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THEORETICAL STUDIES ON THE UNIMOLECULAR  
DECOMPOSITION OF METHANOL

Lawrence B. Harding

Theoretical Chemistry Group, Chemistry Division  
Argonne National Laboratory, Argonne, IL 60439

H. B. Schlegel

Department of Chemistry, Wayne State University  
Detroit, MI 48202

R. Krishnan and J. A. Pople

Department of Chemistry, Carnegie-Mellon University  
Pittsburgh, PA 15213

I. INTRODUCTION

Reactive collisions typically involve dramatic changes in the electronic structure of the species, and it is necessary to account for these to calculate accurate potential energy surfaces, particularly in the critically important saddle-point or transition-structure regions. As a consequence a realistic theoretical description of reactive potential energy surfaces requires very accurate electronic wave functions;<sup>1-3</sup> large flexible basis sets are necessary and the effects of electron correlation must be included. To date relatively few such studies have been carried out on systems involving more than three or four atoms. In this report we present the results of an *ab initio* study of the H<sub>4</sub>CO potential energy surface focusing on the species





along with the saddle points for the reactions



Reactions (1)-(3) together with the simple bond cleavage processes



are the most likely pathways for unimolecular decomposition of methanol. The bond cleavage reactions (4)-(6) are expected to involve no barriers in excess of the reaction endothermicities and thus reliable activation energies for these processes can be obtained simply from experimental heats of formation of the corresponding radicals.

Reactions (1) and (2), when considered in the reverse direction, are both carbene insertion reactions, which by analogy to the  $\text{CH}_2(^1\text{A}_1) + \text{H}_2$  insertion,<sup>4</sup> are expected to have at most small barriers. Reaction (3), however, when considered in the reverse direction is a 2 + 2 asymmetric addition and is thus formally a forbidden reaction. It is expected then that the elimination of  $\text{H}_2$  from methanol forming formaldehyde will possess a barrier much larger than the reaction endothermicity. Thus although  $\text{H}_2 + \text{H}_2\text{CO}$  is the thermodynamically most stable product resulting from decomposition of methanol it is likely that the radical products (4)-(6) and possibly the carbene products (1) and (2) may be kinetically preferred.

## II. METHODS

A. Computational Details

The method used here for including the effects of electron correlation is Møller-Plesset perturbation theory carried out to second (MP2), third (MP3), and fourth (MP4) orders. This method has been applied to the determination of a large number of equilibrium geometries<sup>5,6</sup> and to several simple reactions<sup>1,7</sup> and has been found to be an efficient and reliable procedure for obtaining correlated electronic wave functions.

Briefly, the starting point for Møller-Plesset calculations is either an unrestricted Hartree-Fock (UHF) calculation or a closed-shell restricted Hartree-Fock (RHF) calculation. The zero order Hamiltonian,  $H_0$ , is then taken to be the sum of the one-electron Fock operators,  $F_p$ , and the perturbation,  $V$ , is defined as the difference between  $H_0$  and the full, many-electron Hamiltonian. Introducing an expansion parameter,  $\lambda$ , then gives,

$$H_\lambda = H_0 + \lambda V = \sum_p F_p + \lambda V$$

where  $H_\lambda$  reduces to the correct Hamiltonian when  $\lambda = 1$ . The eigenvalues and eigenvectors of  $H_\lambda$  are then expanded in powers of  $\lambda$ ,

$$E_\lambda = E^{(0)} + \lambda E^{(1)} + \lambda^2 E^{(2)} + \dots$$

$$\psi_\lambda = \psi^{(0)} + \lambda \psi^{(1)} + \lambda^2 \psi^{(2)} + \dots$$

and the resulting power series are truncated at some finite order, typically second, third, or fourth order. The details of the methods used to solve these equations have been presented in an earlier series of papers.<sup>8,9</sup> The calculations on closed-shell species reported here employ the spin-restricted formalism (RMPn) while the calculations on radical species ( $\cdot\text{CH}_3$ ,  $\cdot\text{OH}$ , etc.) employ the spin-unrestricted formalism (UMPn). In all calculations the frozen core approximation has been applied, by which it is meant that excitations out of the inner shell (1s) orbitals are not included in the perturbation theory calculations; these orbitals are however obtained self-consistently in the Hartree-Fock calculations.

