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ON THE ROLE PLAYED BY EXCITED ELECTRONIC STATES AND MOLECULAR VIBRATIONS IN ADDITION REACTIONS—I

TRANS-ADDITION TO THE CARBON–CARBON TRIPLE BOND

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Abstract—A mechanism is suggested for the electrophilic additions to acetylene and to acetylenic compounds which implies the intervention of the *trans* bent ^1A_u state. Perturbation calculations have been made on a system consisting of a molecule of acetylene and of a proton, for various modes of approach of the latter. It is found that certain modes of approach enable considerable admixture of the distorted state wave function with that of the ground state. The effect is large enough for the *trans* bent molecule to become more stable than the linear one. The proton's drawing closer thus favor a *trans* distortion of the molecule, which suggests a relation between the *trans*-addition and the shape of acetylene in its first excited state.

IT IS well known that in the mechanism proposed heretofore for the additions, either homolytic or heterolytic, to multiple CC bonds, the substrate is in general assumed to be at its equilibrium configuration. One considers the mutual polarizations of the substrate and the reagent, but molecular distortions are generally not taken into account. The purpose of the present study is to investigate the possibility that the first stages of the reactions would involve distortions of the substrate, which would actually favor the following steps of the addition.

Prior to this work the question of the role played by the molecular distortions in chemical reactions had in fact already been raised. Thus, the importance of the changes in electronic structure induced by the vibrations had been emphasized by Duchesne some time ago.[1] Also, Bader has studied recently the connection between molecular distortions, excited states and reactivity.[2]

This first paper will be devoted to the electrophilic additions to acetylenic compounds. The reactivity of the ethylenic derivatives will be treated in the next paper. As regards the reactions we are concerned with here, they are known to proceed in a *trans*-fashion, as appears from the numerous articles which have treated this question. We will merely give here a few examples of this now well established type of reaction. Acetylenedicarboxylic acid adds the halogens to give the dihalofumaric acids;[3–5] with the hydrogen halides it also undergoes *trans*-addition.[6] Similarly, methyl propiolic acid (CH_3—C≡C—COOH) reacts with HCl to give β-chlorocrotonic acid.[7] As far

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[1] J. Duchesne, *J. Chem. Phys.* **18**, 1120 (1950); *Bull. Acad. Roy. Belg. Cl. Sci.* **58**, 197 (1952).
[2] R. F. W. Bader, *Canad. J. Chem.* **40**, 1124 (1962).
[3] A. Michael, *J. Prakt. Chem.* [2] **52**, 289 (1895).
[4] E. Ottrand and K. Packendorff, *Ber. Dtsch. Chem. Ges.* **64**, 1327 (1931).
[5] L. Eichelberger, *J. Amer. Chem. Soc.* **48**, 1321 (1926).
[6] A. Michael, *J. Prakt. Chem.* [2] **46**, 209 (1892).

as acetylene itself is concerned, there is also evidence that it gives rise to a *trans*-addition when reacting with the halogens.[8] Note that recently it has been established that the same feature characterizes also the nucleophilic additions to the triple CC bonds.[9] Experimental evidence has actually led Miller to suggest a rule of *trans*-addition for nucleophilic reactions with C≡C bonds.[10]

The model currently used by chemists for the electrophilic type of reactions consists first in an attack of the substrate by a positive ion (proton or halide ion, according to the case), and the formation of a π complex. Then a negative halide ion attacks the complex on the side opposite to that where the positive ion lies.[11] This model thus interprets the *trans*-addition by the mode of attack of the π complex by the anion. As it will be shown, by considering distorted states of the substrate as intermediate steps a somewhat different mechanism can be arrived at.

