

tone there was isolated a 42% yield of *p,p'*-tetramethyldiaminotriphenylcarbinol.

A 1:1 mixture of Michler ketone and phenyllithium, in either benzene or ether, forms no stable complex and the only product isolated in excellent

yields is the carbinol, which is an intermediate in the color test.

Other aspects of coordination compounds in organometallic chemistry are considered.

AMES, IOWA

RECEIVED MARCH 18, 1940

[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, OHIO STATE UNIVERSITY]

## Spectroscopic Evidence for Hydrogen Bonds: The Hexyl Alcohols. I<sup>1</sup>

BY SPENCER C. STANFORD<sup>2</sup> AND WALTER GORDY<sup>3</sup>

Many papers dealing with the infrared absorption spectra of the alcohols have appeared since the discovery that such spectra give direct evidence of the linkage involved in association through hydrogen bonding. The work on the alcohols through 1938 has been summarized by Freymann.<sup>4</sup>

Previous work, pertinent to the present discussion, may be summarized briefly as follows. In the region of the —OH fundamental vibration band, there is found, in the pure liquid at ordinary temperatures, a broad, intense band with its center at 2.95–3.00  $\mu$ . On dilution with an inert solvent such as carbon tetrachloride, or on increasing the temperature, the broad band begins to decrease in intensity. Because of this behavior the band is attributed to the presence of associated molecules. As the broad band diminishes in intensity a sharp band appears at 2.75  $\mu$ . This band increases in intensity with increased dilution or temperature and is attributed to single alcohol molecules.

Work on the overtones gives results similar to those on the fundamental. However, in the overtone regions, traces of the monomer bands are found, even in the pure liquids at ordinary temperatures, in alcohols above methyl alcohol. The increased symmetry of the potential energy curve of the proton due to hydrogen bonding causes the overtone association bands to be weak in comparison to the fundamental association band, hence the monomer band is not overlapped as much by the association band.<sup>5</sup>

(1) A summary of this paper was read at the Ohio-Michigan Regional Meeting of the American Chemical Society, East Lansing, Michigan, October 28, 1939.

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(4) Freymann, *J. phys. radium*, **9**, 517 (1938).

(5) See, for example, Errera and Sack, *Trans. Faraday Soc.*, **24**, 728 (1938).

So far as the authors know, no research has been done on a complete series of isomeric alcohols. It appeared of interest to us to study one such series to see if there are detectable differences in association due to variations in structure. Fortunately the hexyl alcohols were available to us, through the courtesy of Dr. Frank Hovorka, of Western Reserve University. The present paper reports the results of the investigation of eight of the seventeen possible hexyl alcohols.

**Experimental Technique.**—The preparation and purification of hexanol-1, -2, -3, 2-methylpentanol-1, -2, and -4 has been described in the literature.<sup>6</sup> The preparation of 3-methylpentanol-1 and 2-ethylbutanol-1 will be described in publications soon to appear. The boiling point range did not exceed  $\pm 0.02^\circ$  in any of the alcohols studied. The spectrometer and experimental method have been described in a previous paper of this series.<sup>7</sup>

### Results and Discussion

The transmission curves for the pure liquids are given in Fig. 1. There is no trace of the monomer band at 2.75  $\mu$ . The minimum of the association band is at 2.97  $\mu$  for hexanol-1 and 3-methylpentanol-1, the other bands have their minima at 2.95  $\mu$ . This slight shift appears to be real, since we were able to reproduce the position of the minima.

There is a gradual increase in the per cent. transmission at the minimum and a decrease in the breadth of the band as one goes from hexanol-1 to hexanol-3. These and differences in intensity among the other pure liquid curves could possibly be due to error in reproducing cell thickness with such thin cells. It is probable, however, that

(6) (a) Hovorka, Lankelma and Naujoks, *THIS JOURNAL*, **55**, 4820 (1933); (b) Hovorka, Lankelma and Stanford, *ibid.*, **60**, 820 (1938).

(7) Gordy and Stanford, *ibid.*, **62**, 497 (1940).

