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EXCITATION OF THE HYDROCARBON DOUBLE BOND

By A. KEITH BREWER

THE mechanism for the excitation of the hydrocarbon double bond possesses an academic interest in itself. The major interest, however, should be in its implementations, physical, chemical, and biological. In this paper, three types of excitation means will be discussed, i.e., electron impact, ultraviolet light irradiation, and thermal. Possible implementations and applications will be considered.

The writer first became interested in double bond excitation when he observed in 1931 that microorganisms could be made to fluoresce and phosphoresce upon exposure to λ 2536. A study of the literature revealed that the underlying basis for this observation had long received the critical attention of many outstanding physicists in Europe.

An initial crude attempt to excite this double bond by electron impact met with failure. A later extension using the mass spectrometer revealed that the phenomena involved in excitation were much more complicated than had initially been supposed. As a consequence of this study it has been possible to construct a model for the excited bond which not only will account for associated observations, but has made it possible to suggest new methods for microorganism detection and analysis, as well as to explain many phenomena involved in vital processes. The proposed model is one that shows excitation to be a similar process whether induced by radiation, heat, or electron impact. The actual distribution of energy between the various processes involved may, however, not be independent of means of excitation.

Excitation of the Double Bond by Electron Impact

The mass spectrometer cracking patterns for hydrocarbons provide a means for studying the mechanism involved in the excitation of the hydrocarbon double bond. In practice, ions are formed by bombardment with 50 volt electrons [1]. This voltage is sufficient to break down the hydrocarbon molecule into a variety of fragmentation products. By sweeping the bombardment voltage, the appearance potential for the various fragments can be determined; this is not a part of the present study except to note that double bonds are very much more stable than single bonds.

Four types of peaks occur in the 50 volt cracking patterns of most hydrocarbons. These are (1) singly charged masses consisting of the whole molecule and its breakdown fragments; (2) doubly charged fragments;

(3) ghosts; and (4) rearrangement masses. These will be discussed separately.

Singly Charged Fragmentation Masses: The cracking pattern for most hydrocarbons upon bombardment by 50 volt electrons shows singly charged masses corresponding to essentially all possible fragmentation products. The C mass itself seldom appears. Time of travel measurements in the conventional ionization chamber shows that fragmentation takes place in less than 10^{-7} sec; the exact time may be as short as 10^{-13} sec.

Double Charged Ions: Double charged masses appear only for groups in which the binding energy is high, such as double bonded molecules or radicals.

Resonance Masses: Resonance mass fragments occur at larger mass numbers than can be realized from direct fractionation of the parent molecule. Thus, mass 15 in the cracking of ethylene can only result from the transfer of an H atom from C-1 to C-2.

Typical examples of resonance masses are listed in Table 1.

The mechanism involved in resonance mass formation is illustrated in Figure 1.

The normal molecule (A) $H_2C=CHR$ is struck by an electron, (e) possessing sufficient energy to eject an electron from the molecule leaving it with a positive charge. The energy of impact also excites an H atom on C_2 enhancing its amplitude of oscillation between atoms C_1 and C_2 . The number of H atoms within the field of the C_1 ion is thus either 2 or 3 depending on the position of the oscillating H atoms at the instance of the fracture of the $C_1=C_2$ bond. The ratio of the two masses will then be determined by the fraction of time the H atom is predominantly in the field of each of the two C atoms; i.e., by its amplitude and its oscillation path.

Reference to Table 1 brings out a number of significant facts. These are listed briefly:

The ratios for various rearrangement masses show that resonance amplitude is determined by the bond itself as is illustrated with ethylene and acetylene.

The most significant point to note is that the resonance ratios are directly related to the atomic configurations associated with the double bond. This is clearly illustrated by comparing 15/14 for ethylene and butadiene.