If one takes into account the fact that the vibration of lowest frequency of acetylene is the bending mode π_g, which corresponds to a *trans* distortion, and, further, that the molecule is *trans* bent in its first singlet excited state,[12,13] it seems indeed legitimate to wonder if there might be a relation between those two facts and the *trans*-addition. The idea upon which our model rests is that, at some stage of the reaction, the molecule can be described by a wave function containing a significant contribution from the bent excited state, and that this admixture is large enough for the molecule to adopt the *trans*-shape. Actually, the hypothesis of a connection between the *trans*-addition and the shape of acetylene in its first excited state had already been introduced by Ingold.[14]

It should be noted that in its excited *trans* (^1A_u) state, the molecule is particularly apt to engage in an addition reaction. As a consequence of the change of hybridization (sp to sp^2), one has indeed now two sp^2 hybrids located *trans* to each other. Molecular orbitals can be built from these two hybrids in the usual fashion: one will be made up by their in-phase superposition, whereas in the other MO they will be out of phase. In the A_u *trans*-state, the first MO (which corresponds to the π bond orbital affected by the bending), is doubly occupied, and the antibonding one contains one electron.[15] Since the hybrids overlap only slightly, they may be considered as non bonding orbitals (containing 1 1/2 electron each) which will tend to saturate by forming a bond with the attacking reagent. As a plausible mechanism which would bring the molecule to the state considered, one may think of an excitation of the π_g vibration, which would be followed by a radiationless transition to the excited state. The radiationless transition is made possible because the potential energy curves of the first two singlet states of acetylene intersect each other, as appears from Fig. 1, which gives the

[7] R. Friedrich, *Liebig's Ann.* **219**, 368 (1883).
[8] H. G. Viehe, private communication.
[9] W. E. Truce, J. A. Simms and M. M. Bondiakian, *J. Amer. Chem. Soc.* **78**, 695 (1956); W. E. Truce and J. A. Simms, *Ibid.* **78**, 2756 (1956).
[10] S. I. Miller, *J. Amer. Chem. Soc.* **78**, 6091 (1956).
[11] See, for instance, E. S. Gould, *Mechanism and Structure in Organic Chemistry*, p. 520. Holt, Rinehart and Winston, New York (1959).
[12] C. K. Ingold and G. W. King, *J. Chem. Soc.* 2702 (1953).
[13] K. K. Innes, *J. Chem. Phys.* **22**, 863 (1954).
[14] C. K. Ingold, *J. Chim. Phys.* **53**, 472 (1956).
[15] For a more detailed description of the electronic structure of the molecule in its A_u state, see Refs 12–14.

position of the two levels as a function of the bending angle α. The Fig. is based on the results of calculations made by Howard and King.[16] Note that the calculations have been carried out for $\alpha = 0°$ and $\alpha = 60°$ only, and that the curves of the Fig. are nothing more than a reasonable guess. This model, however, gives rise to several difficulties. First, the radiationless transition is symmetry forbidden, since the two states involved belong to two different symmetry species (A_g and A_u), which prevents

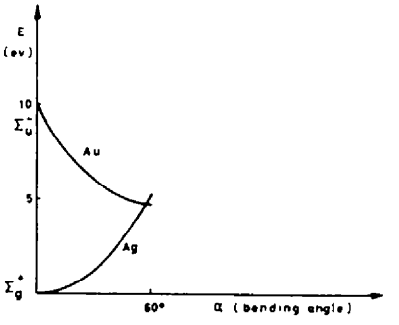

FIG. 1. Energy curves of acetylene in its two lowest singlet states, as a function of the bending angle

the interaction. Also, the model implies the accumulation of a considerable quantity of vibrational energy in a single mode of vibration, which must be very hard to realize in view of the flow of energy taking place inevitably among the various modes. Furthermore, the mechanism requires an activation energy of the order of 5 ev, which is definitely much higher than the values usually found for chemical reactions.

But these difficulties disappear if one takes into account the effect of the approaching reagent, which we have ignored so far. In order to introduce this effect in the treatment, perturbation theory will be used. As will be seen later, certain modes of approach of the reagent are such that an interaction between the A_g and A_u state becomes possible. This suppresses the forbiddenness of the radiationless transition. On the other hand, a consequence of the mixing is that the two curves repel each other, and if the interaction is sufficiently large this will considerably reduce the activation energy.

