[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

A Raman Spectra Study of Hydrogen Bond in Acetoxime

BY C. N. CAUGHLAN, H. V. TARTAR AND E. C. LINGAFELTER

Acetoxime was chosen as a suitable substance for further study of hydrogen bonding. The presence of two very electronegative atoms near the active hydrogen should be expected to produce strong hydrogen bonds. Molecular weight determinations in benzene[1] show association to form a dimer in quite dilute solution and association to higher polymers in more concentrated solutions. Previous work on the Raman spectrum of acetoxime[2] indicates the presence of an association band in the region of 3400 cm.$^{-1}$, the region for OH ··· O vibration. The data reported below are from Raman spectra of pure acetoxime taken at 70, 100, 110, 120, 130 and 136° and from 25, 50 and 75% solutions in carbon tetrachloride at 60°.

Experimental

Preparation and Purification of Materials.—The oxime was prepared by neutralizing an aqueous solution of very pure hydroxylammonium chloride with potassium hydroxide and adding an excess of acetone with vigorous shaking. The oxime was quite completely removed from the aqueous solution by three extractions with equivoluminal amounts of ether. The ether solution was then distilled, removing successively the ether, the water, and finally the oxime at a temperature of about 130°.

Purification of the acetoxime was carried out by fractional distillation and final recrystallization from petroleum ether; the crystals were dried in a vacuum desiccator over phosphorus pentoxide. The oxime was finally distilled directly into the Raman tube which was immediately sealed. This product had a melting point of 60.8° and boiling point 136.2° at 760 mm.

The carbon tetrachloride was purified by careful fractional distillation over barium oxide to remove any water and stored under moisture-free air; the boiling point was 76.6° and the refractive index was 1.45737 at 25°, "I.C.T." value is 1.45732.[3]

Apparatus.—The apparatus was essentially the same as that used by Houlton and Tartar.[4] To control the temperature within the range desired, the mercury arc and Raman tube were placed in an air thermostat controlled by a toluene-type regulator. Since the arc itself supplied more heat than was required at the lower temperatures, copper cooling coils, through which flowed cold water, were installed at the bottom of the thermostat along with a fan which gave a good circulation of cool air. Other intermittent heaters were necessary for satisfactory operation at the higher temperatures. The control was to about 1°; better regulation was difficult to obtain because of the large amount of heat from the arc.

Several light-filtering solutions were tried and a solution of sodium nitrite saturated at room temperature was chosen as the most desirable. The filtering jacket on the Raman tube was filled with the solution and sealed. The 4358 Å. mercury line was used for excitation and the light from the Raman tube passed through a small opening in the thermostat to the Hilger constant deviation spectrograph which gave a dispersion of 40 Å./mm. at 4400 Å.

The Raman spectra were analyzed by making microphotometer tracings from all the plates. The positions of the lines were also accurately determined for pure acetoxime at 70 and 130° with a comparator and wave lengths were calculated using the Hartman interpolation formula. All lines or bands present in any of the spectra appeared on these two plates. The calculation of wave lengths from the comparator readings gave values with an accuracy of one or two ångström units depending on the sharpness of the line; this amounts to about ten to twenty cm.$^{-1}$.

Results

Excellent spectra were obtained for the pure acetoxime at all the temperatures, the time of exposure being one hour. The frequencies are reported in Table I. The lines were sharp except as noted. Figure 1 presents representations of the microphotometer tracings.

TABLE I

THE RAMAN SPECTRA OF ACETOXIME AT 70° AND 130°

Temperature, 70°		Temperature, 130°	
Frequency,[a] cm.$^{-1}$	Frequency, cm.$^{-1}$	Frequency, cm.$^{-1}$	Frequency, cm.$^{-1}$
356b	1381	346b	1379
486	1433	481	1431
596	1664	594	1661
810	2738	810	2753
950	2924d	923	2795
1070	3185ba	1072	2921d
1270	3537e	1270	3198ba
			3622e

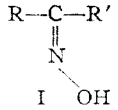
[a] b = broad; ba = band; d = diffuse with sharp maximum; e = edges.

The spectra of the solutions in carbon tetrachloride were not as clear as those for the pure substance. The slight cloudiness of the solution produced a strong background. Reproductions of the microphotometer tracings are given in Fig. 2. The values for the ordinates are not given in the figures because the curves have been relatively displaced and fitted into a single graph to save space. With this arrangement, however, the curves do afford an approximate comparison of the intensities of the lines. In both figures a and b represent the 4358 and 4916 Å. mercury lines, respectively.

