LBL-12815
Preprint

NRCC NATIONAL RESOURCE FOR COMPUTATION IN CHEMISTRY

Submitted to the Journal of Chemical Physics

ELECTRONIC STRUCTURE OF VINOXY RADICAL CH_2CHO

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July 1981

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Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48 and for the National Science Foundation under Interagency Agreement CHE-7721305

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Abstract

Ab initio multiconfiguration Hartree-Fock (MCHF) wavefunctions have been used to describe the electronic structure of vinoxy radical CH_2CHO. The energy difference between the ground $^2A''$ state and the first excited $^2A''$ state is found to be 3.22 eV using a double zeta quality basis set, in good agreement with the observed transition at 3.57 eV. In addition the calculations predict a near infrared electronic transition.

This work was supported 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. W-7405-ENG-48, and by the National Science Foundation under Grant No. CHE-7721305.

I. Introduction

Alkoxy radicals play an important role in combustion processes and in photochemical oxidation. The vinoxy radical CH_2CHO is assumed to be a primary product of the photolosis of ethyl vinyl ether,[1] of the photosensitized decomposition of methyl vinyl ether,[2] and of the thermal decomposition of divinyl ether.[3] In addition, many recent experiments indicate that the CH_2CHO radical is a primary product of the reaction of $O(^3P)$ with C_2H_4. Lee et al.[4] detected by mass spectrometry some products of a crossed molecular beam $O(^3P) + C_2H_4$ reaction, which they assigned to ionized derivatives of CH_2CHO. Inoue and Akimoto[5] observed the laser induced fluorescence originating from an electronic state at 3.57 eV of CH_2CHO produced in a fast flow reactor. Kleinermanns and Luntz[6] excited the same fluorescence from the products of a crossed molecular beam reaction of $O(^3P)$ and C_2H_4. Wendt et al.[7] detected the same electronic transition of CH_2CHO using kinetic optical absorption spectroscopy in the reaction of $O(^3P)$ with C_2H_4.

In light of all the experimental evidence of the role of the vinoxy radical, there is a need for an accurate theoretical characterization of its low lying electronic states. A previous theoretical study by Baird et al.[8,9] described the resonance interaction of two valence bond structures CH_2=CH-O and CH_2-CH=O which play an important role in the description of the ground state structure. Baird et al. used a minimal basis set (MB) in conjunction with a configuration interaction (CI) expansion. The minimal basis set favors the CC double-bonded structure over the CO double-bonded structure and while the CI expansion improves the electronic description of the ground state, there

is still a discrepancy between the theoretical and experimental CC and CO bond lengths and bond orders.[5]

In this paper we present ab initio calculations of selected ground and excited states of CH_2CHO. We find that double zeta plus polarization (DZP) basis set Hartree-Fock (HF) calculations of the resonance structures CH_2=CH-O and CH_2-CH=O favor the latter over the former structure. Furthermore, double zeta (DZ) quality basis set multiconfiguration Hartree-Fock (MCHF) calculations place the $X^2A'' \rightarrow 1^2A''$ electronic transition at 3.22 eV, and predict a near infrared $X^2A'' \rightarrow 1^2A'$ transition.

This paper is organized as follows: Section II summarizes the computational method; Section III presents a qualitative discussion of the electronic structure of CH_2CHO and Section IV provides details on the dominant HF resonance structures. Section V describes the results of ground and excited state calculations of the radical and conclusions of this study form the content of Section VI.

II. Computational Method

Spin restricted HF and MCHF calculations of the ground and first excited $^2A''$ states and of the $^2A'$ state of CH_2CHO were carried out using Pople's STO-3G[10] (MB) and 3-21G[11] (DZ) basis sets. In addition Dunning's (3s,2p) contraction[12] of Huzinaga's (9s,5p) basis set augmented with polarization functions ($\alpha_d^C = 0.75$ on carbon, $\alpha_d^O = 0.85$ on oxygen and $\alpha_p^H = 1.0$ on hydrogen), a basis denoted DZP, was used for HF calculations.

