LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2003 issue.

NOTES

On the feasibility of chemi-ion formation in the system CH₂CH($\tilde{a}\,^4A''$)+O(^3P)
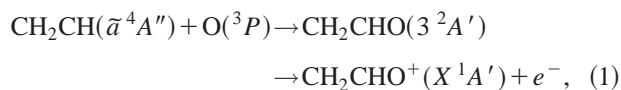
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We have investigated theoretically the possibility that the CH₂CH($\tilde{a}\,^4A''$) radical can generate the CH₂CHO⁺($X\,^1A'$) ion upon collisions with O(^3P). We have concluded that this is very unlikely because the minimum of the ground-state potential-energy surface of the ion is at about the same level as the potential energy of the asymptotic CH₂CH($\tilde{a}\,^4A''$)+O(^3P) fragments. In addition the Franck–Condon factors should not be favorable because of a drastic change in the geometry of the ion. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1623478]

The vinoxy radical can be generated by reactions involving collisions of O(^3P) with olefins, with ethylene and with vinyl bromide as well as by photodissociation of an alkyl vinyl ether.[1–3] Its ground and first excited states are planar of $^2A''$ and $^2A'$ symmetries, respectively, and differ only in the location of the unpaired electron on the oxygen atom as has been shown by theoretical studies of this radical.[4,5] Further theoretical work has shown that the vinoxy radical can also be formed in collisions of O(^3P) with a vinyl radical.[6]

There is strong evidence that in a reaction mixture involving collisions of O(^3P) with 2-butyne, the first quartet state of the methylcarbyne radical (the isomer of the vinyl radical) is present in this mixture. Upon collisions of this radical with O(^3P), the primary chemi-ion CH₃CO⁺ is generated via the neutral intermediate CH₃CO.[7–9] The first quartet states of both the vinyl and the methylcarbyne radicals are stable because they are separated by a high barrier of about 50 kcal/mol.[10,11] Thus, it is of interest to investigate the possibility that the first quartet state of the vinyl radical can also generate chemi-ions. While in its ground state the vinyl radical is planar, in its excited first quartet state it has the staggered geometry shown in Fig. 1 of Ref. 11. At a similar staggered geometry (see Fig. 1 below), the third excited $^2A'$ state of vinoxy correlates to CH₂CH($\tilde{a}\,^4A''$)+O(^3P). Thus the purpose of the present work is to investigate the feasibility of the reaction chain:

$$\mathrm{CH_2CH}(\tilde{a}\,^4A'') + \mathrm{O}(^3P) \rightarrow \mathrm{CH_2CHO}(3\,^2A')$$

$$\rightarrow \mathrm{CH_2CHO}^+(X\,^1A') + e^-, \quad (1)$$

with the intermediate neutral in the staggered geometry shown in Fig. 1. For this to happen, the third excited state of the neutral intermediate must be bound and the potential energy surface (PES) of the ion must penetrate the PES of the neutral well enough for their vibrational levels to interact and thus induce autoionization. Also, the Franck–Condon factors should be favorable.

The correlation consistent basis sets of Dunning and co-workers[12,13] were employed: The aug-cc-pVTZ basis set on the C and O atoms and the cc-pVTZ basis set on the H atoms. The calculations were done at the MCSCF level using the MOLPRO package of programs.[14] There are 17 valence electrons but only 11 of them were distributed among twelve active orbitals. The other six were left in the three lowest valence orbitals, which were not in the active space due to the large amount of memory space required. All geometry
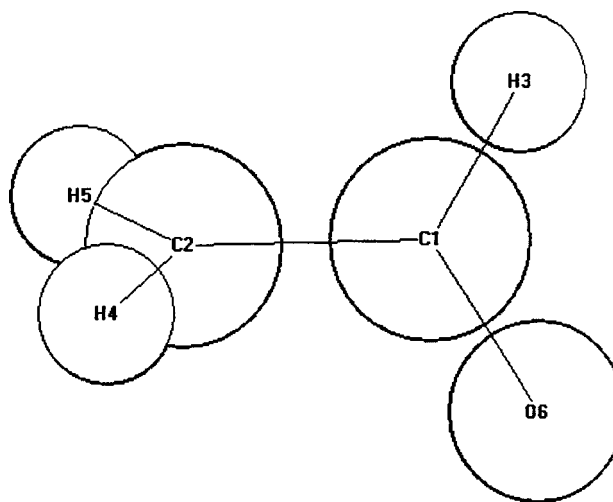

