First Experimental Observation on Different Ionic States of the *tert*-Butoxy [$(CH_3)_3CO^\bullet$] Radical

Zheng Sun,[a,b] Shijun Zheng,[b] Jing Wang,[a] Maofa F. Ge,[a] and Dianxun Wang*[a]

Abstract: A continuous *tert*-butoxy $(CH_3)_3CO^\bullet$ radical beam is produced in situ by respective pyrolysis of both $(CH_3)_3CONO$ at 115(±0.5) °C and $(CH_3)_3COOC(CH_3)_3$ at 87(±0.5) °C. By combining the HeI photoelectron (PE) spectrum with the improved density function theory (DFT) calculations, we have concluded that the $(CH_3)_3CO^\bullet$ radical has C_{3V} symmetry and $\tilde{X}^2E$ ground state. The study does not only provide the ionization energies of different ionic states of the $(CH_3)_3CO^\bullet$ radical for the first time, but also the first example in which there have been similar vibrational structures in different ionic states caused by removal of the electron on an orbital. It is also pointed out that $(CH_3)_3CONO$ is a good source for obtaining the $(CH_3)_3CO^\bullet$ radical beam, and that NO is a stable regent for the active radical. The results will promote the studies in electron spin resonance (ESR) research on the mechanisms of both the initiation of the formation of a new radical and the radical-chain polymerization in which the $(CH_3)_3CO^\bullet$ radical participates.

Keywords: density functional calculations · ionic states · photoelectron spectroscopy · radicals

Introduction

As an initiator, the *tert*-butoxy [$(CH_3)_3CO^\bullet$] radical has been widely used on the radical chain polymerization, also in electron spin resonance (ESR) research for initiating the formation of a new radical;[1–5] however the study of the character of the radical itself is almost nil because of its shorter lifetime and unstability. Recently, Ramond et al. studied the electron affinity of the $(CH_3)_3CO^-$ anion by negative-ion photoelectron spectroscopy.[6] To our knowledge, there is no any report on its ionization energy until now, but the ionization energies, especially the first ionization energy for the species, are among the most important physical and chemical data, because numerous physical and chemical properties can be deduced from its ionization energies. Also the discovery of a good source for obtaining the $(CH_3)_3CO^\bullet$ radical will promote the study on the radical character.

Our laboratory has demonstrated the ability to generate a continuous radical beam through the pyrolysis of parent species or the microwave discharge of a selected compound; this allows us to perform HeI photoelectron spectroscopy (PES) studies on reactive open-shell species.[7–12] Recently, we reported the first experimental observation on different ionic states of both the $CH_3O^\bullet$ and $CH_3S^\bullet$ radicals.[13] In this paper, we present a PES study on ionization energies of the $(CH_3)_3CO^\bullet$ radical and point out that the $(CH_3)_3CONO$ is a good source for obtaining the $(CH_3)_3CO^\bullet$ radical and that the pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ provides an opportunity for studying decomposition kinetic of the $(CH_3)_3CO^\bullet$ radical. To assign the PES bands of the $(CH_3)_3CO^\bullet$ radical, the improved density function theory (DFT) calculations on different ionic states of the $(CH_3)_3CO^\bullet$ radical have been also performed, because they have used successfully for the assignment of the PES bands of radicals.[9–13]

Results and Discussion

The $(CH_3)_3CO^\bullet$ radical obtained by pyrolysis of the $(CH_3)_3CONO$: The $CH_3O^\bullet$ radical was successfully generated by pyrolysis of CH_3ONO at 275(±0.5) °C and its photoelectron (PE) spectrum was also recorded in situ.[13] Similarly, it is thought that the pyrolysis of the $(CH_3)_3CONO$ should generate the $(CH_3)_3CO^\bullet$ radical by losing NO. During the pyrolysis $(CH_3)_3CONO$, the PE spectrum[14] of the $(CH_3)_3CONO$ is always observed if the pyrolysis temperature is too low. A new and constant PE spectrum, which is completely different to that of $(CH_3)_3CONO$ is recorded at 115(±0.5) °C. Figure 1 gives the PE spectrum of the species generated by the pyrolysis of $(CH_3)_3CONO$ at 115(±0.5) °C.

