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 experimental[26] 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 Moskowitz[16] produced an energy of -113.8917, the minimal basis set STO calculation of Newton and Palke[14] 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 and Hackmeyer[2] 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.

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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 paper[1] 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 space[2] makes a detailed knowledge of its photochemistry of potential importance in understanding the primordial processes. The availability of detailed spectroscopic analysis of the formaldehyde spectrum[3] 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

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[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.

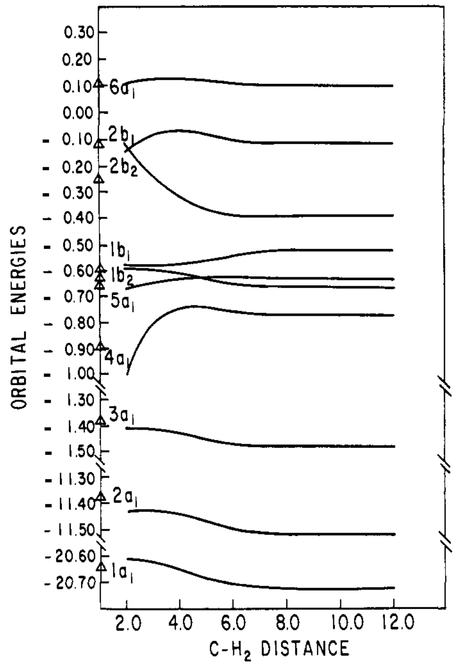

Figure 1. The change of molecular orbital eigenvalues along a path representative of dissociation to molecular products is displayed for the lowest triplet state.

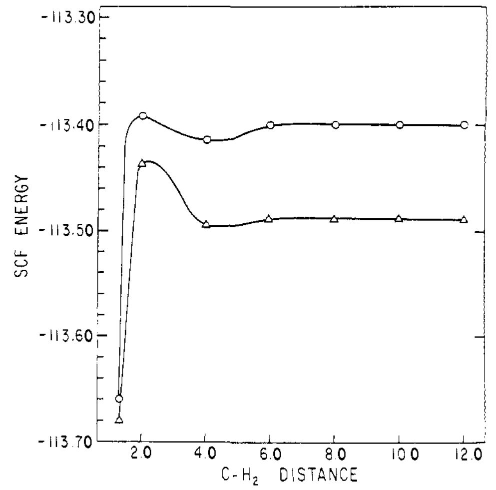

Figure 2. The calculated SCF potential surface is displayed for the first excited singlet (O) and triplet (Δ) states. For the molecular decomposition, the SCF calculation correctly represents the dissociation process.

two paths, to radical products and to molecular products, is also presented along with some inferences about the photolysis based upon the additional insight afforded by the theoretical data.

Results of Calculations

Ideally in the calculation of a photochemically interesting potential surface, one would perform calculations varying all geometric parameters and choosing the lowest energy conformation along each step to dissociation. Unfortunately such an approach is economically prohibitive. In the absence of being able to vary all geometric parameters, some arbitrary choice of a representative dissociation path must be made. The excited-state equilibrium geometry differs from that of the ground state by being nonplanar (out of plane angle = 31°) and with a somewhat longer C–O bond distance. The desired molecular dissociation products are H_2 and CO. It was decided to adopt a representative path by modifying the ground-state geometry by (a) bending the H's out of plane by 31°; (b) closing the HCH angle to such an extent that the H–H distance takes on the value found in molecular hydrogen; (c) moving the hydrogens symmetrically away from the carbon atom maintaining C_s symmetry at all times. Such an adopted path will artificially overemphasize the steep rise in energy close to the formaldehyde geometry, but if not too much quantitative importance is attached to this initial result, the dissociation should be qualitatively reasonably represented.

