

## Mass Spectrometry of Free Radicals

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### I. Introduction

The detection and characterization of free organic radicals has been one of the most important challenges for mass spectrometry during the past 60 years, and, for decades, free radicals have been fascinating species to chemists, mainly because of their elusive nature as intermediates in numerous chemical processes, such as atmospheric and interstellar chemistry, combustion, or chemical vapor deposition phenomena, which can make difficult the understanding of even the apparently most simple chemical processes.<sup>1</sup> If most of the information concerning the reactions of free radicals has come from kinetic studies in which the presence and behavior of radicals are mainly deduced from the nature of the reaction products and from the dependence of the observed reaction rates on various experimental



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Toshihiro Fujii received both his B.Sc. and his Ph.D. in inorganic chemistry from Kyoto University, Japan. In 1974, he joined the National Institute for Environmental Studies (Japan), where he is now the Deputy Director of the Environmental Chemistry Division. He also teaches at Tsukuba University. His current research is focused on the development of  $\text{Li}^+$  ion attachment mass spectrometry, which is aimed at exploring the possibilities for an extremely high sensitivity detection method for intermediary radical species in the gas phase. He is interested in hyperthermal surface ionization as an ionization method for mass spectrometry and in the potential of *ab initio* molecular orbital methods (Gaussian) for environmental toxicology studies.

parameters, mass spectrometry has early appeared as a direct method to study radical intermediates due to its immediate response in the analysis of representative samples of a reaction mixture.

Another invaluable field where mass spectrometry of free radicals provided a wealth of information encompasses the field of bond energy determinations. When this thermochemical information is accurately known, it yields enthalpic criteria that can be used to discriminate between plausible reaction mechanisms since, according to current chemical theory,

chemical equilibria are determined primarily by the differences in enthalpy between the reactants and the products. Bond dissociation energies for molecules are directly related to the enthalpies of formation of their counterpart radicals. Unfortunately, while most organic chemists might have the impression that bond energies are well defined, it must be recognized that we are only just establishing reliable bond strengths for the simplest hydrocarbon compounds, and some domains can be considered as poorly completed.<sup>2</sup>

Determinations of bond energies by mass spectrometric studies necessitate the construction of thermochemical cycles, generally referred to as positive or negative thermochemical cycles depending on the ions involved as well as the quantities measured, ionization energy measurements in the first case, electron affinity measurements in the second. The advent of laser-based spectroscopic methods has obviously favored the opportunities for such detailed studies on organic reactive intermediates and their thermochemical quantities, complementing the early data accessible from the first mass spectrometric thermochemical-derived data reported principally from electron ionization experiments.

Nevertheless, the real issue of thermochemical studies of radicals might be the determination of quantities that can test and quantify conceptual models. There is a plethora of examples that could be reported to argue this point. The enthalpic criterion usually referred to in order to distinguish between concerted and nonconcerted mechanisms can be frustrating if differences in enthalpy of activation for the experimental and hypothetical models impinge on the validation of one or the other alternative. To conceive a transition state for the modeling of one route of reaction involves the breaking and making of covalent bonds, finally reducing the task to the knowledge of enthalpy of formation of the appropriate individual radicals, or of the dissociation energy of similarly appropriate bonds.<sup>3</sup> A wealth of data has been reported from kinetic studies<sup>4–7</sup> or materialized in the so-called additivity method.<sup>8,9</sup> However, the development of experimental techniques for the measurements of bond dissociation energies has unavoidably been conducted to note the vulnerability of the compiled values and has been conducted to question reasonably their reliability. The clear-sighted impetus for upward revision of the enthalpy of formation of the simplest organic free radicals was later revealed to be justified<sup>3</sup> and fed discussion on the study of reaction mechanisms.<sup>10</sup> Similarly, accurate experimental thermochemical values are necessary to implement reliable theoretical models to derive regiochemical patterns.<sup>11,12</sup> Noteworthy, in just over two decades thermochemical quantities collected by mass spectrometry of free radicals has noticeably expanded with the development of specific experiments mostly related to the work of a few dedicated laboratories.

The main purpose of this article is to provide to the reader an extensive overview of radical data obtained by mass spectrometry methods. A correlated aim was to retrace the evolution of mass spectrometry of free radicals since the period when the first

experiments done in this area were reported. However, for the sake of brevity, the quoted list of references has been principally focused on the last 20 years to review the most recent work available.

The review is organized in three main parts. The first part considers the pioneering work and instrumentation of mass spectrometry of free radicals. The historical perspective of the instrumental development of mass spectrometers in this field has been deliberately emphasized because it illustrates well the amazing progress presented by mass spectrometry during the past decades and the unremitting work of pioneering groups in this field that allowed the completion of actual data. Nevertheless, no attempt will be made in this section to give a detailed account of the experimentation since a large number of compilations are available on these particular topics.<sup>13–17</sup> Only the basic useful characteristics of the techniques that will be referred to in the other sections are included here.

The second part presents in four subsections the data collected for thermochemistry. However, this part will concentrate on the thermochemical applications rather than the spectroscopic results, which would enlarge the scope of the paper too much. Consequently, photoelectron spectroscopy of excited states as well as resonance-enhanced multiphoton ionization (REMPI) of Rydberg states are only cited if necessary as illustrative of the investigations.<sup>18</sup> There is also no particular desire to add another compilation of data to those already available<sup>5–9,18</sup> but rather to report comparative data to help the reader in the understanding of what has been the benefit offered by one particular mass spectrometry technique compared to another. Tables 2, 3, and 4 must be considered in this spirit. Our intention was not to give an exhaustive review on one particular radical, or class of radicals, which are fully reported elsewhere.<sup>19–26</sup> Kinetic studies on radical reactions have been omitted in this review because the authors considered that they are more specifically related to the very large field of chemical kinetics, which might be artificially disconnected from ionic and excited species if described in a review on mass spectrometry and free radicals. Nevertheless, the data resulting from kinetic studies have been included if it appeared that they were necessary for the completion of the subject. Ion-atom reactions are not reported here because this subject has been previously reviewed.<sup>27</sup>

The third part of this review is devoted to the field of applications of mass spectrometry in radical detection. However, this part encompasses some data related to information gained under chemical kinetic conditions that would have been difficult to omit for the benefit of illustrative work conducted in this field.

It was difficult to ignore the information obtained through neutralization–reionization mass spectrometry (NRMS) experiments which represent a very quickly evolving field in terms of investigative chemistry. However, due to the specificity of the results obtained by NRMS, it appeared necessary to report them separately when direct links could be connected to the main subjects tackled in the relevant sections. Consequently, the results relative to NRMS are only

**Table 1. List of Acronyms, Abbreviations, and Terms Used in the Text and Tables**

AE	appearance energy
CIDI	collision-induced dissociative ionization
$D_0$	bond dissociation energy (corrected value at 0 k)
DH <sub>298</sub>	bond dissociation energy at 298 k
EA	electron affinity
EI	electron ionization
FTICR	fourier transform ion cyclotron resonance
IAMS	ion attachment mass spectrometry
ICR	ion cyclotron resonance
IE	ionization energy
MPI	multiphoton ionization
NIDD	neutral and ion decomposition difference
NIPES	negative ion photoelectron spectroscopy
NRMS	neutralization-reionization mass spectrometry
PA	proton affinity
PEPICO	photoelectron-photoion coincidence
PES	photoelectron spectroscopy
PIMS	photoionization mass spectrometry
REMPI	resonance-enhanced multiphoton ionization
RPD	retarding potential difference
SIFT	selected ion flow tube
VUV	vacuum ultraviolet
ZEKE	zero electron kinetic energy

briefly reported here since reviews have been compiled extensively on the most recent developments of the past few years,<sup>28–31</sup> and insights will be given only to recent experiments subsequent to the latest available reviews.<sup>31</sup>

Finally, the purpose of the review will be attained if the constant influence of mass spectrometry in the field of radicals appears in the course of the reading.

Table 1 gives a list of acronyms, abbreviations, and terms used in the text. As a convention, a bond dissociation energy at 298 K is related to the abbreviation DH<sub>298</sub>; a bond dissociation energy at 0 K is related to the abbreviation  $D_0$ .<sup>4</sup> If different temperature measurements are specified in the quoted papers, the notation DH<sub>T</sub> has been adopted to define the corresponding measured or deduced values. All the thermochemical data are reported in kcal/mol because most of the quoted references have traditionally adopted this convention. Energy-unit conversions in this review are taken from the 1998 CODATA revision of fundamental constants<sup>32</sup> with the following conversion: 1 eV = 23.06035 kcal/mol, 1 cal = 4.184 J, 1 eV = 8065.544<sub>77</sub> cm<sup>-1</sup>.

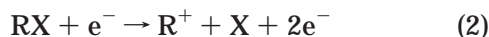
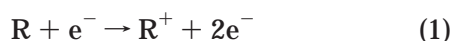
## II. Radical MS Overview

### A. Pioneer Works

The first free radical studies by mass spectrometry have schematically followed two parallel directions. In one type of study, the purpose of the investigation was the detection and the identification of radicals generated in flame, by thermal decomposition or by other chemical processes. In the other approach, the investigation was centered on a particular radical with an effort to produce this radical in high concentration to permit measurements of ionization potentials and calculation of the relevant dissociation energies of precursors.

In both cases, the principle of operation was residing on the same chemical basis. Considering a mass spectrometer in which radicals, R, could be generated by thermal decomposition of molecules RX directly introduced into the ion source, the resulting ionized

radical,  $R^+$ , can be produced in general by two processes that are summarized in the following reactions, eqs 1–2:



The minimum energy for reaction 1 is the ionization energy (IE) of the radical  $R$ , and the minimum energy for dissociative ionization reaction 2 is the appearance energy (AE) of the radical  $R$ . These two thermodynamic quantities are associated through eq 3:

$$AE(R) = IE(R) + DH_{298}(R-X) + eKE \quad (3)$$

where  $DH_{298}(R-X)$  refers to the bond dissociation enthalpy of the  $R-X$  bond, and  $eKE$  to the kinetic energy release of the electron in reaction 2. Thus, by employing electrons with energies of less than  $AE(R)$  but greater than  $IE(R)$  it is, in principle, possible to eliminate any ions produced by the dissociative ionization process and only ionize the free radical  $R$ .

Historically, the feasibility of detecting free radicals and elusive intermediate products of chemical reactions by means of mass spectrometry was pioneered by Eltenton,<sup>33,34</sup> and Hipple and Stevenson.<sup>35</sup> In his exploratory work, Eltenton used a heated reaction chamber coupled to a magnetic mass spectrometer to follow the growth and the decay of methyl radical concentration as a function of reactor temperature in a low-pressure mixture of lead tetramethyl in different carrier gases.<sup>33</sup> A few years later, investigation of both thermal decomposition processes at low pressures and combustion reactions at higher pressures was presented in an extensive paper, proving the utility of mass spectrometry to extend the applicability of radical detection methods to pressure regimes not attainable with the other contemporary methods.<sup>34</sup> In the same period, Hipple and Stevenson<sup>35</sup> reported the measurement of ionization energies of methyl and ethyl radicals produced by thermal decomposition of lead alkyl precursors through a heated furnace directly connected to the ion source of a mass spectrometer. The experimental values of the ionization energies for these two radicals were in good agreement with those obtained by indirect calculations from electron-impact data on hydrocarbons. It must be noted that this study was appearing at a time when the association of appearance energy data with ionization energies to deduce bond dissociation energies was being questioned.<sup>36</sup>

In both studies, experiments were performed on a 180-degree Dempster-type magnetic mass spectrometer for which the location of the ion source limited the available space to connect an efficient high-speed pumping system required to increase the absolute flow of free radicals. Lossing and Tickner<sup>37</sup> used a reactor design similar to those employed by Eltenton, but with an improved pumping efficiency to permit the quantitative determination of methyl radical concentration in thermally decomposing gases. The thermal decomposition of mercury dimethyl and of di-*tert*-butyl peroxide was found to yield methyl radicals in sufficient quantitative amounts to obtain

a relation between the partial pressure of methyl radicals and the corresponding remaining signal at  $m/z$  15 after the correction of all other contributions to the ionization process. Consecutive works have completed this study in investigating the decomposition of ethylene and propylene oxide,<sup>38</sup> have been applied to the measurement of the methyl recombination rate,<sup>39,40</sup> and have been extended to the investigation of benzene-derivative decomposition.<sup>41</sup>

The experimental difficulty of transferring a sample from a relatively high-pressure reactor to the very low-pressure mass spectrometer without losing radicals in a high proportion through collisions in the gas-phase or on surfaces has been the principal limitation of the method at a time when effective pumping capacities were limited. The previous experiments usually adopted a pinhole leak system with a hole sparked in the thin tip of a quartz thimble, or with a hole drilled in a gold diaphragm. However, this pinhole leak system gives a beam of molecules distributed over a wide angle favorable to collisions with the walls of the ion source before ionization of the entering sample. A different approach has been taken in the molecular beam system developed by Foner and Hudson<sup>42</sup> to detect atoms and radicals generated in hydrocarbon flames. The characteristics of the interface between the furnace and the ion source have focused on the rapid removal of the intermediate species from the reaction zone and on the limitation of collisions with the walls of the instrument. A hybrid molecular beam sampling system has been designed where a change in the flow character (from viscous to molecular as the pressure drops) and collimation characteristics of the effusing jet have been conducted to prevent scattering of the gas sample during the transfer path from the furnace to the ion source. By incorporating a molecular beam chopper system and employing phase detection of the ion current signal background signals have been virtually eliminated, resulting in a drastic increase in the sensitivity of the method. Until this time, experiments on free radicals were employing a slow scanning of mass spectra, and Foner and Hudson<sup>42</sup> were the first to make use of the fast scanning possibilities of mass spectrometers for radical detection.

In 1957, the list of radicals and atoms generated by various methods (thermal decomposition, combustion flames, electric discharges, bimolecular reactions) and detected by mass spectrometry was already noteworthy.<sup>43</sup> As a pertinent example, the detection of  $HO_2^{\cdot}$  radicals was reported as one of the early successes of the mass spectrometric methods compared to the other spectroscopic methods.<sup>44</sup>

## B. Brief Survey of the First Instrumental Developments for Radical Studies

In the approach taken by people using mass spectrometry techniques to investigate processes generating free radicals, it appears that the studies following the above-cited pioneer works were mainly related to the improvement of sampling systems evolving between Knudsen effusion and isentropic expansion conditions.<sup>45–47</sup> Milne and Greene<sup>48,49</sup> focused their work on aerodynamic molecular beam

formations for the direct mass spectrometric sampling of flames at pressures equal to or higher than atmospheric pressure. Goldfinger and co-workers<sup>50</sup> reported the use of a rapid scanning system adapted to a conventional mass spectrometer for the analyses of molecular beams issuing from a photochemical reactor at pressures up to one atmosphere. Foner and Hudson extended the scope of their molecular beam sampling system by coupling it to a short-duration pulsed electrical discharge to analyze long-lived states of excited species in an ammonia and nitrogen–helium mixture,<sup>51</sup> and they later used a crossed-molecular beam system<sup>52</sup> to observe and characterize free radical products of elementary gas-phase reactions. More detailed information on these instrumental developments is given in the review articles summarizing the first stages of mass spectrometry history in this field.<sup>43–46,53,54</sup>

Early studies investigating radicals in the gas-phase by mass spectrometry were performed by electron impact for the ionization of radicals. Nevertheless, structural information and thermochemical data were difficult to assess unambiguously, and with the advent of photoionization methods, the drawbacks of electron ionization methods have been clearly emphasized.<sup>55</sup> By definition, ionization potentials measured by electron impact are considered to correspond to a vertical transition in the Franck–Condon sense and, as such, are slightly higher than the adiabatic values obtained from spectroscopic techniques. This resulted in an unavoidable ambiguity for the exact attribution of ionization energies. However, as stated by Lossing,<sup>43</sup> at the end of the 1950s, no alternative to the electron impact values was available except for very few cases. By principle, a plot of the detected ion current against the electron energy should enable one to determine the ionization and appearance energies of the radical at the threshold. Several empirical methods have been used for this purpose. But, due to the Maxwell-Boltzmann distribution of the ionizing electron energy and due to irreproducible effects in the electron source or in the ion source, data derived from electron impact studies could not be accepted without reservation. Experimental techniques existed for minimizing the effect of the distribution of energy in the electron beam, but, unfortunately, their uses suffered from the disadvantage that any gain in precision was obtained to the detriment of the overall sensitivity of the instruments so necessary for radical investigations. Among the several attempts to produce an electron beam with a sufficiently well-resolved ionization energy, the retarding potential-difference method of Fox and co-workers<sup>56</sup> appeared to be the most successful practical improvement for the design of ion sources with collimated ionization energy. This method was further applied with an absolute accuracy of 0.1 eV for the determination of alkyl radical ionization energies<sup>57,58</sup> at a time when the resolution of photoionization experiments was not comparable to the values accessible nowadays. Similarly, an electrostatic energy selector was later introduced with an energy half-width of 0.06–0.12 V for the electron beam<sup>59</sup> and has been greatly used thereafter (cf. section III-A).

If the electron beam energy is a crucial parameter in using electron ionization for threshold ionization energy measurements, important uncertainties arise when a change in geometry appears between the neutral radical and the resulting ion. As a consequence, the reliability of the measured values must be considered with great care. For this reason, the development of vacuum ultraviolet photoionization methods could be regarded as one of, if not the most important, improvement over mass spectrometric methods used to investigate radicals during the past 40 years. The high-energy resolution of the technique was often proposed as its main advantage. Preliminary experiments reported by Lossing<sup>60</sup> with a far-ultraviolet source showed that methyl radicals generated by decomposition of mercury dimethyl were efficiently photoionized. Ionized methyl radicals were detected with a resulting ion current noticeably lower than those obtained by electron impact, suggesting the necessity for a 10- to 100-fold increase of the absorbed quanta ratio by the parent ion precursor for applicability in accurate photoionization threshold measurements. However, the first photoionization experiments<sup>61</sup> on alkyl radicals were rapidly presented with a measured value for the ionization energy of the methyl radical in agreement with the reported spectroscopic data, demonstrating, for the first time, the reliability of the method used for the production and ionization of free radicals with a light source. The most evident advantage of photoionization data compared to electron impact data certainly resided in the expected clear differentiation between vertical and adiabatic ionization energies due to a higher energy resolution. However, uncertainties for the determination of true thresholds remained since noticeable experimental improvements were obtained in using windowless vacuum ultraviolet monochromators, extending drastically the accessible energy range for ionization, or quadrupolar lens systems to recollect most parts of the generated ion beam. It was therefore possible to obtain reliable threshold data as well as fine structures usually blurred in the electron impact method. The ionization energy of the trifluoromethyl radical was then reported<sup>62</sup> with an ionization efficiency curve showing characteristic features in accordance with the expected different equilibrium configurations for the ion and the neutral precursor.

Since the advent of the modern molecular beam and laser techniques, experimental approaches for radical investigations have followed their own evolution with major developments in relation to the expansion of photoelectron and photoionization techniques. These developments related to the studies of radical species will be introduced in the next section.

## C. Instrumental Methods

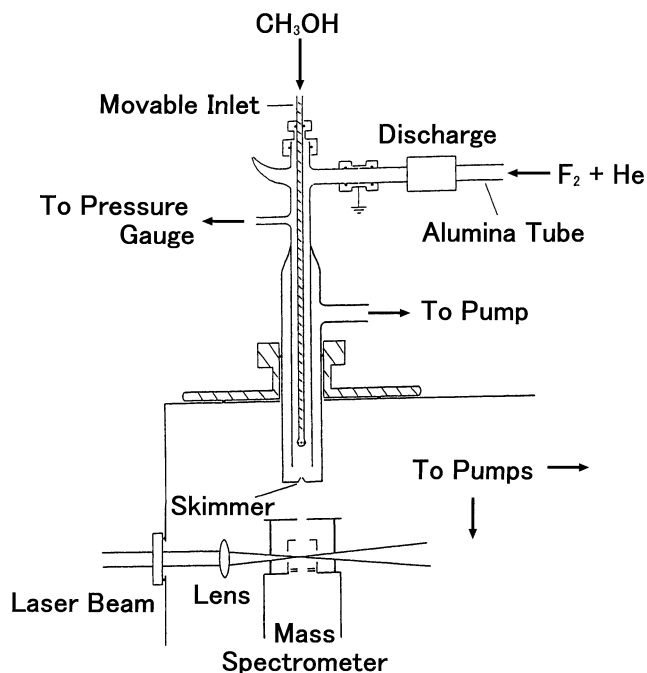
### 1. Radical Formation

A large set of mass spectrometric methods have been employed for the generation and study of radicals including thermal reactions, pyrolysis, photolysis, flames, or electrically induced plasmas.<sup>45–47,53</sup> Most of these methods are well-established techniques, which have been extensively utilized in other areas such as gas-phase kinetic studies. Among them,

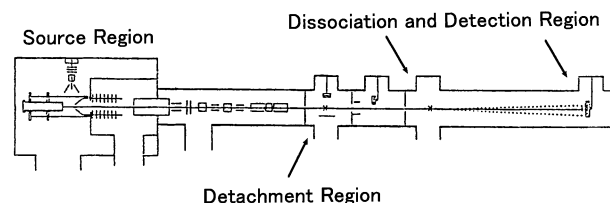
thermal decomposition processes involving both heterogeneous and homogeneous reactions have provided a lot of data on free radicals with, as major inconveniences, first, the difficulty of finding a suitable precursor to generate the expected radical at a sufficiently low temperature to avoid its rapid decomposition and, second, the difficulty of controlling the effective temperature of the radical product. Photolysis was presented as a chance of producing, at low temperature, radicals that are unstable at the usual temperatures necessary for pyrolysis. However, conventional photolytic reactions suffer from relatively low concentrations of radicals relative to stable molecules. The usual low-absorption coefficient of organics is responsible for this fact and results in inefficient absorption mechanisms along the physical path lengths of experimental setups. To circumvent the drawbacks of a low concentration of radical species, it was then necessary to resort to mercury-photosensitized decomposition methods, where excited mercury atoms induce higher yields of decomposition, or flash photolysis, where more energy is available for the radical formation process. In addition to the former methods, the intrinsic simplicity and directness of producing radicals by electrical discharges (radio frequency or microwave-induced plasmas) have served as an impetus for their use in studies of free radicals by mass spectrometry and resulted in a constant use of plasmas from the beginning of these investigations.

**Flow-Beam Reactor.** Recently, most of the new radical species have been discovered or studied using gas-phase reactions in generating transient unstable species, typically fast atom-molecule reactions. These experiments have been successfully applied to the selective formation and study of organic free radicals especially for electron-based spectroscopy techniques where this method of radical formation is widely employed besides photolysis.

A low-pressure flow reactor of a design initially set up by Anderson and Bauer<sup>63</sup> has been extensively used in resonance-enhanced multiphoton ionization (REMPI) studies for the generation of free radicals through abstraction reactions by atomic reactants, mainly atomic fluorine.<sup>64</sup> Basically, the reactor depicted in Figure 1 consisted of three concentric glass tubes, with a skimmer mounted on the end of the largest tube to sample a small portion of the reaction product, which expands into the mass spectrometer ionizer. Design parameters of the flow reactor are optimized to maximize the intensity of the sample in the ionization region and retaining fidelity of composition during the transfer of the sample from the reactor to the mass spectrometer. So, equal areas are required to ensure a constant flow velocity within the reactor, and the place of the sampling orifice is determined to minimize disturbance in the flow pattern. A dilute mixture of fluorine in a helium buffer passes through a microwave discharge to generate fluorine atoms which travel down to the reactor and react uniformly with the reagent (here, CH<sub>3</sub>OH) at the end of the inner central tube. The bulk of the reactants, products, and buffer gas is pumped away, and the portion of reactants sampled



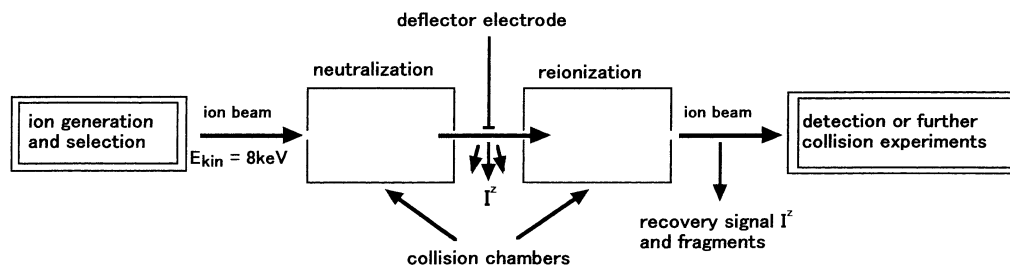
**Figure 1.** Schematic view of a discharge low-pressure flow reactor and mass spectrometer's ionizer used for the generation of free radicals through abstraction reactions by atomic reactants. Reprinted with permission from ref 64. Copyright 1983 American Chemical Society.



**Figure 2.** Schematic illustration of new fast radical beam apparatus designed to study the photodissociation of mass-selected radicals. Reprinted with permission from ref 67. Copyright 1992 American Institute of Physics.

through the skimmer is photoionized by a laser beam. Maximum radical density is estimated at  $10^{10}$ – $10^{11}$  radicals  $\text{cm}^{-3}$ , and efficiency for the irradiation process is assumed to be around 23 000 radicals<sup>65</sup> for a density of  $5 \times 10^{10}$  radicals  $\text{cm}^{-3}$ .

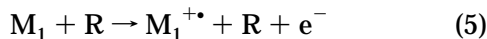
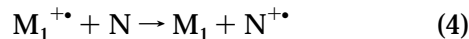
**Fast-Beam Translational Spectrometer.** A new fast-radical beam-apparatus has been built by Neumark and co-workers<sup>66,67</sup> to study the photodissociation of mass-selected radicals. The principle of the apparatus is based on the neutralization of a fast negative ion beam by photodetachment: anions are produced and cooled in a pulsed free-jet expansion, then accelerated and mass-selected by a time-of-flight analyzer before photodetachment of the anion radical precursor (Figure 2). The technique allows one to study the dissociative electronic states of well-characterized radicals with a defined internal energy for avoiding any precursor contamination. In addition, the internal energy of the radicals can be precisely controlled by conducting the photodetachment process near the threshold, ensuring the generation of a beam of internally cold free radicals. Two types of experiments can be performed with this experiment: photodissociation cross-section measurements at variable photodissociation wavelengths and



**Figure 3.** Schematic representation of a neutralization–reionization mass spectrometry experiment for mass-selected ion beam  $I^z$  of charge  $z$  ( $z = \pm$  charges). Reprinted with permission from ref 31. Copyright 1994 American Chemical Society.

photofragment time-of-flight distribution measurement with kinetic energy release determination at fixed photodissociation wavelengths. This experiment presents some conceptual similarities to the neutralization–reionization mass spectrometry technique.

**Neutralization–Reionization Mass Spectrometry (NRMS).** Neutralization–reionization mass spectrometry (NRMS) can be presented as a technique to generate radicals as well as a technique to probe the chemistry of a neutral, taking advantage of the fact that the corresponding ion may have a higher stability to be “trapped” and selected compared to its neutral counterpart.<sup>28,29,31</sup> NRMS presents the advantage of opening up all techniques available for the generation of a precursor ion of interest and allows the investigation of its neutral counterpart without being restricted to thermal or photochemical processes for its formation. In a typical experiment (Figure 3), a beam of ions selected by the first-stage analyzer of a double-focusing mass spectrometer collides at a translational energy of 4–10 keV with a neutral target gas in the first collision chamber under near single-collision conditions. The neutral beam then generated enters the second collision chamber where it is reionized upon collision with a second target gas, typically, molecular oxygen. The reionization energy is provided by the kinetic energy content of the fast neutral beam. The reionized beam is then sampled by a second mass analyzer before detection or submitted to subsequent collision experiments. The overall process can be summarized by the following equations, eqs 4–5:



where  $N$  is the neutral target gas and  $R$  is the reionizing gas. With a kilovolt collision energy range, the ionizing process, eq 5, produces  $M_1^{+*}$  with sufficient energy to fragment allowing the resulting mass spectrum of the intermediate  $M_1$  species to be used for identification of  $M_1$ . The resulting neutralization–reionization mass spectrum is generally recognized to be similar to the electron ionization mass spectrum of the molecule  $M_1$  or the collision-activated dissociation spectrum of the odd electron cation  $M_1^{+*}$ . Obviously, NRMS rapidly appeared as a complementary technique to generate elusive species, which are usually experimentally known through spectroscopic measurements of species generated in energetic processes such as electrical discharges. The

fast-beam velocity of the neutral (ca.  $10^5$  m  $s^{-1}$ ) minimizing the occurrence of bimolecular perturbing reactions, and the time-scale of experiments for both neutral, eq 4 (in the  $\mu s$  range providing a crucial test for the stability of the neutral), and ionic species, eq 5 (ca.  $10^{-5}$  s lifetime), are the main advantages presented by the technique.<sup>29</sup> The NRMS technique has been extended to newly developed methods such as *collision-induced dissociative ionization* (CIDI), where the neutral beam is obtained from the metastable decomposition of appropriate mass-selected precursor ions, eq 6:



and the *neutral and ion decomposition difference* (NIDD), in which normalized charge reversal spectra are subtracted from neutralization–reionization spectra to attribute fragmentations to the neutral  $M_1$ , eq 4, or to the recovered ion  $M_1^{+*}$ , eq 5.<sup>68</sup>

## 2. Electron Ionization Methods

Electron impact techniques have been widely used over the years in experiments directed toward measurements of ionization energies and appearance energies. Ionization threshold measurements are achieved by the interaction of neutral species with an electron beam, resulting in ionization of the precursor (eq 1) or dissociative ionization (eq 2). This class of techniques suffers however from two main problems: (i) a quite large energy spread of the electron beam used for ionizing the sample due to the Maxwell-Boltzman distribution of velocities of the ionizing electrons emitted from a heated filament, and (ii) a variation of the energy maximum of the beam which can noticeably differ from the nominal expected energy deduced from applied electrode potentials (in addition, for dissociative ionization, the ejected fragments have a kinetic energy difficult to define accurately, which, nevertheless, cannot be ignored). Rosenstock divided into three categories the electron impact techniques used for ionization energy measurements,<sup>69</sup> ranking them in a decreasing order of refinement and quality as follows: (a) monoenergetic, (b) quasi-monoenergetic, and (c) conventional.

Using electric fields to produce monoenergetic electron beams appears in principle to be a direct way. However, the factors involved in the optimization of such an electrostatic monochromator design have to reconcile a low operating electron energy to achieve a good resolution at half-width with a large susceptibility to stray from the magnetic fields at this

low energy. As a result, the monoenergetic electron beam technique using a two-stage double-hemispherical electron monochromator<sup>59</sup> appears to be the most reliable technique, offering typical energy spreads varying from 60 to 120 meV at half-maximum for an incident electron beam operated between 10 and 30 V. Indeed, experimental values obtained by this method agreed within  $\pm 0.03$  eV of those of photoionization results.<sup>15</sup>

The quasi-monoenergetic retarding potential difference (RPD) technique<sup>56</sup> has been introduced for eliminating the difficulties arising from uncertainties in the energy of the ionizing electron beam during ionization energy measurements and has been widely adopted since. This technique implies the use of a rapidly varied voltage electrode in the electron path to define the electron beam energy so that only a narrow portion of the electron beam corresponding to the central part of its distribution curve is effectively used for the ionization process. Reported accuracies lie in the 0.1 eV range.<sup>57</sup>

Conventional, or nonmonoenergetic, techniques have in common that they employ a broad energy electron beam and use a differing method for extrapolating the threshold values.<sup>69</sup> Obviously, accuracy ranges from less than 0.1 eV to more than 0.5 eV and is consequently subject to large and unpredictable errors in the interpretation of experimental data. Indeed, threshold energy measurements by electron ionization techniques, and more especially for the conventional techniques, are complicated by the analytical problem of defining a linear threshold law of appearance for which the applicable energy range is generally not known. If electron ionization experiments have potential for accurate measurements, their reliability is correlated to the use of a monochromator to narrow the energy distribution of the ionizing electron beam and associated with an accurate electron energy calibration.<sup>15</sup> Reliability of these data might be more controversial for dissociative ionization processes where kinetic shifts and excess of internal energy are perturbing factors more difficult to control and assign.

### 3. VUV Ionization Methods

The field of vacuum ultraviolet (VUV) spectroscopy of radicals encompasses a large set of experiments carried out with conventional UV light sources, VUV lasers, more rarely synchrotron radiation, and multiphoton ionization even if not technically a pure VUV source. As stated above, the advent of photoionization methods has been related to the development of light sources with high photon flux. The current available VUV light sources<sup>70</sup> provide photon flux/s in the range of  $10^{11}$ – $10^{13}$ .

The simple threshold law, eq 7, generally admitted to depict at least approximately a variety of threshold processes, permits description of sensitive and high-resolution ionization threshold energy measurements.

$$\sigma(E) = \sigma_0 \frac{(E - E_0)^n}{E^m} \text{ if } E > E_0 \quad (7)$$

$$\sigma(E) = 0 \text{ if } E < E_0$$

$\sigma(E)$  is the cross-section (proportional to ionization, or reaction probability),  $\sigma_0$  is a scaling factor depending on the intrinsic reaction strength or reaction probability,  $E_0$  is the state-to-state threshold energy, and  $n$ ,  $m$  are specific parameters related to the process (ionization, collision, reaction). This simple law can be applied to photoionization processes. However, the density of transient species must be substantially high in the target region to distinguish between zero signal and threshold onset for the measurements of energy. Accurate ionization energies (IE) and electron affinities (EA) of the corresponding precursors may be obtained from the threshold removal of an electron when the photon energy  $h\nu$  is increased, as depicted in eq 8–9:



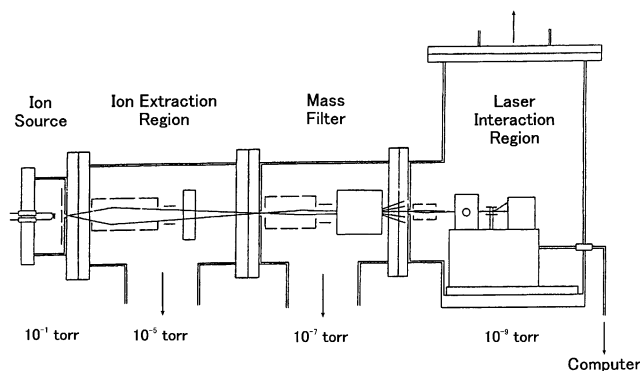
The threshold energy measurements,  $h\nu_0$  and  $h\nu'_0$ , correspond to the direct measurement of the adiabatic ionization energy and electron affinity, respectively, if the transition intensities are mainly governed by good Franck–Condon overlap between the vibrational states of the precursors and the products at 0 K. This simple picture is often complicated by non-Franck–Condon behavior, like autoionization resonances, eq 10, including or not a convergence from Rydberg states to excited vibrational states of the neutral before ionization (hot bands effects), or large geometrical changes during the ionization processes, eqs 8–9.<sup>15</sup>



Obviously, reliability and accuracy of VUV photoionization techniques compared to electron ionization techniques are usually considered to rely on the step-function character of the threshold law for photoionization of neutrals compared to its linear character for electron ionization.<sup>15</sup>

Two methods of VUV photoionization have rapidly emerged in the field of radical chemistry,<sup>55</sup> namely, photoelectron spectroscopy (PES) and photoionization mass spectrometry (PIMS). In its usual configuration, PES employs a monochromatic light source, and an electron energy analyzer to measure the kinetic energy spectrum of the ejected photoelectrons, but without concomitant mass analysis. The photon energy is fixed at a value higher than the expected IE or EA, and the ejected photoelectron kinetic energy is measured upon reaction processes under investigation, eqs 8–9. The difference between the incident photon energy,  $h\nu$ , and the expelled electron kinetic energy,  $eKE$ , determines the electron binding energy,  $eBE$ . The photoelectron spectrum consequently yields information on the structure of the upper charge states of the precursor, and the energy difference between the ground states of the neutral and the ion gives the adiabatic values of IE and EA. PIMS uses a tunable VUV light source and records the mass spectrum of generated photoions as a function of the incident VUV source wavelength. Direct measurements of adiabatic ionization potential may





**Figure 4.** Overview of a mass spectrometer used for negative ion photoelectron spectroscopy experiments. Negative ions are generated in a discharge ion source and then extracted into a high-vacuum region before mass-selected separation. Electron photodetachment takes place in the laser interaction region. Reprinted with permission from ref 72. Copyright 1983 American Institute of Physics.

be obtained more precisely in part due to the elimination of unwanted species, precursors or impurities.<sup>55</sup>

Negative ion photoelectron spectroscopy (NIPES) has been used to measure electron affinities of radicals and to examine the structure of ground and excited states of the corresponding neutral.<sup>71</sup> Compared to PES, the initial mass analysis of the negative ion beam eliminates uncertainties on the assignment of the precursors of the neutral product. The method has also demonstrated its ability to investigate neutrals that are difficult to generate for classical optical techniques. Among the couple of advantages that this technique has to offer is the direct measurement of the electron affinity of the neutral generated during the electron detachment process, eq 9, as well as the location of the various electronic and vibrational states in which the neutral is left. The principle of the experiment resides in the formation of a thermolyzed negative ion beam interacting with a laser of fixed wavelength. The energy imparted by the laser causes an electron to be expelled, forming a neutral and a kinetically excited electron. Typically, a hemispherical electron analyzer measures the kinetic energy of the detached electrons,  $eKE$ , which can be simply converted to a measure of electron binding energy,  $eBE$ , by subtracting it from the energy of the laser,  $h\nu$ , eq 11.

$$eBE = h\nu - eKE \quad (11)$$

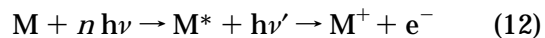
Negative ion formation is usually conducted through a discharge ion source.<sup>72</sup> The generated ions are extracted into a high vacuum region and focused into a beam sent through a Wien filter to give a mass selected anion beam finally crossed by a monochromatic laser beam in the laser interaction region (Figure 4). Currently, resolution of the electron energy analyzer lies in the 20–25 meV range (fwhm) but has been recently improved to the 10 meV range (fwhm).<sup>73</sup>

A flowing afterglow ion source has been developed by Lineberger and co-workers<sup>74</sup> because of the advantages presented by this selective device for the generation of rotationally and vibrationally relaxed anions, and for its increased synthetic versatility, as a wide variety of anions can be generated by ion-

molecule reactions under well-characterized conditions. For both of these experiments, the achieved energy resolution usually lies in the 10 meV range over the entire energy range of analysis.<sup>15</sup>

Beside the photodetachment spectroscopy techniques, ion cyclotron resonance (ICR) mass spectrometry has been the predominant experimental method to study photodetachment processes of trapped negative ions, and has been extended to the investigation of radicals by the group of Brauman.<sup>16</sup> A pulsed-mode of operation of the ICR apparatus has extended the inherent versatility of these types of mass spectrometers for the generation of precursor anions through proton abstraction or electron impact ionization. Details on the principle of electron photodetachment spectroscopy of trapped negative ions have been extensively compiled in a preceding issue of this journal.<sup>16</sup>

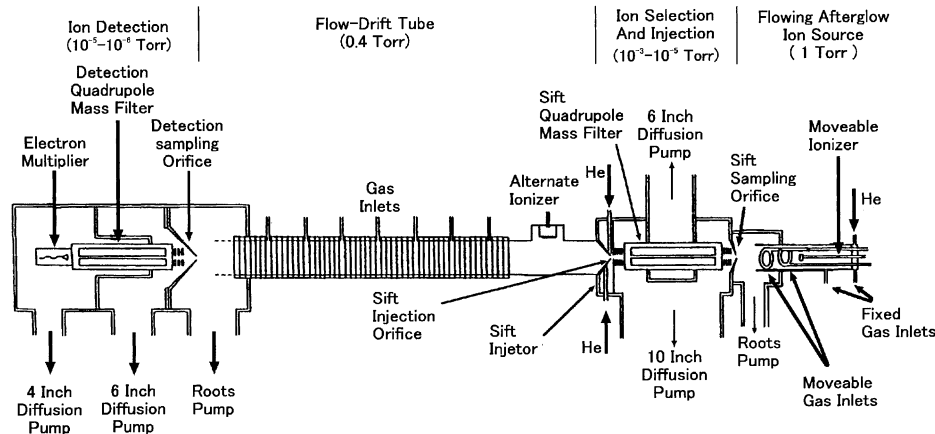
Not purely involved in the domain of VUV ionization techniques, multiphoton ionization (MPI) must however reasonably be referred to here for its implications in experiments that have concerned free radicals, and have mainly employed resonance-enhanced multiphoton ionization (REMPI). Early on, MPI was revealed to be a simple and efficient technique for recording electronic spectra of molecules, especially providing insight into electronic states not easily amenable to study by conventional spectroscopic methods.<sup>75,76</sup> In addition, for radical studies, the sensitivity of the technique is one of its main advantages since today's available laser powers allow only a few molecules to be needed under normal conditions of use of the ionization cell of MPI experiments. Selectivity of the technique, in addition, affirmed it as a powerful method for the elucidation of excited-state structures, as the most commonly appearing resonances belong to Rydberg states in MPI spectra. Compared to PES, the fact is that REMPI information is carried out by ions accessible to mass spectrometry analysis and, then, provides good opportunity for accurately establishing the identity of radicals involved in the example of a  $[n + 1]$  REMPI process, eq 12:



where  $n$  is an integer, and  $\nu$ ,  $\nu'$  are the respective wavelengths of the photons involved in photoionization. In addition, REMPI mass spectra seldom show high fragmentation yields, displaying principally the molecular ions certainly related to the consequence that ionization of radicals leads to the formation of stable closed-shell ions unlikely to undergo subsequent photofragmentation.<sup>65</sup> Most of the radical electronic states observed under these conditions are Rydberg states.

#### 4. Ion-Molecule Reaction Experiments

On the route of determining thermochemical data of a neutral unstable species, it is possible to obtain an experimental estimate of the enthalpy change for a particular process by the use of a technique referred to as "ion-molecule reaction bracketing", in which an ion of interest is reacted with a series of molecules chosen to scale the appropriate thermochemical



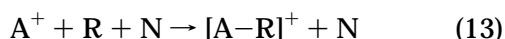
**Figure 5.** Drawing of a tandem flowing afterglow selected ion flow tube (SIFT)-drift instrument. Reprinted with permission from ref 77. Copyright 1987 Elsevier Science Publishers.

parameter (e.g., proton affinity). This technique has been applied in the early days of ion cyclotron resonance (ICR) mass spectrometry and later on in Fourier transform ion cyclotron resonance mass spectrometry (FTICR).<sup>13,15</sup> Ion–molecule reaction experiments have been employed for the determination of relevant data for radicals. This approach is based on the preliminary assumption that an endothermic reaction will not be observed due to its low efficiency. Consequently, one expects that the approximate onset energy lies on the energy scale at a point where the rate of reaction starts to rise. The remaining problem is the exact determination of the threshold, which, in particular, is drastically related to the sensitivity of the experiments.<sup>15</sup>

An illustrative example of such experiments is the tandem flowing afterglow selected ion flow tube (SIFT) drift instrument developed at the University of Colorado, Boulder<sup>77</sup> (Figure 5). Precursor ions are generated in the flowing afterglow source, extracted and focused into the SIFT quadrupole mass filter and mass-selected before injection into the drift tube where they are reacted with neutral reagents. Energies of the reaction can be controlled by the application of an electric field on the flow-drift tube, varying from thermal to elevated kinetic energies. Typically, gas-phase acidities of radicals have been derived from kinetic measurements of proton-transfer reactions by this technique.

### 5. Ion Attachment Mass Spectrometry

Lithium ion attachment mass spectrometry (IAMS) has been introduced as a new method for detection and identification of radical species in the gas phase.<sup>78</sup> This method provides mass spectra of quasi-molecular ions formed by lithium-ion attachment to the radical species under high-pressure conditions in a similar way to that proposed for the detection of stable molecules.<sup>79</sup> Briefly, thermal alkali-metal ion association reactions are described by the termolecular process, eq 13:



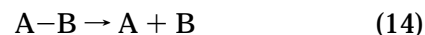
where A denotes a positively charged alkali metal ion, R is a radical species, and N acts as a third-body.

The binding energy of the radical R to the alkali cation  $A^+$  is defined by the enthalpy change for the preceding reaction. Deriving primarily from electrostatic forces, the binding energy of the reagent alkali metal ion  $A^+$  to the radical must be high enough to permit a significant number of adducts to be formed at the partial pressure used in the experiments. Cationized adducts are generally stable and give away a direct information on the molecular weights of the neutral counterpart of the  $[A + R]^+$  adduct. The relative binding energies of radicals have been estimated by theoretical calculations,<sup>80,81</sup> indicating that the binding energies of a wide range of such species with the alkali ion are high enough to be detectable at low concentrations. The advantages of this method for radical detection are a measure of mass as a guide for radical identification without fragmentations, adaptability to a large range of steady-state pressures, and direct continuous measurements of any species emerging from dynamic systems. In addition, the technique allows one to probe at the same time both the ionic and radical species flowing out from the investigated systems (plasmas in general), which make possible to obtain correlations between them.

## III. Radical Characterization

### A. Threshold Measurements by Electron Ionization: Ionization Energy, Enthalpy of Formation, and Bond Dissociation Energy Collection

A great quantity of thermochemical information on neutrals has been obtained through the threshold measurements of ionization and appearance energies using electron ionization methods.<sup>7</sup> Considering the homolytic bond dissociation energy ( $DH_{298}$ ) of a neutral AB as resulting from the following fragmentation process, eq 14:



where  $DH_{298}(A-B) = \Delta H_{298} = \Delta_f H_{298}^0(A) + \Delta_f H_{298}^0(B) - \Delta_f H_{298}^0(A-B)$  and refers usually to the AB species at 298 K.  $DH_{298}$ 's may be determined directly by

measuring the enthalpy change in eq 14 at 298 K or may be obtained if the three heats of formation are known from independent experiments. If the values of  $\Delta_f H_{298}^0(\text{AB})$  could be known through calorimetric techniques, the remaining problem is one of determining  $\Delta_f H_{298}^0(\text{A})$  and  $\Delta_f H_{298}^0(\text{B})$ . The missing thermochemical information for the neutral species A and B can be obtained with the use of thermochemical cycles introducing positive ions and their relevant ionization energy and appearance energy, as reported in eqs 15–16.

$$\text{DH}_{298}(\text{A}-\text{B}) = \text{DH}_{298}(\text{A}^+-\text{B}) + \text{IE}(\text{AB}) - \text{IE}(\text{A}) \quad (15)$$

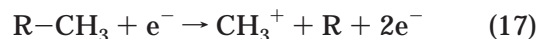
$$\text{DH}_{298}(\text{A}-\text{B}) = \text{AE}(\text{A}^+, \text{AB}) - \text{IE}(\text{A}) \quad (16)$$

Relative heats of formation of positive ions can be subsequently determined and can be anchored with accessible absolute values such as the heats of formation of atoms, measured spectroscopically.