In order to test this idea, we have applied it to a system consisting of a molecule of acetylene and a proton. To take a proton as reagent of course greatly facilitates the calculation, since in this case the perturbation term is due to coulombic interaction and no spin effect arises. Nevertheless, this model is not too unrealistic, since the electrophilic addition consisting in the attack by a positive ion and particularly in the case of the addition of hydrogen halides it may be considered as a satisfactory representation of the actual situation.

The treatment neglects the hydrogen atoms and the CH bonds and includes the six electrons of the CC bond. For the unperturbed linear molecule, the following wave functions have been used.

$$\psi_0 = \psi(^1\Sigma_g^+) = |(\sigma_g\alpha)(\sigma_g\beta)(\pi_u\alpha)(\pi_u\beta)(\bar{\pi}_u\alpha)(\bar{\pi}_u\beta)|$$

$$\psi_1 = \psi(^1\Sigma_u^-) = \tfrac{1}{2}\{|(\sigma_g\alpha)(\sigma_g\beta)(\pi_u\alpha)(\bar{\pi}_g\beta)(\bar{\pi}_u\alpha)(\bar{\pi}_u\beta)| + |(\sigma_g\alpha)(\sigma_g\beta)(\bar{\pi}_g\alpha)(\pi_u\beta)(\bar{\pi}_u\alpha)(\bar{\pi}_u\beta)| - |(\sigma_g\alpha)(\sigma_g\beta)(\pi_u\alpha)(\pi_u\beta)(\bar{\pi}_u\alpha)(\pi_g\beta)| - |(\sigma_g\alpha)(\sigma_g\beta)(\pi_u\alpha)(\pi_u\beta)(\pi_g\alpha)(\bar{\pi}_u\beta)|\},$$

[16] H. Howard and G. W. King, *Canad. J. Chem.* 37, 700 (1959).

where the σ-bond and π-bond orbitals have been represented by the standard notations.

In the *trans* bent molecule, these wave functions become respectively

$$\psi_0 = \psi(^1A_g) = |(a_g\sigma_g\alpha)(a_g\sigma_g\beta)(b_u\pi_u\alpha)(b_u\pi_u\beta)(a_u\bar{\pi}_u\alpha)(a_u\bar{\pi}_u\beta)|$$

and

$$\psi_1 = \psi(^1A_u) = \frac{1}{\sqrt{2}}\{|(a_g\sigma_g\alpha)(a_g\sigma_g\beta)(b_u\pi_u\alpha)(b_u\pi_u\beta)(a_u\bar{\pi}_u\alpha)(a_g\pi_g\beta)| + |(a_g\sigma_g\alpha)(a_g\sigma_g\beta)(b_u\pi_u\alpha)(b_u\pi_u\beta)(a_g\pi_g\alpha)(a_u\bar{\pi}_u\beta)|\}$$

Here each orbital is indicated by the symmetry species of the group C_{2h} to which they belong, but for the sake of clarity, we have also indicated the corresponding symbols which label them in the linear molecule. Perhaps a brief description of the various orbitals of the bent molecule will be useful. The σ-bond orbital, $a_g\sigma_g$, is formed by the superposition of two sp^2 hybrids pointing to each other; $b_u\pi_u$ and $a_g\pi_g$ are respectively the bonding and antibonding MOs formed by the two trans sp^2 hybrids and described p. 2; $a_u\bar{\pi}_u$ is the bonding orbital formed by the $2p\pi$ AOs perpendicular to the plane of the distorted molecule. The analytical expressions of the MOs are readily obtained and are not given here. They may be found in Howard and King's paper.[16] For the 2s AO of carbon, we have used a nodeless Slater type orbital, with an orbital exponent of 1·59, which value was also used for the 2p orbitals.

It will be noticed that we have neglected the configuration interaction between the two possible states of A_u symmetry, but for our purpose, this point is of minor importance.

