

atoms. This appears not to be an unhappy situation, in terms of shell effect, since its neighboring C atom does not carry anymore a large negative charge. This is exactly what is shown by the population analyses and what is expressed by eq 4. The consequence is that the CH₂ group in propane is electron deficient and, finally, that the ethyl group appears to be a better electron donor than methyl. Similar arguments can also be applied to isobutane and neopentane.

It follows, from these considerations, that methyl groups cannot simply be regarded as electron donors with the implication that the electron donation toward a center is increased as the number of methyl groups attached to this center is increased. Hence, the argument which is occasionally invoked that "a tertiary carbonium ion is more stable than the secondary or primary one since there are more methyl groups that can release electrons toward the positive center" should not be retained. Anyway, the charges are distributed so as to minimize their total energy and, consequently, any subsequent charge pushing is unnecessary. The order of stabilization of carbonium ions can be interpreted in terms of eq 4, which indicates that a positive center is favored by neighboring negatively charged atoms.

This interpretation has a further consequence. Since a positive site appears to be favored by negative neighbors, the methyl group is expected to be more

effective in favoring a carbonium ion than, say, a *tert*-butyl group, whose central C atom is electron deficient with respect to the methyl C atom. Clearly, from a consideration of the shell effect, the alkyl groups are expected to favor a positive site in the order methyl > ethyl > isopropyl > *tert*-butyl, *i.e.*, in the so-called "hyperconjugative order." This is illustrated, both on experimental and theoretical grounds, by a detailed study of the formation of zwitterionic carbocations from the decomposition of 1,2,3-trioxolanes (primary ozonides), in terms similar to the arguments presented here.^{17,18}

It is, hence, concluded that the shell effect (eq 4) is capable of explaining both the inductive order (*tert*-butyl > ... > methyl) and the "hyperconjugative" order (methyl > ... > *tert*-butyl) of reactivity exhibited by alkyl groups.

Acknowledgments. The author thanks Professor C. Sándorfy for helpful comments and Professor D. Z. Simon and Mr. J. Sygusch for assistance in several calculations. The financial aid given by the National Research Council of Canada is gratefully acknowledged.

(17) S. Fliszár, J. Renard, and D. Z. Simon, *J. Amer. Chem. Soc.*, **93**, 6953 (1971).

(18) Any over generalization of the present interpretation of the "hyperconjugative order" could, however, be misleading since, in a number of cases, solvolysis may be responsible for the ordering of effects exhibited by alkyl groups.

All-Electron Nonempirical Calculations of Potential Surfaces.

I. Dissociation of Formaldehyde into Radical Products

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Abstract: *Ab initio* calculations on the lowest two singlet and triplet states of formaldehyde have been performed using excited-state SCF orbitals as an expansion set in a modest CI. The calculations were repeated for several molecular geometries representative of the dissociation path to radical products. The nature of the dissociation as examined in terms of the molecular orbital energies and coefficients as well as the weighting coefficients of electronic configurations is discussed. The calculated values for spectral excitations of formaldehyde and formyl radical and the H-HCO bond dissociation energy are compared with experiment and with previous calculations where available.

The success of recent efforts to perform SCF calculations for ground-state polyatomic molecules has stimulated a need for at least equally satisfactory methods for molecular excited states. The present work is an attempt to find a suitable compromise between accuracy and economy of application so that investigation of excited-state potential surfaces can be carried out with some degree of reliability. The difficulties of open shell SCF calculations are widely recognized and have been discussed by Berthier.¹ For carefully selected problems, primarily those involving a single electron outside a closed shell core, SCF calculations

may be sufficient to yield good results for spectral excitation energies. However, for most molecular spectra the problem is more difficult and consideration must be taken of possible changes in correlation energy upon excitation. If one is interested in the change of molecular energy as a function of internuclear geometry, as in chemical reactions, the SCF result has the additional disadvantage that frequently the calculated energies misbehave at asymptotic values of the geometric parameters. The dissociation of molecular hydrogen in the MO approximation to a fictitious energy of equal weights of (H⁻ + H⁺) and of (2H) is the simplest example of this misbehavior.

In the present work it was hoped to evolve a relatively economic scheme which would somewhat overcome

(1) G. Berthier, "Molecular Orbitals in Physics, Biology, and Chemistry," P. Lowdin and B. Pullman, Ed., Academic Press, New York, N. Y., 1965.