Unless otherwise noted, the geometry optimizations were all carried out at the Hartree-Fock level employing the 6-31G\* polarization basis set.<sup>10</sup> Perturbation theory calculations employing a basis set augmented with hydrogenic p-polarization functions (6-31G\*\*), were then carried out at the optimized HF equilibrium (or transition structure) geometries. In a preceding paper a detailed comparison was made of the results obtained using HF geometries compared to

RMP2 geometries.<sup>11</sup> It was found that optimization of the geometries at the RMP2 level led to only minor changes in calculated heats of reaction and activation energies. One reason for this good agreement is that the HF calculations lead to reasonably accurate heats of reaction for the processes considered here. As Truhlar<sup>12</sup> has pointed out, it is generally necessary to have accurate energetics in order to make an accurate determination of saddle point geometries.

In all cases the geometry optimizations were carried out using the gradient method, in which the first derivative of the energy with respect to the nuclear coordinates is calculated analytically at each point and the result used to determine the direction of steepest descent. In addition, at the optimized RHF/6-31G\* geometries, analytic second derivatives of the energy with respect to nuclear coordinates were calculated in order to obtain harmonic vibration frequencies and zero point energies. The computational details of the second derivative calculations have been presented previously.<sup>13</sup> All calculations were carried out using the GAUSSIAN 80/CMU program on a Digital Equipment Corporation VAX 11/780 digital computer.

### B. Basis Sets

In the calculations presented in the subsequent sections of this report the 6-31G\* basis sets<sup>10</sup> were used to determine optimum geometries and 6-31G\*\* basis sets were used to obtain the final relative energies of the species. In this section we discuss briefly results from calculations with smaller less flexible basis sets.

In Table I we summarize the calculated activation energies for addition of H<sub>2</sub> to H<sub>2</sub>CO forming methanols obtained with STO-3G, 4-31G, 6-31G\* and 6-31G\*\* basis sets. From this table we see that the calculated activation energies with the smaller basis sets are significantly larger than the 6-31G\*\* results at all orders of perturbation theory. Neglect of even the hydrogenic polarization functions results in a ~6 kcal increase in the calculated activation energy (relative to 6-31G\*\*).

Perhaps more important are the differences in the effect of correlation on the activation energy obtained with different basis sets. At the STO-3G level fourth order perturbation theory increases the calculated activation by 10 kcal/mol. With the 4-31G basis set correlation appears to have no effect on the calculated activation energy while with the 6-31G\* and 6-31G\*\* basis sets, correlation decreases the activation energy 5-6 kcal/mol. It should be concluded then that attempts to determine the effect of correlation with small basis sets are likely to lead to spurious results.

Table 1  
 Comparison of 6-31G\*\*, 6-31G\*, 4-31G, and STO-3G  
 RMP activation energies (kcal/mol) for the reaction  
 $\text{H}_2 + \text{H}_2\text{CO} \rightarrow \text{H}_3\text{COH}$ .

Basis Set	Method			
	RHF	RMP2	RMP3	RMP4
STO-3G	136.1	146.1	147.7	146.1
4-31G	93.8	93.9	93.6	93.9
6-31G*	88.9	82.1	83.4	83.7
6-31G**	82.7	74.5	75.6	76.1

### C. Comparison of Møller-Plesset and CI Calculations on $\text{H}_2\text{CO}$

Many important features of the  $\text{H}_2\text{CO}$  potential energy surface have been well characterized with both experimental and theoretical techniques. Thresholds for photodissociation of formaldehyde forming both  $\text{H}_2$  and  $\text{H}\cdot$  are known. In addition there is some experimental evidence indicating the presence of a lower energy decomposition route (reversible) leading to hydroxycarbene.<sup>14</sup>

On the theoretical side, Jaffe and Morokuma<sup>15</sup> have reported small basis set (4-31G) MCSCF calculations on the photodissociation pathways of formaldehyde. More recently, Goddard and Schaefer<sup>16</sup> have completed an extensive CI study of the  $\text{H}_2\text{CO}$  surface including transition structures leading to both  $\text{H}_2 + \text{CO}$  and hydroxycarbene. In this section we compare the results of Møller-Plesset calculations to the CI calculations of Goddard and Schaefer.

Four minimum-energy structures

$\text{H}_2 + \text{CO}$	(IX)
$\text{H}_2\text{CO}$	(X)
HCOH (cis)	(XI)
HCOH (trans)	(XII)

and the saddle points for the reactions

Table 2  
Comparison of RMP/6-31G\*\* and CI/DZP activation energies (kcal/mol).

