A Reinvestigation of the First Band in the Photoelectron Spectrum of the Ethyl Radical

J. M. Dyke,* A. R. Ellis, N. Keddar, and A. Morris

Department of Chemistry, The University, Southampton S09 5NH, U.K. (Received: September 14, 1983)

The first photoelectron band of the ethyl radical, produced from the reaction of fluorine atoms with ethane, has been recorded with a new multidetector photoelectron spectrometer using He I radiation. A regular vibrational series (with average separations of $400 \pm 30 \text{ cm}^{-1}$) was observed which is attributed to excitation of the pyramidal bending mode in the ion. The vertical ionization energy of the observed band is measured as 8.51 ± 0.01 eV and an upper limit of the adiabatic ionization energy is obtained as $8.26 \pm 0.02 \text{ eV}$. Two other methods of generating the ethyl radical, namely, pyrolysis of azoethane and pyrolysis of *n*-propyl nitrite, are shown to be less suitable sources for PES investigations of this radical.

Introduction

The first band in the photoelectron spectrum of the ethyl radical presents a challenging problem as use of well-established heats of formation, $\Delta H_{f^{o}_{298}}$, for the molecule and ion in their ground electronic states $(1.21 \pm 0.04^{1-3} \text{ and } 9.37 \pm 0.04 \text{ eV},^{4-6} \text{ respec-}$ tively) leads to a reliable estimate of the first adiabatic ionization potential (IP) of this radical as 8.16 ± 0.08 eV. However, as the ion has a hydrogen-bridged equilibrium geometry and the molecule has a classical equilibrium structure,⁷⁻¹¹ the change in equilibrium geometry on ionization is expected to be large. Consequently, the vertical and adiabatic ionization energies are not equal and a broad first photoelectron band is expected. This proved to be the case in the three photoelectron spectra that have been published for this radical¹²⁻¹⁴ and in all cases the true first adiabatic IP could not be measured directly.

In the first investigation Houle and Beauchamp¹² produced the radical by pyrolysis of *n*-propyl nitrite and the first photoelectron band of C_2H_5 was recorded with He I α (21.22 eV) radiation. Three vibrational components were observed, separated by 1000 cm⁻¹. The first was measured as 8.30 ± 0.02 eV and the third, investigation,¹³ however, these workers identified the feature at 8.30 ± 0.02 eV to a vibrational component of the first band of nitric oxide ionized by He I β (23.09 eV) radiation. This was reasonable as nitric oxide is a major product of the pyrolysis of *n*-propyl nitrite and the first photoelectron band of NO ionized by He I α radiation was clearly seen in the experimental spectrum. In the same study,¹³ a Ne I (16.84 eV) spectrum recorded for the first band of the radical revealed two components at 8.39 ± 0.02 and 8.51 ± 0.02 eV, which were assigned to the adiabatic and vertical ionization potentials. The separation of these components (0.12 eV) was the only vibrational interval resolved and some suggestions were made for its assignment.¹³

Subsequent to these studies, we have also published the result of a preliminary investigation of the photoelectron spectrum of the ethyl radical, produced in our case from the reaction of fluorine

(1) Castelhano, A. L.; Griller, D. J. Am. Chem. Soc. 1982, 104, 3655. (2) Castelhano, A. L.; Marriott, P. R.; Griller, D. J. Am. Chem. Soc. 1981, 103. 4262.

- (3) Tsang, W. Int. J. Chem. Kinet. 1978, 10, 821.
 (4) Baer, T. J. Am. Chem. Soc. 1980, 102, 2482.
- (5) Rosenstock, H. M.; Buff, R.; Ferreira, M. A. A.; Lias, S. G.; Parr, A.
- C.; Stockbauer, R. L.; Holmes, J. L. J. Am. Chem. Soc. 1982, 104, 2337. (6) Traeger, J. C.; McLoughlin, R. G. J. Am. Chem. Soc. 1981, 103, 3647. (7) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P.v.R. J.
- Am. Chem. Soc. 1981, 103, 5649. (8) Zurawski, B.; Ahlrichs, R.; Kutzelnigg, W. Chem. Phys. Lett. 1973, 21. 309.