The structures reported in this paper correspond to fully optimized lowest energy structures obtained by the gradient method. The calculations were carried out with the HONDO program[13] which includes a Newton-Raphson orbital optimization procedure for MCHF wavefunctions[14] and the GUGA-CI program developed by Brooks[15] for configuration interaction (CI) calculations.

III. Electronic Structure of CH_2CHO

The ground state X^2A'' and the first excited state of $^2A''$ symmetry result from the resonance interaction of the ethenyloxy radical $CH_2{=}CH{-}O^{\cdot}$ and the formyl methyl radical $\dot{C}H_2{-}CH{=}O$. Valence bond pictures of these two resonance structures are shown in Fig. 1.

The ethenyloxy radical has a C-C double bond, an "out-of-plane" π unpaired electron located on the oxygen atom, an "in-plane" σ lone pair of electrons also on the oxygen atom and therefore conforms to $^2A''$ symmetry. The formyl methyl radical $\dot{C}H_2{-}CH{=}O$ has an "out-of-plane" π unpaired electron located on the methylene carbon atom, a C-O double bond, a σ lone pair of electrons on the oxygen atom and therefore also has $^2A''$ symmetry. The resonance interaction of these two structures results in a π-electron system delocalized over the C-C-O bonds.

In addition to the $^2A''$ structure described above, the ethenyloxy radical has a $^2A'$ structure shown in Fig. 1. It differs from the $^2A''$ structure in the occupation of the π and σ orbitals located on the oxygen atom. In the $^2A'$ structure, the oxygen lone pair occupies a π orbital, while the unpaired electron occupies a σ orbital. There exists no other low-lying $^2A'$ structure. The energy correlation diagram in Fig. 2 follows from these qualitative considerations. It is based on the HF (DZP) calculations described in section IV.

From the above qualitative description of the valence states of CH_2CHO, it is easy to formally write a compact wavefunction which can describe the resonance interaction. For the $^2A''$ states we consider the three π orbitals built from the three atomic out-of-plane functions. The 8 configurations, obtained by distributing the three π electrons in all possible ways among the three π orbitals, contain the electron spin recoupling configurations needed to describe the resonance interaction. For the $^2A'$ state the configurations obtained by distributing four electrons among the three π orbitals and keeping an unpaired electron in the oxygen σ orbital (total of 9 configurations) describe the most important electron correlation effects.

IV. The HF Resonance Structures of CH_2CHO

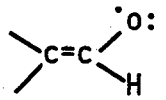
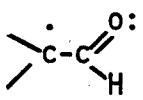
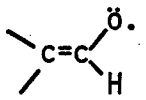
Interestingly enough, the HF model provides two local minima on the $^2A''$ potential energy hypersurface, corresponding to the ethenyloxy radical structure and to the formyl methyl radical structure. Only one minimum is found on the $^2A'$ hypersurface. The most important geometric parameters obtained with the DZP basis set are given in Table I, while the total and relative energies obtained with the various basis sets are given in Table II.

For comparison with the results given in Table I, we note that the DZP basis set gives R(CC) = 1.325 Å for ethylene, R(CO) = 1.192 Å and R(CC) = 1.508 Å for acetaldehyde $CH_3CHO(^1A_1)$, R(CO) = 1.402 Å for methanol CH_3OH, and R(CC) = 1.523 Å for ethane.[16] On the basis of the calculated structures of the $^2A'$ minimum and of the two $^2A''$ minima, we assign these minima to the ethenyloxy and formyl methyl radical structures. In the $^2A''$ ethenyloxy structure, the CC bond length (1.316 Å) corresponds to an almost pure π bond while the CO bond length (1.384 Å) is shorter than the CO σ bond length in CH_3OH. These features can be attributed to the interaction of the unpaired electron on the oxygen atom with the CC π bond. In the $^2A''$ formyl methyl structure, the CO bond length (1.217 Å) corresponds to an almost pure π bond, while the CC bond length is shorter than the CC σ bond length (1.523Å) in ethane. Here also the unpaired electron on the methylene group relaxes slightly the double bond in a β position to the radical center.

