

Short Communications

Structures and Thermodynamic Stabilities of the C₂H₄O Isomers: Acetaldehyde, Vinyl Alcohol and Ethylene Oxide

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Ab initio molecular orbital theory with a sequence of basis sets ranging from minimal to triple zeta plus polarization and with electron correlation incorporated using Möller–Plesset perturbation theory terminated at third order (MP3) is used to examine the structures and relative energies of the C₂H₄O isomers, acetaldehyde, vinyl alcohol and ethylene oxide. Acetaldehyde is indicated to be the most stable isomer with vinyl alcohol lying 45 kJ mol⁻¹ and ethylene oxide 114 kJ mol⁻¹ higher in energy. The theoretical structures and energies are in reasonable agreement with the best available experimental data.

Key words: Acetaldehyde – Vinyl alcohol – Ethylene oxide.

1. Introduction

Of the C₂H₄O isomers, acetaldehyde and ethylene oxide have been experimentally known for some time while vinyl alcohol was first observed only quite recently [1]. A large number of *ab initio* calculations have been previously reported [2–10] for acetaldehyde (**1**), vinyl alcohol (**2**) and ethylene oxide (**3**) but there has been no systematic study of the three molecules together. We have previously reported STO-3G structures for all three molecules [3, 4] and a 4-31G structure for vinyl alcohol [5]. In this paper, we supplement these data with 4-31G structures for acetaldehyde and ethylene oxide. In addition, we report new calculations with considerably larger basis sets and which incorporate electron correlation, thus yielding more reliable energy comparisons. Our results are compared with available experimental data.

2. Methods and Results

Theoretical structures for the three C₂H₄O isomers were obtained at the self-consistent-field level with the minimal STO-3G [11] and split-valence 4-31G

Table 1. Calculated total energies (hartrees) for C₂H₄O isomers at their experimental geometries

Method	Acetaldehyde	Vinyl alcohol ^a	Ethylene oxide
RHF/4-31G ^b	-152.68519	-152.66858	-152.62490
RHF/6-31G	-152.84197	-152.82619	-152.78274
RHF/6-31G ^{*c}	-152.91369	-152.88755	-152.86605
RHF/6-31G ^{**}	-152.92040	-152.89957	-152.87280
RHF/DZ	-152.86838	-152.85464	-152.81004
RHF/DZd	-152.94315	-152.91815	-152.89479
RHF/DZdp	-152.95156	-152.93169	-152.90326
RHF/TZ	-152.89226	-152.87924	-152.83822
RHF/TZd	-152.96304	-152.94097	-152.91441
RHF/TZdp	-152.97071	-152.95241	-152.92275
RHF/DZd'p'	-152.94962	-152.92997	-152.90034
MP3/DZd'p'	-153.42242	-153.40398	-153.37758

^a Estimated experimental structure from Ref. [5].

^b Using STO-3G geometries, RHF/4-31G results are -152.68499, -152.66632 and -152.62444 for **1**, **2** and **3** respectively.

^c Using STO-3G geometries, RHF/6-31G^{*} results are -152.91347, -152.88506 and -152.86455 for **1**, **2** and **3** respectively.

[12] basis sets using a gradient optimization procedure. In order to obtain improved energy comparisons and to study the effect of basis set enhancements and of electron correlation on the predicted relative energies, additional calculations were carried out with a sequence of basis sets ranging from split-valence to triple-zeta plus polarization functions, and with electron correlation incorporated at the level of third-order Möller-Plesset perturbation theory (MP3) [12]. The gaussian atomic basis sets used were the 4-31G [13] and 6-31G [13] split-valence bases, the Huzinaga-Dunning [4s2p/2s] double-zeta (DZ) basis [14], and a triple-zeta [6s3p/3s] basis (TZ) formed by contraction of van Duijneveldt's (11s6p/5s) primitive atomic basis [15]. A hydrogen scale factor $\eta^2 = 1.44$ was used for the DZ and TZ bases. Calculations were performed with these unpolarized basis sets and, except for the 4-31G basis, with first the addition of d-functions on carbon and oxygen (6-31G,^{*} DZd, TZd) and then the further addition of p-functions on hydrogen (6-31G,^{**} DZdp, TZdp). For the 6-31G basis set, the polarization function exponents were taken from reference [16] ($\zeta_{\text{dC}} = \zeta_{\text{dO}} = 0.80$, $\zeta_{\text{pH}} = 1.1$) while those for the DZ and TZ bases were based on the values of reference [17] ($\zeta_{\text{dC}} = 0.75$, $\zeta_{\text{dO}} = 0.98$, $\zeta_{\text{pH}} = 1.0$). The MP3 calculations were carried out using the DZ basis augmented with polarization functions (DZd'p') whose exponents ($\zeta_{\text{dC}} = 0.70$, $\zeta_{\text{dO}} = 1.25$, $\zeta_{\text{pH}} = 0.70$) were taken from published optimization studies for correlated wavefunctions [18–20]. To avoid the effects of possible errors in the theoretical structures, our energy comparisons are based on calculations carried out on the experimental structures [21, 22] for **1** and **3** and an estimated experimental structure [5] for **2**, although for comparison, the 4-31G and 6-31G^{*} calculations were also performed on the STO-3G geometries. The SCF calculations were carried out using a modified version [23] of the Gaussian

