The oxygen consumption curves of heptaldehyde and butyraldehyde are somewhat similar to that of *n*-octane, but the difference in the nature of the early reaction is shown by the fact that in the case of the aldehydes the oxygen consumption corresponds to the carbon oxides formed, while in the case of octane the early stage involves very little of these oxidation products. Altogether it appears that the interpretation of the oxidation phenomena outlined above is in excellent agreement with the experimental facts and affords a simple explanation of most of the phenomena observed.

V. Summary

1. The vapor phase oxidation of *n*-octane, *n*-heptaldehyde and *n*-butyraldehyde has been studied in detail.

2. The results may be simply interpreted on the theory that the initial oxidation product of *n*-octane is octaldehyde, which in turn is further oxidized to aldehydes of successively smaller number of carbon atoms, carbon monoxide and some carbon dioxide being simultaneously formed.

3. The existence of luminescent "chain" reactions is indicated, apparently corresponding to the oxidation of the aldehydes to lower aldehydes, carbon monoxide and water.

YONKERS, NEW YORK

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

TAUTOMERISM OF HYDROXYTRIARYLCARBINOLS. II

BY L. C. ANDERSON

RECEIVED FEBRUARY 5, 1929 PUBLISHED JUNE 5, 1929

By the combination of spectroscopic and chemical evidence presented in a previous paper[1] it has been shown that the quinonoid modification of 3-methyl-4-hydroxytriphenylcarbinol is not a mixture of the fuchsone and the benzenoid form of the carbinol. Further studies of the absorption spectra of the above-mentioned carbinols, of 3-methoxy-4-hydroxytriphenylcarbinol and of the 5-chloro- and 5-bromo-derivatives of 3-methyl-4-hydroxytriphenylcarbinol have given further evidence of the quinonoid forms of these hydroxytriarylcarbinols.

The quantitative absorption curves of ether solutions of the methanes, benzenoid modifications, quinonoid modifications and the fuchsones of the aforementioned carbinols have been determined and the points in the visible and ultraviolet portions of the spectrum (7600–2350 Å.) at which a maximum and a minimum of energy is absorbed by these solutions have been located. We have found in the curves for some of the quinonoid forms that the absorption band in the violet region and in the ultraviolet region adjacent to the visible is at a position different from that which it has in the corresponding fuchsone (Table I). This is a positive indication in

---

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

itself that the color of our colored carbinol is not due to the presence of small quantities of the fuchsone and hence that this compound must itself be a quinonoid carbinol.

The quinonoid curve as compared to that of the fuchsone is displaced toward the shorter wave lengths in 5-chloro- and 5-bromo-*o*-cresyldiphenylcarbinols and toward the longer wave lengths in 4-hydroxy-triphenylcarbinol. In *o*-cresyldiphenylcarbinol and guaiacyldiphenylcarbinol the displacement is within our experimental error of determining the position of these peaks.

The similarity of the curves of the members within each class, the methanes, the benzenoid carbinols, the quinonoid carbinols and the fuchsones is very striking. As the molecular weight in each group of compounds is increased some of the peaks for the corresponding derivative in each class are shifted toward the longer wave lengths and some are shifted in the direction of shorter wave lengths. The positions of the bands between frequencies 2800 mm.$^{-1}$ and 2600 mm.$^{-1}$ in the curves for the fuchsones and for the quinonoid carbinols are displaced toward the longer wave length as the molecular weights of each type increase, but the displacement bears no simple relationship to the increase of molecular weight.