Reaction	Activation energy					
	RHF/6-31G**	RHF/DZP <sup>a</sup>	RMP2	RMP3	RMP4	CI(1+2) <sup>a</sup> CI(1+2) + QC <sup>b</sup>
H <sub>2</sub> CO → H <sub>2</sub> + CO	105.0	105.1	96.1	98.2	95.5	97.3 93.6
H <sub>2</sub> CO → HCOH (trans)	100.6	100.7	89.6	93.6	91.0	91.8 88.8
HCOH (trans) → HCOH (cis)	27.7	27.7	32.2	30.8	31.1	27.4 <sup>c</sup> 27.5 <sup>c</sup>

a. DZ + POL results from reference 16

b. DZ + POL singles and doubles CI with quadruples correction reference 16

c. DZ results (no polarization functions)



have been examined here. The calculated activation energies using the RHF/6-31G\* geometries are given in Table 2 along with the corresponding results from the Goddard-Schaefer study. We find the calculated RHF/6-31G\*\* activation energies agree to within 0.2 kcal/mol of the DZ+POL results of Goddard and Schaefer; this indicates that differences in the basis sets are probably insignificant. The RMP4 activation energies are found to lie between the singles and doubles CI results and the results obtained by adding the Davidson formula<sup>17</sup> correction for unlinked cluster quadruple excitations. The RMP4 calculations represent a more accurate estimate of the effects of quadruple excitations and thus we conclude that in this case the Davidson formula leads to a slight overestimate of these effects.

Of the three reactions (7)-(9), experimental data<sup>18</sup> is available only for one, reaction (7). Photodissociation of formaldehyde to produce molecular hydrogen has been observed at energies near the S<sub>1</sub> origin (80.6 kcal/mol).<sup>19</sup> The difference then between the most accurate calculated barrier to dissociation (88.0 kcal/mol) and the observed threshold in this process can be attributed either to errors in the calculated energetics or to tunneling effects (as suggested by Goddard and Schaefer<sup>16</sup> and supported by Miller<sup>20</sup>). We note though that an error in a calculated activation energy of 8 kcal/mol is not unexpectedly large. Indeed errors of similar magnitude are found in the relative energies of several H<sub>4</sub>CO species (*vide infra*).

### III. RESULTS AND DISCUSSION

The calculated relative energies of species (I)-(VIII) together with activation energies for methanol decomposition *via* pathways (1)-(3) are summarized in Table 3. A more detailed tabulation of these results including calculated geometries, vibrational frequencies, and total energies has been presented in a previous report.<sup>11</sup>

Of the eight species considered, accurate experimental heats of formation are available for four, CH<sub>3</sub>OH, H<sub>2</sub> + H<sub>2</sub>CO, CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) + H<sub>2</sub>O, and CH<sub>3</sub> + OH. In Table 4 we compare calculated and experimental relative energies of these species along with those of several closely related molecules. From these results we see that the RMP4/6-31G\*\* calculations yield relative heats of formation of closed-shell species accurate to approximately ±5%. Typically the largest errors involve comparison of species with drastically different structures; for

Table 3  
Relative energies (kcal/mol) from MPn/6-31G\*\* calculations based on HF/6-31G8 geometries.

Reaction	HF	MP2	MP3	MP4	Zero Point Energy
CH <sub>3</sub> OH	0.0	0.0	0.0	0.0	34.7
H <sub>2</sub> + H <sub>2</sub> CO	28.7	26.7	29.6	26.9	24.9
H <sub>2</sub> + HCOH (cis)	83.3	90.0	89.1	86.5	24.4
H <sub>2</sub> + HCOH (trans)	77.8	84.7	83.9	81.3	24.8
CH <sub>3</sub> + OH	57.6	96.9	89.6	89.7	(23.5) <sup>a</sup>
CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> ) + H <sub>2</sub> O	92.2	109.8	104.9	103.9	25.7
H <sub>2</sub> C···OH <sub>2</sub>	84.0	94.8	91.9	90.1	30.1
H <sub>2</sub> C···HOH	86.5	103.2	98.6	97.8	28.0
CH <sub>3</sub> OH↔H <sub>2</sub> + HCOH	101.5	97.3	97.2	95.9	28.8
CH <sub>3</sub> OH↔CH <sub>2</sub> ( <sup>1</sup> A <sub>1</sub> ) + H <sub>2</sub> O	98.3	(89.8)	(92.3)	(89.9)	(29.6)
CH <sub>3</sub> OH↔CH <sub>2</sub> O + H <sub>2</sub>	111.4	101.2	105.2	103.0	28.7

a. experimental zero point energy from reference 23

example the calculated energy of CH<sub>2</sub>(<sup>1</sup>A<sub>1</sub>) + H<sub>2</sub>O relative to H<sub>2</sub> + H<sub>2</sub>CO is in error by 8.8 kcal/mol. Similarly calculated heats of reaction involving bond cleavage, forming radical species, are typically low by about 10 kcal/mol. For example cleavage of the C-O bond of methanol leads to a calculated MP4 dissociation energy of 89.7 kcal/mol compared to an experimental value of 98.0 kcal/mol (corrected to remove zero point effects). At this point it is not clear whether the remaining errors are due to limitations in the basis sets or to truncation of the perturbation series expansion at fourth order. Recent results however indicate that in some cases the effect of triple excitations at fourth order (neglected in the calculations reported here) can be quite substantial.<sup>21</sup>