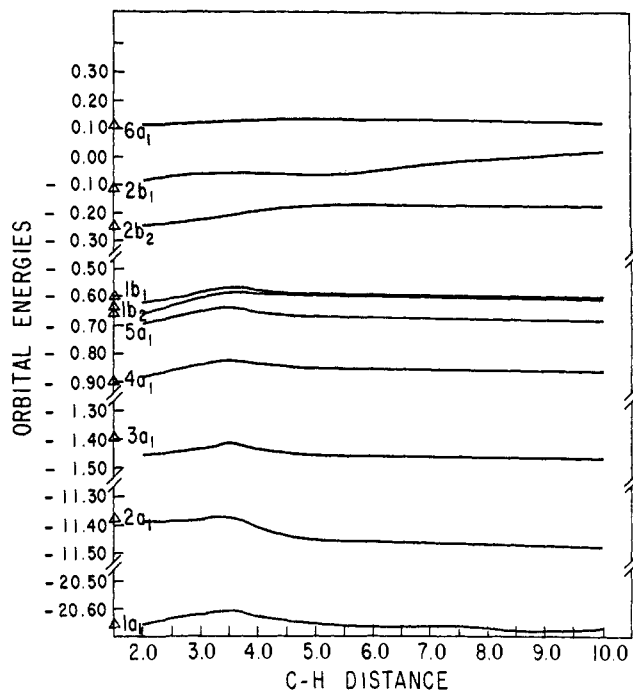


Figure 1. The change of molecular orbital eigenvalues as a function of increasing H to formyl distance is displayed for the first excited triplet state along the dissociation path described in the text.

these two difficulties of SCF calculations. The most straightforward solution to both of them is to add a configuration interaction calculation to be performed after the initial SCF solution has been reached. The slow convergence rate of CI calculations has been well established and is a target of much current research.²⁻⁴ With the constraint of employing only a few configurations, the present work does not seriously address itself to the correlation problem, but a few configurations are all that is required to rid the SCF solution of its misbehavior at large distances. It is then hoped that, by performing open shell SCF calculation and using the resultant orbitals as an expansion set for a small CI calculation, proper dissociation products will be obtained and that any very serious changes in correlation energy will at least be detected if not adequately calculated.

Hopefully, such a small CI scheme will produce reasonable values for excitation energies, that is for molecular spectra; it will yield information about the photochemical processes which molecular excited states may undergo, and it will enable a more general examination of ground-state reaction surfaces than has previously been possible. In order to accomplish these ends, it must be sufficiently inexpensive that several calculations as a function of internuclear geometry may be carried out. Compromises among the requirements of accuracy, reliability, and ease of computation must be made and it was decided to settle on a reasonable but smallish number of determinants to be included in the CI. In the present calculations about 50 determinants were considered suitable.

An interesting test of this straightforward and simple calculational scheme is presented by formaldehyde.

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 (3) A. Pipano and I. Shavitt, *Int. J. Quantum Chem.*, **2**, 741 (1968).
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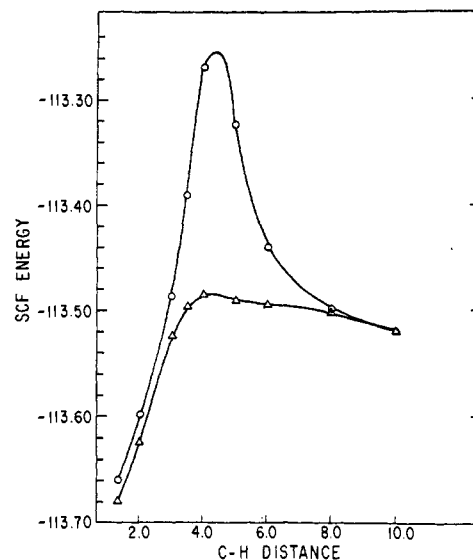


Figure 2. A view of the calculated SCF potential surface along the dissociation path described in the text is displayed for the triplet (Δ) and singlet (O) first excited states. The singlet state dissociation is incorrectly represented.

