References and Notes

(1) (a) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960); (b) C. Walling and P. J. Wagner, *ibid.*, **85**, 2333 (1963); (c) C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964); (d) C. Walling and V. Kurkov, *ibid.*, **88**, 4727 (1966); (e) C. Walling, *Pure Appl. Chem.*, **15**, 69 (1967), and references therein; (f) C. Walling and J. A. McGuinness, *J. Am. Chem. Soc.*, **91**, 2053 (1969).

(2) (a) D. J. Carlsson, J. A. Howard, and K. U. Ingold, *J. Am. Chem. Soc.*, **88**, 4725 (1966); (b) D. J. Carlsson, J. A. Howard, and K. U. Ingold, *ibid.*, **88**, 4726 (1966); (c) B. R. Kennedy and K. U. Ingold, *Can. J. Chem.*, **44**, 2381 (1966); (d) D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 4891 (1967); (e) D. J. Carlsson and K. U Ingold, *ibid.*, **89**, 4885 (1967); (f) K. U. Ingold, *Pure Appl. Chem.*, **15**, 49 (1967).

(3) (a) A. A. Zavitsas and S. Ehrenson, *J. Am. Chem. Soc.*, **87**, 2841 (1965); (b) A. A. Zavitsas and J. D. Blank, *ibid.*, **94**, 4603 (1972); (c) A. A. Zavitsas and J. A. Pinto, *ibid.*, **94**, 7390 (1972).

(4) J. A. Howard, *Adv. Free Radical Chem.*, **4**, 49 (1971).

(5) (a) A. L. Williams, E. A. Oberright, and J. W. Brooks, *J. Am. Chem. Soc.*, **78**, 1190 (1956); (b) H. Sakurai and A. Hosomi, *ibid.*, **89**, 458 (1967); (c) J. K. Stoddart, A. Nechvatal, and J. J. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 473 (1974).

(6) In the case of the related methoxy radicals their half-life in methanol has been estimated as 106 ns from the extrapolation of a study of their reaction with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine: D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. R. Soc. London, Ser. A*, **328**, 23 (1972).

(7) S. Weiner and G. S. Hammond, *J. Am. Chem. Soc.*, **91**, 2182 (1969).

(8) M. C. R. Symons, *J. Am. Chem. Soc.*, **91**, 5924 (1969).

(9) We have recently used the same type of techniques in the study of biradical reactions. For a more detailed description of the experiments and assumptions, see R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828 (1977), and *ibid.*, **81**, 2126 (1977); *Chem. Phys. Lett.*, **50**, 431 (1977).

(10) The transient absorptions were monitored using a pulsed 450-W Xe lamp and monochromator system. The signal from an RCA-1P28 photomultiplier tube was terminated into 93 Ω and then displayed upon a Tektronik 7623 storage oscilloscope. The rise time of the detection system was ≤5ns.

(11) For a review on photoreduction, see J. C. Scaiano, *J. Photochem.*, **2**, 81 (1973/74).

(12) (a) M. R. Topp, *Chem. Phys. Lett.*, **32**, 144 (1975); (b) A. Beckett and G. Porter, *Trans. Faraday Soc.*, **59**, 2038 (1963).

(13) These experiments were carried out using an attenuation of ~1:20 for the laser pulse to avoid the second-order decay of the *tert*-butoxy radicals. The adequate range of pulse intensities was determined from a study of the dependence of the time profiles on the energy in the incident pulse. Attenuation of the pulses not only prevented the second-order decay, but also avoided significant heating effects. Diphenylmethanol was sublimed twice, to eliminate impurities, in particular benzophenone, and the samples were never pulsed more than six–eight times to avoid the accumulation of benzophenone produced via radical disproportionation. All the samples were degassed by three freeze–pump–thaw cycles to a residual pressure of ~2 × 10⁻⁵ Torr. Further details will be given in a full paper.

(14) The β cleavage of Buᵗ0· radicals to acetone and methyl radicals is unimportant under our experimental conditions.[1b,c]

(15) A. F. Trotman-Dickenson and G. S. Milne, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. 9 (1968); E. T. Denisov, "Liquid Phase Reaction Rate Constants", Plenum Press, New York, N.Y., 1974, p 283.

