Pullman and Pullman,[21] in characterizing the K and L regions, employed a complex index which includes the atom localization energy having the lowest value for the two carbon atoms which define the corresponding region, A_m. Finally, it should be stated that to avoid undue computation, only the *para*-localization energies were calculated for the non-angular derivatives; the free valences indicated that the remaining compounds studied possess relatively inactive L regions.

In Table VIII the corresponding values for the electrophilic and radical reactions are shown.

A comparison of the results in Table VIII shows that the variation of the complex index that characterizes the K region is more uniform for radical reactions than for electrophilic ones. For the latter, 3,4,5,6-dibenzocarbazole, the most carcinogenic of these compounds, should have the minimum index value, but 1,2-benzocarbazole and 1,2,7,8-dibenzocarbazole have even smaller values. On the other hand, there is no marked difference in the index values of the three groups of compounds (inactive, weakly and strongly carcinogenic). Thus, the complex dynamic indexes do not permit us to define threshold values from which we can predict whether a compound of this type is carcinogenic.

From these results, we conclude that there is a better correlation between the carcinogenic activity and the static complex indexes of these carbazole derivatives than between the carcinogenic activity and the dynamic complex indexes; however, more results are necessary to establish this finding for the nitrogen heterocyclics.

Acknowledgments.—We are indebted to Prof. C. A. Coulson for having read this manuscript and to the Instituto de Cálculo del C. S. I. C. (Madrid) for assistance with the calculations.

VALENCIA, SPAIN

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

Characteristic Integrated Intensities of Bands in the Infrared Spectra of Carboxylic Acids[1]

BY JOSEPH WENOGRAD[2] AND ROBERT A. SPURR

RECEIVED MAY 31, 1957

The integrated intensities of the free and bonded hydroxyl and carbonyl stretching bands in the spectra of carboxylic acids were measured and found to be characteristic properties of acids. The bands were all more intense in acids in which the carbonyl function was part of a conjugated system. In all cases there was an increase in intensity when the absorbing group was hydrogen-bonded. The integrated intensities of the free hydroxyl bands were 1.2 units for non-conjugated acids and 1.7 units for acids in which the carbonyl function was part of an aromatic or dienoic system. The corresponding intensities for the associated hydroxyl bands were 10.6 and 15.5 units. The integrated intensities of the free carbonyl stretching bands were 3.6 and 4.6 units and for the associated carbonyls 4.5 and 5.9 units for the two types of acids. Each carbon–hydrogen bond in the acids studied absorbed with an intensity of about 0.46 unit near 3000 cm.$^{-1}$. Equilibrium constants for the dimerization of several acids were determined spectroscopically. These dissociation constants were near 4.5×10^{-4} mole/l. for the non-conjugated acids and near 2.2×10^{-4} mole/l. for the conjugated acids.

Introduction

In drawing conclusions from the frequencies of infrared absorption maxima one uses only part of the information available from infrared spectra. Further information about the identity and nature of the absorbing material may be obtained from a consideration of band intensities. It is true that until recently it has been difficult to evaluate the absolute intensities of infrared bands. Ramsay[3] has shown, however, how to calculate intensities from the infrared spectra of compounds in solution. The increased reliability and improved dispersion of the infrared instruments currently available, moreover, make it possible to obtain reproducible measurements.

The utility of intensity measurements in the characterization of unknown structures depends upon the relationship between the intensity and the nature of an absorbing group. If the absolute intensity of an infrared band can be shown to be characteristic of a functional group or of the molecular environment of such a group, it will be possible to use such data to supplement band frequency measurements.