Formaldehyde was the first polyatomic molecule for which a full rotational analysis was completed⁵ and its spectrum has subsequently become the most thoroughly examined and understood of all polyatomic molecules.⁶ The primary photochemical process in formaldehyde has also been the subject of numerous investigations.⁷⁻¹² There is therefore a well-established experimental background with which to compare the calculated results. There have also been several nonempirical calculations on the ground state of formaldehyde¹³⁻¹⁶ and more recently several papers^{2,17,18} have considered calculations of the electronic excitation energies, while a qualitative molecular orbital theory discussion of formaldehyde photochemistry appeared earlier.¹⁹ The present work attempts to expand the scope of theoretical calculations to a representation of the potential surface relevant to the photodissociation process. The existence of these previous attempts at excitation energy calculations provides a theoretical comparison in the neighborhood of the ground-state equilibrium geometry. Ideally to get an impression of the potential surfaces relevant to photodissociation one would calculate many

- (5) G. H. Dieke and G. B. Kistiakowsky, *Phys. Rev.*, **45**, 4 (1935).
 (6) Review material is given in (a) G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967; (b) G. W. Robinson, "Methods of Experimental Physics, Vol. 3, Molecular Physics," L. Maston, Ed., Academic Press, New York, N. Y., 1962; (c) G. W. Robinson and V. Erdmanis DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958).
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 (13) J. M. Forster and S. F. Boys, *Rev. Mod. Phys.*, **32**, 303 (1960).
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 (15) P. Ros, *ibid.*, **49**, 4902 (1968).
 (16) D. B. Neumann and J. W. Moskowitz, *ibid.*, **50**, 2216 (1969).
 (17) N. W. Winter, T. H. Dunning, and J. H. Letcher, *ibid.*, **49**, 1871 (1968).
 (18) R. J. Buenker and S. D. Peyerimhoff, *ibid.*, **53**, 1368 (1970).
 (19) E. W. Abrahamson, J. G. F. Littler, and K.-P. Vo, *ibid.*, **44**, 4082 (1966).

Table I. Change of $2b_1$ Orbital upon Occupation

| Basis orbital | A_1 | A_2 |
|---------------|----------|----------|
| S_1 (O) | -0.00015 | -0.00020 |
| S_2 (O) | 0.01905 | 0.01527 |
| S_3 (O) | -0.00306 | -0.00457 |
| $2P_z$ (O) | -0.05953 | 0.57886 |
| $2P_y$ (O) | 0.00000 | 0.00000 |
| $2P_x$ (O) | -0.00096 | -0.04154 |
| S_1 (C) | 0.00027 | 0.00171 |
| S_2 (C) | -0.03508 | -0.19656 |
| S_3 (C) | 0.00530 | 0.03477 |
| $2P_z$ (C) | 0.00484 | -0.92185 |
| $2P_y$ (C) | 0.00000 | 0.00000 |
| $2P_x$ (C) | 0.00584 | 0.12890 |
| H_1 | -0.00689 | 0.07535 |
| H_2 | -0.00689 | 0.07535 |
| 3S | 0.02824 | -0.06517 |
| $3P_z$ | 0.78044 | -0.05503 |
| $3P_y$ | 0.00000 | 0.00000 |
| $3P_x$ | -0.62512 | 0.01100 |

points for variations in all of the internuclear geometries going toward the dissociation products of interest. Again, however, compromises must be made. The

= 31°) and with somewhat increased C-O bond distances. Preliminary SCF calculations on the ground-state geometry (both ground-state and excited-state electronic configurations), the excited-state geometry (both ground-state and excited-state electronic configurations), and intermediate geometries derived from the ground state by bending the hydrogens out of the plane by 15 and 31° (excited-state configuration), respectively, were performed. These latter were carried out with several C-H distances out to 4.0 bohr (au). There were quantitative differences between these latter two sets of energies and molecular orbitals, but they were qualitatively sufficiently similar that it was decided to follow only the 31° path to dissociation in the interest of economy. It is about the 31° path that the majority of the following discussion will refer, although occasional explicitly stated reference to the other geometries will be made.

