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Publication Date

1977

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January 1977

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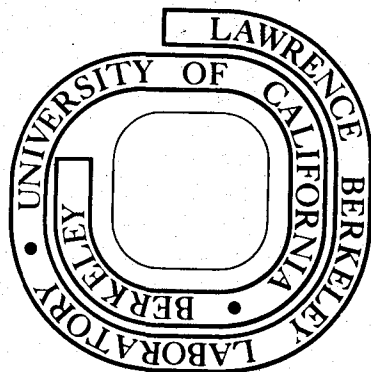
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Metal-Carbene Complexes and the Possible Role of Hydroxycarbene
in Formaldehyde Laser Photochemistry

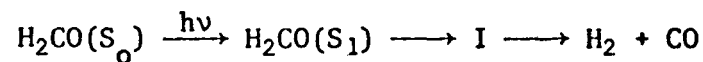
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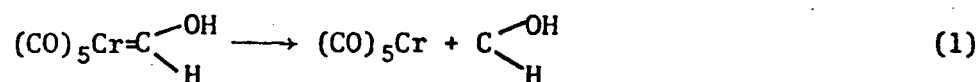
Abstract

Transition metal-carbene complexes represent one of the important advances in organometallic chemistry over the past decade. Of particular interest here are the hydroxycarbenes $(CO)_5MC \begin{smallmatrix} \text{OH} \\ \text{R} \end{smallmatrix}$ prepared by Fischer and coworkers. Such complexes are known to split off the carbene ligand, which subsequently rearranges to give the much more stable aldehyde. It is pointed out that this isomerization reaction may possibly identify the intermediate state I in the photodissociation of formaldehyde

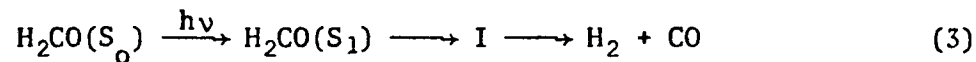


Ab initio configuration interaction studies of hydroxycarbene HCOH have been carried out to provide additional insight into the plausibility of this hypothesis.

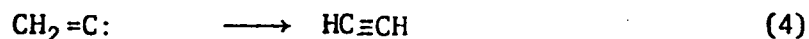
Hydroxycarbene CHOH is probably the most important very simple carbene which has not been characterized experimentally. First, one would like to relate the properties of hydroxycarbene to those of other simple carbenes [e.g. CH_2 , CHF , CHCl , CHBr , and CHCN] for which experimental data is available.¹⁻³ Secondly CHOH may be considered the simplest alkoxy-carbene $\text{C} \begin{smallmatrix} \diagup \text{OR} \\ \diagdown \text{R} \end{smallmatrix}$, and alkoxy-carbenes have proven extremely difficult to prepare via conventional synthetic methods.^{4,5} Third, the Fischer type transition metal carbenes⁶ $(\text{CO})_5\text{M}=\text{C} \begin{smallmatrix} \diagup \text{OR} \\ \diagdown \text{R} \end{smallmatrix}$ which have been one of the most exciting developments in organometallic chemistry during the past decade, contain the alkoxy-carbene fragment. In fact, as related by Fischer in his Nobel address⁷, the very first metal carbene complexes prepared were of the hydroxy variety $(\text{CO})_5\text{W}=\text{C} \begin{smallmatrix} \diagup \text{OH} \\ \diagdown \text{R} \end{smallmatrix}$. And, in fact, metal carbene complexes are even today considered^{2,7} the most realistic source of the extremely reactive alkoxy-carbene radicals. When the carbene ligand is split off from the metal, it appears⁷ that a hydrogen shift occurs almost immediately yielding an aldehyde product. A simple example of this process would be



Our interest in hydroxycarbene arose from recent experimental studies^{8,9} of the laser photodissociation of formaldehyde. Despite the simplicity of this system and the sophistication of the experimental techniques employed, there is still no adequate molecular explanation of the experimental results. Specifically, neither triplet formaldehyde T_1 nor the excited vibrational manifold of the ground state S_0 can be satisfactorily invoked as the intermediate I for the observed process



However, if some hitherto unrecognized molecular species were involved in the photodissociation, a coherent picture might emerge. One conceivable such "intermediate state" would be hydroxycarbene⁸, which is of course an isomer of formaldehyde. Here we wish to point out that experiments on Fischer-type carbenes lend credence to this hypothesis. As shown in (1) it is accepted by organometallic chemists^{6,7} that hydroxycarbenes spontaneously undergoes isomerization to yield formaldehyde. It must be noted of course that the hydroxycarbene in (1) may possess as internal energy some of the exothermicity resulting from the rupture of the metal-carbene bond. Nevertheless, it seems likely that there is a relatively small activation energy for rearrangement (2). This conclusion is supported by detailed theoretical studies¹⁰, incorporating the effects of electron correlation, of the related vinylidene rearrangement



for which a barrier of no more than 8 kcal/mole is predicted.

