2. The initial rates have been shown to be represented by the equation $-dBr_2/dt = k \times [R_2S_2(Br_2)_2]$ where k is a function of the rate of shaking.

3. The first steps in the oxidation of ethyl disulfide by bromine in the presence of water are suggested as

$$R_2S_2 + 2Br_2 \rightleftarrows 2RSBr_2, \text{ and} \quad (1)$$

$$RSBr_2 + H_2O = RSO + 2H^+ + 2Br^- \quad (2)$$

DAVIS, CALIF. RECEIVED DECEMBER 11, 1936

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WHEATON COLLEGE]

Raman Spectra. II. Monomethoxy Derivatives of Ethyl Benzoate

BY DOROTHY D. THOMPSON

The Raman spectra of several derivatives of benzoyl chloride were determined[1] in an attempt to find a relationship between this property and the rates of esterification of the acid chlorides, and these spectra were compared with those of the corresponding ethyl esters.[2] Since, however, the spectra of the methoxy derivatives of ethyl benzoate had not been determined, it was thought advisable to prepare them and study their Raman spectra.

Experimental

Apparatus.—The same Hilger E-439 glass spectrograph,[3] system of filters, light source, Raman tube and photograph plates were employed as were described in a previous paper.[1] The frequencies of the lines were determined as before except that the deviation curves were made from the difference from linear dispersion in terms of wave numbers instead of wave lengths. The accuracy is about the same as before (±1 for the strong, sharp lines, but a greater error up to ±4 cm.$^{-1}$ for very weak diffuse lines).

Purification of Compounds.—The esters were prepared from the corresponding acid chloride and absolute alcohol or by the action of absolute alcohol saturated with hydrogen chloride on the corresponding acid (*o*-methoxybenzoic acid prepared by methylation of salicylic acid with dimethyl sulfate; *p*-methoxybenzoic acid was Eastman White Label). The esters were washed rapidly with ice-cold sodium carbonate and several times with cold water, then dried over calcium chloride. They were distilled *in vacuo* from an ordinary Claisen flask several times or until the index of refraction of the major portion remained constant. One distillation through a modified Vigreux[4] column showed that the boiling point range was in every case not greater than 0.2°. The densities were determined in the usual way with a pycnometer having a capacity of 5 ml. The average deviations of three to five independent determinations never exceeded one part in twenty thousand. The calculations were made in the usual way correcting for the buoyancy of air and for the expansion of glass. The indices of refraction were measured with an Abbé refractometer and the molecular refractions calculated from the equation of Lorenz and Lorentz.

Data

Explanation of Tables.—The values of the Raman spectra have been summarized in the usual way. The value for the Raman shift is followed by a number in parentheses indicating the relative intensity (estimated)—the large numbers indicating greater intensity, the letter "b" for broad and "d" for diffuse. This is followed by letters indicating the mercury exciting lines as follows: a = 24,705 cm.$^{-1}$, b = 24,516 cm.$^{-1}$, c = 23,039 cm.$^{-1}$, d = 22,995 cm.$^{-1}$ and e = 22,938 cm.$^{-1}$. Each compound was photographed four times—twice with "Greenish Nultra" filter only, with long and short exposure times, once with "Greenish Nultra" + quinine sulfate, and once with "Red-Purple Ultra" glass + sodium nitrite. Each Raman line occurred on at least two plates unless indicated with a *.

Ethyl *o*-Methoxybenzoate.—Boiling point 104.4–104.5° at 2 mm.; n^{20}_D 1.5224; d^{20}_4 1.1124; d^{25}_4 1.1077; R_M calcd. 48.40, obsd. 49.42.

$\Delta\nu$ = 80(0)(a, +b, c, e); 115(00)(a, e); 230(00)(a, e); 276(0)(a, e); 305(00)(a, e); 333(4)(a, b, c, e); 395(00)(a, e); 434(0)(a, d, e); 459(00)(a, e); 523(0)(a, e); 563 ± 5(1b)(a, e); 582(2)(a, b, d, e); 657(2)(a, b, ±e); 780 ± 10(4band)(a, d, e); 854(2)(a, e); 877(1)(a, e); 1020(0b)(a, e); 1049(6)(a, b, c, e); 1166(4)(a, b, d, e); 1251(8b)(a, b, d, e); 1302(2d)(a, b, e); 1354(00)(a, e); 1448(0)(a, c, e); 1491(0)(a, e); 1600(6)(a, c, d, e); 1721(2d)(b, d, e); 2929(1)(a); 3077(2)(a).

Ethyl *m*-Methoxybenzoate.—Boiling point 97.6–97.8° at 1 mm.; n^{20}_D 1.5161; d^{20}_4 1.0993; d^{25}_4 1.0949; R_M, calcd. 48.40, obsd. 49.50.

$\Delta\nu$ = 94(00)(a, +b); 107(00)(a); 128(00)(a, e); 192(0)(e); 223(00)(a, e); 252(00)(a, e); 263(0)(e); 301(0)(a, e); 330(2)(a, e); 390(00)(a, e); 416(00)(a, e); 452(2)(a, b, e); 482(0)(e); 550(00)(a, e); 572(2d)(a, e); 588(0)(a); 667(3)(a, e); 765(2)(a, e); 804(2b)(a, e); 863(2d)(a, e); 996(10)(a, b, c, d, e); 1038(00)(a, e); 1102(0b)(a, e); 1172(1)(a, b, e); 1235(00)(a, e); 1281(10b)(a,

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(1) Thompson and Norris, THIS JOURNAL, 58, 1953 (1936).

(2) Kohlrausch and Pongratz, *Monatsh.*, 63, 427 (1933–1934); Kohlrausch and Stockmair, *ibid.*, 66, 323 (1935).

(3) The author wishes to express appreciation to the Research Laboratory of Organic Chemistry of the Massachusetts Institute of Technology for the use of this apparatus and to the Physics Department for the use of their Hilger comparator.

(4) Thanks are due to Mount Holyoke College Chemical Laboratory for this column.

* Occurred on one plate only.

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.

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

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[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.

[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).