The theoretical study of molecular orbital character for the $(CH_3)_3CONO$ shows also that the bonding strength between

---

[a] Prof. D. Wang, Z. Sun, S. Zheng, J. Wang, Dr. M. F. Ge
State Key Laboratory for
Structural Chemistry of Unstable and Stable Species
Institute of Chemistry, The Chinese Academy of Sciences
Beijing 100080, (People's Republic of China)
Fax:(+86) 10-62559373
E-mail: wangdx@xx1.icas.ac.cn

[b] Open Laboratory of Computational Quantum Chemistry
Hebei Normal University, Shijiazhuang 050091
(People's Republic of China)

0947-6539/01/0714-2995 $ 17.50+.50/0

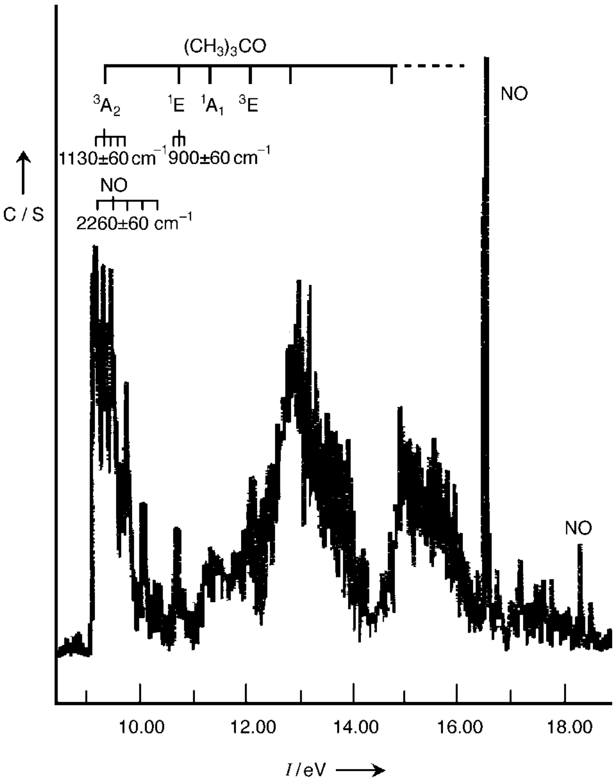

Figure 1. HeI PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3CONO$ at 115(±0.5) °C.

$(CH_3)_3CO$ and NO groups is weakest.[14] So an intuitive guess for the PE spectrum of the species generated by the pyrolysis of $(CH_3)_3CONO$ is that the PES bands of NO should appear in the spectrum.

In Figure 1, a very sharp peak at 16.56 eV is clearly seen in the PE spectrum of the species generated by the pyrolysis of $(CH_3)_3CONO$. This is considered as an indication of of the formation of NO, because both ionization energy 16.56 eV and the highest intensity of the PE signal are characteristic NO.[15] Similarly, the sharp peak at 18.32 eV is also characteristic of NO.

An expanded PE spectrum with the fine vibrational structure of the first PES band of the species generated by the pyrolysis of $(CH_3)_3CONO$ in the low ionization energy region (11.0 eV) is given in Figure 2. From the Figure 2 it is found that the five peaks at 9.26, 9.54, 9.82, 10.10, 10.38 eV with vibrational spacing of 2260 ± 60 cm^{-1} are also characteristic of the first PES band of NO,[15] that is, the pyrolysis of the $(CH_3)_3CONO$ at 115(±0.5) °C gives NO by generation of the $(CH_3)_3CO^{\bullet}$ radical [Eq. (1)]:

$$(CH_3)_3CONO \xrightarrow{115(\pm 0.5)\,^{\circ}C} (CH_3)_3CO^{\bullet} + NO \qquad (1)$$

The high intensity of the first vibrational peak at 9.26 eV is attributed to the overlap of the first vibrational peak of NO with the PES peak of the $(CH_3)_3CO^{\bullet}$ radical, because the vibrational peak with the highest intensity on the first PES band of NO is at 9.54 eV. Clear peaks at 9.40 and 9.68 eV are also considered as the peaks for the first PES band of the $(CH_3)_3CO^{\bullet}$ radical, that is, the first PES band of the $(CH_3)_3CO^{\bullet}$ radical should have vibrational spacing of 1130 ± 60 cm^{-1}, corresponding to the interval between 9.26 and 9.40 eV. So the adiabatic and vertical ionization energies on the first PES band of the $(CH_3)_3CO^{\bullet}$ radical should be 9.26 and 9.40 eV, respectively, because the peak at 9.40 eV has the highest intensity. That is to say, the first PES band of the $(CH_3)_3CO^{\bullet}$ radical includes at least five vibrational peaks at 9.26, 9.40, 9.54, 9.68, and 9.82 eV.