- (9) Lischka, H.; Kohler, H. J. J. Am. Chem. Soc. 1978, 100, 5297.
 (10) Pacansky, J.; Dupuis, M. J. Chem. Phys. 1978, 68, 4276.
 (11) Lathan, W. A.; Hehre, W. J.; Pople, J. A. J. Am. Chem. Soc. 1971, 93, 808.
- (12) Houle, F. A.; Beauchamp, J. L. Chem. Phys. Lett. 1977, 48, 457.
- (13) Houle, F. A.; Beauchamp, J. L. J. Am. Chem. Soc. 1979, 101, 4067.
 (14) Dyke, J. M.; Jonathan, N.; Morris, A. Int. Rev. Phys. Chem. 1982,

2, 3.

atoms with ethane.¹⁴ The first band, recorded with He I radiation, showed vertical and adiabatic ionization energies of 8.53 ± 0.02 and 8.32 ± 0.04 eV, respectively. Additionally, this band showed a regular vibrational series with at least nine vibrational components separated by $370 \pm 40 \text{ cm}^{-1}$. This structure was assigned to excitation of the out-of-plane CH₂ bending mode in the ethyl cation.¹⁴ Clearly, therefore, the published spectra of the first band of C_2H_5 are inconsistent particularly with regard to the measured adiabatic first ionization energy and the resolved vibrational structure.

Recently, we have developed a multidetector photoelectron spectrometer which has been designed specifically for the rapid acquisition of spectra of short-lived molecules,¹⁵ hence reducing problems associated with contamination of the ionization region during the course of the experiment. A reinvestigation of the ethyl photoelectron spectrum was therefore undertaken with this instrument in order to obtain an improved spectrum of the first band and hopefully to identify the reasons for the discrepancies between the published spectra.

Experimental Section

Three methods were used to produce the ethyl radical in the gas phase: (1) the rapid reaction of fluorine atoms with ethane,¹⁶ (2) pyrolysis of *n*-propyl nitrite, and (3) pyrolysis of azoethane. This last route was also investigated as pyrolysis of 2,2'-azoisobutane and azomethane have been used successfully previously to record the photoelectron spectra of the *tert*-butyl and methyl radicals.17,18

For the $F + C_2H_6$ reaction, most of the experiments were performed on the multidetector apparatus¹⁵ although a number of pilot experiments were also carried out on a single-detector apparatus.¹⁹ On both spectrometers, the most intense spectra were recorded at a reagent mixing distance of 0.5-1.0 cm above the photon beam. Fluorine atoms were generated by microwave discharge (2.45 GHz) of a 5% molecular fluorine in helium mixture.

The *n*-propyl nitrite used in this study was prepared from 1-propanol and nitrous acid by standard methods²⁰ and azoethane was synthesized via N,N'-diethylsulfamide.²¹ Pyrolysis of the azoethane and *n*-propyl nitrite was achieved by using an inductively heated tantalum furnace on a single detector spectrometer as described earlier.17-19

- Morris, A. Rev. Sci. Instrum., 1984, 55, 172.
 (16) Jones, W. E.; Skolnik, E. G. Chem. Rev. 1976, 76, 563.
 (17) Dyke, J. M.; Jonathan, N.; Lee, E.; Morris, A.; Winter, M. Phys. Scr. 1977, 16, 197.
- (18) Dyke, J. M.; Jonathan, N.; Lee, E.; Morris, A. J. Chem. Soc., Faraday Trans. 2 1976, 72, 1385.
- (19) Dyke, J. M.; Jonathan, N.; Morris, A. "Electron Spectroscopy"; Ac-(20) Noyes, W. A. "Organic Syntheses"; Blatt, A. H., Ed.; Wiley: New
- York, 1443; Collect Vol. II, p 108.
- (21) Ohme, R.; Preuschhof, H.; Heyne, H. U. Org. Syn. 1972, 52, 11.

⁽¹⁵⁾ Dyke, J. M.; Francis, P. D.; Jonathan, N.; Keddar, N.; Mills, J. D.;



Figure 1. The He I photoelectron spectrum of pyrolyzed azoethane recorded with a single detector spectrometer in (a) the 8.0-15.0-eV and (b) the 8.0-10.5-eV ionization energy regions. Methyl iodide has been added in Figure 1b as a calibrant.

For the conditions under which spectra were recorded, the usual resolution was 20-25 meV (fwhm) as measured for argon with He I α radiation. The first band of the ethyl radical was calibrated by adding methyl iodide to the ionization chamber.

