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THEORETICAL STUDIES OF FORMYL RADICAL FORMATION
IN SELECTED COMBUSTION REACTIONS
Final Report

W.A. Lester, Jr. and M. Dupuis

January 1984

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Lawrence Berkeley Laboratory
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Final Report to the
National Aeronautics and Space Administration

Theoretical Studies of Formyl Radical Formation in
Selected Combustion Reactions
(Contract Number A861308)

William A. Lester, Jr., Principal Investigator
Michel Dupuis, Co-Principal Investigator

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I. Proposal Summary

The main component of the proposal dealt with ab initio studies of reaction pathways for selected reactions of combustion chemistry, with emphasis on formyl (HCO) radical formation. Mechanisms leading to HCO in the electronically excited ($A^2\Pi$) state in the reactions $H_2CO + OH$, $CH_2 + O$, and $CH_2 + OH$ were of special interest because of the possible role of that species in flame spectra.

A second component of the proposal dealt with program development of ab initio quantum mechanical methods.

The last component involved exchange of knowledge in the above and related areas with members of the quantum chemistry group of NASA Ames Research Center.

II. Accomplishments

i. Reaction Pathways Studies

Correlation diagrams for the three reactions mentioned in Sec. I were developed and presented in the original proposal. Of the three, the $H_2CO + OH$ reaction was given the most attention because of relevance to the NASA mission. The essential features of the potential energy surface leading to ground state HCO radical were fully characterized using multiconfiguration Hartree-Fock (MCHF) and configuration interaction (CI) techniques. The relative energies of the reactants, transition state, and products were found to be in semiquantitative agreement with experimental data. The structures of stationary points are expected to be accurate, as molecular geometries are usually not very sensitive to

the level of calculation. The findings of this study should prove to be a useful complement to the experimental study of Stief, et al.¹ of the NASA Goddard Space Flight Center on the OH + H₂CO reaction rate constant. A full account of this work is given in Appendix A.

Qualitative considerations given in the proposal and expanded upon in Appendix A suggest that no direct reaction pathway with small activation energy connects the ground state reactants to the electronically excited HCO products. Characterization of the electronically excited surface was attempted but not achieved. The difficulty is associated with this state being the second one of doublet spin. The computed wavefunction was found to collapse to the ground state even with the use of a fully quadratic self-consistent-field technique. The state averaging technique did not yield a transition state structure because the ground state surface and the excited state surface were found to have very different slopes and curvatures. A weighted average energy of the two states showed very erratic behavior even with weights highly favoring the second state.

Similar difficulties were encountered in the study of the O + CH₂ reaction. The dissociation channel H₂CO → HCO + H leads to excited HCO as shown in the proposal and corresponds to the the second state of either singlet or triplet spin. Again, the wavefunction was found to collapse to the ground state. Finally, no attempt was made to characterize the CH₂ + OH reaction pathways leading to excited HCO, in light of the unsuccessful efforts on the two aforementioned systems.

The reaction of oxygen atoms with formaldehyde is another process which leads to HCO formation. This hydrogen atom abstraction reaction was characterized during the contract period, and the results of this study are also included in Appendix A. Another reaction channel for this system is believed to involve oxygen atom addition followed by H atom migration and fragmentation. The H atom migration process was investigated, and the findings are given in Appendix B.

Manuscripts based on Appendices A and B are in preparation for submission for publication in the Journal of Chemical Physics.

ii. Program Development

The most recent version of the computer code HONDO designed for the study of molecular structure and reaction mechanisms was made to run on the CDC 7600 and CRAY 1S computers of the Ames Research Center. The program was fully operational at the end of the contract period, and is available for use by the quantum chemistry group at the Ames Research Center.

The calculations described previously were carried out in part with HONDO, for the determination of the stationary points of the potential energy surfaces using multiconfiguration Hartree-Fock wavefunctions, and with configuration interaction programs available at Ames Research Center.

iii. Scientific Exchange

Michel Dupuis visited the Ames Research Center once a week. Initially the visits were needed to complete the implementation of the HONDO code on the Ames computers. These visits resulted in fruitful scientific exchanges including:

a informal discussions with Dr. R. Jaffe of NASA Ames on quantum mechanical calculations on $\text{Be} + \text{HF}$, $\text{Sr} + \text{HF}$, and on polymers.

b informal discussions with Dr. A. Komornicki of Polyatomic Research Institute (Sunnyvale) who is under contract with NASA. Calculations of the ground state reaction pathway for $\text{OH} + \text{CO}$ (a system of combustion interest) were discussed, as well as calculations of the dipole moments of O_3 . Dr. Komornicki carried out calculations on $\text{OH} + \text{CO}$ using the HONDO computer code. The discussions on O_3 resulted in calculations carried out by M. Dupuis to be published in collaboration with Dr. Komornicki.

NASA will be appropriately cited in all publications arising from this contract and reprints forwarded to the cognizant offices.

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APPENDIX A

LBL-17301

HYDROGEN ATOM ABSTRACTION FROM ALDEHYDES:
OH + H₂CO AND O + H₂CO

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Supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

Abstract

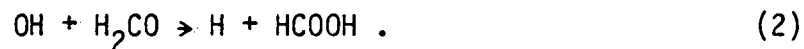
The essential features of the potential energy surfaces governing hydrogen abstraction from formaldehyde by oxygen atom and hydroxyl radical have been characterized with ab initio multiconfiguration Hartree-Fock (MCHF) and configuration interaction (CI) wavefunctions. The results are consistent with a very small activation energy for the $\text{OH} + \text{H}_2\text{CO}$ reaction, and an activation energy of a few kcal/mole for the $\text{O} + \text{H}_2\text{CO}$ reaction. In the transition state structure of both systems the attacking oxygen atom is nearly collinear with the attacked CH bond.

I. Introduction

Formaldehyde is an important intermediate in hydrocarbon oxidation. However, rate constants for loss processes of formaldehyde are uncertain. Temperature studies¹⁻³ for OH + H₂CO products show large discrepancies in preexponential factors and activation energies. In fact the reactive channels for this reaction are not firmly established.^{3,4} The mechanism of the reaction has been assumed to be H-atom abstraction



but addition followed by H-atom elimination can not be ruled out



The mechanism of the O + H₂CO reaction has also been assumed to be H-atom abstraction⁵



However, the observation of CO₂ as a product of the O + H₂CO reaction led Chang and Barker⁶ to suggest a pathway involving addition followed by H-atom migration



Our theoretical study⁷ of the H-atom migration step (5) indicates that

it has a high energy barrier, and most likely is not the second step in Chang and Barker's multistep mechanism.