SCF Calculations

Some of the results of the SCF calculations performed using Nesbet's method of symmetry and equivalence re-

Table II. Change of Singly Occupied Molecular Orbitals with Distance

| Basis orbital | R_{CH} | | | | | | |
|---------------|----------|----------|----------|----------|----------|----------|----------|
| | 2.0 | 3.0 | 4.0 | 5.0 | 8.0 | 10.0 | ∞ |
| $2b_1$ | | | | | | | |
| S_1 (O) | -0.00020 | 0.00001 | -0.00055 | 0.00068 | -0.00059 | -0.00034 | |
| S_2 (O) | 0.01288 | 0.00994 | 0.07716 | -0.08404 | 0.06837 | 0.04026 | |
| S_3 (O) | -0.00471 | 0.00098 | -0.01061 | 0.01382 | -0.01233 | -0.00710 | |
| $2P_z$ (O) | 0.65482 | -0.64194 | -0.41609 | 0.19596 | -0.02474 | -0.00617 | |
| $2P_y$ (O) | 0.00000 | 0.03226 | 0.17950 | -0.15026 | 0.01779 | 0.00605 | |
| $2P_x$ (O) | -0.02533 | 0.05433 | 0.13784 | -0.13479 | 0.06572 | 0.03310 | |
| S_1 (C) | 0.00161 | -0.00231 | -0.00381 | 0.00295 | -0.00106 | -0.00054 | |
| S_2 (C) | -0.18802 | 0.27205 | 0.47019 | -0.37692 | 0.14660 | 0.07455 | |
| S_3 (C) | 0.03242 | -0.04652 | -0.07537 | 0.05723 | -0.01999 | -0.01022 | |
| $2P_z$ (C) | -0.91643 | 0.86267 | 0.50976 | -0.22274 | 0.02923 | 0.00743 | |
| $2P_y$ (C) | 0.00000 | -0.04657 | -0.23174 | 0.18788 | -0.02191 | -0.00728 | |
| $2P_x$ (C) | 0.13076 | -0.17127 | -0.26854 | 0.20095 | -0.07096 | -0.03791 | |
| H_1 | 0.08488 | -0.10489 | -0.15260 | 0.09968 | -0.00178 | 0.00239 | |
| H_2 | 0.08488 | -0.19306 | -0.57464 | 0.77555 | -0.93992 | -0.98358 | 1.00000 |
| 3S | -0.07072 | -0.06309 | -0.39957 | 0.44361 | -0.32984 | -0.18493 | |
| $3P_z$ | -0.08143 | 0.16142 | -0.00693 | 0.00401 | -0.00051 | -0.00012 | |
| $3P_y$ | 0.00000 | 0.05854 | -0.00059 | 0.00008 | 0.00005 | 0.00008 | |
| $3P_x$ | 0.01542 | 0.04219 | 0.00216 | -0.00509 | 0.00335 | 0.00138 | |
| $2b_2$ | | | | | | | |
| S_1 (O) | 0.00000 | -0.00011 | 0.00035 | 0.00039 | 0.00033 | -0.00032 | -0.00033 |
| S_2 (O) | 0.00000 | 0.00661 | -0.02050 | -0.02039 | -0.01248 | 0.01229 | 0.01581 |
| S_3 (O) | 0.00000 | -0.00265 | 0.00882 | 0.00993 | 0.00862 | -0.00857 | -0.00812 |
| $2P_z$ (O) | 0.00000 | 0.01537 | -0.11288 | -0.16679 | -0.18602 | 0.18651 | 0.18858 |
| $2P_y$ (O) | -0.92352 | -0.81175 | 0.64028 | 0.63549 | 0.64477 | -0.64301 | -0.64847 |
| $2P_x$ (O) | 0.00000 | -0.00919 | 0.03261 | 0.06960 | 0.10132 | -0.10296 | -0.10712 |
| S_1 (C) | 0.00000 | 0.00015 | -0.00167 | -0.00295 | -0.00361 | 0.00363 | 0.00363 |
| S_2 (C) | 0.00000 | -0.03671 | 0.19795 | 0.34350 | 0.42391 | -0.42668 | -0.42983 |
| S_3 (C) | 0.00000 | 0.00222 | -0.03445 | -0.06015 | -0.07301 | 0.07345 | 0.07278 |
| $2P_z$ (C) | 0.00000 | -0.03279 | 0.14566 | 0.17299 | 0.17967 | -0.18027 | -0.18063 |
| $2P_y$ (C) | 0.25684 | 0.29728 | -0.43823 | -0.56267 | -0.61913 | 0.62041 | 0.62041 |
| $2P_x$ (C) | 0.00000 | 0.05298 | -0.17108 | -0.25589 | -0.29867 | 0.29993 | 0.29492 |
| H_1 | 0.29338 | 0.27815 | -0.27949 | -0.30704 | -0.31871 | 0.31762 | 0.31056 |
| H_2 | -0.29338 | -0.44350 | 0.46238 | 0.27660 | 0.02196 | -0.00391 | 0.00000 |
| 3S | 0.00000 | -0.12087 | 0.19177 | 0.15739 | 0.09802 | -0.09521 | -0.09138 |
| $3P_z$ | 0.00000 | 0.00723 | -0.00021 | -0.00255 | -0.00360 | 0.00361 | -0.00406 |
| $3P_y$ | 0.00280 | 0.02885 | 0.01846 | 0.01412 | 0.01239 | -0.01224 | 0.01395 |
| $3P_x$ | 0.00000 | 0.02436 | -0.00540 | -0.00512 | -0.00353 | 0.00340 | 0.00672 |

