e); 1320(3)(a, e); 1366(1)(a, e); 1391(0)(a, e); 1430(00)-(a, e); 1455(3d)(a, e); 1600(10b)(a, c, e); 1718 (9)(b, d, e); 2939(2)(a); 2978(00)(a); 3078(3)(a).

Ethyl *p*-Methoxybenzoate.—Boiling point, 104.2–104.4° at 2 mm.; n^{20}_D 1.5254; d^{20}_4 1.1038; d^{25}_4 1.0994; *R*M, calcd. 48.40, obsd. 50.05.

$\Delta\nu$ = 120(00)(a, e); 284(0)(a, b, d, e); 311*(0)(e); 326*(0)(e); 381*(0)(e); 437*(0)(e); 614(2)(a, c, e); 635(3)(a, b, e); 777(0b)(a, e); 801(2d)(a, e); 855(5)(a, b, d, e); 1012(0)(a, e); 1108(3)(a, e); 1169(10b)(a, b, c, d, e); 1216(0)(a); 1257(8)(a, b, d, e); 1277(7)(a, b, e); 1314(3b)(a, b, d, e); 1364(3b)(a, d, e); 1392(0)(a, e); 1420(1)(a, e); 1455(1 v. b.)(a, e); 1577(0)(a, e); 1607(10)-(a, c, e); 1709(8b)(b, c, d, e); 2837(0b)(a); 2875(0)(a); 2933(3)(a); 2969(1b)(a); 3070(3b)(a).

Discussion

When the Raman spectra of these methoxy derivatives of ethyl benzoate are compared with the spectra of other esters which have substituents in corresponding positions, one striking difference appears. The number of weak lines of frequency difference of less than 600 cm.$^{-1}$ is much greater in each of these new spectra than in that of any other corresponding ester—even greater than in the spectrum of its acid chloride, Nor does this seem to be due to a shift toward lower frequencies of normally occurring higher frequencies since the correspondence of the rest of the spectra is almost perfect for all three position substitutions. The difference is probably not due to a difference in technique, for the comparison of the spectra of the acid chlorides determined by the author[1] shows no such disagreement with those of the same compounds determined by Kohlrausch, Pongratz and Stockmair.[5] Perhaps there is a relationship between this phenomenon and the optical exaltation to 1 ml. observed for ethyl *o*-methoxybenzoate of 2 ml. for the para derivative. Although no significant reason for this large number of low frequencies in the methoxy compounds can be advanced now, it was felt that the data should be published so that they will be available for interpretation when Raman spectra are better understood.

Summary

The Raman spectra of pure methoxy derivatives of ethyl benzoate have been determined and compared with the spectra of other derivatives of ethyl benzoate and of benzoyl chloride. The boiling points, densities, indices of refraction and molecular refractions for these compounds have, also, been determined and recorded.

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[5] Kohlrausch, Pongratz and Stockmair, *Monatsh.*, **67**, 104 (1935–1936).

NORTON, MASS. RECEIVED FEBRUARY 8, 1937

[CONTRIBUTION FROM THE PHYSICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Infrared Absorption of Mixtures of Methyl Alcohol with Ethyl Formate and with Ethyl Acetate

BY DUDLEY WILLIAMS[1] AND WALTER GORDY[2]

Recently a series of experiments[3] has been made on the infrared absorption spectra of water, alcohol, and aniline in various solutions of other liquids. In every case when the solvent contained the strongly electronegative atoms, oxygen or nitrogen, having unshared electron pairs, pronounced changes were observed in the intensity and position of the vibrational OH band of alcohol and water, and in the NH band of aniline. In some cases certain changes were likewise observed in the spectrum of the solvent. For example, in mixtures of alcohol with acetone the vibrational band of the OH alcohol group was shifted to the shorter wave lengths, and its intensity was increased, while the CO band of acetone was shifted to the longer wave lengths and its intensity was increased correspondingly. It was suggested that these results indicate some type of interaction, possibly the formation of hydrogen bonds between the solute and solvent molecules. For the purpose of determining whether these results indicate some general type of interaction, the study has been continued, and in the present article results obtained from observations of the absorption spectra of different mixtures of methyl alcohol with ethyl formate and with ethyl acetate are discussed.