We present here an ab initio study of the H-atom abstraction channels (1) and (3). The paper is organized as follows: the computational method is described in Section II and the results are presented and discussed in Section III.

II. Computational Method

Ab initio Hartree-Fock (HF), multiconfiguration Hartree-Fock (MCHF), and configuration interaction (CI) calculations were carried out to characterize the essential features of the potential energy surfaces. Correlation diagrams for $\text{OH} + \text{H}_2\text{CO}$ and $\text{O} + \text{H}_2\text{CO}$ are shown in Figs. 1 and 2. For both systems the abstraction reaction proceeds in the plane of the formaldehyde molecule. The potential energy surface for $\text{OH} + \text{H}_2\text{CO}$ has ${}^2\text{A}'$ symmetry. The energy surfaces of ${}^3\text{A}'$ and ${}^3\text{A}''$ symmetries connect the reactants and products for $\text{O} + \text{H}_2\text{CO}$. Classical valence bond structures of the two systems are shown in Fig. 3. In the $\text{OH} + \text{H}_2\text{CO}$ structure of ${}^2\text{A}'$ symmetry, the unpaired electron of the hydroxyl radical attacks the CH bond of formaldehyde in the plane of the molecule. The repulsive ${}^2\text{A}''$ surface corresponds to the situation where the unpaired electron of OH lies outside the molecular plane. In this case a lone pair of electrons on OH approaches the CH bond resulting in a strongly repulsive interaction.

For the $O + H_2CO$ system there is a second unpaired electron on the attacking oxygen atom (absent in the $OH + H_2CO$ system because of the OH bond). The orientation of this second unpaired electron dictates the symmetry of the energy surfaces. When this electron lies in the molecular plane, the surface has $^3A'$ symmetry, and when it lies outside the molecular plane, the surface is the lower one of $^3A''$ symmetry. The higher strongly repulsive $^3A''$ surface arises when the 2p electron pair on the oxygen atom approaches the CH bond. The second unpaired electron in $O + H_2CO$ is not actively involved in H-atom abstraction. It can be viewed as undergoing only spin recoupling. This situation is reminiscent of H-atom abstraction from H_2 by O and OH. The energy barrier in $O + H_2$ was found to be ~6 kcal/mole higher the barrier than in $OH + H_2$.^{8,9} Thus we expect the energy barrier in $O + H_2CO$ to be slightly higher than the barrier in $OH + H_2CO$. However, the energies and critical structures of the $^3A'$ and $^3A''$ surfaces of $O + H_2CO$ are expected to be very similar.

For the $OH + H_2CO$ ($^2A'$) and $O + H_2CO$ ($^3A'$) surfaces structures of the reactants, transition state, and products were fully optimized using a MCHF wavefunction which accounted for the most important configuration mixing effects due to bond breaking and bond formation. The dots in Fig. 3 represent those electrons which participate actively in the abstraction process for the two systems. During the reaction the two electrons of a CH bond in H_2CO unpair, one electron forms a bonding pair with the unpaired electron on the attacking oxygen atom, and the

other electron remains unpaired on the carbon atom to form the formyl radical HCO. We note that the electron pair of each of the CH bonds in H₂CO must be treated equivalently in the wavefunction of both systems in order to give a symmetrical structure of the reactants. Similarly the electron pair of the hydroxyl radical of OH + H₂CO must be treated at a comparable level of theory in order to give a symmetrical structure for H₂O.

We can describe the CH bonds in H₂CO and the OH reactant and in H₂O each with two orbitals (bonding and antibonding), and the unpaired electrons on OH and O each by one orbital. A MCHF wavefunction which includes all the configurations obtained by distributing seven (six) electrons among seven (six) active orbitals in all possible ways consistent with doublet (triplet) spin, provides a qualitatively correct description of the reactants, transition states, and products for OH + H₂CO (O + H₂CO).

For all the MCHF determined stationary points on the energy surfaces, we carried out HF and CI calculations. The CI calculations included all singly and doubly excited configurations interacting with the HF configuration.¹⁰ An estimate of the contributions from higher excitation was calculated using Davidson's correction.¹¹ It is worth noting that the HF wavefunction was obtained without difficulty at the geometry of the MCHF transition state. However, no HF transition state could be determined. The reason for this is that the HF wavefunction cannot adequately describe bond breaking and bond formation.^{12,13}

All calculations were done with a double zeta plus polarization (DZP) basis set¹⁴ using HONDO¹⁵ and Siegbahn's GUGA¹⁶ computer codes.

III. Computational Results

a. The MCHF (DZP) Structures

The optimized MCHF (DZP) structures of the stationary points are given in Table I for OH + H₂CO and Table II for O + H₂CO following the nomenclature of Fig. 4. The bonding-antibonding orbital pair representation of the CH and OH bonds leads to bond lengths ~0.02Å longer than the corresponding experimental bond lengths. This effect is usually observed in valence-bond type wavefunctions which typically overemphasize left-right electron correlation effects.

The bond lengths of the transition-state structure of the bond being broken and of the bond being formed depend on the energies of the reaction. For OH + H₂CO the calculated exothermicity is -14.2 kcal/mole, compared to the experimental heat of reaction of -32.0 kcal/mole. The true transition state should occur slightly earlier on the reaction pathway but not very far from the calculated structure. For O + H₂CO, the reaction is calculated to be endothermic by 10.0 kcal/mole, while the experimental heat of reaction is -15.2 kcal/mole. Again the true transition state should occur earlier on the reaction pathway but the calculated structure is qualitatively correct. For both the OH + H₂CO and O + H₂CO transition state structures, the attacking oxygen atom is nearly collinear with the attacked CH bond. This feature

was previously found in the $O + H_2$ and $OH + H_2$ reactions,^{8,9} and in the $H + H_2CO$ reaction.¹⁷ It is in accord with one model of the activated complex for $OH + H_2CO$ put forth by Stief, et al.³ However, the calculated $HO...H$ distance (1.30\AA) differs significantly from the large distance ($\sim 4.0\text{\AA}$) in the loose complex suggested by these authors.

b. Relative Energies

The relative energies calculated with the HF, MCHF, and CI wavefunctions for the various species are given in Table III. The HF and CI energies were calculated at the MCHF (DZP) optimized geometries. The energies denoted SDHF correspond to CI wavefunctions including all singly and doubly excited interacting configurations. The energies denoted SDQHF are the CI energies corrected for effects of quadruple excitations. The experimental activation energies and heats of formation are also given. Also included in Table III are the results of Harding and Schatz¹⁷ for $H + H_2CO$. Their SOGVB wavefunction is nearly equivalent to our MCHF wavefunction.

