ELECTRONIC TRANSITIONS IN THE SIMPLE UNSATURATED HYDROCARBONS[1]

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The group of narrow intense bands found in the absorption spectra of all unsaturated hydrocarbons in the Schumann region has been interpreted as the first member of a Rydberg series, the limit of which gives an ionization potential of the molecule. This type of molecular electronic transition is due to the excitation of a π or unsaturation electron of the double bond and is closely analogous to atomic spectra.

The long-wave absorption band which is found in the spectra of all these hydrocarbons is also ascribed to the transition of a π electron and certain characteristics are common to the two groups of bands. In the few hydrocarbons whose spectra show vibrational structure in this region, the pattern is very similar to that in the Schumann region and it is possible to select comparable points for determination of the energy difference between the two electronic levels.

Evidence is presented in support of the interpretation of these long-wave bands as due to an electronic transition which, like the Rydberg transitions, is closely related to atomic spectra. On this basis the energy difference per mole between the two electronic levels would evaluate the difference between two electronic states of the carbon atom in the unsaturated hydrocarbon molecule. These values are given for the molecules whose spectra show sufficient vibrational structure to make the comparison between the two levels unequivocal.

From the heat of hydrogenation and the bond energy for the C—H linkage the heat of the reaction $\underset{|}{H_2C}\text{—}\underset{|}{CH_2} \rightarrow H_2C{=}CH_2$ is calculated. The value per carbon atom per mole would give a thermal measure of the energy difference between two electronic states of the carbon atom in the molecule. The results for the four hydrocarbons, containing one, two, and three double bonds, parallel quite closely the energy difference between the two electronic levels as measured from the absorption spectrum of each compound.

According to the proposed interpretation of the electronic bands of the unsaturated hydrocarbons, it is possible to calculate resonance energy directly from the absorption spectrum. The values for benzene and the cyclohexadienes are in satisfactory agreement with those calculated from thermal data, but there is a marked divergence between the thermal and spectral values for cyclopentadiene.

An extensive study has been made in this Laboratory of the absorption spectra between 4000 A. and 1600 A. of thirty-five or more highly purified hydrocarbons, which included aliphatic and cyclic compounds containing one and two double bonds together with benzene and biphenyl. A group of narrow bands found in the spectra of all these hydrocarbons in the region 2200–1800 A. has been identi-

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fied as belonging to a Rydberg-type transition. The first strong band in each group has been interpreted as constituting the first member of a Rydberg series whose limit is the ionization potential of the molecule (4).

This assignment was confirmed by the work of Price and collaborators, who determined the photoionization potentials of a number of hydrocarbon molecules (13, 14). In the monoölefins the exact position of the bands, characterized as Rydberg bands, and the ionization potential are dependent upon the number of alkyl groups bound to the carbon atoms of the double bond and are independent of the nature of the alkyl group or groups (5). There is a progressive shift toward the visible as the hydrogen atoms of ethylene are replaced by alkyl groups. That is, the energy of this transition is determined by the immediate environment of the carbon atoms of the double bond and is practically independent of the configuration of the molecule as a whole. This is shown by the striking similarity both in the energy of the electronic transition and in the vibrational pattern between *cis*-2-butene and cyclohexene (6). These spectra are quite closely analogous to atomic spectra, and the electron concerned in the transition is one of the more loosely bound π or unsaturation electrons of the double bond. Another type of molecular electronic transition, characterized by Mulliken (10) as an $N \rightarrow V$ transition, bears no analogy to atomic spectra and has very different characteristics. The identification of these two types of transition in the spectral region below 2300 A. for the monoölefins and in a series of eight aliphatic dienes was made in an earlier publication (2). In the monoolefins and in the dienes with isolated double bonds, the maximum of the very intense continuous band of the charge-transfer type ($N \rightarrow V$ transition) is near 1750 A. (57,000 cm.$^{-1}$); where the double bonds are conjugated this band is shifted toward the visible by about 10,000 cm.$^{-1}$, while the narrow bands of the Rydberg transition are not appreciably displaced by conjugation.