FIG. 1. Schematic of the CH₂CHO staggered geometry establishing the atom numbering followed in the text and in Table I.
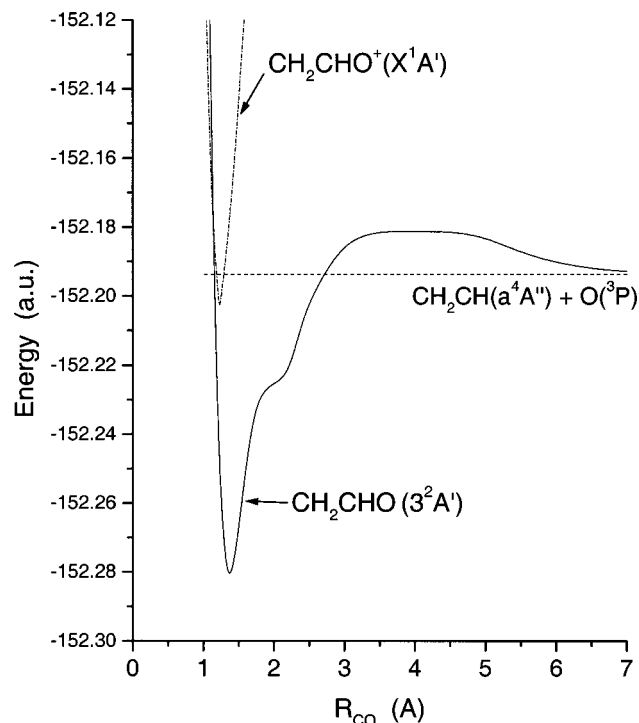
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FIG. 2. Cuts of the potential energy surfaces of the $CH_2CHO(3\,^2A')$ neutral and the $CH_2CHO^+(X\,^1A')$ ionic states along the R_{CO} reaction coordinate for the staggered geometry shown in Fig. 1. See text for optimization details.

TABLE I. The equilibrium and asymptotic geometries, energies and adiabatic ionization energies (AIE) of the indicated species. The accuracy of the entries are at a reduced active space MCSCF level (lengths in Å, angles in degrees).

Coordinates	$CH_2CHO(X\,^2A')$		$CH_2CHO^+(X\,^1A')$	
	Equilibrium	Asymptotic	Equilibrium	Asymptotic
$R_{CC}\ (=R_{12})$	1.5124	1.4509	1.4425	1.3913
$R_{CO}\ (=R_{16})$	1.2159	20.000	1.2385	20.000
R_{13}	1.0937	1.0964	1.0770	1.0667
R_{24}	1.0759	1.0782	1.0772	1.0852
R_{25}	1.0759	1.0782	1.0772	1.0852
Φ_{612}	123.27	180.00	075.08	000.00
Φ_{213}	116.38	110.17	152.07	177.24
Φ_{124}	120.63	120.14	119.91	120.54
Φ_{125}	120.63	120.14	119.91	120.54
	Energies (a.u.)			
MCSCF				
X	−152.470 77	−152.243 14	−152.206 50	−151.942 22
2	−152.307 87	−152.243 14		
3	−152.241 89[a]	−152.193 79		
CCSD(T)	−152.893 07		−152.605 00	
AIE (eV)	7.8			

[a]The MCSCF minimum of this state is −152.285 23 at $R_{CO}\simeq1.4$ Å.

optimizations were done by analytic gradients at the multi-configuration self-consistent field (MCSCF) level.

The equilibrium geometry of the $CH_2CH(\tilde{a}\,^4A'')$ radical is of C_s symmetry (see Fig. 1 of Ref. 11), and we maintained this symmetry during the approach of the O atom, which was kept on the C2C1H3 plane as shown in Fig. 1. We started the calculation for three states at a C–O distance of 20 Å and found that the third state of the vinoxy radical correlates to the quartet state of the vinyl radical plus $O(^3P)$. Then we proceeded inwards using the orbitals of the previous point as guess orbitals of the current point. At each C–O distance we optimized all other ground-state internal coordinates, and then we performed a state averaged calculation involving three states. The interest of course is on the third state, and one hopes that the ground-state optimization will generate a geometry close to that corresponding to the minimum energy of the third state.