The HF activation energies are 28.3 kcal/mole for $OH + H_2CO$ and 42.4 kcal/mole for $O + H_2CO$. The corresponding SDHF values are 10.7 kcal/mole and 19.1 kcal/mole. Thus the correlation corrections from singly and doubly excited configurations amount to 17.6 kcal/mole for $OH + H_2CO$ and 23.3 kcal/mole for $O + H_2CO$. The MCHF activation energies are 16.6 kcal/mole and 30.4 kcal/mole, respectively. The MCHF wavefunctions take into account the most important electron correlation

effects due to bond breaking and bond formation. Remaining electron correlation effects could be described well by CI wavefunctions that include all single and double excitations from the MCHF wavefunctions. The energy lowering due to these remaining electron correlation effects is estimated to be less than the 17.6 kcal/mole for $\text{OH} + \text{H}_2\text{CO}$ and the 23.3 kcal/mole for $\text{H} + \text{H}_2\text{CO}$ obtained with a single configuration as reference. Similar behavior of the correlation energy correction has been observed in the molecular dissociation of formaldehyde.¹⁸ In addition, the effects of basis set errors on the activation energy should also be taken into account. These considerations point to theoretical activation energies in accord with the experimental values.

We note that for all wavefunctions the activation energy is larger for $\text{O} + \text{H}_2\text{CO}$ than for $\text{OH} + \text{H}_2\text{CO}$, in accord with the discussion of Section II. In the former system, the reaction proceeds via spin decoupling of the two unpaired electrons of the attacking oxygen atom. In the latter case no spin decoupling occurs since one electron of oxygen atom is tied up in the electron pair of the OH bond.

The relative energies calculated for $\text{OH} + \text{H}_2\text{CO}$ and $\text{O} + \text{H}_2\text{CO}$ are consistent with the results of Harding and Schatz for $\text{H} + \text{H}_2\text{CO}$. While the configuration mixing included in the MCHF, SOGVB, and other correlated wavefunctions play a key role in determining the transition state structure, as presently applied the MCHF method is unable to provide quantitatively accurate relative energies.

IV. Conclusions

We have characterized the essential features of the potential energy surfaces for hydrogen atom abstraction from H_2CO by OH and by O. The calculated relative energies are in semiquantitative agreement with experimental values. They are consistent with a very small activation energy for the OH + H_2CO reaction, and an activation energy of a few kcal/mole for the O + H_2CO reaction. The geometries of reactants, transition state, and products are generally less sensitive to the method of calculation than the relative energies of these species. The computed structure of the transition state should therefore be useful for the theoretical interpretation of the observed temperature dependence of the reaction rates. In the transition state structure of both systems, the attacking oxygen atom is nearly collinear with the attacked CH bond.

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Table I MCHF(DZP) Structures^a of OH + H₂CO Stationary Points

	H ₂ CO + OH	-TST- ^b	HCO + H ₂ O
R(O ₁ C ₂)	1.18837	1.17375	1.16191
R(C ₂ H ₃)	1.11540	1.12012	1.13085
∠(O ₁ C ₂ H ₃)	122.06	125.14	126.65
R(C ₂ H ₄)	1.11540	1.26937	∞
∠(O ₁ C ₂ H ₄)	122.06	122.57	-
R(H ₄ O ₅)	∞	1.29634	0.96790
∠(C ₂ H ₄ O ₅)	-	177.79	-
R(O ₅ H ₆)	0.97934	0.97943	0.96790
∠(H ₄ O ₅ H ₅)	-	96.29	103.62
E(² A')	-189.358235	-189.331781	-189.380797

a. Bond lengths in Å, angles in degrees, energy in a.u. See Fig. 4 for nomenclature.

b. TST = transition state.

Table II MCHF(DZP) Structures^a of OH + H₂CO Stationary Points

	H ₂ CO + OH	-TST- ^b	HCO + H ₂ O
R(O ₁ C ₂)	1.18837	1.16637	1.16088
R(C ₂ H ₃)	1.11540	1.12015	1.13095
∠(O ₁ C ₂ H ₃)	122.06	126.29	126.68
R(C ₂ H ₄)	1.11540	1.35489	∞
∠(O ₁ C ₂ H ₄)	122.06	121.54	-
R(H ₄ O ₅)	∞	1.22739	0.97922
∠(C ₂ H ₄ O ₅)	-	179.47	-
E(³ A') ^c	-188.730248	-188.681826	-188.714064

- Bond lengths in Å, angles in degrees, energy in a.u. See Fig. 4 for nomenclature.
- TST = transition state.
- For this system the d function exponent on the oxygen atoms was 0.85.

Table III Relative Energies of
Reactants, Transition State, and Products (kcal/mole)

Wavefunction	H ₂ CO + OH	-TST-	HCO + H ₂ O
MCHF	0.0	+16.6	-14.2
HF	0.0	+28.3	- 8.8
SDHF	0.0	+10.7	-20.3
SDQHF	0.0	+ 5.5	-22.1
EXP	0.0	+ 0.2	-32.0
Wavefunction	H ₂ CO + O	-TST-	HCO + HO
MCHF	0.0	+30.4	-10.2
HF	0.0	+42.4	+12.8
SDHF	0.0	+19.1	+ 0.3
SDQHF	0.0	+13.4	- 2.4
EXP	0.0	+ 3.1	-15.2
Wavefunction	H ₂ CO + H	-TST-	HCO + H ₂
SOGV ^a	0.0	+24.0	+ 3.7
GVBCI	0.0	+17.0	- 6.6
POLCI	0.0	+12.7	- 7.7
EXP	0.0	+ 4.1	-14.2

a. All data for H₂CO + H reaction taken from Ref. 17.