The $^2A'$ structure of ethenyloxy radical is similar to the $^2A''$ structure. The out-of-plane orientation of the oxygen lone pair results in a greater electron pair repulsion with the π bond, thereby shortening the CC double bond length and increasing the CO bond length.

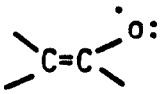
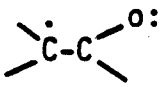
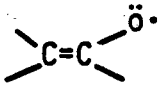
Although the geometry of the valence structures are qualitatively unchanged going from the MB to the DZP basis set, total energies are found to be sensitive to basis set. With the MB basis set the $^2A'$ ethenyloxy structure has the lowest energy followed in order by the $^2A''$ ethenyloxy structure and the $^2A''$ formyl methyl structure, the former being $\sim$9 kcal/mole more stable than the latter. The MB basis set provides a better description of the CC double bond than the CO double bond. As noted by Baird et al.[8,9], it is unable to describe correctly

Table I. HF Resonance Structures[a] of CH_2CHO Radical.

		$^2A''$	$^2A''$	$^2A'$
				
		Ethenyloxy	Formyl methyl	Ethenyloxy
DZ basis	R(CC)	1.316	1.450	1.311
	R(CO)	1.384	1.217	1.386
	<(CCO)	120.8	123.9	124.8
	<(CCH)	122.7	115.1	124.0
DZP basis	R(CC)	1.335	1.464	1.323
	R(CO)	1.325	1.198	1.342
	<(CCO)	120.8	123.9	125.0
	<(CCH)	121.9	115.4	124.2

a. Bond lengths in angstroms, angles in degrees.

Table II. Total[a] and Relative Energies[b] of the HF Structures of CH_2CHO Radical.

		MB basis	DZ basis	DZP basis
	$^2A''$	-150.318890 (+2.4)	-151.429214 (-2.4)	-152.304399 (-2.6)
	$^2A''$	-150.303949 (+11.8)	-151.428499 (-2.0)	-152.323418 (-14.5)
	$^2A'$	-150.322779 (0.0)	-151.425393 (0.0)	-152.300207 (0.0)

a. Total energies in atomic units.

b. Relative energies in kcal/mol, given in parentheses.

the strength of the π components of C=O and C=C bonds. An improvement is observed with the DZ basis set used in this study, however, because the two $^2A''$ structures have nearly identical energies. Baird et al.[8,9] suggested that a double zeta plus polarization basis set is necessary to stabilize the oxygen lone pair by bonding participation through the hydrogens. The DZP results reported here confirm this notion, since the formyl methyl radical is found to be ~ 12 kcal/mol more stable than the $^2A''$ ethenyloxy and ~ 14.5 kcal/mol more stable than the $^2A'$ ethenyloxy radical.

From the relative energies reported in Table II, the importance of the $^2A''$ ethenyloxy structure and $^2A''$ formyl methyl structure in the ground and excited states of vinoxy radical will change dramatically going from the MB basis set to the DZ and DZP basis sets. For the DZ basis set a nearly equal contribution is expected, but for the DZP basis set the formyl methyl structure will have the dominant contribution. The correlation diagram of Fig. 2 corresponds to the DZP results.

V. Ground and Excited States of Vinoxy Radical

The MCHF optimized structures obtained with the DZ basis set are given in Table III (labels are shown in Fig. 3). Total and relative energies for the MB and DZ basis sets are presented in Table IV. The out-of-plane π natural orbitals of the MCHF (DZ) wavefunctions are schematically represented in Fig. 4 and the corresponding occupation numbers are shown also.

The structure of the ground state ($^2A''$) from the DZ basis is nearly half way between the two interacting resonance structures. As pointed out in the previous section, this is to be expected since the two resonance structures are nearly degenerate with a DZ basis set. With the

DZP basis set, one would expect the $^2A''$ ground state to resemble the formyl methyl radical, which is the lower energy resonance structure. The first excited $^2A''$ state has a structure significantly different from the X^2A'' state. The CC and CO bond lengths are much longer (R(CC) = 1.466 Å and R(CO) = 1.397 Å) than in the ground state (R(CC) = 1.405 Å and R(CO) = 1.275 Å). These differences can be explained by considering the natural orbitals displayed in Fig. 4. The orbitals with one and two nodal surfaces have higher occupation numbers in the excited $1^2A''$ state than in the ground X^2A'' state, resulting in longer CC and CO bonds.

