An Electronic Transition of the Rydberg Series Type in the Absorption Spectra of Hydrocarbons

Emma P. Carr and Hildegard Stücklen

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In an analysis of our experimental results on the absorption spectra of a series of dienes, which will be published shortly, a possible theoretical interpretation of our earlier results on mono-olefins and cyclic hydrocarbons[1, 2] has developed which seems to be of significance in the general study of molecular spectra of polyatomic molecules. The seventeen olefin hydrocarbons which have been examined in this laboratory all show a group of narrow diffuse absorption bands of high intensity in the region between 43,000 and 53,000 cm^{-1} and the position of the first band in each compound is determined by the number of alkyl groups bound to the carbon atoms of the double bond but is independent of the nature of the group. There is a progressive shift toward the visible as the number of alkyl groups is increased. If the position of this band for each compound is plotted as a function of the number of such alkyl groups and the corresponding value for ethylene with no substituent is taken as 57,320 cm^{-1}, measured by Price,[3] the result is very nearly a straight line. This relationship was used to justify our assumption that the bands represented an analogous, electronic transition in ethylene and in its derivatives. The electronic band for ethylene was shown by Price to be the first member of a Rydberg series but the diffuseness of the bands in the ethylene derivatives and the variable intensity factors made it difficult to confirm a similar assignment for the more complex hydrocarbons. The results of our study of dienes have shown, however, that the sharpness as well as the relative intensities of the bands is modified profoundly where they are superimposed on a region of continuous absorption due to other electronic transitions. It seems quite certain therefore that these first bands in the Schumann region, which are found in the spectra of all the olefins, constitute the first electronic band system of a Rydberg series which is superimposed on a continuous band of high intensity which, for most of the olefins, has a maximum about 57,000 cm^{-1}. On the basis of theoretical considerations this latter band in the ethylene derivatives is assigned by Mulliken to a charge-transfer transition $(N \rightarrow V)$ characteristic of this type of homopolar molecule.[4]

An important corollary of the identification of the shallow bands of the olefins with a Rydberg series transition, is its application to the interpretation of the benzene spectrum. The parallelism in position between the first bands in the Schumann region of all the hydrocarbons both aliphatic and cyclic having the grouping $C-CH=CH-C$ has been pointed out[2] and the extraordinary similarity between the bands of cyclohexene and *cis*-butene-2[5] is more readily understood if the electronic transition is of the Rydberg series type where the electron concerned is nonbonding and the energy of the transition would be dependent primarily upon the effective nuclear charge of the carbon atom. This effective charge would be strongly influenced and probably determined by the number and arrangement of hydrogen and carbon atoms directly bound to the carbon atoms of the double bond and therefore the energy of excitation of a nonbonding electron would be nearly the same in all

hydrocarbons containing a similar grouping. The identification of the group of strong bands between 48,800 and 54,000 cm^{-1} in the spectrum of benzene as belonging to the first member of a Rydberg series which may be superimposed upon another electronic transition, predicted by Goeppert-Mayer and Sklar[6] as a weak band due to a forbidden electronic transition would explain the anomalous intensity relationship.

EMMA P. CARR
HILDEGARD STÜCKLEN

Department of Chemistry,
  Mount Holyoke College,
    South Hadley, Massachusetts,
      July 14, 1939.

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Activated Adsorption of Nitrogen on Iron at 23° and 100°C, and Ammonia Synthesis

During the recent symposium on "Fundamentals of Heterogeneous Catalysis" (A.C.S. Meeting, Baltimore) ammonia synthetic catalysts were discussed from various angles. In the light of these discussions, it appeared to be of great interest to investigate the adsorption of nitrogen on evaporated iron films. Technique of production of such films was discussed by one of the writers during the same symposium and, among others, adsorption measurements were presented for various gases on nickel films.

As in the case of nickel, very rapid chemisorption was observed for hydrogen on iron at room temperature. In contrast to nickel, however, iron also adsorbs nitrogen at room temperature. The amount adsorbed is roughly one-fifth of the hydrogen adsorption. Whereas, the hydrogen adsorption on iron is practically instantaneous, considerable time is required for the activated adsorption of nitrogen at room temperature. The remaining four-fifths of the surface can be covered with hydrogen bringing the total adsorption to the same number of molecules as in the case of hydrogen alone. Apparently no interaction between the co-adsorbed gases takes place. If the iron film is heated to 100°C, it sinters and the amount of hydrogen it will take up after cooling to room temperature is about 80 percent of that of a film evaporated at room temperature. On such a sintered catalyst, much less than one-fifth of the available surface (as measured by hydrogen adsorption) may be covered with nitrogen at room temperature. If, however, the nitrogen is admitted to the iron film at 100°C again about one-fifth of the total available surface is covered by nitrogen. The rate of this adsorption is considerably faster than that at room temperature on the unsintered catalyst. Attempts to produce ammonia in the gas phase by, for instance, heating the iron film on which nitrogen is actively adsorbed in a hydrogen atmosphere have so far failed. If, however, the iron films on which nitrogen was adsorbed at room temperature or at 100°C are dissolved in hydrochloric acid, the presence of ammonia can be readily shown by distilling with alkali and testing by Nestler's reagent. The

amount of ammonia found was roughly in quantitative agreement with the amount of nitrogen adsorbed. This ammonia synthesis takes place independent of the presence of free or adsorbed hydrogen. No nitrogen is adsorbed either at room temperature or at 100°C and consequently no ammonia is formed if hydrogen is admitted to the iron film first.