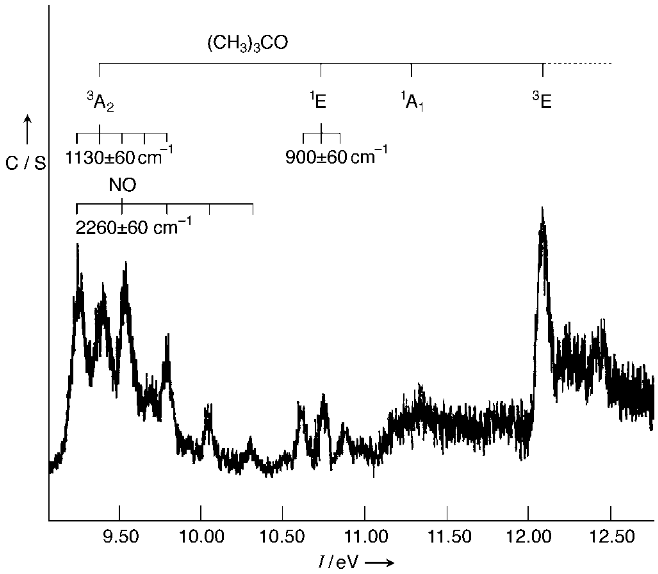

Figure 2. Expanded PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3CONO$ at 115(±0.5) °C in the low ionization energy region (< 12.20 eV).

The bands at vertical ionization energy 10.75 eV, with a vibrational spacing 900 ± 60 cm^{-1}, and at 11.31 and 12.10 eV in the expanded PE spectrum of the species generated by the pyrolysis of $(CH_3)_3CONO$ are also attributed to be the PES bands of the $(CH_3)_3CO^{\bullet}$ radical, because there are no PES bands of NO in this ionization energy region. The band at vertical ionization energy 10.75 eV and with vibrational spacing 900 ± 60 cm^{-1} should be the second PES band of the $(CH_3)_3CO^{\bullet}$ radical. The band centered near 11.31 eV with divergent structure is the third PES band of the $(CH_3)_3CO^{\bullet}$ radical.

The sharp peak at 12.10 eV is considered to be the fourth PES band of the $(CH_3)_3CO^{\bullet}$ radical. Of course, the bands centered near 13.30 and 14.95 eV are also considered as the PES bands of the $(CH_3)_3CO^{\bullet}$ radical, because also there is no the PES bands of NO in this area.

In fact, the PES bands of NO could be also used as a calibration for the new species. In other words, the PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical consists of six clear bands: the first band at vertical ionization energy 9.40 eV, with vibrational spacing 1130 ± 60cm^{-1}, the second one at vertical ionization energy 10.75 eV, with vibrational spacing 900 ± 60cm^{-1}, the third one centered near 11.31 eV with divergent structure, the fourth sharp band at 12.10 eV, and two very broad bands centered near 13.30 and 14.95 eV.

The $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$: It was well known that the thermal, homolytic decomposition of the alkyl peroxides gives the alkyoxy RO$^{\bullet}$ radical.[16] So $(CH_3)_3COOC(CH_3)_3$ is also used as a source for obtaining the $(CH_3)_3CO^{\bullet}$ radical. During the pyrolysis of $(CH_3)_3COOC(CH_3)_3$, the PE spectrum[17] of $(CH_3)_3COOC(CH_3)_3$ was always observed at low temperature. A constant PE spectrum that is completely different with that of $(CH_3)_3COOC(CH_3)_3$ was recorded at 87(± 0.5) °C (See Figure 3). Figure 4 gives the expanded PE spectrum of the species generated by the pyrolysis of $(CH_3)_3COOC(CH_3)_3$ in the low ionization energy region (< 12.50 eV). In Figure 4 the peaks at 9.26, 9.40, and 9.54 eV are clearly seen, with a vibrational spacing $1130 \pm 60\ cm^{-1}$, and are considered as the first PES band of the $(CH_3)_3CO^{\bullet}$ radical, because they match the first PES band of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3CONO$. The PES peak at 9.70 eV, with the highest intensity, is attributed to be the first PES band of the acetone, because its value 9.70 eV, with a vibrational spacing of $1170 \pm 60\ cm^{-1}$ is in excellent agreement with the first PES band of the acetone.[18] The fourth and fifth vibrational peaks at 9.68 and 9.82 eV that belong to the first PES band of the $(CH_3)_3CO^{\bullet}$ radical are buried under the first PES band of the acetone. The vertical ionization energy for the first PES band of the $(CH_3)_3CO^{\bullet}$ radical should be at 9.40 eV, because the peak corresponding to 9.40 eV has the highest intensity in this vibrational progression.

