; thus a film could be built having a thickness of 1, 2, 3 or more layers of molecules. Further development of the method has made it possible to deposit more than 200 layers on glass and on various metals.

This paper will describe experiments in which the thickness of films containing many layers was measured by means of the interference of monochromatic light reflected by the films. These measurements were made with films of calcium or barium soaps of long-chain fatty acids deposited on glass having a high refractive index. Films can be built with fatty acids[4] when deposited on a metal, but fatty acids do not adhere readily to glass.

A monomolecular calcium stearate film is formed on water by placing a small amount of stearic acid, dissolved in benzene, on a clean surface of water containing calcium salts. The stearic acid spreads rapidly in a monomolecular film.[5] If the pH of the water-bath is greater than 5.0, approximately, the Ca ions in the water combine with the carboxyl group of the adsorbed molecules, converting the film to calcium stearate. The film may be neutral soap or an acid soap, depending on the pH of the water. The term "acid soap" is used here in the sense in which it is used by McBain[6] and other writers to refer to compounds of the fatty acid and the neutral soap. Both types of soap will be called "calcium stearate" in this paper.

The film is transferred from water to glass[7] by raising a clean glass slide slowly out of the water on which the film is spread. A constant surface pressure is maintained on the film as the glass is raised through the surface. If the water-bath is alkaline ($p\mathrm{H} > 7.5$), the stearate molecules show a ready tendency to attach themselves to glass, so that the surface pressure causes them to be shoved off the water and onto the glass. Langmuir, Adam and others have demonstrated that the fatty acids tend to orient themselves on a water surface with the —COOH "head" of each molecule in contact with the water and the chain tilted at a more or less steep angle with the plane of the water surface. In the present experiments the monomolecular layer of calcium stearate is similarly oriented and the layer is transferred to glass with the $(\text{—COO})_2\text{Ca}$ heads attached to the glass, and the paired chains perpendicular to the plane of the glass. The exposed upper surface of the film is composed of closely packed CH_3 groups.

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[1] The experiments described in this paper were commenced in collaboration with Dr. Irving Langmuir and were continued while he was traveling in the Orient. The writer is indebted to Dr. Langmuir for urging her to develop further the method described in the previous paper, and for contributing many important suggestions which have been included in this paper.

[2] K. B. Blodgett, THIS JOURNAL, **56**, 495 (1934).

[3] I. Langmuir, *J. Franklin Inst.*, **218**, 153 (1934).

[4] G. L. Clark, R. R. Sterrett and P. W. Leppla, THIS JOURNAL, **57**, 330 (1935).

[5] (a) I. Langmuir, *ibid.*, **39**, 1848 (1917); (b) N. K. Adam, *Proc. Roy. Soc.* (London), **A99**, 336 (1921), and succeeding papers.

[6] J. W. McBain, M. Taylor and M. E. Laing, *J. Chem. Soc.*, **121**, 621 (1922), and other papers.

[7] I. Langmuir, *Trans. Faraday Soc.*, **15**, 62 (1920); reprinted in *G. E. Rev.*, **24**, 1025 (1921).