Results and Discussion

The initial attempts to obtain the photoelectron spectrum of the ethyl radical were made by pyrolyzing the azoethane molecule which, by analogy with azomethane pyrolysis,¹⁸ should be a good and relatively clean source of ethyl radicals. Azoethane gave a photoelectron spectrum which was in good agreement with that published elsewhere.²² He I spectra of pyrolyzed azoethane were recorded over the furnace temperature range 800–1400 K and typical spectra of the pyrolysis products are shown in Figure 1, a and b. The main features observed are bands due to ethylene and the methyl radical which both arise from ethyl radical secondary reactions.^{23,24} It was also observed that although the first band of azoethane showed the anticipated decrease in intensity as the temperature is increased, it developed a slight shoulder on the low ionization energy side. Thus early on in the course of these

Figure 2. The He I photoelectron spectrum obtained from the reaction $F + C_2H_6$ recorded in the ionization energy range 7.5–10.5 eV with a multichannel detector photoelectron spectrometer. It consists of 250 scans recorded in a total time of 40 s. Methyl iodide was added as a calibrant.

experiments it became evident that the first vertical IP of azoethane at 8.77 eV^{22} was overlapping that of the ethyl radical. Furthermore, because the 10.0-15.0-eV IP region contained relatively intense bands arising from ethylene, it was not possible to use the intensity of the higher bands of azoethane to estimate the contribution of the azoethane first band to the band in the 8.0-9.5-eV IP region. It was also not possible to estimate with confidence the temperature at which complete pyrolysis of azoethane occurred in order to ensure that the band in the 8.0-9.5-eV range contained no contribution from azoethane and could be assigned wholly to the ethyl radical. Use of temperatures which were clearly higher than necessary for complete pyrolysis gave a very low yield of the ethyl radical (as judged from the intensity of its first band) and high yields of the secondary products, ethylene and the methyl radical. For these reasons pyrolysis of azoethane was ruled out as a viable source of ethyl radicals for PES investigation.

An alternative method for production of the ethyl radical for PES investigation is by the rapid reaction of fluorine atoms with ethane.¹⁶ The spectrum obtained with the multidetector photoelectron spectrometer in the 8.0-10.5-eV IP region, consisting of 250 scans recorded in a total time of 40 s, is shown in Figure 2. Apart from methyl iodide calibrant bands, this spectrum shows a broad band in the 8.0-9.0-eV IP region which decreases dramatically in intense as the reagent mixing distance is increased beyond 1.0 cm. The vertical IP of this band has been measured over a large number of spectra as 8.51 ± 0.01 eV, in exact agreement with the value obtained by Houle and Beauchamp.¹³ On the basis of this evidence, this band is assigned to the first ionization potential of the ethyl radical. A small band was also seen in Figure 2 at 9.84-eV ionization energy arising from ionization of the methyl radical¹⁸ produced via secondary reactions in the $F + C_2H_6$ reaction scheme.²⁷ No higher bands of the ethyl radical could be positively identified in the 9.0-16.0-eV IP region because of relatively intense bands arising from the reaction products ethylene, acetylene, and vinyl fluoride as well as small contributions from unreacted ethane.

A mass spectrometric study of the $F + C_2H_6$ reaction has been made by Zetzsch,²⁷ and the following mechanism for the production of CH₃ was proposed:

$$F + C_2 H_6 \rightarrow C_2 H_5 + HF \tag{1}$$

$$F + C_2H_3 \rightarrow CH_3 + CH_2F$$
 (2)

$$CH_2F + CH_2F \rightarrow C_2H_3F + HF$$
 (3)

- (26) Field, R. W. J. Mol. Spectrosc. 1973, 47, 194.
- (27) Zetzsch, C. Ph.D Thesis, Georg-August University, Gottingen, 1971.

⁽²²⁾ Houk, K. N.; Chang, Y. M.; Engel, P. S. J. Am. Chem. Soc. 1975, 97, 1824.

⁽²³⁾ Perona, M. J.; Beadle, P. C.; and Golden, D. M. Int. J. Chem. Kinet.
1973, 5, 495.
(24) Sandhu, H. S. J. Phys. Chem. 1968, 72, 1857.

⁽²⁵⁾ Edqvist, O.; Lindholm, E.; Selin, L. E.; Sjogren, H.; Asbrink, L. Ark. Fys. 1969, 40, 439.