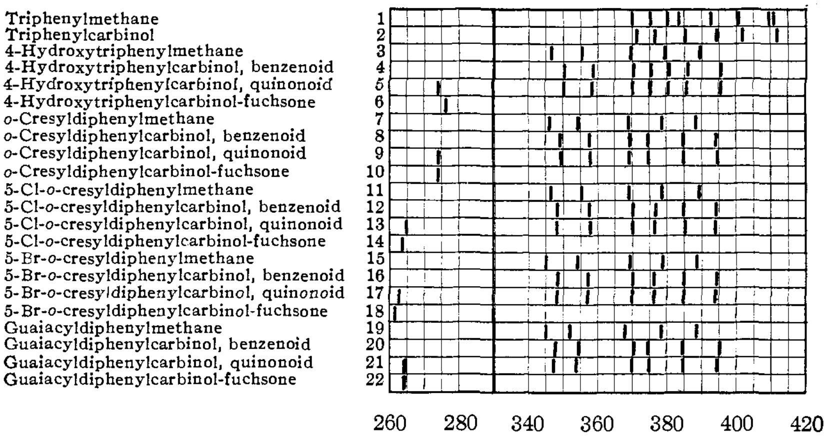

Fig. 1.

Procedure.—The method which we have used in obtaining data for plotting curves to show the quantitative absorption of light by solutions has already been described.[1] For determining the points of maximum and minimum absorption, the relative blackening of the photographed absorption spectra has been measured by means of a Moll recording microphotometer. The spectrograph plate is drawn past the slit of the thermopile at least twice, first, to obtain a curve (a) for the intensity of light in the beam which has passed through the solvent and, second, to obtain a curve (b) for the intensity of light in the beam which has passed through the solution. These curves appear superimposed upon the bromide paper used in the recording instrument. Wherever the two curves have the same slope at a given wave length, there is a point of maximum or minimum absorption. When the solvent curve (a) falls below the solution curve (b) the points of maximum absorption are those wave lengths at which the two curves are farthest apart. Black ink lines ruled upon the plate after exposure and development locate certain frequencies upon the photometer curve and allow any other frequency

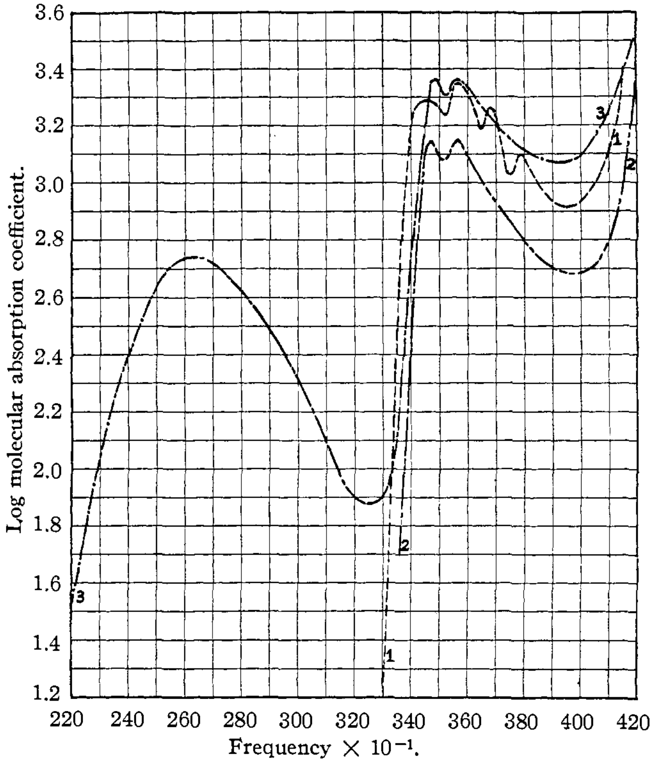

Fig. 2.—5-Chloro-*o*-cresyldiphenylcarbinol: 1, ---, methane; 2, —··—, benzenoid carbinol; 3, —·—, quinonoid carbinol.

Table I

Frequency Numbers

Sample	4-OH-triphenylcarbinol, quinonoid	4-OH-triphenylcarbinol, fuchsone	5-Cl-*o*-cresyldiphenyl-COH, quinonoid	5-Cl-*o*-cresyldiphenyl-COH, fuchsone	5-Br-*o*-cresyldiphenyl-COH, quinonoid	5-Br-*o*-cresyldiphenyl-COH, fuchsone
1	2742	2763	2653	2643	2635	2627
2	2740	2764	2648	2640	2629	2616
3	2738	2767	2650	2640	2628	2621
4	2746	2761	..	..	2630	2617
5	2740	..	..	..	..	..
6	2748	..	..	..	..	..
7	2748	..	..	..	..	..
Av.	2743	2764	2650	2641	2630	2620

to be found from calibration curves. The instrument was calibrated with the spectrograph and comparator by means of the copper spectrum.

