SEPTEMBER 15, 1932 PHYSICAL REVIEW VOLUME 41

Electronic Structures of Polyatomic Molecules and Valence. II. Quantum Theory of the Double Bond

By Robert S. Mulliken

Ryerson Physical Laboratory, University of Chicago

(Received August 4, 1932)

The electronic structure of CH_2 in its probable normal and first excited states is described in terms of molecular orbitals. The formation of C_2H_4 from two (excited) CH_2 radicals is discussed, and it is shown, with the help of the Slater-Pauling overlapping criterion, to be theoretically obvious, in agreement with experiment, that for the normal state of C_2H_4 the energy is surely considerably lower if the two CH_2 are arranged symmetrically in one plane than if their planes make an angle of 90° (Figs. 1, 2). Similar statements apply to the derivatives of C_2H_4. The $C=N$ and $N=N$ double bonds can be treated similarly. The $C=C$ and $O=O$ double bonds are compared. The $(BH_3)=(BH_3)$ bond in B_2H_6 probably resembles the $O=O$ more than the $C=C$ bond. For certain predicted excited states of C_2H_4 and its derivatives, which are probably the upper states of ultraviolet absorption bands of these compounds, it is shown that the energy should be higher for the plane form than for the perp. form (one CR′R″ plane rotated through 90°). Hence the plane form should tend to go over spontaneously by rotation into the perp. form (90°) and on to the other plane form (180°) after absorption of suitable ultraviolet light. In this way the observed transformations of *cis* into *trans* isomers or vice versa by ultraviolet light may be explained.

Introduction

Several attempts have been made to explain quantum-mechanically the well-known double bond of organic chemistry.[1] Hückel formulated the double bond, e.g., in C_2H_4, as consisting of two electron-pairs $[\sigma]^2[\pi]^2$, where $[\sigma]$ has approximate rotational symmetry around the C-C axis, $[\pi]$ an angular distribution approximately proportional to $\sin\phi$ ($\phi=0$ in the common plane of all the nuclei). The stability of the double bond toward rotation is connected with properties of the $[\pi]_{\sin\phi}$ orbital, but Hückel's discussion of this stability is unsatisfactory.

Slater[2] and Pauling[3] give a different explanation using their tetrahedral atomic orbitals (*s*, *p* hybrids), as follows: Each CH_2 has two such orbitals which have formed electron-pair bonds with H atoms, and two which are unpaired. In C_2H_4, the two unpaired CH_2 orbitals form two electron-pairs which determine a plane perpendicular to that in which all the atoms lie, and cause this arrangement to be stable toward rotation.

Although the Slater-Pauling method generally gives a good approximation and a valid explanation of valence angles, the approximation appears to

---

[1] Cf. R. S. Mulliken, Phys. Rev. **41**, 49 and especially 55–61 (1932) for a summary and references.

[2] J. C. Slater, Phys. Rev. **37**, 481 (1931).

[3] L. Pauling, Jour. Am. Chem. Soc. **53**, 1367 (1931).

be relatively crude in the case of C_2H_4 and of double bonds in general, essentially because of the assumption of *s-p* hybridization. As will now be shown, it seems possible by means of a different approximation, resembling Hückel's but going farther, to obtain a more detailed correspondence with existing empirical, especially chemical, knowledge of the behavior of double-bonded molecules.

ELECTRONIC STRUCTURE OF CH_2

It is useful to consider the formation of C_2H_4 from 2 CH_2 for two cases: (*a*) all the atoms lie in one plane ("plane C_2H_4"); (*b*) the planes of the two CH_2 make an angle of 90° ("perpendicular C_2H_4"). For this purpose, it is convenient to describe the molecular electronic structures in terms of molecular orbitals[1] of CH_2 and of C_2H_4. The possible types of molecular orbitals and their symmetry properties depend on the symmetry of the nuclear arrangement. They can be conveniently determined by group theory methods, or in simple cases by inspection. The exact meanings of the term symbols used here for electronic states, e.g., $^1\Gamma_1$, will be explained in a later detailed paper; it should be noted that the meaning of a given symbol may differ according to the nuclear arrangement.

