similar substances nitrogen pentoxide and pinene are nearly the same, seems improbable, we are forced to the conclusion that the rate of reaction is determined by the rate of activation. This is the view to which we are led from a consideration of Lewis and Smith's deduction of this equation.

Summary

1. The rate of racemization of *d*-pinene, both in solution and in the gas phase, has been measured between the temperatures 184° and 237°, and the reaction has been shown to be a simple unimolecular one. This is the first time to the author's knowledge, that a racemization *rate* has been measured in the gas phase.

2. The rates measured in the gas phase, in the pure liquid and in the solvents petrolatum, acetophenone and α-methylnaphthalene over a concentration range of more than 1000-fold, are nearly the same.

3. Evidence is introduced to show that the reaction is mainly a simple racemization and that side reactions come in but to a small extent. The actual rates may be slightly in error but the temperature coefficient is doubtless nearly correct.

4. The heat of activation as calculated from the Arrhenius equation is 43,710 cal. per gram molecule. The value of ν corresponding to this is 4.60×10^{14} sec.$^{-1}$

5. The results show approximate agreement with the equation $k = \nu e^{-Nh\nu/RT}$. The significance of this agreement is briefly discussed.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

INFRA-RED ABSORPTION SPECTRA
II. THE CHLORO-ACETIC ACIDS

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A relation between molecular structure and infra-red absorption spectra was emphasized in a recent publication from this Laboratory.[1] It was shown that completely non-polar molecules such as diatomic hydrogen do not exhibit absorption bands in the near infra-red, and it was reasoned that the progressive increase in polarity of the chloro-acetic acids with increased substitution of chlorine might be reflected in a shift of some band in the near infra-red absorption spectrum.

The present communication is concerned with the description of such a shift. It was found that the band falling at 5.90 μ in acetic acid, moves approximately 0.05 μ toward the shorter wave lengths for each chlorine atom substituted into the methyl group.

[1] Daniels, THIS JOURNAL, **47,** 2856 (1925).

As more chlorine atoms are put into the acetic acid molecule the acid becomes stronger, until trichloro-acetic acid is practically as strong as hydrochloric acid. These facts are explained by G. N. Lewis[2] on the assumption that the chlorine atoms draw the electron pair toward the acetate part of the molecule and permit the positive hydrogen atom to break away more easily. In this way a hydrogen ion and a chloro-acetate ion result. This displacement of the electron pair should produce an unbalanced condition in the molecule, making possible a displacement of atoms within the molecule and giving rise to differences in the near infra-red absorption spectra.

In leading up to the experimental study of the spectrum, certain improvements were made in the apparatus, and certain factors which might affect the infra-red absorption spectrum were studied.

Description of Apparatus

The Spectrometer.—The spectrometer was described in an earlier communication.[1]

It was found that the best way to adjust the position of the thermopile with reference to the concave mirror is to run through a series of absorption measurements on a standard liquid such as chloroform, with different settings. The spectra are then plotted and the thermopile is set at that position which gives the sharpest absorption bands.

A block of concrete set on corks proved to be an excellent base for the galvanometer and a heavy, projecting iron rod was cast into the block to support the galvanometer lamp without vibration.

The Absorption Cell.—The micrometer absorption cell shown in Fig. 1 was made entirely of bronze. The authors are indebted to Mr. O. E. Romare, the University mechanic, for its construction. It is designed so that the thickness of the absorbing liquid can be changed rapidly, and measured accurately with a micrometer scale. The error introduced by reflection at the surface between the liquid and the cell windows is eliminated by passing the light through a very thin layer of liquid, rather than through the empty cell, when taking the zero reading.[3]

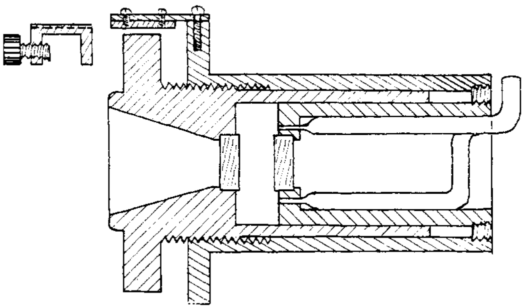

Fig. 1.—Micrometer absorption cell.