Table 4

Comparison of calculated (MPn/6-31G\*\*) and experimental heats of reaction (kcal/mol). All experimental results have been corrected to remove zero point energies.

Reaction	HF	MP2	MP3	MP4	EXPT <sup>a</sup>
$\text{H}_2 + \text{CO} \rightarrow \text{H}_2\text{CO}$	-0.3	-2.9	-5.4	-2.3	-4.6
$\text{H}_2 + \text{H}_2\text{CO} \rightarrow \text{H}_3\text{COH}$	-28.7	-25.6	-29.3	-26.1	-29.0
$\text{H}_2 + \text{H}_3\text{COH} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$	-31.0	-29.7	-30.5	-29.8	-30.3
$\text{CH}_3\text{OH} \rightarrow \text{CH}_2(^1\text{A}_1) + \text{H}_2\text{O}$	92.2	109.9	104.9	103.9	97.7
$\text{H}_2 + \text{H}_2\text{CO} \rightarrow \text{CH}_2(^1\text{A}_1) + \text{H}_2\text{O}$	63.5	84.3	75.6	77.8	68.7
$\text{CH}_3\text{OH} \rightarrow \cdot\text{CH}_3 + \cdot\text{OH}$	57.6	96.9	89.6	89.7	98.0

a. experimental results used are summarized in Table 5

Structures (VII) and (VIII) are loose complexes of  $\text{CH}_2(^1\text{A}_1)$  and  $\text{H}_2\text{O}$ . In one of these structures, (VII), methylene acts as a Lewis acid, involving a delocalization of an oxygen lone pair into the unoccupied methylene  $p\pi$  orbital. In the other, (VIII), methylene is formally a Lewis base and the bonding approximates a hydrogen bond in which a hydrogen of  $\text{H}_2\text{O}$  interacts with the methylene lone pair. Structure (VII) is calculated to be bound by 13.8 kcal/mol relative to  $\text{CH}_2(^1\text{A}_1)$  and  $\text{H}_2\text{O}$  while structure (VIII) is bound by only 6.1 kcal/mol. It should be stressed that both complexes are very loosely bound, each possessing a number of distinct minimum-energy conformations separated by small barriers. Complexes of this kind though may play an important role in the dynamics of reaction (2) and related reactions.

Considering now the activation energies for decomposition of  $\text{CH}_3\text{OH}$  we find the RMP4, 6-31G\*\* calculations predict that the lowest pathway leads to  $\text{H}_2 + \text{HCOH}$ , with an activation energy of 90 kcal/mol. The net reaction is over 70 kcal/mol endothermic compared to the reaction leading to  $\text{H}_2 + \text{H}_2\text{CO}$  which is 16 kcal/mol endothermic but involves an activation energy of 96 kcal/mol. The RMP4 calculations predict an endothermicity for the reaction leading to  $\text{CH}_2(^1\text{A}_1) + \text{H}_2\text{O}$  of 95 kcal/mol, with no barrier in excess of the endothermicity, whereas the most recent experimental heat of formation for  $\text{CH}_2(^1\text{A}_1)$ <sup>22</sup> leads to an endothermicity of 90.0 kcal/mol. It is interesting to note however that RHF calculations predict a barrier of 6 kcal/mol above the endothermicity for this process.

Table 5  
Summary of relevant experimental<sup>a</sup> heats of formation and zero point energies.