Figure 3. The He I photoelectron spectrum of the ethyl radical obtained from the reaction $F + C_2H_6$, recorded in the ionization energy range 8.0-9.0 eV with a multichannel photoelectron spectrometer. It consists of 500 scans recorded in a total time of 20 s.

Although the first photoelectron band of CH₂F has previously been observed with adiabatic and vertical ionization potentials of 9.04 \pm 0.01 and 9.22 \pm 0.01 eV,³³ respectively, this band was not observed in this study probably because the CH₂F radical is too short-lived to be observed at the reagent mixing distances used in this study. Weak bands attributed to CH₃ and vinyl fluoride were, however, seen. The possibility that the band attributed to the first IP of the ethyl radical was contaminated by contributions from the fluoroalkyl radicals, CH₃CHF or CH₃CF₂, was also considered but eliminated as these species are expected to have first adiabatic ionization potentials ≈ 0.4 eV lower than that of the ethyl radical.³⁴

An expanded spectrum of the first band of the ethyl radical is shown in Figure 3. This was recorded with the multidetector system by accumulating 500 scans in a total time of 20 s. As can be seen from this figure, regular vibrational structure was resolved, and the average vibrational spacing measured over 25 spectra, each of 500 scans, was 400 ± 30 cm⁻¹. Vertical and adiabatic ionization energies of the observed band were measured as 8.51 \pm 0.01 and 8.26 \pm 0.02 eV, respectively. The vertical IP and average vibrational separation measured for this band are in reasonably good agreement with earlier values that we obtained from a preliminary investigation of the $F + C_2H_6$ reaction with a single detector spectrometer¹⁴ although, as a result of improved stability (and hence calibration), the adiabatic IP measured in this work is lower than that obtained previously.¹⁴ In both cases, however, there are five vibrational separations between the vertical and adiabatic ionization potentials.

The possibility that the ethyl radical is vibrationally excited when ionization occurs must also be considered. This would lead to a distortion of the observed envelope, irregular vibrational structure particularly in the region of the band onset, and an anomalously low adiabatic IP. Some useful evidence related to this point can be derived by studying the first band of the methyl radical, produced by the $F + CH_4$ reaction, by PES. The F + C_2H_6 and F + CH₄ reactions are similar in that they are both rapid exoergic reactions ($\Delta H = -155 \text{ kJ mol}^{-1}$ for C₂H₆ and -146 kJ mol⁻¹ for CH₄) with small activation energies ($E_a \approx 4 \text{ kJ}$ mol⁻¹).²⁸ Also, in both cases it is well established from infrared chemiluminescence studies²⁸ that most of the energy available to

(30) Pacansky, J.; Dupius, M. J. Am. Chem. Soc. 1982, 104, 415



Figure 4. (a) The He I photoelectron spectrum of pyrolyzed n-propyl nitrite in the ionization energy range 8.0-9.5 eV. The NO⁺⁽¹ Σ ⁺), v' = $0 \leftarrow NO(X^2\Pi) v'' = 1$ component is masked by the He I β band of the first band of H_2CO . (b) The Ne I photoelectron spectrum of pyrolyzed *n*-propyl nitrite recorded in the ionization energy region 8.0-12.0 eV. Both spectra were recorded with a single detector photoelectron spectrometer.

the products goes into the newly formed HF bond ($\approx 70\%$) as vibrational and rotational excitation, with the remainder being partitioned between translational energy of the products and the internal degrees of freedom of the product alkyl radical. It should be noted, however, that C_2H_5 and CH_3 have fifteen and six vibrational modes, respectively, and energy randomization between these modes is likely to be faster in the C_2H_5 case. In the case of the F/CH_4 reaction, there is a marked geometry change at the central carbon atom from pyramidal to planar during the course of the reaction. Hence one would presume that, initially, the totally symmetric out-of-plane deformation vibration might be preferentially excited. Subsequently, internal vibrational energy randomization and indeed energy transfer processes would take place. We have carried out experiments in which the $F + CH_4$ reaction was used to produce CH₃ radicals under conditions very similar to those used to produce the ethyl radical. The well-established vibrational PES band envelope of CH3 was observed and fitted to a vibrational temperature of 340 ± 30 K.¹⁸ This is achieved by measuring the relative intensities of the $0 \leftarrow 0$ and $1 \leftarrow 1$ vibrational components in the ν_2 out-of-plane deformation mode in CH3⁺ and comparing with calculated relative Franck-Condon factors at different vibrational temperatures. Details of this procedure are described elsewhere.¹⁸ Hence this result unambiguously shows that the vibrational mode which should be preferentially excited is not, within the error limits of the experiment, vibrationally enhanced. It must be emphasized that this should not be taken as evidence for the initial energy distribution but rather for the fact that, under the relatively highpressure PES conditions, energy randomization or collisional relaxation has occurred before photoionization takes place. It follows from this result that, since the ethyl radical experiments were carried out under similar conditions, the vibrational distribution in C_2H_5 will correspond closely to that expected at room temperature and any effects due to vibrational excitation in the