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[1] Now at the University of Florida.

[2] Now at Mary Hardin-Baylor College.

[3] (a) Walter Gordy, *J. Chem. Phys.*, **4**, 769 (1936); (b) *Phys. Rev.*, **50**, 1151 (1936); (c) THIS JOURNAL, **59**, 464 (1937).

Experimental

The apparatus and experimental method were the same as those used in the previous investigations[3] and will not be described here. The methyl alcohol and ethyl acetate were Baker "Certified Products." The ethyl formate was prepared by the action of formic acid on absolute ethyl alcohol, the ethyl formate being fractionated off during the reaction.

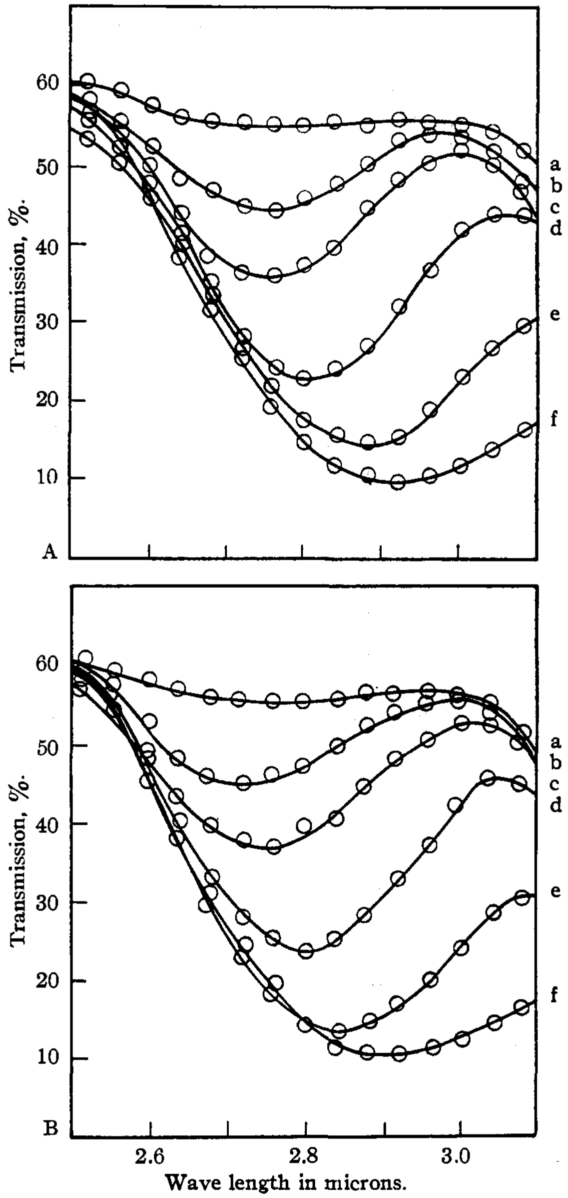

Fig. 1.—A. Transmission of methyl alcohol–ethyl formate mixtures: (a) pure ethyl formate; (b) 6.25% alcohol; (c) 12.5% alcohol; (d) 25% alcohol; (e) 50% alcohol; (f) pure alcohol. B.—Transmission of methyl alcohol–ethyl acetate mixtures: (a) pure ethyl acetate; (b) 6.25% alcohol; (c) 12.5% alcohol; (d) 25% alcohol; (e) 50% alcohol; (f) pure alcohol.