(16) J. P. Lorand and R. W. Wallace, *J. Am. Chem. Soc.*, **96**, 2874 (1974).

(17) C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

(18) A. Padwa, *Tetrahedron Lett.*, 3465 (1964).

(19) The research described herein was supported by the Division of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1801 from the Notre Dame Radiation Laboratory.

**R. D. Small, Jr., J. C. Scaiano***

Radiation Laboratory,[19] University of Notre Dame
Notre Dame, Indiana 46556

*Received September 6, 1977*

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

Sir:

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 A, and alkoxycarbenes have proven ex-

$$C\!\!<^{OR}_{R}$$

A
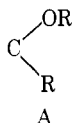
tremely difficult to prepare via conventional synthetic methods.[4,5] Third, the Fischer-type transition metal–carbenes[6] B,

$$(CO)_5M\!\!=\!\!C\!\!<^{OR}_{R}$$

B
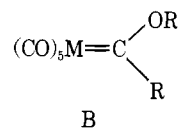
which have been one of the most exciting developments in organometallic chemistry during the past decade, contain the alkoxycarbene fragment. In fact, as related by Fischer in his Nobel address,[7] the very first carbene complexes prepared were of the hydroxy variety C. In fact, metal–carbene complexes

$$(CO)_5W\!\!=\!\!C\!\!<^{OH}_{R}$$

C
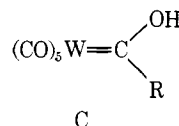
are even today considered[2,7] the most realistic source of the extremely reactive alkoxycarbene radicals. When the carbene ligand is split off from the metal, it appears[7] that a hydrogen shift occurs almost immediately yielding an aldehyde product. A simple example of this process would be

$$(CO)_5Cr\!\!=\!\!C\!\!<^{OH}_{H} \longrightarrow (CO)_5Cr + C\!\!<^{OH}_{H} \tag{1}$$

$$C\!\!<^{OH}_{H} \longrightarrow H_2C\!\!=\!\!O \tag{2}$$
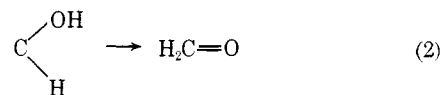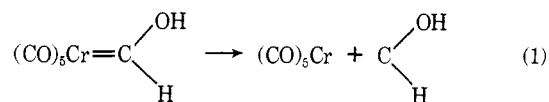
Our interest in hydroxycarbene arose from recent experimental studies[8,9] of the laser photodissociation of formaldehyde. Despite the simplicity of this system and the sophistication of the experimental techniques employed, there is still no adequate molecular explanation of the experimental results. 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

$$H_2CO(S_0) \xrightarrow{h\nu} H_2CO(S_1) \rightarrow I \rightarrow H_2 + CO \tag{3}$$
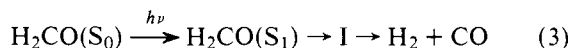
However, if some hitherto unrecognized molecular species were involved in the photodissociation, a coherent picture might emerge. One conceivable such "intermediate state" would be hydroxycarbene,[8] which is of course an isomer of formaldehyde. Here we wish to point out that experiments on Fischer-type carbenes lend credence to this hypothesis. As shown in reaction 1, it is accepted by organometallic chemists[6,7] that hydroxycarbenes spontaneously undergo isomerization to yield formaldehyde. It must be noted of course that the hydroxycarbene in reaction 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 indirectly supported by detailed theoretical studies,[10] incorporating the effects of electron correlation, of the related vinylidene rearrangement

$$CH_2\!\!=\!\!C\!\!: \rightarrow HC\!\!\equiv\!\!CH \tag{4}$$

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

If there is only a small barrier associated with rearrangement 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

Table I. Summary of Energetic Predictions for H_2CO and HCOH Using Different Theoretical Methods[a]

Species	Relative energy, kcal/mol							
	DZ SCF	DZ CI[b]	DZ CI[c]	DZ + P SCF	DZ + P CI[b]	DZ + P CI[c]	DZ + P CI[d]	Expt[e]
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 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. [b] The three lowest SCF orbitals were held doubly occupied and 13 virtual orbitals included in the CI. [c] The two lowest (essentially C and O 1s) orbitals were held doubly occupied and 14 virtual orbitals included in the CI. [d] The two lowest orbitals were held doubly occupied, all virtual orbitals included in the CI, and determinants selected by perturbation theory. [e] Reference 3.

context by Altmann, Csizmadia, Yates, and Yates,[11] and we build on their research in the present study.