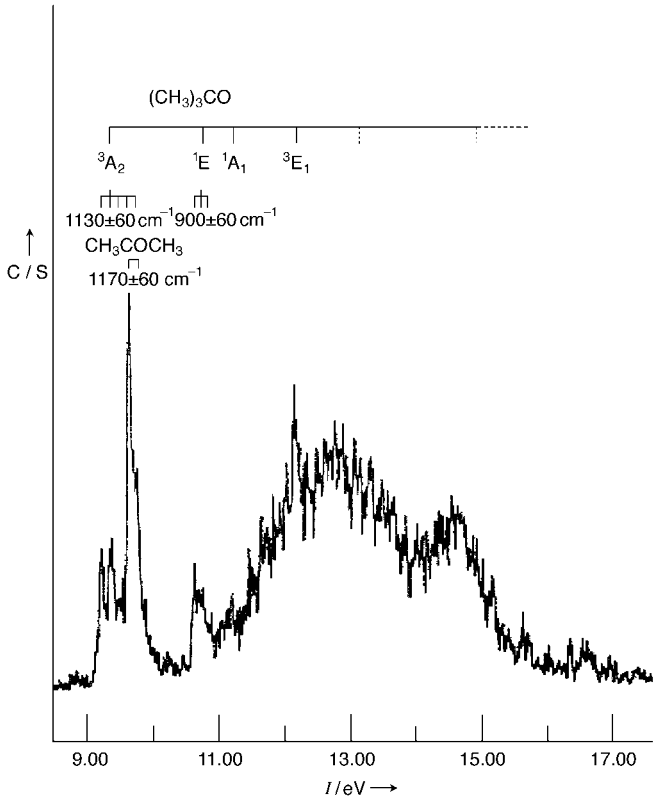

Figure 3. HeI PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ at 87(± 0.5) °C.

The PES peaks at 10.65, 10.76, and 10.87 eV, with vibrational spacing of $900 \pm 60\ cm^{-1}$, are designated to the second band of the $(CH_3)_3CO^{\bullet}$ radical, because both vertical ionization energy 10.76 eV and vibrational spacing are also in excellent agreement with the second PES band of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3CONO$. Similarly, the band centered near 11.32 eV is the third PES band of the $(CH_3)_3CO^{\bullet}$ radical, because it also matches the third PES band of the $(CH_3)_3CO^{\bullet}$ radical generated by pyrolysis of the $(CH_3)_3CONO$.

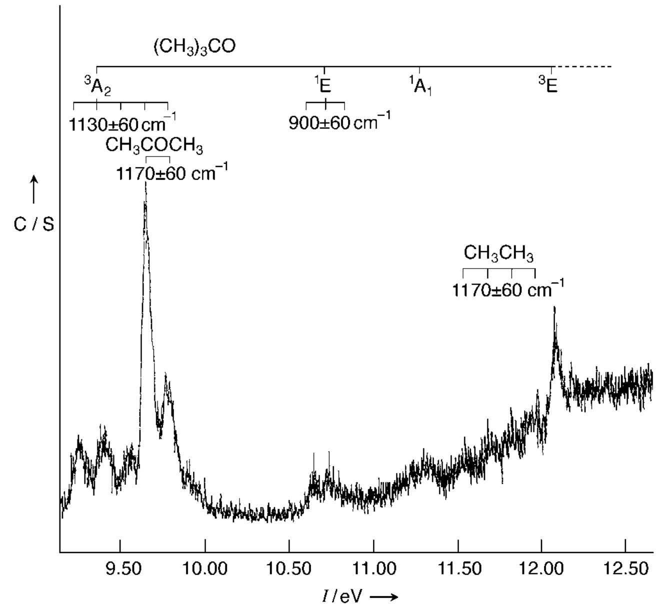

Figure 4. Expanded PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ at 87(± 0.5) °C in the low ionization energy region (< 12.20 eV).