That CH_2 should be triangular, with an angle of perhaps about 110° between the two C-H directions, can be seen most easily by using the Pauling-Slater methods, assuming either pure p valence (predicted angle somewhat over 90°) or tetrahedral bonds (predicted angle slightly larger than the tetrahedral angle), or an intermediate condition. In the following, a z axis will be chosen bisecting the apex angle of CH_2, an x axis perpendicular to the CH_2 plane. [In forming p bonds, Slater and Pauling would use y' and z' axes making angles of 45° with the y and z axes used here.] The probable normal state and the probable lowest excited state of CH_2 can then be described in terms of molecular orbitals as:

$$1s^2[s]^2[y]^2[z]^2,\ ^1\Gamma_1;\ 1s^2[s]^2[y]^2[z][x],\ ^3\Gamma_3. \qquad (1)$$

The symbols $[s]$, $[x]$, $[y]$, $[z]$ stand for orbitals which may be approximately built up as linear combinations respectively of $2s$, $2p_x$, $2p_y$, $2p_z$ of carbon[2,3] and $1s$ of hydrogen; $[s]$ consists mostly of $2s$, some $1s$, and a little $2p_z$; $[x]$ of $2p_x$ only; $[y]$ of $2p_y$ and $1s$; $[z]$ of $2p_z$, some $1s$, and a little $2s$. The C-H binding is taken care of by the $[y]$, $[s]$, and $[z]$ orbitals, especially by the $[y]$.

FORMATION OF C_2H_4 FROM CH_2

The Slater-Pauling criterion of maximum overlapping, which can be applied to formation of pairs of molecular orbitals as well as to formation of electron-pair bonds,[1] can now be used to show that the most stable form of C_2H_4 should be a plane configuration built out of two CH_2 radicals each in the state . . . $[z][x]$, $^3\Gamma_3$ in such a way that the z axes of the two radicals coincide and form what may be called the z axis of C_2H_4. [Although best thought of as built out of two $^3\Gamma_3$, normal C_2H_4 should dissociate adiabatically into two $^1\Gamma_1$ unexcited CH_2 radicals.] With this arrangement, the two $[z]$

orbitals of the two CH_2 overlap strongly to form Hückel's $[\sigma]$ bond, the two $[x]$ orbitals somewhat less strongly to form his $[\pi]$ bond. The resulting (C-C)-bonding orbitals of C_2H_4 are approximately *const.* $\{[z]_A+[z]_B\}$ and *const.* $\{[x]_A+[x]_B\}$, or more briefly, $[z+z]$ and $[x+x]$, where A and B refer to the two CH_2 radicals. The (C-H) bonding orbitals $[s]$ and $[y]$ of the two CH_2 radicals are not very much disturbed by the formation of C_2H_4, and take little part in the (C-C)-bonding, so that one may describe C_2H_4 in its normal state approximately as:

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z+z]^2 [x+x]^2,\ {}^1\Gamma_{1g}. \tag{2}$$

The $[z]$ orbitals, in forming $[z+z]$, withdraw largely from their previous (C-H)-bonding function, their share being taken over by the $[s]$ orbitals; in the process, there is probably a somewhat increased hybridization of $[s]$ and $[z]$ which facilitates the alterations in their bonding roles: for $\alpha[s]+\beta[z]$ and $\beta[s]-\alpha[z]$ are respectively better adapted to C-H and to (C-C)-bonding than are pure $[s]$ and $[z]$.

The interaction between $[y]_A{}^2$ and $[y]_B{}^2$, likewise that between $[s]_A{}^2$ and $[s]_B{}^2$, should be a repulsive one. Instead of $[y]^2[y]^2$ one *might* write $[y+y]^2$ $[y-y]^2$, where $[y+y]$, which means *const.* $\{[y]_A+[y]_B\}$, is (C-C)-bonding, while $[y-y]$ is (C-C)-antibonding. Probably, however, the (C-C)-nonbonding formulation $[y]^2[y]^2$ represents a better approximation here. The difference between the C=C double bond in C_2H_4 and the O=O double bond in O_2 lies chiefly in this last fact. This can be seen on comparing (2) with the following formulations (3) and (4), and noting that $(\pi+\pi)$ and $(\pi-\pi)$ of O_2 (usually called $\pi 2p$ and $\pi^* 2p$) are two-foldly degenerate orbitals, respectively of the types $\{(x+x)$ and $(y+y)\}$ and $\{(x-x)$ and $(y-y)\}$,—or $\{(x+x)\pm i(y+y)\}$, and $\{(x-x)+i(y-y)\}$,—where x and y stand for $2p_x$ and $2p_y$ of the O atom.