A detailed account and discussion of this work will be published in due time. Thanks are due to Messrs. W. A. Cole and A. B. Bullock for help with the experiments and analyses.

OTTO BEECK
AHLBORN WHEELER

Shell Development Company,
Emeryville, California,
July 12, 1939.

Ultrasonic Velocities in and Adiabatic Compressibilities of Mixtures of Acetic Acid and Water

Using the method of Debye and Sears[1] and of Lucas and Biquard,[1] we have measured the velocities of ultrasonic waves of a frequency of 7.4 megacycles per second, at 25°C, in mixtures of varying concentration of acetic acid and water. The trough containing the liquid was mounted on the prism table of a spectrometer to facilitate the measurement of the angle of diffraction of the light. Since the mixtures are electrically conducting, the piezoquartz was immersed in an inner vessel containing xylene. The waves were transmitted through a mica window to the outer vessel containing the conducting liquid. The frequency of the electrical oscillator was measured with a General Radio, 724-A, frequency meter. The adiabatic compressibility β was calculated by means of the equation $v = (1/\rho\beta)^{\frac{1}{2}}$, in which v is the measured velocity of the ultrasonic waves and ρ is the density of the liquid. This equation gives β in dyne^{-1}; in the values recorded below β is in atmos.$^{-1}$ A sodium vapor lamp was used as a source of monochromatic light. The glacial acetic acid used had a purity of 99.5 percent; it was mixed with distilled water to get the desired concentrations. The results are represented in Fig. 1, which shows that the velocity of the supersonic waves reach a maximum at about 30 percent concentration, by weight, of acetic acid, and that the com-
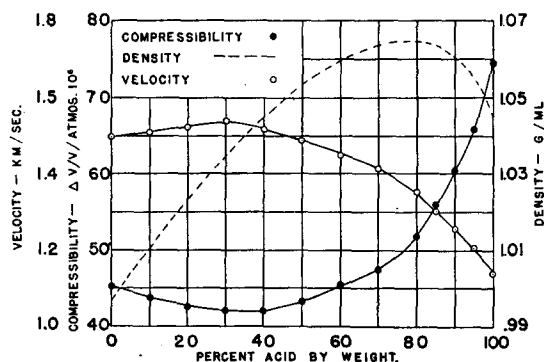

FIG. 1. Velocity of ultrasonic waves and adiabatic compressibility in aqueous solutions of acetic acid.

pressibility has a minimum at this concentration. The variations in ultrasonic velocities and adiabatic compressibilities are somewhat similar to the well-known variations in the density and index of refraction of mixtures of acetic acid and water.

ALVA W. SMITH
LEWIS M. EWING

Mendenhall Laboratory of Physics,
The Ohio State University,
Columbus, Ohio,
June 29, 1939.

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Raman Spectra of Deuterium Substituted Guanidine and Urea

In continuation of earlier work on the Raman spectra of guanidine and urea,[1] we have determined the effect of completely substituting deuterium for hydrogen in the NH_2 groups of these compounds, and have also repeated the earlier measurements on ordinary guanidine and urea. The results are tabulated below. Lines marked P are definitely polarized; those marked D are probably depolarized.[2]

Guanidonium Chloride

$C(NH_2)_3{}^+ Cl^-$ in H_2O		$C(ND_2)_3{}^+ Cl^-$ in D_2O	
536(4b)	D	459(3)	D
1015(8)	P	921(8)	P
1462(0vb)	?	1193(1b)	D
1565(2vb)	D	1278(1)	P
1670(1vb)	?	2127(0?)	—
3212(3b)	—	2374(6)	P(D_2O?)
3290(3b)	—	2433(6)	P
3360–3471(H_2O)		2496–2591(6)(D_2O)	

Urea

$CO(NH_2)_2$ in H_2O		$CO(ND_2)_2$ in D_2O	
534(2)	D	458(1)	D
601(2)	D	548(1)	D
1008(10)	P	890(5)	P
1167(4)	P	997(6)	P
1478(2b)	D	1049(1)	?
1604(4b)	P?	1164(1)	D
1680(3b)	P	1201(1b)	?
3235(5b)	P	1247(3)	P
3385(6vb)	P	1613(3b)	P
3496(5b)	D	2421(5vb)	P
		2506(3)	P?
		2603(3)	D

A detailed analysis of the data will be given later; we may call attention now, however, to the general parallelism of our data on $CO(NH_2)_2$ and $CO(ND_2)_2$ and the data of Engler[3] on $CO(CH_3)_2$ and $CO(CD_3)_2$.

JOHN W. OTVOS
JOHN T. EDSALL

Department of Physical Chemistry,
Harvard Medical School,
Boston, Massachusetts,
July 5, 1939.

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