If there is only a small barrier associated with (2), then from microscopic reversibility we know that formaldehyde may be converted to hydroxycarbene with an amount of energy only slightly greater than the energy difference between the two isomers. The second purpose of this paper then is to evaluate this energy difference using reliable theoretical techniques. This problem has been addressed in a different context by Altmann, Csizmadia, Yates and Yates,¹¹ and we build on their research in the present study.

Using the standard Huzinaga-Dunning¹² double zeta (DZ) basis set, we first determined the equilibrium geometries of triplet and singlet

hydroxycarbene within the single-configuration self-consistent-field (SCF) approximation. This process was immensely simplified by having at our disposal the theoretical structures obtained by Altmann¹³ using a slightly smaller basis, and in fact two sets of structures are nearly indistinguishable.¹⁴ We note here one of Altmann's primary conclusions, namely that singlet hydroxycarbene has stable cis and trans forms (both planar), whereas the triplet state has only one stable geometry, gauche. Relative to the 1A_1 ground state of formaldehyde, the S_0 trans, S_0 cis, and T_1 gauche states of HCOH lie at 46.5, 54.2, and 48.2 kcal, respectively. Some idea of the reliability of these results may be gleaned from the S_0 - T_1 separation in formaldehyde, which is known experimentally³ to be 72.0 kcal/mole. In the present SCF calculations $\Delta E(S_0-T_1)$ is predicted to be 35.5 kcal. This difference of 36.5 kcal, which is also apparent in the Altmann study¹¹, is sufficiently large to bring into serious question the validity of these theoretical predictions.

For this reason, we decided to consider the effects of electron correlation using configuration interaction (CI).¹⁵ Since the DZ SCF geometries should be quite reliable,¹⁶ no geometry search was attempted in the CI studies. All but the final CI included all Slater determinants differing by one or two spinorbitals from the appropriate SCF reference configuration. This procedure was adopted with the restrictions (spelled out in the Table) that certain SCF orbitals were held frozen (i.e. doubly-occupied in all Slater determinants) and some of the highest improved virtual orbitals¹⁷ deleted from the CI. The CI treatments thus described ranged from 1628 to 5697 Slater determinants. In the final, and most reliable set of calculations, Slater determinants were selected (e.g. 5,561 from a total of 57,870 for triplet hydroxycarbene) using the cumulative perturbation theory method of Raffanetti, Hsu, and Shavitt.¹⁸

Our results are summarized in the Table and show that the final CI treatment predicts the formaldehyde S_0 - T_1 separation to be only 3 kcal less than known experimentally. This and the extensive CI methods employed suggest that the predictions in the final theoretical column should be quite reliable.

The most important finding here is that the S_0 trans, S_0 cis, and T_1 gauche electronic states of hydroxycarbene all lie below the formaldehyde S_1 state (80.6 kcal). Thus all three are energetically accessible during the photodissociation (3) of H_2CO . S_0 trans CHOH is a particularly attractive candidate for I [in Eq. (3) above] since it lies ~29 kcal below S_1 H_2CO , and is also favored from least motion considerations.

Finally we must emphasize that the present energy surface results by no means demonstrate that hydroxycarbene is the "intermediate state" in the laser photodissociation of formaldehyde. What we have shown is that this possibility is quite feasible energetically. Rather detailed theoretical dynamical studies and/or additional experiments will be needed to unravel the H_2CO photodissociation mechanism. It remains a formidable challenge to both theory and experiment.

This research was supported by the U.S. Energy Research and Development Administration and by the National Science Foundation, Grant GP-39317.

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Table Summary of energetic predictions for H₂CO and HCOH using different theoretical methods. The total energies obtained for the formaldehyde ground state were -113.8307, -113.9933, -114.0353, -113.8936, -114.0417, -114.0744, and -114.1338 hartrees.

Species	(Relative Energy (kcal/mole))							Experiment ^d
	DZ SCF	DZ CI ^a	DZ CI ^b	DZ+P SCF	DZ+P CI ^a	DZ+P CI ^b	DZ+P CI ^c	
Formaldehyde S ₀	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Formaldehyde T ₁	35.5	56.2	58.6	48.4	66.2	67.1	68.9	72.0
Hydroxycarbene S ₀ trans	46.5	53.2	54.1	47.9	54.2	53.0	51.7	-
Hydroxycarbene S ₀ cis	54.2	60.0	60.8	53.8	58.7	57.6	57.5	-
Hydroxycarbene T ₁ gauche	48.2	66.7	-	55.9	72.6	-	73.0	-

^a The three lowest SCF orbitals were held doubly-occupied and 13 virtual orbitals included in the CI.

^b The two lowest (essentially C and O 1s) orbitals were held doubly-occupied, and 14 virtual orbitals included in the CI.

^c The two lowest orbitals were held doubly-occupied, all virtual orbitals included in the CI, and determinants selected by perturbation theory.

^d Reference 3.

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This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

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