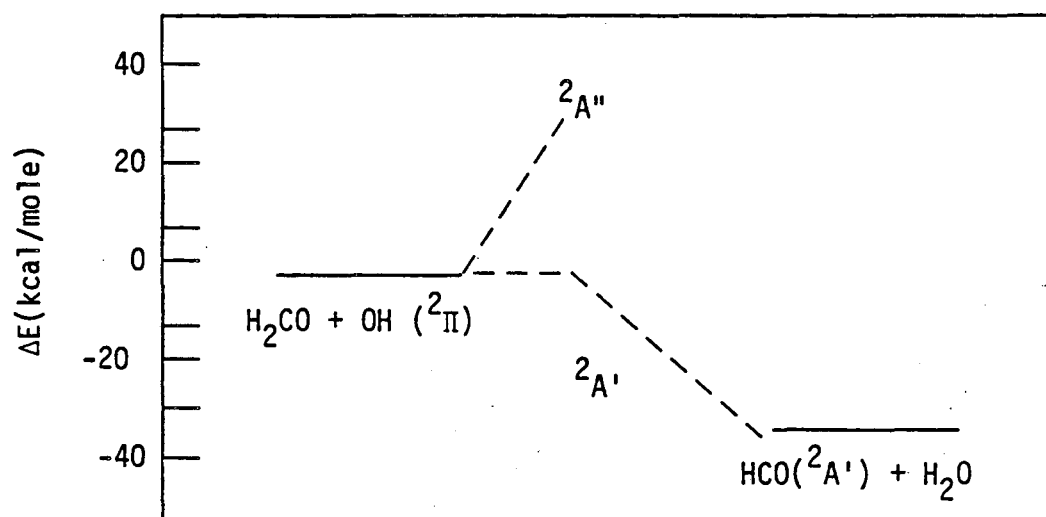
Fig. 1 Correlation Diagram for OH + H₂CO Reaction

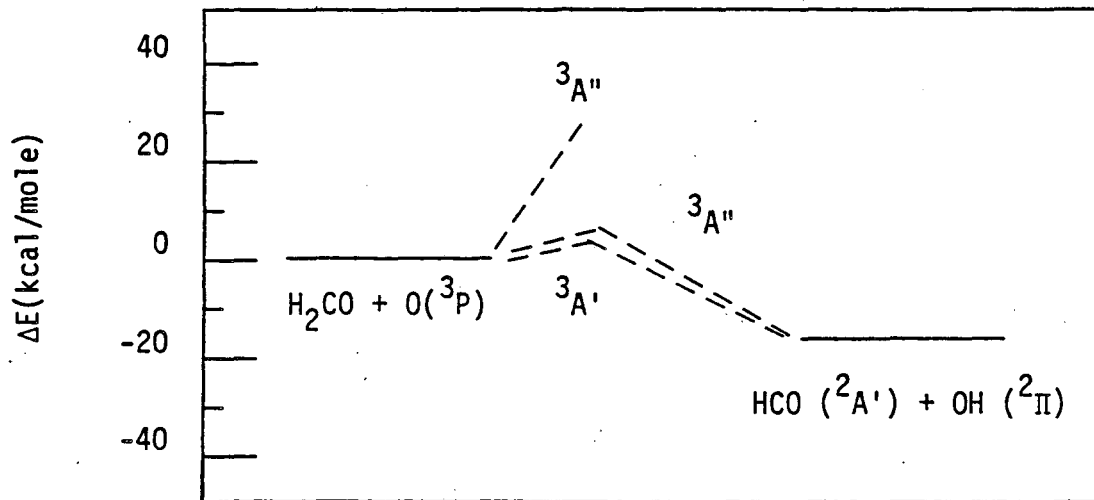
Fig. 2 Correlation Diagram for $O + H_2CO$ Reaction