A sharp peak at 12.11 eV on the Figure 4 is considered as the fourth PES peak of the $(CH_3)_3CO^{\bullet}$ radical, because both the value and relative intensity are in good agreement with the fourth peak at 12.10 eV for the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3CONO$. Also, the PES bands in the high ionization energy region (> 12.00 eV) for the species generated by the pyrolysis of $(CH_3)_3COOC(CH_3)_3$ match those of the species generated by the pyrolysis of $(CH_3)_3CONO$. In other words, the pyrolysis of both $(CH_3)_3CONO$ and $(CH_3)_3COOC(CH_3)_3$ gives a same PE spectrum, that is, that of the $(CH_3)_3CO^{\bullet}$ radical.

From the comparison the Figure 2 with the Figure 4, it is found that there is some fine structure between 11.40 and 12.20 eV on the PE spectrum of the species generated by the pyrolysis of $(CH_3)_3COOC(CH_3)_3$. Four vibrational progressions with $1170 \pm 60 cm^{-1}$ vibrational spacing and the highest intensity at 12.00 eV are in excellent agreement with the first PES band of the ethane,[15] that is, the PES bands of the ethane also appear on the PE spectrum of the species generated by the pyrolysis of $(CH_3)_3COOC(CH_3)_3$. An evident difference in the high ionization energy region (> 12.20 eV) seen between Figures 3 and 1 also supports the above-mentioned assignment for the PES band of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$, because the PES bands with the high intensity for both acetone[18] and ethane[15] overlap with the PES bands of the $(CH_3)_3CO^{\bullet}$ radical. That is to say, the pyrolysis of the $(CH_3)_3$-

0947-6539/01/0714-2997 $ 17.50+.50/0

$COOC(CH_3)_3$ generates the $(CH_3)_3CO^\bullet$ radical, and then the $(CH_3)_3CO^\bullet$ radical decomposes into the acetone and ethane; this comes from the combination of the $CH_3^\bullet$ radical with the shorter lifetime, because the$(CH_3)_3CO^\bullet$ radical, as an initiator, can also initiates itself to form the $CH_3^\bullet$ radical. So the mechanism of the pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ can be given by Equations (2) and (3).

$$(CH_3)_3COOC(CH_3)_3 \xrightarrow{87(\pm 0.5)\,^\circ C} 2\,(CH_3)_3CO^\bullet \tag{2}$$

$$(CH_3)_3CO^\bullet \rightarrow (CH_3)_2CO + CH_3^\bullet \xrightarrow{+CH_3^\bullet} CH_3CH_3 \tag{3}$$

This result is in good agreement with the previous proposal.[19] In fact, the PES bands of the acetone could be also used as a calibration for new species.

According to C_{3V} symmetry proposed by previous studies[6, 20, 21] for the $(CH_3)_3CO^\bullet$ radical, the molecular orbitals of the valence shell would be in the order of increasing energy: $\sim (4e)^4(8a_1)^2(5e)^4(1a_2)^2(6e)^3$

The $(CH_3)_3CO^\bullet$ radical has a $\tilde{X}^2E$ ground state. The ionization of the electron of the HOMO 6e should lead to three ionic states $^3A_2$, ^1E and $^1A_1$ of the $(CH_3)_3CO^+$ cation. The ionization of the electron of the SHOMO $1a_2$ leads to both ^3E and ^1E ionic states.

A careful analysis of the intensity for the PES bands of three vertical ionization energies 9.40, 10.75, and 11.31 eV gives the ratio of the intensity of three bands to be about 3.12:1.97:1.00. This means that the ratio of statistical weights on the ionic states, corresponding to three PES bands should be 3:2:1, that is, the three PES bands correspond to the $^3A_2$, ^1E and $^1A_1$ ionic states, respectively, for the $(CH_3)_3CO^\bullet$ radical. Conversely, the PE spectra of the species generated by the pyrolysis of both $(CH_3)_3CONO$ and $(CH_3)_3COOC(CH_3)_3$ provides experimental evidence for both C_{3V} symmetry and a $\tilde{X}^2E$ ground state for the $(CH_3)_3CO^\bullet$ radical. The sharp peak with ionization energy 12.11 eV is designated to ^3E ionic state, caused by ionization of the electron of the SHOMO $1a_2$, because the SHOMO $1a_2$ of the $(CH_3)_3CO^\bullet$ radical is almost that of a lone-pair orbital on the oxygen atom.