Results

The effects of ethyl acetate and of ethyl formate on the fundamental vibrational band of the OH alcohol group will be evident from Fig. 1. The center of the band in pure methyl alcohol appears at 2.9 μ. When the alcohol is mixed with either of the esters the band appears at shorter wave lengths, and the magnitude of the shift increases as the ester concentration in the mixture is increased. For alcohol concentrations as low as 12.5% in either ester the center of the band appears at about 2.74 μ. The intensity of the band does not decrease in proportion to the number of absorbers. This will be evident from a comparison of some of the experimental curves with theoretical ones for the same mixtures, computed on the assumption that neither component of the mixture influences in any way the spectrum of the other. In Fig. 2 the theoretical curves for mixtures of 12.5 and 6.25% methyl alcohol in ethyl acetate are shown with the experimental curves for the same mixtures. The method used in determining the theoretical transmission of a

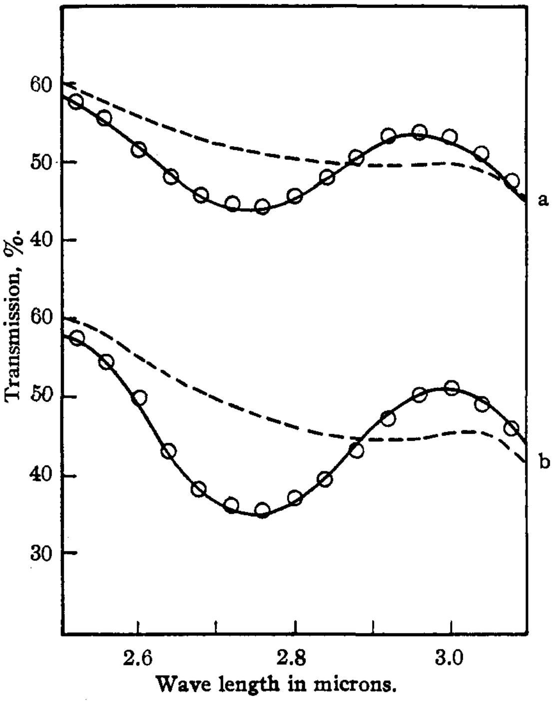

Fig. 2.—Comparison of theoretical with experimental transmission of some methyl alcohol–ethyl acetate mixtures: (a) 6.25% alcohol; (b) 12.5% alcohol.

mechanical mixture has been given in a previous paper[3c] and will not be repeated.