The absolute intensity, A, of an infrared band is defined by the expression

$$A = \int \alpha \mathrm{d}\nu = 1/Cl \int \ln I_0/I \mathrm{d}\nu \qquad (1)$$

where α is the molar absorption coefficient, C is the concentration of the solution in moles/liter, l is the sample thickness in cm., I/I_0 is the transmittance of the solution and ν is the frequency in cm.$^{-1}$. The units of A are cm.$^{-2}$ mole^{-1} l. For convenience, an "intensity unit" is defined as 10^4 cm.$^{-2}$ mole^{-1} l. The quantity A has been evaluated for various bands by two methods. The first involves the measurement of the area under a plot of log I_0/I against frequency and the direct calculation of A through eq. 1. The second method[3] assumes a symmetrical shape for the infrared band in question and requires the measurement of only two quantities from the experimentally determined spectrum: the value of ln I_0/I at the band maxi-

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(1) Taken from a thesis submitted by Joseph Wenograd to the Graduate School of the University of Maryland as partial fulfillment of the requirements for the degree of Doctor of Philosophy. This investigation received the generous financial support of the Office of Army Ordnance. A portion of this work was presented before the Eighth Symposium on Molecular Structure and Spectroscopy, June, 1954, at Columbus, Ohio.

(2) United States Naval Ordnance Laboratory, Silver Spring, Maryland.

(3) D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

mum and the half-intensity band-width, ($\Delta\nu_{1/2}$). The integrated intensity of a band is given by

$$A = K/Cl \ln(I_0/I)_{\nu\max} \Delta\nu_{1/2} \qquad (2)$$

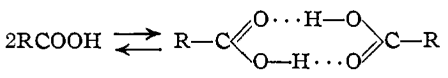
Here K is a constant which has a value near $\pi/2$ and which varies with experimental conditions.

Another function which will be of value is the "integrated density" D, defined as $D = \int \ln I_0/I \, d\nu$ and derived from Ramsay's method

$$D = K \ln (I_0/I)_{\nu\max} \Delta\nu_{1/2} \qquad (3)$$

Thus $A = D/Cl$.

Both in the vapor phase and in solutions in nonpolar solvents, carboxylic acids exist as equilibrium mixtures of monomer and dimer molecules.



The effects of this association on the infrared spectra of carboxylic acids has been discussed.[4,5] In the hydroxyl stretching region near 3 μ these spectra are characterized by two bands: one sharp peak in the neighborhood of 3500 cm.$^{-1}$ attributable to monomer molecules, and a very broad irregular dimer band extending from above 3500 to 2300 cm.$^{-1}$. Incorporated in this broad band are the various C–H stretching modes which absorb near 3000 cm.$^{-1}$. The spectrum of a typical acid in this region is shown in Fig. 1. In the carbonyl region, near 1700 cm.$^{-1}$, the spectra of acids in solution are characterized by two fairly sharp peaks attributable to monomer and dimer molecules.

The equilibrium constant K_d for the dimerization is given by

$$K_d = 2M^2/(C - M) \qquad (4)$$

where C is the total acid concentration and M is the concentration of monomer molecules. While the evaluation of K_d has been undertaken by many investigators using several independent methods,[6-13] there is very little agreement among the values obtained. Since reliable dissociation constants were needed for the calculation of intensities, it was necessary to evaluate these constants for the acids under consideration. This was done by a spectroscopic technique similar to that employed by Harris and Hobbs,[12] to be described below.

Experimental

All measurements were made with a Perkin–Elmer model 12C single-beam spectrometer, adapted by the manufacturer for a double-pass operation. It was equipped with a LiF prism for measurements in the 3 μ region and with a CaF_2 prism for use near 6 μ. The light path was flushed with compressed air which had been passed through a column containing activated alumina.

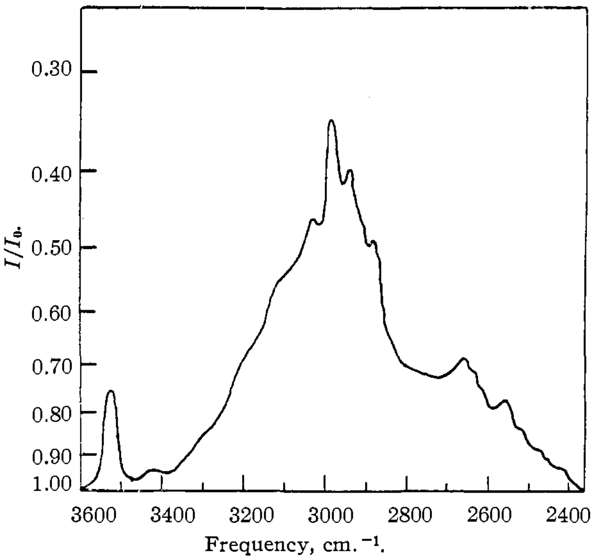


Fig. 1.—Spectrum of propionic acid in hydroxyl stretching region; concn. 0.00254 mole/l., cell 1.45 cm.