present work is directed at the photodissociation to radical products. The geometries of the ground and first excited states of formaldehyde are known to differ,⁶ the excited species being nonplanar (out of plane angle

restrictions are presented in Figures 1 and 2 and in Tables I and II. The basis set used was the Gaussian lobe function basis reported by Whitten for carbon and oxygen,²⁰

(20) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

a five-component Gaussian for the hydrogen atoms,²¹ a three-component 3s orbital centered at the midpoint of the carbonyl group,²² and a single component long-range (approximately 3p) p-type Gaussian also at the midpoint of the carbonyl group. Previous experience in calculations on SCF excited states²²⁻²⁴ suggested that the 3s and 3p orbitals may be required to adequately represent some of the states. The 3p orbitals were not found to participate significantly in any of the states considered here.

The SCF calculations are the base upon which the more interesting CI results are established, but a few of the results at this stage are sufficiently noteworthy to remark upon. For clarity and simplicity orbitals and states in the remainder of the discussion will be referred to by the symbol to which they correlate under the C_{2v} point group where the orientation suggested by Mulliken²⁵ ($X \perp$ to molecular plane) has been used. This is an established practice^{9c} and provides for simplicity of presentation although it must be remembered that during the dissociation process, the only correct designation is simply energy ordering.

Table I shows the expansion coefficients of the $2b_1$ orbital for the excited-state experimental equilibrium geometry of formaldehyde for two different electronic configurations. The column headed A_1 is that resulting for the ground-state electronic configuration $(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(1b_2)^2(1b_1)^2(2b_2)^2(2b_1)^0$, while that headed A_2 is the $2b_1$ orbital when it becomes populated in the first-excited state configuration $(1a_1)^2(2a_1)^2(3a_1)^2(4a_1)^2(5a_1)^2(1b_2)^2(1b_1)^2(2b_2)^1(2b_1)^1$. The result points out, in a very dramatic way, the well-known difficulty associated with using the ground-state virtual orbitals as an expansion set for a CI calculation. The $2b_1$ orbital is unoccupied in the A_1 configuration and consequently sees a field due to 16 electrons or the field appropriate to the formaldehyde negative ion. It is energetically desirable for this orbital to spread out in such a field and the $2b_1$ orbital has taken on a large amount of the diffuse character of the 3p orbitals included in the basis. When the orbital is occupied in the A_2 configuration, however, it experiences an entirely different kind of field, now due to 15 electrons, and changes its character completely, becoming the antibonding π^* orbital.

Table II and Figure 1 show the changes the molecular orbitals undergo along the adopted 31° dissociation path. The results displayed here are those obtained from the A_2 electronic configuration. In Table II the evolution of the $2b_1$ from the antibonding π^* orbital into a pure hydrogen 1s orbital at infinity, while picking up some fairly large 3s character in the intermediate regions, can be seen clearly. The $2b_2$ orbital is also singly occupied in the A_1 configuration and has become strikingly similar to the corresponding orbital of the formyl radical at 10.0-bohr separation between the carbon and the dissociating hydrogen atom. Earlier workers¹⁷ have remarked upon the fairly large contribution of carbon to this n orbital which is also apparent in these calculations.

Figure 1 shows that the field experienced by the more

deeply lying $1b_1$ and $1b_2$ orbitals at large separation is nearly that of a linear molecule as they are nearly degenerate (b_1 and b_2 would correlate to a π orbital for a linear molecule).