In the first essays of radical investigation by mass spectrometry, most of the data relative to dissociation energies were obtained by direct measurements of appearance potentials or by the combination of differences between appearance energies of ions formed by similar dissociation processes, the indirect method.<sup>35</sup> However, scatter in the values reported by certain investigators in the IE measurements suggested problems with the reliability of the instrumental and methodological errors, a fact that can be conciliated in accepting an absolute accuracy of  $\pm 0.1$  eV for these data.<sup>53</sup> This error bar value is in total accordance with the estimated absolute accuracy quoted by Melton and Hamill in their primary attempts to develop the retarding potential difference (RPD) technique for the IE measurements.<sup>57</sup> The error values reported earlier were sometimes more optimistic<sup>82</sup> and finally revealed to be largely underestimated with the advent of complementary photoionization experiments.<sup>61</sup> In addition, the RPD technique and photoionization experiments have shown that the previous data on the ionization energy of alkyl free radicals were generally too high by 0.1 to 0.6 eV.<sup>83</sup> A mix-up between the supposed adiabatic value and the vertical ionization potential value involving transitions corresponding to slightly higher vibrational levels of the neutral precursor was certainly the reason for these over-estimations. Experiments conducted with an accurately controlled monoenergetic electron beam<sup>83,84</sup> have since permitted the accordance of the reassessed values with those obtained by other techniques.

Using electron ionization methods, bond strengths and heats of formation of radicals have mainly been derived from the measurements of appearance potentials of an ion generated in a well-known process and by independently measuring the ionization potential of the radical species, eq 16. However, this method suffers from the disadvantages to require an efficient process to generate solely the concerned radical species, and to correct from excess energy the experimental values to avoid errors in attributing the appearance potentials. An alternative procedure<sup>85,86</sup>

has been introduced to derive valid thermochemical data from appearance energy measurements taking into account the excess energy content of the product ions during the experiments, and using a reaction where these ions for which thermochemistry is well-known, for example,  $\text{CH}_3^+$ , allows the direct determination of the enthalpy of formation of the product radical R, eq 17:



From available thermochemical data, bond strengths of the concerned bonds can be directly derived. This approach has been made possible because a large set of enthalpy of formation  $\Delta_f H^0$  for many organic cations is now well established as those for neutral compounds.<sup>87</sup> An advantage of the method lies in the necessity to investigate only one reaction, avoiding consequent complications due to bimolecular processes and is especially valuable for radicals that are not easily amenable to conventional kinetic studies. Criteria for the success of the method are related to good knowledge of the thermochemistry of the system (i.e., in particular, high-energy resolution experimental data for the AE of the counterion), to the selection of a suitable simple dissociation reaction (e.g., a single-bond cleavage) with the lowest energy requirement if competitive reactions are allowed, and to the well-controlled kinetic energy features of the reaction to ascertain that the measurement is conducted at the thermochemical threshold.<sup>88,89</sup>

### 1. Alkyl Radicals

**Methyl  $\text{CH}_3^\bullet$ .** The simplest alkyl radical, the methyl radical, has been extensively studied by electron ionization. The first measurement of a vertical ionization potential of the methyl radical,  $10.07 \pm 0.1$  eV,<sup>90</sup> was reported on early by Hipple and Stevenson in 1943.<sup>35</sup> An averaged value of  $9.95 \pm 0.03$  eV was later measured by Lossing and co-workers<sup>82</sup> with, as stated above, a clearly unreasonable reported precision of the measurements in the 0.02–0.03 eV range for standard calibration, even if the method of extrapolated voltage differences<sup>91</sup> was used in these experiments to improve the accuracy of the IE measurements. The same authors,<sup>82</sup> using this experimental value, derived a bond dissociation energy,  $\text{DH}_{298}(\text{CH}_3-\text{H})$  of  $102.8 \pm 1.5$  kcal/mol, combining it with the appearance potential measurement of  $\text{CH}_3^+$  with methane as a molecular precursor.<sup>91</sup> However, both of these values, IE and  $\text{DH}_{298}$ , were at that time in agreement with the few available experimental data like the assumed or derived values of McDowell and Warren<sup>91</sup> for IE ( $\text{CH}_3^\bullet$ ) < 9.96 eV, and  $\text{DH}_{298}(\text{CH}_3-\text{H}) = 102.15$  kcal/mol. The first photoionization experiments<sup>61</sup> have permitted the rescaling of the experimental values determined by mass spectrometry for the IE of the methyl radical, which were dispersed among values varying from 9.85 to 11.1 eV.<sup>53</sup> Melton and Hamill<sup>57</sup> applying the RPD technique, first measured a IE( $\text{CH}_3^\bullet$ ) of 9.8 eV, a low value even within the  $\pm 0.2$  eV error range reported for this technique if we compare this IE to the experimental measurement  $\text{IE}(\text{CH}_3^\bullet) = 9.82 \pm$

0.04 eV obtained by photoionization.<sup>61</sup> This difference might be attributed to the thermal excitation of radicals in the reactor where the methyl radicals were generated from the decomposition of nitrite precursors.<sup>57</sup> Using the same RPD technique,<sup>58</sup> IE( $\text{CH}_3^*$ ) was later corrected to  $9.87 \pm 0.05$  eV, and the bond dissociation energy for the carbon–hydrogen bond was derived at  $\text{DH}_{298}(\text{CH}_3\text{–H}) = 104.2$  kcal/mol for methane. As a matter of fact, the values obtained by the RPD technique for the ionization of neutral standards were shown to agree satisfactorily with the spectroscopic and photoionization values within an average deviation of 0.02 and 0.03 eV, respectively. However, these earlier data on the ionization potential of the methyl radical obtained by electron ionization methods have been shown to be generally too high by a few tenths to more than one eV compared to the values determined spectroscopically.<sup>93</sup> These overestimations of the IE are related to the inherent difficulty of selecting the lowest vibrational level of the ion or radical during the EI experiments, keeping in mind in addition that the ionization probability of this ground-state level may be quite small. In comparison, the ionization probability in a Franck–Condon sense may become rapidly larger for the vibrational levels situated only a few tenths of eV higher, and which correspond to the vertical transitions for ionization. The ionization curve of the methyl radical, reinvestigated by electron ionization, using an energy-resolved electron beam from a double-hemispherical energy selector,<sup>83</sup> gave a IE( $\text{CH}_3^*$ ) =  $9.84 \pm 0.03$  eV in excellent agreement with values from PI and spectroscopy.<sup>93</sup> The methyl radicals, generated from the pyrolysis of di-*tert*-butyl peroxide, showed an ionization curve with two well-defined linear sections allowing the measurement of the IE with a relative uncertainty not exceeding 0.03 eV, and the attribution of an observed break 0.36 eV above the threshold to the excitation of a vibrational level of  $\text{CH}_3^+$ , most probably the symmetric C–H bond stretched mode. Aside from this break, the ionization curve appeared to be linear enough for 1.8 eV above the threshold to suggest that no low-lying electronic states were accessible within this region. In particular, the observed breaks at 10.7 and 11.4 eV during the preceding RPD experiments<sup>57</sup> could not be found and were not confirmed from appearance potential measurements for the formation of  $\text{CH}_3^+$  ion fragments with neutral methyl iodide and methane as precursors.

**Ethyl  $\text{C}_2\text{H}_5^*$ .** The first reported IE values for the ethyl radical were  $8.67 \pm 0.1$  eV<sup>35</sup> and  $8.78 \pm 0.05$  eV.<sup>94</sup> Combined with the measured AE of  $\text{C}_2\text{H}_5^+$  ethyl ion from ethane, a derived value  $\text{DH}_{298}(\text{C}_2\text{H}_5\text{–H}) = 98.5 \pm 2.3$  kcal/mol was proposed for the carbon–hydrogen bond energy in ethane.<sup>94</sup> The IE later measured by the RPD technique were considerably lower with IE( $\text{C}_2\text{H}_5^*$ ) =  $8.25 \pm 0.2$  eV<sup>57</sup> and  $8.34 \pm 0.05$  eV,<sup>58</sup> respectively, and in accordance with the upper limit proposed from PI experiments earlier by Elder and co-workers.<sup>61</sup> A calculated energy of 100.3 kcal/mol was proposed for  $\text{DH}_{298}(\text{C}_2\text{H}_5\text{–H})$ .<sup>58</sup> For similar reasons to those presented for the methyl radical, the IE value was reassessed by Lossing and

Semeluk<sup>83</sup> and an IE( $\text{C}_2\text{H}_5^*$ ) =  $8.38 \pm 0.05$  eV was proposed. Heats of formations of alkyl radicals, including the ethyl radical, have been revised upward using the monoenergetic electron impact method on several precursor molecules.<sup>95</sup> The average value for the heat of formation of the ethyl radical from appearance energy measurements with propanol, 1-methyl propanol, 1,1-dimethyl propanol, and 1-methyl, propylamine gave a revised value of  $\Delta_f H^0(\text{C}_2\text{H}_5^*) = 27.8 \pm 0.6$  kcal/mol.

***n*-Propyl, Isopropyl, Butyl, Pentyl Radicals.** Direct measurements of the IE of the propyl and butyl radicals were pioneered by Lossing and De-Sousa<sup>96</sup> to overcome the uncertainties arising from calculations by the use of the indirect method<sup>36</sup> because of the difficulties of assigning the correct structure to the ions produced in the investigated dissociative ionization processes. Unfortunately, re-investigation of these experimental values, IE(*t*- $\text{C}_4\text{H}_9^*$ ) =  $6.93 \pm 0.05$  eV<sup>83</sup> underlined the overestimation of IEs for the *s*-butyl radical, IE(*s*- $\text{C}_4\text{H}_9^*$ ) =  $7.93 \pm 0.05$  eV, and the *tert*-butyl radical, IE(*t*- $\text{C}_4\text{H}_9^*$ ) =  $7.42 \pm 0.05$  eV, even confirming a better accuracy for the indirect value obtained by Stevenson, IE(*t*- $\text{C}_4\text{H}_9^*$ ) = 6.90 eV.<sup>36</sup> Ionization energies attributed to vertical ionization transitions were measured by electron ionization for several pentyl radicals<sup>97</sup> with the corresponding ionic heats of formation, but, even if reported in thermochemical compilations,<sup>93</sup> these values were later recorrected downward by appearance method measurements.<sup>98</sup>

## 2. Unsaturated Aliphatic Radicals

**Vinyl  $\text{C}_2\text{H}_3^*$ .** Contrary to the concordance observed between experimental values and derived values compiled by the indirect method for butyl radicals, the published electron impact measurements of the C–H bond dissociation energy in ethylene showed a large discrepancy, which justified further investigation into the ionization energy and the heat of formation of the vinyl radical.<sup>99</sup> The average value reported for the assigned vertical ionization energy was IE( $\text{C}_2\text{H}_3^*$ ) =  $9.45 \pm 0.05$  eV with a derived value of  $\text{DH}_{298}(\text{C}_2\text{H}_2\text{–H}) = 41 \pm 3$  kcal/mol in the vinyl radical which set this bond energy in the same range as the C–H bond energies reported at that time for ethyl or *tert*-butyl groups in their corresponding alkane precursors.<sup>99</sup> Using an energy-resolved electron beam, IE of the vinyl radical was remeasured by Lossing<sup>100</sup> with an IE( $\text{C}_2\text{H}_3^*$ ) =  $8.95 \pm 0.05$  eV. Extrapolation of the different segments observed in the ionization curve of the vinyl radical confirmed that the first published value<sup>99</sup> corresponded to a vertical IE and returned to the lack of accuracy of the conventional ion sources to explain the missing structure of the ionization energy curve, even if the authors could not entirely rule out the possibility that this measured IE was not the true adiabatic ionization potential. The appearance energy measurement of  $\text{C}_2\text{H}_3^+$  from the ethylene precursor is made difficult by the competing lower energy dissociative process leading to the formation of ionized acetylene,  $\text{C}_2\text{H}_2^+$ , and the release of a hydrogen molecule as a neutral counterpart. However, the assumed heat of formation

of the vinyl ion,  $\Delta_f H^0(\text{C}_2\text{H}_3^+) = 266$  kcal/mol, presupposed that a lower value of IE would be required to corroborate this heat of formation, requiring an IE- $(\text{C}_2\text{H}_3^*)$  downward from about 0.4 eV.<sup>100</sup> Surprisingly, no other experiments using electron ionization methods have been conducted since then to study the vinyl radical. Derived values from appearance energy methods were revised by Holmes and Lossing, with  $\text{DH}_{298}(\text{CH}_2=\text{CH}-\text{H}) = 104 \pm 2$  kcal/mol,<sup>88</sup> considering that the heat of formation  $\Delta_f H^0(\text{C}_2\text{H}_3^*)$  proposed earlier<sup>100</sup> was too low. This  $\text{DH}_{298}$  value was later challenged by photoionization experiments.

**Ethynyl  $\text{C}_2\text{H}^*$ .**  $\text{IE}(\text{C}_2\text{H}^*) = 11.6 \pm 0.5$  eV was determined by Wyatt and Stafford<sup>101</sup> with a derived value for the heat of formation,  $\Delta_f H^0(\text{C}_2\text{H}^*) = 130$  kcal/mol. This value has been one of those which has varied more widely over the years than those of other radicals. However, the heat of formation for the ethynyl radical was reconfirmed by Franklin using the appearance energy method.<sup>85</sup>

**Propargyl  $\text{C}_3\text{H}_3^*$ .** The first reported value for the IE of propargyl was lower,  $\text{IE}(\text{C}_3\text{H}_3^*) = 8.25 \pm 0.08$  eV, than those published later contrary to other experiments conducted with a low-energy resolution that usually gave IE overestimated by a few tenths of eV.<sup>94</sup> Reinvestigation with different precursors has provided a reassessed value,  $\text{IE}(\text{C}_3\text{H}_3^*) = 8.68$  eV, and has attributed the former over-range data to an erroneous voltage scale calibration.<sup>102</sup> The heat of formation of the propargyl radical has been derived by the appearance energy method,  $\Delta_f H^0(\text{C}_3\text{H}_3^*) = 82$  kcal/mol.<sup>85</sup>

**Allyl  $\text{C}_3\text{H}_5^*$ .** The main difficulty in the study of the allyl radicals lies in the formation of secondary compounds during the decomposition process of the allyl precursor, in addition to the fact that  $\text{C}_3\text{H}_5^+$  is one of the most observed fragments in organic mass spectra. Allyl radicals were previously detected by a reaction of methyl radicals with propylene.<sup>34</sup> Lossing and co-workers<sup>82</sup> chose allyl iodide as a precursor to conduct their first investigation on the IE of  $\text{C}_3\text{H}_5^*$  since pyrolysis of allyl iodide did not provide noticeable quantities of products resulting from disproportionation reactions of allyl radicals (propylene, allene). The IE of the allyl radical generated from pyrolysis of allyl iodide has been reported at  $8.16 \pm 0.03$  eV, and  $8.15 \pm 0.07$  eV when generated from the decomposition of 1-butene used to reduce the level of expected 1,5-hexadiene resulting from secondary reactions of allyl radicals.<sup>82</sup> These values have been used to calculate the  $\text{DH}_{298}$  for the R-X bond in allyl iodide, allyl bromide and allyl chloride,  $\text{DH}_{298}(\text{R}-\text{X}) = 34.1 \pm 1.5$ ,  $47.7 \pm 2.5$ , and  $60.4 \pm 3$  kcal/mol, respectively.<sup>92</sup> A good yield of allyl radicals can be generated by pyrolysis of allyl, methyl-nitrite molecules. This precursor has been used to reinvestigate the IE of the allyl radical and gave a value of  $\text{IE}(\text{C}_3\text{H}_5^*) = 8.07 \pm 0.03$  eV.<sup>100</sup> The ionization curve, which is better resolved than for the preceding experiments, tended to prove that the onset at 8.07 eV could be attributed to the adiabatic ionization potential. A derived value for the heat of formation of the allyl radical,  $\Delta_f H^0(\text{C}_3\text{H}_5^*) = 40 \pm 2$  kcal/mol,

was proposed and was reconfirmed later by Franklin.<sup>85,86</sup>

**1-Butene-3-yl  $\text{CH}_3\text{C}^*\text{HCH}=\text{CH}_2$  and 2-Methylallyl Radicals  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}^*\text{H}_2$ .** The appearance potential of  $\text{C}_4\text{H}_7^+$  fragment ions generated from electron impact on  $\text{C}_4\text{H}_8$  and  $\text{C}_5\text{H}_{10}$  isomers have been investigated and shown to provide the same fragment ion with a common structure attributed to either the 1-methylallyl (1-butene-3-yl) or 2-methylallyl radicals.<sup>102</sup> These two radicals directly generated from pyrolysis of nitrite precursors gave IEs of 7.54 and 7.89 eV, respectively. No heat of formation was available for the 2-methyl allyl radical, but an estimate was provided for this quantity,  $\Delta_f H^0(\text{CH}_2=\text{C}(\text{CH}_3)\text{C}^*\text{H}_2) = 28.6 \pm 5$  kcal/mol, on the assumption that the C-H bond energy of the terminal methyl group was bracketed between the bond energy values of the  $\text{CH}_2=\text{CHCH}_2-\text{H}$  bond and the  $\text{CH}_3\text{CH}=\text{CHCH}_2-\text{H}$  bond.<sup>102</sup>

**Dimethylallyl, Dimethylpropargyl Radicals.** The ionization potentials and derived heats of formation of several radicals of formula  $\text{C}_5\text{H}_7^*$  and  $\text{C}_5\text{H}_9^*$  were determined by Lossing and Traeger.<sup>103</sup> The heats of formation of these radicals are mainly estimated by group substitution considerations to derive quantities from expected products. In regard to the inherent assumptions, reported IEs and  $\Delta_f H^0$  are proposed with accuracies within  $\pm 0.2$  eV and  $\pm 3$  kcal/mol, respectively.<sup>103</sup> These data are the only data actually available on these radicals.

The dimethylallyl (3-methyl-1-butene-3-yl) and dimethylpropargyl (1-butyne, 3-methyl) radicals have been formed by electron impact from the 3,3-dimethyl-1-butene and the 3,3-dimethyl-1-butyne, respectively, with  $\text{CH}_3^+$  as counterion.<sup>85</sup> Heats of formation have been derived from appearance energy measurements with reasonable values if one compares them with available  $\text{DH}_{298}$  data of similar neutral compounds (propene, propyne, propane, and substituted isobutane) and the spread in derived values is small enough to be assigned as reliable by the authors. The reported heats of formation are  $\Delta_f H(3\text{-methyl-1-butene-3-yl}) = 19 \pm 3$  kcal/mol and  $\Delta_f H(3,3\text{-dimethyl-1-butyne}) = 59 \pm 3$  kcal/mol.<sup>85</sup>

**1,4-Pentadien-3-yl Radical  $(\text{CH}_2=\text{CH}_2)_2\text{C}^*\text{H}$ .** The pentadienyl radical has been scrutinized for its likely stabilization features due to electron delocalization in the neutral, compared to its ionic counterpart, and compared to the analogous nonallylic radical of corresponding size. The first measurements of its IE were reported at  $7.76 \pm 0.1$  eV<sup>104</sup> and, as expected, the neutral allylic radical appeared to present an increased stability over its saturated analogue, ca. 0.5 eV,<sup>97</sup> which was paralleled by the increased stabilization of its cation. This statement can however be cast in doubt due to the uncertainties in the experiments varying in a similar range to the reported differences. The stability of the pentadienyl radical was reinvestigated by Clark and co-workers<sup>105</sup> combining different techniques. Monoenergetic electron ionization of 3-terbutyl 1,4-pentadiene allowed one to derive the heat of formation of the pentadienyl radical,  $\Delta_f H((\text{CH}_2=\text{CH}_2)_2\text{C}^*\text{H}) = 49.8 \pm 1$  kcal/mol and  $\text{DH}_{298}((\text{CH}_2=\text{CH}_2)_2\text{CH}-\text{H}) = 76.6 \pm 1$  kcal/mol.

**Cycloalkyl Radicals.** The cyclopropyl, cyclobutyl, cyclopentyl, and cyclohexyl radicals have rarely been investigated using electron ionization methods. Pottie and co-workers<sup>106</sup> reported measured IEs for these radicals generated by pyrolysis of the appropriate cycloalkyl nitrites: IE(cyclopropyl) =  $8.05 \pm 0.1$  eV, IE(cyclobutyl) =  $7.88 \pm 0.05$  eV, IE(cyclopentyl) =  $7.79 \pm 0.05$  eV, IE(cyclohexyl) =  $7.66 \pm 0.05$  eV. No other measurements have been conducted by electron ionization except for the IE of the cyclopentyl radical that was remeasured by Lossing and Traeger,<sup>103</sup> IE(cyclopentyl) =  $7.47 \pm 0.2$  eV but with no evidence on the adiabatic or vertical features of the experimental value. In the same study, these authors remeasured the IE of the cyclopentenyl radical correcting the previous measurement of  $7.54$  eV<sup>104</sup> to a lower value, IE(cyclopentenyl) =  $7.0 \pm 0.2$ .<sup>103</sup>

### 3. Aromatic Radicals

**Cyclopentadienyl, Cycloheptatrienyl, and Derivatives.** The cyclic radical, cyclopentadienyl, was first studied by Harrison and co-workers.<sup>107</sup> The cyclopentadienyl radical was assumed to be most likely produced by a decarbonylation reaction of the intermediate phenoxy radical generated from pyrolysis of anisole molecules giving a signal at  $m/z$  65, attributed to the cyclic  $C_5H_5^+$  ion. Measurement of IE provided a value, IE(cyclopentadienyl) =  $8.69 \pm 0.1$  eV,<sup>107</sup> later corrected to  $8.41$  eV.<sup>108</sup>

The cycloheptatrienyl radical, generated from thermal decomposition of bis(7-cycloheptatrienyl), dihydroheptafulvalene, provided an IE, IE(cycloheptatrienyl) =  $6.6 \pm 0.1$  eV.<sup>107</sup> The vertical ionization energies of substituted cyclopentadienyl radicals<sup>109</sup> (cyano-, bromo-, fluoro, chloro-, methyl-, and vinyl-cyclopentadienyl) have been measured by the electron ionization method, at  $9.44 \pm 0.1$ ,  $8.85 \pm 0.1$ ,  $8.82 \pm 0.1$ ,  $8.78 \pm 0.1$ ,  $8.54 \pm 0.1$ , and  $8.44 \pm 0.1$  eV, respectively. At the same time, the IE of the indenyl and fluorenyl radicals have been determined, showing an increase of the ionization energy values with the lower degree of substitution, IE(indenyl) =  $8.35 \pm 0.1$  eV and IE(fluorenyl) =  $7.07 \pm 0.1$  eV.<sup>109</sup>

**Phenyl  $C_6H_5^{\cdot}$ .** The vertical ionization energy of phenyl has been measured by electron ionization at IE( $C_6H_5^{\cdot}$ ) =  $9.2$  eV in reasonable agreement with the values obtained previously by derivation methods.<sup>110</sup> Holmes and Lossing reported later a heat of formation for the phenyl radical,  $\Delta_f H^{\circ}(C_6H_5^{\cdot}) = 75.8 \pm 2$  kcal/mol.<sup>88</sup>

**Benzyl and Derivatives.** No measurements of IE of the benzyl radical were available before the  $7.73 \pm 0.08$  eV value of Lossing and co-workers.<sup>82</sup> Reinvestigated later, this IE has been corrected to  $7.76 \pm 0.08$  eV.<sup>111</sup> The effects of the substituents on the stability of the benzyl radical have been studied as well, confirming their expected electron-attracting or electron-releasing powers with a decreasing of the IE values from a strongly electron-attracting group to a weakly electron-attracting group.<sup>111</sup> Among these compounds, only the benzyl radical has been reinvestigated with energy-resolved electron beams, providing a corrected value of IE( $C_7H_7^{\cdot}$ )  $\leq 7.27 \pm 0.03$  eV.<sup>100</sup>

**Naphthylmethyl and Diphenyl, Methyl Radicals.** The IE of the 1-naphthylmethyl and 2-naphthylmethyl radicals were measured by Harrison and Lossing<sup>112</sup> providing the following IE: IE(1-naphthylmethyl) =  $7.35 \pm 0.1$  eV and IE(2-naphthylmethyl) =  $7.56 \pm 0.1$  eV. During the same experiments, the authors reported the IE(diphenylmethyl) =  $7.32 \pm 0.1$  eV. No other values for the IE of these radicals appear to have been reported in the literature.

**Anilino, Pyridylmethyl.** Continuing their previous work studying the effect of substituting characteristic groups for ring H-atoms, Palmer and Lossing<sup>113</sup> extended their investigation to the measurements of the effect of the substitution of skeletal carbon atoms by nitrogen on 2-, 3-, 4-pyridylmethyl and anilino radicals. The vertical IEs found are given as follows: IE(2-pyridylmethyl) =  $8.17 \pm 0.1$  eV, IE(3-pyridylmethyl) =  $7.92 \pm 0.1$  eV, IE(4-pyridylmethyl) =  $8.4 \pm 0.1$  eV, and IE( $C_6H_6N^{\cdot}$ ) =  $8.26 \pm 0.1$  eV. The difference between the reported IE values has been qualitatively interpreted as a result of the charge delocalization on the resulting cation, and only the 3-pyridylmethyl radical needs not involve a charge delocalization on the nitrogen atom to justify its lower IE. No other measurements have been performed on these radicals.

### 4. Oxygen-Containing Radicals

**Oxygenated Alkyl Radicals.** The first experimental measurements on alkoxy radicals were performed by Williams and Hamill using the RPD method<sup>58</sup> generating the radicals by thermal degradation of the corresponding ethers or alkyl nitrites. IE of the ethoxy, *n*-propoxy, 1-methyl ethoxy, and *n*-butoxy radicals were reported as well as the derived  $DH_{298}$  of the hydrogen-oxygen bond (Table 2). Holmes and Lossing<sup>88</sup> compiled the heat of formation of numerous oxygen-containing free radicals including methoxy,  $\Delta_f H^{\circ}(CH_3O^{\cdot}) = 5.6 \pm 2$  kcal/mol, formyl,  $\Delta_f H^{\circ}(HC^{\cdot}O) = 8.1 \pm 2$  kcal/mol, hydroxymethyl, or  $\Delta_f H^{\circ}(^{\cdot}CH_2OH) = -5.7 \pm 2$  kcal/mol (Table 2). The same authors applying more systematically the appearance energy method for hydroxy-substituted radicals published a set of heat of formation, mostly unknown at that time.<sup>115</sup> A comparison of the bond strengths found for the alcohols with those of the corresponding alkanes is provided and shows that hydroxy substitution on the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -position affects the bond strength in a decreasing manner:  $DH_{298}(CH_3-H) = 104.7$  kcal/mol vs  $DH_{298}(HOCH_2-H) = 94.6$  kcal/mol;  $DH_{298}(CH_3CH_2-H) = 100$  kcal/mol vs  $DH_{298}(HOCH_2CH_2-H) = 94.8$  kcal/mol;  $DH_{298}(CH_3CH_2CH_2-H) = 99.8$  kcal/mol vs  $DH_{298}(HOCH_2CH_2CH_2-H) = 97.1$  kcal/mol, respectively.<sup>115</sup> In addition, this study provided a heat of formation for the hydroperoxy radical  $HO_2^{\cdot}$ ,  $\Delta_f H^{\circ}(HO_2^{\cdot}) = 3.5 \pm 3$  kcal/mol in good agreement with published values and recent experimental measurements by the ion-beam technique.<sup>116</sup>

**Phenoxy  $C_6H_5O^{\cdot}$ .** The phenoxy radical has been detected by mass spectrometry in the thermal decomposition of anisole<sup>107</sup> and allyl phenyl ether.<sup>110</sup> Measurement of the vertical IE of the phenoxy radical has provided a value, IE( $C_6H_5O^{\cdot}$ ) =  $8.84$  eV.<sup>110</sup>

**Table 2. Ionization Energies and Related Data Collected by Electron Ionization, Photoelectron Spectroscopy, and Photoionization Methods**

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Alkyl</b>				
methyl CH <sub>3</sub> <sup>•</sup>	9.8 ± 0.2	EI		57
	9.87 ± 0.05	EI		58
	9.84 ± 0.03	EI		83
	9.825 ± 0.010	PIMS	$\Delta_f H_0^\circ(\text{CH}_2) = 91.9 \pm 1.0$	135
	9.840* ± 0.005	PES		142
	9.8380* ± 0.0004	ZEKE		144
	9.8338 ± 0.0016	PIMS	$DH_{298}(\text{CH}_3\text{-H}) = 104.96 \pm 0.07$ $D_0(\text{CH}_3\text{-H}) = 103.4 \pm 0.07$ $\Delta_f H_{298}^\circ(\text{CH}_3^\bullet) = 35.03 \pm 0.09$ $\Delta_f H_0^\circ(\text{CH}_3^\bullet) = 35.84 \pm 0.09$ $\Delta_f H_{298}^\circ(\text{CH}_3^+) = 262.71 \pm 0.09$	145
ethyl C <sub>2</sub> H <sub>5</sub> <sup>•</sup>	8.25 ± 0.2	EI		57
	8.34 ± 0.05	EI	$DH_{298}(\text{C}_2\text{H}_5\text{-H}) = 100.3 \pm 2$	58
	8.38 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\text{C}_2\text{H}_5^\bullet) = 27.8 \pm 0.6$	95
	8.39 ± 0.02	PES	$\Delta_f H_{298}^\circ(\text{C}_2\text{H}_5^+) = 219.2 \pm 1.1$	143
	8.51* ± 0.02	PES		
		PEPICO	$\Delta_f H_{298}^\circ(\text{C}_2\text{H}_5^+) = 215.3 \pm 1$	147
	8.26 ± 0.02	PES	$\Delta_f H_0^\circ(\text{C}_2\text{H}_5^+) = 218.8 \pm 0.5$	148
	8.117 ± 0.008	PIMS	$D_0(\text{C}_2\text{H}_5\text{-H}) = 99.6 \pm 0.6$ $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_5^\bullet) = 28.9 \pm 0.4$ $DH_{298}(\text{C}_2\text{H}_5\text{-H}) = 101.1 \pm 0.4$ $D_0(\text{C}_2\text{H}_5\text{-H}) = 99.5 \pm 0.5$	149
	DER		14	
1-propyl <i>n</i> -C <sub>3</sub> H <sub>7</sub> <sup>•</sup>	8.15 ± 0.05	EI		57
	8.13 ± 0.05	EI		58
	8.10 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_3\text{H}_7^\bullet) = 22.7 \pm 0.4$	95
	8.15 ± 0.02	PES	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_3\text{H}_7^+) = 210.5 \pm 1.1$	150
	8.43* ± 0.02	PES		
	8.09 ± 0.02	PES		151
8.35* ± 0.02	PES			
isopropyl (1-methyl, ethyl) (CH <sub>3</sub> ) <sub>2</sub> C <sup>•</sup> H	7.52 ± 0.05	EI		57
	7.57 ± 0.05	EI		58
	7.55 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_3\text{H}_7^\bullet) = 19.1 \pm 0.6$	95
	7.36 ± 0.02	PES	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_3\text{H}_7^+) = 187.3 \pm 1.1$	143
	7.69* ± 0.02	PES	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_3\text{H}_7^\bullet) = 17.6 \pm 1.1^d$	
		PES	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_3\text{H}_7^+) = 189.7 \pm 1.1$	150
	PES	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_3\text{H}_7^+) = 189.8 \pm 1.6$	151	
	PES			
7.37 ± 0.02	PES			
7.67* ± 0.02	PES			
1-butyl <i>n</i> -C <sub>4</sub> H <sub>9</sub> <sup>•</sup>	8.01 ± 0.05	EI		58
	8.01 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_4\text{H}_9^\bullet) = 18.1 \pm 0.6$	95
	8.02 <sup>+0.04</sup> <sub>-0.1</sub>	PES	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_4\text{H}_9^+) = 201.9 \pm 3$	150
	8.50* ± 0.04	PES	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_4\text{H}_9^\bullet) = 17.0 \pm 1.2^c$	
2-butyl (CH <sub>3</sub> )C <sup>•</sup> HC <sub>2</sub> H <sub>5</sub>	7.41 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_4\text{H}_9^\bullet) = 18.1 \pm 0.6$	95
	7.25 ± 0.02	PES	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_4\text{H}_9^+) = 201.9 \pm 3$	150
	7.59* ± 0.03	PES	$\Delta_f H_{298}^\circ(\textit{n}\text{-C}_4\text{H}_9^\bullet) = 17.0 \pm 1.2^c$	
		PES		
isobutyl (2-methyl, 1-propyl) <sup>•</sup> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	8.01 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_4\text{H}_9^\bullet) = 15.8 \pm 0.3$	95
	7.93 <sup>+0.03</sup> <sub>-0.1</sub>	PES	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_4\text{H}_9^+) = 197.9 \pm 3$	150
	8.31* ± 0.03	PES	$\Delta_f H_{298}^\circ(\textit{i}\text{-C}_4\text{H}_9^\bullet) = 15.0 \pm 2$	
<i>tert</i> -butyl (CH <sub>3</sub> ) <sub>3</sub> C <sup>•</sup>	6.93 ± 0.05	EI		83
		EI	$\Delta_f H_{298}^\circ(\textit{t}\text{-C}_4\text{H}_9^\bullet) = 9.5 \pm 0.2$	95
		EI	$\Delta_f H_{298}^\circ(\textit{t}\text{-C}_4\text{H}_9^\bullet) = 9.2 \pm 2$	88
			$\Delta_f H_{298}^\circ(\textit{t}\text{-C}_4\text{H}_9^\bullet) = 9.7 \pm 2$	
	6.70 ± 0.03	PES	$\Delta_f H_{298}^\circ(\textit{t}\text{-C}_4\text{H}_9^+) = 162.9 \pm 1.2$	143
	6.92* ± 0.03	PES	$\Delta_f H_{298}^\circ(\textit{t}\text{-C}_4\text{H}_9^\bullet) = 8.4 \pm 1.2^c$	
	DER	$\Delta_f H_{298}^\circ(\textit{t}\text{-C}_4\text{H}_9^\bullet) = 12.3 \pm 0.4$	14	

Table 2 (Continued)

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Alkyl</b>				
1-pentyl $n\text{-C}_5\text{H}_{11}^\bullet$		EI	$\Delta_f H_{298}^\circ(n\text{-C}_5\text{H}_{11}^\bullet) = 10.1 \pm 0.3$	95
	8.13 ± 0.1	PES	$\Delta_f H_{298}^\circ(n\text{-C}_5\text{H}_{11}^+) = 198 \pm 1.15$	152
	8.50* ± 0.03	PES		
2,2-dimethyl, 1-propyl $\bullet\text{CH}_2\text{C}(\text{CH}_3)_3$	7.91 ± 0.05	EI	$\Delta_f H_{298}^\circ(\bullet\text{CH}_2\text{C}(\text{CH}_3)_3) = 5.6 \pm 3$	98
		EI	$\Delta_f H_{298}^\circ(\bullet\text{CH}_2\text{C}(\text{CH}_3)_3) = 10.1 \pm 0.3$	95
	7.88 ± 0.05	PES	$\Delta_f H_{298}^\circ(\text{neo-C}_5\text{H}_{11}^+) = 188.8 \pm 2.3$	150
	8.25* ± 0.03	PES	$\Delta_f H_{298}^\circ(\text{neo-C}_5\text{H}_{11}^\bullet) = 7.1 \pm 2$	
2-pentyl $\text{CH}_3\text{C}\bullet\text{HC}_3\text{H}_7$	7.41 ± 0.05	EI	$\Delta_f H_{298}^\circ(\text{CH}_3\text{C}\bullet\text{HC}_3\text{H}_7) = 7.4 \pm 3$	98
	7.22 ± 0.10	PES	$\Delta_f H_{298}^\circ(2\text{-C}_5\text{H}_{11}^+) = 174 \pm 1.1$	152
	7.51* ± 0.15	PES		
2-methyl, 2-butyl $(\text{CH}_3)_2\text{C}\bullet\text{C}_2\text{H}_5$	6.85 ± 0.05	EI	$\Delta_f H_{298}^\circ((\text{CH}_3)_2\text{C}\bullet\text{C}_2\text{H}_5) = 3.1 \pm 3$	98
1-hexyl $\text{C}_6\text{H}_{13}^\bullet$	8.10 ± 0.03	PES	$\Delta_f H_{298}^\circ(n\text{-C}_6\text{H}_{13}^+) = 193 \pm 1.15$	152
	8.49* ± 0.04	PES		
2-hexyl $(\text{CH}_3)\text{C}\bullet\text{HC}_4\text{H}_{10}$	7.38 ± 0.05	EI	$\Delta_f H_{298}^\circ(2\text{-C}_6\text{H}_{13}^\bullet) = 3.0 \pm 3$	98
	7.17 ± 0.07	PES	$\Delta_f H_{298}^\circ(2\text{-C}_6\text{H}_{13}^+) = 168 \pm 1.15$	152
	7.38* ± 0.07	PES		
2-methyl, 2-pentyl $(\text{CH}_3)_2\text{C}\bullet\text{C}_3\text{H}_7$	6.82 ± 0.05	EI	$\Delta_f H_{298}^\circ((\text{CH}_3)_2\text{C}\bullet\text{C}_3\text{H}_7) = -1.9 \pm 3$	98
1-heptyl $\text{C}_7\text{H}_{15}^\bullet$	8.10 ± 0.04	PES	$\Delta_f H_{298}^\circ(n\text{-C}_7\text{H}_{15}^+) = 188 \pm 1.15$	152
	8.50* ± 0.03	PES		
2-heptyl $\text{CH}_3\text{C}\bullet\text{HC}_5\text{H}_{11}$	7.17 ± 0.05	PES	$\Delta_f H_{298}^\circ(2\text{-C}_7\text{H}_{15}^+) = 163 \pm 1.15$	152
	7.41* ± 0.04	PES		
1-methyl, 1-hexyl $\text{CH}_3\text{C}\bullet(\text{CH}_3)\text{C}_4\text{H}_9$	6.79 ± 0.05	EI	$\Delta_f H_{298}^\circ(\text{CH}_3\text{C}\bullet(\text{CH}_3)\text{C}_4\text{H}_9) = -6.6 \pm 3$	98
<b>Unsaturated Alkyl</b>				
vinyl $\text{C}_2\text{H}_3^\bullet$	8.95 ± 0.05	EI		100
			$\Delta_f H_{298}^\circ(\text{C}_2\text{H}_3^\bullet) = 64 \pm 2^d$	88
	8.59 ± 0.03	PIMS		159
	8.25 <sup>+0.2</sup> <sub>-0.05</sub>	ZEKE	$D_0(\text{C}_2\text{H}_3\text{-H}) = 109.7 \pm 0.8$	161
	PIMS	$\Delta_f H_0^\circ(\text{C}_2\text{H}_3^\bullet) = 71.6 \pm 0.8$	14	
ethynyl $\text{C}_2\text{H}^\bullet$	11.6 ± 0.5	EI		101
		EI	$\Delta_f H_{298}^\circ(\text{C}_2\text{H}^\bullet) = 130 \pm 3$	101, 85
	11.61 ± 0.07 <sup>d</sup>	PEPICO		164
propargyl $\text{C}_3\text{H}_3^\bullet$	8.68 ± 0.05	EI		102
		EI	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_3^\bullet) = 82^e$	85
	8.673 ± 0.001	ZEKE	$\Delta_f H_0^\circ(\text{C}_3\text{H}_3^+) = 281.3 \pm 2$	165
allyl $\text{C}_3\text{H}_5^\bullet$	8.16 ± 0.03	EI		82
	8.15 ± 0.07	EI		82
	8.07 ± 0.03	EI	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_5^\bullet) = 40 \pm 2$	100, 85
		DER	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_5^\bullet) = 41^e$	86
		DER	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_5^\bullet) = 39.3 \pm 2$	88
	8.13 ± 0.02	PES		166
			$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_5^+) = 225.5 \pm 1.1$	
8.153 ± 0.0006	ZEKE		167	
1-butene-3-yl $\text{CH}_3\text{C}\bullet\text{HCH}=\text{CH}_2$	7.54 ± 0.1	EI		102
	7.49 ± 0.02	PES	$\Delta_f H_{298}^\circ(\text{C}_4\text{H}_7^+) = 203.1 \pm 1.4$	168
	7.67* ± 0.02	PES		
2-methylallyl $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}\bullet\text{H}_2$	7.89 ± 0.1	EI	$\Delta_f H_{298}^\circ(\text{CH}_2=\text{C}(\text{CH}_3)\text{C}\bullet\text{H}_2) = 28.6 \pm 5$	102
	7.90 ± 0.02	PES	$\Delta_f H_{298}^\circ(\text{C}_4\text{H}_7^+) = 212.2 \pm 1.6$	168
	7.95* ± 0.02	PES		
but-3-en-1-yl $\bullet\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	8.04 <sup>+0.03</sup> <sub>-0.1</sub>	PES	$\Delta_f H_{298}^\circ(\text{C}_4\text{H}_7^+) = 231.0 \pm 3$	168
	8.47* ± 0.05	PES		
3-methyl,1-butene-3-yl $(\text{CH}_3)_2\text{C}\bullet\text{CH}=\text{CH}_2$	7.13 ± 0.2	EI	$\Delta_f H_{298}^\circ(\text{C}_5\text{H}_9^\bullet) = 19.5 \pm 3^e$	103
		EI	$\Delta_f H_{298}^\circ(\text{C}_5\text{H}_9^\bullet) = 19 \pm 3$	85
1-pentene-3-yl $\text{C}_2\text{H}_5\text{C}\bullet\text{HCH}=\text{CH}_2$	7.3 ± 0.2	EI	$\Delta_f H_{298}^\circ(\text{C}_5\text{H}_9^\bullet) = 25.4 \pm 3^e$	103
2-pentene-4-yl $\text{CH}_3\text{CH}=\text{CHC}\bullet\text{HCH}_3$	7.07 ± 0.2	EI	$\Delta_f H_{298}^\circ(\text{C}_5\text{H}_9^\bullet) = 22 \pm 3^e$	103



Table 2 (Continued)

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Unsaturated Alkyl</b>				
1,4-pentadiene-3-yl CH=CHC•HCH=CH	7.25 ± 0.2 7.76 ± 0.1	EI EI EI	$\Delta_f H_{298}^\circ((CH_2=CH_2)_2C\cdot H) = 49.8 \pm 1$ $DH_{298}^\circ((CH_2=CH_2)_2CH-H) = 76.6 \pm 1$	103 104 105
1-butyne-3-methyl (CH <sub>3</sub> ) <sub>2</sub> C•C=CH	7.44 ± 0.2	EI EI	$\Delta_f H_{298}^\circ(C_5H_7^\cdot) = 63 \pm 3^e$ $\Delta_f H_{298}^\circ(C_5H_7^\cdot) = 59 \pm 3$	103 85
cyclopropyl C <sub>3</sub> H <sub>5</sub> •	8.18 ± 0.03 8.68* ± 0.02	PES PES	$\Delta_f H_{298}^\circ(C_3H_5^+) = 255.5 \pm 0.9$	151
cyclobutyl C <sub>4</sub> H <sub>7</sub> •	7.54 ± 0.02 7.66* ± 0.02	PES PES	$\Delta_f H_{298}^\circ(C_4H_7^+) = 225.1 \pm 1.1$	168
cyclopentyl C <sub>5</sub> H <sub>9</sub> •	7.47 ± 0.2 7.21 ± 0.02 7.45* ± 0.02	EI PES PES		103 169
cyclohexyl C <sub>6</sub> H <sub>11</sub> •	7.15 ± 0.04 7.40* ± 0.04	PES PES		169
cyclopentenyl C <sub>5</sub> H <sub>7</sub> •	7.0 ± 0.2	EI		103, 108
<b>Aromatic</b>				
cyclopentadienyl C <sub>5</sub> H <sub>5</sub> •	8.41	EI		108
phenyl C <sub>6</sub> H <sub>5</sub> •	9.2 <sup>c,d</sup> 8.32 ± 0.04 8.67* ± 0.02	EI EI PES PES	$\Delta_f H_{298}^\circ(C_6H_5^\cdot) = 75.8 \pm 2$	110 88 171
benzyl C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> •	≤ 7.27 ± 0.03 7.76 ± 0.1 7.43* ± 0.06 7.2 ± 0.02 7.2477 ± 0.0017 7.2484 ± 0.0004	EI EI PES PES MPI ZEKE	$\Delta_f H_{298}^\circ(C_7H_7^+) = 211 \pm 1.1$ $\Delta_f H_0^\circ(C_7H_7^+) = 217.5 \pm 1.0$ $D_0(C_7H_7^+-H) = 52.6 \pm 1.0$ $D_0(C_7H_7-H) = 88.9 \pm 1.0$	100 111 172 166 174 174
	7.2487 ± 0.0006	ZEKE		176
cycloheptatrien-1-yl C <sub>7</sub> H <sub>7</sub> •	6.6 ± 0.1 6.28 ± 0.02 6.236 ± 0.005	EI PES PIMS	$\Delta_f H_{298}^\circ(C_7H_7^+) = 210 \pm 2$	107 177 178
indenyl C <sub>9</sub> H <sub>7</sub> •	8.35 ± 0.1	EI		109
fluorenyl C <sub>13</sub> H <sub>9</sub> •	7.07 ± 0.1	EI		109
3-cyano, benzyl C <sub>6</sub> H <sub>4</sub> (CN)CH <sub>2</sub> •	8.58 ± 0.1	EI		111
4-cyano, benzyl C <sub>6</sub> H <sub>4</sub> (CN)CH <sub>2</sub> •	8.36 ± 0.1	EI		111
3-nitro, benzyl C <sub>6</sub> H <sub>4</sub> (NO <sub>2</sub> )CH <sub>2</sub> •	8.56 ± 0.1	EI		111
3-fluoro, benzyl C <sub>6</sub> H <sub>4</sub> (F)CH <sub>2</sub> •	8.18 ± 0.1	EI		111
4-fluoro, benzyl C <sub>6</sub> H <sub>4</sub> (F)CH <sub>2</sub> •	7.78 ± 0.1	EI		111
4-chloro, benzyl C <sub>6</sub> H <sub>4</sub> (Cl)CH <sub>2</sub> •	7.95 ± 0.1	EI		111
2-methyl, benzyl C <sub>8</sub> H <sub>9</sub> •	7.07 ± 0.02 8.88* ± 0.02	PES PES	$DH_{298}(2-CH_3C_6H_4CH_2-H) = 87.3 \pm 1$ $\Delta_f H_{298}^\circ(2-C_8H_9^+) = 202.8 \pm 1$	179
3-methyl, benzyl C <sub>8</sub> H <sub>9</sub> •	7.65 ± 0.1 7.12 ± 0.02 8.92* ± 0.02	EI PES PES	$DH_{298}(2-CH_3C_6H_4CH_2-H) = 87.8 \pm 1$ $\Delta_f H_{298}^\circ(3-C_8H_9^+) = 204.0 \pm 1$	111 179
4-methyl, benzyl C <sub>8</sub> H <sub>9</sub> •	7.46 ± 0.1 6.96 ± 0.02 8.85* ± 0.02	EI PES PES	$DH_{298}(2-CH_3C_6H_4CH_2-H) = 87.6 \pm 1$ $\Delta_f H_{298}^\circ(4-C_8H_9^+) = 200.3 \pm 1$	111 179
4-isopropyl, benzyl C <sub>10</sub> H <sub>13</sub> •	7.42 ± 0.1	EI		111
1-naphthylmethyl C <sub>11</sub> H <sub>9</sub> •	7.35 ± 0.1	EI		112
2-naphthylmethyl C <sub>11</sub> H <sub>9</sub> •	7.56 ± 0.05	EI		112
diphenylmethyl (C <sub>6</sub> H <sub>5</sub> )CH•(C <sub>6</sub> H <sub>5</sub> )	7.32 ± 0.1	EI		112
2-pyridylmethyl C <sub>6</sub> H <sub>6</sub> N•	8.17 ± 0.1	EI		113
3-pyridylmethyl C <sub>6</sub> H <sub>6</sub> N•	7.92 ± 0.1	EI		113