$$C_2H_4\text{: } 1s^2 1s^2 [s]^2 [s]^2 [y+y]^2 [y-y]^2 [z+z]^2 [x+x]^2,\ {}^1\Gamma_{1g} \tag{3}$$

$$O_2\text{: } 1s^2 1s^2 s^2 s^2 (z+z)^2 (\pi+\pi)^4 (\pi-\pi)^2,\ {}^3\Sigma^-{}_g. \tag{4}$$

Here $[y+y]^2[x+x]^2$ of C_2H_4 corresponds to $(\pi+\pi)^4$ of O_2, $[y-y]^2$ to $(\pi-\pi)^2$; but because of the degeneracy involved in $(\pi-\pi)$, which means that $(y-y)$ and $(x-x)$ of O_2 have equal energy unlike $[y-y]$ and $[x-x]$ of C_2H_4, the lowest state of O_2 is a paramagnetic triplet state with one electron in $(x-x)$, one in $(y-y)$, while that of C_2H_4 is a diamagnetic singlet state.

Besides the ${}^1\Gamma_{1g}$ normal state of C_2H_4, the union of two CH_2 each in the state . . . $[z][x]$, ${}^3\Gamma_3$ should give an unstable quintet state and an excited, possibly also unstable (cf. Fig. 1), triplet state of C_2H_1. This and a corresponding singlet state should probably be the lowest excited triplet and singlet state of C_2H_4. They are (cf. (2)):

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z+z]^2 [x+x][x-x],\ {}^3\Gamma_{4u},\ {}^1\Gamma_{4u}. \tag{5}$$

These states should have a very considerably larger equilibrium C-C distance than the normal state. Absorption of suitable ultraviolet frequencies by normal C_2H_4 should take it readily to the ${}^1\Gamma_{4u}$ state, since it can be shown that the transition is in agreement with selection rules appropriate to the case; absorption bands leading to the $^3\Gamma_{4u}$ state should be very weak because of the change in multiplicity. If Fig. 1 is correct, the absorption to the $^3\Gamma_{4u}$ state should consist mostly of a weak continuum causing dissociation into two CH_2.

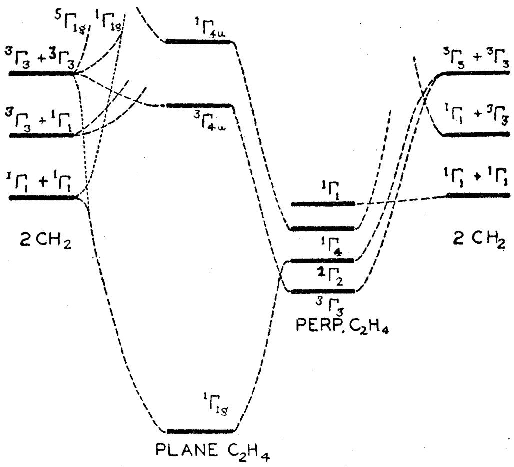

Fig. 1. Probable lowest energy levels of plane C_2H_4 and of perp. C_2H_4 (plane of one CH_2 at 90° to that of the other) and of 2 CH_2, and their adiabatic correlations as given by group theory. (The correlations with 2 CH_2 should not be considered absolutely certain, since the theory has not been carefully checked.) The spacings of the levels are of no more than qualitative significance, and the correct order of some of them may even be the reverse of that shown. It is not impossible that the energy of the $^3\Gamma_{4u}$ state of plane C_2H_4 may be higher than that of 2 $CH_2(^3\Gamma_3)$ so that the state is an unstable repulsive one. The state $^1\Gamma_{4u}$, however, is almost certainly stable. It should be noted that while C_2H_4 in its normal state may be thought of (dotted lines in the figure) as derived from, or to a considerable degree as consisting of, two excited CH_2 radicals both in the state $\cdots [z][x]$, $^3\Gamma_3$ (cf. (2) in the text), normal plane C_2H_4 would probably dissociate adiabatically into two unexcited $^1\Gamma_1$ CH_2 radicals (dashes in the figure). Various states of 2 CH_2 with only slightly higher energy than those shown could be added to the diagram, e.g., $^1\Gamma_1+^1\Gamma_3$, $^1\Gamma_3+^3\Gamma_3$, and $^1\Gamma_3+^1\Gamma_3$, but are not important for our purposes. The equilibrium separation of the two C atoms (r_e) is smallest for the normal state of plane C_2H_4, intermediate in value for the states of perp. C_2H_4, and relatively large for the Γ_{4u} excited states of plane C_2H_4. Diagrams similar to Fig. 1 would apply to *derivatives* of C_2H_4, e.g. $R'R''C=CR''R'''$, although the group theory designations of the electronic states would be different; also, there would be *two* plane forms (*cis* and *trans*) with slightly different energy levels. Further, the dissociation product correlations would be rather different, and some predissociation of the state corresponding to $^1\Gamma_{4u}$ of C_2H_4 seems likely. Perhaps this explains the more structureless character[8] reported for the absorption bands of C_2H_4 derivatives than for C_2H_4 itself.