Discussion and Conclusions

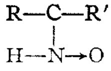
These spectra of acetoxime agree quite well with that reported by Bernstein and Martin.[2]

Of the structures which have been postulated[5] for the oximes only two need be considered here



$\mathrm{R{-}C({=}N{-}OH){-}R'}$

I



$\mathrm{R{-}C(N(H){\rightarrow}O){-}R'}$

II

Bernstein and Martin have assigned the lines of the spectrum to the different frequencies resultant from structure I which they deem to be correct. They also calculated the frequencies of the normal modes of vibration of a molecular model of this configuration and found that the calculated frequencies agreed remarkably well, considering the assumptions made, with those observed; further considerations of this type are unnecessary here.

The effect of temperature on the O–H band is

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(1) Lassettre, *Chem. Revs.*, **20**, 259 (1937).

(2) Bernstein and Martin, *Trans. Roy. Soc. Can.*, (III) **31**, 105 (1937).

(3) "International Critical Tables," Vol. VII, McGraw-Hill Book Co., Inc., New York, N. Y., 1930, p. 77.

(4) Houlton and Tartar, THIS JOURNAL, **60**, 544 (1938).

(5) Hibben, "The Raman Effect and Its Chemical Applications," Reinhold Publishing Corp., New York, N. Y., 1939.

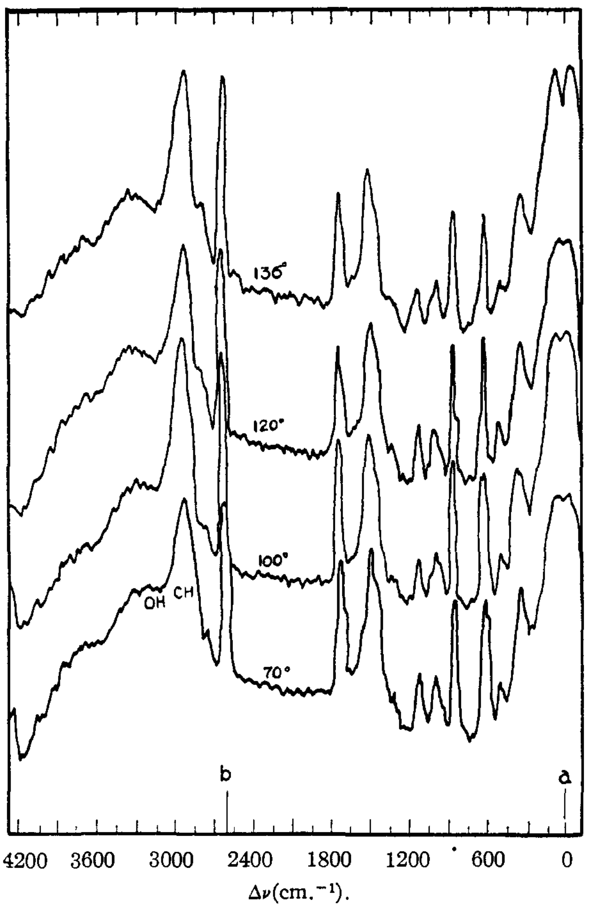

Fig. 1.—Microphotometer tracings for acetoxime, 70, 100, 120 and 136°.

clearly evidenced by the microphotometer tracings for pure acetoxime. The maximum of this broad diffuse band at 70° gradually shifts in position as the temperature rises, and at 130° a more or less sharp but weak line with diffuse edges is present. The band is due to OH ··· O bond while the line at a slightly higher frequency results from OH groups which do not participate in hydrogen bond formation. This line is superimposed upon the association band since there is still a considerable amount of the dimer even near the boiling point. Consequently the change with temperature of this portion of the spectrum is the result of the breaking of hydrogen bonds in the acetoxime polymer.

The spectra of the carbon tetrachloride solutions of acetoxime corroborate the findings for the pure substance. However, the results are less clear due to two complicating factors. First, the solutions were slightly cloudy and produced a continuous background on the plates thus making it more difficult to determine the presence and position of the band. Second, the decreasing concentration of acetoxime made longer exposures necessary; the carbon tetrachloride lines were much overexposed and interfered somewhat with the spectrum of the acetoxime. The higher frequency line resulting from the O—H vibration appears in the spectra of the more dilute solutions indicating the dissociation of the dimer, a change similar to that with increasing temperature on the pure substance.