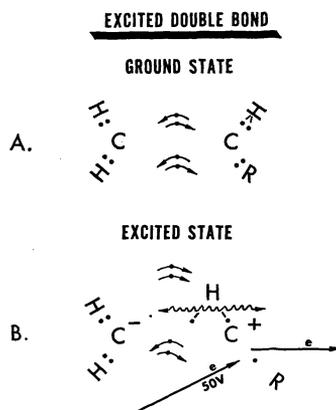


Figure 1

TABLE 1

Compound	Structure	Mass	Ratio
Acetylene	$\begin{array}{c} \text{H} \\ \longleftrightarrow \\ \text{C}\equiv\text{C} \\ \longleftrightarrow \\ \text{H} \end{array}$	14/13	0.042
Ethylene	$\begin{array}{c} \text{H} \\ \longleftrightarrow \\ \text{HC}=\text{CH} \\ \longleftrightarrow \\ \text{H} \end{array}$	15/14	0.093
Propene	$\begin{array}{c} \text{H} \quad \text{H} \\ \longleftrightarrow \\ \text{HC}=\text{C}-\text{CH} \\ \longleftrightarrow \\ \text{H} \quad \text{H} \end{array}$	29/28	0.038
Propadiene	$\begin{array}{c} \text{H} \\ \longleftrightarrow \\ \text{HC}=\text{C}=\text{CH} \\ \longleftrightarrow \\ \text{H} \end{array}$	15/14	0.063
	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \longleftrightarrow \\ \text{HC}=\text{C}-\text{C}-\text{CH} \\ \text{H} \quad \text{H} \end{array}$	27/28	0.8
1 Butene	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\ \longleftrightarrow \\ \text{HC}=\text{C}-\text{C}-\text{CH} \\ \text{H} \quad \text{H} \end{array}$	30/29	0.07
2 Butene	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\ \longleftrightarrow \\ \text{HC}-\text{C}=\text{C}-\text{CH} \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$	29/28	0.45
Isobutene	$\begin{array}{c} \text{H} \\ \text{H} \uparrow \text{C} \backslash \text{H} \\ \downarrow \text{H} \quad \text{C}=\text{CH} \\ \text{H} \uparrow \text{C} / \\ \downarrow \text{H} \quad \text{H} \end{array}$	28/27	1.0
	$\begin{array}{c} \text{H} \quad \text{H} \\ \longleftrightarrow \\ \text{H}_3\text{C}-\text{C}=\text{C}-\text{C}-\text{CH}_3 \\ \text{H} \quad \text{H} \end{array}$	29/27	0.5
Pentene 2	$\begin{array}{c} \text{H} \quad \text{H} \\ \longleftrightarrow \\ \text{H}_3\text{C}-\text{C}=\text{C}-\text{C}-\text{CH}_3 \\ \text{H} \quad \text{H} \end{array}$	43/42	0.021

The very high 27/26 ratio for benzene shows a very strong H resonance. This is of particular interest in that it reflects on the structure of the cyclic molecule. On the basis of the evidence, the Kekule formula would appear to be a statistical configuration, the H atoms actually resonating between the various C atoms. Another significant factor is the tendency for H atoms to split off in pairs. This is a direct consequence of resonance in which an atom penetrates the field of its neighbor. It is basic to the synthesis of benzene derivatives as will be discussed later.

Ghosts: Ghosts are of interest in that they throw light upon the mechanism involved in the metastable state. Ghost peaks are obtained from highly excited ionized masses which pass through the entire accelerating

just insufficient for dissociation, this imposed torque may be sufficient to cause fragmentation.

Since mass 43 has the velocity imparted to mass 58 it will not appear at the 43 mass position but will be resolved according to the equation

$$m'(m'/m)v = Her \quad (1)$$

where v is the velocity upon entering the field H , e is the charge, and r is the deflection radius. Thus, the mass position for the ghost from n -butane is $43^2/58 = 31.9$.

Actually ghost peaks tend to be displaced from 0.1 to 0.2 mass units from that given by equation (1) toward heavier masses; this is to be expected since the drag of the negative portion of the ion at the moment of splitting will tend to increase the radius of curvature. Ghost peaks for 50 volt electrons seldom exceed 0.01 of the source peak. Ghosts may arise from the loss of H_2 , and from C_1 , C_2 , and C_3 radicals singly or in pairs.

The ghost fragmentation is not always a single unit process. It may involve association as illustrated by the appearance of H_2 , and by the 29 peak for isobutene. Again, it may result from a multiple dissociation; for example, the 24.5 peak is due to the loss of mass 30 from mass 72. Mass 42 has an abundant peak while mass 30 exists only as isotope from 29; mass 30, therefore, must represent multiple fragmentation. Mass numbers resulting from the loss of 16 are also examples of multiple dissociation.