The frequencies at which absorption bands have been located in ether solutions of the compounds under discussion are given in Table II and Fig. 1, which also include additional data upon curves already published. We have previously found by visual observation of the spectrograph plates only the four most prominent absorption bands in triphenylmethane and triphenylcarbinol.[2] By using the microphotometer, we have located other peaks in each of the curves and the positions of the bands as now found agree very well with data which have been published by Orndorff, Gibbs, McNulty and Shapiro upon the solutions of these compounds in alcohol.[3]

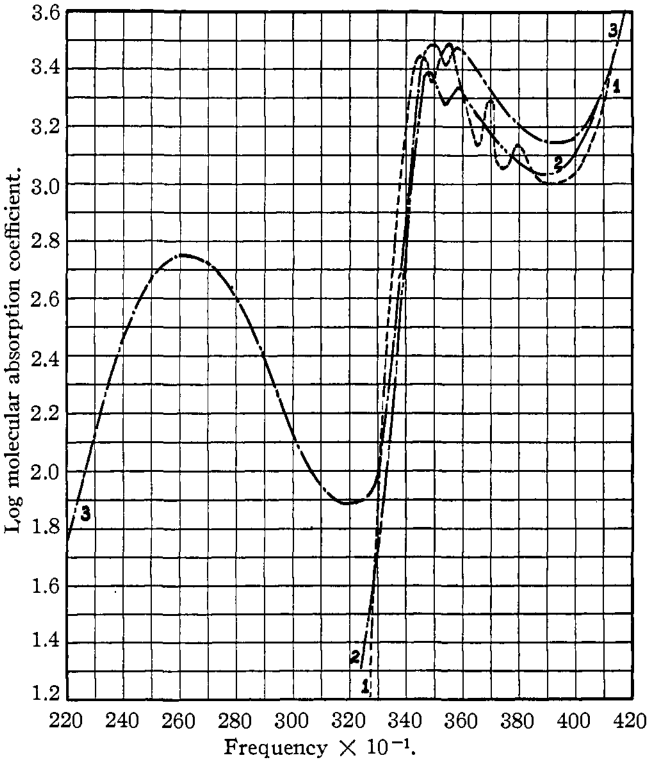

Fig. 3.—5-Bromo-*o*-cresyldiphenylcarbinol: 1, ---, methane; 2, —··—, benzenoid carbinol: 3, —·—, quinonoid carbinol.

Purification of Materials

3-Methyl-4-hydroxy-5-chlorotriphenylmethane was obtained by reducing the corresponding fuchsone with zinc and acetic acid. The substance was recrystallized

---

[2] Anderson, This Journal, **50**, 208 (1928).

[3] Orndorff, Gibbs, McNulty and Shapiro, *ibid.*, **49**, 1541 (1927).

from petroleum ether which had been purified until it showed no selective absorption of light between 2300 and 7500 Å.; m. p. 89–89.5°.

3-Methyl-4-hydroxy-5-chlorotriphenylcarbinol, benzenoid tautomer, was prepared by digesting the fuchsone, or the quinonoid form of the carbinol, with *N* potassium hydroxide solution. The solution was filtered and the colorless filtrate was saturated with carbon dioxide. The crystals were washed and dried; m. p. 145–146°.

3-Methyl-4-hydroxy-5-chlorotriphenylcarbinol, quinonoid tautomer, was prepared by dissolving the corresponding fuchsone in glacial acetic acid. Hot water was added to the solution until the acetic acid concentration had been reduced to 60%. The solution was filtered and the filtrate was allowed to cool very slowly. The crystals produced were filtered, washed with fresh solvent and then dried over a saturated solution of potassium hydroxide in an evacuated desiccator; m. p. 133–134°.