It is instructive to consider what would be expected if two CH_2 each in the state $\ldots [z][x]$, $^3\Gamma_3$ were brought together with their planes at right angles. The orbitals $[z]$ would overlap nearly as strongly as before and their electrons would give a strong bond $[z+z]^2$, but the two $[x]$ orbitals would overlap very little, and give practically zero energy of bonding, as one sees clearly on examining carefully the appropriate interaction integrals, which can conveniently be set up according to the methods of Slater.[4] Hence instead of getting a singlet state $[x+x]^2$ and a triplet state $[x+x][x-x]$ of widely different energy (cf. (2) and (5)), the singlet and triplet should be nearly equal in energy, and both probably fairly stable. There must of course also be an unstable quintet. Examination of the integrals indicates that the triplet state should be slightly below the singlet, but this is not certain. It will be noticed that with perp. C_2H_4 (the two CH_2 planes perpendicular), the x axis of one CH_2 is parallel to the y axis of the other, and vice versa. As can be shown conveniently by group theory, this leads to a degeneracy somewhat resembling the π degeneracy in O_2. One may write for perp. C_2H_4:

$$1s^2 1s^2 [s]^2 [s]^2 [\pi]_y{}^4 [z+z]^2 [\pi]_x{}^2,\ {}^3\Gamma_3,\ {}^1\Gamma_2,\ {}^1\Gamma_4,\ {}^1\Gamma_1. \tag{6}$$

It can be shown that the incomplete group $[\pi]_x{}^2$ yields four electron states ${}^3\Gamma_3$, ${}^1\Gamma_2$, ${}^1\Gamma_4$, ${}^1\Gamma_1$, of which ${}^3\Gamma_3$ and ${}^1\Gamma_2$ are the triplet and singlet state obtained by bringing together two $CH_2 \ldots [z][x]$, ${}^3\Gamma_3$, with their planes at right angles. The states ${}^1\Gamma_4$ and ${}^1\Gamma_1$ probably lie a volt or so above the two lowest states ${}^3\Gamma_3$ and ${}^1\Gamma_2$ of perp. C_2H_4; their structure is as if derived from CH_2^+ plus CH_2^-.[5]

For the ${}^3\Gamma_3$ and ${}^1\Gamma_2$ (but not for the ${}^1\Gamma_4$ and ${}^1\Gamma_1$) one might write instead of (6):

$$1s^2 1s^2 [s]^2 [s]^2 [y]^2 [y]^2 [z+z]^2 [x][x],\ {}^3\Gamma_3,\ {}^1\Gamma_2. \tag{7}$$

This gives expression to the fact that the $[\pi]_y$ and $[\pi]_x$ orbitals of perp. C_2H_1 in (6), in the case of ${}^3\Gamma_3$ and ${}^1\Gamma_2$, really describe essentially the same state of affairs as if one had the original $[y]$ and $[x]$ orbitals of CH_2 unshared, only the $[z]$ orbitals of CH_2 forming a bond.[6]

Comparing plane C_2H_4 with perp. C_2H_4, it can be shown by group theory that (unless possibly other excited states of unexpectedly low energy intervene), the normal state ${}^1\Gamma_{1g}$ of plane C_2H_4 must go over, on rotation of the CH_2 planes, into the low state ${}^1\Gamma_2$ of perp. C_2H_4, and the two excited states ${}^3\Gamma_{4u}$ and ${}^1\Gamma_{4u}$ of plane C_2H_4 into the low states ${}^3\Gamma_3$ and ${}^1\Gamma_4$ of perp. C_2H_4. It is now of interest to consider the relative positions of the various energy levels

---

[4] J. C. Slater, Phys. Rev. **38**, 1109 (1931).

