Summary

The quantitative absorption curves of ether solutions of the methane, the benzenoid carbinol, the quinonoid carbinol and the fuchsone of each—the *p*-hydroxytriphenylcarbinol and *o*-cresyldiphenylcarbinol—have been carefully determined. The spectroscopic results constitute further evidence that *p*-hydroxytriphenylcarbinol and *o*-cresyldiphenylcarbinol exist each in two tautomeric forms, a quinonoid and a benzenoid.

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

THE ABSORPTION SPECTRA OF SOME TRIPHENYLMETHANE DERIVATIVES

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The curves which we have obtained for the quantitative absorption of ultraviolet light by solutions of triphenylmethane and some of its derivatives differ in many respects from those which other investigators have recorded. These differences are due partly to variations in equipment and procedures used at different laboratories but partly, however, to the fact that in some of the recently published work no account was taken of the fact that reaction between the solute and the solvent had given rise to compounds which differed from the original solute and which consequently possessed different absorption spectra.

As previously mentioned,[1] we have found ether to be a very satisfactory solvent to use in this type of work. We have examined layers of pure ethyl ether as thick as two centimeters and in no case has the pure liquid shown selective absorption[2] in the spectrum included by our equipment,[1] which allows measurements to be made at frequencies from 4550 mm.$^{-1}$ to the visible.

The ultraviolet absorption spectra of solutions of triphenylmethane and triphenylcarbinol have been described by Hartley,[3] Baker[4] and Hantzsch[5] who give curves which show absorption only in broad bands. Orndorff, Gibbs, McNulty and Shapiro[6] have given curves which show the quantitative absorption of ultraviolet light by absolute ethyl alcohol solutions of these compounds. They report ten peaks for the solution of triphenylmethane and seven for triphenylcarbinol between 3700 and

[1] Anderson and Gomberg, THIS JOURNAL, **50**, 203 (1928).

[2] See for discussion, Smith, Boord, Adams, and Pease, THIS JOURNAL, **49**, 1335 (1927); De Laszlo, *ibid.*, **49**, 2106 (1927).

[3] Hartley, *J. Chem. Soc.*, 51, 152 (1887).

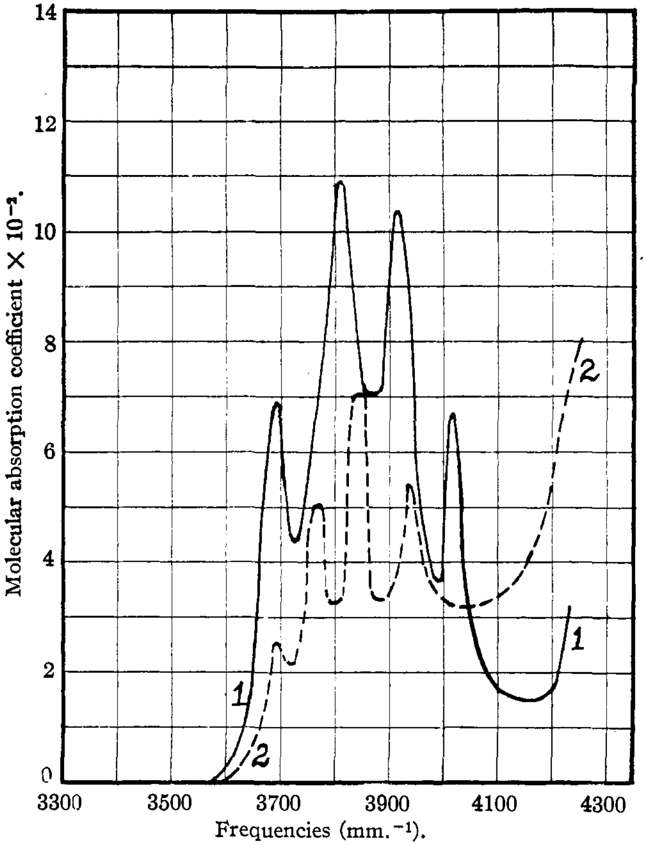
[4] Baker, *ibid.*, 91, 1490 (1907).

[5] Hantzsch, *Ber.*, **52**, 509 (1919).

[6] Orndorff, Gibbs, McNulty and Shapiro, THIS JOURNAL, **49**, 1541 (1927).

4200 mm^{-1}. Using ether solutions we have located only the four prominent peaks of each compound between the above frequencies. A careful examination of our plates has not given any indication of several of the absorption peaks which the latter investigators have found in alcohol solutions.

The quantitative absorption spectra of solutions of the ethyl ether of triphenylcarbinol, whether in ethyl ether or absolute ethyl alcohol, differ only in intensity; the position of the bands at frequencies 3690, 3760, 3840 and 3930 are virtually unchanged by the change of solvent.