^{(28) (}a) Jonathan, N.; Melliar-Smith, C. M.; Slater, D. H. Mol. Phys. 1971, 20, 93. (b) Jonathan, N.; Naylor, J. C., unpublished work.

⁽²⁹⁾ Pacansky, J.; Schrader, B. J. Chem. Phys. 1983, 78, 1033

⁽³¹⁾ Pacansky, J.; Gardini, G. P.; Bargon, J. J. Am. Chem. Soc. 1976, 98, 2665.

⁽³²⁾ Pacansky, J.; Horne, D. E.; Gardini, G. P.; Bargon, J. J. Phys. Chem. 1977, 81, 2149.

⁽³³⁾ Andrews, L.; Dyke, J. M.; Jonathan, N.; Keddar, N.; Morris, A.; Ridha, A. J. Phys. Chem., in press. (34) Williamson, A. D.; Le Breton, P. R.; Beauchamp, J. L. J. Am. Chem.

Soc. 1976, 98, 2705.

observed band can be neglected. The observed vibrational series in Figure 3 is in any case regular and shows no obvious sign of vibrational excitation in the neutral molecule.

It must be a cause of some concern that the band shape and particularly the vibrational spacings in the work just described are markedly different from that reported by Houle and Beauchamp.^{12,13} In order to try to understand these differences we have carried out PES experiments on the pyrolysis of n-propyl nitrite, which was the method used by those workers to produce the C_2H_5 radical. The He I spectrum recorded on pyrolysis of this precursor at a furnace temperature of 890 ± 20 K is shown in Figure 4a. The general features of spectra recorded under these conditions are in agreement with a similar He I photoelectron spectrum reported previously.^{12,13} However, although a broad band was observed on pyrolysis in the 8.0-9.0-eV IP region with a vertical IP of 8.54 ± 0.02 eV, the two vibrational components seen in this band by Houle and Beauchamp^{12,13} in both their He I and Ne I spectra at 8.39 \pm 0.02 and 8.51 \pm 0.02 eV¹³ were not detected. He I spectra recorded separately for nitric oxide, formaldehyde, and n-propyl nitrite led us to believe that the band shown in Figure 4a in the 8.0-9.0-eV IP region is complicated by a small contribution from the first band of n-propyl nitrite recorded with He I β radiation and the $v' = 2, 3 \leftarrow v'' = 0$ vibrational components of the first band of nitric oxide recorded with He I β radiation.^{25,26} After many He I spectra of pyrolyzed propyl nitrite were recorded over a wide temperature range it was concluded that although the first band of the ethyl radical can be clearly observed, no vibrational structure could be definitely resolved in this band. Hence, it was decided to use Ne I radiation as a means of obtaining improved resolution in the ethyl radical first band.

The Ne I photoelectron spectrum of pyrolyzed *n*-propyl nitrite at a furnace temperature of 770 \pm 20 K is shown in Figure 4b. Again the first band of the ethyl radical was observed. However, by recording separate Ne I spectra of nitric oxide and formaldehyde at room temperature, and nitric oxide passed through a heated furnace at temperatures in the range 300-1400 K, a number of other bands were found to overlap with the ethyl radical first band. As indicated in Figure 4b, the first band of H₂CO recorded with Ne I β radiation and vibrationally excited NO recorded with Ne I α radiation were observed on the low and high IP side of the ethyl first band, respectively. Also, evidence of vibrational components of the NO^{+(1 Δ , ¹ Π) \leftarrow NO(X² Π) bands} recorded with Ne II (26.91 eV) radiation was obtained in the ethyl first band as indicated in Figure 4b.25 However, measurement of spectra of the type illustrated in Figure 4b shows that the vertical IP of the band in the 8.0-9.0-eV ip region is measured as 8.53 ± 0.02 eV and a clear band maximum is seen on the low IP side corresponding to the adiabatic component of the NO⁺(¹II) \leftarrow NO(X²II) ionization (18.23 eV ip²⁵) recorded with Ne II (26.91 eV) radiation. This would have an apparent ip in a Ne I (16.85) eV) spectrum of 8.26 eV. Hence it is concluded that, under the conditions of our experiment, investigation of the pyrolysis products of n-propyl nitrite with Ne I radiation will lead to a spectrum of the ethyl radical first band which is seriously overlapped by other bands and this method cannot be used as a reliable way of investigating the details of the ethyl radical band envelope. No evidence was found in either the He I or Ne I spectra of pyrolyzed n-propyl nitrite for the band seen by Houle and Beauchamp at $8.39 \pm 0.02 \text{ eV}.$