For the ground state of the $CH_2CHO^+(X\,^1A')$ ion, assuming the existence of a minimum, and maintaining a staggered C_s symmetry, we initially optimized all internal coordinates. A minimum was indeed found. Starting from there, we proceeded on each side of this minimum exactly as in the case of the neutral species. The purpose, of course was to see whether the ion was bound and what was the relative position of the ground-state ionic PES with respect to the appropriate PES of the neutral species.

Of the three state-averaged states only the $3\,^2A'$ state is relevant to our discussion. The cut of this surface along the reaction coordinate (R_{CO}) is depicted in Fig. 2. Table I lists the optimized internal coordinates at both the asymptotic separation $(R_{CO}=20$ Å$)$ and at the ground-state equilibrium, which is not the equilibrium of the $3\,^2A'$ state but close

enough. The optimizations were done iteratively in groups of two to three internal coordinates at the equilibrium and at the asymptotic region. Within this limitation the minimum of the $3\,^2A'$ state was at $R_{CO}=1.4$ Å. Note that the asymptotic level of the $3\,^2A'$ state may be somewhat lower than the one given in Table I and Fig. 2, since only the ground state was optimized. The C–O bond energy of this state is about 2.49 eV.

The ground state of the ion is the $CH_2CHO^+(X\,^1A')$ state. Table I shows the optimized internal coordinates and the energy at the minimum and at the asymptotic region $(R_{CO}=20$ Å$)$. The adiabatic ionization energy of the neutral $3\,^2A'$ state is then about 2.14 eV. Note the drastic change of the CCO angle at equilibrium with respect to the neutral species, forcing the O atom to face the other end of the vinyl fragment upon separation. Figure 2 shows a cut of the ionic surface along the collision coordinate (R_{CO}). The optimizations were also done iteratively as in the case of the neutral.

It is obvious from both Table I and Fig. 2 that the minimum of the ionic state is at about the same level as the asymptotic level of the $CH_2CH(\tilde{a}\,^4A_2)+O(^3P)$ fragments, and it may even be above it, if the asymptotic level is lowered by a better optimization. Another way of putting it is that given the uncertainties of the optimizations, the ionization energy of the third state of the neutral species and its C–O bond energy are very close to each other, thus rendering autoionization improbable. Also, because of the neutral-ion geometry change, the Franck–Condon factors should not be favorable. Therefore, one concludes that the quartet vinyl radical is not likely to be a precursor of the observed chemiions.

[1] K. Kleinermanns and A. C. Luntz, J. Phys. Chem. **85**, 1966 (1981).
[2] R. J. Buss, R. J. Baseman, G. He, and Y. T. Lee, J. Photochem. **17**, 389 (1981).
[3] H. Su and R. Bersohn, J. Chem. Phys. **115**, 217 (2001).

[4] E. S. Huyser, D. Feller, W. T. Borden, and E. R. Davidson, J. Am. Chem. Soc. **104**, 2956 (1982).

[5] M. Dupuis, J. J. Wendoloski, and W. A. Lester, Jr., J. Chem. Phys. **76**, 488 (1982).

[6] D. J. Donaldson, I. V. Okuda, and J. J. Sloan, Chem. Phys. **193**, 37 (1995).

[7] Z. Hou and K. D. Bayes, J. Phys. Chem. **98**, 6324 (1994).

[8] J. M. Dyke, A. M. Shaw, and T. G. Wright, J. Phys. Chem. **98**, 6327 (1994).

[9] A. Metropoulos, Chem. Phys. Lett. **375**, 26 (2003).

[10] I. M. B. Nielsen, C. L. Jansen, N. A. Burton, and H. F. Schaefer III, J. Phys. Chem. **96**, 2490 (1992).

[11] A. Metropoulos, Chem. Phys. Lett. **368**, 701 (2003).

[12] T. H. Dunning, Jr., Chem. Phys. **90**, 1007 (1989).

[13] A. K. Wilson, T. V. Mourik, and T. H. Dunning, Jr., J. Mol. Struct.: THEOCHEM **388**, 339 (1996).

[14] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf *et al.*