In the near ultraviolet between λ 3000 and λ 2300 all unsaturated hydrocarbons show a region of absorption. For those containing one double bond or isolated double bonds, the absorption consists of a broad structureless band of very low intensity which overlaps the more intense band at shorter wave lengths and thus appears as a "stepout" in the absorption curve. Cyclohexene, cyclopentene, and 1,4-cyclohexadiene show this same type of absorption. The curves for the aliphatic dienes, containing conjugated double bonds, show two such abrupt changes of slope, indicating overlapping bands, but it is only in the cyclic dienes and benzene that the spectra of any of these unsaturated hydrocarbons show sharply marked vibrational structure. In the cyclic dienes these narrow bands are superimposed on a fairly intense continuous band (8, 12). The present discussion is concerned only with a possible interpretation of the former.[2]

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[2] That the two bands represent different types of electronic transition seems probable from a comparison of the absorption curves of cyclohexadiene in the vapor phase (8) and in hexane solution. The narrow bands in the solution curve are shifted toward the visible by about 2300 cm.$^{-1}$, while the broad continuous band is shifted about 600 cm.$^{-1}$ Recent measurements in this laboratory of the absorption spectra of concentrated solutions of benzene in different solvents and of pure liquid benzene indicate the presence of a very low intensity continuous band underlying the narrow bands toward the long-wave end. In

The similarity in vibrational pattern between these bands in the near ultraviolet and those identified as belonging to a Rydberg transition is shown in table 1, which gives the band maxima and the separations of the strong bands in each group.

This parallelism in vibrational pattern between the two band systems suggests closely related electronic transitions. If the assignment of the short-wave bands as an $N \rightarrow R$ transition is correct, it would seem reasonable to assume that these corresponding bands in the long-wave region are also due to an electronic transition which is closely related to atomic spectra. Such an interpretation might explain the selective absorption which is shown by chromophoric groups in the molecule,—a type of absorption quite different from that which is associated with conjugation. It is suggested that this atomic-like absorption may represent an excitation which is somewhat analogous to the forbidden transition of the carbon atom, where there is a change in multiplicity and angular momentum but no change in principal quantum number. From this point of view,

TABLE 1

Frequencies and separations of the strong bands in the two electronic levels of 1,3-cyclohexadiene, cyclopentadiene, and benzene

1,3-CYCLOHEXADIENE				CYCLOPENTADIENE			
Band 1 (8)*		Band 2 (3)		Band 1 (12)		Band 2 (14)	
$cm.^{-1}$		$cm.^{-1}$		$cm.^{-1}$		$cm.^{-1}$	
39,797		48,790		38,880		50,380	
41,038	1615	49,970	1515	39,650	1520	50,850	1440
41,412	1647	50,305	1530	40,400	1540	51,820	1460
42,685	1660	51,500	1515	41,170		52,310	
43,072		51,820					

BENZENE			
Band 1 (7)	$\Delta\frac{1}{\lambda}$	Band 2 (3)	$\Delta\frac{1}{\lambda}$
$cm.^{-1}$	$cm.^{-1}$	$cm.^{-1}$	$cm.^{-1}$
37,495		49,035	
	1130		935
38,625		49,970	
	924		880
39,549		50,850	
	920		840
40,469		51,690	
	922		790
41,391		52,490	
	919		740
42,310		53,220	

* Reference number.

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chloroform solution this band shifts to shorter wave lengths, while the narrow bands show a definite shift toward longer wave lengths.

the long-wave group of bands in these hydrocarbons would represent an electronic transition in which one of the unsaturation electrons changes spin, thus giving a triplet state as the excited state. The low intensity in comparison with the Rydberg transition would be in accord with such an assumption. Mulliken has suggested (11) that in the $N \rightarrow R$ transition there is the transfer of one electron to a 3*s* orbital. If then there are comparable points of reference in the two band systems, the energy difference between the two electronic bands should evaluate the difference in energy between two electronic configurations of a carbon atom in an unsaturated hydrocarbon molecule.

Although, as has been pointed out, the position of the bands in the $N \rightarrow R$ transition for a large number of hydrocarbons has been measured with sufficient accuracy for such calculations, only the cyclic dienes and benzene show the sharp vibrational structure in the long-wave band which is necessary for an accurate determination of this energy difference. Selective absorption in this spectral region has long been recognized as characteristic of the C═C linkage, but in most molecules the band is continuous and appears only as a stepout in the absorption curve. Measurements by Snow and Allsopp (15) for ethylene show a group of very shallow abrupt stepouts at the short-wave end of a broad "shelf." The breadth and separation of these narrow bands would indicate a possible relationship to the bands identified by Price (13) as the first member of a Rydberg series for the ethylene molecule. The first of these bands, as measured by Snow and Allsopp, is taken as the point of reference for comparison with the band identified by Price as the 0–0 transition in the $N \rightarrow R$ transition. Table 2 gives the values for the four hydrocarbons for which measurements in both the long-wave and short-wave regions are available. All values are for vapor-phase measurements.