[5] The preceding results may appear less unfamiliar if it is remarked that ${}^3\Gamma_3$ of the present $[\pi]_x{}^2$ corresponds to ${}^3\Sigma^-{}_g$ of π^2 of a diatomic molecule, ${}^1\Gamma_2$ and ${}^1\Gamma_4$ correspond to ${}^1\Delta_g$ of π^2, and ${}^1\Gamma_1$ corresponds to ${}^1\Sigma^+{}_g$ of π^2. In fact if the H nuclei in perp. C_2H_4 could be united with the C nuclei to form O_2, the four above-mentioned states of $\cdots [\pi]_y{}^4[\pi]_x{}^2$ of perp. C_2H_4 would go over into the three states of $\cdots \pi^4\pi^{*2}$ of O_2, i.e., of $\cdots (\pi+\pi)^4(\pi-\pi)^2$ of (4).

[6] In (6), $[\pi]_y{}^4$ is a degenerate group formed from $[y]_A{}^2$ and $[y]_B{}^2$, where the designation $[y]$ is based on a separate choice of axes for the two CH_2 radicals A and B. If a choice of x and y axes consistent for the *whole* perp. C_2H_4 *molecule* were used, one would have to speak of, say, $[y]_A{}^2$ and $[x]_B{}^2$ instead of $[y]_A{}^2$ and $[y]_B{}^2$. It is this peculiarity which causes these two types to belong to a single degenerate type, here called $[\pi]_y$, of perp. C_2H_4, regardless of whether or not they interact appreciably. Similarly the orbitals which, when expressed in terms of the x, y axes of the separate CH_2's, are called $[x]_A$ and $[x]_B$ of 2 CH_2, become $[x]_A$ and $[y]_B$ in terms of x and y axes consistent for the whole molecule. In C_2H_4 both, somewhat modified by the interaction of the two CH_2 of course, then belong to the degenerate type here called $[\pi]_x$.

of plane and perp. C_2H_4. Roughly, the energy differences depend only on that part of the energy of formation of C_2H_4 which is furnished by the interaction of the two $[x]$ electrons of the two CH_2. In perp. C_2H_4 this is approximately 0 volts (${}^1\Gamma_4$ is perhaps about 1 volt higher). In plane C_2H_4 in its normal state it is the energy of the $[x+x]^2$ bond, say about -2.5 volts. In excited C_2H_4 with $[x+x][x-x]$ we may expect the anti-bonding action of $[x-x]$ to exceed considerably[7] the bonding action of $[x+x]$, giving a net result of say perhaps $+3$ volts. These estimates are plotted in Fig. 1, which shows qualitatively how we may expect the energies of the various states to change on going from plane C_2H_4 to perp. C_2H_4, also the probable correlations of the various states with those of CH_2+CH_2.

OTHER DOUBLE-BONDED COMPOUNDS

From Fig. 1 it will be seen that the normal state of plane C_2H_4 should be stable with respect to a relative rotation of the planes of the two CH_2's, but that the excited states ${}^3\Gamma_{4u}$ and ${}^1\Gamma_{4u}$ shown in Fig. 1 might be expected to rotate spontaneously into the corresponding states ${}^3\Gamma_3$ and ${}^1\Gamma_4$ of perp. C_2H_4. By applying methods similar to the above to ethylene derivatives, such as for example $R_1R_2C=CR_1R_3$, it is easily shown that they should show qualitatively the same behavior as $H_2C=CH_2$ itself, and should have energy level diagrams similar to Fig. 1. Experimentally, their lowest excited energy levels are apparently nearer the normal level than in C_2H_4, since the ultraviolet absorption bands of the derivatives begin at longer wave-lengths than those of C_2H_4 itself, the shift increasing with the complexity of the molecule.[8]

Application of the quantum theory to $C=N$ and $N=N$ double bonds along the lines used for the $C=C$ bond indicate that they also have the structure $[z+z]^2[x+x]^2$ characteristic of the $C=C$ bond (cf. (2)). But the bond in B_2H_6 is probably more like that in O_2, giving a paramagnetic normal state, and has probably almost no stability toward a relative rotation of the two BH_2 groups. Details will be given in later papers.