Table 2 (Continued)

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Aromatic</b>				
4-pyridylmethyl C <sub>6</sub> H <sub>6</sub> N <sup>•</sup>	8.4 ± 0.15	EI		113
anilino C <sub>6</sub> H <sub>5</sub> N <sup>•</sup> H	8.26 ± 0.1	EI		113
<b>Oxygen-Containing</b>				
methoxy CH <sub>3</sub> O <sup>•</sup>		DER	$\Delta_f H_{298}^\theta(\text{CH}_3\text{O}^\bullet) = 5.6 \pm 2$	88
	7.37 ± 0.03	PES		182
	8.13* ± 0.02	PES		
	10.726 ± 0.008	PIMS	$\Delta_f H_{298}^\theta(\text{CH}_3\text{O}^+) \leq 251.2 \pm 1.0$	184
	10.42 ± 0.02	PIMS	$\Delta_f H_{298}^\theta(\text{CH}_3\text{O}^\bullet) = 2.9$ $D_0(\text{CH}_3\text{O}-\text{H}) = 102.0$	186
hydroxymethyl <sup>•</sup> CH <sub>2</sub> OH		DER	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{OH}) = -5.7 \pm 2$	88
	7.56 ± 0.01	PES	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{OH}) = -5.8 \pm 3$	181
	8.14* ± 0.01	PES		181
	7.540 ± 0.006	PIMS	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{OH}) \leq -3.7 \pm 0.7$	184
	7.56 ± 0.02	PIMS		185
		PIMS	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{OH}) = -4.9$	186
			$D_0(\text{HOCH}_2-\text{H}) = 94.0$	186
	7.553 ± 0.006	PIMS	$D_0(\text{HOCH}_2-\text{H}) = 94.46 \pm 0.15$	184
	7.562 ± 0.004	REMPI	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{OH}) = -4.25 \pm 0.3$ $\Delta_f H_0^\theta(\text{•CH}_2\text{OH}) = -2.75 \pm 0.3$ $\Delta_f H_{298}^\theta(\text{CH}_2\text{OH}^+) = 171.2 \pm 0.4$ $\Delta_f H_0^\theta(\text{CH}_2\text{OH}^+) = 171.6 \pm 0.4$	187
	ethoxy CH <sub>3</sub> CH <sub>2</sub> O <sup>•</sup>	9.11 ± 0.1	EI	$DH_{298}(\text{C}_2\text{H}_5\text{O}-\text{H}) = 109.5 \pm 2$
10.29 ± 0.08 <sup>f</sup>		PIMS	$\Delta_f H_0^\theta(\text{CH}_3\text{CH}_2\text{O}^+) \sim 237$	190
1-hydroxy, ethyl CH <sub>3</sub> <sup>•</sup> CHOH	< 6.85	PIMS	$\Delta_f H_{298}^\theta(\text{CH}_3\text{•CHOH}) > -15.6$ $\Delta_f H_0^\theta(\text{CH}_3\text{CHOH}^+) = 145.6 \pm 0.1$	190
2-hydroxy, ethyl <sup>•</sup> CH <sub>2</sub> CH <sub>2</sub> OH	8.35 ± 0.06	PIMS	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{CH}_2\text{OH}) = -8.7 \pm 2$ $\Delta_f H_0^\theta(\text{CH}_2\text{CH}_2\text{O}^+) = 187 \pm 2$	190
<i>n</i> -propoxy C <sub>3</sub> H <sub>7</sub> O <sup>•</sup>	9.2 ± 0.1	EI	$DH_{298}(\text{C}_3\text{H}_7\text{O}-\text{H}) = 110.9 \pm 2$	58
1-methyl, ethoxy (CH <sub>3</sub> ) <sub>2</sub> C(H)O <sup>•</sup>	9.2 ± 0.1	EI	$DH_{298}((\text{CH}_3)_2\text{C}(\text{H})\text{O}-\text{H}) = 110.9 \pm 2$	58
		EI, DER	$\Delta_f H_{298}^\theta((\text{CH}_3)_2\text{C}^\bullet\text{OH}) = -25.6 \pm 3$	115
		EI	$DH_{298}(\text{R}-\text{H}) = 91.7 \pm 3$	
<i>n</i> -butoxy C <sub>4</sub> H <sub>9</sub> O <sup>•</sup>	9.22 ± 0.1	EI	$DH_{298}(\text{C}_4\text{H}_9\text{O}-\text{H}) = 114.1 \pm 2$	58
formyl HC <sup>•</sup> O	8.14 ± 0.04	DER	$\Delta_f H_{298}^\theta(\text{HC}^\bullet\text{O}) = 8.1 \pm 2$	88
	8.27 ± 0.01	PES		182
	9.31* ± 0.01	PES	$\Delta_f H_{298}^\theta(\text{HC}^\bullet\text{O}) = 6.7 \pm 1.3$	191
		PES	$DH_{298}(\text{H}-\text{C}(\text{O})\text{H}) = 84.6 \pm 1.5$	
ethynyl oxy HC=CO <sup>•</sup>		DER	$\Delta_f H_{298}^\theta(\text{HCCO}^\bullet) = 28.8 \pm 2$	88
acetyl CH <sub>3</sub> C=O		DER	$\Delta_f H_{298}^\theta(\text{CH}_3\text{C}^\bullet\text{O}) = -4.5 \pm 2$	88
methoxy, methyl CH <sub>3</sub> OC <sup>•</sup> H <sub>2</sub>	6.94 ± 0.05	EI	$\Delta_f H_{298}^\theta(\text{CH}_3\text{OCH}_2^\bullet) = -2.1 \pm 2$	114
		DER	$\Delta_f H_{298}^\theta(\text{CH}_3\text{OCH}_2^\bullet) = -1.3 \pm 2^d$	88
1-ethyl, methoxy CH <sub>3</sub> C <sup>•</sup> HOCH <sub>3</sub>	≤ 6.5 ± 0.05	DER	$\Delta_f H_{298}^\theta(\text{CH}_3\text{C}^\bullet\text{HOCH}_3) = -13.8 \pm 2$	88
1-hydroxy, ethyl CH <sub>3</sub> C <sup>•</sup> HOH		DER	$\Delta_f H_{298}^\theta(\text{CH}_3\text{C}^\bullet\text{HOH}) = -17.7 \pm 2$	88
		EI, DER	$\Delta_f H_{298}^\theta(\text{CH}_3\text{C}^\bullet\text{HOH}) = -14.5 \pm 3^d$	115
		EI	$DH_{298}(\text{R}-\text{H}) = 93.8 \pm 3$	
propenoyl H <sub>2</sub> C=CHCO <sup>•</sup>		DER	$\Delta_f H_{298}^\theta(\text{H}_2\text{C}=\text{CHCO}^\bullet) = 57.7 \pm 2$	88
		DER	$DH_{298}(\text{HCCH}_2\text{O}-\text{H}) = 99.7 \pm 2$	88
pimethoxy, methyl (CH <sub>3</sub> O) <sub>2</sub> C <sup>•</sup> H		DER	$\Delta_f H_{298}^\theta((\text{CH}_3\text{O})_2\text{C}^\bullet\text{H}) = -44.2 \pm 2$	88
		DER	$DH_{298}((\text{CH}_3\text{O})_2\text{CH}-\text{H}) = 91.1 \pm 2$	88
hydroxypropyl <sup>•</sup> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH		EI, DER	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{CH}_2\text{CH}_2\text{OH}) = -16 \pm 3^d$	115
		EI	$DH_{298}(\text{R}-\text{H}) = 97.1 \pm 3$	
2-hydroxy, propyl <sup>•</sup> CH <sub>2</sub> CHOHCH <sub>3</sub>		EI, DER	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{CHOHCH}_3) = -23 \pm 3^d$	115
		EI	$DH_{298}(\text{R}-\text{H}) = 94.3 \pm 3$	
hydroxy, tertbutyl <sup>•</sup> CH <sub>2</sub> C(OH)(CH <sub>3</sub> ) <sub>2</sub>		EI, DER	$\Delta_f H_{298}^\theta(\text{•CH}_2\text{C}(\text{OH})(\text{CH}_3)_2) = -35.2 \pm 3$	115
		EI	$DH_{298}(\text{R}-\text{H}) = 91.6 \pm 3$	

Table 2 (Continued)

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Oxygen-Containing</b>				
1-hydroxy, 2-propyl $\text{CH}_3\text{C}\cdot\text{HCH}_2\text{OH}$		EI, DER EI	$\Delta_f H_{298}^\circ(\text{CH}_3\text{C}\cdot\text{HCH}_2\text{OH}) = -18.8 \pm 3$ $DH_{298}(\text{R-H}) = 94.3 \pm 3$	115
1,2-dihydroxy, ethyl $\text{HOCH}_2\text{C}\cdot\text{HOH}$		EI, DER EI	$\Delta_f H_{298}^\circ(\text{HOCH}_2\text{C}\cdot\text{HOH}) = -52.6 \pm 3$ $DH_{298}(\text{R-H}) = 92.1 \pm 3$	115
1-ethoxy, methyl $\cdot\text{CH}_2\text{OC}_2\text{H}_5$		EI, DER EI	$\Delta_f H^\circ(\cdot\text{CH}_2\text{OC}_2\text{H}_5) = -10.6 \pm 3$ $DH_{298}(\text{R-H}) = 93.2 \pm 3$	115
1-hydroxy, 2-ethyl $\cdot\text{CH}_2\text{CH}_2\text{OH}$		EI, DER EI	$\Delta_f H_{298}^\circ(\cdot\text{CH}_2\text{CH}_2\text{OH}) = -13.5 \pm 3^d$ $DH_{298}(\text{R-H}) = 94.8 \pm 3$	115
hydroperoxo $\text{HO}\cdot_2$	11.53 $11.67 \pm 0.15$	EI EI EI, DER EI	$\Delta_f H_{298}^\circ(\text{HO}\cdot_2) = 3.5 \pm 3$ $DH_{298}(\text{R-H}) = 88.2 \pm 3$	21 36 115
$\cdot\text{CH}_2\text{C}(\text{O})\text{OH}$		EI, DER	$\Delta_f H_{298}^\circ(\cdot\text{CH}_2\text{C}(\text{O})\text{OH}) = -61.6 \pm 3$ $DH_{298}(\text{R-H}) = 93.9 \pm 3$	115
$\cdot\text{C}(\text{O})\text{OH}$		EI, DER	$\Delta_f H_{298}^\circ(\cdot\text{C}(\text{O})\text{OH}) = -46 \pm 3$ $DH_{298}(\text{R-H}) = 96.6 \pm 3$	115
$\cdot\text{C}(\text{O})\text{O CH}_3$		EI, DER	$\Delta_f H_{298}^\circ(\cdot\text{C}(\text{O})\text{O CH}_3) = -39.9 \pm 3$ $DH_{298}(\text{R-H}) = 97.2 \pm 3$	115
$\cdot\text{CH}_2\text{C}(\text{O})\text{OH}$		EI, DER	$\Delta_f H_{298}^\circ(\cdot\text{CH}_2\text{C}(\text{O})\text{OH}) = -61.6 \pm 3$ $DH_{298}(\text{R-H}) = 93.9 \pm 3$	115
$\text{HC}(\text{O})\text{O}\cdot$		EI, DER	$\Delta_f H_{298}^\circ(\text{HC}(\text{O})\text{O}\cdot) = -37.7 \pm 3^d$ $DH_{298}(\text{R-H}) = 104.7 \pm 3$	115
hydrocarboxyl $\text{HCOO}\cdot$	$8.486 \pm 0.012$	PIMS PIMS PIMS	$\Delta_f H^\circ_0(\text{HCOO}\cdot) = -52.5 \pm 0.6$ $\Delta_f H^\circ_0(\text{COOH}^+) = 143.2 \pm 0.5$ $DH_{298}(\text{H-COOH}) = 89.3 \pm 0.6$	192 194 192
	$8.2^c$	DER	$D_0(\text{H-COOH}) = 87.9 \pm 0.6$ $D_0(\text{H-COOH}) = 94.5^c$	14
$\text{CH}_3\text{C}(\text{O})\text{O}\cdot$		EI, DER	$\Delta_f H_{298}^\circ(\text{CH}_3\text{C}(\text{O})\text{O}\cdot) = -51.7 \pm 3^d$ $DH_{298}(\text{R-H}) = 103.8 \pm 3$	115
vinylxy $\cdot\text{CH}_2\text{CHO}$	10.85	EI EI	$\Delta_f H_{298}^\circ(\cdot\text{CH}_2\text{CHO}) = 0.2 \pm 2$	119 118
$\cdot\text{CH}_2\text{COCH}_3$		EI	$\Delta_f H_{298}^\circ(\cdot\text{CH}_2\text{COCH}_3) = -12 \pm 1.5^d$	118
phenoxy $\text{C}_6\text{H}_5\text{O}\cdot$	8.84 <sup>c</sup> $8.56 \pm 0.02$	EI PES	$\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{O}^+) = 209.0 \pm 2.8$	110 195
<b>Sulfur-Containing</b>				
mercapto $\text{SH}\cdot$	$10.37 \pm 0.01$	PES PIMS	$D_0(\text{H-SH}) = 89.9 \pm 0.01$	196 198
thioformyl $\text{HCS}\cdot$	$\leq 7.499 \pm 0.005$	PIMS	$\Delta_f H^\circ_0(\text{HCS}^+) = 242.6 \pm 2$ $\Delta_f H^\circ_0(\text{HCS}\cdot) = 71.7 \pm 2$	199
methylthio $\text{CH}_3\text{S}\cdot$	$9.262 \pm 0.005$	PIMS	$\Delta_f H^\circ_0(\text{CH}_3\text{S}^+) = 245.0 \pm 0.5$ $\Delta_f H^\circ_0(\text{CH}_3\text{S}\cdot) = 32.5 \pm 2$	202
	$9.225 \pm 0.014$	PIMS	$\Delta_f H^\circ_0(\text{CH}_3\text{S}\cdot) = 35.5 \pm 2$	203
	203	PIMS	$\Delta_f H^\circ_0(\text{CH}_3\text{S}\cdot) = 31.0 \pm 0.4$	204
	204	PIMS		205
mercaptomethyl $\cdot\text{CH}_2\text{SH}$	$7.536 \pm 0.003$	PIMS	$\Delta_f H^\circ_0(\cdot\text{CH}_2\text{SH}) = 37.7 \pm 2$ $D_0(\text{H-CH}_2\text{SH}) = 93.97 \pm 0.13$	202
methylthiomethyl $\text{CH}_3\text{SCH}_2\cdot$	$6.85 \pm 0.03$ $7.16^* \pm 0.03$	PES PES PIMS	$\Delta_f H^\circ_0(\text{CH}_3\text{SCH}_2) = 34 \pm 2.5$ $D_0(\text{H-CH}_2\text{SCH}_3) = 91 \pm 2.5$	206 207
methyl perthiyl $\text{CH}_3\text{SS}\cdot$		EI	$\Delta_f H_{298}^\circ(\text{CH}_3\text{SS}\cdot) = 16.4 \pm 2$ $DH_{298}(\text{RSS-terButyl}) = 52.6 \pm 2$	121
ethyl perthiyl $\text{C}_2\text{H}_5\text{SS}\cdot$		EI	$\Delta_f H_{298}^\circ(\text{C}_2\text{H}_5\text{SS}\cdot) = 10.4 \pm 2$	121
isopropyl perthiyl $\text{C}_3\text{H}_7\text{SS}\cdot$		EI	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_7\text{SS}\cdot) = 3.3 \pm 2$	121
terButyl perthiyl $\text{C}_4\text{H}_9\text{SS}\cdot$	$8.25 \pm 0.08$	EI	$\Delta_f H_{298}^\circ(\text{C}_4\text{H}_9\text{SS}\cdot) = -4.6 \pm 2$	121
$\text{HS}\cdot\text{O}$	$9.918 \pm 0.016^d$	PIMS	$\Delta_f H_{298}^\circ(\text{HSO}^+) = 228 \pm 5$	208

Table 2 (Continued)

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Nitrogen-Containing</b>				
azide N <sub>3</sub> <sup>•</sup>	11.06 ± 0.01	PES	$\Delta_f H^\circ_0(N_3^+) = 366 \pm 5$	209
imidogen NH <sup>•</sup>	13.49 ± 0.01	PES		210
	13.476 ± 0.002	REMPI		211
amino <sup>•</sup> NH <sub>2</sub>		EI, AE	$\Delta_f H^\circ_{298}(^•NH_2) = 41^c$	85
	11.46 ± 0.01	PES		210
	12.0* ± 0.01	PES		
	11.14 ± 0.01	PIMS	$\Delta_f H^\circ_0(^•NH_2) = 45.8 \pm 0.3$ $\Delta_f H^\circ_0(^•NH) = 85.2 \pm 0.4$ $\Delta_f H^\circ_0(NH^+) = 396.3 \pm 0.3$ $\Delta_f H^\circ_0(NH_2^+) = 302.7 \pm 0.1$ $D_0(H-NH_2) = 106.7 \pm 0.3$ $D_0(H-NH) = 91.0 \pm 0.5$ $D_0(H-N) = 79.0 \pm 0.4$	212
methane imine <sup>•</sup> CH <sub>2</sub> NH	9.88 ± 0.05	EI	$\Delta_f H^\circ_{298}(^•CH_2NH) = 22 \pm 3$	124
methyl amino CH <sub>3</sub> N <sup>•</sup> H		EI	$\Delta_f H^\circ_{298}(CH_3N^•H) = 43.6^c$	85
	6.88 <sup>g</sup>	PES		216
	10.16* <sup>g</sup>	PES		
dimethyl amino (CH <sub>3</sub> ) <sub>2</sub> N <sup>•</sup>		EI, AE	$\Delta_f H^\circ_{298}((CH_3)_2N^•) = 39^c$	85
methylene amidogen CH <sub>2</sub> N <sup>•</sup>	9.4 ± 0.1	PIMS		215
amino methyl <sup>•</sup> CH <sub>2</sub> NH <sub>2</sub>	6.2	EI	$\Delta_f H^\circ_{298}(^•CH_2NH_2) = 36 \pm 2$	122
		EI	$\Delta_f H^\circ_{298}(^•CH_2NH_2) = 43^c$	85
		EI	$DH_{298}(R-H) = 94 \pm 2$	123
	6.29 ± 0.03 6.97* ± 0.03	PES PES	$\Delta_f H^\circ_{298}(CH_2NH_2^+) = 180.4 \pm 2.6$	216
methylamino methyl (CH <sub>3</sub> )NHC <sup>•</sup> H <sub>2</sub>	5.9	EI	$\Delta_f H^\circ_{298}(CH_3NHC^•H_2) = 30 \pm 2$	122
		EI	$DH_{298}(R-H) = 87 \pm 2$	123
dimethylaminomethyl (CH <sub>3</sub> ) <sub>2</sub> NC <sup>•</sup> H <sub>2</sub>	5.7	EI	$\Delta_f H^\circ_{298}((CH_3)_2NC^•H_2) = 26 \pm 2$	122
		EI	$DH_{298}(R-H) = 84 \pm 2$	123
1-aminoeth-1-yl (CH <sub>3</sub> )C <sup>•</sup> HNH <sub>2</sub>	5.7	EI	$\Delta_f H^\circ_{298}((CH_3)_2NC^•H_2) = 26 \pm 2$ $DH_{298}(R-H) = 90 \pm 2$	123
2-aminoprop-2-yl (CH <sub>3</sub> ) <sub>2</sub> C <sup>•</sup> NH <sub>2</sub>	5.4	EI	$\Delta_f H^\circ_{298}((CH_3)_2NC^•H_2) = 26 \pm 2$ $DH_{298}(R-H) = 89 \pm 2$	123
cyano CN <sup>•</sup>	14.2 ± 0.3	PIMS	$\Delta_f H^\circ_0(CN^•) = 109$	213
	14.03 ± 0.02 <sup>g</sup>	PIMS	$\Delta_f H^\circ_0(CN^•) = 105.5$	214
cyanomethyl <sup>•</sup> CH <sub>2</sub> CN	10.87 ± 0.1	EI		125
	10.3 ± 0.02	EI	$\Delta_f H^\circ_{298}(^•CH_2CN) = 58 \pm 3$ $DH_{298}(R-H) = 92 \pm 3$	126
1-cyanoethyl	9.76 ± 0.1	EI		125
	9.25 ± 0.02	EI	$\Delta_f H^\circ_{298}(CH_3C^•HCN) = 50 \pm 2$ $DH_{298}(R-H) = 90 \pm 2$	126
2-cyanoethyl	9.85 ± 0.1	EI		125
2-cyano, 2-propyl	9.15 ±	EI		125
	8.48 ±	EI	$\Delta_f H^\circ_{298}(CH_3C^•HCN) = 50 \pm 2$ $DH_{298}(R-H) = 90 \pm 2$	126
α-cyanoisopropyl	8.56 ± 0.06	PES		172
isocyanato <sup>•</sup> NCO	11.76 ± 0.01	PES	$\Delta_f H^\circ_{298}(NCO^+) = 307.8 \pm 3.7$ $D_0(N-CO) = 101.5 \pm 3.7$	217
	11.759 ± 0.006	PIMS	$\Delta_f H^\circ_0(^•NCO) \leq 32.8 \pm 0.7$ $\Delta_f H^\circ_0(NCO^+) \geq 299.6 \pm 0.5$ $D_0(H-NCO) = 110.1 \pm 0.3$	218
hydrazinyl N <sub>2</sub> H <sub>3</sub> <sup>•</sup>	7.61 ± 0.01	PIMS	$\Delta_f H^\circ_0(N_2H_3^•) = 55.3 \pm 0.3$ $D_0(H-NNH_2) = 80.3 \pm 0.3$ $D_0(H-HNNH) = 43.8 \pm 1.1$	219
nitrogen trioxide NO <sub>3</sub> <sup>•</sup>	12.57 ± 0.03	PIMS	$\Delta_f H^\circ_{298}(NO_3^+) = 307.1 \pm 1.7$ $\Delta_f H^\circ_0(NO_3^+) = 308.9 \pm 1.2$	220

Table 2 (Continued)

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Silicon-Containing</b>				
silylydyne SiH•	7.91 ± 0.01	PIMS	$\Delta_f H_0^\circ(\text{SiH}^+) = 272.0 \pm 1.2$ $\Delta_f H_0^\circ(\text{SiH}^\bullet) = 89.6 \pm 1.2$ $D_0(\text{Si-H}) = 68.7 \pm 0.7$	223
silylene SiH <sub>2</sub> •	≤ 9.15 ± 0.02 (9.15 ± 0.02 or 9.02 ± 0.02)	PIMS	$\Delta_f H_0^\circ(\text{SiH}_2^+) = 276.6 \pm 0.6$ $\Delta_f H_0^\circ(\text{SiH}_2^\bullet) = 65.6 \pm 0.7$ or $68.6 \pm 0.8^b$ $D_0(\text{Si}^\bullet\text{H-H}) = 72.6 \pm 1.4$ or $75.6 \pm 1.4^b$	223
		DER	$\Delta_f H_0^\circ(\text{SiH}_2^\bullet) = 69.0 \pm 2$	229
silyl SiH <sub>3</sub> •	8.14 ± 0.01 8.74* ± 0.01 8.01 ± 0.02	PES PES PIMS	$\Delta_f H_{298}^\circ(\text{SiH}_3^+) = 234.2 \pm 1.7$ $\Delta_f H_0^\circ(\text{SiH}_3^+) = 232.4 \pm 1.4$ $\Delta_f H_0^\circ(\text{SiH}_3^\bullet) = 47.6 \pm 1.6$ $D_0(\text{Si}^\bullet\text{H}_2\text{-H}) = 69.6 \pm 2.1$ or $72.5 \pm 2.1^b$ $D_0(\text{Si}^\bullet\text{H}_3\text{-H}) = 88.8 \pm 1.6$	221 223
	8.135 <sup>+005</sup> <sub>-002</sub>	REMPI DER	$\Delta_f H_0^\circ(\text{SiH}_3^\bullet) = 48.5 \pm 1.6$	228 229
disilicon dihydride Si <sub>2</sub> H <sub>2</sub> •	8.2 + 0.01 - 0.02	PIMS	$\Delta_f H_0^\circ(\text{Si}_2\text{H}_2^\bullet) < 100.7$	230
disilicon trihydride Si <sub>2</sub> H <sub>3</sub> •	< 7.59	PIMS	$\Delta_f H_0^\circ(\text{Si}_2\text{H}_3^\bullet) \sim 96$	230
disilanyl Si <sub>2</sub> H <sub>5</sub> •	7.60 ± 0.05	PIMS	$\Delta_f H_0^\circ(\text{Si}_2\text{H}_5^\bullet) < 63.3$	230
<b>Miscellaneous</b>				
phosphino •PH <sub>2</sub>	9.83 ± 0.02	EI	$\Delta_f H_{298}^\circ(\bullet\text{PH}_2) = 33.1 \pm 2$ $DH_{298}(\text{R-H}) = 83.9 \pm 3$	84
	9.824 ± 0.002	PIMS	$D_0(\bullet\text{PH}_2\text{-H}) = 82.46 \pm 0.46$ $D_0(\bullet\text{PH-H}) = 74.2 \pm 2$ $D_0(\bullet\text{P-H}) = 70.5 \pm 2$	232
phosphinidene •PH	10.149 ± 0.008	PIMS		231
trifluoromethyl •CF <sub>3</sub>	9.3 ± 0.2 8.5 ± 0.8 9.25 ± 0.04	EI EI PIMS		128 129 62
dichloromethyl •CHCl <sub>2</sub>	8.32 ± 0.01 8.54* ± 0.01	PES PES		237
trichloromethyl •CCl <sub>3</sub>	8.7 ± 0.1 8.06 ± 0.02 8.109 ± 0.005	EI PES REMPI	$\Delta_f H_0^\circ(\text{CCl}_3^+) = 202.6 \pm 0.8$ $\Delta_f H_0^\circ(\bullet\text{CCl}_3) = 16.7 \pm 0.6$ $\Delta_f H_0^\circ(\text{CCl}_3^+) = 203.7 \pm 0.6$	128 238 240
bromomethyl •CH <sub>2</sub> Br	8.61 ± 0.01 8.72* ± 0.01 8.61 ± 0.01	PES PES PIMS		242 239
tribromomethyl •CBr <sub>3</sub>	7.5 ± 0.2	EI		128
pentafluoroethyl •C <sub>2</sub> F <sub>5</sub>	9.98 ± 0.1	EI		130
<i>n</i> -propyl-heptafluoro •C <sub>3</sub> F <sub>7</sub>	10.06 ± 0.1	EI		130
isopropyl-heptafluoro •CF(CF <sub>3</sub> ) <sub>2</sub>	10.5 ± 0.1	EI		130
oxygen monofluoride FO•	12.77 ± 0.01 13.08* ± 0.01 12.78 ± 0.03	PES PES PIMS	$\Delta_f H_0^\circ(\text{FO}^\bullet) = 26.2 \pm 1.9$	244 245
oxygen monochloride ClO•	10.87 ± 0.01 11.01* ± 0.01 10.88 <sub>5</sub> ± 0.01 <sub>6</sub> 10.85 ± 0.05	PES PES PIMS PIMS	$\Delta_f H_0^\circ(\text{ClO}^+) = 275.2 \pm 0.37$	246 248 249
oxygen monobromide BrO•	10.29 ± 0.01 10.46 ± 0.02	PES PIMS		250 251
oxygen monoiodide IO•	9.66 ± 0.10 <sup>g</sup>	PIMS		252
fluoroformyl FCO•	11.26 ± 0.01 ≤ 9.7 11.16* ± 0.03	PES PIMS PIMS	$\Delta_f H_{298}^\circ(\text{FCO}^+) = 160 \pm 12$ $\Delta_f H_{298}^\circ(\text{FCO}^+) = 178.1 \pm 2.3$ $\Delta_f H_0^\circ(\text{FCO}^\bullet) = 36.5$ $DH_{298}(\text{F-CO}) = 28.9 \pm 2.9$	253 255 255

**Table 2 (Continued)**

radicals	IE (eV) <sup>a</sup>	exptl <sup>b</sup>	derived thermochemical quantities: $\Delta_f H^\circ$ , $D_0$ , $DH_{298}$ (kcal/mol)	ref
<b>Miscellaneous</b>				
1-adamantyl	6.21 ± 0.03	PES		261
	6.36* ± 0.05	PES		
		EI	$\Delta_f H_{298}^\circ(C_{10}H_{15}^*) = 12 \pm 3$	132
2-adamantyl	6.73 ± 0.03	PES		261
	6.99* ± 0.05	PES		
		EI	$\Delta_f H_{298}^\circ(C_{10}H_{15}^*) = 16^e$	132

<sup>a</sup> Reported values are adiabatic values if not otherwise stated. Vertical IEs are quoted with an asterisk. If the accuracy of the measurements is not clearly reported in the relevant reference, the quoted uncertainties of the values are taken to be those reported for the general method used. <sup>b</sup> Abbreviations are those reported in Table 1. The data associated to the abbreviation DER correspond to derived values. <sup>c</sup> No uncertainties available. <sup>d</sup> Averaged value. <sup>e</sup> Estimated value. <sup>f</sup> Value corresponding to the deuterated homologue. <sup>g</sup> Derived values from threshold onset measurements. <sup>h</sup> Correlated to the value of 9.02 or 9.15 for the adiabatic IE of silylene.

However, only an upper limit for the derived heat of formation for the phenoxy radical  $\Delta_f H^\circ(C_6H_5O^*) = 20$  was given.<sup>110</sup>

**Enol Radicals.** Holmes and Lossing<sup>118</sup> reported the heat of formation of the vinyloxy and the acetyl radicals using NRMS for the generation of these two neutrals resulting from the dissociation of vinyl acetate, and from the dissociation of 2-propenyl acetate and acetylacetone, respectively. In both cases, the counterion was the acetyl cation. From appearance energy measurements, the values  $\Delta_f H^\circ(^*CH_2CHO) = 0.2 \pm 2$  kcal/mol and  $\Delta_f H^\circ(^*CH_2COCH_3) = -12 \pm 1.5$  kcal/mol were derived.

### 5. Sulfur-Containing Radicals

Despite the importance of sulfur chemistry, mass spectrometry data related to sulfur-containing radicals by electron ionization methods are scarce. As a consequence, most of the information on their thermochemistry are deduced from indirect methods. The mercapto, methylthio, and phenylthio radicals were investigated by Palmer and Lossing.<sup>120</sup> The IE of the mercapto radical was measured at  $10.5 \pm 0.1$  eV. The corresponding  $DH_{298}(H-S)$  was deduced from the more reliable data available on  $\Delta_f H^\circ(S_{2(g)})$  in obtaining the heat of formation  $\Delta_f H^\circ(S_{(g)})$ , which was not known with certainty at that time. The derived  $DH_{298}(H-S)$  was consequently reported to be less than 84.6 kcal/mol.<sup>120</sup> The methylthio radical was given a value of  $IE(CH_3S^*) = 8.06 \pm 0.1$  eV and a corresponding  $DH_{298}(CH_3S-H) = 89.3$  kcal/mol. For the phenylthio radical only the IE was provided,  $IE(C_6H_5S^*) = 8.63 \pm 0.1$  eV, because no reliable data for the appearance energy of the  $C_6H_5S^+$  cation from dissociation of the methylthio benzene could be obtained due to the suspected high-energy content of  $C_6H_5S^+$ .

The perthiyl radicals were later investigated by the appearance energy method to derive the heat of formation and the  $DH_{298}$  of S-C bonds in selected disulfide compounds.<sup>121</sup> The energy required to fragment mixed disulfides, RSS-terButyl, was found to be independent from the nature of the group R with an averaged value of  $AE(terButyl^+) = 9.08 \pm 0.04$  eV. The  $DH_{298}(RSS-terbutyl)$  was deduced with a value of  $DH_{298}(RSS-terButyl) = 52.6 \pm 2$  kcal/mol. If these results have shown that the nature of the group

R has little or no influence on the  $DH_{298}(RSS-R')$ , it was confirmed that the bond S-R' becomes weaker when R' changes from primary to tertiary alkyl groups in the case of MeSS-R' compounds.  $DH_{298}$  of the S-S bond in tetrasulfides derivatives was reported constant at an average value of  $DH_{298}(RSS-SSR) = 32.3$  kcal/mol in accordance with the previously recommended value of  $33.6 \pm 2$  kcal/mol, given by Benson.<sup>19</sup> IE of terButyl radical was measured at  $IE(terButyl, perthiyl) = 8.25 \pm 0.08$  eV.

### 6. Nitrogen-Containing Radicals

**Aminoalkyl Radicals.** Amino- and amine-substituted methyl radicals were investigated by Franklin<sup>85,86</sup> to determine the heat of formation of the amino, methyl amino, and dimethyl amino radicals reported at 41, 43.6, and 39 kcal/mol, respectively. Investigation on the thermochemistry of the  $\alpha$ -amino alkyl radicals was tackled and detailed by Lossing et al.<sup>122-124</sup> The appearance energy method was utilized to determine the heat of formation of the dimethyl amino  $(CH_3)_2N^*CH_2$ , methyl amino  $(CH_3)NH^*CH_2$ , and  $^*CH_2NH_2$  radicals and to derive the IEs which are the only available values for their IE to date.<sup>122</sup> These values were reported to decrease with increasing the alkylation degree on the nitrogen atom in accordance with the reducing-agent character of such compounds in solution. In the same way, the increasing of the stabilization energy with N alkylation was confirmed later with the study of this effect on the C and N centers in  $\alpha$ -amino alkyl radicals,  $R_2N^*CR'_2$ .<sup>123</sup> A series of ethylenediamines was studied for this purpose by the appearance energy method. The thermodynamic properties of these  $\alpha$ -amino alkyl radicals could be related to the free-radical chemistry of amines: the very weak C-H bond which facilitates hydrogen abstraction reactions, and the low values of IE (the lowest values observed for organic compounds) to explain their high reducing character making them powerful electron donors in photochemical reductions.

The thermochemistry of methane imine has been reinvestigated by energy-resolved electron impact to measure its appearance energy and derive its controversial heat of formation.<sup>124</sup> This heat of formation has been measured at  $\Delta_f H^\circ(^*CH_2NH) = 22 \pm 3$  kcal/mol, and the final recommended value after review-

ing the compiled data leads the authors to quote a value of  $\Delta_f H^\circ(\cdot\text{CH}_2\text{NH}) = 21 \pm 4$  kcal/mol. The measured IE was  $\text{IE}(\cdot\text{CH}_2\text{NH}) = 9.88 \pm 0.05$  eV.

**Cyanomethyl Radical  $\cdot\text{CH}_2\text{CN}$  and Derivatives.** The IEs of four cyanoalkyl radicals were reported early on by Pottie and Lossing.<sup>125</sup> These IEs have been revised using the energy-resolved electron impact appearance energy method<sup>126</sup> and completed by the relative heat of formation. The IE of the cyanomethyl radical was remeasured at 10.3 eV showing a large difference compared to the calculated value of 9.9 eV obtained from the experimental values of the heat of formation for the cyanomethyl radical  $\cdot\text{CH}_2\text{CN}$  and ion  $\text{CH}_2\text{CN}^+$ . This discrepancy has been explained by the assumed geometric distortion of the ion relative to the radical, given that the adiabatic IE is inaccessible with the appearance energy method.<sup>126</sup> Comparison of the bond strength R–H for the three substituted methyl radicals studied with the values reported for alkyls<sup>9</sup> and hydroxy-substituted radicals,<sup>115</sup> confirmed the good correlation between the observed differences and the recommended values for methyl-substitution in established molecular additivity rules. The -CN group substitution is then shown to reduce the bond strength by ca. 7 kcal/mol compared to -CH<sub>3</sub> substitution.

### 7. Miscellaneous

The phosphino radical,  $\cdot\text{PH}_2$ , was studied by McAllister and Lossing,<sup>84</sup> and the IE of the radicals generated from the thermal decomposition of benzylphosphine was measured to be  $\text{IE}(\cdot\text{PH}_2) = 9.83 \pm 0.02$  eV. The derived heat of formation and  $\text{DH}_{298}$  for the  $\text{PH}_2$ –H bond from appearance energy measurements were  $\Delta_f H^\circ(\cdot\text{PH}_2) = 33.1 \pm 2$  kcal/mol and  $\text{DH}_{298}(\text{PH}_2\text{–H}) = 83.9 \pm 3$  kcal/mol, respectively. An approximate value of 8.3 eV was proposed for the  $\text{IE}((\text{CH}_3)_2\text{P}\cdot)$ . No other values are available for the phosphino radical.

Perfluoroalkyl radicals, except the lower analogue  $\cdot\text{CF}_3$ , have hardly been investigated, despite the importance of their chemistry. The measurements of IE of the  $\cdot\text{CF}_3$  radical have shown large discrepancies in the reported values depending mainly on the experimental determination and the choice of precursors, direct electron impact on the  $\cdot\text{CF}_3$  radical, or dissociative ionization of  $\cdot\text{CF}_3$  derivatives. Consequently, IEs reported from electron ionization are quite disperse,  $\text{IE}(\cdot\text{CF}_3) = 10.1 \pm 0.05$  eV,<sup>127</sup>  $\text{IE}(\cdot\text{CF}_3) = 9.3 \pm 0.2$  eV,<sup>128</sup>  $\text{IE}(\cdot\text{CF}_3) = 8.5 \pm 0.8$  eV.<sup>129</sup> The IE value 10.1 eV has been reconsidered to be less than 9.5 eV by the authors in view of its incompatibility with their measurements of the IEs of higher members of the  $\text{C}_x\text{F}_y\cdot$  series.<sup>130</sup> Finally, these experimental determinations might be reconciled with the photoionization measurement of Lifshitz and Chupka.<sup>62</sup> Vertical IE of the pentafluoro-ethyl, *n*-heptafluoroheptyl, and ethyl,1,1,2,2,2-tetrafluoro-1-(trifluoromethyl) radicals were reported by Fisher et al.<sup>130</sup> at 9.98, 10.06, and 10.5 eV, respectively. In addition, the  $\text{CF}_2$  fragment produced from the thermal decomposition of the pentafluoro-ethyl radical gave  $\text{IE}(\text{CF}_2) = 11.7$  eV and a derived value for the heat of formation,  $\Delta_f H^\circ(\text{CF}_2) = 36$  kcal/mol.<sup>130</sup>

The IEs of the trichloromethyl and tribromomethyl radicals were reported by Kime and co-workers<sup>128</sup> at  $\text{IE}(\cdot\text{CCl}_3) = 8.7 \pm 0.1$  eV and  $\text{IE}(\cdot\text{CBr}_3) = 7.5 \pm 0.2$  eV, respectively. The former one is in good agreement with the previous measurements of Farmer et al.<sup>127</sup> at  $8.78 \pm 0.05$  eV.

Few studies have been conducted on the bridge-head radical species.<sup>131,132</sup> A  $\text{C}_7\text{H}_{11}\cdot$  radical detected from the thermal decomposition of 2-norbornylmethyl nitrite which provided IE at 8.1 eV was at first suspected to be the 2-norbornyl and finally attributed to a rearrangement product of ring rupture without further information on its structure.<sup>131</sup> In the course of this study, pyrolysis of 1-bicyclo[2,2,2]octylmethyl nitrite failed to generate the expected 1-bicyclo[2,2,2]octyl radical. However, these experiments tended to prove that the bicyclic radicals are less stable toward ring rupture than the alkyl and alkenyl radicals.<sup>104</sup> The rate of decomposition of these radicals compared to those of their nitrite precursors confirmed that the activation energy for ring rupture might be less than the 36 kcal/mol necessary for nitrite decomposition. Values of the heat of formation for the 1-adamantyl and 2-adamantyl radicals have been derived from appearance energy experiments.<sup>132</sup>

### 8. Remarks on Data Collection of IE and Derived Thermochemical Quantities by Electron Ionization Methods

Two periods could be distinguished from the results reported above with a frontier defined by the application of the RPD technique to radicals<sup>57,58</sup> and the development of an energy selected electron monochromator for IE measurements<sup>59</sup> further applied in the appearance energy method. The first values compiled for IEs, heat of formation, and  $\text{DH}_{298}$ 's before these developments are highly related to the limitations of the techniques in use and their drawbacks, mainly appearing in the low resolved energy of the incident electron beams. Consequently, most of the data published before 1965–1968 are questionable or must be considered with some reserve. However, it is worth noting that the relevant experiments of this first period are for some radicals the only available experiments that report IE or  $\Delta_f H^\circ$  values to date for numerous radicals,<sup>84,103,112,113</sup> and these works have at least the merit to give insights into their unknown thermochemistry.

Following the development of experiments with a better-defined electron beam energy and due to the advent of complementary photoionization experiments, a particular attention has been paid to the interpretation of experimental data and to the influence of the internal thermal energy of reagents and products on the accuracy of the measurements, especially in the case of the appearance energy method.<sup>115,133</sup> As stated above, the requirements for the most precise refinements in the appearance energy method lie in the investigation of a dissociative process, exemplified in eq 17, which does not imply a significant kinetic shift or reverse energy barrier. However, if satisfied, this condition does not preclude the problem inherent in the accurate esti-

mation of the temperature applicable to the product ion or the radical.

Basic difficulties remain in the identification of the meaningful onset energy in the ionization curve and the correction for the contribution of thermal energy to this onset energy. The threshold analysis strategy applied to electron ionization methods usually treats the measured ionization energy IE or the measured appearance energy AE of polyatomic species as a room-temperature value.<sup>15,115</sup> This approach has been advocated by Holmes and Lossing<sup>115,133</sup> arguing that the threshold value measured in appearance energy experiments might not represent a threshold value lower than the corrected value taking into account the integration of heat capacities for the dissociative process. These authors, clearly separating the interpretation of data for small and large molecules, question the necessity to consider that all or a major part of the internal thermal energy participates in the activation process for dissociation of polyatomic ions. This argument is supported by the concordant values obtained for the heat of formation  $\Delta_f H_{298}^0$  of a large set of radicals or neutral molecules generated by different processes without such correction and without providing any precursor-dependent character in the experimental results.<sup>95,115</sup> These authors recommend paying greater attention to the temptation to introduce unjustified correction if no clear evidence for the degree of participation of internal energy in the fragmentation of polyatomic ions appears for the determination of the experimental threshold.<sup>115</sup> A counter argument could be however opposed if one suspects that the self-consistency of the quoted examples could be related to the cancellation of internal energy effects and kinetic shifts, which are acting in opposite directions on the position of the measured onset threshold,<sup>15</sup> considering in conclusion that, generally, there is no reason for exact cancellation of these two effects. This latter argument tends to be supported by photoionization experiments. However, it is clear that electron ionization methods have potential for providing accurate IEs and AEs when associated with an energy-resolved electron impact method and are often in good agreement with the photoionization experiments within the relative error inherent in the technique (see Table 2).