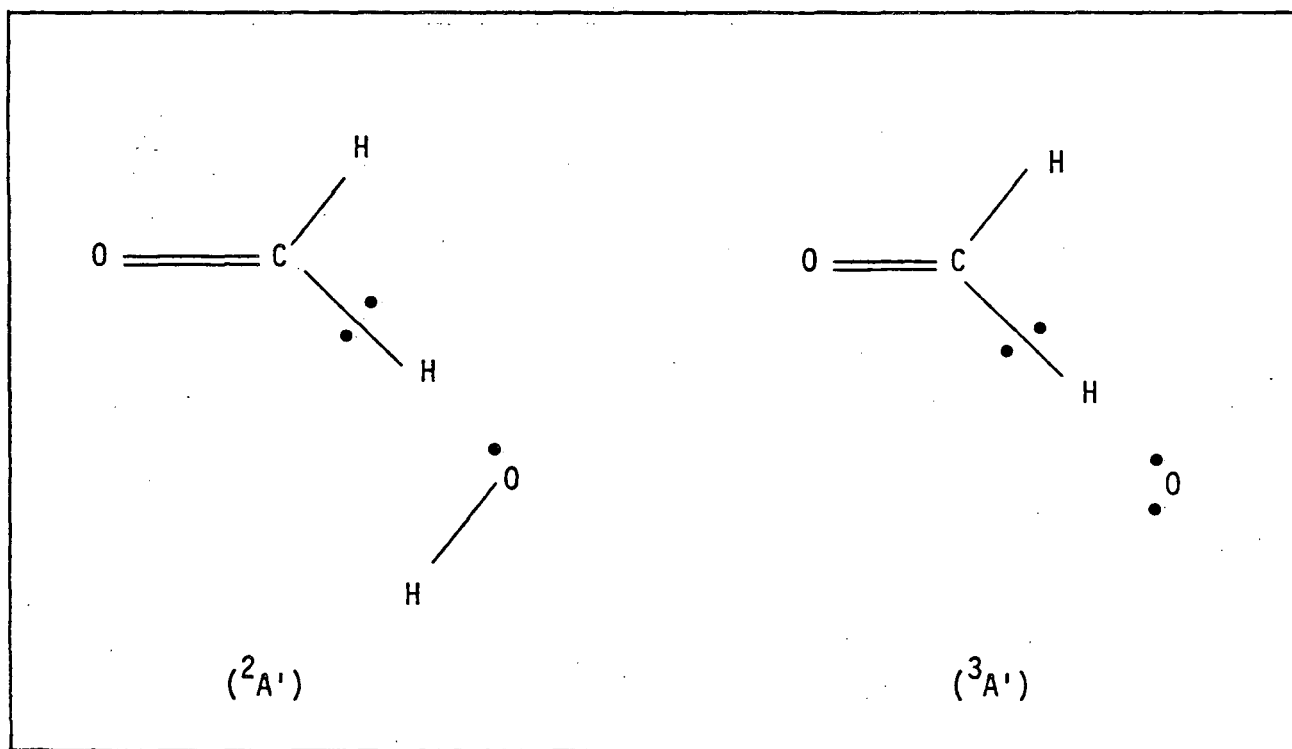
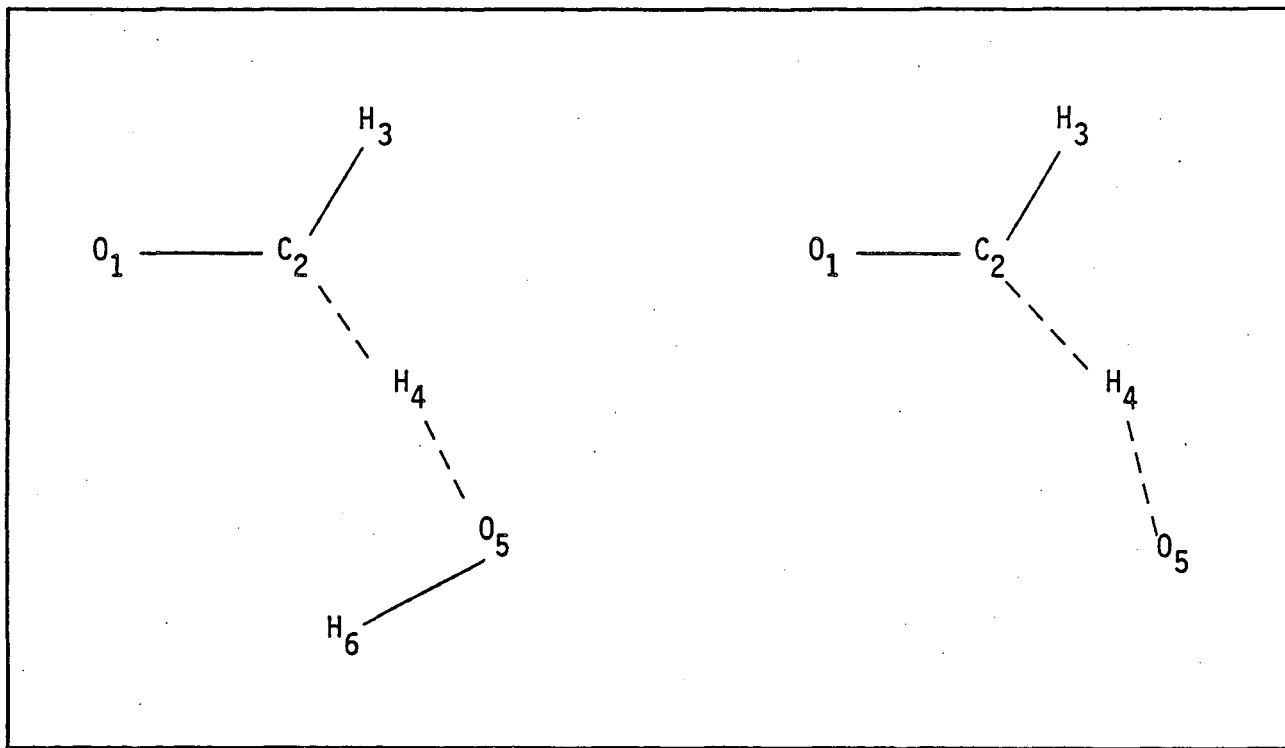
Fig. 3 Valence Bond Structures of OH + H₂CO and O + H₂CO

Fig. 4 Nomenclature for Molecular Structures



HYDROGEN ATOM MIGRATION IN THE OXIDATION OF ALDEHYDES: $O(^3P) + H_2CO$

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*Supported in part by the National Aeronautics and Space Administration under Contract No. A 86130B (LML).

†Also, Department of Chemistry, University of California, Berkeley. Supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

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HYDROGEN ATOM MIGRATION IN THE OXIDATION OF ALDEHYDES: $O(^3P) + H_2CO$

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ABSTRACT

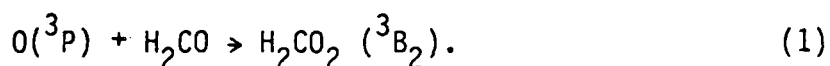
We report an ab initio study of hydrogen atom migration in methylenebis(oxy) H_2CO_2 (3B_2) to form triplet formic acid $HCOOH$ (3A_1). From HF, MCHF, and CI calculated energy barriers, we estimate the activation energy to be no less than 30 kcal/mole. We conclude that the hydrogen migration channel is not accessible in recent room temperature experiments on the $O(^3p) + H_2CO$ reaction.

*Supported in part by the National Aeronautics and Space Administration under Contract No. A 86130B (LML).

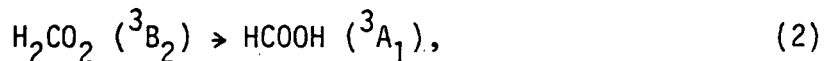
†Also, Department of Chemistry, University of California, Berkeley. Supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098.

I. Introduction

Mechanistic and kinetic studies¹⁻⁷ indicate that the reactions of $O(^3P)$ with aldehydes proceed mostly via abstraction of the weak aldehydic hydrogen atom. In the reaction with H_2CO , the expected products are the formyl and hydroxyl radicals.¹⁻³ However, Chang and Barker⁶ recently reported the measurement of a substantial yield (30 %) of a primary product of mass 44 (presumably CO_2) in that reaction, and suggested that the addition reaction may be an important channel,



The methylenebis(oxy) H_2CO_2 adduct would then undergo isomerization



followed by fragmentation to form $H + HOCO$, $H + HCO_2$, and $HCO + OH$. Further fragmentation of $HOCO$ and HCO_2 would lead to CO_2 . We report here the results of an ab initio study of the H-atom migration reaction channel (2).