TABLE 2

Differences between corresponding bands in the two electronic levels of ethylene, 1,3-cyclohexadiene, benzene, and cyclopentadiene in cm.$^{-1}$ and in kilocalories per mole

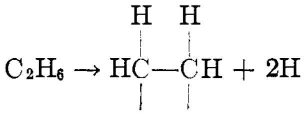
HYDROCARBON	BAND 1	BAND 2	$\Delta\frac{1}{\lambda}$	$\Delta Nh\nu$	REFERENCES
	cm.$^{-1}$	*cm.$^{-1}$*	*cm.$^{-1}$*	*kcal.*	
Ethylene	48,330	57,340	9,010	25.70	(13, 15)
1,3-Cyclohexadiene	39,797	48,790	8,993	25.64	(3, 8)
Benzene	38,625	49,970	11,345	32.33	(3, 7)
Cyclopentadiene	38,880	50,380	11,500	32.78	(12, 14)

Measurements for 1,4-cyclohexadiene have been made in this Laboratory but are not included in table 2 because of our difficulty in obtaining this hydrocarbon completely free from traces of benzene and 1,3-cyclohexadiene. These impurities were discernible only in the long-wave region, where there is a broad stepout whose intensity is of the same order as that in cyclohexene. It is significant, however, that at the short-wave end of this stepout, beginning at about 43,000 cm.$^{-1}$, there is a group of shallow but very sharp stepouts quite similar to those of ethylene but displaced by about 5000 cm.$^{-1}$ In the Schumann region, where the absorption of the 1,4-diene is very intense, there is no evidence of either benzene or the 1,3-diene, and a group of very sharp bands beginning at 51,950 cm.$^{-1}$ is undoubtedly characteristic of 1,4-cyclohexadiene. This gives an energy difference between the two electronic excitations of 25.51 kcal. (8950 cm.$^{-1}$). It should be emphasized that in all of these spectra there seems to be the superposition of two different types of bands in the long-wave region. Only in the conjugated cyclic dienes is the continuous band of high intensity.

The absorption curves of the conjugated aliphatic dienes show two distinct stepouts in this spectral region, but the present discussion is limited to the few molecules in which there is clearly defined vibrational structure, so that the comparison with a corresponding band in the $N \rightarrow R$ transition may be unequivocal.

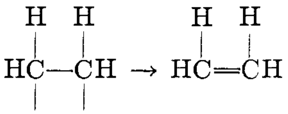
Some years ago attention was called to a relationship between the energy of these two electronic levels and the heats of combustion of saturated and unsaturated hydrocarbons containing the same number of carbon atoms,[3] but no theoretical reason for the existence of such a relationship could be advanced and both spectral and thermal values were of such doubtful accuracy that the paper was not published. With the accurate spectral measurements of the unsaturated hydrocarbons in the short-wave region and the accurate determination of the heats of hydrogenation of these hydrocarbons (9), the correlation of spectral and thermal data has been reconsidered. If the interpretation of the electronic bands which has been presented is valid, it would be reasonable to expect that there might be a relationship between the values of $\Delta Nh\nu$ (table 2) and the energy difference between two electronic states of the carbon atom as evaluated from thermal data. Calculations of the energy change per carbon atom per mole which takes place in the formation of a carbon–carbon double bond have been made from hydrogenation data for each of the compounds, the heat of dissociation of hydrogen, and the bond energy for the C—H linkage. The uncertainty in this calculation is, of course, in this latter value, but inasmuch as most of the recent calculations from thermal data have used Pauling's value of 87.3 kcal., this has been used in calculating the difference in energy between a saturated and an unsaturated carbon atom. The calculation for ethylene is as follows:

$$\mathrm{C_2H_6 \longrightarrow C_2H_4 + H_2} \qquad \Delta H = 32.853 \text{ kcal.} \qquad (1)$$



$$\mathrm{C_2H_6 \rightarrow H\underset{|}{\overset{\overset{H}{|}}{C}}{-}\underset{|}{\overset{\overset{H}{|}}{C}}H + 2H} \qquad \Delta H = 174.6 \qquad (2 \times 87.3) \qquad (2)$$

$$\mathrm{2H \rightarrow H_2} \qquad \Delta H = -103.4 \qquad (3)$$



$$\mathrm{H\underset{|}{\overset{\overset{H}{|}}{C}}{-}\underset{|}{\overset{\overset{H}{|}}{C}}H \rightarrow H\overset{\overset{H}{|}}{C}{=}\overset{\overset{H}{|}}{C}H} \qquad \Delta H = -38.35 \qquad (1-2)-(3)$$