## B. PES/PIMS/REMPI: Structural Information and Thermochemical Data

The difficulties associated with the accurate estimation of the temperature applicable to the product ion or the radical in a photodissociative process, eq 18:



are simplified in photoionization experiments compared to electron ionization methods mainly due to the higher resolution of the experiments and the effectiveness of the threshold assignment in relation to a steplike structure.<sup>15</sup>

Adopting the "electron convention", i.e.,  $\Delta_f H_T^0(e^-) = 0$  at all temperatures, the heat of formation of the

cation  $A^+$  in eq 18 can be expressed under the form:<sup>134</sup>

$$\Delta_f H_T^0(A^+) = AE_T - \Delta_f H_T^0(B) + \Delta_f H_T^0(AB) + \int_0^T C_p(A^+)dT + \int_0^T C_p(B)dT - \Delta H \quad (19)$$

where  $\Delta_f H_T^0$  represents the heat of formation at temperature  $T$ ,  $AE_T$  represents the experimental AE at temperature  $T$ ,  $C_p(i)$  are the heat capacities and  $\Delta H$  corresponds to the enthalpy difference between the products generated at the "quasi-temperature" of the experiment and the products generated at 0 K. Experimentally, the determination of the onset threshold is achieved by linearly extrapolating to zero current a selected post-threshold portion of the curve of the ion yield  $A^+$  plotted against the photon energy. If  $T = 0$  K, eq 19 reduces to the equation normally used to derive the ionic heat of formation from ion AEs, eq 20:

$$\Delta_f H_0^0(A^+) = AE_0 - \Delta_f H_0^0(B) + \Delta_f H_0^0(AB) \quad (20)$$

In a similar way, the IE of radical  $R$  at 0 K is expressed by:

$$IE_0 = \Delta_f H_0^0(R^+) - \Delta_f H_0^0(R) \quad (21)$$

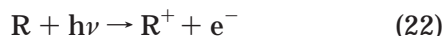
The most direct approach to the determination of the heat of formation of the ion is by measuring the dissociative ionization threshold from the neutral precursor by photoionization (if it is the lowest energy fragmentation path). But AE measurements have the disadvantage of representing an upper limit of the process difficult to correct at the 0 K threshold.

The adiabatic IE is, of course, the link between the heat of formation of both the radical  $R$  and the corresponding ion  $R^+$ . Knowledge of one quantity gives the other, and usually, heat of formation of the ion is determined through adiabatic IE measurements especially when the true heat of formation of the ionics cannot be gained by AE measurements because of disturbing factors such as rearrangements to a more stable ion geometry, appearance of kinetic energy release, and the existence of a large energy barrier. In summary, photoionization experiments mainly provided derived heat of formation of the cation  $R^+$  at 298 or 0 K as will be seen below. However, the reverse way can be followed, and these experiments can, of course, be used to derive a heat of formation for the radical  $R$  as a means to check the validity of compiled data. It is noteworthy to say that a wealth of information gained by photoionization techniques includes bond energies derived at 298 or 0 K, and has been consequently used to check the accuracy of data obtained through other experimental techniques, including halogenation kinetics, shock-tube experiments, or low-pressure pyrolysis.<sup>14</sup>

PIMS and PES are complementary techniques to study the ionization energies of radicals. It appeared difficult to separate the results obtained by one technique from another as they have been, as can be seen below, at the origin of most of the reliable thermochemical data on radicals. But, of course, PES is not a mass spectrometry technique properly speak-



ing as no mass analysis is associated with the electron energy analysis. In PES, a photon of fixed energy (dependent from the light source, generally He(I) or Ne(I)) is used to ionize the radical R and the kinetic energy of the expelled electron is measured upon photoionization, eq 22:



The electron binding energy (eBE) is related to the photon energy and the electron kinetic energy as follow, eq 23:

$$eBE = h\nu - eKE \quad (23)$$

and the PE yields information (structural, thermochemical) on the upper charged state of  $R^+$ . For derivation of thermochemical data, the determined IEs, or AEs, should represent adiabatic values for which the energy difference between the ground states of the radical R and the ion  $R^+$ ,  $IE = eBE(0-0)$ .<sup>15</sup> The PE spectrum band shapes are governed by Franck–Condon factors resulting in a PES spectrum of the radical giving thermochemical and structural information relative to the cation in a particular geometry, usually similar to that of the radical precursor. Isomerization of the cation after ionization will not alter the results since it is only the ejected electron prior to ionization that is analyzed by PES. Reliability of the data is greatly increased by combination with ab initio calculations and computations of all possible ionic states accessible by one-electron ionization.

### 1. Alkyl Radicals

**Methyl  $CH_3^\bullet$ .** The first complete photoionization study of methyl radicals over a wide energy range, 9.5–16.5 eV, was performed by Chupka and Lifshitz<sup>135</sup> providing  $IE(CH_3^\bullet) = 9.825 \pm 0.010$  eV. This IE energy value confirmed the  $IE(CH_3^\bullet) = 9.82 \pm 0.04$  eV determined previously by Elder and co-workers,<sup>61</sup> even if these values were lower than the spectroscopically measured value at  $9.842 \pm 0.002$  eV.<sup>44</sup> The discrepancy between the PI values and the more accurate spectroscopic value was attributed to a possible error in the interpretation of the shape of the ionization efficiency curve in the PI experiment.<sup>135</sup> However, the steplike form of the ionization curve in the threshold region permitted one to conclude that direct ionization was the dominating process with few autoionization features, and no noticeable geometrical change appeared during the ionization of methyl radicals. The appearance energy value for the formation of the  $CH_2^+$  ion from  $CH_3^\bullet$  has been reported at  $15.09 \pm 0.03$  eV with a resulting upper value for the heat of formation of methylene,  $\Delta_f H_0^\circ(CH_2) = 91.9 \pm 1.0$  kcal/mol.<sup>135</sup> A PES spectrum of methyl radicals recorded by Koenig and co-workers<sup>136</sup> reconfirmed the presence of a sharp peak corresponding to an IE of  $9.82 \pm 0.02$  eV, in agreement with a mostly planar geometry for the methyl radical  $CH_3^\bullet$  even if the observed vibrational structure attributed to out-of-plane bending, and symmetric stretching frequencies of the ionic product  $CH_3^+$  conducted the authors to assume a limited nonplanar

character for  $CH_3^\bullet$ . The planarity of the methyl radical is responsible for the absence of visible spectrum for this radical and is in accordance with a  $D_{3h}$  symmetry in its ground neutral state with the resulting impossibility of detecting efficiently  $CH_3^\bullet$  by a one-photon ionization process due to forbidden selection rules. And, as a consequence, the MPI characterization of the  $CH_3^\bullet$  radical through the observation of Rydberg state resonances at 450.8 nm was important for the demonstration of the applicability of the REMPI technique for the detection of nonfluorescing radicals.<sup>137,138</sup> The different state assignments of methyl radicals have been further investigated by the REMPI technique<sup>139,140,20</sup> with their applied detection of the  $CH_3^\bullet$  radical in laser-induced unimolecular reactions.<sup>141</sup> A thorough VUV PES study of methyl radicals combined with ab initio calculations conducted by Dyke et al.<sup>142</sup> also concluded in favor of the planar geometry of the methyl radical in its ground state. Investigation of the vibrational structures associated with the first IE with deuterated methyl radicals did not give any evidence supporting a nonplanar model for the  $CH_3^\bullet$  ground state. The observed associated bands were attributed to the photoionization of slightly vibrationally excited methyl radicals. The reported first IE for the methyl radical was  $IE(CH_3^\bullet) = 9.840 \pm 0.005$  eV.<sup>142</sup> Another PES experiment correlated the two preceding studies with the detection of a sharp peak at  $9.84 \pm 0.02$  eV associated with weak features at higher ionization energies attributed to hot bands.<sup>143</sup> Methyl radicals were shown to undergo no geometrical change upon ionization. The recommended thermochemical values for  $\Delta_f H_{298}^\circ(CH_3^\bullet)$  and  $\Delta_f H_{298}^\circ(CH_3^+)$  were  $34.9 \pm 0.05$  kcal/mol and  $261.8 \pm 0.05$  kcal/mol, respectively. More recently, a zero-electron kinetic energy (ZEKE) spectrum has been reported by Blush and co-workers<sup>144</sup> yielding an adiabatic IE,  $IE(CH_3^\bullet) = 9.8380 \pm 0.0004$  eV. This spectrum has been compared to the photoionization spectrum of the threshold region of methyl radicals recently reported by Litorja and Rušćić,<sup>145</sup> where methyl radicals were generated by hydrogen abstraction from methane and equilibrated at room temperature. The nominal position of the onset threshold energy for the  $CH_3^+$  ions is reported at  $9.8338 \pm 0.0016$  eV some  $70$   $cm^{-1}$  higher ( $0.0087$  eV) than the current PI value and still  $34$   $cm^{-1}$  lower ( $0.0042$  eV) than the ZEKE value. This discrepancy has finally been attributed to rotational autoionization in the threshold region. These results indicate that the spectroscopically measured value might be slightly too high and reconsideration of the IE value for  $CH_3^\bullet$  radicals leads to a reevaluated value for the  $DH_{298}$  of the C–H bond in methane,  $DH_{298}(CH_3-H) = 104.96 \pm 0.07$  kcal/mol at 298 K ( $D_0(CH_3-H) = 103.4 \pm 0.07$  kcal/mol), very slightly higher than the value recommended by Berkowitz and co-workers<sup>14</sup> at  $104.9 \pm 0.1$  kcal/mol. The corresponding reevaluated heat of formation for the methyl radical and methyl ion are  $\Delta_f H_{298}^\circ(CH_3^\bullet) = 35.03 \pm 0.09$  kcal/mol ( $35.84 \pm 0.09$  kcal/mol at 0 K) and  $\Delta_f H_{298}^\circ(CH_3^+) = 262.71 \pm 0.09$  kcal/mol,<sup>145</sup> respectively.

**Ethyl  $C_2H_5\cdot$ .** The ethyl radical has been investigated mainly by PES experiments, even if the first IE measurement conducted by photoionization was reported as early as 1962 with a value for the vertical IE = 8.4 eV,<sup>61</sup> notably lower than the values published from electron impact experiments (see Table 2). The first PES spectrum reported by Houle and Beauchamp<sup>146</sup> revealed strong evidence for the presence of a vibrational structure in the first photoelectron band of the ethyl radical. The adiabatic IE is determined to be  $8.30 \pm 0.02$  eV and the vertical IE  $8.55 \pm 0.02$  eV. The derived heat of formation of  $C_2H_5^+$  was reported to be  $217.1 \pm 1.1$  kcal/mol. Repetition of this early work showed that the feature previously assigned to be the adiabatic IE was due to the photoionization of NO, present as a byproduct in pyrolysis of the propyl nitrite molecule used as  $C_2H_5\cdot$  precursor.<sup>143</sup> So, the adiabatic and vertical IEs under a much higher resolution were reassigned at  $8.39 \pm 0.02$  and  $8.51 \pm 0.02$  eV, respectively. Interpretation of the shape of this first photoelectron band with its two distinguishable peaks, attributed to adiabatic and vertical IEs, and which are not affected by deuterium substitution, lead the authors to suspect that a bridged form of the  $C_2H_5^+$  ion could account for the measurement of the lower IE, the former vertical IE corresponding to the transition between the radical and the classical form of the  $C_2H_5^+$  ion. Finally, the photoelectron data could not be considered as evidence for deducing the geometry of both the ethyl radical and the ethyl cation. In particular, that the assignment of the observed peaks to  $C_s$  symmetry overlaps, suggesting that the adiabatic ionization energy was in fact not determined, could not be completely ruled out. However, a value of  $219.2 \pm 1.1$  kcal/mol was calculated for the heat of formation  $\Delta_f H_{298}^0(C_2H_5^+)$ .<sup>143</sup> A photoelectron-photoion coincidence (PIPECO) study of  $C_2H_5^+$ , generated from the photodissociative ionization of ethyl iodide, led to a revised value of this thermochemical quantity at  $\Delta_f H_{298}^0(C_2H_5^+) = 215.3 \pm 1$  kcal/mol.<sup>147</sup> The author then suggested that, as the calculation of this heat of formation was based on the attribution of the experimentally determined value of the IE of  $C_2H_5\cdot$ , the large discrepancy observed, 4 kcal/mol (corresponding to ca. 0.17 eV), could be due to a misleading determination of the adiabatic IE and would place the adiabatic IE of  $C_2H_5\cdot$  just at the beginning of the broad PES band at 8.21 eV. The discrepancies between these two values of  $\Delta_f H_{298}^0(C_2H_5^+)$  acted in favor of the interpretation of a geometrical change in the structure of  $C_2H_5\cdot$  and  $C_2H_5^+$  upon photoionization. The challenging problem presented by the accurate determination of the adiabatic IE of the  $C_2H_5\cdot$  radical led Dyke and co-workers<sup>148</sup> to reinvestigate the first photoionization band in the PES of the ethyl radical. Owing to the difficulties encountered to reproduce the experiments previously cited with propyl nitrite as the radical precursor,<sup>143,146</sup> these authors chose the reaction of fluorine atoms with ethane as a reliable source of ethyl radicals. The measured adiabatic and vertical IEs for  $C_2H_5\cdot$  were  $8.26 \pm 0.02$  and  $8.51 \pm 0.01$  eV, respectively. However, comparison of the adiabatic

IE measured with those expected from known heat of formation of the molecules and ions showed a difference of 0.10 eV placing the PES value outside of the expected range. This experiment, however, provided evidence for the internal energy excitation of the  $C_2H_5\cdot$  radical formed through reaction with F atoms.

In summary,  $\Delta_f H_{298}^0(C_2H_5^+)$  has been revised downward by ca. 3 kcal/mol while  $\Delta_f H_{298}^0(C_2H_5\cdot)$  was revised upward by 2.5–2.8 kcal/mol, and, consequently, the expected adiabatic IE must lie well below the experimental values in the interval 8.26–8.51 eV. These revisions led Rušćić et al.<sup>149</sup> to reinvestigate the photoionization pattern of  $C_2H_5\cdot$  radicals. Their data supported the measurement of a lower adiabatic IE,  $IE(C_2H_5\cdot) = 8.117 \pm 0.008$  eV in accordance with the predicted value, 8.06 eV, obtained concomitantly by theoretical calculations. Former data were reinterpreted with the attributions of two structures for the ethyl cation, one with a  $C_s$  geometry for the classical  $C_2H_5^+$  ion not located at minimum on the potential energy surface and the other with a nonclassical bridged structure with a  $C_{2v}$  geometry corresponding to the only minimum on the potential energy surface.<sup>149</sup> Similarity between the geometries of the radical and the classical ion form is proposed to result in a most probable transition easily detected in the former experiments and corresponding to the vertical IE. The probable transition to the nonclassical ion structure is supposed to be less intense, which explains the failure to detect this transition in the low-resolution experiments due to thermal excitation of the ethyl radical by the pyrolytic “hot” source of formation. The reassignment of the adiabatic IE at 8.117 eV presented the advantage of reconciling the previously recommended values for the heat of formation of both radical and ion.<sup>93,5</sup> The measured adiabatic value for the IE is consistent with a derived value  $D_0(C_2H_5-H) = 99.6 \pm 0.6$  kcal/mol.<sup>149</sup>

**Branched Alkyl Radicals.** The first measurements of the appearing potential of *n*-propyl and isopropyl radicals using PIMS by Elder and co-workers,<sup>61</sup>  $\leq 8.1$  eV and  $\leq 7.5$  eV, respectively, have the merit of giving the right order of magnitude of the ionization energies remeasured later, and of confirming that the EI values<sup>57,58,83</sup> for *i*- $C_3H_7\cdot$  (Table 2) are closer to the vertical IEs. PES study of the *n*-propyl radical provided values of  $IE(n-C_3H_7\cdot) = 8.15 \pm 0.02$  and  $8.43 \pm 0.02$  eV for the adiabatic and vertical IEs, respectively.<sup>150</sup> Measurements on the isopropyl radical provided values of  $IE(i-C_3H_7\cdot) = 7.36 \pm 0.02$  and  $7.69 \pm 0.02$  eV for the adiabatic and vertical IEs, respectively.<sup>143</sup> These experiments yielded heat of formation  $\Delta_f H_{298}^0(n-C_3H_7^+) = 210.5 \pm 1.1$  kcal/mol<sup>150</sup> and  $\Delta_f H_{298}^0(i-C_3H_7^+) = 187.3 \pm 1.1$  kcal/mol.<sup>143</sup> The reported heat of formation for the *n*-propyl has been calculated with the adiabatic IE value (8.15 eV) since no change in geometry has conclusively been deduced from the PES experiments. The geometry of the  $C_3H_7^+$  cation is proposed to be close to that of the *n*-propyl radical with a probable staggered position of the C–H bonds of the primary carbon.<sup>150</sup> Differences in the heat of formation of

isopropyl radicals<sup>143,150</sup> are due to the use of a slightly higher heat of formation for the isopropyl radical for their calculations revealing in a similar way how the estimation of the IEs influences the derived values for compilation of thermochemical data. So, the vertical IE value is proposed to be preferable for calculation of the heat of formation if a structure closest to the radical is expected, especially when adiabatic and vertical IEs values do not coincide in the PES.<sup>150</sup> This factor must be considered for consistent comparison of data obtained by techniques where the cations are generated in a manner favoring "stabilized" structures (some of the differences reported above for the  $\Delta_f H_{298}^0(\text{C}_2\text{H}_5^+)$  values might be illustrative of this fact). Dyke and co-workers<sup>151</sup> confirmed the data reported previously and deduced that their PES is consistent with the expected appearance of *n*- and isopropyl radicals generated by the fast hydrogen atom abstraction reaction on the propane precursor. Agreement in the measurements of IEs was good for the adiabatic and vertical values in the case of the isopropyl radical (Table 2), and fairly well supported by the use of two different sources for the *i*-C<sub>3</sub>H<sub>7</sub>• radicals. Differences of 0.06 and 0.08 eV observed for the adiabatic and vertical IEs, respectively, in the case of the *n*-propyl radical are attributed to geometry change between the radical *n*-C<sub>3</sub>H<sub>7</sub>• and the resulting cation C<sub>3</sub>H<sub>7</sub><sup>+</sup> proposed to rearrange into a more stable protonated cyclopropane structure. Conversely, it was concluded that the true adiabatic IE was not observed in the case of the *n*-propyl radical.

The pentyl, neo-pentyl, hexyl, and heptyl radicals have been investigated by PES.<sup>150,152</sup> IEs and deduced heat of formation are reported in Table 2. It appears from these studies that one of the main advantages presented by PES over other methods, namely, the radical detection under unimolecular reaction conditions avoiding the perturbing bimolecular processes often inherent in other experimental techniques as it is proven by the lack of significant secondary radical bands in the collected PES spectra. However, reported values for the 2-C<sub>6</sub>H<sub>13</sub>• and the 2-C<sub>7</sub>H<sub>15</sub>• radicals are supposed to correspond to several isomers.<sup>152</sup>

The *n*-butyl, isobutyl, and 2-butyl radicals have been studied by PES,<sup>150</sup> and their adiabatic and vertical IEs as well as the deduced heat of formation for the corresponding cations are reported in Table 2. Combining these results with those obtained for ethyl,<sup>143</sup> *n*-propyl,<sup>143</sup> and neo-pentyl, the authors gave some expected trends in the evolution of adiabatic and vertical IEs, supposed to decrease with increased substitution of the  $\beta$ -carbon for the one-alkyl series. This assumption is confirmed by the experimental results reflecting the increased inductive stabilization with  $\beta$ -methyl substitution.<sup>150</sup> The IE of the *tert*-butyl radical was reported first by Koenig and co-workers<sup>136</sup> with a vertical IE,  $\text{IE}(t\text{-C}_4\text{H}_9\cdot) = 6.95 \pm 0.05$  eV but a suspected considerable geometrical rearrangement during the ionization process. Later reinvestigated by Houle and Beauchamp,<sup>143</sup> this value was revised to  $6.92 \pm 0.03$  eV. The adiabatic IE is attributed to  $\text{IE}(t\text{-C}_4\text{H}_9\cdot) = 6.70 \pm 0.03$  eV allowing one to calculate

a derived heat of formation for the cation  $t\text{-C}_4\text{H}_9^+$ ,  $\Delta_f H_{298}^0(t\text{-C}_4\text{H}_9^+) = 162.9 \pm 1.2$  kcal/mol.<sup>143</sup> The deduced heat of formation for the radical was  $\Delta_f H_{298}^0(t\text{-C}_4\text{H}_9\cdot) = 8.4$  kcal/mol,<sup>143</sup> in significant disagreement with the recommended value of Berkowitz and co-workers,<sup>14</sup>  $\Delta_f H_{298}^0(t\text{-C}_4\text{H}_9\cdot) = 12.3 \pm 0.4$  kcal/mol. At that time, resolution of the first PES band of the  $t\text{-C}_4\text{H}_9\cdot$  radical was found to indicate a nonplanar-to-planar geometrical change during the photoionization. Unfortunately, no more PIMS or PES data are available for this radical to refine this interpretation of the first photoelectron band features. The heat of formation of the  $t\text{-C}_4\text{H}_9\cdot$  radical and the correlated DH<sub>298</sub> of the tertiary C–H bond remain a controversial topic. Gutman<sup>153</sup> reviewed the different experimental ways which have permitted the determination of this heat of formation, concluding that the noted discrepancies in the reported values were finally more related to the uncertainties in the assumed information data needed to perform the calculation than the inaccuracies of experimental determinations, in particular the activation energies of the  $t\text{-C}_4\text{H}_9\cdot + \text{RX}$  reactions. The recommended values for the heat of formation of the *tert*-butyl radical was  $\Delta_f H_{298}^0(t\text{-C}_4\text{H}_9\cdot) = 11.6 \pm 0.4$  kcal/mol with a DH<sub>298</sub>(R–H) =  $95.9 \pm 0.4$  kcal/mol.<sup>153</sup> However, the experimental determinations and the reaction mechanisms proposed for the reactions allowing these determinations have been cast in doubt,<sup>154</sup> and finally, the recommended value of Berkowitz and co-workers<sup>14</sup> remains the reference of the associated DH<sub>298</sub>(R–H) =  $96.5 \pm 0.4$  kcal/mol. A real uncertainty resides in the discrepancies between the heat of formation of the  $t\text{-C}_4\text{H}_9\cdot$  radical and the  $t\text{-C}_4\text{H}_9^+$  cation which suggest a higher value for both adiabatic and vertical IEs of the  $t\text{-C}_4\text{H}_9\cdot$  radical.<sup>155</sup> These possible underestimations of IEs are in agreement with recent theoretical calculations for the adiabatic IE of the  $t\text{-C}_4\text{H}_9\cdot$  radical providing a value  $\text{IE}(t\text{-C}_4\text{H}_9\cdot) = 6.81 \pm 0.06$  eV.<sup>156</sup>

## 2. Unsaturated Alkyl Radicals

**Vinyl C<sub>2</sub>H<sub>3</sub>•.** In a former Triennial International Mass Spectrometry Conference, Holmes reported the surprisingly large discrepancies in experimental data compiled for the vinyl radical over a period of 30 years.<sup>133</sup> McMillen and Golden, in their review of 1982,<sup>5</sup> recommended a value of  $70.4 \pm 2$  kcal/mol for the heat of formation,  $\Delta_f H_{298}^0(\text{C}_2\text{H}_3\cdot)$ . Holmes proposed an average value of  $68 \pm 2$  kcal/mol to reconcile the reported discrepancies when Berkowitz and co-workers<sup>14</sup> a few years later stated a recommended heat of formation,  $\Delta_f H_{298}^0(\text{C}_2\text{H}_3\cdot) = 71.6 \pm 0.8$  kcal/mol. This dispersion of data is related to the *difficult case*<sup>14</sup> presented by the vinyl radical reported as having an ethylene-like structure with a missing hydrogen compared to the molecular ethylene structure. The experimental problem raised by C<sub>2</sub>H<sub>3</sub>• resides in the fact that, upon ionization, it undergoes a large geometrical change from the planar ethylene-like structure for the radical to a classical or nonclassical bridged structure for the cation C<sub>2</sub>H<sub>3</sub><sup>+</sup> proposed to have a very low interconversion barrier,  $\leq 1$  kcal/mol,<sup>157</sup> if any.<sup>158</sup> The first photoionization experi-

ments to determine the IE of the vinyl radical utilized two different sources for the production of  $C_2H_3^{\bullet}$ : the first method used the reaction of F atoms with ethylene, and the second method consisted of pyrolysis of diethyl mercury. Both photoionization-yield curves were similar in shape, and the measured adiabatic IEs were  $8.59 \pm 0.03$  eV with the H abstraction reaction assumed to equilibrate the radical precursor to near room temperature and  $8.43 \pm 0.03$  eV with the pyrolysis method.<sup>159</sup> The lower value was interpreted as being related to a hot band. The proposed upper limit for the adiabatic IE of  $C_2H_3^{\bullet}$  was reported at  $8.59 \pm 0.03$  eV, combined with a lower limit for the C–H bond,  $D_0(C_2H_3-H) = 106.8 \pm 0.8$  kcal/mol.<sup>159</sup> The vinyl radical has finally been reinvestigated by PES with a pulsed nozzle pyrolysis source.<sup>160</sup> Flash pyrolysis of *tert*-butyl ester derivatives was reported as a clean, high-yield, high-number-density continuous source of the vinyl radical with a near-quantitative conversion of precursors to radical products. The measured adiabatic IE for  $C_2H_3^{\bullet}$  was  $IE(C_2H_3^{\bullet}) = 8.25 + 0.2 - 0.05$  eV with a correlated value for the bond dissociation energy at 0 K,  $D_0(C_2H_3-H) = 109.7 \pm 0.8$  kcal/mol.<sup>161</sup> This difference in experimental adiabatic IEs of 0.34 eV leads to an ambiguity of about 3 kcal/mol in the first C–H bond energy in ethylene. In correlation with their measurements, Blush and Chen<sup>161</sup> suggested that these values can barely be correlated to a heat of formation for the cation  $C_2H_3^+$  at 0 K outside the interval of 261.8–267.5 kcal/mol, and they proposed to refine the  $D_0$  value in the interval 263–266 kcal/mol.<sup>162</sup>

**Ethynyl  $C_2H^{\bullet}$ .** Unfortunately, there is no direct determination of the IE of the ethynyl radical by PIMS to complete the values obtained by EI methods. Ono and Ng<sup>163</sup> reported a photoionization study of the appearance energy process for the formation of  $C_2H^+$  ions from acetylene from which they deduced an IE value,  $IE(C_2H^{\bullet}) = 11.31 \pm 0.13$  eV, consistent with an unpublished value of Miller and Berkowitz of 11.51 eV for  $IE(C_2H^{\bullet})$ .<sup>163</sup> Reexamining the same process using the photoelectron-photoion coincidence (PEPICO) technique, Norwood and Ng<sup>164</sup> corrected this value to  $11.61 \pm 0.07$  eV.

**Propargyl  $C_3H_3^{\bullet}$ .** Despite its importance, the propargyl radical  $C_3H_3^{\bullet}$  has scarcely been studied by PIMS. From their ZEKE spectrum of the propargyl radical, Chen and co-workers<sup>165</sup> assigned recently an adiabatic IE at  $8.673 \pm 0.001$  eV for the planar acetylenic  $C_{2v}$  geometry, in agreement with their previous PES measurements at  $8.67 \pm 0.02$  eV. These data are in accordance with the IE value reported earlier by EI methods<sup>102</sup> and refine this value more precisely. These experiments permitted to derive a value  $\Delta_f H_0^{\circ}(C_3H_3^+) = 281.3 \pm 2$  kcal/mol and a resonance energy of  $-28 \pm 3$  kcal/mol, similar in magnitude to the stabilization associated with allylic or benzylic resonance in the relative cations.<sup>162</sup>

**Allyl  $C_3H_5^{\bullet}$ .** PES study of the allyl radical  $C_3H_5^{\bullet}$  showed that the adiabatic and vertical IEs coincide at  $8.13 \pm 0.02$  eV<sup>166</sup> in quite good agreement with previous EI experiments (Table 2). Nevertheless, the observed discrepancy in the lower ionization energy values<sup>82,100,85</sup> measured by electron ionization meth-

ods could be related to the characterization of hot band structures in the first photoelectron band of  $C_3H_5^{\bullet}$  in the PES spectrum reported by Houle and Beauchamp.<sup>166</sup> The derived heat of formation for the allyl cation was proposed at  $\Delta_f H_{298}^{\circ}(C_3H_5^+) = 225.5 \pm 1.1$  kcal/mol. Recently, the adiabatic IE of the allyl radical has been reinvestigated by the ZEKE technique, yielding a refined value at  $8.153 \pm 0.0006$  eV,<sup>167</sup> which can be considered as the true adiabatic IE since the production of radicals as a cold jet allows an accurate determination of this value.

**1-Buten-3-yl, 2-Methylallyl, and But-3-en-1-yl.** PES study of 1-buten-3-yl, 2-methylallyl, and but-3-en-1-yl radicals has been performed with radicals generated from pyrolysis of the nitrite precursors.<sup>168</sup> The 1-methylallyl radical  $CH_3C^{\bullet}HCH=CH_2$  (1-buten-3-yl) showed vibrational structures in the PES spectrum that were attributed to the fact that a pure isomer cannot be generated under experimental pyrolytic conditions, and only a mixture of *cis*- and *trans*-conformation for the radical can be expected. Attempts to differentiate the two conformers by using different precursors failed to resolve the PES spectrum. The experiments finally provided adiabatic and vertical IEs reported at  $7.49 \pm 0.02$  and  $7.67 \pm 0.02$  eV, respectively. Similarly, the resulting cation is expected to be formed in a mixture of *cis*- and *trans*-isomers, justifying the difference of shape observed in the PES spectra of the 1-buten-3-yl and 2-methylallyl radicals. The measured adiabatic and vertical IEs for the 2-methylallyl radical  $CH_2=C(CH_3)C^{\bullet}H_2$  were  $7.90 \pm 0.02$  and  $7.95 \pm 0.02$  eV, respectively. The lower values for the adiabatic IEs of these substituted allyl radicals, 7.49 and 7.90 vs 8.13 eV for the allyl radical, were attributed to a stabilization in the corresponding cation  $C_4H_7^+$  resulting from methyl substitution, this substitution appearing to be more effective at the terminal carbon compared to the central carbon in the allyl cation<sup>168</sup> since the adiabatic IE of the 1-butene-3-yl radical is assigned a lower value. The derived heat of formation of the resulting  $C_4H_7^+$  cations are calculated to be  $203.1 \pm 1.4$  and  $212.2 \pm 1.6$  kcal/mol for the 1-methylallyl and 2-methylallyl cations, respectively. Comparatively, the PES spectrum of the but-3-en-1-yl radical  $\bullet CH_2-CH_2CH=CH_2$  (allylcarbonyl) is not so well resolved and permitted attribution of the adiabatic IE at 8.04 eV and vertical IE at 8.47 eV with a larger uncertainty. The derived heat of formation of the corresponding cation  $C_4H_7^+$  is estimated at  $231.0 \pm 3$  kcal/mol. The broad and featureless first photoelectron band is proposed to correspond to the absence of any local minima on the potential energy surface of the corresponding  $C_4H_7^+$  cation.

**Cycloalkyl Radicals.** Dyke et al. additionally reported in their paper on propyl radicals<sup>151</sup> the first PES investigation of the cyclopropyl radical with adiabatic and vertical IEs measured at  $8.18 \pm 0.03$  and  $8.68 \pm 0.02$  eV. These values are consistent with the IE measured at 8.05 eV by electron impact.<sup>106</sup> The observed photoelectron band however showed an overall asymmetric shape with vibrational peaks between the two adiabatic and vertical components, differentiating in fact the cyclopropyl radical from the

isomeric allyl radical where the adiabatic and vertical IEs coincide at 8.13 eV (cf. supra), indicating no change in the geometry from the radical to the cation  $C_3H_5^+$  in this latter case. The observed vibrational separations in the photoelectron band are much higher compared to the allyl radical to which they are not attributed.<sup>166</sup> In the case of the cyclopropyl radical, ab initio calculations confirmed that these vibrational separations could be assigned to the excitation of the pyramidal bending mode at the  $\alpha$ -CH position in the resulting cation  $C_3H_5^+$  with a good concordance between the theoretical and experimental values.<sup>151</sup> The difference between the two measured IE, adiabatic and vertical ( $0.50 \pm 0.05$  eV), has been considered as representative of the energy difference between equilibrated geometries (equilibrium geometry and parent ion geometry) of the  $C_3H_5^+$  ion. Provided that the true adiabatic IE has been measured, the heat of formation for the corresponding  $C_3H_5^+$  cation is derived at  $\Delta_f H_{298}^{\circ}(C_3H_5^+) = 255.5 \pm 0.9$  kcal/mol. This value (larger than the reported value for the allyl cation,  $225.5 \pm 1.1$  kcal/mol<sup>166</sup>) and the observed geometrical equilibrium between the two proposed forms of the cyclopropyl cation have led the authors to anticipate an energy separation between the allyl and the cyclopropyl cation on their respective potential energy surfaces of  $29.9 \pm 1.8$  kcal/mol for the two corresponding minima.<sup>151</sup> Ionization from the neutral cyclic radical to an open-ring geometry corresponding to an allyl cationic structure has been ruled out in view of the largely lower expected value for the vertical IE in this latter case. The process is conclusively attributed to the ionization of a purely cyclic cationic structure with an adiabatic IE corresponding to ionization of a cyclic  $C_3H_5^+$  cation at its minimum energy geometry.<sup>151</sup>

The PES spectrum of the cyclobutyl radical<sup>168</sup> generated from pyrolysis of the nitrite precursor gave two peaks at  $7.54 \pm 0.02$  and  $7.66 \pm 0.02$  eV in the first photoelectron band attributed to the adiabatic and vertical IEs, respectively. The measured IEs are lower than the value of  $7.88 \pm 0.05$  eV reported by Pottie and co-workers and measured by electron ionization.<sup>106</sup> However, in these experiments, the authors were not completely sure of the structure of the investigated cyclobutyl radical which can be easily transformed through a ring opening reaction under pyrolytic conditions into a presumably allyl-carbinyl  $\cdot CH_2CH_2CH=CH_2$  with a high internal energy content allowing isomerization into 1-methylallyl or thermal decomposition into 1,3-butadiene.<sup>168</sup> Heat of formation of the cyclobutyl cation is calculated to be  $225.1 \pm 1.1$  kcal/mol. The resolved vibrational progression in the photoelectron band ( $990 \pm 100$   $cm^{-1}$ ) has not been assigned, but as the ring of the  $C_4H_7^{\cdot}$  radical is considered to be planar, or nearly so, and as most of the theoretical calculations are reported to assign a special stability to cross-ring interactions in cyclobutyl cations, a ring-puckering mode is assumed to be excited here even if the corresponding vibrational features might not be expected to be resolved in the PES spectrum.<sup>168</sup> In view of the experimental results, the reported  $\Delta_f H_{298}^{\circ}(C_4H_7^+)$  is assigned to a slightly puckered

cyclobutyl cation. The measured adiabatic IE is however slightly higher than expected if one compares it with the IE of other secondary radicals, for example, *i*- $C_3H_7^{\cdot}$  or 2- $C_4H_9^{\cdot}$ , suggesting that additional energy is required to form a cation center in cyclobutane in accordance with a lower stability of the cyclobutyl cation in comparison to other typical  $C_4$  secondary cations ( $\sim 8$ – $5$  kcal/mol). This instability of the  $C_4H_7^+$  cation is proposed to result from the rigid four-membered ring structure, even if a misleading attribution of the adiabatic IE value to a transition other than the expected 0–0 transition remains possible, indicating that the reported heat of formation of 225.1 kcal/mol must be more likely considered as an upper limit.<sup>168</sup>

In their attempt to evaluate the advantages presented by PES as a detection method for the study of chemical decomposition processes, Houle and Beauchamp<sup>169</sup> reported the adiabatic and vertical IEs for the cyclopentyl and cyclohexyl radicals, IE(cyclopentyl) =  $7.21 \pm 0.02$  and  $7.45 \pm 0.02$  eV and IE(cyclohexyl) =  $7.15 \pm 0.04$  and  $7.40 \pm 0.04$  eV, respectively. No similar data are available for the cyclopropenyl radical  $C_3H_3$ . Clauberg and Chen<sup>170</sup> only derived a C–H bond dissociation energy at  $61 \pm 6$  kcal/mol from their PES study of the cyclopropenylidene *c*- $C_3H_2$ .

### 3. Aromatic Radicals

**Phenyl  $C_6H_5^{\cdot}$ .** A study of the phenyl radical by PES was reported by Butcher and co-workers.<sup>171</sup> The measured adiabatic and vertical IEs provided values at  $8.32 \pm 0.04$  and  $8.67 \pm 0.02$  eV, respectively, in accordance with the few available experimental or derived values. Phenyl radicals were generated by a hydrogen abstraction reaction from benzene by fluorine atoms, with monofluorobenzene as a byproduct observed to overlap some of the expected higher photoelectron bands of the phenyl radical. Assignment of the vibrational separations resolved in the first photoelectron band is attributed to excitation of a C–H stretching mode of  $a_1$  symmetry in the ion assumed to be in a planar  $C_{2v}$  equilibrium geometry.<sup>171</sup> On the basis of ab initio calculations, the experimental spectrum could be interpreted as correlated to the ionization process of the ground-state configuration  $X^2A_1$  of the phenyl radical for which only the formation of the phenyl cation in its  $^3B_1$  state is observed. The first adiabatic IE corresponding to the formation of the phenyl cation in its  $X^1A_1$  state deduced to be at  $8.0 \pm 0.1$  eV is not observed.<sup>171</sup>

**Benzyl, Cycloheptatrienyl  $C_7H_7^{\cdot}$ .** Koenig et al.<sup>172</sup> assigned the vertical IE of the benzyl radical at  $7.43 \pm 0.06$  eV. Hoffbauer and Hudgens<sup>173</sup> reported the first REMPI spectrum of benzyl radicals generated by hydrogen abstraction reactions of fluorine and chlorine on toluene. Two-color resonant two-photon ionization technique has been applied by Eiden and Weisshaar<sup>174</sup> to investigate benzyl radicals generated by photolysis of toluene. Their recommended estimate for the adiabatic IE of the benzyl radical established this IE at  $7.2477 \pm 0.0017$  eV, a value corrected to  $7.2484 \pm 0.0004$  eV with a measurement performed by the ZEKE technique.<sup>174</sup> These values are larger

than the PES value reported by Houle and Beauchamp<sup>166</sup> at 7.2 eV. These new results are in better agreement with the upper limit estimated from EI experiments<sup>100</sup> and present the advantage of eliminating any hot band contribution to the determination of the IE since this measurement was performed on an internally cold beam of radicals. A two-color mass resolved excitation spectroscopy study of the benzyl radical was published just after the preceding work and confirmed the adiabatic IE value at 7.236 eV.<sup>175</sup> Eiden and co-workers<sup>176</sup> reported another correction to their measured value of the adiabatic IE of the C<sub>7</sub>H<sub>7</sub><sup>•</sup> radical as well as the attribution of vibrational frequencies measured by ZEKE-PES at cm<sup>-1</sup> resolution.

The cycloheptatrienyl radical has been investigated by both PES and PIMS with reported adiabatic IEs at  $6.28 \pm 0.02$ <sup>177</sup> and  $6.236 \pm 0.005$ ,<sup>178</sup> respectively.

**Methylbenzyl C<sub>8</sub>H<sub>9</sub><sup>•</sup>.** The first photoelectron bands of the 2-, 3-, and 4-methylbenzyl radicals have been investigated by PES.<sup>179</sup> Vertical and adiabatic IE appeared to coincide with each isomer radical with values of  $IE(2\text{-C}_8\text{H}_9^{\bullet}) = 7.07 \pm 0.02$  eV,  $IE(3\text{-C}_8\text{H}_9^{\bullet}) = 7.12 \pm 0.02$  eV and  $IE(4\text{-C}_8\text{H}_9^{\bullet}) = 6.96 \pm 0.02$  eV. If band shapes and vibrational envelopes of the PES spectra of each radicals are similar to each others and to that of the benzyl radical, the difference measured in the IE allows a direct differentiation of isomers by PES. From this study, the homolytic benzyl C–H  $DH_{298}$  has been derived from that of toluene as well as the  $DH_{298}$  values for the R–H benzyl bond and the heat of formation of the corresponding cations (Table 2). Derived heat of formation for the different radicals are similar with a derived value of  $\Delta_f H_{298}^{\circ}(\text{C}_8\text{H}_9^{\bullet}) = 39.8 \pm 1$  kcal/mol.<sup>179</sup>

#### 4. Oxygen-Containing Radicals

**Methoxy CH<sub>3</sub>O<sup>•</sup>, Hydroxymethyl <sup>•</sup>CH<sub>2</sub>OH.** The methoxy CH<sub>3</sub>O<sup>•</sup> radical and its isomer, hydroxymethyl <sup>•</sup>CH<sub>2</sub>OH, play important roles as intermediates in combustion and atmospheric processes justifying the interest that these species have motivated among spectroscopists since many of their fundamental parameters remained undetermined until recently.<sup>180</sup> Dyke and co-workers<sup>181</sup> reported IEs values for the adiabatic and vertical IEs of the hydroxymethyl radical from their PES study of the gas-phase reactions of chloride and fluorine atoms with methanol, with  $IE(^{\bullet}\text{CH}_2\text{OH}) = 7.56 \pm 0.01$  eV for the adiabatic transition. In view of the difficulties encountered in the measurements of AE of the CH<sub>2</sub>OH<sup>+</sup> cation from CH<sub>2</sub>OH by EI methods, this value corrected the former estimated values for the IE of <sup>•</sup>CH<sub>2</sub>OH with more reliability. This value was completed by those obtained for the methoxy radical CH<sub>3</sub>O<sup>•</sup> as well as for the deuterated hydroxymethyl counterparts.<sup>182</sup> Long et al.<sup>183</sup> extended the range of techniques available to probe methoxy radicals with the first detection of CH<sub>3</sub>O<sup>•</sup> by the REMPI technique. The advantage of this experiment appeared in the absence of fragmentation during the REMPI process, enhancing in fact the sensitivity as the signal associated with CH<sub>3</sub>O<sup>+</sup> cation was concentrated into one single mass. However, this preliminary analysis,

limited to a narrow range of irradiating wavelengths, temporarily failed to assign the resonant state of the CH<sub>3</sub>O<sup>•</sup> radical involved in the ionization process. Missing reliable values for the IEs of different electronic states of the methoxy radical were also responsible for the difficulties in assigning the involved state. In addition, it must be stated that most of the ion processes at first attributed to the production of a CH<sub>3</sub>O<sup>+</sup> fragment were finally reattributed to the production of a more stable CH<sub>2</sub>OH<sup>+</sup> product making the determination of the corresponding IE difficult. The predicted adiabatic IE at  $10.5 \pm 0.25$  eV<sup>184</sup> for the CH<sub>3</sub>O<sup>•</sup> radical (extracted from the difference between the heat of formation of the neutral species and of its cation) could not be confirmed during these first REMPI experiments.<sup>183</sup> In addition, this value was challenged by the direct measurement of the adiabatic IE of the methoxy radical reported by Dyke at 8.13 eV<sup>182</sup> one year later using PES experiments.

To resolve this discrepancy, Rušćić and Berkowitz<sup>184</sup> performed PIMS experiments studying the reaction F + CH<sub>3</sub>OH with isotopic substitution of the methanol precursor to distinguish between CH<sub>3</sub>O<sup>•</sup> and <sup>•</sup>CH<sub>2</sub>OH products. They reported adiabatic IE at  $10.726 \pm 0.008$  and  $7.540 \pm 0.006$  eV for these two radicals, respectively. From the IE of the hydroxymethyl radical, they deduced an upper limit for the heat of formation for the radical,  $\Delta_f H_{298}^{\circ}(^{\bullet}\text{CH}_2\text{OH}) = -3.7 \pm 0.7$  kcal/mol.<sup>184</sup> The situation is far more controversial regarding the case of the methoxy radical since the two direct IE measurements are in large disagreement (relaxation of methoxy radicals into the more stable hydroxymethyl radicals resulting in a blurred <sup>•</sup>CH<sub>2</sub>OH PES spectrum instead of a pure CH<sub>3</sub>O<sup>•</sup> PES spectrum was proposed as an explanation for the quoted discrepancy in measured adiabatic IEs<sup>184</sup>). The experimental value at 10.726 eV for the methoxy radical was satisfying for the correlation with former estimations. Rušćić and Berkowitz,<sup>184</sup> assuming a more reliable accuracy in their proposed enthalpy of formation for the methoxy radical, estimated an upper limit for the heat of formation of CH<sub>3</sub>O<sup>+</sup> at  $251.2 \pm 1.0$  kcal/mol in correlation with previously reported values.<sup>93,183</sup>

Klemm and co-workers<sup>185</sup> reported the photoionization spectrum of <sup>•</sup>CH<sub>2</sub>OH using tunable VUV synchrotron radiation combined with an expansion nozzle for the extensive rotational cooling of the precursors; this experiments precluded any thermal effects in the threshold measurement. They measured  $IE(^{\bullet}\text{CH}_2\text{OH}) = 7.56 \pm 0.02$  eV (the uncertainty range must not underestimate the precision of the measurement revealed by the steplike details and the signal-to-background ratio due to the high synchrotron light intensity observed in the PI spectrum). The precedent study was extended to hydroxymethyl, methoxy radicals, and deuterated homologues.<sup>186</sup> Direct photoionization of the CH<sub>3</sub>O<sup>•</sup> radical provided an adiabatic IE reported at  $10.42 \pm 0.02$  eV (10.74 eV for the deuterated homologue) confirming the PIMS value reported at 10.726 eV.<sup>184</sup> An analysis of the photoion efficiency spectrum for the <sup>•</sup>CD<sub>2</sub>OH reveals dissimilarities in the spectra observed during

these experiments compared to those of Rušćić and Berkowitz.<sup>184</sup> IEs reported for hydroxymethyl radicals are, however, generally consistent with previous values, except for the trend of decreasing the IE with increasing the extent of deuteration in the homologue series, compared to PES results.<sup>182</sup> Derived heat of formation and  $DH_{298}$  are reported for  $\cdot\text{CH}_2\text{OH}$ , with  $\Delta_f H_{298}^0(\cdot\text{CH}_2\text{OH}) = -4.9$  kcal/mol,  $D_0(\text{HOCH}_2-\text{H}) = 94.0$  kcal/mol, and for  $\text{CH}_3\text{O}\cdot$ , with  $\Delta_f H_{298}^0(\text{CH}_3\text{O}\cdot) = 2.9$  kcal/mol,  $D_0(\text{CH}_3\text{O}-\text{H}) = 102.0$  kcal/mol.<sup>186</sup> In an extensive study of the structural and thermochemical properties of hydroxymethyl radicals performed by REMPI spectroscopy, Johnson and Hudgens<sup>187</sup> reported corrected values for the heat of formation for the hydroxymethyl radical and the corresponding cation. From experimental results and REMPI spectra analysis of  $\cdot\text{CH}_2\text{OH}$  and deuterated homologues, resulting thermochemical values are shown to differ from previous ones but help to resolve the discrepancies quoted from compiled data, especially for the entropy estimate with a reported value of  $S_{298}^0 = 58.36 \pm 0.004$  cal/(mol K). Reevaluation of the adiabatic IE of  $\cdot\text{CH}_2\text{OH}$  provided a value of  $\text{IE}(\cdot\text{CH}_2\text{OH}) = 7.562 \pm 0.004$  eV. From the literature data, it appears that the variation in the adiabatic IEs confirms how difficult it is to assign the thresholds with accuracy, which can be distorted by the presence of hot bands depending on the way of generating the  $\cdot\text{CH}_2\text{OH}$  radical. One way to improve the accuracy resides in the averaging of the data. Another way consists of augmenting the set of data by adding the measured values for the deuterated homologues, corrected for the difference in zero-point energies relative to the nondeuterated hydroxymethyl radicals.<sup>187</sup> Observed variations in the IEs, taking into account these factors as well as results supported by ab initio calculations, have led the authors to recommend their experimental value,  $\text{IE}(\cdot\text{CH}_2\text{OH}) = 7.562 \pm 0.004$  eV, for the adiabatic IE of the hydroxymethyl radical.<sup>187</sup> From this value, the derived heat of formation for  $\cdot\text{CH}_2\text{OH}$  and  $\text{CH}_2\text{OH}^+$  were  $\Delta_f H_{298}^0(\cdot\text{CH}_2\text{OH}) = -4.25 \pm 0.3$  kcal/mol and  $\Delta_f H_{298}^0(\text{CH}_2\text{OH}^+) = 171.2 \pm 0.4$  kcal/mol, respectively ( $\Delta_f H_0^0(\cdot\text{CH}_2\text{OH}) = -2.75 \pm 0.3$  kcal/mol and  $\Delta_f H_0^0(\text{CH}_2\text{OH}^+) = 171.6 \pm 0.4$  kcal/mol). This value for the heat of formation for the hydroxymethyl radical,  $\Delta_f H_{298}^0(\cdot\text{CH}_2\text{OH})$ , is very slightly different from that reported at the same time by Dobe and co-workers,<sup>188</sup> derived from direct kinetic study of the reaction  $\text{CH}_2\text{OH} + \text{HBr}$  with an estimated  $\Delta_f H_{298}^0(\cdot\text{CH}_2\text{OH}) = -3.97 \pm 0.3$  kcal/mol. Even if this discrepancy reveals the influence of both the evaluation method and the adopted value for the adiabatic IE in the calculation, within the respective  $\pm 0.3$  kcal/mol error limits, both evaluations of these later reported values for  $\Delta_f H_{298}^0(\cdot\text{CH}_2\text{OH})$  agree quite well.