The results of this current investigation highlight the difficulties of using azoethane and *n*-propyl nitrite as precursors for the ethyl radical for PES investigation. In comparing our work on pyrolysis of *n*-propyl nitrite with that of Houle and Beauchamp^{12,13} two objections could be raised. Firstly, the experimental resolution in our work is worse than that achieved in ref 12 and 13. This does not, however, appear to be the case as the resolution obtained on the first band of nitric oxide is comparable in both studies.

Secondly, the intensity of the subsidiary lines He I β , Ne I β , and Ne II may be greater in our discharge lamp than in the photon source of Houle and Beauchamp.^{12,13} Also, the partial pressure ratio [C₂H₅]/[NO] appears to be greater in ref 12 and 13 than in the current *n*-propyl nitrite work. In ref 12, the He I photo-

electron spectrum of pyrolyzed n-propyl nitrite is recorded, the relative band heights (measured from the most intense components) of the first bands of Et and NO are in the approximate ratio of ≈ 1.6 , and a He I β vibrational component of the first band of NO is observed at $8.30 \pm 0.02 \text{ eV}^{.12}$ In ref 13, the Ne I spectra of pyrolyzed n-propyl nitrite are recorded and the corresponding ratio is $\approx 1:8$. In the Ne I spectrum shown in Figure 4b the corresponding ratio is $\approx 1:27$. Clearly the effects of subsidiary photon lines on the first band of the ethyl radical will be greater under these latter conditions. We have, however, recorded Ne I spectra under higher $[C_2H_5]/[NO]$ ratios (up to values ≈ 1.5 from first band heights). The effects of subsidiary lines were, as expected, a lot less under these conditions but we were still not able to resolve any reproducible vibrational structure in the ethyl first band. Obviously these factors need to be considered when comparing spectra obtained via the *n*-propyl nitrite route in this work and in ref 12 and 13. However, in view of the band envelope obtained from the $F + C_2H_6$ route shown in Figure 3, which was obtained reproducibly over many spectra, there is no obvious explanation for the component seen at 8.39 eV by Houle and Beauchamp.¹³ On the basis of the work performed in this paper, it is believed that the $F + C_2H_6$ method provides the best route of generating ethyl radicals for PES investigation.

In order to assign the vibrational structure in the first band of the ethyl radical shown in Figure 3, it is necessary to know the equilibrium geometries in the ground states of both the molecule and ion and the fundamental vibrational frequencies of the neutral molecule. The most detailed ab initio molecular orbital calculations which have been performed show that the neutral radical has a staggered classical geometry with the barrier to an eclipsed form being very small ($\leq 4 \text{ kJ mol}^{-1}$). A nonclassical hydrogenbridged structure is expected to be much higher in energy for the radical. In the ground state of the ion, the hydrogen-bridged form is predicted to be the ground state, being ~29 kJ mol⁻¹ lower in energy than a classical staggered form which is in turn ~4 kJ mol⁻¹ lower in energy than a classical eclipsed form.⁷⁻¹¹