The paper is organized in the following manner. The computational method is described in Section II, the results are given in Section III, and discussion of the findings is presented in Section IV.

II. Computational Method

Ab initio Hartree-Fock (HF), multiconfiguration Hartree-Fock (MCHF) and configuration interaction (CI) calculations were carried out to characterize the essential features of the potential energy surface. Methylenebis(oxy) has a singlet ground state and a low lying triplet state.⁸ H-atom migration for the singlet state leads to ground state formic acid HCOOH (1A_1), and migration for the triplet state to triplet formic acid HCOOH (3A_1). For both surfaces, structures of the reactants, transition state, and products were fully optimized using a MCHF wavefunction which accounted for the most important configuration mixing effects due to bond breaking and bond formation.

Structures of stationary points in $H_2CO_2 \rightarrow HCOOH$ are shown in Fig. 1. For each of the structures the dots represent those electrons which participate actively in the migration process. During the reaction the two electrons of a CH bond in H_2CO_2 unpair, one electron forms a bonding pair with the previously unpaired electron on one of the oxygen atoms, and the other electron remains unpaired on the carbon atom. We note that the electron pair of each of the CH bonds must be treated equivalently in the computations of methylenebis(oxy) in order to give a symmetrical structure.

We can describe the CH bonds in H_2CO_2 each with two orbitals (bonding and antibonding), and the unpaired electrons on the oxygen atoms each by one orbital. A MCHF wavefunction which includes all the configurations obtained by distributing the six active electrons among the six active orbitals in all possible ways consistent with triplet

spin, provides a qualitatively correct description of methylenebis(oxy), the transition state, and formic acid. A similar wavefunction can be constructed for the singlet species.

Additionally, for the three MCHF determined stationary points on the triplet potential surface and for singlet formic acid we carried out HF and CI calculations. The CI wavefunction included all singly and doubly excited configurations interacting with the HF configuration.⁹ An estimate of the contributions from higher excitations was calculated using Davidson's correction.¹⁰ All calculations were done with a double zeta plus polarization (DZP) basis set,¹¹ using HONDO¹² and Siegbahn's GUGA¹³ computer code.

III. Computational Results

a. The MCHF (DZP) Structures

The optimized MCHF(DZP) structures of the various singlet and triplet species are given in Tables I-III, which use the nomenclature of Fig. 1.

The structures for singlet and triplet methylenebis(oxy) are very similar. The bonding-antibonding orbital pair representation of the CH bonds leads to a bond length ~ 0.02 Å longer than typical experimental CH bond lengths for sp^3 hybrid carbon. This effect is usually observed in valence-bond type wavefunctions which typically overemphasize left-right electron correlation effects. Harding and Goddard⁸ have characterized the low lying states of H_2CO_2 . The wavefunction used here includes the configurations needed for a correct description of those states, especially the diradical character of singlet methylenebis(oxy). Harding and Goddard did not optimize the structure of H_2CO_2 , but used a geometry in qualitative agreement with the structures determined here.

The ground state structure of $HCOOH$ (1A_1) is in agreement with the structure calculated by McLean and Ellinger.¹⁴ Here again the CO, OH, and CH bond lengths are ~ 0.015 Å longer than the HF value, due to the electron correlation effects accounted for in the MCHF wavefunction. We note that the CO bond length of the carbonyl group is 1.194 Å in the ground state and 1.366 Å in the triplet state. Indeed the triplet state arises from promotion of a carbonyl oxygen lone pair electron into the antibonding π orbital resulting in a much longer C-O bond length. In triplet formic acid the two CO bonds have single-bond character.

The transition state structures are given in Table II. In the singlet transition state the carbonyl CO bond length is halfway between the single-bond length in methylenebis(oxy) and the double-bond length of formic acid. The migrating hydrogen atom is closer to the carbon atom than to the oxygen atom in accord with the large exothermicity of the singlet state reaction (see next paragraph), and with an "early" transition state. In the triplet transition state the migrating hydrogen atom is closer to the oxygen atom in accord with the small exothermicity of the triplet state reaction. All through the reaction the CO bonds maintain single-bond character.

b. Relative Energies

The relative energies calculated with the HF, MCHF and CI wavefunctions for the various species are given in Table IV. The HF and CI energies were calculated at the MCHF(DZP) optimized geometries. The energies denoted SDHF correspond to CI wavefunctions including all singly and doubly excited interacting configurations. The energies denoted SDQHF are the CI energies corrected for effects of quadrupole excitations. For each category of results the energy of triplet methylenebis(oxy) is taken as the zero of energy. The experimental heats of reactions are also given.⁶

The values listed in Table IV permit an estimate of the true activation energy for the migration process. The HF activation energy is 59.1 kcal/mole, the SDHF value is 42.3 kcal/mole. Thus the correlation correction from singly and doubly excited configurations amounts to 16.8 kcal/mole. The MCHF activation energy is 52.7 kcal/mole. The

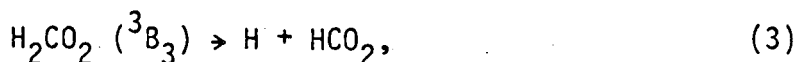
MCHF wavefunction takes into account the most important electron correlation effects due to bond breaking and bond formation. Remaining electron correlation effects could be described well by a CI wavefunction that includes all single and double excitations from the MCHF wavefunction. The energy lowering due to these remaining electron correlation effects most likely will be less than the 16.8 kcal/mole obtained with a single configuration as reference. Similar behavior of the correlation energy correction has been observed in the study of the $\text{H} + \text{H}_2$ exchange reaction,¹⁵ and in the molecular dissociation of formaldehyde.¹⁶ Thus we can reasonably estimate that the activation energy in the DZP basis set is not less than 35.9 kcal/mole. We note that the SDQHF value which includes the effects of some higher than double excitations is 38.6 kcal/mole.

The effect of basis set errors on the barrier height must also be taken into account. In the molecular dissociation of H_2CO , the use of a triple zeta basis set lowered the calculated barrier by 4 kcal/mole.^{16,17} A reasonable estimate of the basis set error for the migration barrier is ~ 6 kcal/mole. Thus a lower limit to the activation energy for this process is estimated at 30 kcal/mole. Finally, we note that the calculated MCHF activation energy on the singlet surface is 13.1 kcal/mole. We expect the true barrier to be of the order of a few kcal/mole.