A comparison of Tables I and III shows that the $^2A'$ state of CH_2CHO has nearly identical HF and MCHF structures. For this state the role of configuration mixing is to describe electron correlation rather than resonance interaction, resulting in slightly increased CC and CO bond lengths (R(CC) = 1.331 Å and R(CO) = 1.391 Å) compared to the HF structure (R(CC) = 1.311 Å and R(CO) = 1.386 Å).

The term energy for the first excited $^2A''$ state is calculated to be 69.6 kcal/mol (3.02 eV) with the MB basis set, and 74.3 kcal/mol (3.22 eV) with the DZ basis set. This is to be compared with the experimentally observed transition at 82.32 kcal/mol (3.57 eV). It is interesting that these small basis set MCHF wavefunctions provide an excitation energy in semiquantitative agreement with experiment. Further improvement could be obtained using the DZP basis set in the MCHF wavefunction, and a more extended CI expansion.

Table III. MCHF (DZ) Optimized Structures[a] of the Ground and Excited States of CH_2CHO Radical.

	$X\text{-}^2A''$	$1\text{-}^2A''$	$^2A'$
Energy (au)	-151.474548	-151.356117	-151.454632
ΔE (kcal/mol)	0.0	+74.3	+12.5
$R(C_1C_2)$	1.405	1.466	1.331
$R(C_2O)$	1.275	1.397	1.391
$R(C_1H_1)$	1.071	1.069	1.071
$R(C_1H_2)$	1.070	1.069	1.071
$R(C_2H_3)$	1.078	1.069	1.073
$<(H_1C_1C_2)$	120.2	120.0	121.7
$<(H_2C_1C_2)$	120.5	119.5	120.2
$<(H_3C_2C_1)$	117.8	120.9	124.3
$<(C_1C_2O)$	122.9	121.5	124.4

a. Bond lengths in angstroms, angles in degrees.

Table IV. MCHF Total[a] and Relative Energies[b] of the Valence Electronic States of CH_2CHO Radical.

	MB basis	DZ basis
$X\text{-}^2A''$	-150.371324 (0.0)	-151.474548 (0.0)
$1\text{-}^2A''$	-150.260371 (+69.6)	-151.356117 (+74.3)
$^2A'$	-150.363920 (+ 4.6)	-151.454632 (+12.5)

a. Total energies in atomic units.

b. Relative energies in kcal/mol given in parentheses.

The excitation energy of the $^2A'$ state is 4.6 kcal/mol (0.20eV) with the MB basis set, and 12.5 kcal/mol (0.54eV) with the DZ basis set. We recall that the $^2A'$ structure is only slightly (2.0 kcal/mol) above the $^2A''$ HF resonance structures with the DZ basis set. With the DZP basis set the $^2A'$ state lies 14.5 kcal/mol above the more stable resonance structure. In section III we pointed out the importance of the polarization functions for a proper description of the π component of the C=O bond or, in other words, for stabilizing the ground state structure through a better π electron description. The $^2A'$ state can be described as having a CC π bond and an out-of-plane π oxygen lone pair. Since both orbitals are doubly occupied, there is no competition between the CC π bond and the CO π bond as in the $^2A''$ states, and polarization functions are not expected to play as crucial a role. Polarization functions and a more extended CI expansion should lower the X^2A'' state more than the $^2A'$ state, resulting in an increased excitation energy. MCHF (DZP) calculations at the respective HF (DZP) minimum energy structures give $E(^2A') - E(X^2A'') = 0.86$ eV. Thus it is reasonable to expect a near infrared $X^2A'' \rightarrow {}^2A'$ transition between 0.9 and 1.25 eV.