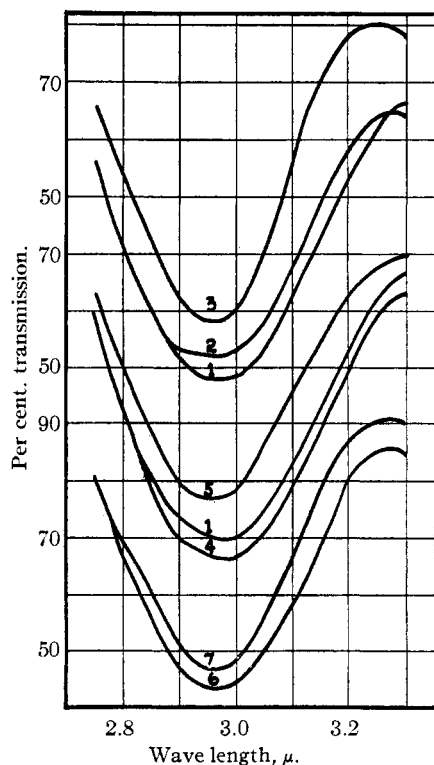


Fig. 1.—Pure liquids, cell thickness, 0.015 mm.: (1) hexanol-1; (2) hexanol-2; 2-methylpentanol-2; (3) hexanol-3; (4) 3-methylpentanol-1; (5) 2-methylpentanol-1; (6) 2-ethylbutanol-1; (7) 2-methylpentanol-4.

they are caused partly by structural differences since similar differences are noted in the solution curves where cell thicknesses are accurate.

For the solutions we have plotted molecular extinction coefficients as a function of wave length. Figure 2 shows the curves for the 0.291 molar solutions. At this concentration there is a distinct monomer band. This band is at  $2.75 \mu$ , within the limits of experimental error, for all the alcohols studied. This fact shows that there is no detectable interaction between the  $-\text{OH}$  and adjacent groups; consequently differences in the association bands may be attributed entirely to differences in association caused by variations in the structure of the alcohol molecules.

The slight differences in the bands of the pure liquids become much more pronounced in the 0.291 molar solutions. Figure 2A shows that there is a marked change in intensity and band position as the hydroxyl is moved from the 1- to the 3-position. The center of the association band for hexanol-2 is at a slightly shorter wave length ( $2.95 \mu$ ) than for hexanol-1 ( $2.97 \mu$ ). The center of the hexanol-3 band is at  $2.88 \mu$ . Figure

2B shows that the primary alcohols with side chains fall in a single group having smaller intensity and maxima at shorter wave lengths than is the case with hexanol-1. The curves for these alcohols are identical, within the limits of experimental error, so only the curve for 2-methylpentanol-1 is given. The secondary alcohol, 2-methylpentanol-4, and the tertiary alcohol, 2-methylpentanol-2, give similar curves. The maxima for these alcohols are at the same wave length ( $2.95 \mu$ ) as for the primary branched chain compounds but the intensity is somewhat less.

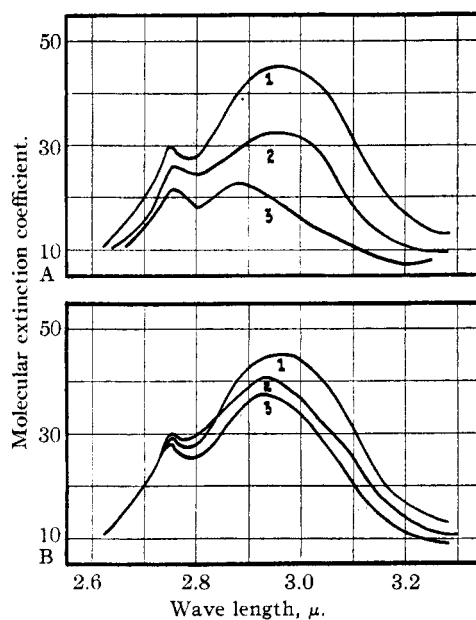


Fig. 2.—Concentration, 0.291 molar; cell thickness, 0.56 mm.: A.—(1) hexanol-1; (2) hexanol-2; (3) hexanol-3. B.—(1) hexanol-1; (2) 2-methylpentanol-1; 2-ethylbutanol-1; 3-methylpentanol-1; (3) 2-methylpentanol-4; 2-methylpentanol-2.

The curves for the 0.1 molar solutions are shown in Fig. 3. The primary alcohols, hexanol-1 and 3-methylpentanol-1 show two well defined components in the association band at  $2.91$  and  $3.03 \mu$ . In hexanol-2 the longer wave length component is not as pronounced and the short wave length component is at  $2.89 \mu$ . In hexanol-3 the long wave length component has completely disappeared and the short wave length component is at  $2.86 \mu$ . The remainder of the alcohols give very similar curves. The short wave length component is at  $2.86 \mu$  and the long wave length component is extremely weak and poorly defined.