Figure 1 shows the changes in the molecular orbital one-electron energies for formaldehyde along the path described above. These were calculated for the triplet excited state. The open triangles on the ordinate mark the position of the corresponding molecular orbital energy in the ground-state experimental geometry, and the orbital designation appropriate to the ground-state C_{2v} geometry has been used throughout the following discussion. It is obvious that the initial distortion of the molecule has resulted in some strong electronic rearrangement, but it is also apparent that further and more severe rearrangement, as evidenced by changes in the molecular orbital energies, takes place as the path to dissociation is followed. In these calculations the orbitals through $1b_1$ were doubly occupied, orbitals $2b_1$ and $2b_2$ were singly occupied, and orbital $6a_1$ was unoccupied. That the orbital pairs ($1b_2$,$5a_1$) and ($2b_2$,$6a_1$) do not become degenerate at large C–H_2 distances is because orbital $6a_1$ remains unoccupied and consequently the full axial symmetry of carbon monoxide is not established. The highest doubly occupied orbital $1b_1$ becomes the hydrogen molecule bonding molecular orbital at large C–H_2 distances. The open-shell SCF calculation will dissociate to the $^{1,3}\Pi$ excited state of carbon monoxide at large C–H_2 distances.

Figure 2 shows the calculated SCF energies for the singlet (open circles) and triplet (triangles) excited states of formaldehyde as a function of increasing C–H_2 distance. The first point plotted in these curves corresponds to the excited-state experimental equilibrium geometry; subsequent points are along the dissociation path described previously. In contrast to the SCF results for dissociation to radical products, the proper dissociation products are obtained for the molecular decomposition because the H_2 fragment is a closed-shell sub system and the singly occupied orbitals correlate properly with the 2π levels of CO. As will shortly be seen the CI treatment modifies these potential surfaces but little. It was remarked earlier that little quantitative significance should be attached to the early part of the dissociation path so that the reality of the small depressions immediately beyond the dissociation barrier is questionable. A much wider ranging search over the potential surface would be required to categorically establish their presence.

Figure 3 shows the final theoretically calculated CI surfaces along the defined path for the ground state and the first two excited singlet (open circles) and triplet (triangles) states. All five states are described at large C–H_2 distances by the hydrogen molecule in its ground state with carbon monoxide in varying states of elec-

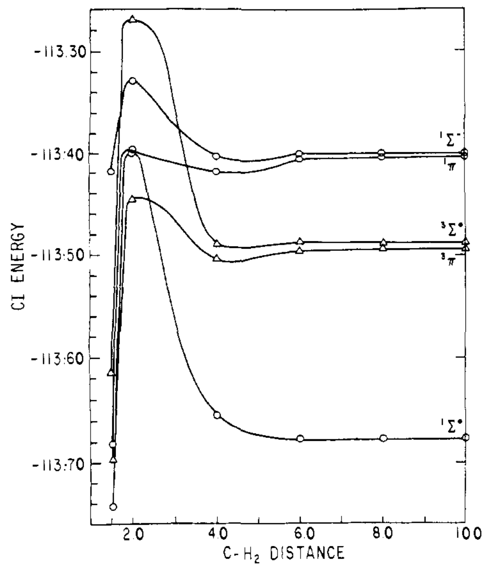

Figure 3. The calculated CI potential surfaces are displayed for the first three singlet (O) states and the first two triplet (Δ) states. The initial steep rise in energy is probably overemphasized because of the path chosen to represent the decomposition.

tronic excitation. For convenience the molecular term symbol for carbon monoxide associated with each respective surface has been placed at the extreme right of Figure 3. The calculations have qualitatively reproduced the dissociation very nicely if the asymptotic products obtained are a valid test. The relative ordering of the carbon monoxide states is exactly that found experimentally including even that of the $^1\Sigma^-$ state, the presence of which has only been inferred experimentally by certain perturbations found in the levels of the $^1\Pi$ state.[4]