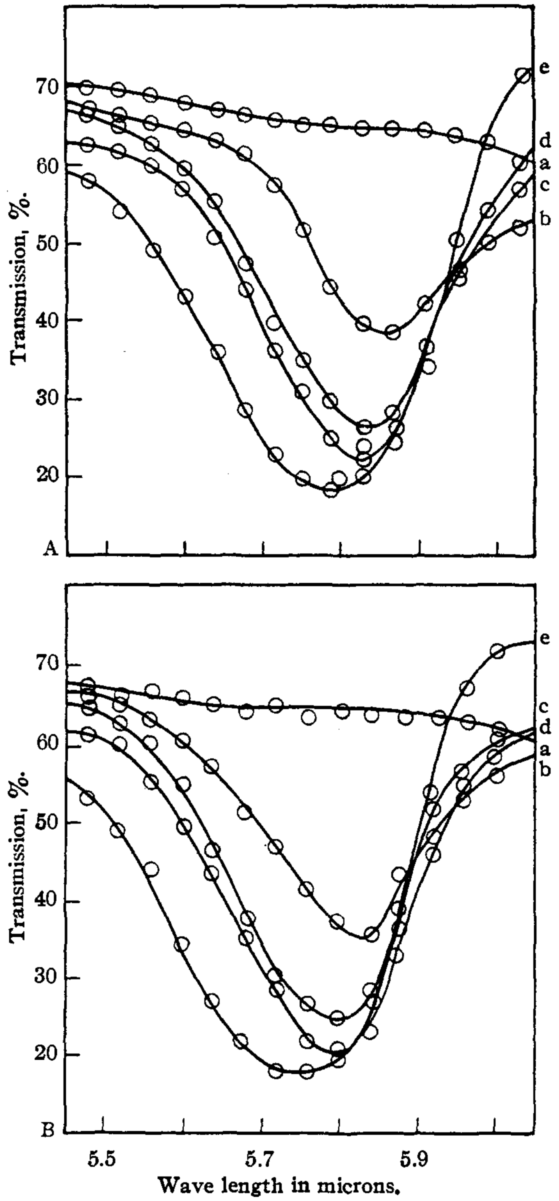

Fig. 3.—A. Transmission of methyl alcohol–ethyl formate: (a) pure alcohol; (b) 6.25% ethyl formate; (c) 12.5% ethyl formate; (d) 25% ethyl formate; (e) 50% ethyl formate; (f) pure ethyl formate. B.—Transmission of methyl alcohol–ethyl acetate mixtures: (a) pure alcohol; (b) 6.25% ethyl acetate; (c) 12.5% ethyl acetate; (d) 25% ethyl acetate; (e) 50% ethyl acetate; (f) pure ethyl acetate.

The vibrational band of the CO group in ethyl formate appears at about 5.79 μ, and in ethyl acetate it appears at about 5.75 μ. Figure 3 shows the effects of methyl alcohol on this band. In each of the esters the band is shifted to the longer wave lengths, and its intensity is increased by the methyl alcohol. The shift amounts to 0.08 μ for alcohol concentrations of 88.5%. Theoretical curves for two of the mixtures are given in Fig. 4. A study was also made of the effects of alcohol on the band appearing at about 8 μ in the two esters. No shifts in the position of the band could be detected. The curves for these mixtures are not shown. Due to the overlapping of bands of the two components it was not found practicable to study other bands appearing between 2.5 and 8.5 μ. The CO band of ethyl acetate was studied for various concentrations of ethyl acetate in isopropyl ether. The ether does not produce shifts and intensity changes in the band as does alcohol.

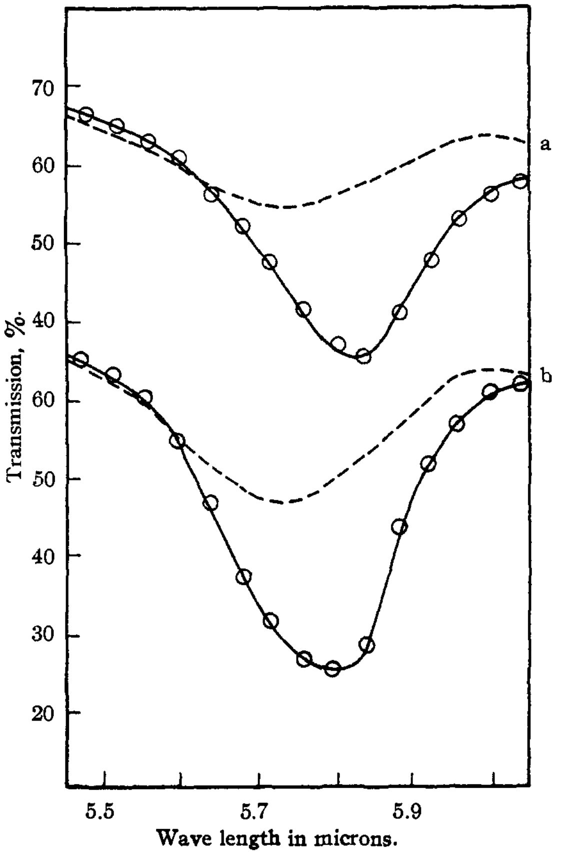

Fig. 4.—Comparison of theoretical with experimental transmission of some methyl alcohol–ethyl acetate mixtures: (a) 12.5% ethyl acetate; (b) 25% ethyl acetate.

