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

# THE QUINONOID STRUCTURE OF SOME TRIPHENYLMETHYL SALTS

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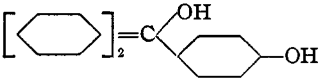
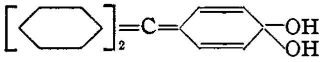
Previous papers from this Laboratory[1] have shown that a very marked change occurs in the quantitative absorption spectra when colorless *p*-hydroxytriarylcarbinols possessing the benzenoid structure (I) are converted to the tautomeric colored quinonoid carbinols (II). This type of change is especially apparent when the benzenoid carbinols are converted to the corresponding fuchsones (III) of whose quinonoid structure no question has ever been raised. It has now been found that this same marked change occurs in the quantitative absorption spectra when a colorless dimethyl sulfate solution of triphenylchloromethane is converted to triphenylmethyl sulfate or perchlorate by silver sulfate or silver perchlorate, respectively. The solution becomes yellow and at the same time the absorption of light by the solution changes in a manner similar to that which has been shown to occur when the benzenoid carbinols are converted to the quinonoid fuchsones. We have found by means of absorption spectra that triphenylchloromethane possesses the same benzenoid structure in dimethyl sulfate solutions that it possesses in ether solutions and from the similarity in the curves obtained from these two sets of reactions—benzenoid carbinols to quinonoid fuchsones and benzenoid chloride (IV) to sulfate or perchlorate—we are led to conclude that the salts, the sulfate and the perchlorate, exist in a quinonoid state (V, VI) in dimethyl sulfate solutions.


I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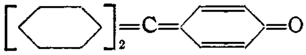
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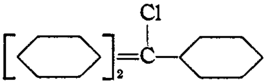
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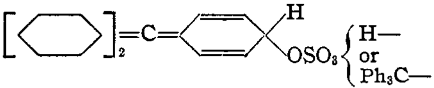
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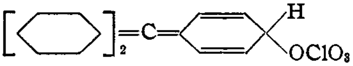
VI

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

This conclusion is in agreement with the chemical evidence presented by Gomberg,[2] who pointed out that the sulfates of the *p*-halogenated triphenylcarbinols are quinonoid compounds. He showed that diphenylquinomethane (fuchsone) was one of the products obtained upon hydrolysis of the sulfate of *p*-bromotriphenylcarbinol.

Former investigators have been unable to study such changes in the spectra of these salts because no one solvent had been used in which all of these compounds could be dissolved without chemical change. Gomberg[3] used dimethyl sulfate as a solvent for the preparation and purification of some of these salts, *e. g.*, the sulfates, and he pointed out that when the solvent had been carefully purified, it yielded colorless solutions of triphenylcarbinol and triphenvlchloromethane. The quantitative absorption spectra of the colorless solutions of triphenylcarbinol and triphenylchloromethane are almost identical with those curves obtained from the ether solutions of these compounds.[4] These data, together with Gomberg's work, show that pure dimethyl sulfate is without chemical effect upon these solutes. The use of dimethyl sulfate as a solvent makes it possible, therefore, for us to compare, in one solvent, the absorption spectra of the benzenoid and quinonoid salts of the triarylcarbinols.

It has been found, also, that the quantitative absorption spectra between frequencies 4200–1350 $\text{mm.}^{-1}$ of solutions of the sulfate and perchlorate salts of triphenylcarbinol in pure sulfuric acid and pure perchloric acid, respectively, are almost identical with those obtained for each salt in its dimethyl sulfate solution; the difference between the two sets of curves lies only in the height of the quantitative curves. The similarity in the absorption bands constitutes evidence in favor of the hypothesis that these salts exist as quinonoid compounds in their solutions in these acids.

In the light of these results it appears that the questions concerning the nature of the constitution of the various salts of triarylcarbinols, which have been discussed in articles recently published by Dilthey,[5] Brand,[6] Madelung,[7] Lund[8] and others have been largely clarified and rather in favor of quinoidation.

## Experimental

A drawing of the apparatus which was used to prepare solutions of the sulfate and perchlorate salts of triphenylcarbinol in dimethyl sulfate is shown in Fig. 1. Absorption

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[2] (a) Gomberg, *Ber.*, **40**, 1853 (1907); (b) Gomberg and Blicke, THIS JOURNAL, **45**, 1770 (1923).

[3] Ref. 2a, p. 1847.

[4] Anderson, THIS JOURNAL, **50**, 208 (1928).

[5] Dilthey, *Z. angew. Chem.*, **37**, 313 (1924).

[6] Brand, *J. prakt. Chem.*, **109**, 17 (1925).

[7] Madelung, *ibid.*, **111**, 100 (1925).