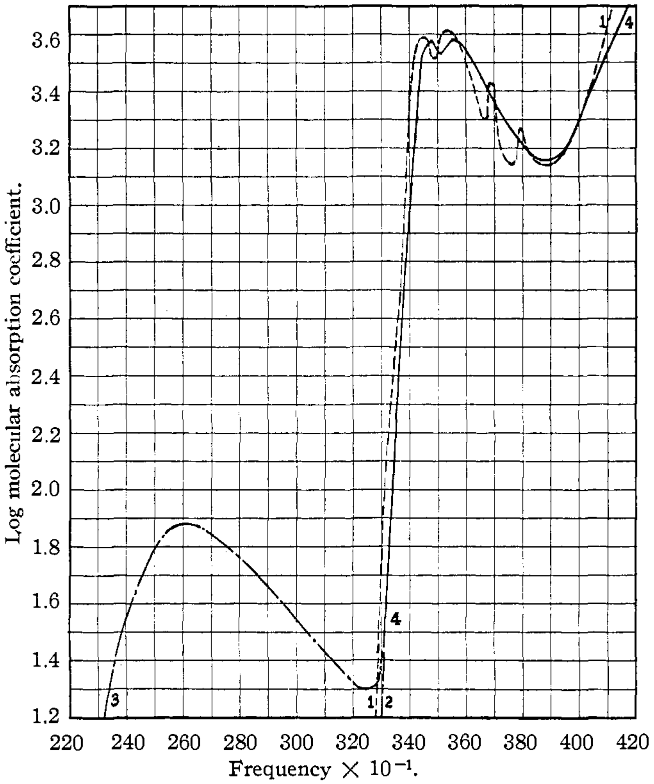

Fig. 4.—Guaiacyldiphenylcarbinol: 1 ---, methane; 2, —··—, benzenoid carbinol; 3, —·—, quinonoid carbinol; 4, —, both benzenoid and quinonoid carbinols.

3-Methyl-4-hydroxy-5-chloroquinodiphenylmethane, that is the fuchsone, was prepared by recrystallizing the corresponding quinonoid carbinol from glacial acetic acid; m. p. 195°.

3-Methyl-4-hydroxy-5-bromotriphenylmethane was prepared by reducing the carbinol with zinc dust and acetic acid. It was crystallized from ether and purified *n*-hexane; m. p. 119°.

3-Methyl-4-hydroxy-5-bromotriphenylcarbinol, benzenoid tautomer, was precipitated by passing carbon dioxide into a solution of the fuchsone in potassium hydroxide. It was crystallized from ether and optically clear petroleum ether; m. p. 144–145°.

3-Methyl-4-hydroxy-5-bromotriphenylcarbinol, quinonoid tautomer, was prepared by adding to a hot solution of the fuchsone in glacial acetic acid enough hot water to reduce the acetic acid concentration to 60%. The yellow crystals were filtered from the cold solution and were dried over "Ascarite" in a desiccator; m. p. 138–139°.

3-Methyl-4-hydroxy-5-bromoquinodiphenylmethane, the fuchsone of 5-bromo-*o*-cresyldiphenylcarbinol, was recrystallized from hot acetic acid. The crystals were washed with absolute ether until free from acid; m. p. 202–203°.