Table 2. Energies (kJ mol⁻¹, relative to acetaldehyde) of C₂H₄O isomers at their experimental geometries

Method	Vinyl alcohol ^a	Ethylene oxide
RHF/4-31G ^b	43.6	158.3
RHF/6-31G	41.4	155.5
RHF/6-31G ^{*c}	68.6	125.1
RHF/6-31G ^{**}	54.7	125.0
RHF/DZ	36.1	153.2
RHF/DZd	65.6	127.0
RHF/DZdp	52.2	126.8
RHF/TZ	34.2	141.9
RHF/TZd	57.9	127.7
RHF/TZdp	48.1	125.9
RHF/DZd'p'	51.6	129.4
MP3/DZd'p'	48.4	117.7

^a Estimated experimental structure from Ref. [5].

^b Using STO-3G geometries, RHF/4-31G relative energies are 49.0 and 159.0 for **2-1** and **3-1** respectively.

^c Using STO-3G geometries, RHF/6-31G^{*} relative energies are 76.4 and 128.4 for **2-1** and **3-1** respectively.

70 [24] and the ATMOL3 [25] systems of programs, and the MP3 calculations using an extended version [26] of Dykstra's SCEP program [27].

Calculated total energies are listed in Table 1 and the corresponding relative energies in Table 2. Calculated and experimental geometries are compared in Fig. 1.

3. Discussion

Theoretical and experimental [21] structural parameters are shown in Fig. 1 for the preferred conformation of acetaldehyde (**1**) in which a methyl C-H bond eclipses C=O. Both STO-3G and 4-31G perform reasonably well for this molecule. For vinyl alcohol (**2**), the preferred conformation has previously been shown, both experimentally [1] and theoretically [3, 5, 8, 10] to be *syn*. Only an incomplete experimental structural determination has been reported for this molecule. We have therefore previously constructed [5] a predicted experimental structure, obtained by systematically correcting the STO-3G and 4-31G structures for known basis set deficiencies. This structure is included in Fig. 1 and has been employed here as the experimental structure for vinyl alcohol. Note particularly the large differences between the "experimental" value of the bond angle at oxygen in **2** and the STO-3G and 4-31G values. The third isomer ethylene oxide (**3**) has been previously optimized at the STO-3G level and a 6-31G^{*}//STO-3G energy reported [4]. We have refined here a recently reported [9] 4-31G structure for **3**. Both the STO-3G and 4-31G geometries agree well with the experimental structure [22] for ethylene oxide. The mean absolute errors for STO-3G and 4-31G structural parameters for acetaldehyde

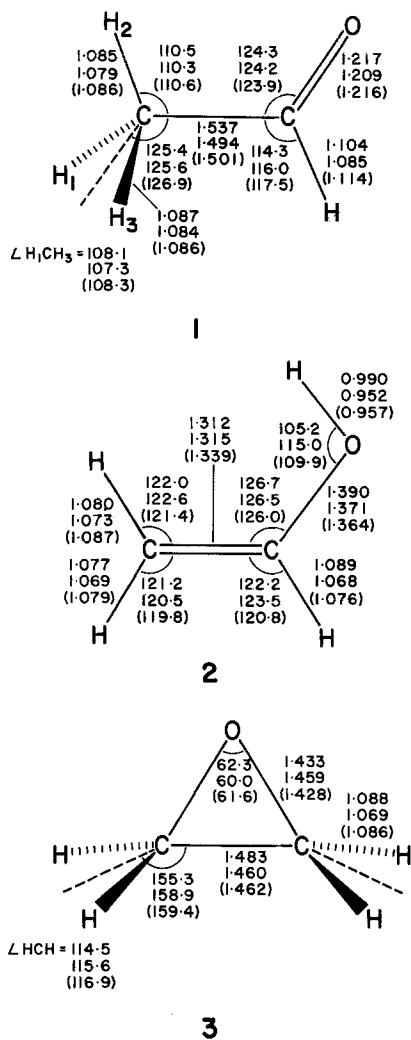


Fig. 1. Theoretical and experimental geometries of acetaldehyde (1), vinyl alcohol (2) and ethylene oxide (3). The "experimental" structural parameters for vinyl alcohol are estimated values from Ref. [5]. STO-3G and 4-31G values are given in that order, followed by experimental values in brackets. Bond lengths are given in Angstroms, bond angles in degrees

and ethylene oxide are 0.01–0.015 Å for bond lengths and 1.0–1.5° for bond angles.

