

3 compares the MIKES/CID spectra of the  $[(\text{CH}_2\text{O})_n\text{H}]^+$  species generated by ion/molecule reactions of paraformaldehyde (heated at 200 °C) and those isomeric ions generated by ion/molecule reactions of trioxane and tetroxocane. Clearly, significant differences are observed in the figure. In particular, the MIKES/CID spectrum of the ionic polymer standard shows bond cleavages at every bond in the backbone, whereas the corresponding species generated from the cyclic oligomers show a series of fragment ions corresponding primarily to loss of monomeric units,  $\text{CH}_2\text{O}$ . These significant spectral differences are indicative of structural differences between the two ionic multimers.

We contend from the results of our MIKES/CID studies on the methylenenitramines<sup>2,6</sup> and the present study that the ionic multimers, generated by gas-phase ion/molecule reactions of the heterocyclic compounds, are indeed cluster ions and not linear polymeric ions. The MIKES/CID results shown here on the methylenenitramines (Figure 1) also show a series of fragment ions corresponding to loss of the monomer,  $\text{CH}_2\text{NNO}_2$ , but no consecutive cleavages of the backbone ( $-\text{CH}_2-/-\text{NNO}_2-/-\text{CH}_2-$ ) are observed. We have discussed the strong intermolecular forces that exist between the paired molecules in the protonated RDX dimer,<sup>2</sup> which must preclude dissociation of the protonated dimers into the molecular entities. This also indicates that at least the dimers are not simple proton-bound dimers, otherwise they would fragment easily into molecular units such as those proton-bound dimers reported in studies by Cooks and co-workers.<sup>7</sup> Consequently, the resulting cluster ions must be composed of intact molecules of the heterocycles, and the intermediate clusters contain monomeric subunits. These cluster ions are held together by rather complex cohesive forces that govern the fragmentation pathways.

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**Registry No.** HMX, 2691-41-0; RDX, 121-82-4; paraformaldehyde, 30525-89-4; tetroxocane, 293-30-1; trioxane, 110-88-3.

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## Alkyl Migration or Carbonyl Migration? Ab Initio MO Study of Reaction Mechanism for Carbonyl Insertion of Pd Complex

Nobuaki Koga and Keiji Morokuma\*

*Institute of Molecular Science  
Myodaiji, Okazaki 444, Japan*

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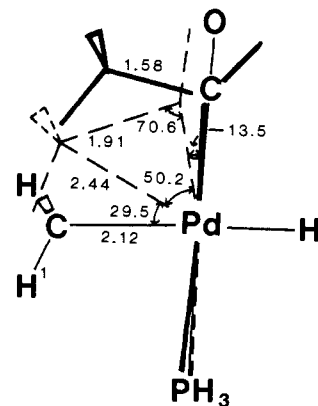
Carbonyl insertion reaction is an important elementary reaction of catalytic processes.<sup>1</sup> One of the most interesting questions concerning this reaction is whether the reaction takes place via alkyl group migration or carbonyl migration.<sup>1,2</sup> It has been proposed recently that the agostic interaction could assist the alkyl group migration.<sup>3</sup> Although some experimental and theoretical studies have appeared to elucidate the mechanism,<sup>4,5</sup> the structure

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**Figure 1.** Optimized geometries (in Å and deg) of  $\text{Pd}(\text{CH}_3)(\text{H})(\text{CO})(\text{PH}_3)$ , the transition state, and  $\text{Pd}(\text{COCH}_3)(\text{H})(\text{PH}_3)$ . The position of the Pd atom and the direction of the PdH bond are fixed. The illustrated positions of atoms are those in  $\text{Pd}(\text{CH}_3)(\text{H})(\text{CO})(\text{PH}_3)$ . The positions shown by the broken lines and the thick solid lines are those at the transition state and in  $\text{Pd}(\text{COCH}_3)(\text{H})(\text{PH}_3)$ , respectively. For clarity, only essential geometrical parameters are shown.

**Table I.** Relative Energy (kcal/mol) for  $\text{Pd}(\text{CH}_3)(\text{H})(\text{CO})(\text{PH}_3) \rightarrow \text{Pd}(\text{COCH}_3)(\text{H})(\text{PH}_3)$

method	reactant	transition state	product
RHF	0.0	25.8	19.1
MP2	0.0	13.5	8.8

of transition state, which could give direct evidence on the reaction mechanism, has never been determined.