1. ——— = Triphenylmethane; 2. ---- = Triphenylcarbinol.

Fig. 1.

It is known that triphenylchloromethane reacts with hot ethyl alcohol to form the ethyl ether of triphenylcarbinol,[7] and we have found that even in the cold the conversion of the chloride to the ether by alcohol is almost

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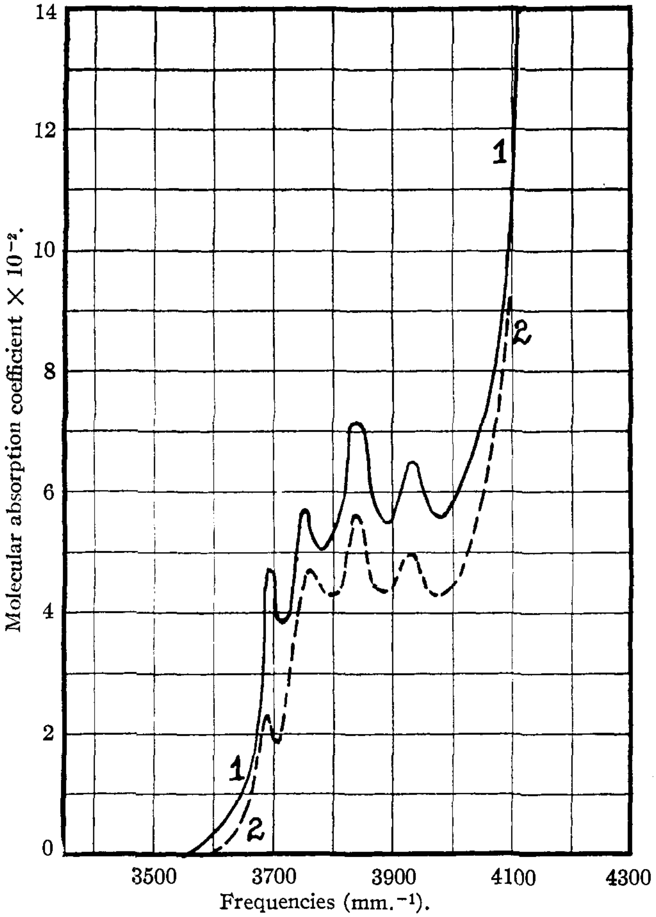
[7] (a) Hemilian, *Ber.*, **7**, 1208 (1874); (b) Friedel and Crafts, *Ann. chim., phys.* [6] **1**, 502 (1884); (c) Frey, *Ber.*, **28**, 2518 (1895).

quantitative. A solution of triphenylchloromethane in ether has absorption bands at frequencies 3660, 3740, 3830 and 3920 mm^{-1}. When, however, the chloride is dissolved in absolute ethyl alcohol (neutral), the frequencies of the absorption peaks become practically identical with those of the pure ethyl ether of triphenylcarbinol, there being only a slight difference in the intensity of the peaks. We conclude that the quantitative absorption curve of a solution of triphenylchloromethane in absolute ethyl alcohol as described by Orndorff, Gibbs, McNulty and Shapiro is not due to triphenylchloromethane but is due to the ethyl ether of triphenylcarbinol.

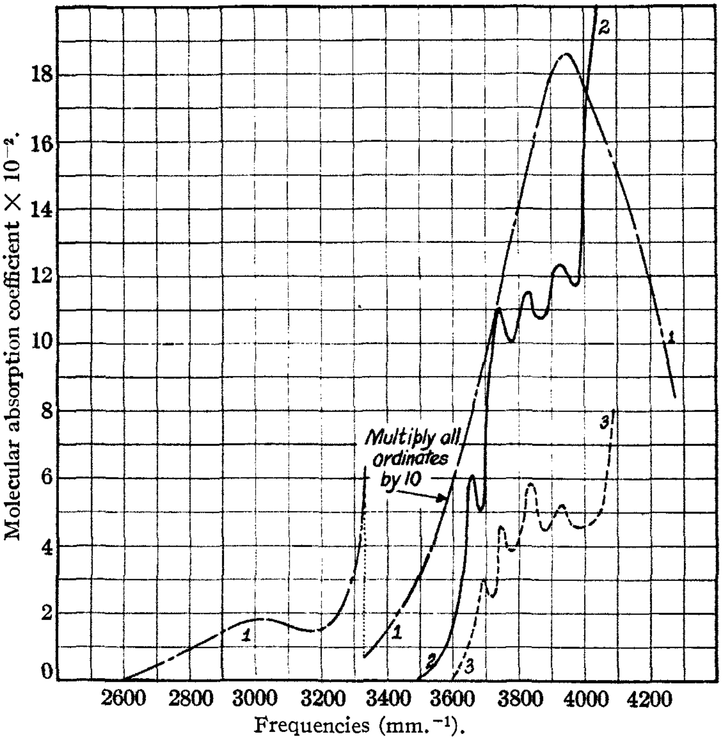


1. ——— = Solution in ether; 2. ---- = Solution in neutral absolute ethyl alcohol.