[2] Lewis, "Valence and the Structure of the Atom," Chemical Catalog Co., New York, **1923**, p. 85.

[3] This principle has been applied to absorption cells of fixed thickness by Taylor and Lewis, *J. Chem. Soc.*, **121**, 665 (1922).

The cell consists of a cylinder and a snugly fitting piston, each containing a fluorite window 2 cm. in diameter. The distance between the windows is varied by rotating the accurately threaded piston. The large contact area on both sides of the piston prevents the leakage of the liquid.

The windows are set in place with LePage's glue, the cell is turned up tight and the glue allowed to harden. An inlet and an outlet of small glass tubing are inserted below and above the fixed window and fastened with LePage's glue. They extend outside the spectrometer box so that the cell can be rinsed and the liquid continually renewed.

Since the threads have a pitch of 1 mm., one complete revolution of the piston gives a difference of cell thickness of 1 mm. The outer ring of the piston is stamped in hundredths of the circumference so that each division corresponds to 0.01 mm. Saddles are made to fit over this ring and they are fastened with set-screws at predetermined cell thicknesses. The piston is rotated until the first saddle is stopped by an arm projecting from the cylinder. After taking a reading at one setting the arm is lifted to let the first saddle pass and it is then lowered to stop the second saddle. In this way, without eye strain, measurements may be made with several different cell thicknesses at each setting of the prism.

In making a determination, the cell is filled with the liquid and the galvanometer deflections are recorded for each setting of the prism at each cell thickness. The galvanometer deflections divided by the galvanometer deflections at the zero setting, give the transmissions in percentages, and these are plotted against wave lengths.

The Effect of Slit Width

Determinations of the spectrum of chloroform were made with slit widths of 0.1, 0.25 and 0.6 mm. A special study was made of the band at 4.22 μ, since this band is unsymmetrical. The band was found to shift less than 0.02 μ for a 2.5-fold increase in slit width, and the slight shift was toward the longer wave lengths, indicating that as the slit was widened, there was a partial overlapping of the band at 4.30 μ.

In the subsequent work the slit width was not changed by more than 25% and any shift due to a change in slit width was less than 0.01 μ and beyond the limits of the sensitivity of the spectrometer.

A narrow slit gives sharper definition with lower minima and higher maxima than a wide one.

The Effect of a Solvent

It was pointed out before,[4] that the galvanometer deflections of a solution divided by the corresponding deflections of the solvent do not give the percentage transmission of the solute when cells of fixed thickness are used. The transmission of the solute may be determined, however,

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[4] Ref. 1, p. 2861.

with the adjustable cell just described because the width of the cell can be changed to include the same quantity of solvent, in the case of the solution and in the case of the pure solvent.

The spectrum of a 20% solution by volume of chloroform in carbon tetrachloride was determined with a cell thickness of 10 mm. A second determination was made with pure carbon tetrachloride in a cell 8 mm. thick. Division of the galvanometer readings of the former by those of the latter gave the percentage transmission for the dissolved chloroform. There was the same number of molecules of carbon tetrachloride in the path of the light in the two cases, since chloroform and carbon tetrachloride form a nearly ideal solution and their volumes in solution are practically additive.