Reproducible measurements of integrated intensities depended to a large extent on the stable operation of the spectrometer. In order to ensure stability the "globar" source and the amplifier were left on continuously.

Four sample cells were used with thicknesses of 0.01, 0.1, 1.48 and 6.10 cm. The former two cell thicknesses were measured interferometrically while the latter were measured directly. The two thicker cells were used in measurements of the hydroxyl band permitting measurements on solutions as dilute as 4×10^{-4} M. All intensities of the hydroxyl dimer band refer to solutions approximately 0.02 M. The carbonyl bands were studied at concentrations near 5×10^{-2}, 5×10^{-3} and $5 \times 10^{-}$ M. All measurements were carried out at 24 ± 1°.

The acids used were the best available grade of commercial material unless otherwise noted. Solid acids were recrystallized from suitable solvents and liquids were fractionally distilled. Eastman spectroscopic grade CCl_4 was used as a solvent.

The integrated intensity of the hydroxyl monomer band is given by $A = D/Ml$. Elimination of M between this expression and eq. 4 gives

$$D = {}^1/_2A^2l^2K_dC/D - {}^1/_2K_dAl \qquad (5)$$

A plot of D *vs.* C/D gives values for both A_{mon} and K_d.[14] There is considerable overlapping between the monomer and dimer hydroxyl stretching bands. For this reason it is not possible to use the solvent spectrum as the line of 100% transmission in studying the monomer band. Instead, the wing of the dimer band is extrapolated on the chart paper and this base line is used as the line of 100% transmission. At high concentrations this base line cannot be extrapolated unequivocally and solutions with concentrations above 0.04 M therefore were excluded from consideration. The intensities of the dimer bands were evaluated by direct integration, using a planimeter, of the areas under plots of log I_0/I against frequency. In these cases the solvent spectra were used as the I_0 curves. The integrated densities of the free and bonded carbonyl bands were determined by Ramsay's method using the solvent spectra as lines of 100% transmission.

It was found that the measurement of the half intensity band width was subject to some variation for each acid considered. Since this variation was independent of concentration, average values of $\Delta\nu_{1/2}$ were used in eq. 3. As the spectral slit widths were small compared to the band widths, no error was introduced by using the value $\pi/2$ for K in eq. 3. In all cases the spectral slit widths were of the order of 20% of the half intensity band widths.

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(4) M. M. Davies and G. B. B. M. Sutherland, *J. Chem. Phys.*, **6**, 755 (1938).

(5) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1954.

(6) M. M. Davies, P. Jones, D. Patniak and E. A. Moelwyn-Hughes, *J. Chem. Soc.*, 1249 (1951).

(7) E. A. Moelwyn-Hughes, *ibid.*, 850 (1940).

(8) H. W. Smith and T. A. White, *J. Phys. Chem.*, **33**, 1953 (1929).

(9) B. von Szysykowski, *Z. physik. Chem.*, **131**, 175 (1927).

(10) H. A. Pohl, M. E. Hobbs and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941).

(11) F. T. Wall and P. E. Rouse, Jr., THIS JOURNAL, **63**, 3002 (1941).

(12) J. T. Harris and M. E. Hobbs, *ibid.*, **76**, 1419 (1954).

(13) G. M. Barrow and E. A. Yerger, *ibid.*, **76**, 5248 (1954).

(14) This equation is analogous to the expression used by Harris and Hobbs,[12] except that they used maximal optical densities instead of "integrated densities" and thus obtained extinction coefficients instead of integrated intensities.