Table I presents a more quantitative comparison of the calculated and experimental energies at the extreme right of Figure 3. Comparison of similar data at the extreme left of Figure 3 was made in ref 1. A CI calculation was performed on the isolated carbon monoxide molecule having the same CO internuclear distance as the fragment left behind by the dissociating H_2 molecule. The excitations calculated for it are given in the column headed CI(∞). In the column headed CI(plateau) are the excitations read directly from the right side of Figure 3. There is astonishingly good agreement between the calculated and experimental excitation energies. The agreement with the experimental thermodynamic value[5] for the dissociation process is quantitatively poor. The calculations do maintain the qualitative ordering of the relative energies of radical products compared with molecular products as may be seen by glancing at Table IV of ref 1 or visually comparing Figure 3 of ref 1 with Figure 3 presented here.

Table I

Transition	Exptl (T_0)	CI (plateau)	CI (∞)
Spectral Data[a] (Carbon Monoxide)			
$^1\Sigma^+-^1\Pi$	65,075	60,100	61,400
$^1\Sigma^+-^3\Pi$	48,688	40,400	43,900
$^1\Sigma^+-^3\Sigma^+$	55,901	41,500	55,900
Thermodynamic Data[b]			
$\Delta E[(H_2 + CO) - (H_2CO)]$	7.5[c]	41.5	52.9

[a] In cm^{-1}. [b] In kcal/mol. [c] From ref 5; $\Delta H_f°_{298}$ corrected for zero-point energies and change in *PV* term.

Formaldehyde Photochemistry. Four primary processes (eq I–IV) have been discussed in the photochemistry of formaldehyde.[6–8]

$$H_2CO\ (^1A_1) \xrightarrow{h\nu} H_2CO\ (^{1,3}A_2)$$

$$H_2CO\ (^{1,3}A_2) \longrightarrow H + HCO \qquad (I)$$

$$H_2CO\ (^{1,3}A_2) \longrightarrow H_2 + CO \qquad (II)$$

$$H_2CO\ (^{1,3}A_2) + H_2CO\ (^1A_1) \longrightarrow H_2COH + HCO \qquad (III)$$

$$H_2CO\ (^1A_1) \xrightarrow{h\nu} 2H + CO \qquad (IV)$$

Process IV will presumably be important only with very short wavelength radiation. The relative importance of the other three processes in the wavelength region of usual photolytic studies is in somewhat of a state of confusion. The difficulties begin because of the absence of a definitive measurement of the H–HCO bond strength, reported values ranging from 68 to 92 kcal/mol.[3b] Walsh and Benson[9] obtained a value of 87 kcal/mol for the bond strength and therefore suggested that process III could account for the photolysis of formaldehyde at 365 nm since predissociation could not occur at this wavelength if the bond dissociation energy were 87 kcal/mol. McQuigg and Calvert[10] concluded, however, that their data demanded setting an upper limit of 85 kcal/mol which could possibly be reduced to 81 kcal/mol, in which case it became unnecessary to include process III in the photolysis.

Both inhibition methods[6,11] and isotope methods[10,12] have been used to assess the relative quantum yields of processes I and II with conflicting results. The former concluded that process II was favored at long wavelengths while the latter concluded that process I was favored at long wavelengths. One may safely conclude that formaldehyde photolysis is a complex reaction. The elucidation of the intricacies of the mechanism of the reaction may require a detailed analysis of the decay processes experienced by individual vibrational bands and levels. The results of Yeung and Moore[13] suggest that the technology of such a study is available and that such experiments may shortly be feasible. Certain reasonable speculations regarding the photolysis of formaldehyde can be made by a combination of available spectroscopic and thermodynamic information and the calculated representative potential surfaces for processes I and II.

Photolysis to Radical Products. If one assumes that the low-energy photolysis of formaldehyde (λ >350 nm) to radical products occurs through a predissociation

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(4) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," Van Nostrand, Princeton, N. J., 1950.

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(11) E. Gorin, *J. Chem. Phys.*, 7, 256 (1939).