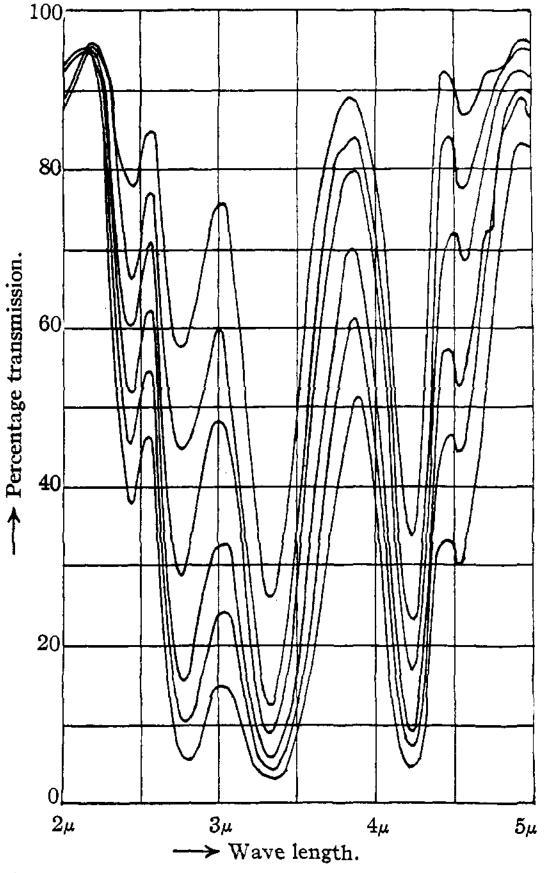

Fig. 2.—Absorption spectra of chloroform. The cell thickness ranged from 1 mm. to 10 mm.

The absorption spectrum of chloroform determined in this way coincided with the spectrum of 2 mm. of pure chloroform and the fact that no shift in the position of the bands could be detected, indicates that with these two liquids, the solvent does not exert any influence on the bands of the solute.

Lambert's Law Applied to Chloroform

The micrometer cell described above is well suited for accurately checking the laws of the absorption of infra-red light. According to Lambert's law, the transmission of light, I/I_0, is related to the thickness, s, of the absorbing medium by the equation $I/I_0 = e^{-ks}$.

If Lambert's law is valid, a straight line should result when the logarithm of the transmission is plotted against the thickness of the absorbing liquid. Failures of this law in the infra-red have sometimes been attributed to loss of light at the window-liquid surface, but the present cell is designed to eliminate these experimental errors.

The absorption spectrum of chloroform was determined for various thicknesses of liquid chloroform, namely, 1, 2, 3, 5, 7 and 10 mm. Two complete curves over this range of thickness were made at different times and found to agree within 1% transmission. The average values are shown in Fig. 2, where absorption bands are evident at 2.44, 2.75, 3.32 and 4.22 μ.

Logarithmic graphs showed that Lambert's law is valid when the transmission is high, but the transmission falls below the calculated value as the thickness of the absorbing liquid is increased beyond 2 or 3 mm. The deviation is most pronounced in the case of the band at 3.32 μ.

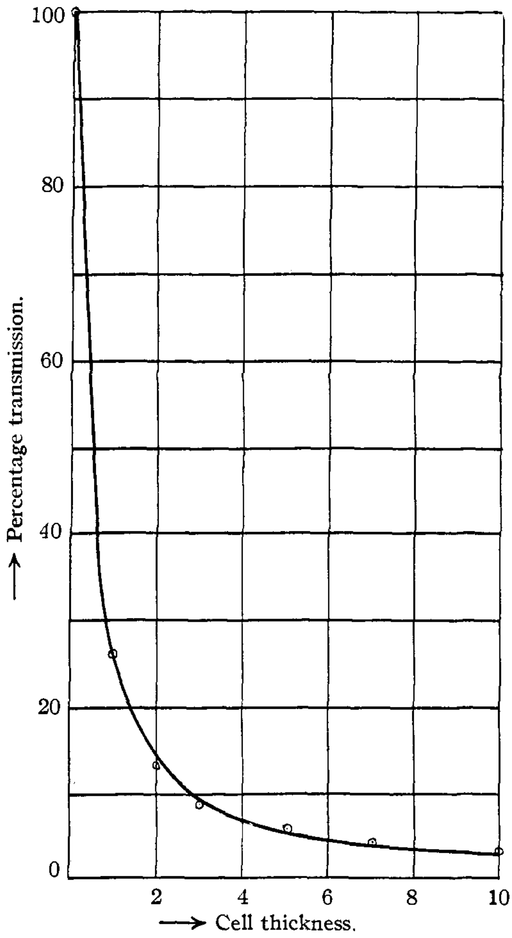

Fig. 3.—Transmission of the band at 3.32μ in chloroform as a function of cell thickness. The circles represent experimental determinations. The line represents the equation $I/I_0 = 1/3.50\ S$.