Results and Discussion

Values of the absolute intensity of the hydroxyl stretching band and the dissociation equilibrium constants were determined for several acids in solutions of CCl_4 by the modified method of Harris and Hobbs; these are shown in Table I. The quantities denoted as saturated aliphatic acids were determined by treating acetic, propionic, valeric and caproic acids together. This procedure, the validity of which is illustrated by Fig. 2, shows graphically that these acids not only have similar absorption intensities but also dissociate in CCl_4 to roughly the same extent. The intensities obtained for the first six acids are all near the value of 1.2 intensity units, obtained from the procedure illustrated by Fig. 2. These acids are similar in that the carbonyl functions of the carboxyl groups are not part of a conjugated system. The intensities for the last three acids also show good agreement with each other, and the acids are characterized by a carbonyl group in conjugation with a long conjugated system.

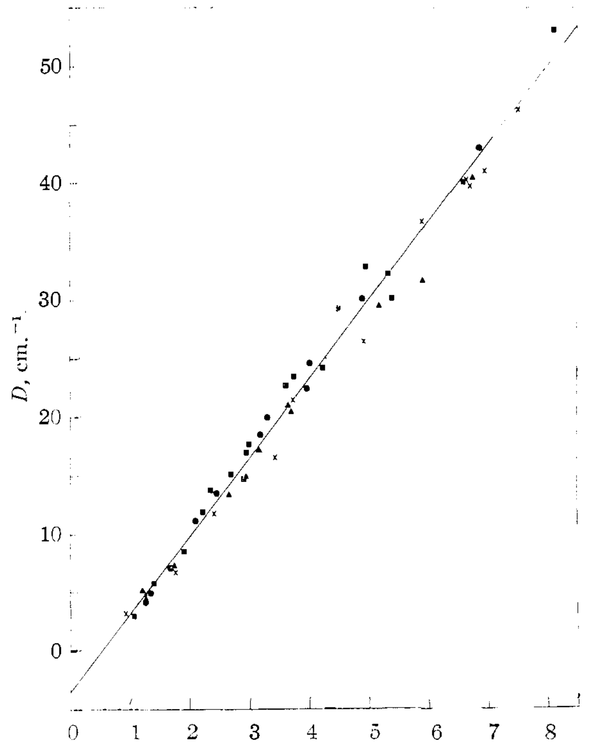

Fig. 2.—Plot of D *vs.* c/D for four saturated aliphatic acids: ●, acetic; ■, propionic; ▲, valeric; ×, caproic.

TABLE I

INTEGRATED INTENSITIES OF MONOMER BANDS AND DISSOCIATION CONSTANTS

Acid	Av. half intensity band width, cm.$^{-1}$	$K_D \times 10^4$	A_{mon}, intensity units
Acetic	24.7	4.21	1.22
Propionic	24.4	4.03	1.25
Valeric	22.9	3.68	1.28
Caproic	22.9	5.37	1.06
Lauric	24.4	5.16	1.18
Phenylacetic	26.3	5.15	1.30
Benzoic	27.0	2.26	1.65
o-Toluic	29.9	3.62	1.72
Sorbic	25.4	1.96	1.71
Satd. aliphatic acids	. .	4.0	1.2

It is now possible to say that the absolute intensity of the stretching band of monomer hydroxyl groups is a characteristic property of a class of carboxylic acids. For non-conjugated acids this intensity is 1.2 units. For conjugated acids this intensity is 1.7 units. These values may be contrasted with the intensity of the free hydroxyl stretching absorption in alcohols of 0.46 unit, as obtained for *n*-propyl alcohol in CCl_4.[15]

The dissociation constants of the saturated aliphatic acids show good agreement with each other, as expected from Fig. 2. There seems to be a trend toward a greater degree of dissociation with increasing chain length.

The constants obtained for the conjugated acids are somewhat lower than those obtained for the saturated acids. As expected from hindering by the *o*-methyl group, *o*-toluic acid associated to a lesser extent than other similar acids. It is significant that both in intensity and equilibrium constant, phenylacetic acid falls among the non-conjugated acids as it should, although its acid dissociation constant is high, falling between sorbic and benzoic acids.