Ten of the 15 vibrational modes in the ground state of C₂H₅ have been observed experimentally in inert gas matrices.²⁹⁻³² Also, theoretical predictions have been made of all 15 vibrational frequencies which confirm the assignments of the ten observed modes and allow a prediction of the frequency and a description in terms of internal coordinates of the remaining five vibrational modes.²⁹ Three vibrational fundamentals are predicted for C₂H₅ below 1000 cm^{-1} , a CH₂ asymmetric bend (A", expected position 499 cm⁻¹), a CH₂ pyramidal distortion (A', expected position 499 cm⁻¹), and a torsion mode (A", expected position 141 cm⁻¹). Of these modes only the pyramidal distortion has been observed (at 540 $\rm cm^{-1}).^{29-32}$ As it is expected that the vibrational structure in the first photoelectron band of C₂H₅ should reflect the classical-to-bridged equilibrium geometry change on ionization, it is reasonable to assign the 400-cm⁻¹ vibrational structure observed in the ethyl radical first photoelectron band to excitation of the pyramidal bending mode in the ion, reduced from 540 cm⁻¹ in the neutral molecule. This is the mode which corresponds to the transition from a bridged ion (at the adiabatic IP) to a classical eclipsed ion (at the vertical ip). The difference between the vertical and adiabatic ionization energies measured in this work is 0.25 ± 0.03 eV (24.4 kJ mol⁻¹), which compares favorably with estimates of 27.2 kJ mol⁻¹ obtained from ab initio calculations including the effects of electron correlation via Moller-Plesset perturbation theory,⁷ 37.6 kJ mol⁻¹ from the IEPA method,⁸ and 30.5 kJ mol⁻¹ from the CEPA method.9

Comparison of the adiabatic IP measured in this work, 8.26 \pm 0.02 eV, with that expected from known heats of formation of the molecules and ion, 8.16 \pm 0.08 eV,⁴⁻⁶ shows that the PES value is outside the expected range. Hence, the adiabatic IP measured in this current work can only be regarded as an *upper limit* of the true adiabatic IP. This work, nevertheless, confirms an earlier estimate of the first vertical IP of the ethyl radical, gives a reliable vibrational envelope for the first PES band, and allows an estimate to be made of the pyramidal bending mode in the ion. It also demonstrates the usefulness of a multidetector spectrometer to

obtain photoelectron spectra of short-lived free radicals. Further work is in progress with the multichannel spectrometer to study the n-propyl and isopropyl radicals produced from the reaction of fluorine atoms with n-propane.

Acknowledgment. We thank the S.E.R.C. for financial as-

sistance, and British Gas and S.E.R.C. for the award of a CASE studentship to A.R.E. The authors gratefully acknowledge the advice of Professor N. Jonathan during the course of this work.

Registry No. Ethyl radical, 2025-56-1; ethane, 74-84-0; fluorine atom, 14762-94-8; azoethane, 821-14-7; *n*-propyl nitrite, 543-67-9.

Photocatalytic Hydrogenation of Alkynes and Alkenes with Water over TiO_2 . Hydrogenation Accompanied by Bond Fission

Masakazu Anpo,* Norikazu Aikawa, Sukeya Kodama, and Yutaka Kubokawa

Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, Sakai, Osaka 591, Japan (Received: October 20, 1983)

Photocatalytic reactions of alkynes and alkenes with water have been investigated over TiO_2 powder. The major photoformed products are those formed by hydrogenation accompanied by C=C or C=C bond fission. Oxidation products such as CO and CO₂ are also formed. From the change in the product yields with the remaining amount of water adsorbed as well as the pressure of water vapor it is concluded that water molecules and not surface OH⁻ groups are responsible for the reaction and also that vacant sites for the alkyne (or alkene) adsorption are necessary for the occurrence of the reaction. The fission of the C=C or C=C bond observed with the hydrogenation is attributed to the interaction of the alkynes (or alkenes) with the trapped e⁻ (Ti³⁺) and h⁺ (OH) pairs. It is suggested that a close association of photoformed electron and hole pairs plays a significant role in the bond fission.

Introduction

As an approach to utilization of solar energy, photodecomposition of water into H₂ and O₂ over metal oxides has recently received a great deal of attention.¹ In connection with this problem, Boonstra and Mutsaers have found that photocatalytic hydrogenation of alkenes and alkynes occurs over TiO2 containing adsorbed water, and proposed that H atoms produced according to the reaction $Ti_s-OH + h\nu \rightarrow Ti_s-O + H$ are responsible for the hydrogenation.² As has been shown by Schrauzer and Guth,³ and Boonstra and Mutsaers,² as well as described previously,⁴ the observed reaction is not a simple hydrogenation, the reaction products undergoing fission of the C=C or C=C bond. Such a fission of the bond is inexplicable by the concept that the reaction is caused by H atoms.² Schrauzer and Guth have suggested that the reaction could be related to the photodecomposition of water.³ We proposed that positive holes generated by UV irradiation participate in the reaction.⁴ Recently we have shown that with supported MoO₃ the charge-transfer complex, $[Mo^{5+}-O^{-}]^*$, formed by the reaction of

$$[\mathrm{Mo}^{6+} = \mathrm{O}^{2^{-}}] \xleftarrow{h\nu}{h\nu'} [\mathrm{Mo}^{5+} - \mathrm{O}^{-}]^*$$

plays a significant role in the fission of the C=C bond of alkenes.⁵ Accordingly, a study was undertaken to clarify the nature of the bond fission in the photocatalytic hydrogenation over TiO_2 . Such