**1-Hydroxy Ethyl, Ethoxy and 2-Hydroxy Ethyl Radicals.** Bogan and Nesbitt,<sup>189</sup> studying hydrogen and deuterium-atom abstraction reactions on deuterated ethanol molecules, showed that the relative IEs of the radicals with a general formula  $[\text{C}_2\text{H}_5\text{O}]\cdot$  generated during these reactions could be finally

determined with more accuracy as it is difficult to form these species by direct dissociative ionization without avoiding carbon skeletal rearrangements. The IEs of the transient ethoxy  $\text{CH}_3\text{CH}_2\text{O}\cdot$ , 1-hydroxy ethyl  $\text{CH}_3\cdot\text{CHOH}$ , and 2-hydroxy ethyl  $\cdot\text{CH}_2\text{CH}_2\text{OH}$  species, generated by reactions of fluorine atoms to ethanol, were measured by Rušćić and Berkowitz.<sup>190</sup> To avoid contamination from other reaction products, such as vinyl alcohol or acetaldehyde, they used the deuterated precursor to generate the  $\text{CD}_3\text{CD}_2\text{O}\cdot$  radical from which adiabatic IE was measured at  $10.29 \pm 0.08$  eV. This value permitted one to derive a heat of formation for the corresponding cation presumably referred to a triplet state ( $\Delta_f H_0^0(\text{CH}_3\text{CH}_2\text{O}^+) = 237$  kcal/mol) and corrected the misleading interpretation of previous electron ionization determinations (see Table 2) which assigned the measured IE to a nitroso methane byproduct. The photoion-yield curve of  $\text{CH}_3\cdot\text{CHOH}$  only allowed bracketing of the IE threshold values between 6.78 and 6.85 eV, giving a value  $\text{IE}(\text{CH}_3\cdot\text{CHOH}) < 6.85$  eV, which has been used to derive a  $\Delta_f H_{298}^0(\text{CH}_3\cdot\text{CHOH}) > -15.6$  kcal/mol. Similarly, the reported value for the adiabatic IE of the 2-hydroxy ethyl radical  $\cdot\text{CH}_2\text{CH}_2\text{OH}$  is  $\text{IE}(\cdot\text{CH}_2\text{CH}_2\text{OH}) = 8.18 \pm 0.08 - 8.35 \pm 0.06$  eV. In both preceding cases, the ionization process is believed to be accompanied by a noticeable geometric change from the radical to the ionic structure. The  $\alpha(\text{C}-\text{H})$  and  $\beta(\text{C}-\text{H})$  bond energy in ethanol at 0 K was tentatively derived at values  $> 91.1$  kcal/mol and at  $98 \pm 2$  kcal/mol, respectively, with in the latter case values based on the difference between the  $\beta(\text{C}-\text{H})$  bond energy in ethanol and bromoethanol.<sup>190</sup> However, these values might be lowered by 1 to 3 kcal/mol as stated by the authors themselves<sup>190</sup> and as reported elsewhere.<sup>14</sup>

**Formyl HC·O.** The formyl radical is illustrative of a case where a large change in the geometrical structure occurring during the ionization process results in a difficult attribution of the corresponding IEs. A partial PES spectrum of the  $\text{HC}\cdot\text{O}$  was first reported by Dyke and co-workers,<sup>191</sup> with a vertical IE measured at  $9.31 \pm 0.01$  eV and an adiabatic IE estimated at  $8.27 \pm 0.01$  eV. Heat of formation of the formyl radical and  $DH_{298}$  of the C-H bond in formaldehyde have been derived from this estimated adiabatic IE and from the established value of  $\Delta_f H_{298}^0(\text{HCO}^+) = 197.2 \pm 1$  kcal/mol.<sup>191</sup> The resulting value for the  $DH_{298}(\text{H}-\text{C}(\text{O})\text{H}) = 84.6 \pm 1.5$  kcal/mol is however lower than the value given by Berkowitz et al.<sup>14</sup> Reinvestigation of the PES of the formyl radical later led to a derived value of  $8.14 \pm 0.04$  eV for the adiabatic IE.<sup>182</sup>

**Hydrocarboxyl HCOO·.** A photoionization mass spectrometric study of the neutral  $\text{COOH}/\text{COOD}$  species was conducted by Rušćić and co-workers,<sup>192</sup> providing the value of the adiabatic IE of the hydroxycarboxyl radical,  $\text{IE}(\text{HCOO}\cdot) = 8.486 \pm 0.012$  eV. These experiments were the first to clearly characterize this species, which have been inferred but not detected in the gas-phase. Previously, Burgers and co-workers,<sup>193</sup> using charge reversal on the formate anion, were able to offer evidence of the stability of the hydroxycarbonyl ion  $\text{HCOO}^+$  that was

shown to survive a few microseconds before rearranging to  $\text{COOH}^+$ . The method chosen to generate  $\text{HCOO}^\bullet$  was the reaction of fluorine atoms with  $\text{HCOOH}$ . The adiabatic IE of the free radical  $\text{HCOO}^\bullet$  was directly measured by PIMS and its heat of formation computed by combining this value with the known value of the heat of formation of  $\text{COOH}^+$ .<sup>194</sup> This lead to  $\Delta_f H_0^\circ(\text{HCOO}^\bullet) = -52.5 \pm 0.6$  kcal/mol.<sup>14,192</sup> Considering that the abstraction reaction of hydrogen atoms by fluorine atoms leads to “cooled”  $\text{HCOO}^\bullet$  radicals since the main part of energy content in the products have been inferred to vibrationally excited DF molecules for the reaction  $\text{F} + \text{DCOOH}$ , the experiment is conclusively presented as evidence for the stability of the hydroxycarbonyl radical  $\bullet\text{COOH}$ , even if the presence of  $\text{HCOO}^\bullet$  could not be completely ruled out. In fact, nothing proves that, in counterpart, this latter radical could not be generated by the same reaction, even if the energy content of the  $\text{DCOO}^\bullet$  radical has been reported to be high compared to HF. From these experiments, the  $\text{DCOO}^\bullet$  radical generated during the reaction  $\text{F} + \text{DCOOH}$  is shown to have a low vibrational excitation level (contrary to HF molecule when the abstraction reaction takes place on the O site), corroborating in fact the hypothesis assuming a rapid dissociation of “hot”  $\text{DCOO}^\bullet$  radicals. The strength of the C–H bond in the hydroxycarbonyl radical is computed at  $89.3 \pm 0.6$  and  $87.9 \pm 0.6$  kcal/mol at 298 and 0 K, respectively. Berkowitz and co-workers<sup>14</sup> have discussed these experiments suggesting that finally, the observed threshold in the photoion-yield curve was not the adiabatic threshold since the presence of a weak but lower step could not be definitely ruled out. They recommended a lower value,  $\text{IE}(\text{HCOO}^\bullet) = 8.20$  eV, inducing a correction which gives  $D_0(\text{H}-\text{COOH}) = 94.5$  kcal/mol.

**Phenoxy  $\text{C}_6\text{H}_5\text{O}^\bullet$ .** Only one PES study is available for the phenoxy radical generated from thermolysis of allyl phenyl ether.<sup>195</sup> This study permitted to reconfirm the order of the adiabatic IE of the allyl radical refining the published data gained by the EI method and to attribute the adiabatic IE at 8.56  $\pm$  0.02 eV. Derivation of the heat of formation for the corresponding ion provided an enthalpy,  $\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{O}^+) = 209.0 \pm 2.8$  kcal/mol.

### 5. Sulfur-Containing Radicals

**Mercapto Radical.** The  $\bullet\text{SH}$  radical produced from the reaction  $\text{F} + \text{H}_2\text{S}$  was studied by Dunlavey et al.<sup>196,197</sup> with an adiabatic IE reported at 10.37  $\pm$  0.01 eV and a vertical IE in the 11–16 eV with concomitant electronic state attributions of  $\text{SH}^+$ . As a complement to this study, a recent investigation reporting the first threshold ion-pair production spectrum for a triatomic molecule permitted one to derive a value of  $D_0(\text{H}-\text{SH}) = 89.9 \pm 0.01$  kcal/mol<sup>198</sup> for the S–H bond in hydrogen sulfide, refining the previously recommended value of Berkowitz and co-workers.<sup>14</sup>

**Thioformyl  $\text{HC}\cdot\text{S}$ .** The thioformyl radical  $\text{HC}\cdot\text{S}$  was studied by Rušćić and Berkowitz<sup>199</sup> in conjunction with the thioformaldehyde transient species  $\text{CH}_2\text{S}$ . An indirect approach for the determination of

the adiabatic IE of the thioformyl radical was favored before this work due to the inherent difficulty of generating the  $\text{HC}\cdot\text{S}$  radical in a proper condition. The choice of the reaction of fluorine atoms with methanethiol revealed subsequent hydrogen abstraction reactions leading to the thioformyl radical in three steps. The relative abundance of  $\text{HC}\cdot\text{S}$  remained small enough to preclude a precise measurement of the adiabatic IE, which has been finally limited to its upper value at  $7.499 \pm 0.005$  eV.<sup>199</sup> In addition, autoionization and the large breadth of the Franck–Condon distribution near the threshold restrained the precision of the measurements. The reported upper value is in quite good agreement with the predicted value  $\geq 7.38 \pm 0.1$  eV deduced from the corresponding heat of formation of  $\text{HC}\cdot\text{S}$  and  $\text{HCS}^+$ . Despite the difficulty to assign with accuracy the threshold for the reason stated above, the shape of the photoion yield permitted detection of a significant change in geometry from a bent-radical geometry to a linear geometry for the ground-state supported by ab initio calculations.<sup>200</sup> Combining the measured adiabatic IE ( $\leq 7.499 \pm 0.005$  eV) with the  $\Delta_f H_0^\circ(\text{HCS}^+)$ , the heat of formation of the thioformyl radical has been bracketted between  $69.7 \pm 2$  and  $73.3 \pm 2$  kcal/mol with a proposed value of  $71.7 \pm 2$  kcal/mol,<sup>199</sup> in good agreement with the heat of formation,  $\Delta_f H_0^\circ(\text{HCS}^\bullet) = 70.8$  kcal/mol, predicted by Curtiss and co-workers.<sup>200</sup> The thioformaldehyde was more conveniently generated from pyrolysis of methanesulfonyl chloride and the adiabatic IE was directly determined from the middle rise of the photoion-yield curve with a reported value of  $9.376 \pm 0.003$  eV,<sup>199</sup> correcting the estimation of 9.30 eV derived from a previous PIMS study of methanethiol.<sup>201</sup> The experimental value for the adiabatic IE was confirmed by measurements on  $\text{CH}_2\text{S}$  generated by pyrolysis of methyl disulfide with, however, a disturbing contribution of hot bands in the same region due to the higher temperature of the experiments (650 vs 370 °C for the pyrolysis of methanesulfonyl chloride). The attribution of the threshold ionization to a  $0 \rightarrow 0$  transition is in accordance with a very small geometry change during the ionization process between the neutral and ion ground states, reported to concern only a slight shortening of the C–S bond. Together with the measurement of the adiabatic IE of  $\text{CH}_2\text{S}$  and the reported value for the heat of formation of the corresponding cation  $\text{CH}_2\text{SH}^+$ , the authors established  $\Delta_f H_0^\circ(\text{CH}_2\text{S}) = 28.3 \pm 2$  kcal/mol with an error bar mainly introduced by the uncertainties of the  $\Delta_f H_0^\circ(\text{CH}_2\text{SH}^+)$ . This value compared well with the results of ab initio calculations which reported a heat of formation of  $\Delta_f H_0^\circ(\text{CH}_2\text{S}) = 28.7$  kcal/mol.<sup>200</sup> Derived values for several bond energies resulting from this work in the  $\text{CH}_n\text{S}$  system are additionally proposed.<sup>199</sup>

**Methylthio, Mercaptomethyl Radicals and Derivatives.** The methylthio radical  $\text{CH}_3\text{S}^\bullet$  obtained from the reaction of fluorine atoms with methanethiol was shown to provide an adiabatic IE of  $9.262 \pm 0.005$  eV, confirmed by  $\text{IE}(\text{CD}_3\text{S}^\bullet) = 9.268 \pm 0.005$  eV, with little geometrical change expected upon ionization between the neutral and the cation.<sup>202</sup>



However, theoretical calculations predicted a  $C_s$  structure for the ground-state methylthio radical with a slightly distorted  $C_{3v}$  geometry due to Jahn–Teller distortions and a local minimum  $C_{3v}$  structure for the corresponding  $\text{CH}_3\text{S}^+$  ion.<sup>200</sup> The IE value corrected the lower value reported by Nourbakhsh and co-workers<sup>203</sup> at  $9.225 \pm 0.014$  eV for the adiabatic IE previously determined by molecular beam PIMS experiments, and the 0.043 eV discrepancy was tentatively attributed to a lower resolved PI experiment in this latter case. Rušćić and Berkowitz<sup>202</sup> deduced a  $\Delta_f H_0^\circ(\text{CH}_3\text{S}^+) = 245.0 \pm 0.5$  kcal/mol inserted in the 244.1–247.7 kcal/mol interval given by Nourbakhsh et al.<sup>203</sup> for this quantity. Kinetic energy release measurements for the photodissociation process of methanethiol in accordance with the 9.225 eV value for the adiabatic IE have led to  $\Delta_f H_0^\circ(\text{CH}_3\text{S}^\bullet) = 35.5 \pm 2$  kcal/mol,<sup>204</sup> with a discrepancy of ca. 4 kcal/mol with the theoretical value of 31.6 kcal/mol reported by Curtiss and co-workers.<sup>200</sup> The measured value of 9.262 eV for the adiabatic IE of the methylthio radical has led to a proposed value of  $32.5 \pm 2$  kcal/mol by Rušćić and Berkowitz<sup>202</sup> in better accordance with the usually achieved accuracy of  $\pm 2$  kcal/mol observed between ab initio calculations and experiments. Recently, the radical  $\text{CH}_3\text{S}^\bullet$  was reinvestigated using fast radical-beam photofragment spectroscopy,<sup>205</sup> providing a refined value for the heat of formation of the methylthio radical,  $\Delta_f H_0^\circ(\text{CH}_3\text{S}^\bullet) = 31.0 \pm 0.4$  kcal/mol, which is in fair agreement with both previous theoretical and experimental values except the 35.5 kcal/mol obtained by molecular-beam PIMS.

The mercaptomethyl  $\text{CH}_2\text{SH}^\bullet$  radical has been studied by PIMS with a first measurement of the adiabatic IE at  $7.536 \pm 0.003$ <sup>202</sup> and a corresponding value of  $7.522 \pm 0.003$  for  $\text{CD}_2\text{SH}^\bullet$ , providing a difference in zero-point energies reported as being in excellent agreement with theoretical calculations. Despite the disparity of collected data which are discussed in their work, Rušćić and Berkowitz,<sup>202</sup> choosing an upper limit for the heat of formation of the corresponding cation at  $211.5 \pm 2$  kcal/mol, deduced a value of  $\Delta_f H_0^\circ(\text{CH}_2\text{SH}^\bullet) = 37.7 \pm 2$  kcal/mol. Their measured IE gave them an upper value for the  $\text{DH}_{298}$  at 0 K for the  $\alpha$  C–H bond in methanethiol by combination with appearance energy measurement results,  $D_0(\text{H}-\text{CH}_2\text{SH}) \leq 93.97 \pm 0.13$  kcal/mol. Using the above-deduced value for the heat of formation of the mercaptomethyl radical led to a lower energy for this C–H bond,  $92.4 \pm 2$  kcal/mol.<sup>202</sup> Noteworthy, the calculated value for the heat of formation of the mercaptomethyl radical is reported at 40.6 kcal/mol<sup>200</sup> in quite disagreement with the above value,  $37.7 \pm 2$  kcal/mol. However, the quoted difference is mainly due to the difference between the theoretical and experimental adiabatic IE, 7.42 vs 7.536 eV, respectively, suggesting that the true adiabatic threshold might not have been located in the PI experiment by reason of a geometrical change upon ionization. No other experimental data are actually available to confirm or deny these IE values. Both theoretical and experimental data, however, conclude in a lower heat of formation for the meth-

ylthio radical  $\text{CH}_3\text{S}^\bullet$  compared to the mercaptomethyl radical  $\text{CH}_2\text{SH}^\bullet$ , a reversed order of those observed for the corresponding oxygenated homologues, methoxy  $\text{CH}_3\text{O}^\bullet$ , and hydroxymethyl  $\text{CH}_2\text{OH}^\bullet$ .

Baker and Dyke<sup>206</sup> reported the PES spectrum of the methylthiomethyl radical  $\text{CH}_3\text{SCH}_2^\bullet$  generated from the reaction of fluorine atoms with dimethyl sulfide. The corresponding adiabatic and vertical IEs were measured at  $6.85 \pm 0.03$  and  $7.16 \pm 0.03$  eV, respectively, refining the upper limit value of 6.88 eV deduced from literature data and PI investigation on dimethyl sulfide.<sup>207</sup> This latter work deduced the heat of formation of  $\text{CH}_3\text{SCH}_2^\bullet$ ;  $\Delta_f H_0^\circ(\text{CH}_3\text{SCH}_2^\bullet) = 34 \pm 2.5$  kcal/mol, as well as the bond energy,  $D_0(\text{H}-\text{CH}_2\text{SCH}_3) = 91 \pm 2.5$  kcal/mol, from the photofragmentation of dimethyl sulfide.<sup>207</sup>

**HS•O Radical.** Despite its possible importance in atmospheric chemistry, the HS•O radical has never been studied by PES and PIMS before the first experiment reported by Cheng et al.<sup>208</sup> HS•O radicals were generated from the reaction of oxygen atoms with organothiol compounds in a discharge-flow photoionization mass spectrometer. The threshold for the ionization of the HS•O radical into the singlet state of the HSO<sup>+</sup> cation was reported at  $9.918 \pm 0.016$  eV. A heat of formation of  $228 \pm 5$  kcal/mol was calculated for the heat of formation of the corresponding HSO<sup>+</sup> cation.

## 6. Nitrogen-Containing Radicals

**Azide, Imidogen, and Amino Radicals.** Azide  $\text{N}_3^\bullet$ , imidogen  $\text{NH}^\bullet$ , and amino  $\text{NH}_2^\bullet$  radicals have hardly been investigated by PES or PIMS. Dyke and co-workers<sup>209</sup> reported the He(I) PES spectrum of the azide radical generated from the reaction of fluorine atoms with hydrazoic acid. They measured the three first adiabatic IEs of the ground  $X^2\Pi$  state of the azide radical in the region 10–13 eV but the PES spectrum above 15 eV could not be confirmed for the other predicted IE because of the intense bands arising from byproducts of the initial reaction of  $\text{F} + \text{N}_3\text{H}$ . The adiabatic IE measured at  $11.06 \pm 0.01$  eV agreed well with the predicted value from ab initio calculations and provided an estimate for the heat of formation of the corresponding  $\text{N}_3^+$  ion,  $\Delta_f H_0^\circ(\text{N}_3^+) = 366 \pm 5$  kcal/mol. The first PES experiments reporting the adiabatic IE of the imidogen radical provided a value of  $\text{IE}(\text{NH}^\bullet) = 13.49 \pm 0.01$  eV.<sup>210</sup> This value was refined by de Beer and co-workers<sup>211</sup> using the REMPI–PES technique with a measured  $\text{IE}(\text{NH}^\bullet) = 13.476 \pm 0.002$  eV confirming the preceding experimental value for the ground-state  $3\Sigma^-$ . Other IEs were reported in this study and were assigned to higher ionic states of the  $\text{NH}^+$  ion. PES spectrum of the amino  $\text{NH}_2^\bullet$  radical prepared by the reaction of fluorine atoms with ammonia was reported by Dunlavey and co-workers<sup>210</sup> with measured IEs at  $11.46 \pm 0.01$  eV and  $12.0 \pm 0.01$  eV for the adiabatic and vertical IEs, respectively. The adiabatic IE was reported at a lower value by Gibson et al.<sup>212</sup> who measured  $\text{IE}(\text{NH}_2^\bullet) = 11.14 \pm 0.01$  eV. The reaction previously used in PES has led to a spectrum blurred by a large band due to  $\text{NH}_3$  in the first photoion band region of the amino radical, making

the assignment of the adiabatic threshold in the spectrum difficult. To overcome these drawbacks, Gibson et al.<sup>212</sup> used the reaction of hydrogen atoms with hydrazine to generate the amino radical investigated by PIMS. Two electronic states of the amino radical have been clearly assigned and resolved, as well as a set of Rydberg states. Several quantities have been derived from the experimental value of the adiabatic IE using the compiled data in thermochemical tables, comprising heat of formation of the radicals and corresponding ions as well as the derived bond energy for the different N–H bonds (Table 2). The heat of formation of the amino radical,  $\Delta_f H_0^\circ(\cdot\text{NH}_2) = 45.8 \pm 0.3$  kcal/mol, combined with the heat of formation of hydrazine,  $\Delta_f H_0^\circ(\text{N}_2\text{H}_4) = 26.16 \pm 0.2$  kcal/mol, gives a measure of the single N–N bond energy through the dissociation reaction of hydrazine into two amino radicals,  $D_0(\text{N–N}) = 65.5 \pm 0.6$  kcal/mol.<sup>212</sup> These thermochemical values have not been corrected in the later compilation of Berkowitz and co-workers.<sup>14</sup>

**Cyano Radical and Derivatives.** Berkowitz,<sup>213</sup> using a Knudsen cell to decompose the cyanogen into CN<sup>•</sup> radicals, measured the adiabatic IE of the cyano radical at  $14.2 \pm 0.3$  eV and deduced a heat of formation,  $\Delta_f H_0^\circ(\text{CN}^\bullet) = 109$  kcal/mol. The adiabatic IE was reconfirmed a few years later with a derived value of  $14.03 \pm 0.02$  eV.<sup>214</sup> In addition, this PIMS study also reported a corrected value for the heat of formation,  $\Delta_f H_0^\circ(\text{CN}^\bullet) = 105.5$  kcal/mol. No corrections have been made since.

The methylene-amidogen radical  $\text{CH}_2\text{N}^\bullet$  generated from the reaction of nitrogen atoms with methyl radicals was investigated by Nesbitt and co-workers<sup>215</sup> using PIMS. The first IEs for the  $\text{CH}_2\text{N}^\bullet$  and its deuterated homologue  $\text{CD}_2\text{N}^\bullet$  were measured at  $9.58 \pm 0.92$  and  $9.62 \pm 0.58$  eV, respectively. Ab initio calculations confirmed that the lower energy radical isomer of formula [C, 2H, N] has the structure  $\text{CH}_2\text{N}^\bullet$ , both the *cis*-HCNH and *trans*-HCNH calculated to be less stable. Derived values of the IEs are reported for these isomers,  $\text{IE}(\text{CH}_2\text{N}^\bullet) = 10.8$  eV,  $\text{IE}(\textit{cis}\text{-CHN}^\bullet\text{H}) = 6.8$  eV, and  $\text{IE}(\textit{cis}\text{-CHN}^\bullet\text{H}) = 7.0$  eV. The two latter values are in accordance with the absence of the *cis*- and *trans*-isomers in the PI spectrum. However, the derived IE for the  $\text{CH}_2\text{N}^\bullet$  radical is too low, leading the authors to assign the measured IE at  $9.4 \pm 0.1$  eV to autoionization from high Rydberg states which can only be in agreement with the calculated singlet ground-state structure of the  $\text{HC-NH}^+$  cation.

The first adiabatic and vertical IEs of the amino methyl  $\cdot\text{CH}_2\text{NH}_2$  radical have been measured by PES at  $6.29 \pm 0.03$  and  $6.97 \pm 0.03$  eV, respectively.<sup>216</sup> Despite the fact that the first photoion band in the PES spectrum was not totally resolved, assignment of the main series in the vibrational structure of  $\cdot\text{CH}_2\text{-NH}_2$  could be attributed to excitation of the stretching mode in the resulting ion in accordance with the geometrical change from a  $C_s$  symmetry for the ground-state radical into a  $C_{2v}$  symmetry for the ground-state ion. Such assignment was supported by computational calculations that also allowed one to determine the values for the IEs of the methyl amino

radical  $\text{CH}_3\text{N}^\bullet\text{H}$ , 6.88 and 10.16 eV for the adiabatic and vertical values, respectively. Heat of formation for the ground-state X1A1 ion  $\text{CH}_2\text{NH}_2^+$  was estimated at  $180.4 \pm 2.6$  kcal/mol.<sup>216</sup>

**Miscellaneous.** The isocyanato radical,  $\cdot\text{NCO}$ , generated from the reaction of fluorine atoms with isocyanic acid, was first investigated by PES.<sup>217</sup> Seven states of the ion have been assigned using the results of ab initio calculations and the adiabatic IE of  $\cdot\text{NCO}$  ( $X^2\Pi$ ) measured at  $11.76 \pm 0.01$  eV.  $\Delta_f H_{298}^\circ(\text{NCO}^+)$  and  $D_0(\text{N–CO})$  have been derived at  $307.8 \pm 3.7$  and  $101.5 \pm 3.7$  kcal/mol, respectively. The shape of the first PES band and derived assignment raised the question of the equilibrium geometry of the corresponding ion upon ionization as  $\text{NCO}^+$  and  $\text{NOC}^+$  are expected to be close in energy at their minimum energy geometry in favor of the latter one assumed to be more stable, but no firm conclusion could be made on that point in the absence of clear evidence. Rušćić and Berkowitz<sup>218</sup> reinvestigated the isocyanato radical  $\cdot\text{NCO}$  by PIMS avoiding drawbacks encountered during PES experiments, i.e., the superposition of bands related to reagents or byproducts of the reaction used to generate the radical. The measured value from the PI spectrum of the  $\cdot\text{NCO}$  radical,  $\text{IE}(\cdot\text{NCO}) = 11.759 \pm 0.006$  eV, confirmed the adiabatic IE value determined previously by PES. In this work, AE of the  $\text{NCO}^+$  ion from isocyanic acid  $\text{HNCO}$  was also measured. Combined with the previous determination of the adiabatic IE of the  $\cdot\text{NCO}$  radical, the following quantities have been derived or bracketed as follows,  $\Delta_f H_0^\circ(\text{NCO}^+) \geq 299.6 \pm 0.5$  kcal/mol,  $28.4 \pm 0.5$  kcal/mol  $\leq \Delta_f H_0^\circ(\cdot\text{NCO}) \leq 32.8 \pm 0.7$  kcal/mol and  $105.6 \pm 0.5$  kcal/mol  $\leq D_0(\text{H–NCO}) \leq 110.1 \pm 0.3$  kcal/mol.<sup>218</sup>

In the course of PIMS study of hydrazine, Rušćić and Berkowitz<sup>219</sup> reported the adiabatic IE of the hydrazinyl radical  $\text{N}_2\text{H}_3^\bullet$ , which was detected by the same authors at a low ratio during a previous investigation on the amino radical in which some thermochemical data on N–H bonds were inferred<sup>212</sup> (Table 2). The adiabatic  $\text{IE}(\text{N}_2\text{H}_3^\bullet)$  was measured at  $7.61 \pm 0.01$  eV refining the preliminary value of  $7.70 \pm 0.05$  eV<sup>212</sup> determined from the study of the reaction of  $\text{H} + \text{N}_2\text{H}_4$ , in which  $\text{N}_2\text{H}_3^\bullet$  is generated as a reaction intermediate. Vibrational progression in the spectrum was attributed to a N–N stretching frequency of a bond with a main double-bond character. By combining the measured AE of the hydrazinyl radical from the hydrazine precursor with the measured adiabatic IE, the authors obtained a value of  $55.3 \pm 0.3$  kcal/mol for the heat of formation of the radical at 0 K, and inferred  $D_0(\text{H–HNNH}) = 43.8 \pm 1.1$  kcal/mol and  $D_0(\text{H–NNH}_2) = 80.3 \pm 0.3$  kcal/mol. This latter value is claimed to be the closest one accessible under these experimental conditions of approaching the N–H bond value in hydrazine. Correlated to previous experimental measurements on different  $\text{NH}_x\text{–H}$  bonds (Table 2), the N–H bond energy in hydrazine is close to the first H addition to nitrogen ( $D_0(\text{H–N}) = 79.0 \pm 0.4$  kcal/mol<sup>212</sup> and quite far from the average bond in ammonia reported at 92.3 kcal/mol.

Monks and co-workers<sup>220</sup> conducted a discharge flow-photoionization MS study of nitrogen trioxide  $\text{NO}_3^{\bullet}$  and reported the measurement of its adiabatic IE. Nitrogen trioxide radicals were generated from the reaction of fluorine atoms with nitric acid. The measurement of the IE gave an adiabatic value of  $\text{IE}(\text{NO}_3^{\bullet}) = 12.57 \pm 0.03$  eV, quite an increase in the progression of IE reported from the other nitrogen oxides  $\text{NO}^{\bullet}$  and  $\text{NO}_2$ , 9.264 and 9.60 eV, respectively. This gap in the IE is explained by the more polar character of the  $\text{NO}_3^{\bullet}$  radical and the resulting higher energy necessary to remove the open-shell electron localized on the  $\text{O}_3$  ring around the N atom in nitrogen trioxide. From the experimental single and very sharp initial step in the photoefficiency curve, as well as support by theoretical calculations, it was concluded that neutral and cation symmetries were similar in a  $D_{3h}$  equilibrium symmetry to account for this argument. Derived values for the heat of formation of the corresponding cation  $\text{NO}_3^+$  were reported at  $\Delta_f H_{298}^{\circ}(\text{NO}_3^+) = 307.1 \pm 1.7$  kcal/mol and  $\Delta_f H_0^{\circ}(\text{NO}_3^+) = 308.9 \pm 1.2$  kcal/mol.

### 7. Silicon-Containing Radicals

Silicon-containing radicals have been the subject of compilation<sup>21</sup> and recent review articles<sup>25,26</sup> in view of the important chemistry they bear. As a consequence, they will be only briefly reported in this section as extensive information can be found in previous articles and references herein. Data obtained by photoionization concerning silicon-containing radicals are for the most part related to the  $\text{SiH}_x$  series, mainly, silyldiyne  $\text{SiH}^{\bullet}$ , silylene  $\text{SiH}_2^{\bullet}$ , silyl  $\text{SiH}_3^{\bullet}$ , or the  $\text{Si}_2\text{H}_x^{\bullet}$  radicals. At the time when a general account of the  $\text{DH}_{298}$  values of silicon-containing compounds was published,<sup>21</sup> it was certainly thought that these values were well-established. However, it appears that some discrepancies between experimental and theoretical calculations, as well as between experiments, cast a degree of doubt on some of these values, primarily due to an error in the estimation of the heat of formation of the silylene radical.<sup>55</sup>

Silyl or hydride-silicon-based radicals are usually generated from a hydrogen abstraction reaction with halogen atoms (F, Cl).<sup>221,222</sup> The first direct determination of the adiabatic IE of the silyl radical by PES was performed by Dyke and co-workers<sup>221</sup> who reported values of  $8.14 \pm 0.01$  and  $8.74 \pm 0.01$  eV for the adiabatic and vertical IEs of  $\text{SiH}_3^{\bullet}$ , respectively. This first band in the PE spectrum was consistent with a pyramidal equilibrium geometry for the ground electronic state of  $\text{SiH}_3^{\bullet}$  and a planar geometry for that of  $\text{SiH}_3^+$ , in contrast to the case of the methyl radical where both  $\text{CH}_3^{\bullet}$  and  $\text{CH}_3^+$  are reported to be planar (see above).<sup>142</sup> From the determination of the adiabatic IE, a derived value of  $\Delta_f H_{298}^{\circ}(\text{SiH}_3^+) = 234.2 \pm 1.7$  kcal/mol was reported.

Some controversy cropped up concerning silylated radicals because of the very slight differences reported between the measured AEs and adiabatic IEs of some radicals of the  $\text{SiH}_x^{\bullet}$  series, inducing probable confusion in the assignment of threshold values at the basis of derivation of the recommended heat of

formation.<sup>223</sup> In addition, experimental determinations of the proton affinity of the silylene radical<sup>224</sup> and theoretical calculations<sup>225,226</sup> were raising some additional questions about the validity of recommended data. Investigation of the adiabatic IEs for the  $\text{SiH}_x^{\bullet}$  series using PIMS led to the following values:<sup>223</sup>  $\text{IE}(\text{SiH}_3^{\bullet}) = 8.01 \pm 0.02$  eV,  $\text{IE}(\text{SiH}_2^{\bullet}) \leq 9.15 \pm 0.02$  eV,  $\text{IE}(\text{SiH}^{\bullet}) = 7.91 \pm 0.01$  eV. No direct data measured using mass spectrometry were available before for silyldiyne  $\text{SiH}^{\bullet}$ ; only one derived value was reported in the case of silylene  $\text{SiH}_2^{\bullet}$  at  $9.47 \pm 0.03$ <sup>227</sup> and, finally, the 8.01 eV<sup>223</sup> value reported for  $\text{SiH}_3^{\bullet}$  refined the previous value determined by PES,<sup>221</sup> as well as the  $8.31 \pm 0.07$  eV value combined from AE measurements on  $\text{SiH}_4$ .<sup>225</sup> Differences between the two adiabatic IE values of 8.01 eV<sup>223</sup> and 8.14 eV<sup>221</sup> were explained by the impossibility in the PE spectrum of  $\text{SiH}_3^{\bullet}$  of extracting a reliable threshold value because of the presence of an impurity band just in the place where computation on the Franck–Condon envelope showed the expected onset of  $\text{SiH}_3^+$ .<sup>223</sup> The attribution of the adiabatic IE for the silylene radical brought about some difficulties due to the presence of the singlet and triplet ground states of the cation  $\text{SiH}_2^+$ , the reported IE value of  $8.24 \pm 0.02$ <sub>5</sub> eV<sup>223</sup> corresponding to the metastable triplet state ( $a^3\text{B}_1$ ). Ambiguity for the adiabatic IE of the singlet state could not be removed in the presence of the  $\text{SiH}_2^{\bullet}$  triplet state. Both supposed values for the adiabatic IE are reported at  $9.15 \pm 0.02$  and  $9.02 \pm 0.02$  eV.<sup>223</sup> Thermochemical data resulting from these experiments at first reported the heat of formation of  $\text{SiH}_2^+$ ,  $\Delta_f H_0^{\circ}(\text{SiH}_2^+) = 276.6 \pm 0.6$  kcal/mol. More interesting are the relative values for the heat of formation at 298 K of the corresponding silylene radical since the recommended value of Walsh,<sup>21</sup> 58 kcal/mol, was questioned by the experimental value of Shin and Beauchamp at  $69 \pm 3$  kcal/mol,<sup>224</sup> and by theoretical values calculated at 63.4 kcal/mol by Pople et al.<sup>225</sup> and at 68.1 kcal/mol by Ho and co-workers.<sup>226</sup> Recalling the ambiguity in the experimental adiabatic IEs due to the presence of both singlet and triplet states of the  $\text{SiH}_2^+$  ion, Rušćić and Berkowitz, however, corrected this heat of formation at  $\Delta_f H_{298}^{\circ}(\text{SiH}_2^{\bullet}) = 65.2$  kcal/mol (9.15 eV) or  $\Delta_f H_{298}^{\circ}(\text{SiH}_2^{\bullet}) = 68.4$  kcal/mol (9.02 eV). Stepwise bond energies were finally deduced from the collected data (Table 2). A REMPI study<sup>228</sup> of the silyl radical resulted in a corrected value at 8.135 eV for the adiabatic IE of  $\text{SiH}_3^{\bullet}$ . This value is in better agreement with the former value reported by Dyke et al.<sup>221</sup> The authors stated that due to the large geometrical change upon ionization the resulting Franck–Condon factors might be expectedly small, rendering difficult a precise attribution of the onset at threshold, as well as the presence of hot bands that cannot be avoided (effectively observed in the REMPI experiments). Consequently, their spectroscopic data can be considered as reliable and are confirmed by the complementary data given by the ion-beam experiments of Boo and Armentrout<sup>229</sup> in accordance with a lower value for the adiabatic IE of  $\text{SiH}_3^{\bullet}$ , reported at  $8.11 \pm 0.07$  eV. These later experiments cause one to have some reservations regarding the derived thermochemical

data previously reported. Resulting from the ion-beam measurements, some corrections might be necessary for the corresponding heat of formation of the related radicals as well as the  $\text{DH}_{298}$ . The recommended heat of formation for silyl and silylene radicals of Boo and Armentrout are then  $\Delta_f H_0^\circ(\text{SiH}_3^\bullet) = 48.5 \pm 1.6$  kcal/mol and  $\Delta_f H_0^\circ(\text{SiH}_2^\bullet) = 69.0 \pm 2$  kcal/mol, respectively.<sup>229</sup> The latter value definitely agrees with the necessity of correcting the heat of formation reported by Walsh<sup>21</sup> in 1981 and seems to accord the value of the adiabatic IE of the silylene radical, deduced at  $8.11 \pm 0.07$  eV with the measurement at 9.02 eV reported by Berkowitz et al.<sup>223</sup> Recent refinements of the uncertainties in these quantities are discussed in the review of Jasinski and co-workers<sup>25</sup> and show an increase in the agreement between experimentalists and theoreticians on this matter with a recommended value of 65.2 kcal/mol for  $\Delta_f H_0^\circ(\text{SiH}_2^\bullet)$ .

### 8. Miscellaneous

**Phosphinidene, Phosphino Radicals.** Phosphinidene  $\bullet\text{PH}$ <sup>231</sup> and phosphino  $\bullet\text{PH}_2$ <sup>232</sup> radicals have been investigated by PIMS with the goal of presenting photoion-yield curves for these two radicals, and to demonstrate that similarities can be observed in the corresponding photoion yield curves of another pnictogen group V element As, together with the photoion curves of arsenic monohydride  $\bullet\text{AsH}$  and  $\bullet\text{AsH}_2$ .<sup>233</sup> Photoionization studies in the Argonne National Laboratory have been extended to other radicals including  $\bullet\text{SeH}$ ,<sup>234</sup>  $\bullet\text{B}_2\text{H}_5$ ,<sup>235</sup> and  $\bullet\text{GeH}_3$ .<sup>236</sup>

**Halogenated Methyl Radicals.** Halogenated methyl radicals have been investigated using PES and PIMS for fluorinated, chlorinated, and brominated radicals including  $\bullet\text{CF}_3$ ,<sup>30</sup>  $\bullet\text{CHCl}_2$ ,<sup>237</sup>  $\bullet\text{CCl}_3$ ,<sup>238</sup> and  $\bullet\text{CH}_2\text{Br}$ .<sup>239</sup> Determination of the adiabatic IE of the trifluoromethyl radical was one of the early demonstrations of the powerful capacity offered by PIMS for such measurements. The experimental value at  $9.25 \pm 0.04$  eV<sup>62</sup> compares well to the electron ionization value measured later by Kime and co-workers<sup>128</sup> and introduces some reservations on the recent experimental measurements of Tarnovsky and Becker,<sup>129</sup> who reported an IE of 8.5 eV. However, the recommendation of Lifshitz and Chupka<sup>62</sup> to verify their experimental value of 9.25 eV by using PIMS has not been done yet. PE spectrum of the dichloromethyl radical has been reported by Andrews and co-workers,<sup>237</sup> suggesting a planar geometry for both the radical  $\bullet\text{CHCl}_2$  and the corresponding ion  $\text{CHCl}_2^+$ . The reported values for the adiabatic and vertical IEs are  $8.32 \pm 0.01$  and  $8.54 \pm 0.01$  eV, respectively. However, the presence of reactants and byproducts, especially HF in the region of 8.2–9.0 eV, resulting from the use of the reaction of  $\text{F} + \text{CH}_2\text{Cl}_2$  for the formation of the  $\bullet\text{CHCl}_2$  radical could have disturbed this measurement which has not been confirmed by PIMS. The trichloromethyl radical  $\bullet\text{CCl}_3$  generated by flash pyrolysis from bromotrichloromethane was investigated by Robles and Chen<sup>238</sup> using PES. The measured adiabatic IE was reported at  $8.06 \pm 0.02$  eV in quite fair accordance with the value of 8.109 eV obtained by extrapolation of the

Rydberg series detected by REMPI.<sup>240</sup> Using the correction in the value of the heat of formation of the  $\bullet\text{CCl}_3$  radical reported by Hudgens and co-workers<sup>241</sup> with  $\Delta_f H_0^\circ(\bullet\text{CCl}_3) = 16.7 \pm 0.6$  kcal/mol, the derived value for the heat of formation of  $\text{CCl}_3^+$ ,  $\Delta_f H_0^\circ(\text{CCl}_3^+) = 202.6 \pm 0.8$  kcal/mol,<sup>238</sup> is in fairly good agreement with the 203.7 kcal/mol value derived from the REMPI experiments. Gaussian-2 calculations have been performed to compare the experiments, and have predicted the values for the adiabatic IE and the heat of formation for  $\bullet\text{CCl}_3$  and  $\text{CCl}_3^+$ , with  $\text{IE}(\bullet\text{CCl}_3) = 7.954$  eV,  $\Delta_f H_0^\circ(\bullet\text{CCl}_3) = 17.3$  kcal/mol and  $\Delta_f H_0^\circ(\text{CCl}_3^+) = 200.73$  kcal/mol, in quite fair agreement with the experimental data,<sup>238,241</sup> even if in the case of the cation the quantity was slightly lowered. Concordance between theory and experiments was a clue that the value reported by kinetic measurements<sup>241</sup> provided the most reliable  $\Delta_f H_0^\circ(\bullet\text{CCl}_3)$ . The adiabatic IE of the bromomethyl radical  $\bullet\text{CH}_2\text{Br}$  has been reported at  $8.61 \pm 0.01$  eV<sup>239</sup> by PIMS measurement on a pulsed jet of dibromomethane diluted in argon. From the sharp onset of the ion-yield signal in the PI spectrum, it was deduced that structures of the radical and of the ion might be similar with no noticeable geometrical change, which was more or less confirmed by the standard ab initio calculations predicting a planar  $C_{2v}$  structure for  $\text{CH}_2\text{Br}^+$  and a slightly deviant planar structure for  $\bullet\text{CH}_2\text{Br}$ .<sup>239</sup> At a higher level of calculations, it was proposed that the planar radical structure was only 0.12 kcal/mol less stable than a  $C_s$  pyramidal structure. Noteworthy is the excellent agreement between the measured adiabatic IE and the value reported from previous PES experiments,<sup>242</sup> strongly suggesting that the true adiabatic IE was measured by PIMS.

The spectrum of the fluoromethylene radical in its singlet state generated from a reaction of fluorine atoms with methane or preferably fluoromethane, has been observed and assigned in combining experiments using the REMPI technique and theoretical calculations.<sup>243</sup> Even if this study was more related to the domain of spectroscopy with the vibrational and partial rotational resolution of the reported Rydberg state, it must be quoted for the estimation of the corresponding adiabatic IE at  $10.06 \pm 0.05$  eV.