Figure 2 displays the potential surface calculated for the A_2 electronic configurations by the SCF results along the 31° dissociation path. The first points plotted in Figure 2 are for the excited-state equilibrium geometry. The triangles denote the triplet state curve for which the SCF was carried out; the open circles are the singlet state obtained using the same orbitals. The maximum energy for the singlet state is reached at 4.0 bohr, approximately twice the normal C-H bond distance. As the difference between the singlet and triplet surfaces is just twice the exchange integral between the two singly occupied orbitals, it is evident from Figure 2 that the maximum in the singlet potential curve is due to this exchange integral, a point which has been mentioned also in the photodissociation of H_2O .²² As the 3s character of the $2b_1$ orbital at this C-H distance reaches a maximum, the nature of the dissociation is surprisingly similar in the two cases. At larger distances than the maximum, the singlet SCF potential curve misbehaves badly, dissociating to the same asymptotic energy as the triplet state. Since the ground-state 1A_1 configuration must dissociate to the same limiting energy as the 3A_2 , the 1A_2 state should dissociate to an excited state of the formyl radical. There is no flexibility in the SCF wave function to provide for this possibility and the resulting misbehavior is a serious shortcoming of the SCF result for the interpretation of the photodissociation.

Configuration Interaction Calculations

The molecular orbitals obtained from the SCF calculations discussed above were then used as an expansion set of orbitals for a limited CI calculation. Whitten and Hackmeyer² have described a means of selecting the configurations to be included in a CI which is aimed at obtaining highly accurate excitation energy calculations. The present work is directed at a lower accuracy calculation in the interest of being able to trace out portions of molecular potential surfaces. The choice of configurations to be included becomes highly problematical and no mechanical scheme for choosing them can be offered; only a rationale can be suggested for the particular choices made.

Referencing the rationale for the choice of orbitals to the A_2 electronic configuration, examination of Figure 1, and similar information for the higher virtual orbitals not shown there gives a grouping of the orbitals according to their one-electron energies as the five deeply lying inner core orbitals, the higher two closed shell orbitals, the two singly occupied orbitals, two low-lying virtual orbitals, one higher virtual orbital, and then the remaining virtual orbitals which are very high. It was felt that a minimum number of configurations should be included and that it would be best to try to have a final solution which would be fairly sure of being stable to first order for both the ground-state and the first excited-state singlet and triplet. The following excitations were included again referenced to the A_2 electronic configuration. (a) Excitations out of the singly occupied orbitals into the lowest three virtual orbitals. (b) Single excitations from the upper two

(21) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1969).

(22) J. A. Horsley and W. H. Fink, *ibid.*, **50**, 750 (1969).

(23) W. H. Fink, *ibid.*, **49**, 5054 (1968).

(24) W. H. Fink, *ibid.*, **54**, 2911 (1971).

(25) R. S. Mulliken, *ibid.*, **23**, 1997 (1955).

closed shell orbitals to the singly occupied orbitals and the lower two virtual orbitals. (c) Excitations from one singly occupied orbital to the other. These excitations result in a total of 50 determinants in the CI.

Figure 3 displays the calculated potential surfaces for the first two singlet and triplet states. As for the SCF curves, the first point plotted corresponds to the excited-state equilibrium geometry, and the singlet curves are again represented by open circles and the triplets by triangles. Table III shows the weighting coefficients of

Table III. Coefficients of the Two Limiting Configurations of the First Excited Singlet as a Function of C-H Distance

| R_{CH} | $(2b_2)^1(2b_1)^0(6a_1)^0$ | $(2b_2)^0(2b_1)^1(6a_1)^1$ |
|---------------------|----------------------------|----------------------------|
| Excited state equil | 0.68740 | 0.00000 |
| 3.0 | 0.67257 | 0.00171 |
| 4.0 | 0.40658 | 0.08776 |
| 5.0 | 0.10978 | 0.16246 |
| 8.0 | -0.00168 | 0.69182 |
| 10.0 | 0.00009 | 0.70387 |