The above-mentioned assignment for the PES bands of the $(CH_3)_3CO^\bullet$ radical is supported by the improved DFT calculation. Table 1 gives the PES ionization energies (I_V in eV), the DFT computed ionization energies (E_V in eV) according to C_{3V} symmetry and relative intensities of the PES signals observed for the $(CH_3)_3CO^\bullet$ radical. The first PES band with both vertical ionization energy 9.40 eV and vibrational spacing $1130 \pm 60 cm^{-1}$ comes from removal of the electron of the HOMO 6e, corresponding to ionization of the $(CH_3)_3CO$ ($\tilde{X}^2E$) to $(CH_3)_3CO^+$ ($\tilde{X}^3A_2$), because the value 9.40 eV matches the DFT computed ionization energy 9.497 eV for the $^3A_2$ ground state of the $(CH_3)_3CO^+$ cation, and also the HOMO 6e is a π anti-bonding orbital with dominant weight of oxygen atom that should lead to the band with some fine structure. The second PES band with a vertical ionization energy of 10.75 eV is designated to the ^1E ionic state, caused by removal of the electron of the HOMO 6e, because the value 10.75 eV is very close to the DFT computed value 10.520 eV for the ^1E ionic state, and also vibrational structure ($\tilde{\nu} = 900 \pm 60\ cm^{-1}$) is observed. The third PES band centered near 11.31 eV is designated to $^1A_1$ ionic state, caused also by removal of the electron of the HOMO 6e, because the value 11.31 eV is in good agreement with the DFT computed value 11.200 eV, and the band is also divergent. That is to say, the ionization of the electron on an orbital should lead the PES bands with the same structural characters. The ratio of the intensity of three PES bands at vertical ionization energies 9.40, 10.75, and 11.31 eV (i.e., 3.12:1.97:1.00), also supports the above-mentioned assignment for the $^3A_2$, ^1E, and $^1A_1$ three ionic states, because the ratio is in excellent agreement with the ratio of three ionic statistical weights. To our knowledge, this is the first example for the species studied in which there have been the similar vibrational structures at different ionic states caused by electron ionization of an orbital.

Table 1. The PES vertical ionization energies (I_V in eV), the DFT computed ionization energies (E_V in eV) according to C_{3V} symmetry, and relative intensities of signals observed from different ionic states of the $(CH_3)_3CO^\bullet$ radical.

PES$_{exptl}$ I_V [eV][a]		DFT $_{calcd}$ E_V [eV]	Cationic states	Relative intensities this work[b]	stat. ratio
	9.26				
9.40	9.40	9.497	$^3A_2$^{c}	3.12	3
	9.54				
	9.68				
	9.82				
	10.64				
10.75	10.75	10.520	^1E[c]	1.97	2
	10.86				
11.31		11.200	$^1A_1$[c]	1.00	1
12.10		12.001	^3E[d]		
13.30		13.411	^1E[d]		

[a] ± 0.01 eV. [b] Corrected for analyzer sensitiviy ± 0.02 eV. [c] Ionic states come from electron ionization of the HOMO 6e for the $(CH_3)_3CO^\bullet$ radical. [d] Ionic states come from electron ionization of the SHOMO $12a_2$ for the $(CH_3)_3CO^\bullet$ radical.

A sharp peak at 12.11 eV is assigned to ^3E ionic state, caused by removal of the electron of the SHOMO $1a_2$, because the value 12.11 eV is very close to the DFT computed ionization energy 12.001 eV for ^3E ionic state of the $(CH_3)_3CO^+$ cation. The PES bands in the high ionization energy region (> 12.50 eV) are very broad. This means that the ionization corresponding to these broad PES bands comes from result of removal of the electron of the bonding orbital or several orbitals. The assignment of the PES bands for the high ionization energy region (> 12.50 eV) is also supported by the DFT calculation.(see Table 1)