IV. Discussion

An energy correlation diagram is shown in Fig. 2. It is based on the experimental heats of formation,⁶ and on the activation energies estimated in Section III. Methylenebis(oxy)⁶ lies ~ 14.3 kcal/mole below $O(^3P) + H_2CO$. Because Chang and Barker's experiment was carried out at room temperature, a collision energy of at most a few kcal/mole, there is insufficient total energy for the postulated adduct H_2CO_2 to undergo hydrogen atom migration on the triplet surface.

The carbon dioxide observed in Chang and Barker's experiment must originate from a different reaction than the hydrogen migration pathway. Assuming the initial addition occurs, collision induced intersystem crossing to singlet methylenebis(oxy) followed by fragmentation, and H-atom elimination from triplet methylenebis(oxy), i.e.,



followed by further fragmentation are two possible sources of CO_2 . We note that H-atom elimination is a primary channel in the isoelectronic $O(^3P) + C_2H_4$ reaction.²⁰

Similar conclusions are expected to be valid for the $O(^3P) + CH_3CHO$ reaction under similar experimental conditions. Thus addition followed by migration and fragmentation would not be a source of OH radicals in accord with Kleinermanns and Luntz's⁷ experimental findings.

We note that a high barrier to hydrogen migration has also been found in calculations on similar systems. In the $O(^3P) + C_2H_4$ reaction, the migration barrier from open-ring triplet ethylene oxide to form triplet acetaldehyde was found to be ~ 45 kcal/mole.¹⁸ In the $O(^3P) + C_2H_2$ reaction, Harding¹⁹ calculated a high barrier (~ 53 kcal/mole) to migration on the triplet surface. In each case the high barrier can be attributed to the strong repulsive interaction of two spatially close triplet-coupled orbitals of the transition state.

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Table I. MCHF(DZP) Structures^a of Methylenebis(oxy) H₂CO₂

	H ₂ CO ₂ (¹ A ₁)	H ₂ CO ₂ (³ B ₂)
R(C ₁ O ₂)	1.36136	1.36599
R(C ₁ O ₃)	1.36136	1.36599
∠(O ₂ C ₁ O ₃)	117.76	115.34
R(C ₁ H ₄)	1.11165	1.11254
R(C ₁ H ₅)	1.11165	1.11254
∠(H ₄ C ₁ H ₅)	108.72	108.05
E	-188.741158	-188.740099

a. Bond lengths in Å, angles in degrees, energy in a.u. See Fig. 1 for nomenclature.

Table II. MCHF(DZP) Structures^a of Transition States

	TST (¹ A ₁)	TST (³ A ₁)
R(C ₁ O ₂)	1.27529	1.35697
R(C ₁ H ₄)	1.10881	1.10467
∠(O ₂ C ₁ H ₄)	117.30	111.38
R(C ₁ O ₃)	1.34395	1.35077
∠(O ₃ C ₁ O ₂)	124.19	115.96
∠(O ₃ C ₁ H ₄)	114.67	118.64
R(O ₃ H ₅)	1.55324	1.23023
R(C ₁ H ₅)	1.19099	1.29297
∠(C ₁ O ₃ H ₅)	47.88	59.91
τ(H ₅ O ₃ C ₁ O ₂)	96.79	114.76
E	-188.720279	-188.656158

a. Bond lengths in Å, angles in degrees, energy in a.u. See Fig. 1 for nomenclature. TST stands for Transition State.

Table III. MCHF(DZP) Structures^a of Formic Acid HCOOH

	HCOOH(¹ A ₁)	HCOOH(³ A ₁)
R(C ₁ O ₂)	1.19433	1.36626
R(C ₁ H ₄)	1.10397	1.09945
∠(O ₂ C ₁ H ₄)	124.08	111.75
R(C ₁ O ₃)	1.33337	1.35618
∠(O ₃ C ₁ O ₂)	124.87	113.79
∠(O ₃ C ₁ H ₄)	111.05	112.86
R(O ₃ H ₅)	0.96743	0.96443
∠(C ₁ O ₃ H ₅)	108.56	110.02
τ(H ₅ O ₃ C ₁ O ₂)	0.00	65.72
E	-188.880152	-188.732943

a. Bond lengths in Å, angles in degrees, energy in a.u. See Fig. 1 for nomenclature.

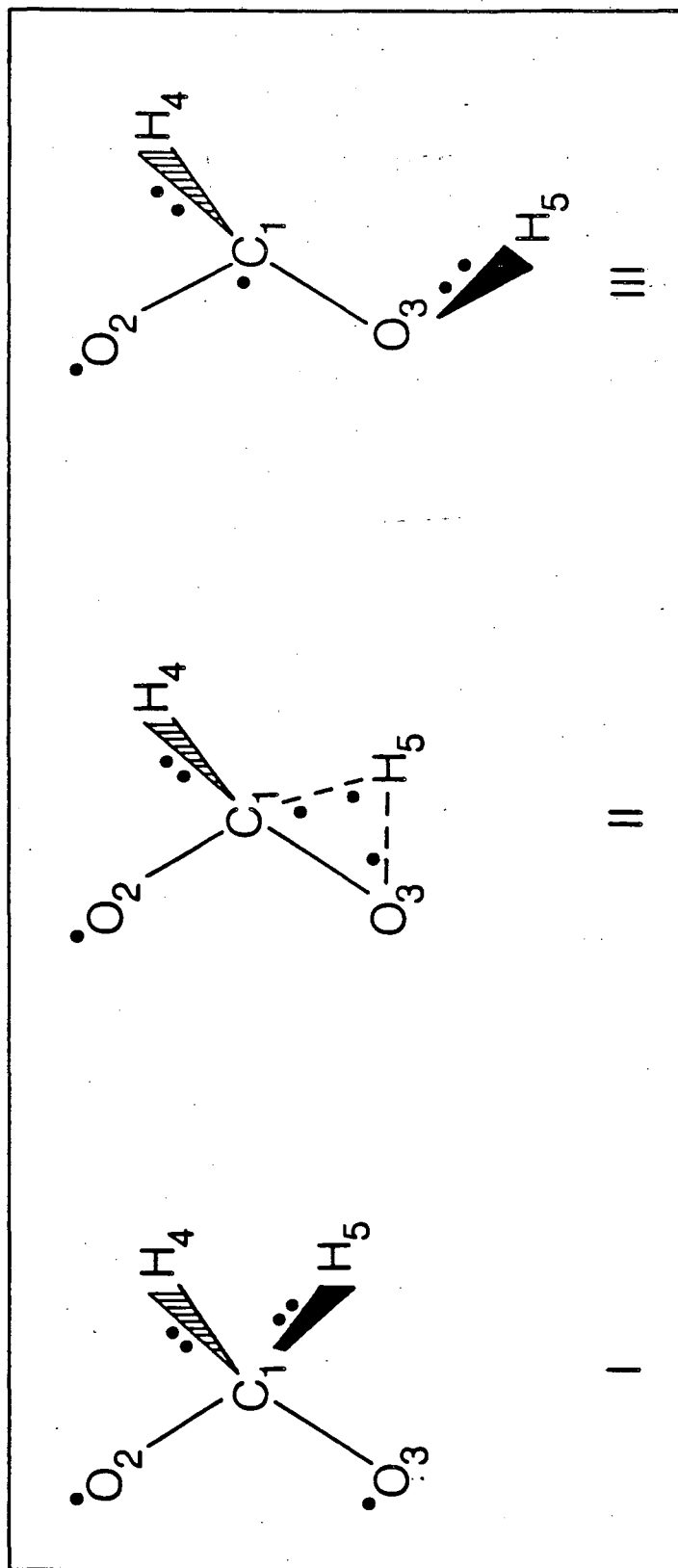
Table IV. Relative Energies (Kcal/mole)