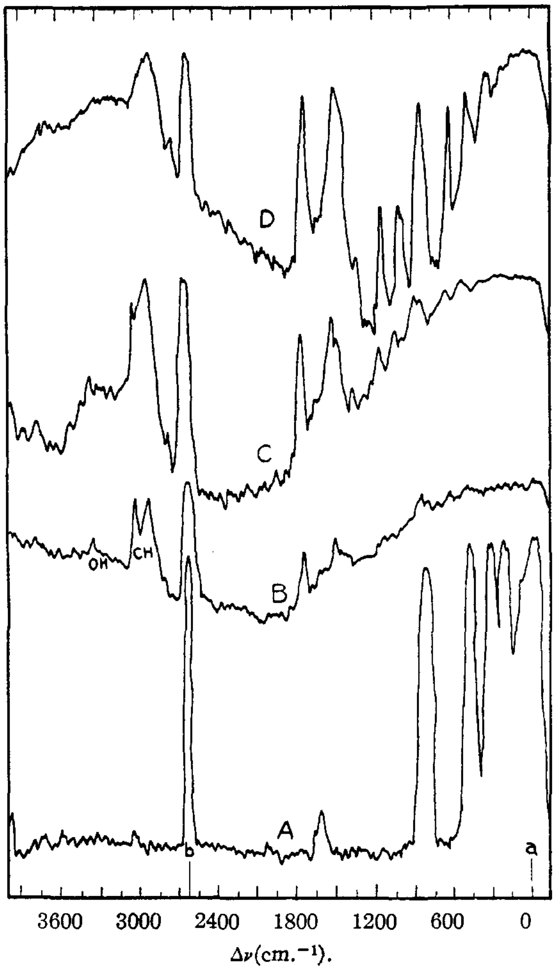

Fig. 2.—Microphotometer tracings for carbon tetrachloride mixtures: A, 100% CCl_4; B, 25%; C, 50%; D, 75% acetoxime.

Badger and Bauer[6] have shown that the magnitude of the shift of the OH frequency due to hydrogen bond formation may be taken as a measure of the strength of the bond, the shift being about 35 cm.$^{-1}$ per kilocalorie. Considering the frequency shift for the pure oxime to be from the lower edge of the band at 70° to the monomeric line which is clearly visible in the microphotometer tracings at 130°, the difference in frequency is 230 cm.$^{-1}$ which gives 6.6 kcal. as an approximate value for the strength of the hydrogen bond in acetoxime.

In addition to the change of the band maximum for the oxime, it will be noted that in the region between 2700 and 2800 cm.$^{-1}$ there appear to be two lines at 130° and only one at 70°. Both of these lines are very weak and might have been overlooked by Bernstein and Martin[2] since they reported that an exposure of 40 to 60 hours was required to obtain the OH band whereas in this study it was clearly shown on the plates in one hour. The line of lower frequency is at 2738 cm.$^{-1}$; the other line is at 2795 cm.$^{-1}$. A similar change is also shown in the carbon tetrachloride solutions at 60° with increasing dilution.

While these findings deserve further experimental study, the authors wish to point out at this time

(6) Badger and Bauer, *J. Chem. Phys.*, **5**, 839 (1937).

that it is in this region that fundamental C–H frequencies occur; also that extensive work on N–H frequencies[7,8] has shown them to occur in about the same region as those due to C–H frequencies. The line at 2795 cm.$^{-1}$ (appearing only at the high temperature) may be due to a N–H vibration. The other line (appearing at both low and high temperatures) suggests the possibility of the N–H—O bond.[9] The changes occurring with temperature as well as a recent observation in this Laboratory of a weak band in the corresponding position in the infrared absorption spectrum indicate that this is not a mercury line. Investigation is being continued to decide more definitely the nature of the bond to which this vibration must be ascribed.

Summary

1. Raman spectra have been taken of pure acetoxime at various temperatures from 70 to 130° and of carbon tetrachloride solutions of acetoxime at various concentrations at 60°.

2. Microphotometer tracings of the spectra show that the O–H band at 3400 cm.$^{-1}$ gradually changes position and shows a sharp line at temperatures greater than 100° and in dilute solutions. These changes are due to the breaking of hydrogen bonds in the acetoxime.

3. Evidence is also presented which may indicate that acetoxime exists in tautomeric forms.

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[7] Edsall, *J. Chem. Phys.*, **5**, 225 (1937).

[8] Bernstein and Martin, *Trans. Roy. Soc. Can.*, III, **31**, 95 (1937).

[9] Pauling, "The Nature of the Chemical Bond," Cornell University Press., Ithaca, N. Y., 1939.

[10] Original manuscript received June 15, 1944.