Stablizing function of the NO species: It was well known that as a famous molecule, NO has marvelous action in the human body. From the difference of pyrolysis actions between the $(CH_3)_3CONO$ and the $(CH_3)_3COOC(CH_3)_3$, it is found that the $(CH_3)_3CONO$ is a better source for obtaining the $(CH_3)_3CO^\bullet$ radical, because there is no decomposition of the $(CH_3)_3CO^\bullet$ radical obtained by pyrolysis of the $(CH_3)_3CONO$, even if the pyrolysis temperature (115(±0.5) °C) of $(CH_3)_3CONO$ is higher than that (87(±0.5) °C) of $(CH_3)_3COOC(CH_3)_3$. This fact shows that NO generated by pyrolysis of the $(CH_3)_3CONO$ may be considered as a stablizing reagent for the $(CH_3)_3CO^\bullet$ radical. The decomposition of the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ is attributed to the self-initiation of the $(CH_3)_3CO^{\bullet}$ radical. That is to say, as an initiator, the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ initiates the formation of the $CH_3^{\bullet}$ radical through the generation the acetone. At the same time, the decomposition of the $(CH_3)_3CO$ obtained by pyrolysis of the $(CH_3)_3COOC(CH_3)_3$ provides also an opportunity for studying the decomposition kinetics of the $(CH_3)_3CO^{\bullet}$ radical, because the PES technique was used successfully to the kinetic study of a chemical reaction.[22]

Conclusion

A continuous $(CH_3)_3CO^{\bullet}$ radical beam is produced by pyrolysis of both $(CH_3)_3CONO$ at 115(±0.5) °C and $(CH_3)_3COOC(CH_3)_3$ at 87(±0.5) °C . The complete PE spectrum with the fine vibrational structure for the $(CH_3)_3CO^{\bullet}$ radical has been recorded in situ for the first time. By combining PES with the improved DFT calculation, we conclude that the $(CH_3)_3CO^{\bullet}$ radical has C_{3V} symmetry and $\tilde{X}^2E$ ground state. The PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical provides also the first example in which similar vibrational structures on different ionic states have been observed, caused by removal of the electron of an orbital. The PE spectrum is, therefore, able to provide both the orbital energy levels and also molecular symmetry.

$(CH_3)_3CONO$ is found to be a good source for obtaining the $(CH_3)_3CO^{\bullet}$ radical. NO is a stablizing reagent for the $(CH_3)_3CO^{\bullet}$ radical obtained by pyrolysis of the $(CH_3)_3CONO$, because there is no decomposition of the $(CH_3)_3CO^{\bullet}$ radical in period of running PE Spectrum.

The results will promote the studies in electron spin resonance (ESR) research on the mechanisms of both the initiation of the formation of a new radical and the radical-chain polymerization in which the $(CH_3)_3CO^{\bullet}$ radical participates.

Experimental Section

The PES experiment was performed with a double-chamber UPS Machine-II, which was built specially to detect transient species as described elsewhere.[23] A continuous $(CH_3)_3CO^{\bullet}$ radical beam was produced by pyrolysis of both $(CH_3)_3CONO$ at 115(±0.5) °C and $(CH_3)_3COOC(CH_3)_3$ at 87(±0.5) °C compounds in a quartz tube with a double-heater inlet system, but the heater was capable of producing 1200 °C. Both $(CH_3)_3CONO$ and $(CH_3)_3COOC(CH_3)_3$ compounds were bought from Aldrich and their purities were 98%. The PE spectrum of the $(CH_3)_3CO^{\bullet}$ radical was measured in situ at a resolution of about 25 meV as indicated by the $Ar^+(^2P_{3/2})$ photoelectron peak. Unless otherwise stated, the experimental ionization energy values are quoted to an estimated accuracy of ±0.01 eV. Spectra were recorded by using a chart recorder in the usual way. Digitized spectra, time-averaged of around 40 min were also obtained. Experimental ionization energies (I_V in eV) were calibrated by simultaneous addition of a small amount of argon and methyl iodide to the sample.

Density functional theory (DFT) calculations: In order to assign the PES bands of the $(CH_3)_3CO^{\bullet}$ radical, the improved DFT calculation was performed on the ^2E ground state of the $(CH_3)_3CO^{\bullet}$ radical with C_{3V} symmetry, and the ground and several ionic states of the $(CH_3)_3CO^+$ cation, because the DFT calculation was applied successfully to the assignment of the PES bands for the open-shell radicals.[9–13] The DFT calculations[9, 10] were carried out with the Amsterdam Density Functional (ADF) program package, in which a density fitting procedure was used to obtain the Coulomb potential, and a elaborate three-dimensional numerical integration technique was employed to calculate the Hamiltonian matrix elements. The Vosko–Wilk–Nusair parameterization of uniform electron gas data was used for the exchange-correlation energy and potential; this is usually called the local spin density approximation (LSDA). The gradient correction of exchange energy by Becke and that of correlation energy developed by Perdew were performed in a post SCF manner. The molecule orbitals were expanded in uncontracted triple-ζ STO basis set augmented by two polarization basis functions. The DFT computed ionization energies (E_V in eV) were obtained from the difference of the total energy of the resulting cation/^2E ground state in C_{3V} symmetry, because the PES ionization energy of the radical were given by using the vertical ionization energies (I_V in eV), chosen as the maxima of the PES peak or band. To calculate the total energy of the singlet states described by multideterminantal wave function, the sum method proposed by Ziegler–Rauk–Baerends was used. The geometry used in the calculation was taken from optimization results at the UMP2/6–31G* level of theory.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (Contract No.29973051). Z.S. and J.W. would liked to thank the Chinese Academy of Sciences for receipt of scholarship during the period of this work. M.F.G. gratefully acknowledges the support of K. C. Wong Education Foundation, Hong Kong.