An equation was found to fit the facts rather well, as shown in Fig. 3. The curve is calculated from the equation $I/I_0 = 1/ks$ where, I/I_0 is the transmission, s is the thickness and k is a constant which has the value 3.50 for the band at 3.32 μ. The circles represent the experimentally determined values of the transmission for this band.

The other bands of chloroform could not be fitted so satisfactorily with this equation, possibly due to complicating action of weak bands adjacent to the main band.

It is possible that the deviations from Lambert's law may be due to imperfections in the spectrometer resulting in scattered radiation. It is probable that they are the result of an averaging effect on the fine structure of the band.

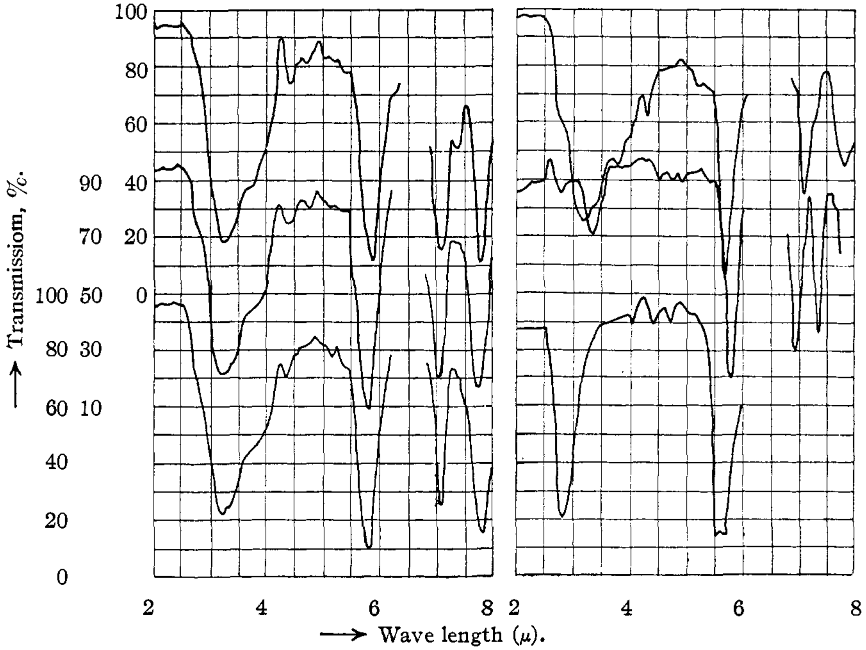

Fig. 4.—Absorption spectra of acetic acid and its derivatives.

Upper curve—CH_3COOH
Middle curve—$CH_2ClCOOH$
Bottom curve—$CHCl_2COOH$

Upper curve—CCl_3COOH
Middle curve—CH_3COOCH_3
Lower curve—$(CH_3CO)_2O$

The Chloro-acetic Acids

The spectra of acetic acid, and mono-, di- and trichloro-acetic acids are shown in Fig. 4. Methyl acetate and acetic anhydride are also included. These acids, even at the zero thickness of the micrometer cell, were too opaque to give sufficient deflections or clear-cut bands, and solutions of acetic acid in carbon tetrachloride were made up in 0.333, 0.1, 0.033, 0.01, 0.005 and 0.002 M concentration. It was found that the 0.005 M concentration gave the clearest spectrum and this concentration was used for all the acids in a cell of about 2 mm. thickness. Carbon tetrachloride is transparent, except at 6.4 μ.