Time-independent perturbation theory has been used for various values of the distance proton-acetylene; the perturbation term of the Hamiltonian comprises the coulombic attraction between the six electrons and the proton, plus the repulsion between the latter and the two carbon nuclei, which have been taken to have a charge of +3e. The CC distance has been taken equal to 2·2714 a.u. (1·202 Å) in the linear configuration and to 2·6135 a.u. (1·383 Å) in the bent configuration. The energy of the perturbed system has been calculated by the well known formula[17]

$$E = \tfrac{1}{2}(E_0 + E_1 + V_{00} + V_{11}) \pm \{\tfrac{1}{4}(E_0 - E_1 + V_{00} - V_{11})^2 + |V_{01}|^2\}^{\frac{1}{2}}$$

which applies for any two interacting states, whether their energy curves intersect or not. In this expression,

$$V_{ij} = \int \psi_i^* \, V\psi_j \, dt,$$

where V is the perturbation term in the Hamiltonian.

Disregarding momentarily the nuclear repulsion term, the following expressions are readily found for the V_{ij} integrals.

In the linear molecule:

$$V_{00} = -2(H:\ \sigma_g\sigma_g) - 2(H:\ \pi_u\pi_u) - 2(H:\ \bar{\pi}_u\bar{\pi}_u)$$

$$V_{11} = -2(H:\ \sigma_g\sigma_g) - \tfrac{3}{2}\{(H:\ \pi_u\pi_u) + (H:\ \bar{\pi}_u\bar{\pi}_u)\} - \tfrac{1}{2}\{(H:\ \pi_g\pi_g) + (H:\ \bar{\pi}_g\bar{\pi}_g)\}$$

$$V_{01} = 0$$

[17] See for instance, L. D. Landau and E. M. Lifschitz, *Quantum Mechanics, Non-relativistic Theory* p. 263. Pergamon Press, London (1958).

In the bent molecule:

$$V_{00} = \quad 2(H:\ a_g\sigma_g a_g\sigma_g) \quad 2(H:\ b_u\pi_u b_u\pi_u) - 2(H:\ a_u\bar{\pi}_u a_u\bar{\pi}_u)$$

$$V_{11} = -2(H:\ a_g\sigma_g a_g\sigma_g) - 2(H:\ b_u\pi_u b_u\pi_u) - (H:\ a_u\bar{\pi}_u a_u\bar{\pi}_u) - (H:\ a_g\pi_g a_g\pi_g)$$

$$V_{01} = -\sqrt{2}\,(H:\ a_u\bar{\pi}_u a_g\pi_g)$$

Here, $(H:\ \phi_i\phi_j)$ represents the nuclear attraction integral

$$\int(\phi_i^*\phi_j)/r_H\,dt.$$

Of special interest is the term V_{01}, which measures the interaction between the two states, and on the magnitude of which depends the probability of the radiationless

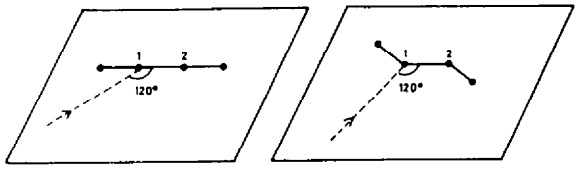

FIG. 2 Mode of approach of the proton—Case 1

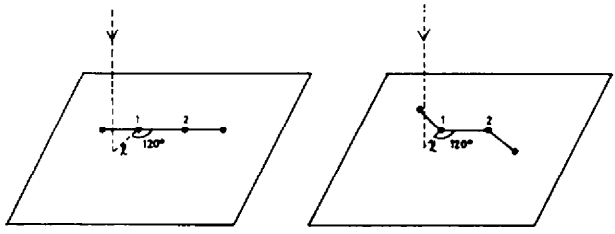

FIG. 3 Mode of approach of the proton—Case 2

transition $A_g \rightarrow A_u$. Of the two MOs involved in this term in the bent configuration, a_u has a node in the plane of the distorted molecule, whereas a_g is located in this plane. It follows that if the proton lies in the molecular plane, V_{01} will be zero. Thus in that case the molecule must necessarily remain in its ground state, access to the A_u state being forbidden.