Since peak 58 is moderately large in the cracking pattern for n -butane and since peak 31.9 is about 0.01 in comparison, it follows that only a small fraction of the metastable 58 mass can be dissociated by the imposed magnetic torque. The resonance concept presented here suggests that fracture occurs when the position in the cycle coincides with the time at which the torque is applied, thus increasing the amplitude to the point where rupture is possible.

Excitation of the Double Bond by Ultraviolet Light

The fluorescence and phosphorescence of microorganisms upon irradiation by ultraviolet light are to be expected from the double bonds present in amino acids. Fluorescence involves the emission of light in the ultraviolet (uv) region upon irradiation by uv of a shorter wave length. The emission takes place primarily in 10^{-8} (10^{-7} to 10^{-9}) seconds following irradiation. Phosphorescence refers to the emission of visible light following irradiation by uv light; the emission may last for many seconds up to one minute or more.

History: Induced luminescence was discovered by Robert Boyle in 1648. Sir John Herschel in 1845 reported on induced luminescence in quinine. A year later Sir David Brewster observed a similar effect in chlorophyll. Sir George Stokes, starting with quinine, examined many organic mate-

rials. He then enunciated Stokes Law, which states that the emitted light is always of a longer wave length than the exciting light. Stokes first suggested the term fluorescence.

E. Becquerel in 1867 devised a phosphorescope for studying long-lived emissions from sulfides and organic crystals; he showed that the phosphorescent light intensity decayed exponentially with time. In 1892 Lenard concluded that the spectrum of phosphorescent light consists of a number of overlapping bands. In 1895 Sir James Dewar showed that many organic substances when cooled to liquid air temperatures would phosphoresce upon uv irradiation. A short while later Lenard, Onnes, and Pauli reported that "for each band in the spectrum of a body excited to phosphorescence there is a certain range of temperatures within which it is phosphorescent, and above and below which no phosphorescence of long duration occurs, although fluorescence may be present."

In 1904 Lenard and Klat analyzed some 800 phosphors, primarily metallic and organic sulfides. They concluded that phosphorescence was due to the falling back of an electron which had been separated to the surrounding space. The return must involve collisions hence $-dn/dt = \lambda n$, and thus

$$i = I_0 e^{-\lambda t} \quad (2)$$

where I is the initial intensity and λ is the decay constant.

Werner showed the process was more complicated than suggested by equation (2), and that the phosphorescent intensity for many substances was given by

$$i = I_0 e^{-\lambda t^m} \quad (3)$$

where m for most of the materials tested varied from 0.2 to 1.

Werner's results were in agreement with Lenard's suggestion that "the vibrations set up on a phosphorescent substance are analogous to those of an electric oscillator having a period dependent on inductance and capacity, and that the wave length of a band is proportional to the square root of the dielectric constant of the medium."

Between World War I and II work lagged in this field. Possibly the most impressive work was that of Jablonski (*Zeits f. Physik*, 94, 38, 1935) who set up a workable energy diagram. This diagram was elaborated during World War II by Lewis, and by Franck and their co-workers.

Lewis modified the Jablonski theory and showed that fluorescence is a singlet-ground transition while phosphorescence results from a singlet to triplet shift with emission following the triplet to ground transition. Lewis further extended the work to a very large number of hydrocarbons containing double bonds. All were shown to fluoresce and to phosphoresce under proper excitation conditions.

Recent work has taken two directions, one to show that organic mate-

rials can be made to fluoresce and to phosphoresce [2], and the other to embellish the singlet-triplet state theory [3]. Unfortunately, there has been little attempt to use phosphorescence decay as an analytical tool. Essentially no work has been done in determining the fine structure of the fluorescence spectrum or in its use in quantitative analysis.

A number of papers have appeared showing fluorescence and phosphorescence in biological materials. The decay constants observed were of the type given in equation (3). In general, it has been concluded that "organic structures are too complicated to obey a simple decay law," hence no attempts have been made to evaluate much less explain the exponent m .

Theory: The mechanism for fluorescence and phosphorescence described here has been developed to explain the observed phenomena, as related to the $C = C$ bond, and to provide a means for the practical

analytical applications of the processes involved. Figure 2 is a modified Jablonski energy diagram.