[8] Lund, THIS JOURNAL, **49**, 1346 (1927); see also Girbes, "Dissertation," Rijks University, Gröningen, **1928.**

flasks were available which had a capacity in bulb H of either 50 or 100 cc. together with absorption cells K which were fitted with parallel quartz plates through which the light was passed to be absorbed and in which the distance between the inside faces of the quartz plates was 2.4, 5.0, 7.5 or 10.0 mm. Pure silver sulfate or silver perchlorate was placed in the tube I, and a small sample of pure triphenylchloromethane, weighed directly into a micro-beaker L, was placed in the upper part of the absorption flask. In order to seal the apparatus and yet not contaminate the solvent with the lubricant, stopcocks G,G and the ground-in stopper M had very small amounts of stopcock grease on the outside edges of the ground surfaces only. Dimethyl sulfate, previously distilled under reduced pressure, was placed in flask A and the whole apparatus was evacuated by means of a water aspirator. When the manometer N indicated a pressure of 12–15 mm. of mercury within the apparatus, the silver salt in I was heated to 120–130° for fifteen to twenty minutes by means of a small electrically heated coil. After the silver salt had been dried and cooled the dimethyl sulfate was distilled through the fractionating column B and condenser C. Having collected the first fraction in F, the main portion was diverted by means of stopcock D through a 30-cm. column of freshly ignited potassium carbonate which had been placed in tube E, and from there was led into the bulb H. When H and I had been filled, stopcock D was turned to allow the last portions of the dimethyl sulfate to collect in F. The volume of the solvent contained in H and I was ascertained from calibrated graduations on the tube J immediately above the bulb H; a correction for the volume occupied by the solid silver salt in I was always applied. Following this, air was slowly admitted through the calcium chloride tube O until the pressure inside the apparatus was again equal to atmospheric. Stopcocks G,G were closed and the absorption flask, after being disconnected from the distillation set-up, was inverted to dissolve the triphenylchloromethane. The mixture was then shaken until the reaction was completed.

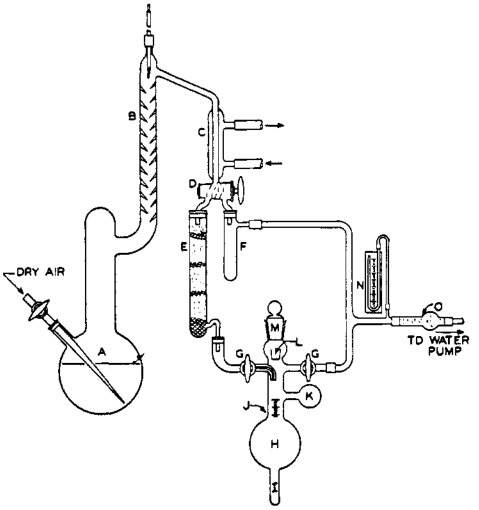

Fig. 1.

Silver perchlorate reacts rapidly with triphenylchloromethane in dimethyl sulfate and the solution acquires a brilliant yellow color. The silver chloride that is formed in the reaction is very finely divided but when the solution is allowed to stand, settles out readily. It possesses the property, however, in the dimethyl sulfate solutions, of adhering to the walls of the vessel and care was taken in the method of shaking to see that none of it was introduced into the quartz absorption cell K.

In preparing the *n*-sulfate of triphenylcarbinol it was necessary to keep the solution at 50–55° for a day or two before the reaction was completed and a mechanical shaking machine in an enclosed air-bath was employed. The delay in the completion of this reaction is believed to be due to the very slight solubility of silver sulfate as compared to silver perchlorate in dimethyl sulfate. The quantitative absorption spectrum of each solution was determined within a few minutes after making up the solution, and was redetermined at intervals thereafter until it was certain that the reaction was at an end.

From the fact that the absorption curves for the solutions prepared in the above manner approach a height only one-half that reached by the corresponding solutions in either sulfuric acid or dimethyl sulfate containing sulfuric acid leads to the inference that the solutes are different in the two cases. We therefore infer that in the former case, in the purified dimethyl sulfate, we were dealing with a solution of the *n*-sulfate.

When the potassium carbonate was omitted in the purification of the dimethyl sulfate, colored solutions were instantly obtained with either triphenylchloromethane or triphenylcarbinol. From the similarity of the absorption curve (Curve 1, Fig. 2) with that of the acid sulfate in sulfuric acid (Curve 1, Fig. 3) the inference was drawn that we were here dealing with solutions of the acid sulfate. These data corroborate the conclusion reached by Gomberg[3] that the last traces of sulfuric acid cannot be removed from dimethyl sulfate by distillation.

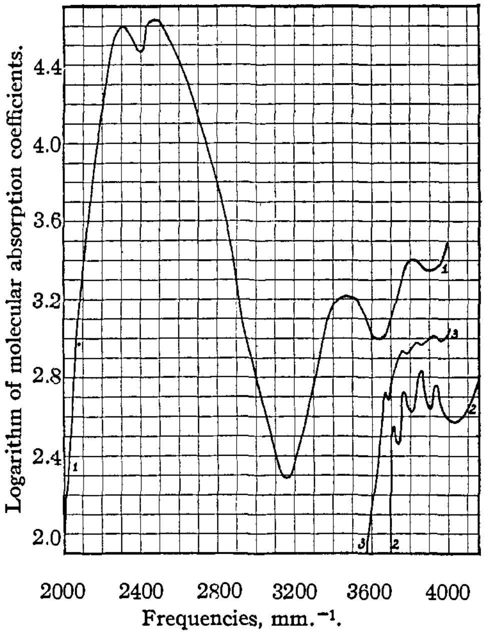

Fig. 2.—1, Triphenylmethyl acid sulfate in dimethyl sulfate; 2, triphenylcarbinol in dimethyl sulfate; 3, triphenylchloromethane in dimethyl sulfate.