(12) R. Klein and L. J. Schoen, *ibid.*, 24, 1094 (1956).

(13) E. S. Yeung and C. B. Moore, *J. Amer. Chem. Soc.*, **93**, 2059 (1971).

mechanism, there are certain necessary consequences. The initial excitation almost certainly will be to a singlet state. Robinson and DiGiorgio[14] pointed out that excitation with these wavelengths necessarily involved a hot band. A temperature-dependent chemical yield of the photolysis is therefore indicated. It is possible that the photolysis mechanism would involve transfer to the first excited triplet surface followed by predissociation of that triplet to ground state H and HCO products, but a simpler mechanism would involve transfer to the ground-state potential surface with subsequent direct dissociation. Such a mechanism is simpler since it would not necessitate involving spin–orbit coupling to effect the transfer to the triplet state. However, the final products of both mechanisms are the same; it may be an academic point as to which is operative since distinguishing between the two would probably require an intricate coincidence experiment. Since the hot bands responsible for the absorption at these wavelengths involve high rotational sublevels of the 0^+ or $0^+ + \nu_2'$ bands,[14] one might expect formyl radicals from such levels to have high rotational energy.

If one assumes the mechanism proposed by Walsh and Benson[9] and by DeGraff and Calvert,[6] process III, the initial acquisition of energy would of course be the same and be highly temperature dependent. However, because III involves molecular collisions, the yield should be a function of total gas pressure and would also lead to a more thermalized distribution of the rotational energy among the reaction products.

Higher energy photolysis (λ <350 nm) to radical products must involve a predissociative mechanism. As the energy is raised, more predissociating paths to ground-state products would become available. At some wavelength lying between 313 and 280 nm (the range is occassioned by the maximum range of reported values for the H–HCO bond energy), dissociation to an electronically excited formyl radical will become possible. Emission from this species would in principle become observable while the H atoms formed would have very low translational energy. If predissociation remained predominantly to ground-state products, no emission from formyl radicals could be observed and quite energetic H atoms would be formed, the H atom and formyl radical sharing something between 10 and 30 kcal/mol of energy in their nuclear motions.

Photolysis to Molecular Products. Decomposition to molecular products is thermodynamically possible at very low energies as may be seen from the data of Table I, something less than 10 kcal/mol being required. However, to execute the nuclear motion to dissociated products two normal vibrational modes must be simultaneously excited, an angle bending mode to bring the hydrogens together and the C–H symmetric stretching mode to move them away from the CO fragment. The low-energy requirement suggests that photolysis to molecular products may be possible by irradiation with near ir wavelengths and also that some vibrational combination bands of the ground-state molecule may be predissociated. The possibility of a bimolecular reaction to molecular products at low energies should not be overlooked and as in the case of radical products, one would expect a more thermal distribution of the available energy if the bimolecular mechanism is dominant.

At higher available photolysis energies, the extra energy will probably be carried off within the nuclear motions of the products as the first excited singlet state of carbon monoxide does not occur until about 65,000 cm^{-1} above the ground state, and even the first triplet dissociation could not become operative until a radiation wavelength of about 185 nm was used. The excess energy would be predominantly carried away by translation and vibration of H_2, with that carried away by CO being predominantly rotational and vibrational. Unfortunately the details of the shape and height of the potential surfaces along this dissociation path will severely affect the rate of this process and, as mentioned earlier, the calculated values are not sufficiently refined to be reliable to the degree required for a quantitative treatment of the dissociation rate.