two configurations for the second singlet root as a function of increasing C-H distance. The essential character of the ground-state curve and the lowest triplet root are reasonably represented by their respective SCF determinants alone and consequently none of their CI weighting coefficients have been presented. The second singlet root (first excited singlet state) is more interesting as Table III shows. The configuration $(2b_2)^0(2b_1)^1(6a_1)^1$ at an infinite C-H distance would be describing the formyl radical in its first excited state and the ground-state hydrogen atom and would have a weighting coefficient of $1/\sqrt{2}$. This weight has almost been reached by 10.0 au. The configuration $(2b_2)^1(2b_1)^0(6a_1)^0$ is the dominant term in the first excited singlet state of formaldehyde near the equilibrium excited-state geometry. The smooth transition between these configurations afforded to this state by the CI treatment enables a proper description of the dissociation process as can be seen in Figure 3 where the ground state and first excited triplet have the same asymptotic energy whereas the first excited singlet and the second triplet have the same asymptotic energy. The transition from one configuration to the other sets in at about 4.0 bohr as can be seen in Table III. The missing weight at 5.0 au is borne predominantly by the configuration $(2b_2)^1(2b_1)^0(6a_1)^1$ as one might expect. Here in the CI calculation as well as in the SCF results, one sees that in the region of the dissociation path at about 4.0 au severe electronic rearrangement must take place for dissociation to proceed.

Comparison with Previous Work. It is somewhat difficult to relate the results of these calculations to the photochemical mechanism for dissociation to radical products proposed by Abrahamson, Littler, and Vo.¹⁹ In their qualitative molecular orbital discussion they used a localized orbital representation, whereas these calculations have been carried out with the canonical delocalized molecular orbitals. The configuration interaction calculations also go beyond the orbital approximation in order to adequately represent the surfaces at all values of the geometrical parameters. However from their proposed mechanism one would expect to find appreciable weight in the CI root of the

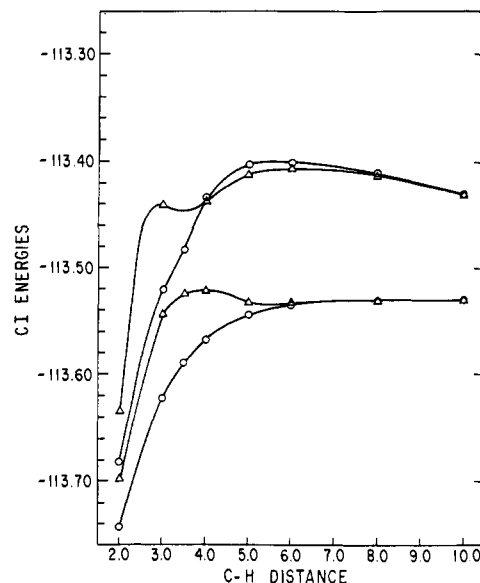


Figure 3. A plot of the calculated CI potential surface is presented along the dissociation path representative of the photolysis to radical products. The first two singlet states (O) and the first two triplets (Δ) are shown.

excited singlet state due to the configuration $(2b_2)^1(2b_1)^0(6a_1)^0(3b_2)^1$. This weight is not found in the calculations reported here. Instead, as mentioned above, the configuration $(2b_2)^1(2b_1)^0(6a_1)^1$ which they suggested as being important for the decomposition to molecular products seems to be effective in the decomposition to radical products as well.

Table IV presents a comparison of the calculated values with experimental values for certain asymptotic differences between the potential surfaces. The cal-

Table IV

| Transition | Experimental ^b | | Theoretical | |
|-------------------------------|---------------------------|--------|-------------|----------------|
| | Band limits | T_0 | SCF | CI |
| Spectral Data ^a | | | | |
| Formaldehyde | | | | |
| $^1A_1 \rightarrow ^1A_1$ | 28,300-43,500 | 28,188 | 26,100 | 23,900 |
| $^1A_1 \rightarrow ^3A_2$ | 25,300-27,800 | 25,194 | 20,850 | 19,500 |
| Formyl radical | | | CI(plat) | CI(∞) |
| $^2A' \rightarrow ^2A''(\pi)$ | 11,620-21,750 | 9,294 | 22,400 | 19,750 |
| Thermodynamic Data | | | | |
| H-CHO bond dissociation | 69.6-87 | | CI(plat) | CI(∞) |
| | | | 134 | 96.2 |

^a In cm^{-1} . ^b From ref 6a. ^c Lower value from ref 6a, upper limit ref 25. In kcal/mol.