Conclusions

Ab initio calculations using MCHF wavefunctions of the X^2A'', $1^2A'$ electronic states of CH_2CHO place the $X^2A'' \rightarrow 1^2A''$ electronic transition at 3.22 eV in good agreement with the experimentally observed transition at 3.57 eV, and predict a near infrared $X^2A'' \rightarrow 1^2A'$ transition between 0.9 and 1.25 eV. It is found that a double zeta plus polarization basis set is necessary for a quantitative description of the C-C and C-O bonds of the vinoxy radical. As this manuscript was in preparation

Hunziker et al.[17] reported the detection of a near infrared transition of CH_2CHO in the $O + C_2H_4$ reaction with a O-O band head at 0.99 eV.

Acknowledgements

The authors gratefully acknowledge many stimulating discussions with Drs. H. E. Hunziker, A. C. Luntz and L. B. Harding. This work was supported 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. W-7405-ENG-48 and by the National Science Foundation under Grant No. CHE-7721305.

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Table Captions

Table I. HF Resonance Structures of CH_2CHO Radical.

Table II. Total[a] and Relative Energies[b] of the HF structures of CH_2CHO Radical.

a. Total energies in atomic units.

b. Relative energies in kcal/mol given in parentheses.

Table III. MCHF (DZ) Optimized structures of the ground and excited states of CH_2CHO Radical.

Table IV. MCHF Total[a] and Relative [b] Energies of the Valence Electronic States of CH_2CHO Radical.

a. Total energies in atomic units.

b. Relative energies in kcal/mol given in parentheses.

Figure Captions

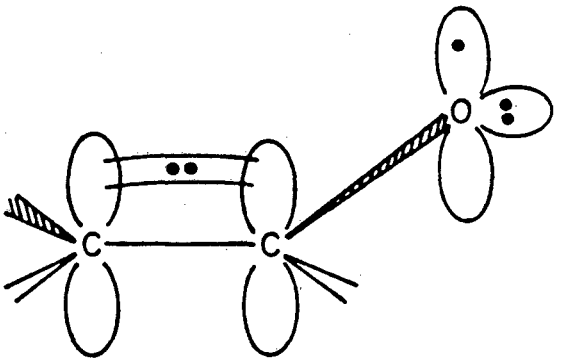
Fig. 1. Valence bond structures of the vinoxy radical.

Fig. 2. Correlation diagram for the $^2A''$ and $^2A'$ structures of CH_2CHO radical.

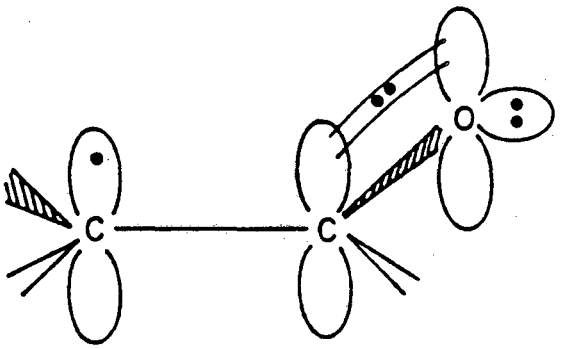
Fig. 3. The vinoxy radical.

Fig. 4. π Natural orbitals[a] of the MCHF (DZ) wavefunctions of the valence states of CH_2CHO radical.

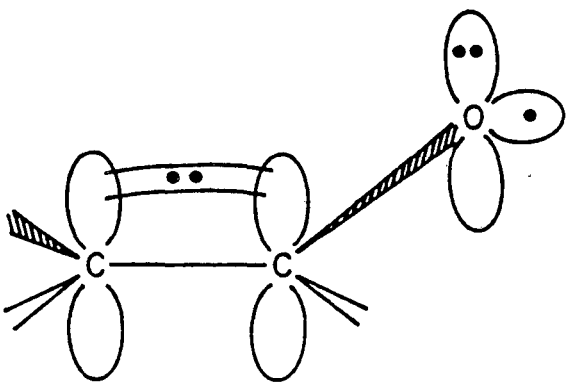
a. Occupation numbers given in parentheses.