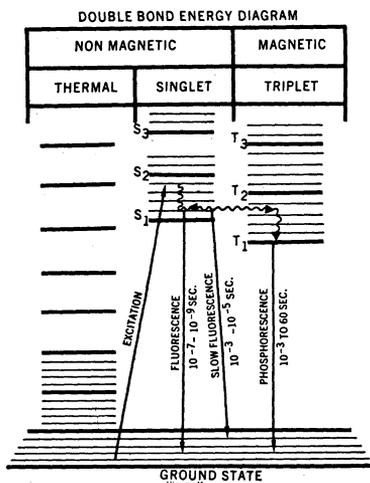


Figure 2

The double bond depicted in A of Figure 1 is irradiated with ultraviolet light of wave length in the range $2700 \text{ \AA} \pm 200$. The electron is raised to a level in the S range as shown. The electron here may take a number of paths. It may drop back to the ground state in a time of the order of 10^{-8} seconds with the emission of fluorescent light having a wave length $500 \pm 400 \text{ \AA}$ longer than the exciting light; this is ordinary fluorescence. It may oscillate between the S and T states and then

fall back to ground in a time of the order of 10^{-4} sec; this is slow fluorescence.

Again it may oscillate between the S and T states, but if the bond is stabilized by incorporation in a crystal lattice or preferably by cooling to liquid nitrogen temperature, then the electron will have time to go into parallel spin with its paired electron. In this state the electron is magnetically stabilized and will continue to rotate until it picks up energy by collision from an outside source.

Upon collision, which is determined by probability, the electron will be knocked out of its stabilized state. It can then fall back to the ground level with the emission of phosphorescent light. The wave length is, in general, in the visible range primarily $5000 \pm 1000 \text{ \AA}$.

The number of collisions is given by $-dn/dt = \lambda n$ hence

$$i_t = I_0 e^{-\lambda t} \quad (2a)$$

In the magnetically stabilized state the bond is paramagnetic and should exhibit paramagnetic spin resonance. It follows then that the decay in paramagnetic spin resonance must be concomitant with the decay in phosphorescence.

Reference to Table 1 reveals that the field existing at a double bond is dependent upon the atoms associated with the bond. This is illustrated figuratively in Figure 1B.

In virtue of the above it is not too surprising that Lenard, almost 100 years ago, should conclude that, in phosphorescence decay, the bonds act like tuned circuits. Nor is it surprising that the decay should be expressed by $i = I_0 e^{-\lambda t}$, although the real significance of the deviation from a pure exponential was missed.

On the basis of information presented in Table 1, the writer suggested some years ago that the decay in light intensity from an organic material, such as protein, which contains a plurality of double bonds, should be expressed by the following equation:

$$i = I_1 e^{-\lambda_1 t} + I_2 e^{-\lambda_2 t} \dots I_n e^{-\lambda_n t} \quad (4)$$

where i is the integrated intensity from all the resonators, and 1, 2 . . . n refer to the emissivity from specific bond configurations.

That this equation can be applied as a means for the analysis of organic materials will be shown in the last section of this paper.

Since the resonance of the H atoms associated with double bonds is characterized by the associated atomic configurations, it is to be expected that light absorption frequencies will also be so associated. In general, the more complex the molecular configuration, the longer the threshold for uv absorption; this wave length may range from 1900 Å for ethylene to 3000 Å or more for large molecules.

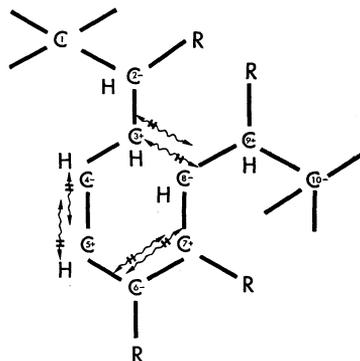


Figure 3

Thermal Excitation of the Double Bond

The resonance concept presented in Figures 1 and 2 suggests that this type of activation should be induced by heat as well as by electron impact, and by radiation. The possibility was tested by placing about one milligram of various polymers in the side arm of a small still that could be

heated electrically. The main body of the still was evacuated, sealed off, and then immersed in liquid air. The design was such that gaseous fragmentation products could be removed directly from the polymer sample without the chance of secondary reactions.

The results revealed that gaseous products could be frozen out from all the polymers tested. A residue remained in the cell in each instance. A mass spectrographic analysis of the gaseous pyrolysis products showed the presence of cyclics or substituted benzene rings for many polymers. No tests were made on the solid residue.