The results for the 0.05 molar solutions are plotted in Fig. 4. At this concentration the long

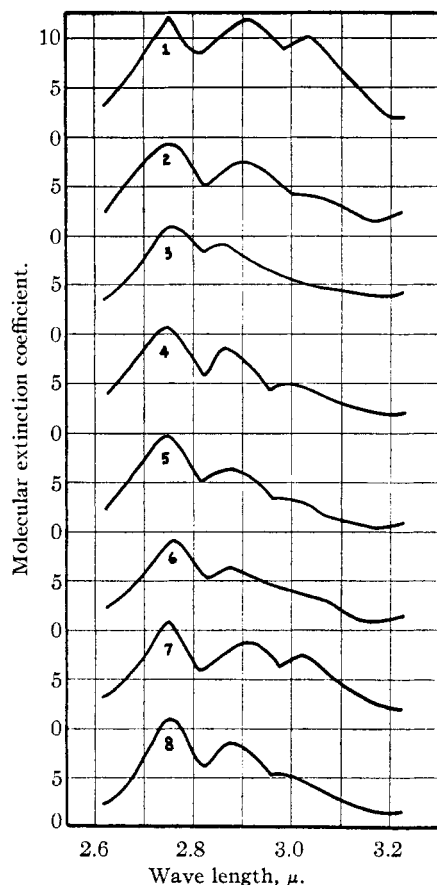


Fig. 3.—Concentration, 0.1 molar; cell thickness, 1.63 mm.: (1) hexanol-1; (2) hexanol-2; (3) hexanol-3; (4) 2-methylpentanol-1; (5) 2-methylpentanol-2; (6) 2-methylpentanol-4; (7) 3-methylpentanol-1; (8) 2-ethylbutanol-1.

wave length component of the association band has disappeared. The curves fall into the same groups found with the 0.1 molar solutions. In hexanol-1 and 3-methylpentanol-1 there is a distinct band at about  $2.86 \mu$ . Hexanol-3 shows only the monomer band at  $2.75 \mu$ . In the remaining curves there is a slight indication of absorption in the region of the association band, showing that at this concentration these alcohols are not completely broken down into monomers.

Fox and Martin,<sup>8</sup> studying aliphatic alcohols in carbon tetrachloride at a concentration of 0.112 molar, resolved the association band into two components. Their results were similar to ours, in that they found the long wave length component predominant in the primary alcohols, and the short wave length component predominant in tertiary butyl alcohol. They suggested that

(8) Fox and Martin, *Proc. Roy. Soc. (London)*, **A162**, 419 (1937).

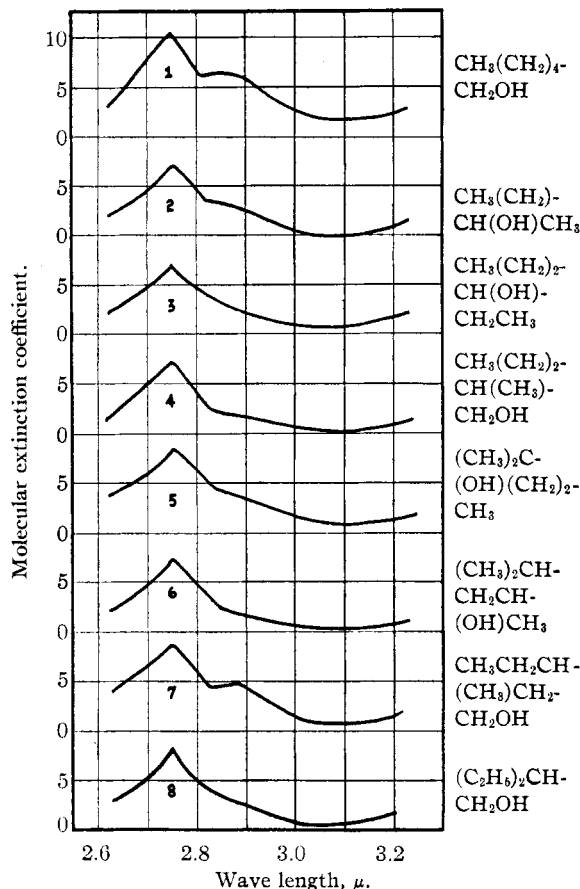
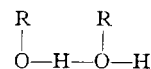


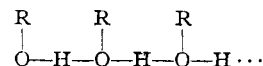
Fig. 4.—Concentration, 0.05 molar; cell thickness, 3.31 mm.: (1) hexanol-1; (2) hexanol-2; (3) hexanol-3; (4) 2-methylpentanol-1; (5) 2-methylpentanol-2; (6) 2-methylpentanol-4; (7) 3-methylpentanol-1; (8) 2-ethylbutanol-1.

the two components might be due to dimers and higher polymers.