**Oxygenated Halogen Radicals.** The oxygen monofluoride radical has been investigated by PES<sup>244</sup> filling the lack of data relative to this halogen monoxide. The  $\text{FO}^\bullet$  radical was generated from the reaction of  $\text{F} + \text{O}_3$  and was shown to present a lifetime largely compatible with the time scale of the experiments. However, the main drawback for this way of generating the radical was the presence of photoelectron bands attributable to the reactants, F and  $\text{O}_3$ , and byproducts, O atoms, molecular  $\text{O}_2$  or  $\text{SiF}_4$ , resulting from the reaction of fluorine atoms with the glass inlet system. Ozone and molecular oxygen were particularly disturbing in the assignment of the ground-state IEs, as well as other expected ionic onsets supposed to be accessible with He(I) radiation. The adiabatic and vertical IEs of  $\text{FO}^\bullet$  were measured at 12.77 and 13.08 eV, respectively.<sup>244</sup> Assuming that the  $\text{FO}^+$  ion dissociates into  $\text{F}^+ + \text{O}$ ,

the ionic dissociation energies of several ionic states of  $\text{FO}^+$  were estimated, that of the ground-state being  $D_e(\text{FO}^+) = 160.5 \pm 3.7$  kcal/mol. A PIMS study appeared to complete this former study providing an adiabatic IE for the same transition at  $12.78 \pm 0.03$  eV<sup>245</sup> in excellent agreement with the PES study.  $\text{FO}^\bullet$  radicals were generated from the reaction of fluorine atoms with  $\text{NO}_3$  or, less efficiently due to recombination reactions, via a  $\text{F}_2/\text{O}_2$  discharge. The PIMS experiments preclude the noted overlapping bands to obscure the PES spectrum. A computed value of 26.2 kcal/mol was reported for the heat of formation of  $\text{FO}^\bullet$  at 298 K.<sup>245</sup>

The complete He(I) PE spectrum of  $\text{ClO}^\bullet$ , formed from the reaction of Cl, H, or O atoms on several oxygenated precursors ( $\text{O}_3$ ,  $\text{ClO}_2$ ,  $\text{Cl}_2\text{O}$ ), has been reported by Bulgin et al.<sup>246</sup> with the computation of all possible ionic states accessible by one-electron ionization using  $\Delta\text{SCF}$  calculations. The adiabatic and vertical IE resolved in the first PE band were determined at  $10.87 \pm 0.01$  and  $11.01 \pm 0.01$  eV for the  $X^2\Pi_{3/2}$  ground-state,<sup>246,247</sup> for a computed value of 10.96 eV. Similar to the monofluoride radical, overlapping bands were the main problem for an accurate assignment of the computed IEs, and the authors were calling for complementary spectroscopy techniques to characterize in more detail the ionic states detected in their work. The PI spectrum of  $\text{ClO}^\bullet$  was reported by Thorn and co-workers<sup>248</sup> in the course of an investigation of the dichlorine monoxide  $\text{ClO}_2$ . The oxygen monochloride radicals were generated from the in situ reaction of fluorine atoms with the reactant  $\text{Cl}_2\text{O}$ . The reported adiabatic IE for  $\text{ClO}^\bullet$  at  $10.88_5 \pm 0.01_6$  eV agrees well with the previous PES value, and the PI spectrum was sufficiently resolved to detect the spin-orbit coupling between the  $X^2\Pi_{3/2}$  ground-state and the immediate upper  $X^2\Pi_{1/2}$  state of  $\text{ClO}^\bullet$  (IE =  $10.84_7 \pm 0.01_6$  eV). At the same time, experiments performed using a monochromatic synchrotron source for the photoionization of  $\text{ClO}^\bullet$  generated from the reaction of  $\text{Cl} + \text{O}_3$  provided a threshold value of  $10.85 \pm 0.05$  eV.<sup>249</sup> In accordance with previous PES experiments, the PI spectrum additionally showed steplike features, observed with increasing photon energy at 10.87, 11.00, and 11.125 eV, and attributed to the vibrational fine structure of the  $\text{ClO}^+ X^3\Sigma^-$  state resulting from the ionization of the  $\text{ClO}^\bullet$  ground-state  $X^2\Pi_{3/2}$ .

The first IE of the oxygen monobromide radical  $\text{BrO}^\bullet$  measured by PES was reported by Dunlavey and co-workers<sup>250</sup> with a vertical value of  $\text{IE}(\text{BrO}^\bullet) = 10.29 \pm 0.01$  eV. This value was attributed to the  $\text{BrO}^+ (X^3\Sigma^-) \leftarrow \text{BrO}^\bullet (X^2\Pi_{3/2})$  transition, with which a dissociation energy of  $D_e(\text{BrO}^+) = 91.5 \pm 0.7$  kcal/mol<sup>250</sup> was associated. Monks and co-workers,<sup>251</sup> reinvestigating the same transition by PIMS, obtained an adiabatic IE of  $10.46 \pm 0.02$  eV.

No direct determinations of the IEs of the oxygen moniodide radical are available, only a derived value at  $9.66 \pm 0.10$  eV being reported by Monks and co-workers<sup>252</sup> in the course of their PI study on the hypoiodous acid  $\text{HIO}$ .

The fluoroformyl radical  $\text{FCO}^\bullet$  has been investigated with both He(I) and Ne(I) PES, and the IE

corresponding to the lowest  $X^2A'$  state has been reported at  $11.26 \pm 0.01$  eV in good accordance with a calculated value of 11.47 eV.<sup>253</sup> As in the case of the oxygen monofluoride radical, byproducts contributed in broad bands in the higher energy region of the PE spectrum, impinging on the identification of the higher  $\text{FCO}^\bullet$  bands. In a manner similar to that encountered for the attribution of the corresponding adiabatic IEs in the case of the formyl radical,  $\text{FCO}^\bullet$  did not directly lead to the assignment of the adiabatic IE. This IE was predicted at a value of  $8.76 \pm 0.32$  eV by SCF calculations,<sup>253</sup> and this is the later estimated value that has been used to derive the heat of formation of the cation  $\text{FCO}^+$ ,  $\Delta_f H_{298}^0(\text{FCO}^+) = 160 \pm 12$  kcal/mol. However, the interpretation of a single bending progression in the experimental PE spectrum to account for the observed bands in the 10–12 eV region and the correlated attribution of the vertical IE at 11.26 eV<sup>253</sup> have been questioned. In fact, additional ab initio calculations on the PE spectrum involving the ground states of  $\text{FCO}^+$  and  $\text{FCO}^\bullet$ <sup>254</sup> have led to an estimated value for the vertical IE of 10.93 eV, 0.33 eV lower than the experimental value reported at 11.26 and 0.54 eV lower than the calculated value of Dyke et al.<sup>253</sup> Buckley and co-workers reported the PI spectrum of  $\text{FCO}^\bullet$ <sup>255</sup> and proposed an upper limit of 9.7 eV for its experimental adiabatic IE. The measured vertical IE was reported at  $11.16 \pm 0.03$  eV, in very good agreement with a calculated value at 11.15 eV using a Gaussian procedure, which is surprising considering the energy of the ion at the geometry of the neutral. The adiabatic IE was calculated at  $9.30 \pm 0.10$  eV. From the data obtained by photoionization of  $\text{CF}_2\text{O}$ , the following quantities have been derived:  $\Delta_f H_{298}^0(\text{FCO}^+) = 178.1 \pm 2.3$  kcal/mol,  $\Delta_f H_0^0(\text{FCO}^\bullet) = 36.5$  kcal/mol and  $\text{DH}_{298}(\text{F}-\text{CO}) = 28.9 \pm 2.9$  kcal/mol.<sup>255</sup>

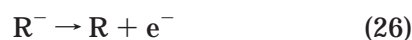
**Others.** Few inorganic radicals have been investigated by REMPI experiments, which provided measured or estimated adiabatic IEs from the origin of the observed Rydberg series. The adiabatic IE of aluminum monofluoride has been reported at  $9.729 \pm 0.001$  eV<sup>256</sup> in good agreement with the measured PES value at  $9.73 \pm 0.01$  eV.<sup>257</sup> The adiabatic IE of the short-lived indium monochloride  $\text{InCl}$  has been extrapolated at  $9.60 \pm 0.08$  eV.<sup>258</sup> From the REMPI study of new Rydberg states of the phosphorus dichloride  $\text{PCl}_2$ , ab initio calculations predicted an adiabatic IE at 8.51 eV.<sup>259</sup> The electronic absorption spectrum of the boron difluoride radical  $\text{BF}_2$  has recently been reported by Atkinson et al.<sup>260</sup> with estimated IEs of 8.66 and 10.44 eV for the adiabatic and vertical values.

Kruppa and Beauchamp<sup>261</sup> reported a PES investigation of the adamantane-derived radicals generated from pyrolysis of 1- and 2-adamantylmethyl nitrite. The corresponding adiabatic and vertical IEs are  $6.21 \pm 0.03$  and  $6.36 \pm 0.05$  eV for the 1-adamantyl radical and  $6.73 \pm 0.03$  and  $6.99 \pm 0.05$  eV for the 2-adamantyl radical, respectively. From the measured IEs, from gas-phase experimental heat of reaction for the hydride transfer, and from the derived heat of formation of the *tert*-butyl radicals

$C_4H_9$ ,<sup>143</sup> the absolute value for the tertiary C–H  $DH_{298}$  in adamantane was derived at  $98.5 \pm 1.5$  kcal/mol, ca. 3.7 kcal/mol greater than in isobutane. These results tended to confirm that more strains than expected appeared in the adamantane radical structure resulting from the distortion in the tetrahedral ring system, and a stronger preference for planarity can be expected for alkyl radicals.<sup>261</sup> From comparison of estimated heat of formation reported in the literature for adamantane, the authors recommended a value of  $\Delta_f H_{298}^0(\text{adamantane}) = -31.6 \pm 0.6$  kcal/mol. For the calculation of the heat of formation of the corresponding cation  $C_{10}H_{15}^+$ , the authors concluded that the failure of the group additivity method in this particular case was due to the underestimated influence of the substantial energy strain in structures used for this calculation, namely, 1-adamantyl chloride or 1-adamantyl bromide. They recommended a value of  $\Delta_f H_{298}^0(C_{10}H_{15}^+) = 158 \pm 3$  kcal/mol.<sup>261</sup>

### C. Negative Ion Photodetachment Studies: Electron Affinity Measurements

The previous section, devoted to photoionization techniques, introduced a positive ion cycle to derive thermochemical data relative to radicals or corresponding cations. Similarly, a negative ion cycle can be used to derive bond energies if relative values are known for electron affinity of the radical R and for the acidity of the compound RH.<sup>14,15,16,71,262</sup> The negative ion cycle is then expressed as follows, eqs 24–26:



where the corresponding enthalpies of the reactions 24, 25, and 26 represent the acidity of the compound RH, the IE of hydrogen and the EA of the radical R, respectively. The energy of the bond R–H,  $DH_{298}(R-H)$ , can then be expressed by eq 27:

$$DH_{298T}(R-H) = \Delta_{\text{acid}} H^0(RH) - IE(H) + EA(R) \quad (27)$$

and be corrected at 0 K to give the quantity  $D_0(R-H)$  since the quantity  $\Delta_{\text{acid}} H^0$  is generally measured at room temperature, contrary to the IE and EA, which are 0 K measurements. In addition, if some absolute values exist, as is the case for the electron affinities of halogen atoms which are known with great accuracy, the relative data can be put on an absolute basis. Obviously, reliable data on  $DH_{298}$  can be expected only if independent and precise measurements of both EA and  $\Delta_{\text{acid}} H^0$  are available, since any error in one of these quantities would be propagated into the derived  $DH_{298}$  value.

The negative ion cycle described in eqs 24–26 was used to provide the C–H bond enthalpies  $DH_{298}$  of fundamental organic compounds such as methane, ethylene, acetylene, and benzene<sup>71</sup> and has been extended to radicals, especially when the correspond-

ing stable anions can be generated to target the R–H bond energy. To illustrate this point, alkoxide anions are certainly among the most striking examples since  $DH_{298}(RO-H)$  of alcohols can be accurately extracted from EA and gas-phase  $\Delta_{\text{acid}} H^0$  determinations as will be discussed below.

Among the experimental techniques used, negative ion photodetachment studies have provided precise measurements of EAs if correct assignment of the observed vibrational and electronic origin transition in the experimental PE spectrum can be obtained. As a consequence, this technique has been extensively used to gain information on the structure of ground and excited states of radicals<sup>17,71</sup> and is particularly suited for the investigation of neutral free radicals since open-shell systems have in general positive EAs. In addition, negative ion photoelectron spectroscopy appears to be very efficient to probe systems in which the anion is stable to rearrangement but the corresponding neutral is not (with a lifetime in the low picosecond range). The development of accurate calculation methods permits much more detailed pictures of bonding in both the anion and the radical resulting from the electron detachment.<sup>71</sup> They have been used to complete the PE spectra which suffer from limited numbers of vibrational active modes mainly corresponding to the total symmetric modes of the radical which make the extraction of geometrical information difficult. These results will be tentatively compiled here.

#### 1. Alkyl and Unsaturated Aliphatic Radicals

**Methyl  $CH_3^-$ .** Investigations on alkyl anions are greatly perturbed by the experimental difficulties encountered in generating them in a sufficient quantity to study their properties and perform thermochemical measurements.<sup>263</sup> The standard mass spectrometric methods including chemical ionization or dissociative electron attachment failed to generate larger alkyl anions than the experimentally detected methyl anion  $CH_3^-$ .<sup>264</sup> Theoretical studies have shown that ab initio calculations on energy and structures of anions may present some problems if uncorrect functions or basis sets are used<sup>265</sup> as well as for the derived acidities.<sup>266</sup> EAs of several alkyl anions have been predicted to be negative, from which one induces that, in the absence of a kinetic barrier to electron detachment, these anions would not be expected to exist as a long-lived isolated species and would therefore not be detected. Gas-phase acidity studies of alkanes using trimethylsilyl derivatives as precursors to generate the anions have predicted negative EAs for alkyl radicals from ethyl to *tert*-butyl, and isobutyl was the first radical of this series showing a slightly positive value (0.8 kcal/mol).<sup>267</sup> Graul and Squires,<sup>263</sup> using the technique of collision-induced decarboxylation of alkanate ions, failed to generate low homologues of the alkyl anions except  $CH_3^-$  during their experiments. They observed that only the neopentyl carboxylate anion, among the acyclic  $C_2$ – $C_4$  carboxylate precursors dissociated by CID, provided a long-lived neopentyl anion ( $\tau > 25 \mu\text{s}$ ), suggesting at the same time that a stabilizing  $\beta$ -substitution effect makes it possible to counterbal-

ance the destabilizing inductive effect of the  $\alpha$ -alkyl substituents which are thought to account for the instability of the  $C_2$ – $C_4$  alkyl anions and their consequent low acidity.<sup>267</sup> Experimental determination of the EA of methyl radical by PES has led to a value of  $EA(CH_3^\bullet) = 0.08 \pm 0.03$  eV,<sup>264</sup> and the geometry of the corresponding carbanion has been assigned to be pyramidal. Methyl radical was confirmed to be planar from both experimental and computed PES with a potential inversion barrier considered to be less than ca. 0.4 kcal/mol if any.<sup>264</sup>

**Vinyl  $C_2H_3^\bullet$ .** Combining negative ion photoelectron spectroscopy (NIPES) and gas-phase proton-transfer kinetic measurements, Ervin et al.<sup>268</sup> investigated the vinylidene radical anion and measured the EA of the vinyl radical,  $EA(C_2H_3^\bullet) = 0.667 \pm 0.024$  eV, as well as its gas-phase acidity with a molar Gibbs energy value,  $\Delta_{acid}G_{298}^0(C_2H_3^\bullet) = 377.6 \pm 3.1$  kcal/mol. Experimental values of EA and  $\Delta H_{acid,298}^0$  were first used to determine  $R-H$   $DH_{298}(C_2H_3-H)$  in a thermochemical cycle identical to that expressed in eq 27, and afterward to derive the heat of formation for the vinyl radical. The derived value for the first C–H bond in ethylene is  $D_0(C_2H_3-H) = 109.7 \pm 0.8$  kcal/mol in excellent agreement with the value later reported from PI experiments (Table 2). As noted in the preceding section, unsaturated aliphatic radicals and the reported values for the  $DH_{298}$  of the first C–H bond in ethylene were quite disperse with one set of values averaged at ca. 105 kcal/mol, while the other set is averaged at ca. 110 kcal/mol. The recommended value was finally given at  $109.7 \pm 0.8$  kcal/mol.<sup>14</sup> The combined experiments of Ervin et al.<sup>268</sup> showed that, if the lower set of values were considered for the  $D_0(C_2H_3-H)$ , the correlated EA of the vinyl radical might have been 0.46 eV rather than the 0.667 eV experimentally measured by NIPES. This 0.46 eV value was nevertheless not compatible with the observed ion–molecule reactions between vinylidene anion  $C_2H_3^-$  and molecular oxygen under flow-tube conditions, as well as the gas-phase acidity measured for ethylene at 401 kcal/mol was not in accordance with the 105 kcal/mol range for the bond energy and would necessitate lowering the acidity of ethylene from about 5 kcal/mol, which is unacceptable in view of the experimental error assumed in flow-tube measurements. These combined experiments provided a good example of the capabilities offered by using complementary techniques to derive thermochemical data in good agreement with PI data for a case of study at the very least quite controversial.<sup>14</sup>

**Ethynyl  $C_2H^\bullet$ .** In the course of their experiments, the same authors<sup>268</sup> reported an upper value for the acidity of the ethynyl radical,  $\Delta_{acid}G_{298}^0(C_2H^\bullet) > 341.5 \pm 1.9$  kcal/mol, and an EA of  $2.969 \pm 0.010$  eV. Similar to the case of ethylene, the experimental  $DH_{298}$  values of acetylene are controversial ranging between 127 and 133 kcal/mol at the time when this work was published.<sup>268</sup> The reported value of  $D_0(C_2H-H) = 131.3 \pm 0.7$  kcal/mol, in disagreement with previously measured low range values, refined the preceding  $DH_{298}$  reported at  $130.4 \pm 5$  kcal/mol<sup>269</sup> from the derivation of data from eq 27 and was revealed to be in very good agreement with the value

of  $131.1 \pm 0.7$  kcal/mol which was derived from photoion-pair formation experiments.<sup>270</sup> The determined value for the EA was in very good agreement with the PES value measured by Ervin and Lineberger,<sup>271</sup>  $EA(C_2H^\bullet) = 2.969 \pm 0.006$  eV. Recently, Taylor and co-workers<sup>272</sup> using negative PES reported a slightly lower value,  $EA(C_2H^\bullet) = 2.956 \pm 0.020$  eV, but without any further discussion. Their negative PES study provided the first measurements for EA of  $C_4H^\bullet$ ,  $C_6H^\bullet$ , and  $C_8H^\bullet$  radicals at  $3.558 \pm 0.015$ ,  $3.809 \pm 0.015$ , and  $3.966 \pm 0.010$  eV, respectively.<sup>272</sup>

**Vinylidene  $H_2CC^\bullet$ .** Ervin and co-workers<sup>273</sup> reported an experimental value for the EA of the ground-state vinylidene radical at  $0.490 \pm 0.006$  eV. The singlet–triplet splitting between the ground-state  $X^1A_1$  and the triplet state  $^3B_2$  was measured for the first time at  $47.60 \pm 0.14$  kcal/mol. A derived value for the second C–H bond energy in the vinyl radical is reported at  $80.0 \pm 5.0$  kcal/mol in accordance with the quantity  $D_0(H_2CC-H) = 81.0 \pm 3.5$  kcal/mol given by Ervin and co-workers.<sup>268</sup> The enthalpy change for the acetylene–vinylidene isomerization reaction using this derived value was calculated at  $46.4 \pm 5.5$  kcal/mol, questioning a larger value based on arguments used for bond additivity rules.<sup>274</sup>

**Propargyl  $C_3H_3^\bullet$ .** Two NIPES studies have reported measurements of the EA of the propargyl radical.<sup>275,276</sup> The first study reported  $0.893 \pm 0.025$  eV for the EA of a propargyl radical  $C_3H_3^\bullet$  with a planar acetylene-like structure ( $X^2B_1$  ground-state).<sup>275</sup> The large Franck–Condon envelope observed in the photodetachment spectrum was interpreted as characteristic of a large geometrical change between the anionic structure, assumed to be allenic  $CH_2=C=CH^-$ , and the  $\bullet CH_2C\equiv CH$  radical structure. An upper limit of 2.60 eV was attributed to the  $CH_3CC^\bullet$  radical structure. The EA value for the  $\bullet CH_2C\equiv CH$  radical was refined at  $0.918 \pm 0.008$  eV from the NIPES study of the allenyl anion  $CH_2=C=CH^-$ , but with no distinction between the acetylene-like and allene-like radical structures. The EA of the  $CH_3CC^\bullet$  radical structure was determined at  $2.718 \pm 0.008$  eV from the spectrum of the 1-propynyl  $CH_3CC^-$  anion.<sup>276</sup> This later study provided derived  $DH_{298}$ 's for both  $H-CH_2CCH$  and  $CH_3CC-H$  structures (but neglecting the EA conversion from 0 to 298 K), with  $DH_{298}(H-CH_2CCH) = 90.3 \pm 3$  kcal/mol and  $DH_{298}(CH_3CC-H) = 130.2 \pm 3$  kcal/mol.<sup>276</sup>

**Allyl and 2-Methyl Allyl Radicals.** The EA of the allyl radical was first measured by Zimmerman and Brauman<sup>277</sup> by electron photodetachment spectroscopy combined with ICR mass spectrometry. The reported value,  $EA(C_3H_5^\bullet) = 0.550 \pm 0.054$  eV, was expected to correspond to a ground-state to ground-state transition, even if it was considered possible that the rapid increase in the relative cross-section of the allyl anion was due to an electronic transition in the anion followed by autodetachment. However, the shape of the threshold in the photodetachment spectrum led the authors to consider their value as an upper limit associated with a value bracketed between 0.529 and 1.06 eV. Combined fits of the theoretical and experimental curves provided the

above EA value. Oakes and Ellison<sup>278</sup> later measured a lower value at  $0.362 \pm 0.020$  eV by PES of the allylic anion. Resolution of the PE spectrum is, however, not good enough to resolve the observed vibrational structures in order to avoid misleading assignments. Taking into account gas-phase reaction data on the allylic anion, and more especially the exothermicity of the reaction of allylic anion with molecular oxygen, the authors bracketed their EA affinity value between 0 and 0.44 eV. Comparing the experimental data to that deduced from a negative ion thermochemical cycle which would lead to an EA value of 0.38 eV, they reported a raw value of 0.362 eV corrected for rotational and spin-orbit contributions at 0.020 eV.<sup>278</sup> They computed a value of  $39.3 \pm 0.8$  kcal/mol for the heat of formation of the allyl radical. The structure of the allyl anion is attributed to a planar  $C_{2v}$  geometry where only the vibronic in-plane skeletal bending of the allyl radical is observed.<sup>278</sup> Wenthold and co-workers<sup>279</sup> corrected the previous EA value during their NIPES study of the allyl and 2-methyl anions. They reported a value of  $0.481 \pm 0.008$  eV attributed from a better-resolved PE spectrum dominated by a single vibrational progression assigned to the CCC bending mode of the allyl radical previously observed by Oakes and Ellison.<sup>278</sup> Two weaker modes attributed to a mixing of stretching, scissoring, and rocking modes of the CCC and  $CH_2$  group in the allyl radical as well as a  $CH_2$  out-of-plane bending mode were reported. The discrepancies between the previous EA value<sup>278</sup> and that measured by NIPES experiments<sup>279</sup> are attributed to the way of formation of the allylic anion (discharge ion source) generating vibrationally excited ions and could be explained by a wrong attribution of the origin band in the NIPES spectrum. This band is tentatively assigned to a transition from a  $\nu = 2$  level of the CCC bend mode of the anion to a  $\nu = 0$  level in the radical. Measured EA for the allyl and 2-methyl allyl radicals are used to derive the bond energies in propene and 2-methyl propene with the following quantities:  $DH_{298}(CH_2CHCH_2-H) = 88.8 \pm 0.4$  kcal/mol and  $DH_{298}(CH_2C(CH_3)CH_2-H) = 88.3 \pm 2.3$  kcal/mol, which are sufficiently similar to make Wenthold et al.<sup>279</sup> conclude in an ineffective methyl substitution in position 2 to stabilize the corresponding anion.

**Others.** Zimmermann and co-workers<sup>280</sup> reported electron photodetachment cross-section measurements for the pentadienyl and heptatrienyl anions for which the lowest  $\pi-\pi^*$  transition is expected to be easily characterized especially due to its pronounced red shift increased by conjugation in the systems. The corresponding EA values are  $EA(C_5H_7^-) = 0.91 \pm 0.03$  eV and  $EA(C_7H_9^-) = 1.27 \pm 0.03$  eV.

NIPES investigation of several  $C_7H_7^-$  anion precursors generated by deprotonation reaction with amide or hydroxide anions was reported by Gunion et al.,<sup>281</sup> and the corresponding EAs were measured. It appeared from the experimental PE spectrum observed for the quadricyclanide anion that two undiscernible isomeric structures resulting from deprotonation in position 1 or 2 in the quadricyclane occurred, resulting in no definite assignment of the EAs for each of the corresponding radicals. The  $C_1$

deprotonation position was, however, suggested to provide the lower EA value. Comparatively, the norbornadiene deprotonates at only one position through reaction with the amide anions. In the absence of any gas-phase reactivity data with a strong base, the position from which the 1,6-heptadiene was deprotonated has not been experimentally determined, deprotonation was proposed to appear at the carbon end or at the  $C_3$  position leading to an acetylide-like anion or an allenyl anion, respectively. The PE spectrum for the cycloheptatriene was complicated by the presence of linear forms of the anion  $C_7H_7^-$ , with at least three products resulting from deprotonation reactions. Only the cycloheptatrienyl radical structure is unambiguously assigned with an EA of 0.39 eV.<sup>281</sup>

## 2. Aromatic Radicals

**Phenyl  $C_6H_5^\bullet$ .** In the course of their studies of small organic rings by PES for which the only previous study dealt with ortho-benzyne,<sup>282</sup> Gunion et al.,<sup>283</sup> in the extending their work to fully aromatic systems, reported an EA of  $0.960 \pm 0.006$  eV for the phenyl radical, correcting the derived values calculated at 1.1 eV from acidity measurements.<sup>284</sup> The PE spectrum of the phenide anion  $C_6H_5^-$  generated from the reaction of benzene with fluorine atoms could not avoid the presence of the benzyne anion as a contaminant in the phenide anion hot band region precluding the exact determination of vibrational frequencies. However, two active vibrational modes were found at 600 and 968  $cm^{-1}$  in the experimental spectrum and tentatively assigned to possible active modes in the  $A_1$  symmetry of the phenide anion with the support of ab initio calculations. From the complex PE spectrum obtained, it was clearly revealed that a ring distortion was observed upon conversion from the anion to the radical and the calculated normal modes for the possible peak positions associated with this distortion were in good agreement with experimental values. Nevertheless, deuteration of the benzene precursor could not permit the absolute identification of the higher frequency mode observed at 968  $cm^{-1}$  in the  $C_6H_5^-$  PE spectrum. From the reported  $DH_{298}$  of the C-H bond in  $C_6H_6$ ,<sup>5</sup> a value for the  $\Delta_{acid}H_{298}^\circ$  of benzene was derived at  $399 \pm 2$  kcal/mol.<sup>283</sup>

**Benzyl  $C_7H_7^\bullet$ .** The same authors<sup>283</sup> reported an EA value of  $0.912 \pm 0.006$  eV for the benzyl radical  $C_7H_7^\bullet$ . This value must be compared with the previous data obtained by photodetachment experiments using ICR mass spectrometry with EA values reported at  $0.88 \pm 0.06$  eV<sup>285</sup> and  $0.86 \pm 0.01$  eV.<sup>286</sup> No discussion was provided on the observed discrepancies. Comparison of the substituent effect led Gunion and co-workers<sup>283</sup> to consider that the electron pair was localized on the substituent if one compares the EA value for the benzyl radical to that of the heptatrienide  $C_7H_9^-$  radical at 1.27 eV for which a fully conjugated  $\pi$  system is implicated with an electron pair contribution in this conjugation. In addition, the ring was thought to have a large stabilizing effect on the lone pair, as proven by the comparison of EAs of  $C_7H_7^\bullet$  with those derived for the alkyl radicals, which do



not have any conjugated system as in the case of ethyl,  $EA(C_2H_5^\bullet) = -0.26$  eV, or propyl radicals,  $EA(C_3H_7^\bullet) = -0.07$  eV.<sup>267</sup>

**Cyclopentadienyl, Methylcyclopentadienyl, Indenyl, and Fluorenyl Radicals.** The upper limit for the EA of the cyclopentadienyl radical  $C_5H_5^\bullet$  was first reported by Richardson et al.<sup>287</sup> with a value of  $1.84 \pm 0.03$  eV. This EA value has been more recently corrected to  $1.786 \pm 0.02$  eV by Engelking and Lineberger,<sup>288</sup> and then confirmed at  $1.789 \pm 0.047$  eV by McDonald and co-workers.<sup>289</sup> In this latter experiment, the authors used a flowing afterglow source known to provide rotational and vibrational relaxation of the precursor ions. Consequently, they explained their 0.003 eV difference compared to the previous PES value of Engelking and Lineberger by way of the elimination of hot band intensities which were reduced at the noise level in their resolved spectrum.

Indenyl and fluorenyl radicals have been investigated using ICR laser photodetachment spectroscopy,<sup>290</sup> providing the only experimental measurements for their EAs at  $1.853 \pm 0.014$  and  $1.864 \pm 0.014$  eV, respectively. From the values of EAs of the three radicals pentadienyl  $C_5H_5^\bullet$ , indenyl  $C_9H_7^\bullet$ , and fluorenyl  $C_{13}H_9^\bullet$ , the process of electron photodetachment in the gas-phase has been compared to its solution-phase electrochemical oxidation counterpart in DMSO, each process leading in both cases to the conversion of a closed-shell anion into a radical upon the loss of one electron. Trends are shown to be reversed between the gas-phase and the condensed-phase for the series and mainly reveals the magnitude of solvation effects.<sup>290</sup>

### 3. Oxygen-Containing Radicals

**Methoxy  $CH_3O^\bullet$ .** Oxygen-containing radicals are one class of radicals that have been among the most studied by electron photodetachment methods.<sup>71</sup> One reason might be related to the fact that alkoxide anions are stable and quite easy to characterize at the opposite to alkoxide cations. Consequently, the reliability in extracted values for RO–H bond energies is good when EAs data are combined to gas-phase acidity measurements.

Reed and Brauman<sup>291</sup> were the first to show the applicability of photodetachment experiments to measure EAs of alkoxy radicals using ICR mass spectrometry. This study provided an upper limit value of  $1.591 \pm 0.039$  eV for the EA of the methoxy radical  $CH_3O^\bullet$ . This value was confirmed later using the same technique at  $1.59 \pm 0.04$  eV.<sup>292</sup> Engelking and co-workers<sup>293</sup> refined this value to  $1.570 \pm 0.022$  eV, establishing a  $CH_3O^-$  structure for the alkoxide precursor rather than a  $CH_2OH^-$  structure. More recently, Osborn et al.<sup>294</sup> reported a value of  $1.568 \pm 0.005$  eV for the EA of  $CH_3O^\bullet$  at a higher resolution level of experiments. At the same time, they reinterpreted the vibrational structures observed in the PE spectrum. The former attribution of the vibrational structure to the  $\nu_2$   $a_1$ -symmetry mode is considered to be only weakly active while the degenerate modes of e-symmetry are thought to account for the features of the PE spectrum of the methoxide<sup>294</sup> in accordance

with the degeneracy of the ground-electronic state of  $CH_3O^\bullet$  in its  $C_{3v}$  geometry configuration (which leads additionally to the Jahn–Teller dominant active modes<sup>295</sup>). Rotationally corrected measurements of the EAs of alkoxy radicals resulted to a value of  $1.572 \pm 0.004$  eV for  $EA(CH_3O^\bullet)$  reported by Ramond and co-workers using NIPES.<sup>295</sup> Values for the enthalpy of formation as well as the  $DH_{300}$  of the RO–H bond have been extracted from this experimental EA and gas-phase thermochemical data.<sup>296</sup> The value derived for the bond energy RO–H at 300 K (105.2 kcal/mol) was shown to be in a fairly good agreement with the value at 0 K reported by DeTuri and Ervin,<sup>296</sup>  $D_0(CH_3O-H) = 103.5 \pm 0.7$  kcal/mol, from threshold collision-induced dissociation experiments.

**Ethoxy and Hydroxy-Substituted Alkyl Radicals.** The first experimental values of the EAs of alkoxy radicals were compiled by Janousek and Brauman.<sup>297</sup> A few years later, Ellison et al.<sup>298</sup> reported the values of the EAs for the ethoxy radical  $CH_3CH_2O^\bullet$ , *n*-propoxy  $CH_3CH_2CH_2O^\bullet$ , 1-methyl ethoxy  $(CH_3)_2C(H)O^\bullet$ , and 1,1,1-trimethyl methoxy  $(CH_3)_3CO^\bullet$  radicals, respectively. The reported value for the EA of  $CH_3CH_2O^\bullet$  was  $1.726 \pm 0.033$  eV.<sup>297</sup> This value was corrected to  $1.715 \pm 0.007$  eV by Dang and co-workers,<sup>299</sup> but the derived  $DH_{298}$  value for the O–H bond is in very good agreement with the previous derived value from PES experiments. Recently, NIPES experiments<sup>295</sup> have conducted to a refined value,  $EA(CH_3CH_2O^\bullet) = 1.712 \pm 0.004$  eV and have permitted with the derived values for the  $DH_{298}$  and the enthalpy of formation at 300 K,  $DH_{300}(C_2H_5O-H) = 105.4 \pm 1.4$  kcal/mol and  $\Delta_f H_{300}^\circ(C_2H_5O^\bullet) = -2.9 \pm 1.7$  kcal/mol. This latter value was quite different from that reported by Ellison's group<sup>298</sup> and slightly smaller than the  $\Delta_f H_{298}^\circ$  value put forth by DeTuri and Ervin<sup>296</sup> at  $-3.3 \pm 1.2$  kcal/mol for the formation of the ethoxy radical. EAs values for the 1-methyl ethoxy  $(CH_3)_2C(H)O^\bullet$  and 1,1,1-trimethyl methoxy  $(CH_3)_3CO^\bullet$  radicals have been recently refined<sup>295</sup> as well as the derived  $DH_{298}$ 's and enthalpies of formation which are found to be in good agreement with the derived values of DeTuri and Ervin,<sup>296</sup> with values for  $\Delta_f H_{300}^\circ((CH_3)_2C(H)O^\bullet) = -11 \pm 1.2$  kcal/mol<sup>295</sup> vs  $-11.5 \pm 1.2$  kcal/mol<sup>296</sup> and for  $\Delta_f H_{300}^\circ((CH_3)_3CO^\bullet) = -19.8 \pm 1.2$  kcal/mol<sup>295</sup> vs  $-20.3 \pm 0.7$  kcal/mol,<sup>296</sup> respectively.

**Enolate Radicals.** PES experiments conducted by Ellison et al.<sup>298</sup> have established an EA value of  $1.817 \pm 0.023$  eV for the vinyloxy radical  $CH_2CHO^\bullet$ , which is in agreement with the value of  $1.824 \pm 0.005$  eV reported by Jackson and co-workers.<sup>300</sup> Both of these measurements confirmed the previous low-resolution value of  $1.808 \pm 0.06$  eV (upper value of  $1.834 \pm 0.06$  eV depending on the reaction used to generated the precursor enolate anion) determined by Zimmerman and co-workers.<sup>301</sup> The photoelectron study of the enolate anion  $C_2H_3O^-$  completed by ab initio calculations on the anion and the two lowest electronic states of the vinyloxy radical were carried out by Alconcel et al.<sup>302</sup> The major change between the anion and the neutral geometry was shown to be centered on the CC and the CO bonds as well as the CCO bond angle. Enolate anion provided photodetachment to

both the ground ( ${}^2A''$ ) and first excited ( ${}^2A'$ ) states of the radical, leading respectively to the  $\cdot\text{CH}_2\text{CHO}$  formyl methyl form when an electron is ejected from the HOMO nonbonding  $\pi$   $a''$  molecular orbital, and to the  $\text{CH}_2=\text{CHO}\cdot$  vinyloxy form when an electron is ejected from the oxygen  $\sigma(2p_x)$  orbital.<sup>302</sup> The peaks corresponding to the  ${}^2A'$  state in the simulation of the PE spectrum were however not observed in the experimental spectrum. The measured value reported for the EA was  $1.795 \pm 0.015$  eV, with an estimated value by ab initio calculations of 1.82 eV and attributed to the lowest excited state of the vinyloxy radical. The separation energy between the two states of the radical is reported at  $1.015 \pm 0.015$  eV,<sup>302</sup> a value slightly higher than that measured at 0.99 eV by Osborn and co-workers.<sup>303</sup>

The EAs for the 1-methyl vinyloxy  $\text{CH}_3\text{CH}=\text{CHO}\cdot$  and 2-methyl vinyloxy  $\text{CH}_2=\text{C}(\text{CH}_3)\text{O}\cdot$  radicals were reported by Ellison et al.<sup>298</sup> at  $1.611 \pm 0.023$  and  $1.757 \pm 0.033$  eV, respectively, in good agreement with the values previously reported by Zimmerman and colleagues.<sup>301</sup> The EA value for the 1-methyl vinyl radical was refined to  $1.617_5 \pm 0.008_7$  eV for the (*E*)-isomer by Römer and Brauman<sup>304</sup> with a complementary measured value of  $1.735 \pm 0.013$  eV for the (*Z*)-isomer, both generated from the reaction of fluoride anions with the corresponding trimethylsilyl enol ethers. The PE spectrum obtained from the enolate generated by deprotonation of the propionaldehyde was interpreted as resulting from a mixture of the two *Z* and *E* isomers. Similar experimental values for the (*E*)-isomer, and the previous EA measured by Ellison and co-workers<sup>297</sup> were in accordance with the assignment of the EA value to the (*E*)-enolate radical in this latter case.

EA of the acetyl radical was reported by Nimlos et al.<sup>305</sup> at  $0.423 \pm 0.037$  eV. The derived values for the heat of formation of the radical  $\text{CH}_3\text{CO}\cdot$  and the  $\text{DH}_{298}$  of the C–O bond at 298 K are reported at  $-5.4 \pm 2.1$  and  $10.6 \pm 2.2$  kcal/mol, respectively.

**Ethynyl Oxy HCCO $\cdot$ .** Oakes and co-workers<sup>306</sup> reported a NIPES study of the ethynyl oxy radical from the electron photodetachment of the  $\text{HCCO}^-$  anion generated from the ketene  $\text{CH}_2\text{CO}$  precursor. EA of the  $\text{HCCO}\cdot$  radical was measured at  $2.350 \pm 0.020$  eV, and the derived heat of formation  $\Delta H_{298}^\circ$  for the radical was reported at  $42.4 \pm 2.1$  kcal/mol. This latter value was refined by Mordaunt and colleagues<sup>307</sup> who put forward a 0 K value,  $\Delta H_0^\circ$  ( $\text{HCCO}\cdot$ ) =  $42.0 \pm 0.7$  kcal/mol.

**Peroxy Radicals.** Photoelectron spectroscopy of the  $\text{HO}_2^-$  anion has been reported by Oakes and co-workers,<sup>308</sup> giving an EA value for the corresponding hydroperoxy radical  $\text{HO}_2\cdot$  of  $1.078 \pm 0.017$  eV. This value was in good agreement with the deduced value from the flowing afterglow experiments of Bierbaum et al.<sup>309</sup> at 1.16 eV, corrected to 1.079 eV by reason of a change in the reference in acidity scale.<sup>93</sup> From the experimental EA value and the derived heat of formation of the  $\text{HO}_2^-$  anion, the preceding authors<sup>308</sup> derived a quantity  $\Delta_{\text{acid}}H_{298}^\circ$  ( $\text{H}_2\text{O}_2$ ) =  $376.4 \pm 0.6$  kcal/mol in accordance with the measured value corrected to  $375.6 \pm 2.1$  kcal/mol from the experiments of Bierbaum and co-workers.<sup>309</sup> The NIPES

study of the  $\text{HO}_2^-$  anion and the *tert*-butyl hydroperoxide anion  $(\text{CH}_3)_3\text{COO}^-$  reported by Clifford and associates<sup>310</sup> provided the EAs for the corresponding radicals,  $\text{EA}(\text{HO}_2\cdot) = 1.089 \pm 0.006$  eV and  $\text{EA}((\text{CH}_3)_3\text{COO}\cdot) = 1.196 \pm 0.011$  eV, respectively.

#### 4. Sulfur-Containing Radicals

The cross-section for electron photodetachment from the  $\text{HS}^-$  anion was measured by Janousek and Brauman,<sup>311</sup> providing a value of  $\text{EA}(\text{HS}\cdot) = 2.314 \pm 0.003$  eV, confirmed by the value published by Breyer and coauthors<sup>312</sup> of  $2.317 \pm 0.002$  eV. Recently, Shiell et al.<sup>313</sup> used a value of 2.315 eV for the reported bond dissociation energy  $D_0(\text{H}-\text{SH}) = 89.9 \pm 0.01$  kcal/mol resulting from threshold ion-pair spectroscopy measurement. No data are available for the thioformyl radical  $\cdot\text{CHS}$  and only one PES study on the thioformaldehyde transient species has provided an EA value, which is  $\text{EA}(\text{CH}_2\text{S}) = 0.465 \pm 0.023$  eV.<sup>314</sup> The first electron photodetachment study reporting an experimental value for EA of the methylthio radical  $\text{CH}_3\text{S}\cdot$  was published by Engelking and co-workers,<sup>293</sup> with  $\text{EA}(\text{CH}_3\text{S}\cdot) = 1.882 \pm 0.024$  eV. The same study reporting experiments on the methoxy radical  $\text{CH}_3\text{O}\cdot$  permitted one to report striking differences in both experimental PE spectra with different sets of vibrations implicating mostly the C–S modes for the methylthio radical in detriment to the S–H modes. The previous value for the EA of the methylthio radical has been corrected by two different studies using ICR mass spectrometry and PES. Janousek and colleagues<sup>315</sup> reported a value of  $1.861 \pm 0.004$  eV, while Moran and Ellison<sup>316</sup> measured an EA of  $1.871 \pm 0.012$  eV. Within the experimental error bars, these values are in good agreement. The presence of several vibronic transitions revealed in the threshold region in the measurement of the electron photodetachment cross-section and the low resolution of the apparatus used in the first report could explain the discrepancy between the last set of two values and the value reported by Engelking and co-workers<sup>293</sup> at 1.882 eV, which can reasonably be considered the upper limit. The derived value for the  $\text{DH}_{298}$  of the S–H bond was reported at  $88.1 \pm 2$  kcal/mol.<sup>315</sup> This value was 0.19 kcal/mol weaker than the corresponding S–H bond in the deuterated  $\text{CH}_3\text{-SD}$  homologue. This difference was thought to provide evidence for a  $\beta$  secondary deuterium isotope effect acting on the donation features between filled  $p$  orbital on sulfur and filled and unfilled  $\pi, \pi^*$  molecular orbital respectively in the methyl group.<sup>315</sup> The thiomethyl anion  $\text{CH}_2\text{SH}^-$  was studied in a variable-temperature flowing afterglow mass spectrometer by Kass et al.,<sup>317</sup> providing the only experimentally derived value for the EA of the mercapto-methyl radical  $\cdot\text{CH}_2\text{SH}$  of  $0.67 \pm 0.13$  eV. EAs of the ethylthio  $\text{C}_2\text{H}_5\text{S}\cdot$ , *n*- and isopropylthio  $\text{C}_3\text{H}_7\text{S}\cdot$ , *n*- and isobutylthio  $\text{C}_4\text{H}_9\text{S}\cdot$ , as well as the pentylthio  $\text{C}_5\text{H}_{11}\text{S}\cdot$  radicals were reported by Janousek's group<sup>315</sup> in the 2.00–2.09 eV range with no other complementary experimental determinations except for the ethylthio radical. The two experimental values for this latter radical are in fairly good agreement with an EA first measured at  $1.953 \pm 0.006$  eV<sup>315</sup> and later confirmed at  $1.947 \pm 0.013$  eV.<sup>316</sup> In addition, the later study

provided the EAs for the methylthiomethyl  $\text{CH}_3\text{SCH}_2\cdot$  and the methylthio  $\text{CH}_3\text{SS}\cdot$  radicals permitting assessment of some trends in the variation of the EA, depending on the substituents, and also comparison of these trends with those of the oxygenated analogues  $\text{RO}\cdot$ . For the anions scrutinized, it appeared that adding a substituent to one of the sulfur atoms of the disulfur anions in the series  $\text{S}_2$ ,  $\text{HS}_2$ ,  $\text{CH}_3\text{S}_2$  led to increasing EA while decreasing the S–S stretching frequencies in the neutral. The effect of adding an alkyl substituent in the mono sulfur compounds thus decreasing their ability to bind an electron resulted in lower EAs, and the electron-donating nature of the alkyl groups was proposed to account for the destabilization of the counteranions. Comparison between EAs values of oxygen and sulfur analogues<sup>316</sup> led to the conclusion that replacing an oxygen atom with a sulfur atom increases the EAs by a few tenths of eV,  $\text{EA}(\text{CH}_3\text{X}\cdot) = 1.570$  vs  $1.871$  eV,  $\text{EA}(\text{C}_2\text{H}_5\text{X}\cdot) = 1.726$  vs  $1.947$  eV (for  $\text{X} = \text{O}$  and  $\text{S}$ , respectively). This trend was considered to result from the stabilization of the relative anion due to the location of the extra electron in a larger 3p-valence shell in the sulfur atom, thus minimizing unfavorable interactions.<sup>316</sup> Comparison of vibration frequencies showed that both R–X and X–X types are lower for the sulfur species ( $\text{R} = \text{H}$ ,  $\text{CH}_3$ ;  $\text{X} = \text{O}$ ,  $\text{S}$ ) with stretching frequencies decreased by about 30% when going from  $\text{X} = \text{O}$  to  $\text{X} = \text{S}$  due almost entirely to the shorter bond length and higher bond strengths in the O–H bonds.<sup>316</sup>

### 5. Nitrogen-Containing Radicals

**Azide, Imidogen, and Amino Radicals.** The azide radical  $\text{N}_3\cdot$  was first studied by Jackson and colleagues,<sup>318</sup> who reported the formation of the azide anion  $\text{N}_3^-$  in the gas-phase using double resonance experiments in an ICR mass spectrometer with azidotrimethylsilane as a precursor. Two thresholds were observed in the corresponding electron photodetachment spectrum with the lowest energy onset attributed to photodetachment from the trimethylsilylnitrene precursor anion, and even if the authors could not preclude the formation of hot azide anions under the experimental conditions, they reported the first EA value of  $\text{EA}(\text{N}_3\cdot) = 2.70 \pm 0.12$  eV. Illenberger et al.<sup>319</sup> put forward the formation of the azide anion by dissociative electron attachment to benzyl azide precursor molecules. From this method, the azide anion was formed efficiently as a primary dissociation product. An EA of  $2.76 \pm 0.04$  eV was measured and correlated with a calculated value of 2.73 eV. The enthalpy of formation for the azide radical as well as the  $\text{DH}_{298}$  of the N–H bond were derived from this experiment (Table 3). Continetti and co-workers<sup>66</sup> presented a PES study of cold azide radicals generated in a similar way. The reported EA value corresponded however to a quantity lower by ca. 0.05–0.08 eV compared to the previously measured values.