Theory: Figure 3 is an attempt to describe graphically the effect of the thermally induced resonance of the hydrogen atoms on the reactions within the polymer. The tetrahedron configuration of the C atoms may result in atoms C-3 being physically near C-8. Resonance of the H atoms on C-3 and C-8 will induce penetration into the fields of each other. In consequence, H₂ can split off from C-3 and C-8 with the establishment of a linkage between these two atoms. The result is the formation of a closed ring structure. Since the H atoms on C-4 and C-5 are again in resonance, H₂ will split off to form the double bonds characteristic of the benzene ring. This splitting off of H₂ from adjacent C atoms is a highly probable reaction. The benzene rings so formed may contain ortho, meta, or para substitutions, depending on the positions of the associated R radicals.

Applications

The resonance concept presented in Figure 1 is one that suggests a number of practical applications; it is also one that can be employed in explaining the mechanism involved in a number of observed phenomena.

Phosphorescence: It was pointed out in a preceding section that the periodicity and hence the phosphorescence decay for double bonds will depend on their associated atomic groupings. Equation (3) was proposed to represent the overall decay from complex organic structures containing a multiplicity of double bonds. With this in mind it was proposed that the sequence of decay constants (λ s) should be specific for various microorganisms. A test of this theory carried out at the Naval Medical Research Institute showed this to be the case. Preliminary results presented in *Nature* [4], revealed that the phosphorescence pattern for a specific microorganism consisted of a summation of the response from a plurality of resonators which were peculiar to the organism. The culture media and washing solutions were without measurable effect.

Within the limit of error in this study, which, due to the recording means, was quite high, it was not possible to distinguish between living cells and autoclaved cells; any difference that may exist between living

and dead cells would appear to be of second order. Again the contributions from the centrifuged fractions showed the wall, the cytoplasm and the capsule to possess the same decay pattern individually as in the whole cell.

Fluorescence: The fact that double bonds can be induced to fluoresce when exposed to suitable uv frequencies and that this fluorescence is essentially temperature independent, as shown in Figure 2, has made it possible to suggest a method and means for the detection of microorganisms in the air at distances of several miles as well as for the detection of double bonded materials in general. This is being covered in a patent application.

Figures 1 and 2 indicate that the fluorescence spectrum should be specific for various double bonds. The available data suggest a semblance of fine structure; it may be possible, therefore, to use fluorescence as an analytical tool, as well as a means for detection.

In addition to applications of the type just presented, the resonance mechanism proposed can be used to account for a number of existing phenomena. A few of these will be summarized.

Cancer: Carcinogens are complex molecules containing benzene rings with substitutions in the meta position. Figure 3 shows how such compounds can be synthesized from polymers upon excitation. In the illustration the excitation was thermal. The result, however, will be the same when the polymer is subjected to electron bombardment, irradiated by uv and X-rays, or by α , β , and γ rays. It is not surprising therefore that cancer can be induced in the skin by exposure to uv, by long exposure to heat, and by penetrating radiation. Also it is not surprising that carcinogens appear in both the particulate matter and the vapor arising from the pyrolysis of certain polymers. Again, burned protein such as meat and uv irradiated proteins have been shown to be carcinogenic upon subcutaneous injection.

Cell Reactions: The excited double bond shown in Figure 1B should be as reactive as a positive ion to oxygen. The quenching of phosphorescence and fluorescence by oxygen is to be expected. This rapid combination of the bond with oxygen should destroy the natural behavior of the cell wall. In addition, radiation would result in the synthesis of compounds within the cell by the mechanism depicted in Figure 3. Further, the excited bonds within molecular groups associated with DNA should be very responsive to hydrogen bonding and thus induce somatic changes within the cell.

The resonance mechanism presented here can be employed to explain a wide variety of phenomena in addition to those just described. Among these are: sunburn; radiation-induced cancer; the hardening of rubber; cross linkage involved in the aging process; etc.

Summary

The excitation of the C=C bond has been investigated from the standpoint of electron bombardment, ultraviolet absorption, and heat. A resonance mechanism has been proposed which has made it possible to propose a number of new analytical procedures. Among these are (1) the phosphorescence decay method for the analysis of microorganisms, and (2) the fluorescence technique for the long range detection of microorganisms in the air. In addition, the mechanism has been used to account for the presence of carcinogens in the pyrolysis products of polymers and tissues, and in many organic materials upon irradiation.

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