For the proton to provoke a radiationless transition, it must thus lie outside of the molecular plane. In order to study what happens in the two cases $V_{01} = 0$ and $V_{01} \neq 0$, we have considered two different modes of approach of the proton. In case 1 (illustrated in Fig. 2), it approaches toward one of the carbon atoms along a line making an angle of 120° with the CC bonds. In case 2, it approaches along the line indicated by an arrow in Fig. 3. The distance l has been taken equal to 2 a.u. The three-center integrals which appear in the treatment have been calculated by the Mulliken approximation. In view of the approximate character of the present work, their exact calculation would be an unnecessary refinement.

In considering case 1, our purpose was to determine whether the presence of the proton would favor a bending of the molecule, the latter remaining in its ground state.

TABLE 1. ENERGY IN A.U. OF THE SYSTEM ACETYLENE + H^+
(Relative to the energy of the isolated linear molecule); Case 1

Linear molecule			
Distance proton-carbon 1	Electronic energy ($^1\Sigma_g^+$ state)	Nuclear repulsion	Molecular energy
5·0	−1·0644	1·0656	0·0012
4·5	−1·1673	1·1693	0·0020
4·0	−1·2922	1·2955	0·0033
3·5	−1·4469	1·4529	0·0060
3·0	−1·6424	1·6551	0·0127
2·5	−1·8943	1·9257	0·0314
2·0	−2·2206	2·3105	0·0899
Trans bent molecule			
Distance proton-carbon 1	Electronic energy (^1A_g state)	Nuclear repulsion	Molecular energy
5·0	−0·8847	1·0477	0·1630
4·5	−0·9895	1·1480	0·1585
4·0	−1·1178	1·2700	0·1522
3·5	−1·2784	1·4218	0·1434
3·0	−1·4844	1·6166	0·1322
2·5	−1·7537	1·8774	0·1237
2·0	−2·1063	2·2487	0·1424

Values of the energy of the perturbed system for several distances proton-carbon 1 are given in Table 1. Fig. 4 illustrates the results. It shows the energy curves concerned respectively with the linear molecule in its ground state, the bent molecule in the same electronic state, and the bent molecule in its excited ^1A_u state. It is noticed that the ground state energy of the bent molecule decreases somewhat as the proton draws closer, but the effect (which in this case results from the application of first-order perturbation theory) is not very important. The energy required to bring the molecule in this configuration decreases up to 3·4 ev, which is still considerable. On the other hand, the energy of the bent excited state decreases constantly and eventually becomes lower than that of the linear molecule. However, as stated earlier, the radiationless transition which would bring the molecule into the ^1A_u state is forbidden. Thus in this case, access to a twisted configuration either requires too much energy or is forbidden, and the process is not very efficient as regards the reaction we are interested in.

In view of the shapes of the curves represented in Fig. 4, one would expect that case 2, where V_{01} is different from zero and hence a radiationless transition is allowed, would give rise to a much more favourable situation. The results of the calculation given in Table II and represented graphically in Fig. 5*, are in agreement with this expectation. The curves of the figure are somewhat similar to those of Fig. 4, with

* Let us recall that due to the perturbation, one may actually no longer talk about a ^1A_g or a ^1A_u state of the bent molecule. The two states involved are actually a mixture of ^1A_g and ^1A_u. When it is in the field of a proton, a molecule moving along the potential curve corresponding to the (original) ^1A_g state of Fig. 1 will in fact have a larger probability to switch over to the curve relative to the (original) ^1A_u state than to stay on the same curve.