In this paper we report the optimized transition-state structure for the carbonyl insertion reaction of  $\text{Pd}(\text{CH}_3)(\text{H})(\text{CO})(\text{PH}_3)$  (**1**) and show that the reaction takes place via methyl migration. This system has been chosen as a model of an intermediate considered to exist in the experimentally studied reaction of *trans*- $\text{Pd}(\text{CH}_3)_2(\text{PR}_3)_2$  and  $\text{CO}$ .<sup>4d</sup> We used for the geometry optimization the energy gradient technique at the restricted Hartree-Fock (RHF) level with the relativistic effective core potential approximation.<sup>6</sup> A smaller basis set (valence double  $\zeta$  except for  $\text{PH}_3$ ) was used for structure optimization and a larger basis set (all valence double- $\zeta$ ) and the second-order Møller-Plesset perturbation method (MP2) were used for energy calculations at the RHF optimized geometries.<sup>7</sup>

The structures of **1**, the product ( $\text{Pd}(\text{COCH}_3)(\text{H})(\text{PH}_3)$ ), and the transition state between them are shown in Figure 1 and their relative energies are in Table I. During the course of reaction, the structure of the  $\text{H}_3\text{PPdH}$  fragment remains nearly unchanged, the angle  $\text{PPdH}$  being about 90°. The methyl group, with its pseudo  $C_3$  axis kept nearly horizontal, moves up halfway toward the carbonyl group at the transition state and proceeds further to form a CC bond with the carbonyl group in the product. At the transition state the carbonyl group moves slightly toward the methyl group as if to facilitate its migration. This result indicates

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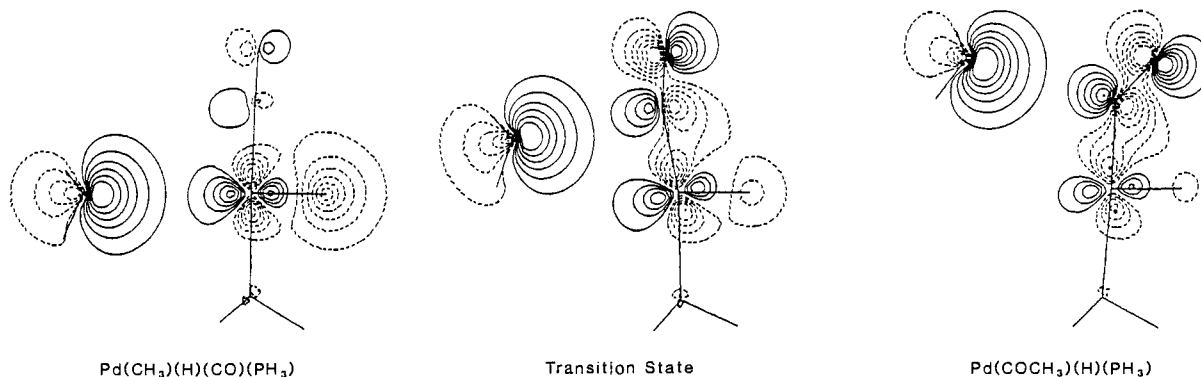
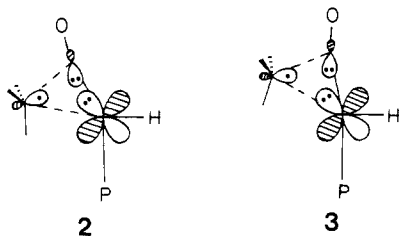


Figure 2. Interactive hybrid molecular orbitals of  $\text{CH}_3$  and  $\text{Pd}(\text{H})(\text{CO})(\text{PH}_3)$  for (left) the reactant, (middle) the transition state, and (right) the product.

that the reaction coordinate is methyl migration through a three-center transition state, consistent with the experimental results.<sup>4d</sup> The  $\text{CH}^1$  bond lengths of the product and the transition state are 1.089 and 1.090 Å, respectively, and thus the agostic interaction which would make the  $\text{CH}$  bond longer is absent.<sup>8</sup>

Here two questions emerge; the first one is why the carbonyl group does not migrate and the second one is what kind of factor stabilizes the three-center transition state.

In order to answer the first question, we assume the transition state for the carbonyl group migration in which the angles ( $\text{C}-\text{O})\text{Pd}(\text{H})$  and  $(\text{CH}_3)\text{Pd}(\text{PH}_3)$  of the true transition state are exchanged. The assumed transition state is less stable by about 7 kcal/mol than the true transition state. This instability is ascribed to the repulsion between two carbonyl lone pair electrons and  $d_{xy}$  electrons, as shown in 2. The repulsion in the true transition state, as shown in 3, is weaker, because the carbonyl lone pair is no longer directed toward the Pd  $d_{xy}$  electrons and because the long distance and the small electron density ( $\sim 1$ ) keep the increase of the methyl  $\text{sp}^3$ -Pd  $d_{xy}$  repulsion to a minimum. Therefore, the alkyl group migration is expected to be common in late transition-metal complexes.