Competition between Processes. A possible interpretation of the relative importance of processes I and II can be obtained by mentally superimposing Figure 3 of ref 1 on Figure 3 of this work. The qualitative features of the two dissociation paths are reflected by the calculated surfaces. The ease of abstraction of H from ground-state formaldehyde is indicated by the absence of any activation barrier in the ground-state surface as a function of increasing HCO–H distance. The possibility of a low-energy Herzberg type II predissociation (same electronic state) to molecular products while forbidding the radical dissociation until higher energy is clearly evident by the asymptotes reached at the right by the ground-state curves. By contrast, the possibility of a second electronic state becoming operative for the radical dissociation, but not for the molecular dissociation, is also apparent. A molecule excited to the first excited singlet potential surface above the H–CHO bond dissociation energy can transfer to the ground-state singlet surface or to the first triplet surface. If it transfers to the ground-state surface, it will still find itself inside a bound well as far as process II is concerned and it must yet undergo a Herzberg type II predissociation or a barrier tunneling process to obtain dissociation. However, for process I, the transfer to the ground-state potential surface leads to immediate dissociation. One would expect a much smaller temperature independent preexponential factor for the rate of process II than that for process I. If the electronically excited molecule should be below the bond dissociation energy threshold, however, process I is not an available option and process II is the only predissociation path available to it. Dissociation may occur but at a much slower rate *via* a tunneling process to molecular products. The presence of an efficient quenching gas to rapidly cool the excited molecule, removing some vibrational energy so that it was below the bond dissociation energy threshold, could enhance process II, making it a dominant process even though process I were favored. DeGraff and Calvert[6] considered this possibility for reconciling their results but felt propylene would not be an effective quencher.

When this work was undertaken it was hoped that there would be a sufficiently large qualitative difference between the two representative dissociation paths that an unequivocal prediction could be made of the trend of the ratio of quantum yields ϕ_{I}/ϕ_{II} with increasing

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[14] G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958).

wavelength of irradiation. Although the pathways were found to be qualitatively different, it is possible to construct qualitative arguments based on these differences which argue nearly equally well for either trend of the ratio ϕ_I/ϕ_{II} with increasing wavelength. The discussion above has pointed out that the calculated potential surfaces are not regarded as sufficiently reliable to be used uncritically for the calculation of quantum yields so that an unequivocal prediction from these data cannot be made.

It is believed, however, that the qualitative interpretation of the photodecomposition along the calculated dissociation pathways is more acceptable if the arguments favoring a decrease in the ratio ϕ_I/ϕ_{II} with increasing wavelength are given. The possibility of a Herzberg type II predissociation or a tunneling mechanism operating for process II at energies below the threshold required by process I is the central feature of this interpretation. At energies in excess of the threshold for process I, but below the barrier height for process II, the radical decomposition, process I, should become dominant because of the simpler nuclear motion involved in that dissociation. That an increasing ratio of ϕ_I/ϕ_{II} with increasing wavelength is found in the higher aldehydes can be understood in this interpretation because the groups involved in the tunneling mechanism are so much more massive that this mode is effectively blocked to them.

Summary

The theoretically calculated potential surfaces for dissociation paths representative of processes I and II coupled with known spectroscopic and thermodynamic data suggest a photolysis mechanism which is a complex competition among several processes and which may be critically dependent on experimental conditions. There may be combination tones of vibrationally excited ground-state formaldehyde which have access to a dissociation path to molecular products *via* a barrier tunneling mechanism. These levels may be activated by a combination of exciting radiation and the presence of a fairly efficient quenching gas. The radical product decomposition can occur *via* either the triplet excited state surface or the ground-state surface, but the latter can proceed in the absence of strong spin orbit coupling. Singlet excited molecules with energies corresponding to excitations of somewhere between 313 and 280 nm above the ground state may predissociate to an electronically excited level of the formyl radical.

In view of the limitations on the theoretical calculations reported here and the current confusion in the determinations of relative quantum yield of processes I and II as a function of wavelength, the speculative nature of the interpretation given here need hardly be stressed. The calculations produced surfaces which were qualitatively or semiquantitatively correct at asymptotic values of the geometrical parameters, however, and the interpretation may be able to reconcile the divergent experimental results to an extent.

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