Wfn	H ₂ CO ₂	-TST-	HCOOH
HF (triplet)	0.0	+59.1	+ 4.7
HF (singlet)	---	---	-69.2
MC (triplet)	0.0	+52.7	+ 4.5
MC (singlet)	-0.7	+12.4	-87.9
SDHF (triplet)	0.0	+42.3	- 2.1
SDHF (singlet)	---	---	-95.7
SDQHF (triplet)	0.0	+38.6	- 2.8
SDQHF (singlet)	---	---	-99.5
Exp. (triplet)	0.0	---	- 9.5
Exp. (singlet)	---	---	-109.3

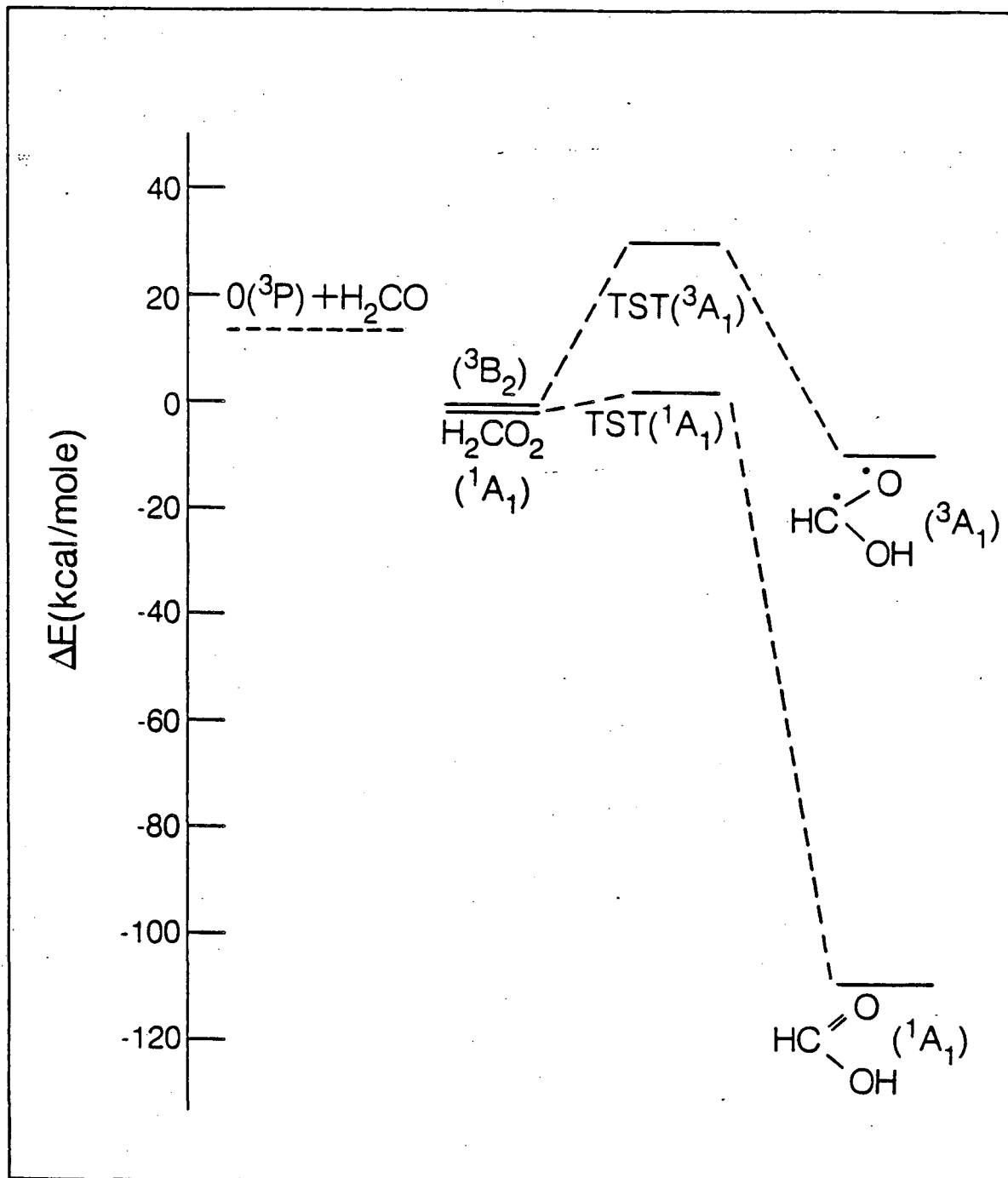
FIGURE CAPTIONS

Fig. 1. Structures of stationary points for $\text{H}_2\text{CO}_2 \rightarrow \text{HCOOH}$.

Fig. 2. Energy correlation diagram for $\text{H}_2\text{CO}_2 \rightarrow \text{HCOOH}$.



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