Fig. 2.—Ethyl ether of triphenylcarbinol.

Purification of Compounds.—Benzophenone was distilled under reduced pressure and, after three repeated crystallizations from alcohol, it was recrystallized from ether; m. p. 47°. It was used by us to check our curves with data that have been given in the literature. Our results agree very well with those of the most recent investigator.[8]

Triphenylmethane was prepared by the reduction of triphenylcarbinol with zinc dust and acetic acid. It was recrystallized from benzene and then twice from ether; m. p. 92°.



1. — — — = Benzophenone in alcohol; 2. ——— = Triphenylchloromethane in ether; 3. - - - - = Solution obtained by dissolving triphenylchloromethane in neutral absolute ethyl alcohol.

Fig. 3.

Triphenylcarbinol, made from benzophenone by the Grignard reaction with phenylmagnesium bromide, was recrystallized once from benzene and then twice from ether; m. p. 162°.

Triphenylchloromethane was made by the reaction between a benzene solution of triphenylcarbinol and dry hydrogen chloride in the presence of anhydrous calcium chloride. It was recrystallized from absolute ether just prior to being used; m. p. 111–112°.

The ethyl ether of triphenylcarbinol was prepared by adding pure triphenylchloromethane to an alcohol solution of sodium ethylate. After it was crystallized twice from ether, it melted at 83°. The ethoxy compound was also made by allowing a solu-

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[8] Scheibe, *Ber.*, **59**, 2626 (1926).

tion of pure triphenylchloromethane in neutral absolute ethyl alcohol to stand at room temperature overnight. The solvent was evaporated under reduced pressure in a desiccator which contained fused calcium chloride. Samples of the dried residue melted at 81–82° and the melting point of mixtures of this residue and the purified ether, which was prepared as first described, showed that the residue was practically pure ethyl ether of triphenylcarbinol.

The absolute ethyl alcohol which was used as solvent was obtained by a careful fractionation of 99.5% ethyl alcohol which had been distilled from anhydrous potassium hydroxide. A two centimeter layer of the liquid was perfectly transparent at all frequencies within the limit of our equipment. The ether that was used as solvent was in most cases a product obtained on the market as "Reagent Ether Anhydrous." This ether, without further purification, was optically clear and was without effect upon the solute; however, for some of the work, it was distilled from fresh metallic sodium.

Summary

1. Curves are presented which show the quantitative absorption spectra in the ultraviolet of ether solutions of triphenylmethane, triphenylcarbinol, triphenylchloromethane and the ethyl ether of triphenylcarbinol; also curves which show the absorption of absolute ethyl alcohol solutions of benzophenone and the ethyl ether of triphenylcarbinol.
2. It has been shown that the curve obtained from a solution of triphenylchloromomethane in neutral absolute ethyl alcohol is in reality the absorption curve of the alcohol solution of the ethyl ether of triphenylcarbinol.

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[Contribution from Kent Chemical Laboratory, University of Chicago]

THE REACTION OF ISOPROPYL IODIDE WITH MERCURIC CHLORIDE

By Ben H. Nicolet and William McDaniel Potts[1]

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Conant and others[2] have recently studied the reaction $RCl + KI = RI + KCl$ (R representing a considerable variety of alkyl and other radicals) in some detail. With the simpler alkyl chlorides, it took place some 60 times more rapidly for primary than for secondary chlorides. They found the reaction quite strictly of the second order, and so slightly reversible that the opposing reaction (if any) did not need to be considered in the calculation of velocity constants.

Nevertheless, Oppenheim[3] in 1860 reported that ethyl chloride and amyl chloride could be obtained by the action of mercuric chloride on the

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[1] The material here presented was used by William McDaniel Potts in partial satisfaction of the requirements for the degree of Master of Science, at the University of Chicago, 1927.

[2] (a) Conant and Kirner, This Journal, **46**, 352 (1924); (b) Conant and Hussey, *ibid.*, **47**, 476 (1925); (c) Conant, Kirner and Hussey, *ibid.*, **47**, 488 (1925).

[3] Oppenheim, *Ann.*, **140**, 207 (1860).