The answer to the second question is given by the paired interactive hybrid molecular orbitals (IHMO's), as shown in Figure 2, into which the dominant orbital interactions between the methyl group and the remaining part of the complex are condensed.<sup>9</sup> Although the IHMO of the methyl group remains almost unchanged during the course of reaction, that of the  $\text{Pd}(\text{H})(\text{C}-\text{O})(\text{PH}_3)$  fragment changes its shape smoothly. While the pair of IHMO's for the reactant describes the  $\text{CH}_3$ -Pd bond and that for the product describes the  $\text{CH}_3$ -CO bond, at the transition state the pair of IHMO's has a character between the two and shows that the three-center transition state is stabilized by the interaction

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(9) (a) One can attain pairs of fragment orbitals by diagonalizing  $\mathbf{P}^+\mathbf{P}$ , where  $\mathbf{P}$  is the rectangular overlap population matrix between AO's of  $\text{CH}_3$  and those of  $\text{Pd}(\text{H})(\text{CO})(\text{PH}_3)$ . The overlap population matrix element is nonzero only within the pair and zero between orbitals in different pairs. Of these pairs, only a few with largest eigenvalues, i.e., overlap populations, play a dominant role in the interaction and thus are called IHMO's. In the present case, we show the most important pair of IHMO's for each geometry. (b) Fujimoto, H.; Koga, N.; Fukui, K. *J. Am. Chem. Soc.* **1981**, *103*, 7452. (c) Fujimoto, H.; Koga, N.; Endo, M.; Fukui, K. *Tetrahedron Lett.* **1981**, *22*, 3427.

between the methyl group  $\text{sp}^3$ -like orbital and  $\text{CO } \pi^*$  and the Pd ( $d + p$ ) orbitals.

The activation energy for the carbonyl insertion reaction of **1** is low, consistent with the experimental fact that the reaction of the Pd complex proceeds easily.<sup>10</sup> On the other hand, the Pt complex is known to be less reactive.<sup>10</sup> Actually, we obtained an activation energy for the reaction of  $\text{Pt}(\text{CH}_3)(\text{H})(\text{CO})(\text{PH}_3)$  to be higher by 8 kcal/mol. The analysis of the difference between Pd and Pt complexes and other details of the present calculations will be published elsewhere.

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### Exciton Delocalization of the Excited Singlet State of Chlorophyll *a* Monohydrate Dimer and Fluorescence Lifetimes of Translationally Equivalent Aggregates

F. K. Fong,\* M. S. Showell,<sup>†</sup> and A. J. Alfano<sup>‡</sup>

Department of Chemistry, Purdue University  
West Lafayette, Indiana 47907

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Recently, it was found that the triplet states of the in vivo P700 Chl *a* dimer<sup>1</sup> and the in vitro monohydrate Chl *a* dimer,  $(\text{Chl } a \cdot \text{H}_2\text{O})_2$ , are not delocalized by exciton interactions.<sup>1,2</sup> On the other hand, exciton interactions are generally assumed to play a role in the excited singlet state properties of these dimers, although hitherto there has been little clear-cut evidence for such interactions. The redshifts observed for the P700 and  $(\text{Chl } a \cdot \text{H}_2\text{O})_2$  bands at 695 nm compared<sup>3</sup> to the 662-nm absorption band of Chl *a*· $\text{H}_2\text{O}$  are largely due to bathochromic shifts arising from intermolecular interactions participating in the dimer structures. Earlier interpretations<sup>4,5</sup> of exciton splittings in the observed P700<sup>+</sup> minus P700 absorption-change spectra have recently been disputed.<sup>6,7</sup> In this paper we report evidence, based on fluorescence lifetime measurements, for exciton delocalization in the  $(\text{Chl } a \cdot \text{H}_2\text{O})_2$   $S_1$  state and provide two criteria for using fluorescence lifetime measurements as a diagnostic tool for determining the size of an *n* aggregate.

Freed considered<sup>8</sup> the radiative decay and internal conversion

\*Present Address: Ivorydale Technical Center, Proctor and Gamble Co., Cincinnati, OH 45217.

<sup>†</sup>Present Address: Rockwell Science Center, Thousand Oaks, CA 91360.

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