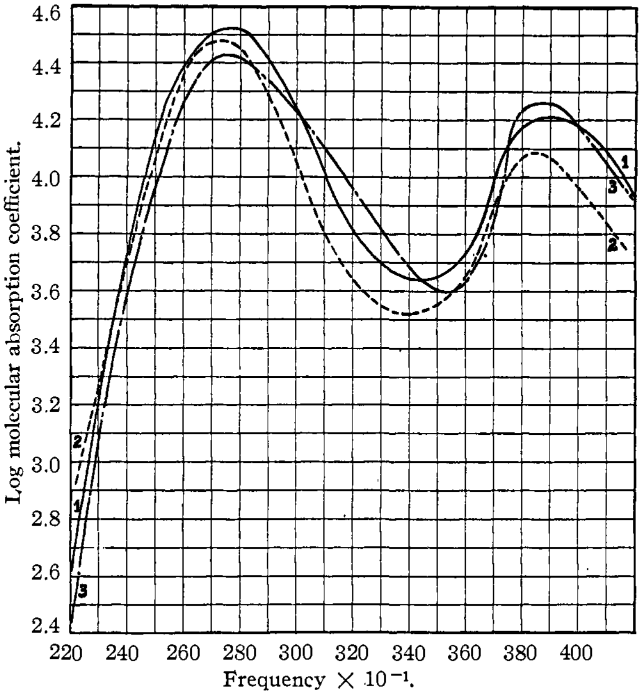

Fig. 5.—Fuchsones of: 1, ———, 5-chloro-*o*-cresyldiphenylcarbinol; 2, - - - -, 5-bromo-*o*-cresyldiphenylcarbinol; 3, —·—, guaiacyldiphenylcarbinol.

3-Methoxy-4-hydroxytriphenylmethane was prepared by the reduction of the carbinol with zinc and acetic acid. The colorless crystals were recrystallized from ether and *n*-hexane; m. p. 108°.

3-Methoxy-4-hydroxytriphenylcarbinol, benzenoid tautomer, was purified by several crystallizations from petroleum ether; m. p. 159°.

3-Methoxy-4-hydroxytriphenylcarbinol, quinonoid tautomer, was prepared by recrystallizing the benzenoid tautomer from 60% acetic acid. The bright yellow crystals were filtered off and dried either over saturated potassium hydroxide solution in an evacuated desiccator or over "Ascarite" at atmospheric pressure; m. p. 154°. This compound has been previously described as brown crystals which melt at 147°.[4]

---

[4] Gomberg and Van Stone, This Journal, 38, 1592 (1916).

3-Methoxy-4-hydroxyquinodiphenylmethane, the fuchsone of guaiacyldiphenylcarbinol, was prepared by crystallizing the quinonoid tautomer from glacial acetic acid. The yellow crystals were heated at 80° for several hours and were then recrystallized from ether; m. p. 182–183°.

Table II

Frequency Numbers of Bands in Ether Solutions

	Triphenyl-	4-OH-Tri-phenyl-	*o*-Cresyl-diphenyl-	5-Cl-*o*-cresyl-diphenyl-	5-Br-*o*-cresyl-diphenyl-	Guaiacyl-diphenyl-
Methane	3700	3463	3462	3465	3452	3451
	3756	3550	3548	3554	3542	3521
	3801	3696	3692	3695	3692	3685
	3831	3793	3787	3789	3789	3787
	3923	3891	3884	3893	3888	3890
	4013					
	4090					
	4108					
Carbinol, benzenoid form	3712	3500	3493	3485	3482	3483
	3764	3582	3577	3575	3581	3548
	3853	3701	3692	3701	3708	3708
	3941	3754	3748	3770	3762	3747
	4015	3802	3849	3850	3851	3858
	4112	3850	3946	3942	3944	3951
		3945				
Carbinol, quinonoid form		2741	2743	2650	2629	2648
		3502	3496	3483	3483	3479
		3589	3583	3580	3575	3548
		3703	3700	3701	3698	3702
		3753	3751	3767	3765	3751
		3806	3854	3853	3850	3848
		3856	3950	3942	3940	3941
		3952				
Carbinol, fuchsone		2764	2740	2641	2620	2648

Summary

1. Curves and tables have been prepared which show the quantitative absorption of ultraviolet light by ether solutions of the methane, the benzenoid carbinol, the quinonoid carbinol and the fuchsone of each of the following compounds: 5-chloro-*o*-cresyldiphenylcarbinol, 5-bromo-*o*-cresyldiphenylcarbinol and guaiacyldiphenylcarbinol.

2. Data have been tabulated which supplement those already published upon the quantitative absorption of light by ether solutions of triphenylmethane, triphenylcarbinol and the methane, benzenoid carbinol, quinonoid carbinol and the fuchsone of each, 4-hydroxytriphenylcarbinol and the *o*-cresyldiphenylcarbinol.

3. Further evidence based on spectroscopic data is presented to prove the existence of a quinonoid modification of hydroxytriarylcarbinols.

Ann Arbor, Michigan