Using the standard Huzinaga–Dunning[12] double ζ (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 Altmann[13] 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 experimentally[3] to be 72.0 kcal/mol. 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 study,[11] 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 spin orbitals from the appropriate SCF reference configuration. This procedure was adopted with the restrictions (spelled out in Table I) that certain SCF orbitals were held frozen (i.e., doubly occupied in all Slater determinants) and some of the highest improved virtual orbitals[17] 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., 5561 from a total of 57 870 for triplet hydroxycarbene) using the cumulative perturbation theory method of Raffenetti, Hsu, and Shavitt.[18]

Our results are summarized in Table I 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 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 form-

aldehyde. What we have shown is that this possibility is quite "feasible". 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.

References and Notes

(1) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971.
(2) M. Jones and R. A. Moss, "Carbenes", Vol. 1, 1973, Vol. II, 1975, Wiley, New York, N.Y.
(3) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1966.
(4) R. M. McDonald and R. A. Kueger, *J. Org. Chem.*, **31**, 488 (1966).
(5) W. J. Baron, M. R. DeCamp, M. E. Hendrick, M. Jones, R. H. Levin, and M. B. Sohn, ref 2, Vol. I, p 129.
(6) E. O. Fischer and A. Maasböl, *Angew. Chem., Int. Ed. Engl.*, **3**, 580 (1964).
(7) E. O. Fischer, *Adv. Organomet. Chem.*, **14**, 1 (1976); a more practical (than ref 6) route to hydroxycarbene complexes has been reported by E. O. Fischer, G. Kreis, and F. R. Kreisel, *J. Organomet. Chem.*, **56**, C37 (1973).
(8) P. L. Houston and C. B. Moore, *J. Chem. Phys.*, **65**, 757 (1976), and references therein.
(9) R. S. Lewis, K. Y. Tang, and E. K. C. Lee, *J. Chem. Phys.*, **65**, 2910 (1976); K. Y. Tang and E. K. C. Lee, *Chem. Phys. Lett.*, **43**, 232 (1976).
(10) C. E. Dykstra, unpublished work. Electron correlation was explicitly considered using the theory of self-consistent electron pairs (SCEP); see C. E. Dykstra, H. F. Schaefer, and W. Meyer, *J. Chem. Phys.*, **65**, 2740 (1976).
(11) J. A. Altmann, I. G. Csizmadia, K. Yates, and P. Yates, *J. Chem. Phys.*, **66**, 298 (1977).
(12) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965); T. H. Dunning, *ibid.*, **53**, 2723 (1970).
(13) J. A. Altmann, unpublished work. We thank Professor C. B. Moore for bringing Altmann's work to our attention.
(14) The three structures are available on request from R.R.L. The largest differences between the present structures and those of Altmann occurred for the gauche triplet: the present C–O distance is 1.371 Å, compared to Altmann's 1.359 Å, and our dihedral angle is 108.5°, compared to 104.9°.
(15) BERKELEY, an open ended configuration interaction (CI) program designed for minicomputers: R. R. Lucchese, B. R. Brooks, J. H. Meadows, W. C. Swope, and H. F. Schaefer, *J. Comput. Phys.*, in press.
(16) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974).
(17) W. J. Hunt and W. A. Goddard, *Chem. Phys. Lett.*, **3**, 414 (1969).
(18) R. C. Raffenetti, K. Hsu, and I. Shavitt, "Selection of Terms for a CI Wavefunction to Preserve Potential Surface Features", ICASE Report No. 76-20, Institute for Computer Applications in Science and Engineering, NASA Langley Research Center, Hampton, Va., July 8, 1976.

Robert R. Lucchese

Department of Chemistry and Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720

Henry F. Schaefer III*

Research School of Chemistry
Australian National University
Canberra, A.C.T. 2600, Australia
Received January 1, 1977