---

[1] D. Griller, K. U. Ingold, *Acc. Chem. Res.* **1976**, *9*, 13.

[2] "Peroxy Compounds": C. S. Sheppard in *Encyclopedia of Polymer Science and Engineering, Vol. 11* (Eds.: H. F. Mark, N. M. Brikales, C. G. Overberger, G. Menges), Wiley-Interscience, New York, **1988**.

[3] "Radical Polymerization": C. H. Bamford, in *Encyclopedia of Polymer Science and Engineering, Vol. 13* (Eds.: H. F. Mark, N. M. Brikales, C. G. Overberger, G. Menges), Wiley-Interscience, New York, **1988**, pp. 708–867.

[4] D. L. Haire, E. G. Janzen, *Can. J. Chem.* **1982**, *60*, 1515.

[5] V. P. Kurkov, *J. Am. Chem. Soc.* **1967**, *89*, 4895.

[6] T. M. Ramond, G. E. Davico, R. L. Schwartz, W. C. Lineberger, *J. Chem. Phys.* **1999**, *112*, 1158.

[7] D. X. Wang, Y. Li, S. Li, H. Q. Zhao, *Chem. Phys. Lett.* **1994**, *222*, 167.

[8] D. X. Wang, C. H. Li, X. M. Qian, S. D. Gablin, *J. Electron Spectrosc. Relat. Phenom.* **1998**, *97*, 59.

[9] D. X. Wang, P. Jiang, X. M. Qian, G. Y. Hong, *J. Chem. Phys.* **1997**, *106*, 3003, and references therein.

[10] C. H. Qiao, G. Y. Hong, D. X. Wang, *J. Phys. Chem. A* **1999**, *103*, 1972.

[11] C. H. Qiao, M. F. Ge, D. X. Wang, *Chem. Phys. Lett.* **1999**, *305*, 359.

[12] M. F. Ge, J. Wang, X. J. Zhu, Z. Sun, D. X. Wang, *J. Chem. Phys.* **2000**, *113*, 1866.

[13] X. J. Zhu, M. F. Ge, J. Wang, Z. Sun, D. X. Wang, *Angew. Chem.* **2000**, *112*, 2016; *Angew. Chem. Int. Ed.* **2000**, *39*, 1940.

[14] Z. Sun, S. J. Zheng, D. X. Wang, *J. Chin. Chem. Soc.*, in press.

[15] D. W. Turner, C. Baker, A. D. Baker, C. R. Brundle, *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London, **1970**.

[16] G. Odian, *Principles of Polymerization*, 3rd ed., Wiley, New York, **1991**.

[17] C. Batich, W. Adam, *Tetrahedron Lett.* **1974**, *16*, 1467.

[18] K. Kimura, S. Katsumata, Y. Achiba, T. Yamazaki, S. Iwata, *Handbook of HeI Photoelectron Spectra of Fundamental Organic Molecules*, Japan Scientific Societies Press, Tokyo, **1980**, p. 156.

[19] C. Walling, P. J.Wagner, *J. Am. Chem. Soc.* **1964**, *86*, 3368

[20] B. K. Janousek, A. H. Zimmerman, K. J. Reed, J. I. Brauman, *J. Am. Chem. Soc.* **1978**, *100*, 6142.

[21] K. B. Wiberg, *J. Am. Chem. Soc.* **1990**, *112*, 3379.

[22] D. X. Wang, X. M. Qian, P. Jiang, *Chem. Phys. Lett.* **1996**, *258*, 149.

[23] H. Q. Zhao, D. X. Wang, G. Z. Xu, *J. Anal. Instrum.* **1992**, *4*, 23.

Received: February 19, 2001 [F3080]