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Researches on Dichroism of Planar Complexes. I

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Absorption spectra of crystals are very important from both the theoretical and experimental points of view. For example, since molecules or ions are considered to be fixed in the crystal, measurement of pleochroism is expected to give certain information about the difference of bonds in different directions as well as the arrangement of ions or molecules. It is due to technical difficulties that measurements of absorption spectra of crystals have been so scarce.[1] Formerly, Tsuchida invented a new method,[2,3] which enables us to make measurements of dichroism in the visible and the near ultraviolet region with microscopic crystals easily obtainable in ordinary procedures of preparation. By this method, researches on absorption spectra of crystals have been carried out, some of which were about dichroism of metallic complex compounds[3,4] and dichroism of the benzene ring.[5] The present paper deals with the dichroism measurement of compounds with planar complex ions.

Experimental

Materials.—K_2PdCl_4 was prepared according to the direction of Gutbier and Krell.[6] It forms orangish-brown, tetragonal crystals. The structure of the crystal was analyzed by R. G. Dickinson.[7]

K_2PtCl_4 was obtained as red, prismatic, tetragonal crystals by reducing K_2PtCl_6 with potassium oxalate. The crystal analysis was made by R. G. Dickinson.[7]

$K_2PdBr_4 \cdot 2H_2O$ was prepared by the method of Gutbier and Krell.[6] The brown prismatic crystals belong to the rhombic system.

$K_2PtBr_4 \cdot 2H_2O$ was prepared as purplish-red, rhombic crystals by the same method as in K_2PtCl_4.

$Pd(NH_3)_4Cl_2 \cdot H_2O$ was prepared according to the direction of Cox.[8] The crystal structure was determined by B. N. Dickinson.[9]

$Pt(NH_3)_4Cl_2 \cdot H_2O$ was prepared by the method of Cox.[8] The crystal structure analysis was carried out by Dickinson.[9]

$K_2Pd(CN)_4 \cdot 3H_2O$ was obtained from K_2PdCl_4 and KCN as colorless, triclinic prisms.

$BaNi(CN)_4 \cdot 4H_2O$ was prepared according to the method of Brasseur.[10] The crystal structure was determined by him.

Quantitative Measurement of Dichroism of Microscopic Crystals.—In the present research was applied the microcrystal method,[2,3] which makes it possible to measure absorption spectra of solid substances in microcrystalline state. It is in most cases very difficult to make measurement of absorption of solid substances by ordinary methods which implies raising a considerably large, single crystal and preparing from it a thin plane-parallel section by polishing. Principal part of the apparatus consists of a quartz microscope and a quartz spectrograph with a sectorphotometer. Both spectra of light through the crystal and of light for comparison were photographed on the plate. Measurements were made in the region from about 6000 Å. to nearly 2000 Å. with linearly polarized light parallel and perpendicular to the principal axis. The extinction coefficient per mm., α, is given by the expression

$$\alpha = 0.9/d \log a_0/a$$

where d is thickness in mm. of the crystal, and a_0 and a are angles of the rotating sector for light through the crystal and the light for comparison. The results of dichroism measurement were shown in the figures 1 to 4. The $||$ or $\perp$ denotes absorption by polarized light with electric vector parallel or perpendicular to the planes of planar complex ions, respectively. Thickness of the crystals used was several hundredths of mm.

Discussion of Results

Previously Tsuchida,[11] in his general theory on the absorption bands of metallic complex compounds, explained many data by classifying four kinds of absorption bands, the first, second, third

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[1] Krishnan and Seshan, *Proc. Indian Acad. Sci.*, **8**, 487 (1938); Scheibe, *Z. angew. Chem.*, **52**, 631 (1939); Le Roux, *Compt. rend.*, **196**, 394 (1933) etc.

[2] Tsuchida and Kobayashi, *Bull. Chem. Soc. Japan*, **13**, 619 (1938); *J. Chem. Soc. Japan*, **60**, 769 (1939).

[3] Tsuchida and Kobayashi, "The Colours and the Structures of Metallic Compounds," Osaka, Japan, 1944.

[4] Tsuchida, Yamada and Yoneda, *J. Chem. Soc. Japan*, **69**, 145 (1948); Tsuchida and Yamada, *ibid.*, **70**, 44 (1949).

[5] Tsuchida, Kobayashi and Nakamoto, *ibid.*, **70**, 12 (1949).

[6] Gutbier and Krell, *Ber.*, **38**, 2385 (1905).

[7] R. G. Dickinson, THIS JOURNAL, **44**, 2404 (1922).

[8] Cox and Preston, *J. Chem. Soc.*, 1089 (1933).

[9] B. N. Dickinson, *Z. Krist.*, **88**, 281 (1934).

[10] Brasseur, De Rassenfosse and Pierard, *ibid.*, **88**, 210 (1934).

[11] Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 388, 436 (1938).