In the dimer association



the energy of a single hydrogen bond is supplied by two separate  $-\text{OH}$  groups of different molecules. Here neither  $-\text{OH}$  group acts both as a proton donor and as a proton acceptor, as do the  $-\text{OH}$  groups (with the exception of the end group) of long chain polymers,



where the number of hydrogen bonds per  $-\text{OH}$  group approaches one as the chain increases in length. If the hydrogen bonds in the dimer are of the same order of strength as those in the higher

polymer, one for the above reasons would expect the dimer association to produce less disturbance of the —OH band than the longer chain polymerization. Thus for alcohols which form long chain polymers, one would expect, as is observed, a shift to shorter wave lengths of the —OH band as the length of the chains is diminished either by dilution in an inert solvent or by an increase of temperature. When the dimer stage is reached further breaking down of the polymer would of course cause a sudden jump of the band to the position of monomeric absorption.

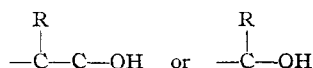
Application of this hypothesis suggests that hexanol-3 in the liquid state (Fig. 1) consists chiefly of lower polymers, possibly dimers, since the band is less intense than that for hexanol-1 and the maximum occurs at the shorter wave length. The other alcohols give curves which are more difficult of interpretation, but the results indicate that these compounds tend to form more dimers than hexanol-1.

Apparently hexanol-3, in 0.291 molar solution in carbon tetrachloride, consists almost entirely of dimers. The rest of the alcohols, at this concentration, appear to form a group intermediate between hexanol-1 and hexanol-3.

In 0.1 molar solution three well-defined groups are found. The primary alcohols, hexanol-1 and 3-methylpentanol-1, show two distinct bands with the short wave length component predominant, indicating that at this concentration more of the molecules exist as dimers than as higher polymers. Hexanol-3 is in a class by itself, with only a weak dimer band. The remainder of the alcohols form a group with very similar bands. In these alcohols there is still a trace of the higher polymer band.

In 0.05 molar solution hexanol-3 is present entirely as monomer. Hexanol-1 and 3-methylpentanol-1 still contain an appreciable amount of dimers. The rest of the alcohols show slight absorption in the region of the association band, indicating that the associated molecules are not completely broken down in these compounds.

It is evident that in all the alcohols studied, with the exception of hexanol-1 and 3-methylpentanol-1, there is something which tends to hinder the formation of polymers higher than dimers. These alcohols have the structure



hence it appears probable that the R groups tend to prevent orientations which are favorable to the production of the higher polymers.

These results are in substantial agreement with those obtained from X-ray work.<sup>9</sup> This seems to confirm the validity of the interpretation of the two components of the association band as being due to dimers and higher polymers.

Some time ago, Hovorka, Lankelma and Stanford<sup>6a</sup> measured the viscosity and density of five of the alcohols over a wide temperature range. It was found that the density and viscosity of hexanol-1 changed rather slowly with temperature. These properties varied much more rapidly in the case of hexanol-3. Hexanol-2, 2-methylpentanol-1, and -4 showed density and viscosity changes intermediate between those of the above two alcohols. The slope of the curves was nearly the same for the last three compounds. The results were interpreted as being due to different types of association and to different rates of dissociation of the associated molecules. The data of the present research are in excellent agreement with this interpretation.

The results obtained thus far indicate that the type and extent of association of a member of an isomeric series of alcohols depends chiefly on the immediate environment of the —OH group rather than on the length of the carbon chain. One would, therefore, expect to find rather similar bands in other alcohols in which the —OH group has a like environment.

In conclusion the authors wish to express their appreciation to Dr. H. H. Nielson and Dr. Alpheus W. Smith for the use of their equipment and for their constant interest in this work, and to Dr. Frank Hovorka of Western Reserve University for providing the alcohols, which made this study possible. They also wish to acknowledge a very helpful conversation with G. B. B. M. Sutherland of Cambridge University.

### Summary

1. The infrared absorption spectra of hexanol-1, -2, -3, 2-methylpentanol-1, -2, -4, 3-methylpentanol-1 and 2-ethylbutanol-1 have been determined in the 3  $\mu$  region, for the pure liquids and for 0.291, 0.1 and 0.05 molar solutions in carbon tetrachloride.