The value reported in Table I for the dissociation constant of acetic acid lies between the two values previously measured for the same acid in the same solvent by spectroscopic techniques.[12,13] As expected, however, it is quite close to one of the values reported by Harris and Hobbs.[12] These dissociation constants do not agree with values obtained by the distribution method.[6]

The other techniques used for the study of acid dissociation constants have not been applied to CCl_4 solutions, and no direct comparisons are available. It is felt that the distribution dissociation constants, applying as they do to moist solvents, are not applicable to the essentially anhydrous solvents used in spectroscopic work. It is probable that Szysykowski's treatment[9] of this problem, which considers only the enhanced solubility of the acid in moist solvent, is an oversimplification of the problem.

The dissociation constant and monomer intensity of propionic acid in $CHCl_3$ were determined by the same method. On the basis of four experimental points, propionic acid has a dissociation constant of 5.43×10^{-3} mole/liter and an absolute hydroxyl monomer intensity of 1.59 units. The enhancement of intensity, as evidenced by propionic acid, appears to be general and has been observed previously for the intensity of the carbonyl group.[16,17] The increase in K_d in $CHCl_3$ is also quite general and has been reported before.[16] Both of these effects can be explained on the basis of the formation of weak hydrogen bonds between the solute and the solvent.

There are some objections to the method adopted for the evaluation of A_D and K_{mon}. If Davies and

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[15] S. A. Francis, *J. Chem. Phys.*, **19**, 505 (1951).

[16] G. M. Barrow, *ibid.*, **21**, 2008 (1953).

[17] R. N. Jones, D. A. Ramsay, D. S. Keir and K. Dobriner, THIS JOURNAL, **74**, 80 (1952).

Sutherland[4] are correct in believing that the value of A changes with concentration, then it becomes impossible to determine A and K_d by a spectroscopic technique unless this variation is fully understood. The contention by Barrow and Yerger[13] that K_d varies with concentration would if correct preclude the calculation of A and K_d by a graphical procedure. That these two factors are not important at the concentrations studied in this work is demonstrated by the linearity of plots of the type suggested by eq. 5 and Fig. 2. Because of these objections, however, the values of A and K_d reported herein do not necessarily apply outside the concentration ranges of their measurement.

The characteristic nature of integrated intensities is shown in a more graphic style by measurements on the dimer band. Integrations of the dimer band were carried out over the very broad frequency range of 3500 to 2300 cm.$^{-1}$. The overlapping of the monomer band was negligible because of the much greater concentration and intensity of the dimer molecules. The values given in Table II were obtained for the acids shown over a twofold concentration range.

TABLE II

INTEGRATED INTENSITIES OF DIMER BANDS

Acid	Concn. range, moles/l.	No. of C–H bonds	Integrated intensity (intensity units)
Acetic	0.02	3	10.6
Propionic	0.025	5	11.3
Butyric	0.01–0.02	7	12.9
Isobutyric	0.02–0.03	7	12.6
Valeric	0.02	9	13.9
Caproic	.02	11	14.4
Isocaproic	.02	11	14.4
Lauric	.015	23	19.9
Palmitic	.01	31	22.8
Stearic	.01	35	25.2
Phenylacetic	.02	7	12.7
Furoic	.02	3	15.6
Benzoic	.015	5	16.8
Cinnamic	.02	7	17.7
o-Toluic	.015	7	17.7
Sorbic	.015	7	17.4

Because of the approximate constancy of the dissociation constants for each type of acid, these values refer to solutions having roughly the same per cent. of dimer. Since, as has been shown, the integration of the dimer band includes all the carbon–hydrogen stretching absorption, the values for the integrated intensity are expected to increase with the number of such bonds. A consideration of the quantities in Table II shows that this is the case. If the intensities given in Table II are plotted against the number of carbon–hydrogen bonds in the molecule, as in Fig. 3, it can be seen that two straight lines are obtained. The lower line includes all the saturated acids and phenylacetic acid. The upper line represents the values for acids in which the carboxyl group is conjugated with a dienoic or aromatic system.