The calculated relative energies show a wide variation at the different levels of theory. For the vinyl alcohol-acetaldehyde comparison, both *d*- and *p*-polarization functions are important. In particular, it can be seen that the effect of adding hydrogen *p*-functions to a basis already containing *d*-functions roughly halves the effect on the keto/enol energy difference of *d*-functions alone, so that the DZd quality results differ as much from the full DZdp results as do the unpolarized DZ values. For this system, it appears therefore that hydrogen *p*-functions must be included in the set of polarization functions along with the heavy atom *d*-functions to ensure a balanced treatment of the two isomers. Work is in progress to generalize this observation.

The correlation contribution to the vinyl alcohol-acetaldehyde energy difference is small, in agreement with our previous PNO-CEPA results [7]. However, although small in magnitude, the PNO-CEPA and MP3 correlation contributions to the energy difference have opposite signs, indicating that some caution is necessary in assessing the reliability of these methods when chemical accuracy ($\sim 5 \text{ kJ mol}^{-1}$) is required.

The ethylene oxide-acetaldehyde energy difference reflects the pattern expected [4] for a comparison of a small ring with its acyclic isomer, with polarization functions differentially favoring the cyclic isomer. For this energy difference, the effect of electron correlation has the same sign but about half the magnitude of the effect of the polarization functions. In contrast to the keto/enol comparison, the energy differences calculated with *p*-polarisation functions included do not differ significantly from those involving *d*-functions alone.

Our best relative energies at the SCF level are the TZdp results while our only results that include an electron correlation contribution come from the MP3 calculations carried out with the slightly inferior DZd'p' basis set. Estimates of the MP3/TZdp results can be obtained by assuming that the correlation corrections are the same for the DZd'p' and TZdp basis sets. This yields the best estimates of relative energies in the present study, namely 45 kJ mol^{-1} for vinyl alcohol and 114 kJ mol^{-1} for ethylene oxide, both relative to acetaldehyde.

In order to obtain experimental relative energies (corresponding to stationary nuclei at 0°K) which may be compared with our theoretical results, we have taken the $\Delta H_f^\circ(0^\circ)$ values [28] for acetaldehyde and ethylene oxide (-155.4 and $-40.1 \text{ kJ mol}^{-1}$, respectively) and corrected these for zero-point vibrational energies. The latter were calculated as $\frac{1}{2}\sum_i h\nu_i$ where ν_i are the experimental fundamental vibration frequencies for acetaldehyde [29] and ethylene oxide [30]. This results in an experimental relative energy for ethylene oxide of $111.7 \text{ kJ mol}^{-1}$ (compared with an uncorrected value of $115.3 \text{ kJ mol}^{-1}$) which is slightly lower than our best estimate of 114 kJ mol^{-1} .

No direct experimental thermochemical data have yet been reported for vinyl alcohol. An indirect estimate of $\Delta H_f^\circ(298^\circ)$ of -111 kJ mol^{-1} , obtained [31] assuming bond energy additivity, yields (using $\Delta H_f^\circ(298^\circ) = -166.2 \text{ kJ mol}^{-1}$ for acetaldehyde) an energy of 55 kJ mol^{-1} for **2** compared with **1**. A gas-phase experimental (ICR) value [32] for the energy difference between the closely related systems acetone and its enol, propen-2-ol, is $58 \pm 8 \text{ kJ mol}^{-1}$. This value can be compared with our best estimate of 45 kJ mol^{-1} for the vinyl alcohol-acetaldehyde energy difference.

4. Conclusions

STO-3G and 4-31G structures for acetaldehyde, vinyl alcohol and ethylene oxide are in reasonable agreement with available experimental data although

there are some deficiencies characteristic of the individual basis sets. Satisfactory relative energies are only realised with basis sets which include both *d*- (on C and O) and *p*- (on H) polarization functions. Electron correlation preferentially favors the cyclic ethylene oxide structure over its acyclic isomers but its effect is less than that of the polarization functions. Our best calculations predict that acetaldehyde is the most stable isomer with vinyl alcohol lying 45 kJ mol⁻¹ and ethylene oxide 114 kJ mol⁻¹ higher in energy.