culated vertical excitation energies for the formaldehyde molecule are presented. These should most nearly correlate with the experimental value at the Franck-Condon maximum although these are not listed. The column headed SCF is the difference in energy between SCF calculations for the ground and first excited state electronic configurations, both at the ground-state experimental geometry. The orbitals for both the excited states were obtained from the triplet state SCF. The results in the column headed CI were obtained by using the excited state triplet orbitals as an expansion set. The agreement between calculated and experimental values is not brilliant but is reputable. For the formyl

radical excitation two values are reported. The first, headed CI(plat), is that obtained when the dissociating H atom has reached 10.0-au distance from the carbon atom of the carbonyl group. The second value, headed CI(∞), is a calculation performed on the formyl radical alone, but at the same geometry obtained from the preceding calculation by simply removing the H atom. The calculated bond dissociation energy is that obtained by taking the difference in energy between the ground-state experimental geometry and the dissociated fragments; again two values are reported as for the formyl radical excitation energy. Agreement between calculated and experimental²⁶ values is at least semiquantitative.

A further sense of the reliability of the present calculations can be obtained by comparison with previous theoretical results. The near Hartree-Fock calculation of Neumann and Moskowitz¹⁶ produced an energy of -113.8917 , the minimal basis set STO calculation of Newton and Palke¹⁴ yielded -113.4496 , whereas the present SCF energy for the ground-state experimental geometry is -113.717 . The best values for the formaldehyde vertical excitation energies obtained by Whitten

(26) R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 4570 (1966).

and Hackmeyer² were 27,200 and 30,600 for the triplet and singlet excitation, respectively, while those obtained in the present work are 19,500 and 23,900.

As a summary conclusion of these comparisons one must acknowledge that the compromises which were made have degraded the results obtained perhaps somewhat below a level one might have hoped for, but the asymptotic differences remain semiquantitatively reliable. It would be unwise to place much faith in a calculation of the photolysis quantum yield based on the present potential curves, but they are probably semiquantitatively reliable and qualitatively represent the situation which must pertain experimentally. A comparison of the potential surface obtained along this dissociation path and that along a path to molecular products with inferences on the photolytic process will be the subject of a forthcoming paper.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. The hospitality of the Centre Européen de Calcul Atomique et Moléculaire and the computer time provided by CNRS for some of these calculations are also gratefully acknowledged.

All-Electron Nonempirical Calculations of Potential Surfaces. II. Dissociation of Formaldehyde into Molecular Products

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Abstract: Results of a modest configuration interaction calculation employing a set of expansion orbitals obtained from an excited state SCF calculation of the first triplet excited state of formaldehyde are reported. The primary processes in formaldehyde photolysis are discussed and a possible interpretation of the available conflicting results is presented in the light of the calculated representative dissociation paths on the molecular potential surfaces.

The present work is the second in a series of papers which employ configuration interaction following an SCF open-shell calculation as a theoretical tool to examine the potential surfaces of molecules undergoing reaction. These first two papers have considered the low-lying states of formaldehyde which should be important in the normal photolysis of this molecule. The preceding paper¹ elaborated in some detail on the method of calculation and the identical approach has been used here. The same basis set was used, the same open-shell Hamiltonian was employed, and the same configurations were included in the CI. The reader who is interested in these details is referred to ref 1.

The photolysis of formaldehyde has had a renewed interest recently as have many photolytic reactions associated with atmospheric contamination. As a prototype for the photochemistry of the carbonyl group, however, formaldehyde photolysis takes on an importance

beyond that which it deserves in its own right. Further, the recent discovery of formaldehyde in interstellar space² makes a detailed knowledge of its photochemistry of potential importance in understanding the primordial processes. The availability of detailed spectroscopic analysis of the formaldehyde spectrum³ will be an enormous aid in the detailed understanding of the primary photolytic process. A theoretical calculation of regions of the potential surface relevant to the photolysis seemed a natural complement to the spectroscopic information available. Presented here is the result of calculations along a dissociation path representative of cleavage to molecular products. A discussion of the

(2) L. E. Snyder, D. Buhl, B. Zuckerman, and P. Palmer, *Phys. Rev. Lett.*, **22**, 679 (1969).

(3) (a) V. Sethuraman, V. A. Job, and K. K. Innes, *J. Mol. Spectrosc.*, **33**, 189 (1970). (b) Review material is available in G. Herzberg, "Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1967.

(1) W. H. Fink, *J. Amer. Chem. Soc.*, **94**, 1073 (1972).