$^2A''$ ethenyloxy radical



$^2A''$ formyl methyl radical



$^2A'$ ethenyloxy radical

Fig. 1

XBL816-2320

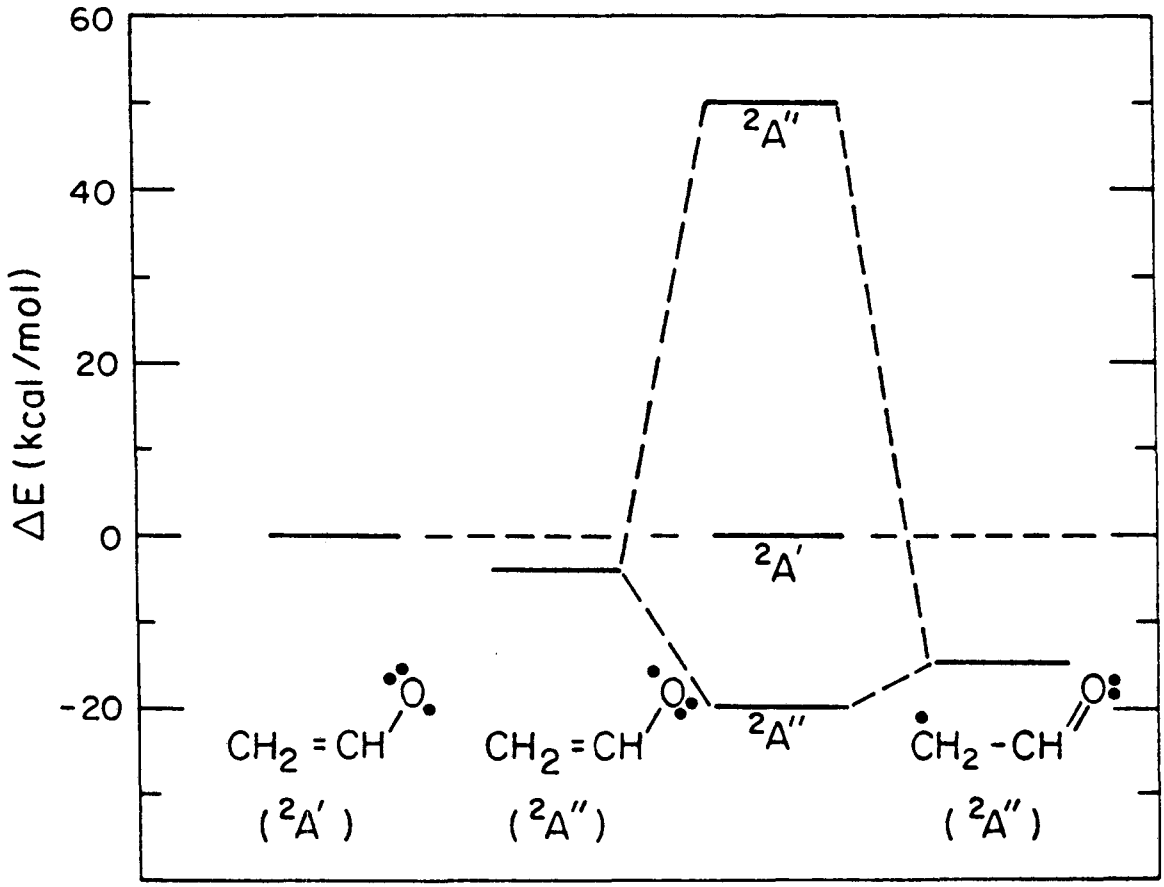
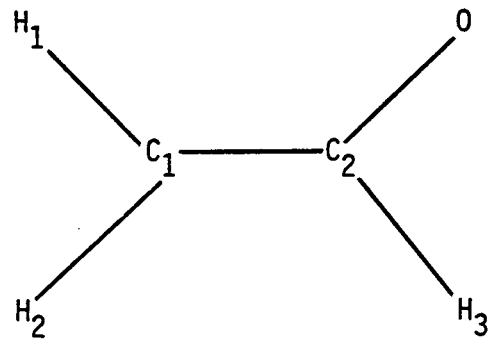