2. From the behavior of the —OH band of the different liquids upon dilution in carbon tetra-

(9) Stewart, *Chem. Rev.*, **6**, 483 (1929); *Phys. Rev.*, **35**, 726 (1930); Pierce and MacMillan, *This Journal*, **60**, 779 (1938).

chloride, something of the nature of association can be ascertained.

3. It was found that hexanol-3 in concentrated solutions consists chiefly of dimers and that its rate of dissociation with dilution is greater than that for the other alcohols. Hexanol-1 and 3-methylpentanol-1 show the presence of higher polymers down to and including a concentration of 0.1 molar. The rate of change of association

with dilution is least for hexanol-1. The remainder of the alcohols form intermediate cases between hexanol-1 and hexanol-3, both in respect to the presence of higher polymers and rate of dissociation with dilution.

4. The difference in behavior of the hexyl alcohols has been interpreted in terms of the structural environment of the —OH group.

COLUMBUS, OHIO

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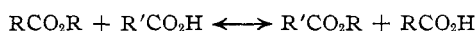
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

## The Equilibrium Constants for the Systems Alkyl Formates and Alkyl Acetates with Stearic Acid

BY CHAS. BARKENBUS, C. A. ROSWELL AND A. ELEANOR MITTS

Ester interchange with alcohols or alcoholysis has received considerable attention in the last few years. A similar type of interchange between ester and acid and called acidolysis has not been so extensively studied. Since very little work has been done from a quantitative viewpoint it was thought advisable to determine the equilibrium constants for a series of alkyl esters with stearic acid and to see how these constants varied with change of alkyl group.

The general reaction, *i. e.*



has been used to prepare certain esters where the conditions were favorable.<sup>1</sup> The first quantitative study of acidolysis was made by Reid<sup>2</sup> who determined the equilibrium constants for the systems benzoic acid-benzyl acetate and *p*-bromobenzoic acid-ethyl benzoate. The equilibrium mixture was analyzed by determining the density and the constants obtained checked within 5% with those calculated from the esterification constants.

Sudborough and Karve<sup>3</sup> obtained an equilibrium constant of unity for the two systems trichloroacetic acid-methyl acetate and trichloroacetic acid-ethyl acetate.

Gault and Chablay<sup>4</sup> have recently studied the system methyl palmitate-acetic acid. They de-

termined the time needed to reach equilibrium and found that fifty hours were necessary at 100° when sulfuric acid was used as a catalyst. In their latest paper they give the equilibrium constants for methyl palmitate with acetic acid, propionic acid, *n*-butyric acid, *n*-valeric acid, and *n*-caproic acid. The analysis of equilibrium mixtures of this type is simplified by the determination of the water soluble or water insoluble acids.

Sowa<sup>5</sup> has determined the rate of reaction using acetic acid with various alkyl esters of propionic, benzoic and salicylic acids. He was able to show that the main reaction was one of straight interchange but that larger normal alkyl groups of esters rearrange to secondary alkyl groups when changing to the other acid. This is probably due to the intermediate formation of an olefin. It was stated that only 4% of the new ester was due to this type of reaction. To see whether this observation held for the higher fatty acids, a large scale run was made using *n*-butyl stearate and acetic acid. The butyl acetates when separated and fractionally distilled through a ten-plate Podbielniak column showed that only 2% of the esters was *s*-butyl acetate.

In this work the equilibrium was obtained by heating in a sealed glass tube at 100° about 0.02 mole of stearic acid, 0.1 mole of the ester and 0.1 g. of *p*-toluenesulfonic acid as a catalyst. The tubes were heated at various lengths of time and equilibrium was considered established when the tubes heated the longest checked with those heated next in length of time. From seventy-two to one hundred and twenty hours were usually required.

(1) Lowig, *J. prakt. Chem.*, [1] **83**, 130 (1861); Lorin, *Bull. soc. chim.*, [2] **49**, 344 (1888); Norman, *Chem. Umschau*, **30**, 250 (1924); Forneau, *Bull. soc. chim.*, **45**, 834 (1929); Pistor, *Z. angew. Chem.*, **38**, 1118 (1925); Graves, U. S. Patent 1,882,808.

(2) Reid, *Am. Chem. J.*, **45**, 479 (1911).

(3) Sudborough and Karve, *Indian Inst. Sci.*, **5**, 1 (1922).

(4) Gault and Chablay, *Compt. rend.*, **203**, 729 (1936); **207**, 293 (1938).

(5) Sowa, *THIS JOURNAL*, **60**, 654 (1938).