Engelking and Lineberger<sup>320</sup> measured an EA of  $0.38 \pm 0.03$  eV for the imidogen radical  $\text{NH}\cdot$  and a rough energy difference of 1.579 eV between the two states  $^1\Delta - ^3\Sigma$ . In an original experiment, Neumark's

group<sup>321</sup> reported the first infrared vibration–rotation spectrum of the gas-phase negative ion  $\text{NH}^-$  based on the excitation of a vibrational level of the anion to induce autodetachment from this excited level. They deduced an upper bound of 0.374 eV for the EA with a given value of  $0.370 \pm 0.004$  eV.

The most recent measurement of the EA of the amino radical  $\cdot\text{NH}_2$  was performed by Wickham-Jones and co-workers<sup>322</sup> and yielded a refined value for the EA of  $\cdot\text{NH}_2$  of  $0.771 \pm 0.005$  eV compared to the previous electron photodetachment measurement of Smyth and Brauman,<sup>323</sup>  $\text{EA}(\cdot\text{NH}_2) = 0.744 \pm 0.022$  eV suffering from quite a large uncertainty. Using the value determined by PIMS for the enthalpy of formation of the amino radical at 45.8 kcal/mol (Table 2), they derived a heat of formation for the anion  $\text{NH}_2^-$ ,  $\Delta H_0^\circ(\text{NH}_2^-) = 28.0 \pm 0.4$  kcal/mol.<sup>322</sup>

**Methylene Amidogen  $\text{CH}_2\text{N}\cdot$  and Methyl Nitrene  $\text{CH}_3\text{N}\cdot$  Radicals.** Cowles and associates<sup>324</sup> reported a study of the PE spectrum of the negative anion  $\text{CH}_2\text{N}^-$  and found an EA value of  $0.511 \pm 0.008$  eV for the corresponding methylene amidogen radical  $\text{CH}_2\text{N}\cdot$ , refining the value established by Kass and DePuy<sup>325</sup> of around  $0.5 \pm 0.1$  eV. This experimental value permitted the derivation of the following thermochemical data:  $D_0(\text{CH}_2\text{N}-\text{H}) = 85 \pm 5$  kcal/mol and  $D_0(\text{H}-\text{CHN}\cdot) = 23 \pm 6$  kcal/mol.

An extensive study of the methyl nitrene ion was reported recently by Travers et al.<sup>326</sup> and has provided an EA value for the methylnitrene radical,  $\text{EA}(\text{CH}_3\text{N}\cdot) = 0.022 \pm 0.009$  eV. The methyl nitrene ion was generated from decomposition in the ion source of the methyl azide  $\text{CH}_3\text{N}_3$  precursor. The PE spectrum of methyl nitrene showed some resemblance to that of the imidogen precursor anion  $\text{NH}^-$  with two band systems separated by ca. 1.5 eV, assigned to detachment from triplet and singlet states of the  $\text{CH}_3\text{N}\cdot$  radical (the triplet–singlet splitting was measured at  $1.352 \pm 0.011$  eV). Substantial geometry changes were expected between the anion and both states of the nitrene radical in view of the features in the PE spectrum. However, lacking the possibility to synthesize an isotopically substituted analogue  $\text{CD}_3\text{N}\cdot$  of the nitrene radical, not knowing properties of the corresponding anion resulting from ab initio calculations, and in the absence of a good estimate of the Jahn–Teller distortion reasonably expected in the anion, a Franck–Condon analysis of the PE spectrum could not be conducted. In consequence, approximate geometries of the radical states must be assumed to be a  $\text{C}_{3v}$  geometry for the radical states, even if a break from  $\text{C}_{3v}$  to  $\text{C}_s$  geometry in the case of the triplet state  $^3\text{A}_2$  provided a good reproduction of the experimental trace of the corresponding band in the PE spectrum. This study was the first to provide by NIPES experiments the evidence for the detection of a non “persistent radical”, namely, the singlet nitrene state, which was thought too unstable for its detection because of a rapid rearrangement to an imine structure. The time scale of the photodetachment measurements seemed to permit the trapping of this metastable configuration on the “methylnitrene side” of the former rearrangement energy surface between the singlet  $^1\text{CH}_3\text{N}\cdot$  methyl-

**Table 3. Data Collected through EA Measurements**

radicals	EA (eV)	derived thermochemical quantities: $\Delta_{\text{acid}}H_0^\circ$ ; $\Delta_{\text{acid}}G_0^\circ$ ; $DH_{298}$ ; $D_0$ (kcal/mol)	ref
<b>Alkyl and Unsaturated Aliphatic</b>			
methyl $\text{CH}_3^\bullet$	$0.08 \pm 0.03$		264
vinyl $\text{C}_2\text{H}_3^\bullet$	$0.667 \pm 0.024$	$\Delta_{\text{acid}}G_{298}^\circ(\text{C}_2\text{H}_3^\bullet) = 377.6 \pm 3.1^a$ $D_0(\text{C}_2\text{H}_3\text{-H}) = 109.7 \pm 0.8$ $\Delta_f H_0^\circ(\text{C}_2\text{H}_3^\bullet) = 72.7 \pm 0.8$	268
ethynyl $\text{C}_2\text{H}^\bullet$	$2.969 \pm 0.010$	$\Delta_{\text{acid}}G_{298}^\circ(\text{C}_2\text{H}^\bullet) > 341.5 \pm 1.9$ $D_0(\text{C}_2\text{H-H}) = 131.3 \pm 0.7$ $\Delta_f H_0^\circ(\text{C}_2\text{H}_3^\bullet) = 134.3 \pm 0.7$	268
	$2.969 \pm 0.006$		271
	$2.956 \pm 0.020$		272
vinylidene $\text{H}_2\text{CC}^\bullet$	$0.490 \pm 0.006$	$D_0(\text{H}_2\text{CC-H}) = 80.0 \pm 5$ $D_0(\text{H}_2\text{CC-H}) = 81.0 \pm 3.5$ $\Delta_f H_0^\circ(\text{H}_2\text{CC}^\bullet) = 102.1 \pm 4.0$	273 268
$\text{C}_3\text{H}_3^\bullet$			276
$^\bullet\text{CH}_2\text{C}=\text{CH}$ (propargyl)	$0.918 \pm 0.008$	$DH_{298}(\text{H-CH}_2\text{C}=\text{CH}) = 90.3 \pm 3$ $DH_{298}(\text{CH}_2=\text{C}=\text{C-H}) = 88.7 \pm 3$	276
$\text{CH}_3\text{C}=\text{C}^\bullet$	$2.718 \pm 0.008$	$DH_{298}(\text{CH}_3\text{C}=\text{C-H}) = 130.2 \pm 3$	
allyl $\text{C}_3\text{H}_5^\bullet$	$0.550 \pm 0.054$		277
	$0.481 \pm 0.008$	$DH_{298}(\text{CH}_2\text{CHCH}_2\text{-H}) = 88.8 \pm 0.4$	279
2-methyl allyl $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}^\bullet\text{H}_2$	$0.505 \pm 0.006$	$DH_{298}(\text{R-H}) = 88.3 \pm 2.3$	279
pentadienyl $\text{C}_5\text{H}_7^\bullet$	$0.91 \pm 0.03$		280
heptatrienyl $\text{C}_7\text{H}_9^\bullet$	$1.27 \pm 0.03$		280
$\text{C}_4\text{H}^\bullet$	$3.558 \pm 0.015$		272
$\text{C}_6\text{H}^\bullet$	$3.809 \pm 0.015$		272
$\text{C}_8\text{H}^\bullet$	$3.966 \pm 0.010$		272
1-quadracyclanyl	0.868		281
2-quadracyclanyl $\text{C}_7\text{H}_7^\bullet$	0.962		
norbornadienyl $\text{C}_7\text{H}_7^\bullet$	1.286		281
cycloheptatrienyl $\text{C}_7\text{H}_7^\bullet$	$0.39 \pm 0.04$		280, 281
<b>Aromatic</b>			
phenyl $\text{C}_6\text{H}_5^\bullet$	$0.960 \pm 0.006$	$\Delta_{\text{acid}}H_{298}^\circ(\text{C}_6\text{H}_6) = 399 \pm 2$	283
benzyl $\text{C}_7\text{H}_7^\bullet$	$0.88 \pm 0.06$		285
	$0.86 \pm 0.01$	$DH_{298}(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 85.3 \pm 2.3$	286
	$0.912 \pm 0.006$	$\Delta_{\text{acid}}H_{298}^\circ(\text{C}_6\text{H}_5\text{CH}_2\text{-H}) = 380.5 \pm 1.5$	283
anilino $\text{C}_6\text{H}_5\text{NH}^\bullet$	$1.70 \pm 0.03$		286
cyclopentadienyl $\text{C}_5\text{H}_5^\bullet$	$1.786 \pm 0.02$		288
	$1.789 \pm 0.047$		289
		$DH_{298}(\text{C}_5\text{H}_5\text{-H}) = 81.5 \pm 2.7$	290
indenyl $\text{C}_9\text{H}_7^\bullet$	$1.853 \pm 0.014$	$DH_{298}(\text{C}_9\text{H}_7\text{-H}) = 81.1 \pm 2.4$	290
fluorenyl $\text{C}_{13}\text{H}_9^\bullet$	$1.864 \pm 0.014$	$DH_{298}(\text{C}_{13}\text{H}_9\text{-H}) = 81.2 \pm 2.4$	290
<b>Oxygen-Containing</b>			
methoxy $\text{CH}_3\text{O}^\bullet$	$< 1.59 \pm 0.04$		292
	$1.570 \pm 0.022$		293
	$1.568 \pm 0.005$		294
	$1.572 \pm 0.004$	$\Delta_f H_{300}^\circ(\text{CH}_3\text{O}^\bullet) = 5.0 \pm 1$ $DH_{300}(\text{CH}_3\text{O-H}) = 105.2 \pm 0.7$	295
ethoxy $\text{CH}_3\text{CH}_2\text{O}^\bullet$	$1.726 \pm 0.033$	$D_0(\text{C}_2\text{H}_5\text{O-H}) = 102 \pm 2$ $\Delta_f H_{298}^\circ(\text{C}_2\text{H}_5\text{O}^\bullet) = -6 \pm 2$	298
	$1.715 \pm 0.007$	$D_0(\text{C}_2\text{H}_5\text{-H}) = 102.2 \pm 2$	299
	$1.712 \pm 0.004$	$DH_{300}(\text{C}_2\text{H}_5\text{O}^\bullet) = 105.4 \pm 1.4$ $\Delta_f H_{300}^\circ(\text{C}_2\text{H}_5\text{O}^\bullet) = -2.9 \pm 1.7$	295
<i>n</i> -propoxy $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}^\bullet$	$1.789 \pm 0.033$		298
1-methyl, ethoxy $(\text{CH}_3)_2\text{C}(\text{H})\text{O}^\bullet$	$1.839 \pm 0.029$		298
	$1.847 \pm 0.004$	$DH_{300}((\text{CH}_3)_2\text{C}(\text{H})\text{O-H}) = 106.4 \pm 1$ $\Delta_f H_{300}^\circ((\text{CH}_3)_2\text{C}(\text{H})\text{O}^\bullet) = -11 \pm 1.2$	295
1,1,1-trimethyl, methoxy $(\text{CH}_3)_3\text{CO}^\bullet$	$1.912 \pm 0.029 - 0.05_4$		298
	$1.909 \pm 0.004$	$DH_{300}((\text{CH}_3)_3\text{CO}^\bullet) = 106.8 \pm 1$ $\Delta_f H_{300}^\circ((\text{CH}_3)_3\text{CO}^\bullet) = -19.8 \pm 1.2$	295

Table 3 (Continued)

radicals	EA (eV)	derived thermochemical quantities: $\Delta_{\text{acid}}H_0^\circ$ ; $\Delta_{\text{acid}}G_0^\circ$ ; $DH_{298}$ ; $D_0$ (kcal/mol)	ref
<b>Oxygen-Containing</b>			
vinyloxy $C_2H_3O^\bullet$	1.817 $\pm$ 0.023		298
	1.824 $\pm$ 0.005		300
	1.795 $\pm$ 0.015		302
1-methyl,vinyloxy $CH_3CH=CHO^\bullet$	1.611 $\pm$ 0.023		298
	1.687 $\pm$ 0.052		301
	1.617 <sub>5</sub> $\pm$ 0.008 <sub>7</sub>		304
2-methyl,vinyloxy $CH_2=C(CH_3)O^\bullet$	1.757 $\pm$ 0.033		298
	1.761 $\pm$ 0.056		301
acetyl $CH_3C^\bullet=O$	0.423 $\pm$ 0.037	$\Delta_f H_{298}^\circ(CH_3C^\bullet O) = -5.4 \pm 2.1$ $DH_{298}(CH_3-C^\bullet O) = 10.6 \pm 2.2$	305
ethynyl oxy $HC=CO^\bullet$	2.350 $\pm$ 0.020	$\Delta_f H_{298}^\circ(HC=CO^\bullet) = 42.4 \pm 2.1$	306
		$\Delta_f H_0^\circ(HC=CO^\bullet) = 42.0 \pm 0.7$	307
hydroperoxo $HO_2^\bullet$	1.078 $\pm$ 0.017	$\Delta_{\text{acid}} H_{298}^\circ(H_2O_2) = 376.4 \pm 0.6$	308
	1.089 $\pm$ 0.006		310
tertbutyl peroxide $(CH_3)_3COO^\bullet$	1.196 $\pm$ 0.011		310
phenoxy $C_6H_5O^\bullet$	2.253 $\pm$ 0.006	$\Delta_{\text{acid}} H_{298}^\circ(C_6H_5O-H) = 348.5 \pm 2$	283
<b>Sulfur-Containing</b>			
mercapto $SH^\bullet$	2.314 $\pm$ 0.003		311
	2.317 $\pm$ 0.002		312
		$D_0(H-SH) = 89.9 \pm 0.01$	313
methylthio $CH_3S^\bullet$	1.882 $\pm$ 0.024		293
	1.861 $\pm$ 0.004	$D_0(CH_3S-H) = 88.1 \pm 2$	315
	1.871 $\pm$ 0.012	$D_0(CH_3S-H) = 88.3 \pm 2$	316
ethylthio $C_2H_5S^\bullet$	1.953 $\pm$ 0.006		315
	1.947 $\pm$ 0.013	$D_0(CH_3CH_2S-H) = 88.9 \pm 2$	316
methylthiomethyl $CH_3SCH_2^\bullet$	0.868 $\pm$ 0.051	$D_0(CH_3SCH_2-H) = 99.6 \pm 2.2$	316
methyledithio $CH_3SS^\bullet$	1.757 $\pm$ 0.022		316
<b>Nitrogen-Containing</b>			
azide $N_3^\bullet$	2.70 $\pm$ 0.12		318
	2.76 $\pm$ 0.04	$\Delta_f H_0^\circ(N_3^\bullet) = 113 \pm 4.6$	319
	2.68 $\pm$ 0.01	$D_0(N_3-H) = 92.2 \pm 4.6$	34
imidogen $NH^\bullet$	0.38 $\pm$ 0.03		320
	0.370 $\pm$ 0.004		321
amino $\bullet NH_2$	0.771 $\pm$ 0.005	$\Delta_f H_0^\circ(NH_2^-) = 28.0 \pm 0.4$	322
methylene amidogen $CH_2N^\bullet$	0.511 $\pm$ 0.008	$D_0(CH_2N-H) = 85 \pm 5$	324
		$D_0(H-CHN^\bullet) = 23 \pm 6$	
methyl nitrene $CH_3N^\bullet$	0.022 $\pm$ 0.009		326
cyano $CN^\bullet$	3.862 $\pm$ 0.004		328
isocyanato $\bullet NCO$	3.609 $\pm$ 0.005		328
		$\Delta_f H_0^\circ(\bullet NCO) = 30.5 \pm 1$	35
		$\Delta_f H_0^\circ(\bullet NCO) = 31.4 \pm 0.7$ $D_0(N-CO) = 54 \pm 0.7$	330
thiocyanato $\bullet NCS$	3.537 $\pm$ 0.005	$DH_{298}(H-NCS^\bullet) = 96 \pm 6$	328
methanetetraylbis aminogen $NCN^\bullet$	2.484 $\pm$ 0.006	$DH_{298}(H-NCN) = 83.2 \pm 1$ $D_0(H-NCN) = 81.7 \pm 1$ $\Delta_f H_{298}^\circ(NCN^\bullet) = 108 \pm 4$	331
	2.481 $\pm$ 0.008		333
		$\Delta_f H_0^\circ(NCN^\bullet) = 111.4 \pm 0.7$	334
cyanoamino $HN^\bullet CN$	2.622 $\pm$ 0.005	$DH_{298}(H-NHCN) = 96.7 \pm 2.3$ $D_0(H-NHCN) = 95.2 \pm 2.3$ $\Delta_f H_0^\circ(HN^\bullet CN) = 77 \pm 3$ $D_0(H-NCN) = 64.6 \pm 0.5$ $\Delta_f H_0^\circ(HN^\bullet CN) = 77.3 \pm 0.5$	331
			335
CNN $^\bullet$	1.771 $\pm$ 0.010	$DH_{298}(H-CNN) = 79 \pm 4$	336
		$\Delta_f H_0^\circ(CNN^\bullet) = 142.1 \pm 1.2$	337
diazomethyl $HCNN^\bullet$	1.685 $\pm$ 0.006	$DH_{298}(H-CHNN) = 97 \pm 2$	336
		$\Delta_f H_0^\circ(HCNN^\bullet) = 115.8 \pm 4.2$	337

Table 3 (Continued)

radicals	EA (eV)	derived thermochemical quantities: $\Delta_{\text{acid}}H^{\circ}$ ; $\Delta_{\text{acid}}G^{\circ}$ ; $DH_{298}$ ; $D_0$ (kcal/mol)	ref
<b>Nitrogen-Containing</b>			
nitromethyl $\cdot\text{CH}_2\text{NO}_2$	2.475 $\pm$ 0.010		338
cyanomethyl $\cdot\text{CH}_2\text{CN}$	1.507 $\pm$ 0.018		277
	1.560 $\pm$ 0.006	$DH_{298}(\text{H}-\text{CH}_2\text{CN}) = 94.2 \pm 2$	339
	1.543 $\pm$ 0.014	$\Delta_f H_{298}^{\circ}(\cdot\text{CH}_2\text{CN}) = 59.7 \pm 2$ $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{CN}^-) = 24.1 \pm 2$	340
phenyl nitrene $\text{C}_6\text{H}_5\text{N}^{\cdot}$	1.461 $\pm$ 0.013		341
	1.45 $\pm$ 0.02		342
	1.429 $\pm$ 0.011		343
<b>Miscellaneous</b>			
phosphino $\cdot\text{PH}_2$	1.271 $\pm$ 0.010		344
	1.25 $\pm$ 0.03	$D_0(\cdot\text{PH}_2-\text{H}) \leq 81 \pm 4$	345
phosphinidene $\cdot\text{PH}$	1.028 $\pm$ 0.010		344
selenium monohydride $\cdot\text{SeH}$	2.21 $\pm$ 0.03		346
germyl $\cdot\text{GeH}_3$	$\leq 1.74 \pm 0.04$		348
	1.61 $\pm$ 0.12 <sup>b</sup>	$\Delta_f H_0^{\circ}(\cdot\text{GeH}_3) = 56.9 \pm 2.2$	349
silyldiyne $\text{SiH}^{\cdot}$	1.277 $\pm$ 0.009		351
silylene $\text{SiH}_2^{\cdot}$	1.124 $\pm$ 0.020		351
silyl $\text{SiH}_3^{\cdot}$	1.406 $\pm$ 0.014	$DH_{298}(\text{SiH}_3-\text{H}) = 90.3 \pm 2.4$	352
		$\Delta_f H_{298}^{\circ}(\text{SiH}_2^{\cdot}) = 69 \pm 3$	
	1.405 $\pm$ 0.026	$DH_{298}(\text{SiH}_3-\text{H}) = 91.6 \pm 2$	353
trimethylsilyl methyl $(\text{CH}_3)_3\text{SiCH}_2^{\cdot}$	0.95 $\pm$ 0.01		354
trimethylsilyl $(\text{CH}_3)_3\text{Si}^{\cdot}$	0.971 $\pm$ 0.026	$D_0(\text{R}_3\text{Si}-\text{H}) \geq 91.0 \pm 2$	353
methylsilyl $(\text{CH}_3)\text{SiH}_2^{\cdot}$	1.193 $\pm$ 0.035	$D_0(\text{R}_3\text{Si}-\text{H}) = 92.2 \pm 3$	353
$(\text{C}_6\text{H}_5)(\text{CH}_3)\text{SiH}^{\cdot}$	1.331 $\pm$ 0.039	$D_0(\text{R}_3\text{Si}-\text{H}) = 91.3 \pm 3$	353
$(\text{C}_6\text{H}_5)\text{SiH}_2^{\cdot}$	1.435 $\pm$ 0.004	$D_0(\text{R}_3\text{Si}-\text{H}) = 90.2 \pm 2$	353
dichloromethyl $\cdot\text{CHCl}_2$	1.472 $\pm$ 0.043 <sup>b</sup>		355
trichloromethyl $\cdot\text{CCl}_3$	2.25 $\pm$ 0.01 <sup>b</sup>	$\Delta_f H_{298}^{\circ}(\text{CCl}_2^{\cdot}) = 52.1 \pm 3.4$	356
trifluoromethyl $\cdot\text{CF}_3$	2.01		357
		$\Delta_f H_{298}^{\circ}(\cdot\text{CF}_2) = -39.4 \pm 3.4$	356
oxygen monofluoride $\text{FO}^{\cdot}$	2.272 $\pm$ 0.006		359
oxygen monochloride $\text{ClO}^{\cdot}$	2.276 $\pm$ 0.006		359
	2.2775 $\pm$ 0.0013		360
oxygen monobromide $\text{BrO}^{\cdot}$	2.353 $\pm$ 0.006		359
oxygen monoiodide $\text{IO}^{\cdot}$	2.378 $\pm$ 0.006		359
$\text{ClO}_3^{\cdot}$	4.25 $\pm$ 0.10		363
$\text{ClO}_4^{\cdot}$	5.25 $\pm$ 0.10		363

<sup>a</sup> Averaged value. <sup>b</sup> Derived value.

nitrene and the  $\text{CH}_2=\text{NH}$  imine. No evidence was found for the existence of a noticeable barrier between the  $^1\text{CH}_3\text{N}^{\cdot}$  and the  $\text{CH}_2=\text{NH}$  imine structure and its value was estimated to lie between a few kcal/mol and zero.

**Isocyanato Radical  $\cdot\text{NCO}$ .** Using low-energy electron attachment reactions, Oster and Illenberger<sup>327</sup> reported the formation of the isocyanide  $\text{NCO}^-$  and derived an EA value for the isocyanato radical  $\cdot\text{NCO}$ ,  $\text{EA}(\cdot\text{NCO}) = 3.8 \pm 0.2$  eV. This value refined that which was proposed by Jackson and co-workers<sup>318</sup> who found that the  $\text{NCO}^-$  anion has an electron photodetachment threshold greater than that of  $\text{F}^-$ , measured at 3.54 eV at that time, finally placing a lower limit of 3.401 eV<sup>93</sup> on the EA of the isocyanato radical. A photoelectron spectroscopy study of three

“pseudohalide” anions,  $\text{CN}^-$ ,  $\text{NCO}^-$ , and  $\text{NCS}^-$ , was conducted by Bradforth and co-workers<sup>328</sup> and the EA of the isocyanato radical was measured at  $3.609 \pm 0.005$  eV but with some uncertainties in calibration. This experimental value lies in the interval range of the two previously proposed limits, 3.401 and 3.8 eV, and is close to the calculated value of  $3.6 \pm 0.2$  eV reported by Wight and Beauchamp.<sup>329</sup> A fast-beam study of state-selected  $\cdot\text{NCO}$  radicals<sup>67</sup> was conducted by the same authors providing a corrected enthalpy of formation of this radical at  $30.5 \pm 1$  kcal/mol by characterizing the  $\text{N} + \text{CO}$  fragment-product energy distribution. This value differed by ca. 6 kcal/mol from the current literature value. Recently, the dissociation dynamics from the same radical state<sup>330</sup> were characterized using an improved photofragment

coincidence detection scheme providing higher energy resolution than in the previous study. The corrected value for the  $\Delta H_0^\circ(\text{NCN})$  was  $31.4 \pm 0.7$  kcal/mol.

**Methanetetraylbis, Aminogen  $\cdot\text{NCN}$ , Cyanoamino  $\text{HN}\cdot\text{CN}$ ,  $\cdot\text{CNN}$ , and Diazomethyl  $\text{HCNN}\cdot$  Radicals.** Data collection on elusive species such as those reported here is obviously related to the development of experimental techniques able to probe them within a short time scale. If the precursor anions  $\text{NCN}^-$  and  $\text{HNCN}^-$  are readily produced from cyanamide  $\text{H}_2\text{NCN}$  providing the corresponding  $\cdot\text{NCN}$  and  $\text{HN}\cdot\text{CN}$  radicals by electron photodetachment,<sup>331</sup> the problem is quite different for the direct generation of the radicals in the gas-phase and it appears that, recently, only charge-stripping of  $\text{NCN}^-$  precursor ions in NRMS experiments permitted a possible synthesis of the cyanonitrene radical  $\cdot\text{NCN}$ .<sup>332</sup> As a consequence, if the  $\cdot\text{NCN}$  and  $\text{HN}\cdot\text{CN}$  radicals have been studied by spectroscopic methods before the PES study of Clifford and co-workers,<sup>331</sup> neither the EA nor the enthalpies of formation of these species were yielded before this study. The EAs of the two  $\cdot\text{NCN}$  and  $\text{HN}\cdot\text{CN}$  radicals are reported at  $2.484 \pm 0.006$  and  $2.622 \pm 0.005$  eV, respectively. These experimental findings are accurately reproduced by complementary ab initio calculations with respective values of  $2.51 \pm 0.03$  and  $2.60 \pm 0.03$  eV. Thermochemical parameters have been extracted from the EA values and available values of acidity for the protonated radical providing the corresponding bond energies,  $\text{DH}_{298}(\text{H}-\text{NCN}) = 83.2 \pm 1$  kcal/mol ( $D_0(\text{H}-\text{NCN}) = 81.7 \pm 1$  kcal/mol) and  $\text{DH}_{298}(\text{H}-\text{NHCN}) = 96.7 \pm 2.3$  kcal/mol ( $D_0(\text{H}-\text{NHCN}) = 95.2 \pm 2.3$  kcal/mol). Of the photon energy used during the experiments, only the ground state of the cyanonitrene radical  $\cdot\text{NCN}$  that was accessible led Taylor and co-workers<sup>333</sup> to reinvestigate with larger photon energies the PE spectrum of the  $\text{NCN}^-$  precursor ion in order to access both the ground  $X^3\Sigma_g^-$  and the lower  $a^1\Delta_g$  and  $b^1\Sigma_g^-$  electronic excited states. The remeasured experimental EA is in excellent agreement with the previous value,  $\text{EA}(\cdot\text{NCN}) = 2.481 \pm 0.008$  eV. Precise spacing between the ground-state and the two  $a^1\Delta_g$  and  $b^1\Sigma_g^-$  electronic states was provided, referring them more accurately to the ground state with a measured energy difference of  $1.010 \pm 0.010$  and  $1.629 \pm 0.010$  eV, respectively. Reinvestigation of the photodissociation dynamics of the cyanonitrene radical using fast-beam photofragment translational spectroscopy<sup>334</sup> provided a refined value for the enthalpy of formation at 0 K,  $\Delta H_0^\circ(\text{NCN}\cdot) = 111.4 \pm 0.7$  kcal/mol. In addition to the dominant  $\text{N}_2 + \text{C}$  fragmentation channel, the  $\text{CN} + \text{N}$  channel was also observed at a higher photon energy for one of the electronically excited state of the radical, giving an upper limit for the associated dissociation barrier height at ca. 9 kcal/mol. A similar reinvestigation of the cyanoamino radical  $\text{HN}\cdot\text{CN}$ <sup>335</sup> provided the refined values  $D_0(\text{H}-\text{NHCN}) = 64.6 \pm 0.5$  kcal/mol and  $\Delta H_0^\circ(\text{HN}\cdot\text{CN}) = 77.3 \pm 0.5$  kcal/mol, the latter value being in good agreement with the previously derived value of  $77 \pm 3$  kcal/mol.<sup>331</sup>

Clifford et al.<sup>336</sup> used NIPES experiments to measure the EAs of the  $\text{CNN}\cdot$  radical and the diazomethyl

radical  $\text{HCNN}\cdot$  at  $1.771 \pm 0.010$  and  $1.685 \pm 0.006$  eV, respectively. These values are accurately reproduced by complete basis set ab initio calculations with corresponding values of  $1.83 \pm 0.03$  and  $1.69 \pm 0.03$  eV. Using these experimental values together with determined gas-phase acidities, the  $\text{DH}_{298}$  of the  $\text{H}-\text{CNN}$  bond and  $\text{H}-\text{CHNN}$  bond were extracted (Table 3). Using the technique of fast-beam photofragment translational spectroscopy, Bise and co-workers<sup>337</sup> have examined the photodissociation spectroscopy and dynamics of the ground state of the  $\text{CNN}\cdot$  radical showing that the  $\text{C}^3\text{P} + \text{N}_2$  channel was dominated by extensive rotational excitation of the  $\text{N}_2$  fragment. From this experiment, the authors derived a value of  $\Delta H_0^\circ(\text{CNN}\cdot) = 142.1 \pm 1.2$  kcal/mol. Coupled with the values of  $\text{DH}_{298}$  determined by Clifford et al.,<sup>336</sup> a value of  $115.8 \pm 4.2$  kcal/mol was reported for the  $\Delta H_0^\circ(\text{HCNN}\cdot)$ .

**Nitromethyl  $\cdot\text{CH}_2\text{NO}_2$  and Cyanomethyl  $\cdot\text{CH}_2\text{CN}$  Radicals.** The PE spectrum of the nitromethyl radical  $\cdot\text{CH}_2\text{NO}_2$  was published by Metz and colleagues,<sup>338</sup> providing a raw EA value of  $2.475 \pm 0.010$  eV. The main progression in the spectrum is in accordance with a planar  $C_{2v}$  geometry for the  $\text{CH}_2\text{NO}_2^-$  anion as well as the radical. A structure with a localized charge on the oxygen atoms and a carbon–nitrogen double bond was proposed as the dominant resonance form for the anion, and the major geometrical change upon electron detachment concerns the change from a double  $\text{C}=\text{N}$  to a single  $\text{C}-\text{N}$  bond as evidenced by a lengthening of the  $\text{C}-\text{N}$  bond and a drop in the torsion barrier for the radical.

EA of the cyanomethyl radical was reported by Zimmerman and Brauman<sup>277</sup> from an electron photodetachment cross-section measurement at  $1.507 \pm 0.018$  eV. This value has been successively corrected to  $1.560 \pm 0.006$  eV<sup>339</sup> and  $1.543 \pm 0.014$  eV.<sup>340</sup> From the analysis of the PE spectrum of cyanide anion  $\text{CH}_2\text{CN}^-$ , Moran and co-workers<sup>340</sup> concluded that the cyanomethyl radical was completely planar with a  $C_{2v}$  symmetry, while the precursor anion was slightly nonplanar, which can almost be described by a  $\text{CH}_2=\text{C}=\text{N}^-$  geometry with an hydrogen slightly bent out of the molecular plane. Attribution of EA at  $1.543$  eV in combination with the gas-phase acidity of  $\text{CH}_3\text{-CN}$  led to a derived  $\text{DH}_{298}$  value for the  $\text{C}-\text{H}$  bond,  $\text{DH}_{298}(\text{H}-\text{CH}_2\text{CN}) = 94.2 \pm 2$  kcal/mol. The two quantities,  $\Delta H_{298}^\circ(\cdot\text{CH}_2\text{CN})$  and  $\Delta H_{298}^\circ(\text{CH}_2\text{CN}^-)$  were similarly extracted (Table 3).

**Phenyl Nitrene  $\text{C}_6\text{H}_5\text{N}\cdot$ .** The photodetachment spectrum near the threshold for the phenyl nitrene anion was measured by Drzagic and Brauman,<sup>341</sup> providing an EA value for the triplet ground-state,  $\text{EA}(\text{C}_6\text{H}_5\text{N}\cdot) = 1.461 \pm 0.013$  eV. Energy-splitting between the first two singlet states and this triplet ground state of the radical provided values of  $0.186 \pm 0.02$  and  $0.382 \pm 0.02$  eV. The EA later redetermined by Travers and co-workers<sup>342</sup> was in good agreement with the previously reported value, this value being  $1.45 \pm 0.02$  eV. The value obtained by McDonald and Davidson<sup>343</sup> was however lower with  $\text{EA}(\text{C}_6\text{H}_5\text{N}\cdot) = 1.429 \pm 0.011$  eV.

## 6. Miscellaneous

**Phosphinidene, Phosphino, Selenium Monohydride, and Germyl Radicals.** The EAs of the phosphinidene  $\cdot\text{PH}$  and phosphino  $\cdot\text{PH}_2$  radicals were measured by Zittel and Lineberger<sup>344</sup> by investigation of the corresponding anions using laser photoelectron spectroscopy. In addition to the EA value reported for the phosphino radical at  $1.271 \pm 0.010$  eV, in good agreement with the value previously published by Smyth and Brauman<sup>345</sup> at  $1.25 \pm 0.03$  eV, the geometry of the  $^1\text{A}_1$  ground state for the  $\text{PH}_2^-$  anion was shown to be very similar to the geometry of the  $^2\text{B}_1$  ground-state phosphino radical. The measured EA for the phosphinidene radical was  $1.028 \pm 0.010$ . The little change in the internuclear distance on adding an electron to the radical was interpreted as resulting from filling a nonbonding  $\pi$  orbital, primarily an atomic p orbital of the phosphorus atom.<sup>344</sup>

EA of the selenium monohydride  $\cdot\text{SeH}$ , as well as the first report on the measurement of the molecular fine structure of this species through its spin-orbit coupling constant determination was reported by Smyth and Brauman.<sup>346</sup> No other measurements have been performed by mass spectrometry on this species and the EA value at  $2.21 \pm 0.03$  eV is in quite good agreement with the determination of Stoneman and Larson<sup>347</sup> by photodetachment threshold measurement in a magnetic field ( $2.213 \pm 0.002$  eV). However, the upper limit proposed for the H-SeH bond at 92 kcal/mol<sup>346</sup> was quite high compared to the value derived from PIMS experiments.<sup>234</sup>

Reed and Brauman<sup>348</sup> reported an upper limit at  $1.74 \pm 0.04$  eV for the EA of the germyl radical  $\cdot\text{GeH}_3$ , assumed to be in its vibronic ground state. By equilibrium measurement for the reaction of  $\text{GeH}_4$  with  $\text{PH}_2^-$  in the cell of a pulsed ICR mass spectrometer, they proposed a  $\text{DH}_{298}(\text{GeH}_3\text{-H}) < 92.3 \pm 4.6$  kcal/mol. This value was later refined by Decouzon and co-workers<sup>349</sup> at  $85.6 \pm 2.2$  kcal/mol. Relatively little attention has been paid to negative ions derived from germane and, consequently, uncertainties remain about the EA value of the germyl radical. Ortiz<sup>350</sup> reported a calculated EA of 1.49 eV and the NIST Chemistry Webbook reports a  $1.61 \pm 0.12$  eV value.<sup>93</sup> From their value of the  $\text{DH}_{298}(\text{GeH}_3\text{-H})$ , Decouzon and co-workers<sup>349</sup> extracted a 0 K enthalpy value  $\Delta H_0^0(\cdot\text{GeH}_3) = 56.9 \pm 2.2$  kcal/mol, in fair agreement with that suggested by Rušćić et al.<sup>236</sup> from PIMS experiments.

**Silylidyne SiH $\cdot$ , Silylene SiH $_2\cdot$  and Silyl SiH $_3\cdot$  Radicals.** The only experimental measurements of EAs of silylidyne and silylene radicals were reported by Kasdan and colleagues.<sup>351</sup>  $\text{SiH}_2\cdot$  was depicted as a planar species with a singlet ground state and a first excited triplet state situated about 0.75 eV above this ground state, in a strict reverse order for the respective degeneracy of the first excited state and ground state of its carbon analogue,  $\text{CH}_2$ . Comparatively, the silyl radical has been the subject of more investigation, with a first estimation of its EA by Reed and Brauman<sup>348</sup> by electron photodetachment cross-section measurement,  $\text{EA}(\text{SiH}_3\cdot) = 1.44 \pm 0.03$  eV. Nimlos and Ellison,<sup>352</sup> reinvestigating this species, measured the PE spectrum of the  $\text{SiH}_3^-$  ion and

reported a value of  $\text{EA}(\text{SiH}_3\cdot) = 1.406 \pm 0.014$  eV. Experimental parameters were in quite reasonable agreement with computational values for the simulation of the active vibrational modes, and it has been concluded that both radical and anion present a pyramidal geometry. However, from the Franck-Condon profile of the PE spectrum, the authors suggested revising the ionization profile upward in assigning the IE at 8.23 eV rather than 8.14 eV, which has since been contradicted by PI experiments.<sup>223,228</sup> A value of  $90.3 \pm 2.4$  kcal/mol has been extracted for the first Si-H bond in  $\text{SiH}_4$ . The heat of formation of the silylene radical was deduced at  $69 \pm 3$  kcal/mol, in excellent agreement with the value reported by Boo and Armentrout<sup>229</sup> resulting from collisional threshold dissociation measurements. Cross-section measurements for the electron photodetachment of organosilyl anions provided an EA for the silyl radical at  $1.405 \pm 0.03$  eV.<sup>353</sup> Both of these experimental values are in good agreement with the calculated value of 1.355 eV obtained by Ortiz<sup>350</sup> using large basis sets. The ICR experiments provided a derived value of  $91.6 \pm 2$  kcal/mol for the first Si-H bond in  $\text{SiH}_4$  in good agreement with the previous value of Nimlos and Ellison.<sup>352</sup> In the same experiment, EAs of larger organosilyl radicals were determined and the corresponding  $\text{DH}_0$  was derived (Table 3).

**Halogenated Methyl Radicals.** Reported data for the halogenated methyl anions appeared by far to be subject of caution in their interpretation of the main reason the electron detachment process from such species might be inefficient due to poor Franck-Condon overlap between the anion and the radical potential energy surfaces and consequently provide experiments which are difficult to interpret. This can explain why most of the data are in fact derived from gas-phase acidity measurements or appearance energy determinations. Some of the available EAs as well as the derived thermochemical quantities are quoted in Table 3. But, in general, the EA values are either rare or quite widely distributed in the thermochemical compilations. Nevertheless, Born and co-workers<sup>355</sup> reported a derived value of  $1.472 \pm 0.043$  eV for the dichloromethyl radical which is the only available value for the EA of  $\cdot\text{CHCl}_2$ . Paulino and Squires<sup>356</sup> derived a value of  $2.25 \pm 0.01$  eV for the trichloromethyl radical clarifying a set of experimental values quite disperse and principally obtained from EI methods.<sup>93</sup>

The trifluoromethyl radical illustrates clearly how difficult it is to get reliable data on the EA for such kinds of species since no less than seventeen values are proposed in the NIST Webbook ranking from 1.8 to 3.15 eV, these values were mainly obtained from appearance energy measurements which assume, by definition, that there is no excess energy associated with the products. In their measurements of threshold energies for collision-induced halide ion dissociation in a flowing afterglow apparatus, Paulino and Squires<sup>356</sup> reported a measured onset for the  $\text{F}^-$  loss from the  $\text{CF}_3^-$  anion (2.4 eV) higher in energy than the EA value measured by Richardson and co-workers<sup>357</sup> at ca. 2.01 eV from electron photodetach-



ment measurements. This latter study suggested that a significant difference (of ca. 0.8 eV) exists between the photodetachment threshold of  $\text{CF}_3^-$  and the adiabatic EA of the trifluoromethyl radical, which can be rationalized by a pronounced geometry change in going from a pyramidal neutral structure to a cation planar structure.<sup>357</sup> Such a picture has already been proposed for the assignment of the adiabatic IE from the PE spectrum of  $\cdot\text{CF}_3$  (see above, section B). Consequently, contrary to the case of the trichloromethyl radical, competition cannot be ruled out between electron detachment and fluorine atom loss, suggesting a possible shift in the appearance curve for the  $\text{F}^-$  loss process to higher energies.<sup>356</sup> In the absence of reliable electron-scavenging experiments, it was not possible to clarify the role of electron detachment at threshold for the  $\text{CF}_3^-$  anion nor to deduce any value for the EA of  $\cdot\text{CF}_3$ . Bartmess et al.<sup>358</sup> reported a value of  $\text{EA}(\cdot\text{CF}_3) = 1.82 \pm 0.07$  eV (uncorrected for acidity-scale change) in accordance with the final EA value previously proposed by Richardson and co-workers<sup>357</sup> and with their appearance energy measurements using tetrafluoromethane and hexafluoroethane as precursors. The true adiabatic EA was assigned in this latter case at a value lowered of ca. 1 eV from the photodetachment threshold to take into account the geometrical change upon electron detachment.<sup>357</sup>

**Oxygenated Halogen Radicals.** The PE spectra of halogen monoxide anions were reported by Gilles et al.<sup>359</sup> and provided the respective EA values,  $\text{EA}(\text{FO}^-) = 2.272 \pm 0.006$  eV,  $\text{EA}(\text{ClO}^-) = 2.276 \pm 0.006$  eV,  $\text{EA}(\text{BrO}^-) = 2.353 \pm 0.006$  eV,  $\text{EA}(\text{IO}^-) = 2.378 \pm 0.006$  eV. The differences between the neutral and anion dissociation energies were reported for all the halogen monoxides studied in the experiments, and were shown to agree with what can be anticipated from the filling of an antibonding orbital in the anion, namely, an increased dissociation energy for the radical compared to the anion.<sup>359</sup> The heat of formation of the corresponding anions  $\text{XO}^-$  at 298 K were determined from the measured EAs and the reported heat of formation for the radicals. The oxygen monochloride radical was reinvestigated recently by Distelrath and Boesl<sup>360</sup> using ZEKE spectroscopy with a measured value of  $2.2775 \pm 0.0013$  eV, in good agreement with the previous value of 2.276 eV. Both experiments refined the first reported value of  $2.17 \pm 0.23$  eV by Lee and co-workers<sup>61</sup> by photodetachment. For the oxygen monobromide radical, the measured EA can be quite fairly correlated to the adiabatic value calculated by Francisco and co-workers<sup>362</sup> at  $2.411 \pm 0.08$  eV.

Recently, the EAs of higher order chloride oxide radicals  $\text{ClO}_3\cdot$  and  $\text{ClO}_4\cdot$  have been determined for the first time by PES of the chlorate and perchlorate anions.<sup>363</sup> The corresponding measured values were especially high for organic radicals at  $4.25 \pm 0.10$  eV and  $5.25 \pm 0.10$  eV for  $\text{ClO}_3\cdot$  and  $\text{ClO}_4\cdot$ , respectively.

#### D. Gas-Phase Proton Affinity Measurements

Negative ion cycles were introduced in the preceding section to express how bond energies can be derived from the measurement of the electron affinity

of the radical R combined with the gas-phase acidity of the compound RH, eqs 24–27. Proton-transfer reactions have been extensively studied in the gas-phase over a long period of time, and have led to the establishment of a relative gas-phase basicity scale<sup>364</sup> currently updated.<sup>93</sup> Techniques for the measurements of proton affinities are well documented<sup>365</sup> and, in regard to radicals, mainly include ICR techniques and flowing afterglow experiments.

To measure the gas-phase basicity,  $\text{GB}(\text{R})$ , and the proton affinity,  $\text{PA}(\text{R})$ , at temperature  $T$  for the radical R, the following proton-transfer equilibrium is used, eq 28:



where B represents a well-characterized reference base. The quantities  $\Delta\Delta H^0$  and  $\Delta\Delta G^0$  for the reaction 28 are directly related to the proton affinities and the gas-phase basicities of the compounds R and B, respectively. The equilibrium ratio  $k_{\text{eq}}(T)$  is directly measured by ICR techniques, eq 29:

$$k_{\text{eq}}(T) = \frac{[\text{R}][\text{BH}^+]}{[\text{RH}^+][\text{B}]} = e\left(\frac{-\Delta\Delta G^0}{RT}\right) \quad (29)$$

while the two reactions  $k_{29}$  and  $k_{-29}$  are usually measured in separate experiments with flowing afterglow apparatus. However, the reference base B does not always exist or the reverse reaction  $k_{-29}$  cannot be measured in each case. Then bracketing techniques are used to inscribe the unknown proton affinity between those of two reference bases  $\text{B}_1$  and  $\text{B}_2$  as follows, eq 30:

$$\text{PA}(\text{B}_1) < \text{PA}(\text{RH}) < \text{PA}(\text{B}_2) \quad (30)$$

Nevertheless, it must be quoted that proton affinity data relative to radicals are not abundant for obvious reasons, principally residing in the elusive nature of the radical R making the measurement of the corresponding thermochemical quantities difficult.