These two straight lines may be extrapolated to zero abscissa. The values of these intercepts represent the absorption due to the amounts of dimer present in the solutions studied. The slopes of these lines represent the integrated intensity for each carbon–hydrogen bond. A least squares treatment of the values for the unconjugated acids gives an intercept of 9.52 intensity units and a slope of 0.44 intensity unit. If an average K_d of 4.5 × 10^{-4} and a concentration of 0.02 M are assumed for these acids, the degree of dissociation under the conditions of these experiments is 10.0%. Using this value, the integrated intensity per mole of hydrogen bonded hydroxyl groups is 9.52/0.90 or 10.6 intensity units. For the conjugated acids the intercept is 14.21 intensity units and the slope is 0.49 intensity unit. Taking as average values a K_d of 2.2 × 10^{-4} and a concentration of 0.015 M, the degree of dissociation is 8.2%. The value of the integrated intensity for the stretching band of the associated hydroxyls is then 15.5 intensity units.

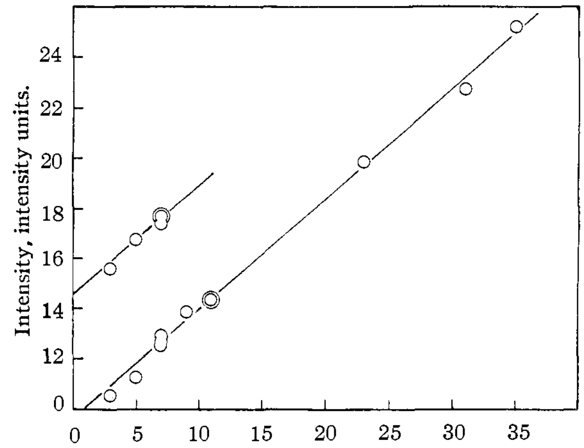

Fig. 3.—Intensities of dimer bands.

The integrated intensity of the infrared absorption between the limits 3500 and 2300 cm.$^{-1}$ in the spectrum of a non-conjugated acid can be given by

$$A = 10.6(1 - \alpha_d) + 0.44n$$

where α_d is the degree of dissociation into monomer molecules and n is the number of carbon–hydrogen bonds. A similar expression for the absorption intensity of the conjugated acids between the same limits may be written

$$A = 15.5(1 - \alpha_d) + 0.49n$$

It is of considerable interest to note the marked enhancement in the intensity of the hydroxyl group absorption caused by association. The ratios of the absorptions of bonded and free hydroxyl groups are 10.6/1.2 = 8.8 in the case of the saturated acids, and 15.5/1.7 = 9.1 in the case of the conjugated acids. These values are comparable to the ratio of 12.6 reported by Francis[15] for the hydroxyl stretching absorptions in n-propyl alcohol.

They are also comparable with the more recent results of Barrow[18] and of Tsubomura.[19] Barrow[18] reports the changes in the integrated intensity of the hydroxyl stretching band in a series of alcohols and phenols caused by changing the solvent

[18] G. M. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).

[19] H. Tsubomura, *J. Chem. Phys.*, **24**, 927 (1956).

from CCl_4 to diethyl ether to triethylamine. Roughly tenfold enhancements in intensity were observed between the free hydroxyls in CCl_4 and the solvent bonded groups in triethylamine. Tsubomura[19] measured the intensity of the free hydroxyl absorption in CCl_4 and *n*-heptane. These intensities were compared to values obtained when acceptor molecules, *viz.*, chlorobenzene, acetonitrile, ethyl acetate, were added to the solutions. Intensities were increased by as much as fivefold by means of the stronger acceptors.

It is apparent that hydrogen bonding causes profound changes in the nature of the hydroxyl vibration. Francis[15] has shown that these results are not explainable on the basis of a simple electrostatic picture for this bond.[20] Both Tsubomura and Barrow show that this marked enhancement in hydroxyl intensity upon hydrogen bonding can be accounted for by attributing to the bond a variable ionic character.