It is well known that derivates of ethylene, e.g., $R_1R_2C=CR_1R_3$, exist in two forms called *cis* and *trans*, where in the *cis* form the two R_1's are on the

---

[7] The difference between $[x+x]^2$, ${}^1\Gamma_{1g}$ and $\cdots$ $[x+x][x-x]$, ${}^1\Gamma_{4u}$ of plane C_2H_4 is analogous to that between $\cdots$ $(\pi+\pi)^4(\pi-\pi)^2$, ${}^3\Sigma^-_g$ and $(\pi+\pi)^3(\pi-\pi)^3$, ${}^3\Sigma^-_u$ of O_2, unless possibly the electron configuration assigned in the latter case is wrong. In this O_2 case the energy difference is 6.1 volts from $v=0$ of the ${}^3\Sigma_g^-$ to $v=0$ of the ${}^3\Sigma_u^-$. Another example of the dominant effect of antibonding electrons is the case of H_2, where the energy of $(1s_A+1s_B)^2$, ${}^1\Sigma^+_g$ is -4.4 volts compared with $H+H$, while for the same internuclear distance the energy of $(1s_A+1s_B)(1s_A-1s_B)$, ${}^3\Sigma^+_u$ is about $+5$ volts.

[8] Cf. J. Stark and collaborators, Jahrbuch der Rad. und Elek. **10**, 10–188 (1913); and data in Int. Crit. Tables, Vol. 5. It seems likely that the "first band" of Stark corresponds in each case to a transition to the state analogous to the ${}^1\Gamma_{4u}$ of C_2H_4. (In the case of C_2H_4 itself, Stark's "second band" near λ2000 is probably really the "first band.") The transition to the state analogous to ${}^3\Gamma_{4u}$ of C_2H_4 is perhaps represented by weak absorption at longer wave-lengths, not carefully investigated by Stark. It is perhaps best not to venture an interpretation of Stark's second band at shorter wave-lengths, except to suggest that *possibly* it may belong to the same transition as the first band,—but more probably not. In regard to the structures of the "first bands," cf. remark at end of the Fig. 1 caption.

same side of the z axis (C-C axis), in the *trans* form on opposite sides.[9] Usually both forms are stable at low temperatures, but the higher-energy form (usually *cis*) can usually be transformed into the lower-energy form (*trans*) by heating. The "energy of activation" for this process is evidently the energy difference between the normal state of the plane form ($^1\Gamma_{1g}$ for C_2H_4 in Fig. 1) and the lowest state of the perp. form ($^3\Gamma_3$ of perp. C_2H_4 in Fig. 1). Experimentally, there is evidence that this energy of activation is lower in the ethylene derivatives than is indicated by Fig. 1 for ethylene itself.[9]

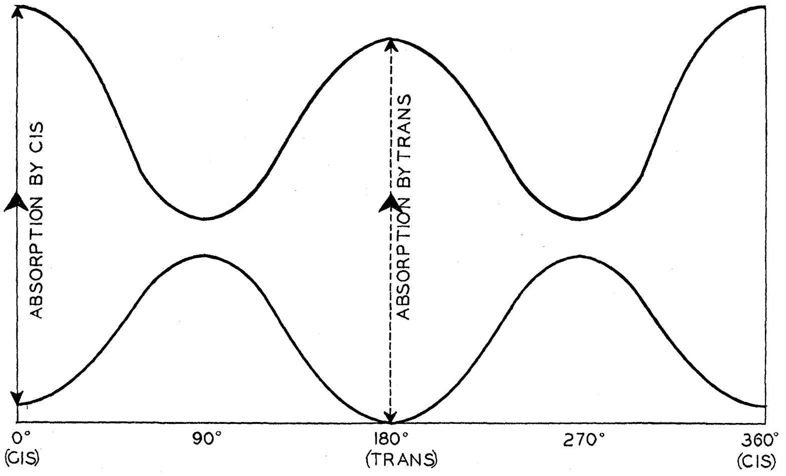

Fig. 2. Curves of electronic energy for a derivative of C_2H_4, for the normal state (lower curve) and (upper curve) for an excited state analogous to $^1\Gamma_{4u}$ of C_2H_4 in Fig. 1. The curves are of no more than qualitative significance. The *cis* form would probably usually correspond to 0°, the *trans* form to 180°, in a figure of the type of Fig. 2. The process of absorption of ultraviolet light by either form is indicated by vertical arrows. After such absorption, the molecule performs rotational vibrations about, or rotations through, the energy maxima at 0° and 180°. If light is emitted, or the energy is lost in a collision, when the angle of rotation away from the original angular position exceeds 90°, the molecule has been transformed from *cis* into *trans*, or vice versa.