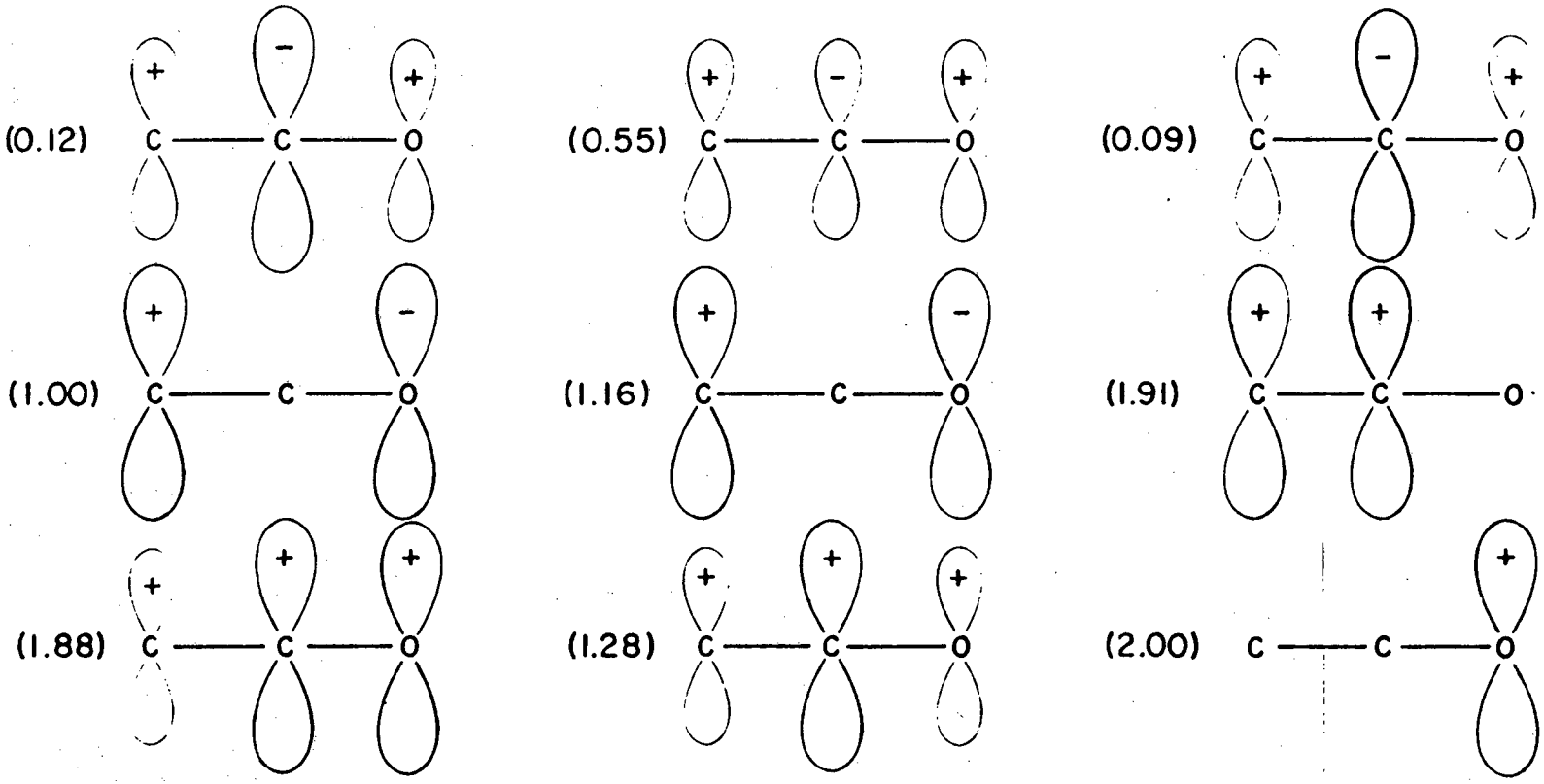


Fig. 2

XBL816-2321

Fig. 3. The vinoxy radical CH_2CHO





a. Occupation numbers given in parentheses.

Fig. 4

XBL 816 - 2322

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