Molecule	Zero point energy (kcal/mol)	$\Delta H_f^\circ$ (kcal/mol)	
		0 K	298 K
H <sub>2</sub>	6.30	0.0	0.0
CO	3.10	-27.20	-26.42
•OH	5.34	9.29	9.4
H <sub>2</sub> O	12.88	-57.103	-57.798
H <sub>2</sub> C( <sup>1</sup> A <sub>1</sub> )	10.5 <sup>b</sup>	101.7 ± 0.5 <sup>c</sup>	
•CH <sub>3</sub>	18.18	35.7	34.9 ± .15 <sup>d</sup>
H <sub>2</sub> CO	16.11	-25.05	-25.95 ± 0.11 <sup>e</sup>
CH <sub>4</sub>	27.10	-15.99	-17.895
CH <sub>3</sub> O•			3.5 <sup>f</sup>
•CH <sub>2</sub> OH			-6 <sup>g</sup>
CH <sub>3</sub> OH	31.13 <sup>h</sup>	-45.355 <sup>i</sup>	-47.96 <sup>i</sup>

- a. except where noted these results are from reference 23  
b. reference 30  
c. reference 22  
d. reference 24  
e. reference 31  
f. reference 25  
g. obtained assuming  $D(\text{H}-\text{CH}_2\text{OH}) = D(\text{H}-\text{CH}_2\text{OCH}_3) = 94.1$  kcal/mol (reference 25)  
h. reference 32  
i. reference 33

Table 6  
Summary of theoretical and experimental 0 K heats of reaction and activation energies for the unimolecular decomposition of methanol (all results in kcal/mol).

Product	$\Delta H_{\text{RXN}}$	$E_a$
RMP4/6-31G**		
H <sub>2</sub> + H <sub>2</sub> CO	16.4	96.5
H <sub>2</sub> + HCOH	71.1	90.2
CH <sub>2</sub> + H <sub>2</sub> O	94.9(90.0) <sup>a</sup>	94.9(90.0) <sup>a</sup>
Experimental		
•CH <sub>3</sub> + •OH	90.2	90.2
CH <sub>3</sub> O• + H•	102.1	102.1
•CH <sub>2</sub> OH + H•	92.5 ± 3	92.5 ± 3

a. obtained using the experimental endothermicity for this reaction with the assumption that there is no barrier in excess of the endothermicity (as found in RMP4 calculations)

Competing with the decomposition routes are three radical cleavage processes (4)-(16). Since each of these reactions is a simple covalent-bond cleavage we expect the required activation energies to be equal to the overall endothermicity of the reactions.

Using the experimental, free-radical heats of formation at 298 K as summarized in Table 5,<sup>23-25</sup> we obtain heats of reaction for (4)-(6) of 92.3, 103.6 and 94.1 kcal/mol respectively. Correcting these to 0 K leads to the results shown in Table 6 where we have assumed that the activation energies for reaction (4)-(6) are equal to the endothermicities.

Considering the activation energies alone, then it would appear that reactions (1)-(3) should be competitive with the free radical reactions (4)-(6). In order to obtain an estimate of the A factors for these reactions we apply the simplified transition state theory

expression<sup>26</sup>

$$A_{\infty} = \frac{\nu_1 \nu_2 \cdots \nu_{\eta}}{\nu_1^{\ddagger} \nu_2^{\ddagger} \cdots \nu_{\eta-1}^{\ddagger}}$$

where the reactant and transition-structure vibrational frequencies,  $\nu_i$  and  $\nu_i^{\ddagger}$ , are obtained from RHF/6-31G\* calculations.<sup>11</sup> This leads to A factors for reactions (1) and (3) of  $6.0 \times 10^{13}$  and  $1.7 \times 10^{14}$  s<sup>-1</sup> respectively. These are over two orders of magnitude smaller than experimental estimates<sup>27,28</sup> of the A factor for reaction (4),  $2 \times 10^{15}$  s<sup>-1</sup>. We conclude then that reactions (1)-(3) will not play an important role in the high-temperature decomposition of methanol. These reactions however may be important as low-temperature chain-initiating steps. This would certainly be true if the calculated activation energy for reaction (9) is 5-10 kcal/mol above the true threshold for this reaction as found for the elimination of H<sub>2</sub> from formaldehyde (*vide supra*).

Finally we note that a recent crossed-beam experiment<sup>29</sup> designed to determine the fragmentation pattern of "hot" methanol led to the conclusion that elimination of molecular hydrogen does not occur in the gas phase when methanol is formed with about 135 kcal/mol of excess energy (from CH<sub>4</sub> + O). This conclusion is consistent with the small A factors for elimination of H<sub>2</sub> obtained in the present calculations.

#### IV. CONCLUSIONS

Combining the results of calculations on reactions (1)-(3) with experimental results on reactions (4)-(6) we obtain the estimates for heats of reaction and activation energies for the unimolecular decomposition of methanol shown in Table 6. From these results we see that although the lowest energy route levels to hydroxycarbene, due to the low A factor for this process, it should not be competitive with C-O cleavage at moderate to high temperatures.

#### V. ACKNOWLEDGMENTS

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