INTERPRETATION OF PHOTOCHEMICAL EXPERIMENTS

Experimentally it is well known that the absorption of ultraviolet light can convert *cis* into *trans* forms and vice versa.[10] Probably the absorption carries the molecule to the singlet level analogous to $^1\Gamma_{4u}$ of C_2H_4 (Fig. 1), where it is unstable with respect to rotation into the perp. form.[11] [Olson[12] has pre-

---

[9] Cf. E. Hückel, Zeits. f. Physik **60,** 423 (1930) for a review of the experimental evidence on the behavior and nature of double-bonded compounds. This includes definite evidence for a plane arrangement of the six atoms nearest to the double bond.

[10] R. Stoermer and collaborators. Ann. d. Chemie **342,** 1 (1905); Chem. Ber. **42,** 4865 (1909); **44,** 637 (1911) and later articles.[9]

[11] Most absorbed frequencies would give rise to strong vibrations as well as to relative rotation of the CH_2 groups, but this has no necessary primary effect on the *cis-trans* transformation discussed here, except for absorbed frequencies causing direct dissociation or predissociation of $R_1R_2C_2R_1R_3$ into CR_1R_2 and CR_1R_3. Experimentally, the ultraviolet frequencies which cause the *cis-trans* change usually do not produce much decomposition.

[12] A. R. Olson, Faraday Soc. Trans. **27,** 69 (1931).

viously discussed the possible transformation of the *cis* into the *trans* isomer or vice versa by relative rotations of the CR′R″ groups as a result of ultraviolet absorption, but did not consider the simple mechanism which the present theory indicates.] The momentum of the rotation should, however, carry the molecule past the perp. form (90° rotation) into the form (*trans* or *cis*, as the case may be) opposite to that (*cis* or *trans*) in which it started (180° rotation): cf. Fig. 2. If the molecule is undisturbed, many rotations or rotational vibrations should take place, until eventually the energy is lost by a collision or by radiation, or sometimes perhaps by predissociation. For any individual molecule which has absorbed suitable light, the chances should then be nearly equal of returning to the original form or of ending in the isomeric form. Experiments of Warburg,[13] however, on the isomeric acids fumaric (*trans* form, higher energy) and maleic (*cis* form) of formula $(H\cdot C\cdot COOH)_2$ show only from 3 to 12 percent conversion of either isomer into the other per light quantum absorbed. Quite possibly this discrepancy can be attributed to disturbing factors, e.g., perhaps interference by collisions before completion of a single rotation or rotational vibration, since the experiments were made in water solution.

Prolonged exposure of ethylene derivatives to ultraviolet light tends to set up a photochemical equilibrium. Apparently this equilibrium is usually such that the lower-energy isomer is changed rather completely into the higher-energy isomer.[10] In the case of maleic and fumaric acid, equilibrium exists when there is about 75 percent of maleic acid;[13] the equilibrium ratio, however, apparently depends on the absorbed wave-lengths. Such results can be readily understood in terms of the present theory. They depend somewhat on the relative heights of the *cis* and *trans* maxima of the excited-state curve in Fig. 2, but probably more, or more directly at least, on differences in the absorption coefficients of the two isomers, which cause one to be transformed more rapidly than the other.

In conclusion, it may be remarked that the correctness of the preceding interpretation of the excited levels of ethylene and its derivatives, and of the effect of ultraviolet light on them, has not been proved. For the interpretation depends in part on estimates of the relative positions of energy levels which may conceivably be wrong to a sufficient extent to upset it. The interpretation should, however, be capable of experimental testing, and might also be the subject of theoretical calculations.

---

[13] E. Warburg, Sitzungsber. der Preuss. Akad. der Wiss., No. 50, p. 964 (1919).