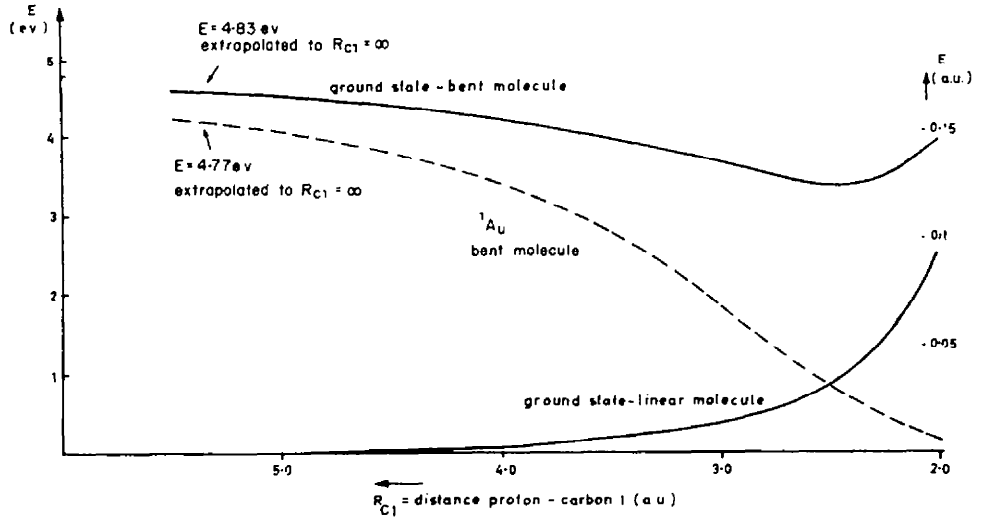

FIG. 4. Energies of the system acetylene + proton vs distance proton-carbon 1—Case 1

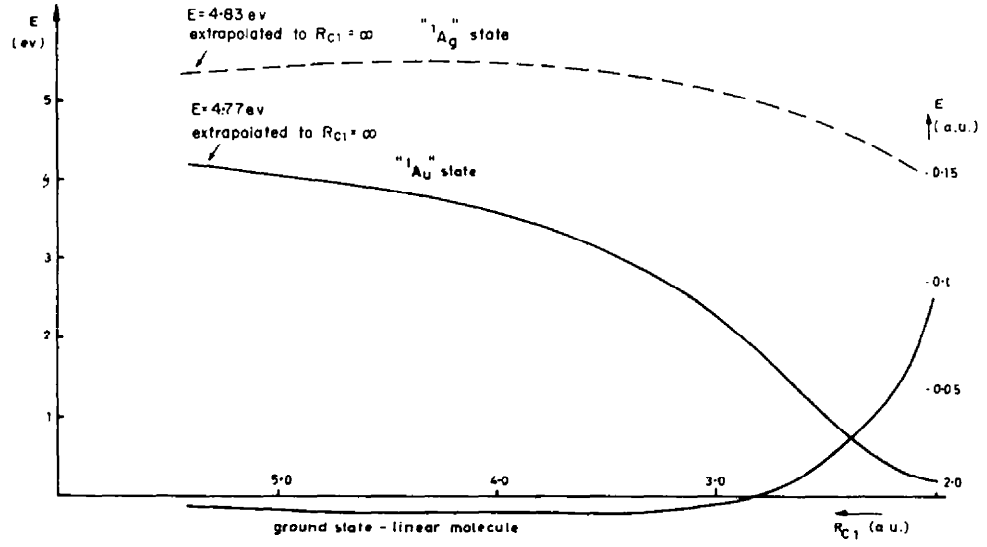

FIG. 5. Energies of the system acetylene + proton vs distance proton-carbon 1—Case 2

TABLE 2. ENERGY IN A.U. OF THE SYSTEM ACETYLENE + H^+ (Relative to the energy of the isolated linear molecule). Case 2

Linear molecule				
Distance proton-plane of reference	Distance proton-carbon 1	Electronic energy ($^1\Sigma_g^+$ state)	Nuclear repulsion	Molecular energy
5·0	5·39	−1·0448	1·0393	- 0·0055
4·0	4·47	- 1·2284	1·2213	−0·0071
3·0	3·60	−1·4690	1·4617	−0·0073
2·0	2·83	−1·7709	1·7737	0·0028
1·3	2·39	−1·9938	2·0223	0·0285
1·0	2·24	−2·0782	2·1241	0·0459
0·5	2·06	- 2·1825	2·2584	0·0759
0·00	2·00	−2·2206	2·3105	0·0899
Trans bent molecule				
Distance proton-molecular plane	V_{01}	Electronic energy "^1A_u state"	Nuclear repulsion	Molecular energy
5·0	−0·0188	−0·8731	1·0253	0·1522
4·0	−0·0258	- 1·0620	1·2007	0·1387
3·0	−0·0373	−1·3169	1·4314	0·1145
2·0	−0·0538	1·6627	1·7305	0·0678
1·3	−0·0598	−1·9420	1·9698	0·0278
1·0	−0·0560	--2·0536	2·0680	0·0144
0·5	--0·0356	−2·1955	2·1981	0·0026
0·0	0	- 2·2481	2·2487	0·0006