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[3] Paper presented by Emma P. Carr before the Division of Physical and Inorganic Chemistry at the 78th Meeting of the American Chemical Society, which was held at Minneapolis, Minnesota, September, 1929.

By similar calculations, the heats of formation of two double bonds in dienes and three double bonds in benzene have been evaluated from the heats of hydrogenation of these compounds, and the results are given in column 1 of table 3. Column 2 gives the energy change per carbon atom per mole, and for comparison column 3 gives the energy difference between electronic states as calculated from the absorption spectrum.

The values calculated from thermal data (column 2) are all lower than those from spectral measurements. The significance of the results lies not so much in any close agreement but in the parallelism between the two sets of values. This is particularly true with benzene and cyclohexadiene, where the hydrogenation product is the same for both hydrocarbons. There is a much wider divergence between the two values for cyclopentadiene where there are undoubtedly more complicating factors, such as ring strain and lack of constancy of the C—H bond energy, which affect the thermal value. The close agreement between the spectral values for the carbon atom of benzene and of cyclopentadiene may be merely fortuitous, but in the light of the aromatic character of the reactions of cyclopentadiene this result is of particular interest. No value for the heat of hydrogenation of 1,4-cyclohexadiene is available, but it would probably be twice that of cyclohexene, which would give an energy change per carbon atom per mole of 21.3 kcal. The energy difference between the two electronic bands is 25.51 kcal. It should be emphasized that these calculations have been made for *all* the simple hydrocarbons which show sufficiently marked vibrational structure for comparison of the two bands. Values for the alkylbenzenes might be calculated, but heats of hydrogenation and the energy difference of the two electronic bands parallel so closely those for benzene that the results would be practically identical with the values for benzene itself.

TABLE 3

Comparison of energy difference between electronic states calculated from thermal data and from absorption spectra

HYDROCARBON	1	2	3
	kcal.	*kcal.*	*kcal.*
Ethylene	−38.35	19.17	25.70
1,3-Cyclohexadiene	−87.1	21.8	25.64
Benzene	−163.8	27.3	32.33
Cyclopentadiene	−91.6	22.9	32.78

Thermal calculations for ethylene, using the more recent (1) value of 99 kcal. for the C—H linkage of ethane, give an energy change per carbon atom per mole of 30.87 kcal. This value is about as much above the spectral value as the value in table 3 is below. A similar relationship would be shown for the thermal values in the other compounds, but the exact agreement or the disagreement between the two sets of values is less significant than the parallelism in the amount of change from compound to compound. For example, from spectral measurements the difference between cyclohexadiene and benzene (per carbon atom) is 6.69 kcal.; by thermal measurements it is 5.5 kcal. (table 3) or 5.37 kcal., using the higher bond energy.

If the interpretation of these spectra which has been presented is correct, it is possible to calculate the resonance energy of the molecule directly from its absorption spectrum. The energy difference per carbon atom for ethylene, 1,4-cyclohexadiene, and 1,3-cyclohexadiene is closely the same; the greater energy difference between the two electronic levels in benzene (32.33 kcal.), as compared with the corresponding difference in ethylene (25.70 kcal.), would represent a stabilization or resonance energy of 6.63 kcal. per carbon atom in benzene, or six times this amount (or 39.8 kcal.) per mole of benzene. This value is 4 kcal. greater than that calculated from heats of hydrogenation. On the basis of their spectra, neither of the cyclic hexadienes would have any resonance energy, while the spectrum of cyclopentadiene gives a value of 28.3 kcal., as compared with only 4.2 kcal. from heats of hydrogenation. If, however, the aromatic character of a molecule is associated with its resonance energy, the spectral value for cyclopentadiene would seem to be in better accord with its chemical activity.

A number of other applications of the theory that has been proposed are possible, but until the fundamental assumptions are established through the critical analysis of data on the simple hydrocarbons, it is inadvisable to attempt the interpretation of more complex problems.

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