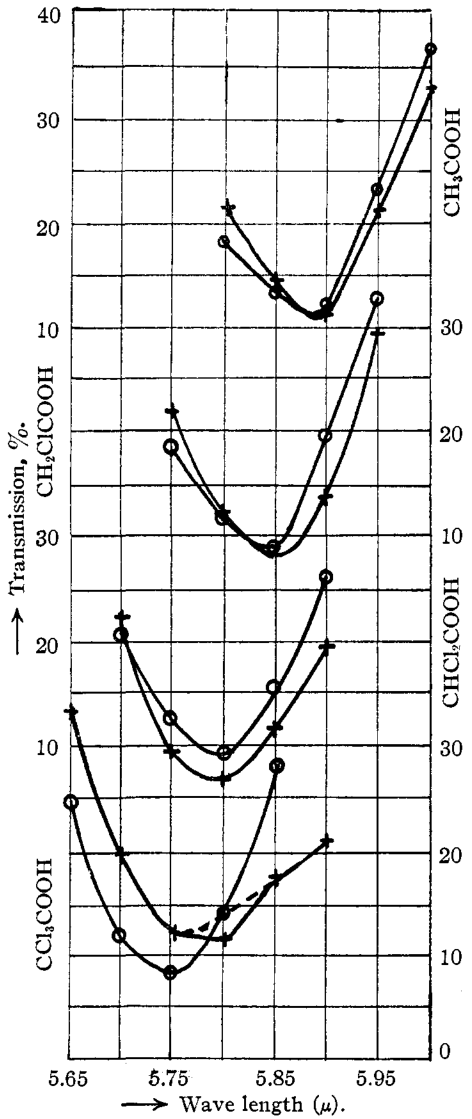

Fig. 5.—Enlarged spectra, showing the shift of the band at 5.90 μ as chlorine is substituted for hydrogen in the acetic acid molecule.

The acids are hygroscopic and particular care had to be taken to prevent their exposure to the moisture of the air for any length of time, in weighing them, as the strong water bands would affect the spectra. Two sets of solutions were made up at different times; one set was exposed to the air for about three minutes and the other for about half an hour. Differences were found in the spectra, but they were slight. The set of shorter exposure to the air was considered the more accurate in the calculations.

In all of these compounds, there are bands at 3.25 μ and 3.70 μ which could not be studied quantitatively on account of insufficient resolution. There are bands at about 7.05 μ and 7.80 μ which could not be located accurately since the deflection of the galvanometer was too small.

There is one outstanding band at about 5.8 μ and it is this band with which this research is particularly concerned. Proceeding in the order of the acids named above, this band shifts steadily to the shorter wave lengths as more chlorine atoms are introduced. The minima come at 5.89 μ, 5.85 μ, 5.80 μ and 5.75 μ, respectively. The minimum for methyl acetate comes at about 5.8 μ and for acetic anhydride the minimum, which is wider, extends from 5.50 to 5.70 μ.

Fig. 5 shows the bands on a larger scale and the manner of locating the points of maximum absorption. The curves for each acid were made with different solutions, weighed out at the same concentrations on different days. The curves denoted by the small circles are the determinations made with the liquids of shorter exposure to the air, while the crosses represent the liquids containing more moisture. It is seen that the spectra all check except the trichloro-acetic acid and a later check showed that this irregularity was due to experimental error.

The band at 5.9 μ is the only one which gives an appreciable shift and it seems reasonable to associate it with the bond (the electron pair) which holds the hydrogen to the rest of the molecule; for example, the O:H group of the carboxyl unit. Certainly this is the bond which is changed by the substitution of chlorine as evidenced by the increasing ionization constants of the chloro-substituted acetic acids, when dissolved in water.

It is interesting that Coblenz[5] observed after examining a large number of organic compounds that those compounds which contain a carboxyl group have a band at 5.9 μ. LeComte[6] also associated the band at 5.9 μ with the carboxyl group.

Summary

1. A micrometer absorption cell has been constructed for the rapid and accurate determination of spectra of liquids at different thicknesses.

2. The absorption spectra of the following compounds have been determined: acetic acid, monochloro-acetic acid, dichloro-acetic acid, trichloro-acetic acid, methyl acetate, acetic anhydride.

3. As the molecule becomes more polar by the substitution of chlorine for hydrogen, the band at 5.90 μ, corresponding to the carboxyl band, shifts about 0.05 μ to the shorter wave lengths for each chlorine atom.

Madison, Wisconsin

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[5] Coblenz, "Investigation of Infra Red Spectra," Carnegie Institution of Washington, **1905**, vol. 1, p. 69.

[6] LeComte, *Compt. rend.*, **178**, 1531 (1924).