Discussion

Since the discovery of the hydrogen bond[4] it has been generally believed that alcohols in

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[4] W. M. Latimer and W. H. Rodebush, THIS JOURNAL, 42, 1419 (1920).

the liquid state are associated through the formation of hydrogen bonds. The OH band appears at longer wave lengths and is much broader in the liquid than in the vapor state.[5] The changes in the character of this band as the alcohol passes from the vapor state to the liquid state are evidence that the OH group participates in the association process. Although in ethyl acetate and in ethyl formate the OH band is shifted to the shorter wave lengths, and this may indicate the breaking of hydrogen bonds between the alcohol molecules, the band does not become sharp, as it does for alcohol in the vapor state. It may be possible to interpret these results by assuming that as the ester content in the mixture is increased the polymerization of the alcohol is decreased and that the alcohol becomes associated to some degree with the ester through the formation of weak hydrogen bonds between the hydroxyl group of the alcohol and the carbonyl group of the ester. This would account for the shift to the longer wave lengths and the increase in intensity of the band associated with the carbonyl group, and it is in accord with the results of the previous investigations.[3]

The writers wish to express gratitude to Dr. E. K. Plyler for the use of his laboratory facilities.

Summary

Ethyl formate and ethyl acetate were found to shift the OH band of methyl alcohol to the shorter wave lengths and to increase its intensity. The CO band of the esters was shifted to the longer wave lengths by the alcohol, and its intensity was increased correspondingly. As a possible means of accounting for these results it was suggested that the esters may tend to decrease the polymerization of the alcohol, and to become associated with it, to some degree, through the formation of weak hydrogen bonds.

CHAPEL HILL, N. C. RECEIVED JANUARY 6, 1937

(5) E. L. Kinsey and J. W. Ellis, *Phys. Rev.*, **49**, 105 (1936).

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Pinacol Rearrangement of *cis*- and *trans*-1,2-Dimethylcyclohexanediol-1,2 and the Relationship of the Walden Inversion to the Mechanism of Molecular Rearrangements

BY PAUL D. BARTLETT AND IRVING PÖCKEL

The course of a molecular rearrangement has been observed in some cases to depend upon the conditions of the rearrangement[1] and upon the configuration of the rearranging compound.[2] The dependence of the course of reaction upon configuration in the alicyclic series has been studied hitherto only for cases of *semi*-pinacolic rearrangements such as that of 1-methylcyclohexanediol-1,2. When the *cis*-isomer of this compound forms 2-methylcyclohexanone on dehydration, it is ascribed to a direct elimination of water, molecular rearrangement occurring to an important extent only in the *trans*-isomer, where ring contraction makes the rearrangement evident.

We have undertaken the study of an actual pinacol rearrangement, where vinyl dehydration is impossible, and where the results tell us directly the effect of configuration upon the relative ease of migration of two organic radicals. There is little doubt of the configurations of the 1,2-diols in the cyclohexane series. The ultimate criterion in this series is the resolution of the *trans*-cyclopentanediol and *trans*-cyclohexanediol into optical isomers.[3] A number of independent criteria, most of them due to Böeseken and his co-workers, support the generalization that where the two isomeric diols can be prepared, one by hydration of the corresponding epoxide and the other by aqueous permanganate oxidation of the corresponding cyclohexene, the former has the *trans* and the latter the *cis* configuration. The isomeric 1,2-dimethylcyclohexanediols-1,2 have been prepared by these methods, and hence although neither of them has been resolved, their configurations are known with a high degree of probability.

The *trans*-pinacol, m. p. 92–92.5°, prepared by hydrolysis of the oxide, was rearranged by Namet-

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(1) Bartlett and Rosenwald, THIS JOURNAL, **56**, 1990 (1934).

(2) Tiffeneau and Tchoubar, *Compt. rend.*, **199**, 360, 1624 (1934); *ibid.*, **202**, 1931 (1936).

(3) Derx, *Rec. trav. chim.*, **41**, 333 (1922); Van Loon, Thesis, Delft, 1929, p. 51; Helferich, Burkhardt and Hiltmann, *Ber.*, **70**, 308 (1937).