The two slopes in Fig. 3 give values for the integrated intensity of the carbon–hydrogen stretching bands of acids in the neighborhood of 3000 cm.$^{-1}$. These values are 0.44 for the saturated acids and 0.49 for the conjugated acids. The difference between these values should not be regarded as significant. It is possible, however, that the carbon–hydrogen bonds on aromatic or dienoic systems give rise to absorptions of slightly greater intensity than aliphatic bonds. Francis[21] reported a value of 0.78 intensity unit for the intensity of the carbon–hydrogen bonds of methylene groups in aliphatic hydrocarbons. Half this value (0.39) agrees approximately with the value of 0.44 intensity unit obtained for aliphatic carbon–hydrogen absorption in the present work. The slightly higher value of the present result may be explained by the fact that the integration involved here included the entire wing of the carbon–hydrogen band, while Francis terminated his integrations at arbitrary limits.

Intensities of free and bonded carbonyl stretching absorptions, as determined using eq. 2, are shown in Table III. Concentrations for use in this equation were calculated from the dissociation constants obtained from studies of the free hydroxyl band. These intensities are seen to be characteristic for each type of absorption. Because of the complicating effects of the 6μ water band the values in Table III are only good to within about 10%.

TABLE III

INTENSITIES OF FREE (A_{mon}) AND BONDED (A_d) CARBONYL GROUPS OF ACIDS IN CARBONYL STRETCHING REGION

Acid	A_{mon}, intensity units	A_d, intensity units
Acetic	3.9	4.5
Propionic	3.3	4.5
Benzoic	4.9	6.0
o-Toluic	4.4	5.8

As in the case of the hydroxyl bands, it is found that there is an increase in intensity upon conjugation. This observation is in agreement with the work of previous investigators.[17] An enhancement in carbonyl intensity upon hydrogen bonding is also evident. This enhancement is not so pronounced as is the similar effect involving the hydroxyl group.

SILVER SPRING, MD.

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[20] N. D. Coggeshall, *J. Chem. Phys.*, **18**, 978 (1950).

[21] S. A. Francis, *ibid.*, **18**, 861 (1950).

[CONTRIBUTION, ISSUED AS N.R.C. NO. 4504, FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL]

Ionization and Dissociation of Allene, Propyne, 1-Butyne, and 1,2- and 1,3-Butadienes by Electron Impact; the $C_3H_3^+$ Ion

BY J. COLLIN[1] AND F. P. LOSSING

RECEIVED JULY 1, 1957

The ionization potentials of allene, 1,2-butadiene and 1,3-butadiene have been found to be 10.16, 9.57 and 9.18 volt, respectively. The appearance potentials of the $C_3H_3^+$ ion from these compounds and from propyne and 1-butyne have been measured. From the results it is concluded that the $C_3H_3^+$ ion formed from these compounds by electron impact has the propargyl ($CH{\equiv}C{-}{}^+CH_2$) structure in each case, and that the hydrogen migration required to form this ion from 1,3-butadiene must occur with almost zero activation energy. The following bond dissociation energies have been derived: $D(C_3H_3{-}H)$ in allene $\leqslant 81.2$ kcal./mole, $D(C_3H_3{-}H)$ in propyne $\leqslant 82.8$ kcal./mole, $D(C_3H_3{-}CH_3)$ in 1,2-butadiene $\leqslant 68.2$ kcal./mole, $D(C_3H_3{-}CH_3)$ in 1-butyne $\leqslant 67.5$ kcal./mole. The heat of formation of C_3H_3 radical = 75 kcal./mole, and of $C_3H_3^+$ ion = 265 kcal./mole.

Introduction

The electron impact technique for the determination of appearance potentials of gaseous ions has been used extensively and undoubtedly has thrown considerable light on ionization potentials of molecules and free radicals. In a number of cases, it has been possible to deduce quite satisfactory values for certain bond dissociation energies. In combination with known heats of formation of molecules, appearance potential data have been widely used to calculate heats of formation of radicals and molecular and radical ions. In some cases a choice between different possible structures of ions and radicals can be made, and a mechanism for their formation can be suggested.

In connection with a mass spectrometric study of the mercury photosensitized decomposition of allene and butadienes, we have determined the appearance potentials of certain ions in the mass spectrum of these molecules. Of particular interest is the C_3H_3 ion and radical since, on the one hand, the radical plays an important role in the

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[1] National Research Council of Canada Postdoctorate Fellow 1956–1957.