The quantitative absorption spectra of triphenylcarbinol and triphenylchloromethane in dimethyl sulfate were obtained from solutions made in a manner identical with that used for the preparation of the *n*-sulfate and perchlorate except that no silver salt was present. Solutions of the carbinol and the chloride in dimethyl sulfate have been kept for more than a week without any development of color or of change in their absorption spectra.

Solutions for the determination of the quantitative absorption spectra of triphenylmethyl sulfate and perchlorate in sulfuric acid (95%) and perchloric acid (72%), respectively, were made by dissolving weighed amounts of either triphenylcarbinol or triphenylchloromethane in known volumes of the pure acid and taking the absorption spectra of successive dilutions.

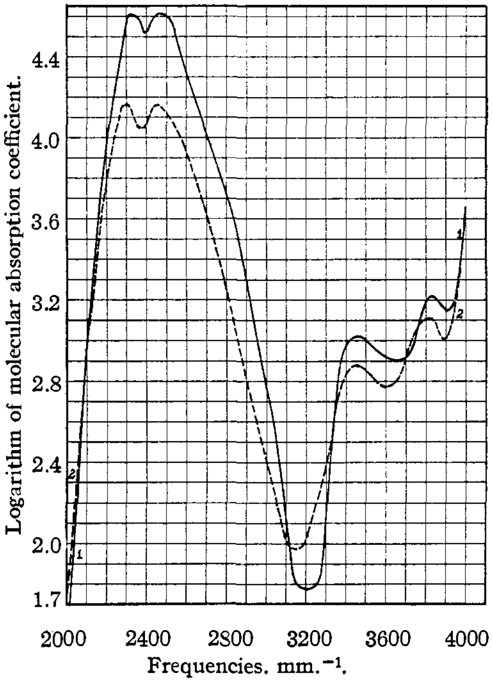

Fig. 3.—1, Triphenylmethyl acid sulfate in sulfuric acid (95%); 2, triphenylmethyl normal sulfate in dimethyl sulfate.

Attempts were made to determine the absorption spectrum of triphenylmethyl nitrate. The results thus far have not been quantitative. Silver nitrate is quite insoluble in dimethyl sulfate, and before all the triphenylchloromethane is converted to the nitrate, part of the nitrate already formed undergoes decomposition. The results that have been obtained, however, indicate that its quantitative absorption spectrum is very similar to that of the sulfate and perchlorate.

The points of maximum absorption of each—the sulfates, perchlorate and nitrate of triphenylcarbinol—were determined by a method which has been previously described[1b] and were found to be identical with each other within experimental limitations. The averages of the determinations of these points of maximum absorption lie at frequencies 2305, 2467, 3432, 3825 mm.$^{-1}$.

The writer wishes to acknowledge his deep indebtedness to Professor M. Gomberg for the suggestions and advice which have made this work possible.

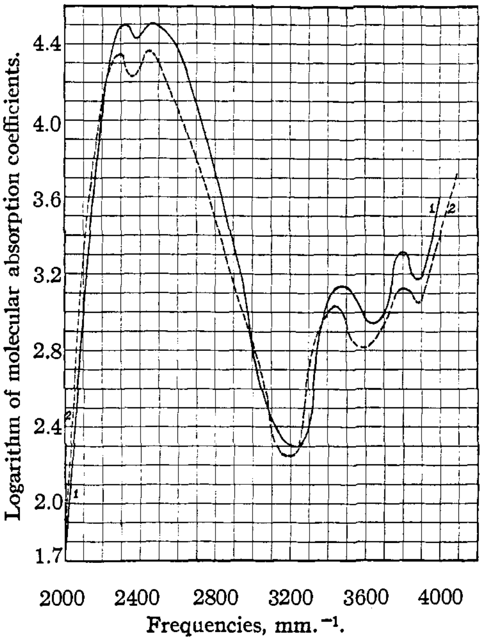

Fig. 4.—1, Triphenylmethyl perchlorate in perchloric acid (72%); 2, triphenylmethyl perchlorate in dimethyl sulfate.

## Summary

1. The quantitative absorption spectra of solutions of triphenylcarbinol, triphenylchloromethane, triphenylmethyl sulfate and triphenylmethyl perchlorate in dimethyl sulfate and of solutions of the acid sulfate and of the perchlorate in sulfuric acid and perchloric acid, respectively, have been ascertained.

2. The data obtained from the absorption spectra of the above salts constitutes evidence in favor of the hypothesis that triphenylmethyl *n*-sulfate, acid sulfate and perchlorate exist in a quinonoid modification in their solutions in dimethyl sulfate, in sulfuric acid or perchloric acid, respectively.

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