TABLE I: Yields of the Hydrogenated Products Formed in the Photoreaction of Various Unsaturated Hydrocarbons with Water over TiO_2 at 300 K

reactants	photohydrogenated products, μ mol
СН≡СН	CH_4 (1.65), C_2H_4 (0.112), $n-C_4H_8$ (0.378), ^b
	$C_{3}H_{8}$ (0.089)
$CH_3 - C = CH^a$	C_2H_6 (4.86), CH_4 (0.451), C_3H_6 (0.312)
C₂H₅-C≡CH	$C_{3}H_{8}$ (4.65), CH_{4} (1.10), $C_{4}H_{6}$ (0.380),
	C_2H_6 (0.147), $CH_3CH=C=CH_2$ (0.295)
$CH_2 = C = CH_2$	C_2H_6 (2.27), CH_4 (0.023), C_4H_{10} (0.436)
$CH_2 = CH_2$	CH_4 (0.301), C_2H_6 (0.045), C_3H_8 (0.011)
$c-C_3H_6$	C_2H_6 (0.272), C_3H_8 (0.090), CH_4 (0.029)

^aSmall amounts of CH₃CHO, C₂H₅CHO, and CH₃COCH₃ were detected. Others were not measured. TiO₂: 0.30 g; reactant: 63.0 μ mol. ^bThis value is not conclusive. The mechanism of its formation is unclear.

information appears to be necessary for a more complete understanding of the photocatalytic reactions over TiO_2 caused by the active species formed from water.

Experimental Section

Materials. The TiO₂ was obtained from the Japan Aerosil Co. (P-25, Degussa, BET; surface area: 40 m²/g; average particle size: 0.029 μ m; purity: 97%). All the alkynes and alkenes used in the present study as well as H₂ were of extrapure grade from the Takachiho Kogyo Co. They were used without further purification. Commercial tank oxygen was purified by low-temperature distillation. Deionized double-distilled water was degassed by alternate freezing and thawing in vacuo. D₂O of 99.75% isotopic purity (E. Merck Darmstadt) was used without further purification.

Apparatus and Procedure. Two types of quartz cells were used. One was about 10 cm long and 5.0 cm in diameter with a total volume of about 300 cm³, and another was smaller, having a volume of about 30 cm³. The catalyst could be moved between the window section and the furnace section, so that its temperature could be raised from room temperature to about 1200 K. The cell was connected to a conventional vacuum system. Ultimate

⁽¹⁾ A. Mills and G. Porter, J. Chem. Soc., Faraday Trans. 1, 78, 3659 (1982); S. Sato and J. M. White, J. Phys. Chem., 85, 592 (1981); T. Sakata, T. Kawai, and K. Hashimoto, Chem. Phys. Lett., 88, 50 (1982); C. Leygrof, M. Hendewrk, and G. A. Somorjai, J. Catal., 78, 341 (1982); S. C. Tsai, C. C. Kao, and Y. W. Chung, J. Catal., 79, 451 (1983); R. I. Bickley, Spec. Period. Rep.: Catal., 5, 308 (1982), and references therein.

⁽²⁾ A. H. Boonstra and C. A. H. A. Mutsaers, J. Phys. Chem., 79, 2025 (1975).

⁽³⁾ G. N. Schrauzer and T. D. Guth, J. Am. Chem. Soc., 99, 7189 (1977).
(4) C. Yun, M. Anpo, S. Kodama, and Y. Kubokawa, J. Chem. Soc., Chem. Commun., 609 (1980).

Chem. Commun., 609 (1980). (5) M. Anpo and Y. Kubokawa, J. Catal., 75, 204 (1982); M. Anpo, I. Tanahashi, and Y. Kubokawa, J. Chem. Soc., Faraday Trans. 1, 78, 2121 (1982).