the difference, however, that access to the "^1A_u" state is now allowed. For a distance proton-carbon 1 smaller than 2·4 a.u., this state becomes actually more stable than the linear one.

It thus appears from the calculations that in such a case as the one just described, the approach of the reagent causes a distortion of the molecule, through the intervention of the excited state of the latter. To our knowledge, the possibility of those distortions has so far received very little attention. In a recent work by Ruffa and Griffing,[18] a similar effect has been studied in a simpler system, consisting of two hydrogen molecules approaching each other along a collinear path. Diatomic molecules, with a single degree of internal freedom, seem to us to represent a particularly favourable example. Moreover, the small number of electrons involved in the problem has enabled Ruffa and Grifing to use a more or less rigorous method, which calculates LCAO MOs by treating the four atom system as a whole. The calculations indicate that as the two molecules approach each other they undergo an elongation; this result is evidently very similar to the one we obtain, and the agreement is encouraging as regards the validity of our approximate treatment. It is certain that we have applied the perturbation method in a range where its use is questionable, because of the very large interaction which takes place. The quantitative results must therefore not be taken in too strict a sense and should rather be considered as giving a general trend of the energy curves. It is undeniable that in case 2 the perturbation causes a

[18] A. R. Ruffa and V. Griffing, *J. Chem. Phys.* **36**, 1389 (1962).

steady important lowering of the energy of the ^1A_u state. The essential point is that the approach of the proton makes the excited state much more easily accessible, whether or not the curves of Fig. 5 intersect each other. If they do not, it certainly would require very little vibrational energy for the molecule to reach the bent state.

It is to be noted that the only type of distortion which has been considered in this work is the *trans*-bending. It is quite possible that the simultaneous intervention of other distortions, such a twisting, for example, may facilitate the process some more. Simple symmetry considerations show indeed that if the molecule is bent and twisted, the two electronic states involved will belong to the same irreducible representation, which favors the radiationless transition. The proton may then come closer along the axis of a hybrid as in case 1, give rise to large V_{00} and V_{11} terms* and at the same time provoke a transition as in case 2. If the energy required to twist the molecule is smaller than the gain due to the position of the proton, this might be a possible mechanism.

A last point which should be stressed is that the mechanism suggested here implies that the second step of the reaction, i.e. the attack by the negative ion, takes place at a very short time after the first one. The interval between the two steps must be very short, so as to prevent a rearrangement which would bring the system into a more symmetrical configuration. However, it should be realized that this requirement is probably not a stringent one and that it does not apply in a general way. For instance, in the addition to the double CC bond, the configuration involving a symmetrical position of the proton with respect to the two carbons has a higher energy than that where the proton is closer to one of the two carbon atoms, as will be seen in the next paper.[19] Moreover, in the case of protonated acetylene itself, Hoffmann has found by using the extended Hückel MO method[20] that a non-symmetrical configuration, involving the bending of a CH bond, is actually the most stable.[21] This feature may very well help relax the condition concerning the time lag between the two stages of the process.

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* That V_{00} and V_{11} in the bent molecule are larger when the proton lies on the axis of a sp^2 hybrid clearly appears from the formulae of page 2406.

[19] L. Burnelle, following paper of this series, *Tetrahedron*.

[20] R. Hoffmann, *J. Chem. Phys.* **39**, 1397 (1963).

[21] R. Hoffmann, *J. Chem. Phys.* to be published.