References

1. Saito, S.: Chem. Phys. Letters. **42**, 399 (1976)
2. Richards, W. G., Walker, T. E. H., Hinkley, R. K.: A bibliography of ab Initio molecular wave functions. Oxford: Clarendon Press 1971; Richards, W. G., Walker, T. E. H., Farnell, L., Scott, P. R.: Supplement for 1971–1973. Oxford: Clarendon Press 1974; Richards, W. G., Scott, P. R., Colbourn, E. A., Marchington, A. F.: Supplement for 1974–1977. Oxford: Clarendon Press 1978
3. Bouma, W. J., Poppinger, D., Radom, L.: J. Am. Chem. Soc. **99**, 6443 (1977)
4. Lathan, W. A., Radom, L., Hariharan, P. C., Hehre, W. J., Pople, J. A.: Fortsch. Chem. Forsch. **40**, 1 (1973)
5. Bouma, W. J., Radom, L.: J. Mol. Struct. **43**, 267 (1978)
6. Bouma, W. J., Vincent, M. A., Radom, L.: Int. J. Quantum Chem. **14**, 767 (1978)
7. Rodwell, W. R., Bouma, W. J., Radom, L.: Int. J. Quant. Chem. in press.
8. Samdal, S., Seip, H. M.: J. Mol. Struct. **28**, 193 (1975)
9. Hopkinson, A. C., Lien, M. H., Csizmadia, I. G., Yates, K.: Theoret. Chim. Acta (Berl.) **47**, 97 (1978)
10. Larson, J. R., Epiotis, N. D., Bernardi, F.: J. Am. Chem. Soc. **100**, 5713 (1978)
11. Hehre, W. J., Stewart, R. F., Pople, J. A.: J. Chem. Phys. **51**, 2657 (1969)
12. Møller, C., Plesset, M. S.: Phys. Rev. **46**, 618 (1934); Pople, J. A., Binkley, J. S., Seeger, R.: Int. J. Quant. Chem., Quant. Chem. Symp. **10**, 1 (1976)
13. Ditchfield, R., Hehre, W. J., Pople, J. A.: J. Chem. Phys. **54**, 724 (1971); Hehre, W. J., Ditchfield, R., Pople, J. A.: J. Chem. Phys. **56**, 2257 (1972)
14. Dunning, T. H.: J. Chem. Phys.: **53**, 2823 (1970)
15. van Duijneveldt, F. B.: IBM Technical Research Report RJ 945 (#16437), December 1971
16. Hariharan, P. C., Pople, J. A.: Theoret. Chim. Acta (Berl.) **28**, 213 (1973)
17. Urban, M., Kellö, V., Čársky, P.: Theoret. Chim. Acta (Berl.) **45**, 205 (1977)
18. Ahlrichs, R., Lischka, H., Staemmler, V., Kutzelnigg, W.: J. Chem. Phys. **62**, 1225 (1975)
19. Botschwina, P., Meyer, W.: Chem. Phys. **20**, 43 (1977)
20. Pople, J. A., Binkley, J. S., Seeger, R.: Int. J. Quantum Chem. **S10**, 1 (1976)
21. Kilb, R. W., Lin, C. C., Wilson, E. B.: J. Chem. Phys. **26**, 1695 (1957)
22. Hirose, C.: Bull. Chem. Soc. Jpn. **47**, 1311 (1974)
23. Poppinger, D., Vincent, M. A., Hinde, A. L., Radom, L.: unpublished
24. Hehre, W. J. *et al.*: QCPE **11**, 236 (1973)
25. Saunders, V. R., Guest, M. F.: 'ATMOL3 Users Guide', Science Research Council, Daresbury, Warrington, England
26. Rodwell, W. R.: unpublished
27. Dykstra, C. E., Schaefer, H. F., Meyer, W.: J. Chem. Phys. **65**, 2740 (1976)
28. Rosenstock, H. M., Draxl, K., Steiner, B. W., Herron, J. T.: J. Phys. Chem. Ref. Data **6**, suppl. 1 (1976)
29. Hollenstein, H., Gunthard, H. H.: Spectrochim. Acta, **27A**, 2027 (1971)
30. Cant, N. W., Armstead, W. J.: Spectrochim. Acta, **31A**, 8391 (1975)
31. Holmes, J. L., Terlouw, J. K., Lossing, F. P., J. Phys. Chem. **80**, 2860 (1976)
32. Pollack, S. K., Hehre, W. J.: J. Am. Chem. Soc. **99**, 4845 (1977)

Note added in proof

Since submission of this manuscript, two unpublished experimental estimates of the vinyl alcohol-acetaldehyde energy difference have been brought to our attention. The first, 32 kJ mol⁻¹, is derived from an ion cyclotron resonance spectroscopy study (Hehre, W. L.: unpublished data). The second, 52 kJ mol⁻¹, is derived using a recently measured ionization potential for vinyl alcohol (9.04 ± 0.05 eV, Holmes, J. L., Lossing, F. P.: unpublished data) in conjunction with a previously reported ionization potential for acetaldehyde (10.23 eV) and energy difference between the molecular ions of acetaldehyde and vinyl alcohol (44 kJ mol⁻¹) (c.f. Ref. [31]). We are indebted to Professors Warren Hehre and John Holmes for providing us with this information.