##### 1. Alkyl and Unsaturated Alkyl Radicals

DeFrees and co-workers<sup>366</sup> published in 1979 a study applied to the determination of heat of formation of gaseous radicals using the pulsed ion cyclotron double resonance bracketing technique. In conjunction with previously determined gas-phase basicities of reference bases, they determined the heat of formation of free radicals by first bracketing the PA of the radical R with these reference bases and then deriving the  $\text{DH}_{298}(\text{R}-\text{H})$  in combining the PA value with the ionization energy,  $\text{IE}(\text{RH})$ . The heat of formation  $\Delta H_{298}^0(\text{R})$  was directly extracted from the expression:  $\text{DH}_{298}(\text{R}-\text{H}) + \Delta H_{298}^0(\text{RH}) - \Delta H_{298}^0(\text{H}^+)$ . Electron impact upon a mixture of RH, a reference base B, and an excess of buffer gas M chosen for its high IE value was used to generate the corresponding radical cations  $\text{RH}^{+\cdot}$  and  $\text{B}^{+\cdot}$ . Double resonance experiments permitted one to determine if the reactant  $\text{RH}^{+\cdot}$  was a precursor for the product ion  $\text{BH}^+$ , eq 28.

Nicholas and co-workers,<sup>367,368</sup> in following up their investigations on the  $pK_a$  values of radical cations, proposed to establish relationships between acidities of radicals in the gas-phase and in solution to properly estimate the solvation energies of organic radical ions. From the half reaction  $RH^{+\bullet} \rightarrow R + H^+$  of the proton-transfer equilibrium, eq 28, they expressed the  $pK_a$  of the radical cation  $RH^{+\bullet}$  with an equation introducing the Gibbs energy,  $\Delta_{\text{acid}}G^0(R)$ , and they derived at the same time the PA(R) of the radical R as a function of the IE(RH), IE( $H^+$ ), and  $DH_{298}(R-H)$ .<sup>368</sup> Several hydrocarbon radical cation acidities have been estimated in this way as well as the PA of the corresponding radicals including the methyl and ethyl radicals, unsaturated alkyl radicals, and the phenyl and benzyl radicals (Table 4). For the methyl radical, the thermochemically derived value of the PA( $CH_3^{\bullet}$ ) was found to be unexpectedly larger than the calculated value for all extended basis sets, assumed to result from an underestimate zero-point energy contribution of the methyl radical compare to that of  $CH_4^{+\bullet}$ .<sup>368</sup> However, the derived acidity of methane revealed to be overestimated by the method employed.<sup>93</sup> Comparatively, PA values for the benzyl, allyl, and vinyl radicals compared better with the values previously reported by DeFrees and co-workers,<sup>366</sup> and those derived for the vinyl, allyl, and ethynyl radicals are in good agreement with compiled data.<sup>369</sup> The ethynyl radical presented a difference of ca. 20 kcal/mol between thermochemical and ab initio values, and this divergent trend was not observed with the other radicals investigated. These values refined the previous value of 173 kcal/mol extracted by Wyatt and Stafford<sup>370</sup> from equilibrium partial pressure measurements. The validity of the thermochemical value of  $176 \pm 1$  kcal/mol could be more precisely corrected with the  $DH_{298}(C_2H-H)$  value of  $132.8 \pm 0.7$  kcal/mol derived from EA and gas-phase proton-transfer kinetics measurements by Ervin and co-workers.<sup>268</sup> Holmes and Lossing<sup>371</sup> reported a PA value for the allyl radical, which confirmed the value previously derived<sup>368</sup> in detriment to the measured value obtained from bracketing experiments.<sup>366</sup>

## 2. Aromatic Radicals

The limitation of the bracketing method to measure precisely the PA of the radical R, eq 28, lies in the fact that the transition between strongly exothermic reactions, usually fast, to thermoneutral reactions (expectedly slower) is not so abrupt in terms of kinetics measurements since endothermic reactions can still proceed at detectable rates during the experiments. To improve the accuracy of thermochemical measurements limited due to the foregoing reason within  $\pm 2$  kcal/mol, Meot-Ner<sup>372</sup> proposed to measure rate constants for the reaction of  $RH^{+\bullet}$  with a set of reference bases whose PAs are closely spaced to quantify more precisely the transition from fast to slow kinetics. By this method, the benzyl radical  $C_6H_5CH_2^{\bullet}$  was used to first relate the PAs of the reference bases to the absolute value of PA( $C_6H_5-CH_2^{\bullet}$ ), which can be derived from thermochemical data, and then to exploit this value to measure experimentally the PAs of several alkylbenzene

radicals. The value proposed for the benzyl radical was 199.2 kcal/mol.<sup>372</sup> The efficiency of the reaction of  $RH^{+\bullet} + B$  was measured by the variation of ratio  $k_{\text{exp}}/k_{\text{ADO}}$  with the PA of the reference bases B ( $k_{\text{exp}}$  is the experimental rate constant value and  $k_{\text{ADO}}$  is the average dipole orientation (ADO) theory collision rate<sup>13</sup>). The falloff of the different curves observed for different radical precursors  $RH^{+\bullet}$  provided the experimental values for the PA of the investigated radical R. This method, based on kinetic measurements, permitted one to clearly distinguish between PA values of only ca. 0.4 kcal/mol, a difference of only 0.3 kcal/mol being characterized as still meaningful by the author. The results, in fact, were in accordance with a similar level of accuracy for this original method and a charge-transfer equilibria study ( $\pm 0.2$  kcal/mol). The heat of formation  $\Delta H_{298}^0$  for the different radicals derived from these experiments are reported in Table 4.

Bracketing experiments<sup>366</sup> to determine the PA of the phenyl radical failed primarily because of the reactivity of the radical cation  $C_6H_6^{+\bullet}$  which did not conduct to a noticeable reaction channel ratio for the proton-transfer reaction with the reference bases compared to the charge transfer, for example. The compiled value for the PA of  $C_6H_5^{\bullet}$ <sup>369</sup> was obtained by other means.

## 3. Heteroatom-Containing Radicals

The PA value for the phenoxy radical  $C_6H_5O^{\bullet}$  was determined at  $204.4 \pm 2$  kcal/mol through proton-transfer reaction experiments.<sup>366</sup> Dimethyl sulfide (with a proposed PA at 205.4 kcal/mol) appeared to be the weakest available reference base to abstract a proton from  $C_6H_5OH^{+\bullet}$  while ethyl isopropyl ether (with a proposed PA at 203.3 kcal/mol) was the weakest reference base which did not abstract a proton from  $C_6H_5OH^{+\bullet}$ . However, correction of the currently accepted values for the PAs of 2-ethoxypropane and diethyl sulfide at 201.4 and 204.8 kcal/mol, respectively,<sup>369</sup> would moderate the accuracy of the lower boundary limit slightly decreasing the expected value of PA( $C_6H_5O^{\bullet}$ ) from about 1 kcal/mol. This value at 204.4 kcal/mol has, however, been confirmed by Hoke and co-workers<sup>373</sup> using the kinetic method of Cooks,<sup>374</sup> reporting a PA value, PA( $C_6H_5O^{\bullet}$ ) =  $205.6 \pm 0.3$  kcal/mol. An independent check on both experiments utilizing the compiled values for the IE of phenol, the  $DH_{298}$  of the corresponding C-H bond and the IE of the hydrogen atom confirmed a value for PA( $C_6H_5O^{\bullet}$ ) of  $204.8 \pm 2.0$  kcal/mol clearly confirming the reliability of the kinetic method experiments for the determination of the PA of the phenoxy radical.<sup>373</sup> During the same experiments, the PAs of isomeric methylphenoxy and hydroxybenzyl radicals have been measured and differentiated.

Holmes and Lossing<sup>371</sup> reported some PA values for oxygen and nitrogen containing radicals bearing alcohol, amine, or keto functions (see Table 4). The amino methyl radical's value has since been corrected downward.<sup>369</sup>

The thermokinetic technique introduced by Bouchoux and co-workers<sup>375,15</sup> has been used recently to determine the basicity of simple  $\beta$ -carbonyl radi-

**Table 4. Proton Affinity Measurements and Derived Enthalpies of Formation**

radicals	PA (kcal/mol)	derived enthalpies of formation $\Delta_f H$ (kcal/mol)	ref
<b>Alkyl</b>			
methyl $\text{CH}_3^\bullet$	$\leq 127.1^a$		368
ethyl $\text{C}_2\text{H}_5^\bullet$	$149 \pm 1^a$		368
<b>Unsaturated Alkyl</b>			
vinyl $\text{C}_2\text{H}_3^\bullet$	$182.6 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_2\text{H}_3^\bullet) = 71.5 \pm 2.2$	366
	$\leq 180 \pm 2^a$		368
ethynyl $\text{C}_2\text{H}^\bullet$	$176 \pm 1^a$		368
propargyl $\bullet\text{CH}_2\text{C}\equiv\text{CH}$	177		371
allyl $\text{C}_3\text{H}_5^\bullet$	$180.2 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_5^\bullet) = 43.7 \pm 2.2$	366
	$176-175 \pm 1.5^a$		368
	176		371
2-methylallyl $\text{C}_4\text{H}_7^\bullet$	186		371
cyclopropenyl $\text{C}_3\text{H}_3^\bullet$	$180.2 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_3^\bullet) = 105.1 \pm 4.1$	366
cyclopropyl $\text{C}_3\text{H}_5^\bullet$	$187.5 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_3\text{H}_5^\bullet) = 66.5 \pm 2.7$	366
<b>Aromatic</b>			
benzyl $\text{C}_7\text{H}_7^\bullet$	$198.3 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_7\text{H}_7^\bullet) = 48.0 \pm 2.2$	366
	$198 \pm 1.5$	198 $\pm$ 1.5	368
	199.2	199.2	372
cyclopentadienyl $\text{C}_5\text{H}_5^\bullet$	$198.8 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_5\text{H}_5^\bullet) = 63.2 \pm 2.7$	366
cycloheptatrienyl $\text{C}_7\text{H}_7^\bullet$	$200.2 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_7\text{H}_7^\bullet) = 69.0 \pm 3.1$	366
3-fluoro, benzyl $\text{C}_6\text{H}_4(\text{F})\text{CH}_2^\bullet$	197.2		372
1-phenyl, 1-ethyl $\text{C}_6\text{H}_5\text{CH}^\bullet\text{CH}_3$	197.9	$\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{CH}^\bullet\text{CH}_3) = 41.3$	372
1-phenyl, 1-propyl $\text{C}_6\text{H}_5\text{CH}^\bullet\text{C}_2\text{H}_5$	199.1	$\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{CH}^\bullet\text{C}_2\text{H}_5) = 35.9$	372
2-phenyl, 2-propyl $\text{C}_6\text{H}_5\text{C}^\bullet(\text{CH}_3)_2$	199.6	$\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{C}^\bullet(\text{CH}_3)_2) = 35.0$	372
anilino $\text{C}_6\text{H}_5\text{NH}^\bullet$	221.5	$\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{NH}^\bullet) = 54.7$	372
<b>Hetero-Atom-Containing</b>			
phenoxy $\text{C}_6\text{H}_5\text{O}^\bullet$	$204.4 \pm 2$	$\Delta_f H_{298}^\circ(\text{C}_6\text{H}_5\text{O}^\bullet) = 11.6 \pm 2.3$	366
	$205.6 \pm 0.3$		373
4-fluoro, phenoxy	$204.5 \pm 0.3$		373
2-methyl, phenoxy	$208.6 \pm 1.0$		373
2-hydroxy, benzyl	$212.3 \pm 1.0$		373
3-methyl, phenoxy	$209.3 \pm 1.0$		373
3-hydroxy, benzyl	$213.0 \pm 1.0$		373
4-methyl, phenoxy	$210.7 \pm 1.0$		373
4-hydroxy, benzyl	$214.6 \pm 1.0$		373
hydroxymethyl $\bullet\text{CH}_2\text{OH}$	166		371
2-hydroxy, ethyl $\bullet\text{CH}_2\text{CH}_2\text{OH}$	178		371
$\bullet\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	176		371
hydrocarboxyl $\bullet\text{COOH}$	149		371
acetyl $\text{CH}_3\text{C}^\bullet\text{O}$	156		371
$\bullet\text{CH}_2\text{COCH}_3$	196		
$\bullet\text{CH}_2\text{CHO}$	185		371
$\bullet\text{CH}_2\text{COOH}$	184		371
$\bullet\text{CH}_2\text{COOCH}_3$	195		371
amino methyl $\bullet\text{CH}_2\text{NH}_2$	203		371
	199		369
amino ethyl $\bullet\text{CH}_2\text{CH}_2\text{NH}_2$	212		371
vinylxy $\bullet\text{CH}_2\text{CHO}$	$183.9 \pm 0.6$	$\Delta_f H_{298}^\circ(\bullet\text{CH}_2\text{CHO}) = 2.37 \pm 0.9$	376
2-methyl vinylxy $\text{CH}_2=\text{C}(\text{CH}_3)\text{O}^\bullet$	$194.3 \pm 0.3$	$\Delta_f H_{298}^\circ(\text{CH}_2=\text{C}(\text{CH}_3)\text{O}^\bullet) = -8.3 \pm 2$	376
silylene $\text{SiH}_2^\bullet$	$201 \pm 3$	$\Delta_f H_{298}^\circ(\text{SiH}_2^\bullet) = 69 \pm 3$	224
oxygen monofluoride $\text{FO}^\bullet$	$122.3 \pm 2.4^a$		245

<sup>a</sup> Derived value.

calcs,<sup>376</sup> namely, the vinylxy radical,  $\text{C}_2\text{H}_3\text{O}^\bullet$ , and the 2-methyl vinylxy radical,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{O}^\bullet$  (Table 4).

These experiments conducted by means of a Fourier transform ion cyclotron resonance mass spectrometer

**Table 5. Applications**

systems	methods of formation of radicals	species	refs
hydrazine	electrodeless discharge mw discharge <sup>a</sup> in H <sub>2</sub> , N <sub>2</sub>	NH <sub>2</sub> <sup>•</sup> , N <sub>2</sub> H <sub>3</sub> <sup>•</sup>	412
halogen atoms + ozone	mw discharge, atom-molecule reactions	FO <sup>•</sup> , ClO <sup>•</sup> , BrO <sup>•</sup> , IO <sup>•</sup>	417
methane	rf discharge <sup>b</sup>	CH <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•</sup> , C <sub>3</sub> H <sub>7</sub> <sup>•</sup>	420
methane	mw discharge	CH <sub>2</sub>	424
methane	rf discharge	CH <sub>3</sub> <sup>•</sup> , CH <sub>2</sub>	426, 427
methane	mw discharge	C <sub>n</sub> H <sub>2n-1</sub> , C <sub>n</sub> H <sub>2n+1</sub>	428, 431
methane/oxygen	mw discharge	C <sub>n</sub> H <sub>2n+2</sub> OH <sup>+</sup> , C <sub>n</sub> H <sub>2n+2</sub> O <sub>2</sub> H <sup>+</sup> , C <sub>n</sub> H <sub>2n</sub> OH <sup>+</sup> , C <sub>n</sub> H <sub>2n-1</sub> O <sup>+</sup> C <sub>n</sub> H <sub>2n+2</sub> O, C <sub>n</sub> H <sub>2n+2</sub> O <sub>2</sub> , C <sub>n</sub> H <sub>2n</sub> O, C <sub>n</sub> H <sub>2n</sub> O <sub>2</sub>	432, 433
methane/nitrogen	mw discharge	C <sub>m</sub> H <sub>n</sub> CN, NC(CH <sub>2</sub> ) <sub>n</sub> CN, C <sub>m</sub> H <sub>n</sub> NH <sub>2</sub> , C <sub>m</sub> H <sub>n</sub> N <sub>2</sub> H <sub>3</sub> , CN <sup>•</sup> , NH <sup>•c</sup>	434
ethane	rf discharge	CH <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•c</sup>	436
ethylene	rf discharge	C <sub>2</sub> H <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•</sup>	435
ethylene	mw discharge	C <sub>3</sub> H <sub>5</sub> <sup>•</sup> , C <sub>4</sub> H <sub>3</sub> <sup>•</sup> , C <sub>4</sub> H <sub>5</sub> <sup>•</sup> , C <sub>4</sub> H <sub>7</sub> <sup>•</sup> C <sub>5</sub> H <sub>5</sub> <sup>•</sup> , C <sub>5</sub> H <sub>7</sub> <sup>•</sup> , C <sub>5</sub> H <sub>9</sub> <sup>•</sup> C <sub>6</sub> H <sub>3</sub> <sup>•</sup> , C <sub>6</sub> H <sub>5</sub> <sup>•</sup> , C <sub>7</sub> H <sub>7</sub> <sup>•</sup>	437
acetylene	rf discharge	C <sub>2</sub> H <sub>n</sub> <sup>+</sup> , C <sub>4</sub> H <sub>n</sub> <sup>+</sup> , C <sub>6</sub> H <sub>n</sub> <sup>+</sup>	438
acetylene	mw discharge	C <sub>2</sub> H <sup>•c</sup> , H(C=C) <sub>n</sub> H	439
acetylene	mw discharge	C <sub>m</sub> H <sub>n</sub> C <sub>n</sub> <sup>•</sup> , C <sub>n</sub> H <sub>2</sub> <sup>•</sup> , C <sub>n</sub> H <sub>4</sub> <sup>•</sup>	441, 442
acetylene/nitrogen	mw discharge	C <sub>m</sub> H <sub>n</sub> CN, NC(CH <sub>2</sub> ) <sub>n</sub> CN, NC(C) <sub>n</sub> CN, C <sub>m</sub> H <sub>n</sub> NH <sub>2</sub> , C <sub>m</sub> H <sub>n</sub> N <sub>2</sub> H <sub>3</sub>	443
CF <sub>4</sub>	rf discharge	F <sup>•</sup> , F <sub>2</sub> , C <sub>2</sub> F <sub>6</sub> , CF <sub>3</sub> <sup>•c</sup>	447
CF <sub>4</sub> /O <sub>2</sub>	rf discharge	F <sup>•</sup> , F <sub>2</sub> , COF <sub>2</sub> , CO <sub>2</sub> , CO	447
CF <sub>4</sub> , Si	rf discharge	F <sup>•</sup> , F <sub>2</sub> , C <sub>2</sub> F <sub>6</sub> , SiF <sub>4</sub> , SiF <sub>x</sub> <sup>•c</sup>	447
CF <sub>4</sub> , Si	rf discharge	F <sup>•</sup> , F <sub>2</sub> , COF <sub>2</sub> , CO <sub>2</sub> , CO, SiF <sub>4</sub> , SiF <sub>x</sub> <sup>•c</sup>	447
CF <sub>3</sub> H	rf discharge	HF, CF <sub>4</sub> , C <sub>2</sub> F <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>2</sub> HF, C <sub>2</sub> H <sub>2</sub> , CF <sub>x</sub> <sup>•c</sup>	448
C <sub>2</sub> F <sub>4</sub>	rf discharge	C <sub>2</sub> F <sub>4</sub> , C <sub>2</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>6</sub> , C <sub>3</sub> F <sub>8</sub> , C <sub>4</sub> F <sub>8</sub> , CF <sub>2</sub>	449
C <sub>2</sub> F <sub>6</sub> /acetylene	rf discharge	HF, CF <sub>4</sub> , CHF <sub>3</sub> , C <sub>2</sub> F <sub>4</sub> , CF <sub>2</sub>	450
SiH <sub>4</sub> /Ar	rf/dc discharge	SiH <sub>3</sub> <sup>•</sup>	457
SiH <sub>4</sub> /Ar	dc discharge	SiH <sub>3</sub> <sup>•</sup> , Si <sub>2</sub> H <sub>2</sub> <sup>•</sup> , Si <sub>2</sub> H <sub>n</sub> <sup>•</sup>	460
SiCl <sub>4</sub> /Ar; SiCl <sub>4</sub> /Ar/H <sub>2</sub>	mw discharge	SiCl <sub>3</sub> <sup>•</sup> , SiCl <sub>2</sub> <sup>•</sup>	458
Si(s); SiH <sub>4</sub> /N <sub>2</sub>	rf discharge	SiH <sub>3</sub> <sup>•</sup> , Si <sub>2</sub> H <sub>n</sub> <sup>•</sup> , SiH <sub>n</sub> <sup>•</sup>	462
H <sub>2</sub> /O <sub>2</sub>	mw discharge	HO <sub>2</sub> <sup>•</sup>	463
H <sub>2</sub> O/H <sub>2</sub> O <sub>2</sub>			467
H <sub>2</sub> O <sub>2</sub> , H <sub>2</sub> /H <sub>2</sub> O <sub>2</sub> ; O <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	mw discharge	HO <sub>2</sub> <sup>•</sup>	465
H <sub>2</sub> /O <sub>2</sub>	furnace	HO <sub>2</sub> <sup>•</sup>	469
acetylene/O <sub>2</sub>	mw discharge	C <sub>2</sub> H <sup>•</sup> , C <sub>4</sub> H <sup>•</sup> , C <sub>6</sub> H <sup>•</sup> , C <sub>3</sub> H <sub>2</sub> <sup>•</sup> , C <sub>2</sub> <sup>•</sup>	486
acetylene/O <sub>2</sub>	flame	C <sub>6</sub> H <sub>5</sub> <sup>•</sup> , C <sub>3</sub> H <sub>2</sub> <sup>•</sup> , CH <sub>2</sub>	486, 488
acetylene/O <sub>2</sub>	flame	C <sub>2</sub> <sup>•</sup> , C <sub>2</sub> H <sup>•</sup> , C <sub>3</sub> H <sup>•</sup> , C <sub>4</sub> H <sup>•</sup> , CH <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•</sup> , C <sub>2n</sub> H <sub>3</sub> <sup>•</sup> , C <sub>6</sub> H <sub>5</sub> <sup>•</sup> , C <sub>3</sub> H <sub>2</sub> <sup>•</sup> , C <sub>5</sub> H <sub>2</sub> <sup>•</sup>	490
ethylene/oxygen	flame	C <sub>2</sub> <sup>•</sup> , C <sub>2</sub> H <sup>•</sup> , CH <sub>2</sub> , C <sub>3</sub> H <sub>2</sub> <sup>•</sup> , C <sub>2n</sub> H <sub>3</sub> <sup>•</sup> , CH <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•</sup> , C <sub>4</sub> H <sub>5</sub> <sup>•</sup> , C <sub>6</sub> H <sub>5</sub> <sup>•</sup>	490
1,3-butadiene/oxygen	flame	C <sub>2</sub> <sup>•</sup> , C <sub>2</sub> H <sup>•</sup> , C <sub>3</sub> H <sub>2</sub> <sup>•</sup> , C <sub>2n</sub> H <sub>3</sub> <sup>•</sup> , CH <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•</sup> , C <sub>4</sub> H <sub>5</sub> <sup>•</sup> , C <sub>6</sub> H <sub>5</sub> <sup>•</sup> , C <sub>3</sub> H <sub>4</sub> O, C <sub>4</sub> H <sub>4</sub> O, C <sub>4</sub> H <sub>6</sub> O	490
methane/oxygen	flame	CH <sub>3</sub> <sup>•</sup> , C <sub>2</sub> H <sub>5</sub> <sup>•</sup> , C <sub>2</sub> H <sub>3</sub> <sup>•</sup> , CH <sub>2</sub> , CH <sub>3</sub> O <sup>•</sup>	490
benzene/oxygen	flame	C <sub>x</sub> H <sub>y</sub> <sup>•</sup> (x = even, odd number, x = 18–70, y = odd number) C <sub>26</sub> H <sub>13</sub> <sup>•</sup> , C <sub>34</sub> H <sub>15</sub> <sup>•</sup> , C <sub>36</sub> H <sub>15</sub> <sup>•</sup> , C <sub>42</sub> H <sub>17</sub> <sup>•</sup> , C <sub>44</sub> H <sub>17</sub> <sup>•</sup> , C <sub>46</sub> H <sub>19</sub> <sup>•</sup> C <sub>5</sub> H <sub>5</sub> <sup>•</sup> , C <sub>7</sub> H <sub>7</sub> <sup>•</sup> , C <sub>9</sub> H <sub>7</sub> <sup>•</sup>	492
methane/nitrogen	mw discharge	H <sub>2</sub> C=NH, NC(CH <sub>2</sub> ) <sub>n</sub> CN, H <sub>2</sub> NCN, hydrazines	493

<sup>a</sup> mw discharge: microwave discharge generally monitored at 2.45 GHz. <sup>b</sup> rf discharge: radio frequency discharge generally monitored at 13.56 MHz. <sup>c</sup> Suspected reagents in the plasma.

and supported by ab initio molecular orbital calculations have afforded the derived heat of formation,  $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{CHO}) = 2.37 \pm 0.9$  kcal/mol and  $\Delta_f H_{298}^{\circ}(\text{CH}_2=\text{C}(\text{CH}_3)\text{O}^{\bullet}) = -8.3 \pm 2$  kcal/mol, refining the previous value reported by Holmes and Lossing<sup>118</sup> for the vinyloxy radical,  $\Delta_f H_{298}^{\circ}(\text{CH}_2\text{CHO}) = 0.2 \pm 2$  kcal/mol. Finally, the reported values after comparison with available data in the

literature have led to the following recommended averaged values  $\Delta_f H_{298}^{\circ}$  of 3.1 kcal/mol and -8.1 kcal/mol for the C<sub>2</sub>H<sub>3</sub>O<sup>•</sup> and CH<sub>2</sub>=C(CH<sub>3</sub>)O<sup>•</sup> radicals, respectively.<sup>376</sup> Estimation of the resonance stabilization energy due to the delocalization of the unpaired electron over the three-center  $\pi$ -system is in accordance with a value close to 5.5 kcal/mol for the two  $\beta$ -carbonyl radicals considered, correcting up-

ward the low or negligible quantities usually reported for these species.

Using the techniques of Fourier transform ion cyclotron resonance spectroscopy, Shin and Beauchamp<sup>224</sup> reported the PA of the silylene radical  $\text{SiH}_2\cdot$  at  $201 \pm 3$  kcal/mol, leading to a value for the heat of formation  $\Delta_f H_{298}^\circ(\text{SiH}_2\cdot)$  of  $\text{SiH}_2\cdot$  equal to  $69 \pm 3$  kcal/mol in large disagreement with the value proposed by Walsh,<sup>21</sup> 11 kcal/mol lower. This value has been confirmed by PI experiments<sup>223</sup> and collisional dissociation threshold measurements.<sup>229</sup>

#### 4. Topical Proton Affinities

Recent NRMS experiments, based on the kinetic competitive features of exothermic protonation in ion/molecule reactions in the gas-phase, have provided accurate information on specific sites of protonation in heterocyclic organic compounds. Nguyen and Tureček<sup>377</sup> reported the gas-phase protonation study of pyridine with various bases by variable-time NRMS in which radicals derived from the protonated aromatic cation  $\text{C}_5\text{H}_6\text{N}^+$  are generated by vertical neutralization. This vertical "reduction process" was shown to allow the determination of the site of protonation by the use of deuterated bases in the generation of the protonated intermediate  $[\text{C}_5\text{H}_5\text{N}, \text{D}]^+$ , assuming that the derived radical dissociates through single-bond cleavage to recreate the pyridine precursor. Depending on the N- or C-site of protonation and the corresponding H and/or D loss, the recovered ionized products finally permitted one to assign the protonation site. Introduction of a variable-time parameter in the observation of both intermediate neutrals and dissociated ions allowed detection of short-lived species as well as the determination of unimolecular rate parameters involved in the different processes.<sup>377</sup> Ab initio calculations completed the experiments to gauge the relative stabilities of ions and radicals. The 1H-pyridinium radical was shown to be a stable species at the time-scale of the experiment when generated by neutralization of N-protonated pyridine, and ab initio calculations gave the PAs of the different N, C-2, C-3, and C-4 sites of the pyridine cycle in accordance with a preferential protonation at the N-site for base of the PA = 164.9 kcal/mol.<sup>377</sup> A value of 25.8 kcal/mol is derived for the  $\text{DH}_{298}$  of the corresponding N–C bond.

A recent review<sup>378</sup> stated how such experiments on transient radicals derived from simple heterocycles might provide insights into the radical chemistry of nucleobases. Probing of the chemistry of hydroxypyridine showed that the more stable radical produced under collisional neutralization conditions was the 2-hydroxypyridinium radical,<sup>378</sup> whereas pyrimidium and uracil yielded protonation on the N- and (C4)O-sites, respectively, in the most stable radical structures. The presence of the amino group in the 2- and 4-amino pyrimidine affected the protonation thermochemistry of these compounds in providing competitive protonation under CI conditions and in increasing the topical proton affinities by electron-donating effects. In both cases, the N-ring position was preferred for protonation in view of the reported

stabilities in the radicals detected. The imidazole ring yielded different features in contrast with the other heterocyclic radicals since, if the protonation appeared to favor the imine nitrogen position, formation of the stable radical structure by vertical neutralization was accompanied by a quasi-total dissociation resulting from H loss and ring cleavage, such that the survivor ion afforded a very weak signal in the resulting NR mass spectrum. In addition, deuterium labeling showed partial exchange of the N and C-2 hydrogen atom in the intermediate radical. Calculations revealed that the expected most stable radical generated after protonation on the imine position was weakly bound against dissociation to the imidazole and hydrogen atom, and that vertical neutralization of the precursor ion was accompanied by a large Franck–Condon effect resulting in vibrational excitation of the radical formed. Concurrently to dissociation, this radical could rearrange to a more stable form where the hydrogen atom is bound to the C-2 carbon explaining the partial H scrambling observed during dissociation.<sup>378</sup> Experiments were extended to tetrahydroxyphosphorane radicals  $\cdot\text{P}(\text{OH})_4$  formed from  $\text{P}(\text{OH})_4^+$  precursor ions. The NR mass spectrum of the latter ion did not show any survivor ions nor any stable molecule products formed by simple cleavage of P–O bonds. Interpretation of this spectrum with the aid of ab initio calculations revealed that the  $\cdot\text{P}(\text{OH})_4$  radical must be characterized by several stereoisomeric forms resulting from Berry pseudorotations. Dissociations by O–H and P–O bond cleavage must overcome substantial activation barriers whereas the formation of the  $\cdot\text{P}(\text{OH})_4$  radical from the  $\text{P}(\text{OH})_4^+$  ion by vertical neutralization necessitates a large geometrical change from a distorted tetrahedral structure in the ion to a  $\text{C}_s$  trigonal pyramide geometry in the radical. The resulting vibrational excitations were proposed to explain the fast dissociation observed in phosphoric acid.<sup>378</sup> All these experiments were completed by ab initio calculations, providing the PAs of the different positions in the heterocyclic structures investigated.

The 3-hydroxypyridinium radical has been similarly investigated by Wolken and Tureček.<sup>379</sup> This radical, generated by femtosecond collisional electron transfer to the s-hydroxy-(1H)-pyridinium cation, was shown to be the most stable structure among the other isomers accessible by hydrogen atom addition in 3-hydroxypyridine by ca. 2 to 5 kcal/mol, depending on the H atom position. Dissociation patterns were reported and ab initio calculations provided the topical proton affinities of the relative N-, C-, and O-positions of the heterocycle. NRMS study of the 2-hydroxypyridinium and the 2-(1H) pyridone radicals completed by ab initio and density functional theory calculations was reported by Wolken and Tureček.<sup>380</sup> Gas-phase protonation of 2-hydroxypyridinium and 2-(1H) pyridone appeared to occur preferentially at the nitrogen and the oxygen sites respectively, yielding a single 2-hydroxypyridinium ion. The corresponding 2-hydroxy-(1H)-pyridinium radical was generated by collisional neutralization of this ion and was found to be stable in the experiment time scale. Contrary to its counterpart ion where a scram-

bling of H atoms was observed before dissociation, the 2-hydroxy-(1H)-pyridinium radical showed a highly regiospecific loss of hydrogen (or D, in the deuterated precursor) from the N–H and O–H positions. Geometrical optimizations yielded local minima for the expected radical structures, helping in the interpretation of the observed fragmentation channels, but the most informative results certainly provided in evidence for the likely appearance of bimodal energy distributions in molecules and radicals due to the population of excited electronic states upon femtosecond collisional electron transfer.<sup>380</sup> Similar experiments have been conducted on pyrrole,<sup>381</sup> pyrimidine, and pyridamine<sup>382</sup> as well as uracil<sup>383</sup>-derived radicals.

## IV. Applications

### A. Gas-Phase Reactivity

In 1986, McEwen<sup>384</sup> reviewed the field of radical detection using analytical mass spectrometry, focusing on the potentialities that radicals might have to influence the nature of acquired mass spectra in classical ionization techniques. This review also quoted references on radical formation observed in field ionization and fast atom bombardment ionization processes. In fact, ionization of byproducts resulting from fast radical/molecule reactions could lead to misinterpretation of the data contained in the mass spectra acquired by electron ionization methods. Nevertheless, the observation of such radical/molecule reaction products is rare under classical analytical conditions, and special conditions must be realized to favor their detection. The ability to trap radicals with neutral compounds has been proposed for studying radical and ion populations in chemical ionization sources. Contrary to electron ionization (EI) where a two-step mechanism is unlikely to ionize radical fragments resulting from a primary ionization process, chemical ionization (CI) might basically be more favorable to secondary product ionization, including radicals, even if few studies have reported such observations.<sup>385</sup> Indeed, McEwen and Rudat,<sup>385</sup> in their preliminary work, reported for the first time the characterization of ions resulting from radical addition to the 7,7,8,8-tetracyanoquinodimethane (TCNQ) under both negative and positive methane CI conditions. The ions attributed to the addition of H<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, and C<sub>2</sub>H<sub>5</sub><sup>•</sup> to the TCNQ were postulated to arise from a common radical addition reaction with the molecular radical cation or molecular radical anion of the TCNQ molecule. The main interest of these experiments resides in the opportunity offered to trap the alkyl radicals potentially formed by different hydrocarbon gases with the 7,7,8,8-tetracyanoquinodimethane reactant for the purpose of structural identification. Radical trapping in a CI ion source was extended to tetracyanoethylene and tetracyanopyrazine as a reagent and has permitted the determination of the elemental composition and structures of carbon-centered radicals produced in plasmas generated from methane, isobutane, di-*tert*-butyl peroxide, octanol, and toluene as well as the

radical population of a methane plasma generated under Townsend discharge conditions.<sup>386</sup> Several mechanisms have been proposed to account for the radical formation including ion fragmentation, hydrogen abstraction to the CI gas, or ion–electron recombination. This radical trapping technique has been coupled to tandem mass spectrometry providing collisional activation spectra dominated by fragmentation of the original radical and directly interpretable in terms of radical structure.<sup>387</sup> Similarly, the products of isomerization of a number of selected C<sub>n</sub>H<sub>2n-1</sub>, C<sub>n</sub>H<sub>2n+1</sub> hydrocarbon cations corresponding to precursor carbon-centered radicals have been determined quantitatively<sup>388</sup> by using this technique with TCNQ as a trapping molecule, confirming the ability of this technique for structure elucidation of ions with a lifetime of between 10<sup>-4</sup>–10<sup>-5</sup> s, the time scale of the experiments. In such a way, degradation reactions of the thermally produced cyclohexyloxy radical have been investigated with the TCNQ radical trapping agent<sup>389</sup> and showed that, at low temperature (ca. 200 °C), the main fragmentation processes observed correspond to the β-scission of the cyclohexyloxy radicals and loss of the CO fragment from the resulting acyl radicals, leading respectively to ω-formyl hexyl and derived pentyl radicals. Increasing gradually the temperature of the source (above ca. 250 °C) was shown to result in the highest ratio of ethyl and propyl radicals, both resulting from β-scission of the intermediary pentyl radicals in accordance with the admitted competitive scheme between β-scission and disproportionation and hydrogen atom transfer for the chemistry of alkyloxy and cycloalkyloxy radicals. This work refined the previous comparative gas-phase and condensed-phase experiments of Druliner and co-workers<sup>390</sup> on cycloalkyloxy radicals.

Previous experiments reported for the use of a flowing afterglow apparatus as a chemical ionization detector<sup>391</sup> led Gleason and co-workers<sup>392</sup> to employ this technique for the investigation of the role of bisulfite radicals HOS•O<sub>2</sub> in the gas-phase oxidation of the sulfur dioxide SO<sub>2</sub>. The principle of the method for detecting the HOS•O<sub>2</sub> radical resided in its selective ionization by using the appropriate ion/molecule reaction, which causes little or no fragmentation of the radical. However, in the case of HOS•O<sub>2</sub>, direct detection of this radical was not attainable, and its reactivity was followed through the variation of the signal obtained through the gas-phase acid–base reaction of HOS•O<sub>2</sub> with the chlorine chemical ionization reagent Cl<sup>-</sup>, permitting the rate constant measurement of the hydrogen atom abstraction reaction of bisulfite radicals with molecular oxygen. Chemical ionization mass spectrometry has been subsequently used for the investigation of gas-phase reactions of several radicals including trifluoromethylperoxy CF<sub>3</sub>O<sub>2</sub><sup>•</sup> and trifluoromethoxy CF<sub>3</sub>O<sup>•</sup>,<sup>393</sup> methylperoxy CH<sub>3</sub>O<sub>2</sub><sup>•</sup>,<sup>394</sup> isopropylperoxy (CH<sub>3</sub>)<sub>2</sub>CHOO<sup>•</sup>,<sup>395</sup> peroxyacetyl CH<sub>3</sub>C(O)O<sub>2</sub><sup>•</sup>,<sup>396</sup> or peroxyacryl CH<sub>2</sub>=C(CH<sub>3</sub>)C(O)O<sub>2</sub><sup>•</sup>.<sup>397</sup> All the subtlety of the chemical ionization mass spectrometry technique lies in the choice of a chemical ionization reagent allowing a soft ionization process for the detection of the radical of

interest and providing at once a good sensitivity and a good selectivity. So, the sulfur hexafluoride anion  $\text{SF}_6^-$  has been used for the detection of  $\text{CF}_3\text{O}_2^*$  and  $\text{CF}_3\text{O}^*$  by charge-transfer reaction,<sup>393</sup> providing at the same time a lower limit for the EA of  $\text{CF}_3\text{O}_2^*$  at 1.05 eV. The methylperoxy radical  $\text{CH}_3\text{O}_2^*$  was characterized by charge-transfer reaction with  $\text{O}_2^+$ ,<sup>394</sup> while the  $(\text{CH}_3)_2\text{CHOO}^*$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{O}_2^*$  and  $\text{C}_3$  to  $\text{C}_5$  peroxy radicals were detected through electron-transfer reaction with  $\text{O}_2^-$ <sup>395</sup> and  $\text{SF}_6^-$ <sup>397,398</sup> reagent ions, respectively. However, in the case of kinetic measurements for the reaction of the peroxyacetyl  $\text{CH}_3\text{C}(\text{O})\text{O}_2^*$  radical<sup>396</sup> with the nitrogen oxides NO and  $\text{NO}_2$ , the experiments required the use of both  $\text{SF}_6^-$  and  $\text{O}_3^-$  as ionizing reagents for the simultaneous detection of all the products since  $\text{CH}_3\text{C}(\text{O})\text{O}_2^*$ ,  $\text{NO}_2$ , and  $\text{CO}_2$  are the resulting products of the investigated reactions. Measurements of the reaction rate constant of the peroxypropionyl radical  $\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2^*$  with NO<sup>399</sup> exemplified how heterogeneous effects and pressure dependence of concentration gradients can be examined by chemical ionization mass spectrometry, and gave results comparable to the recommended value for the analogous  $\text{CH}_3\text{C}(\text{O})\text{O}_2^*$  with nitrogen monoxide obtained by other methods. Recently, Moise and co-workers<sup>400</sup> reassessed the rate constant and rate coefficient values for the reaction of the peroxyacetyl  $\text{CH}_3\text{C}(\text{O})\text{O}_2^*$  radical with nitrogen monoxide using chemical ionization mass spectrometry detection in accordance with the previous value reported by Villalta and Howard,<sup>396</sup> but these later experiments validate more precisely the recommended value to be used in atmospheric chemistry models.

Similarly, the advantages of gas-phase reaction product analysis, namely, charge transfer and nucleophilic substitution, have been used for the investigation of various species resulting from a microwave discharge in various polyhalogenated methanes.<sup>401</sup> The use of a multiquadrupole mass spectrometer permitted sequentially the selection of the ion probe species ( $\text{Ar}^+$ ,  $\text{Cl}^-$ ,  $\text{FeCO}^+$ ) and the analysis of the mixture composition by studying the reactivity of the generated neutral species with these selected ions. From the polyhalogenated methanes investigated,  $\text{CF}_3\text{Br}$ ,  $\text{CHBr}_3$ ,  $\text{CHCl}_3$ ,  $\text{CFCl}_3$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CCl}_4$ ,  $\text{CF}_4$ , and  $\text{C}_2\text{F}_6$ , conclusions were drawn for the rough composition of expected neutral and radical species depending on the presence of hydrogen and fluorine atoms in the precursor molecules. The most surprising result of these experiments was certainly in the absence of recombination products generated through new carbon-carbon bond formation, contrary to compounds resulting from carbon-halogen bond formation observed in the case of microwave discharges conducted in  $\text{CHCl}_3$  and  $\text{CFCl}_3$  and confirmed by the detection of  $\text{CCl}_4$  in these plasmas.

Due to their important role in the gas-phase chemistry of the atmosphere, peroxy radicals have been the subject of numerous experimental developments for their detection and quantification. Among these, the chemical amplifier technique was proposed in the early 1980s<sup>402</sup> using chain reactions involving peroxy radicals in oxidative processes to finally

characterize the radicals by the detection of the resultant oxidized products, usually  $\text{NO}_2$  or  $\text{CO}_2$ . Recently, Reiner et al.<sup>403</sup> reported a novel method based on the amplifying chemical conversion of peroxy radicals to gaseous sulfuric acid for measuring peroxy radical concentration in in-field and laboratory experiments. The system  $\text{NO}/\text{SO}_2$  was used as a chemical amplifier through which chain reaction leads to the intermediate formation of  $\text{SO}_3$  leading ultimately to the formation of sulfuric acid. Detection of the resulting gaseous  $\text{H}_2\text{SO}_4$  is monitored through ion/molecule reactions with  $\text{NO}_3^-(\text{HNO}_3)_n$  ions permitting peroxy radical concentration measurements in the low  $10^6 \text{ cm}^{-3}$  range with reduced interfering processes.<sup>403</sup> This technique was developed for aircraft-borne measurements in the free troposphere<sup>404,405</sup> with a conversion efficiency in the case of methyl peroxy radicals larger than 80%.

By definition, a free radical R can be deprotonated, similarly to any molecule (eq 24), yielding a radical anion  $[\text{R}-\text{H}]^-$ . Experimental difficulties for the investigation of such species are directly related to the stability of the resulting radical anion because the electron in the  $[\text{R}-\text{H}]^-$  generally has a very small binding energy and sometimes is even unbounded (with a correlated negative EA, see above Part III – C and ref 267). Consequently, data on such species are scarce and only the acidity of some heteroatom bearing radicals  $\text{R}\text{X}\text{H}$  has been more recently studied since the deprotonation reaction of the X–H group might yield the corresponding radical anion of a stable closed-shell molecule. Prototypically substituted methanes<sup>406,407</sup> or phenyl<sup>408</sup> compounds have been studied experimentally and theoretically. In the former case, acidities of the  $\text{CH}_2\text{X}$  radicals are predicted to be correlated with the  $\pi$ -donor or  $\pi$ -acceptor substituent effects, corresponding to a greater or a lower acidity compared to the  $\text{CH}_3\text{X}$  counterpart, respectively.<sup>407</sup> Fourier transform ion cyclotron resonance mass spectrometry studies of the phenyl radical have led to place the gas-phase acidity of  $\text{C}_6\text{H}_5^*$  at  $380.5 \pm 1.9 \text{ kcal/mol}$ <sup>408</sup> confirming its higher acidic character than benzene,<sup>87</sup> and reevaluating the  $\text{DH}_{298}$  of the C–H bond *ortho* to the radical position at 79.8 kcal/mol. Similarly, the  $\text{C}_6\text{H}_4\text{X}^*$  radicals are reported to be more acidic than the  $\text{C}_6\text{H}_5\text{X}$  molecules, with a radical center effect on the acidity which is less pronounced than for the  $\text{C}_6\text{H}_5^*-\text{C}_6\text{H}_6$  system. The method employed in this study for the formation of the conjugate base of the radical, abstraction of a formal  $\text{H}_2^+$  by a  $\text{O}_2^-$  radical anion, permitted one to show, in the case of  $\text{C}_6\text{H}_4\text{F}^*$  radicals with the use of a deuterated precursor that different acidities of isomeric radicals can be expected for the various positions of the radical site.<sup>408</sup> The same authors<sup>409</sup> then reported the gas-phase acidities of the isocyanomethyl  $\text{CH}_2\text{NC}$  and the cyanomethyl  $\text{CH}_2\text{CN}$  radicals at  $378 \pm 2.4$  and  $373.6 \pm 0.7 \text{ kcal/mol}$ , respectively. A few years before, Guo and Grabowski,<sup>410</sup> using a flowing afterglow technique, placed a value on the acidity of the vinyl radical which was  $\Delta H_{\text{acid}}^\circ(\text{CH}_2=\text{CH}^*) = 385 \pm 3 \text{ kcal/mol}$ . This experimental measurement allowed the authors to derive values for the heat of formation and the  $\text{DH}_{298}$  of the

C–H bond in ethylene, but these values were later corrected upward.<sup>14,161</sup>

## B– Plasma and Flame Analysis

### 1. Plasma Analysis

As stated by Fite,<sup>411</sup> there is a well-recognized place for mass spectrometry in remote sampling of systems containing radicals even if optical spectrometry can be considered as the cleanest approach in the sense that it does not interfere with the system being sampled. However, the numerous publications reporting on mass spectrometric plasma or discharge sampling confirm the efficiency of mass spectrometry in these domains (see Table 5). Nevertheless, remote sampling by mass spectrometry methods without interfering or destroying the intrinsic nature of the system investigated is not obvious and the general approach usually chosen is in the use of a small hole permitting a fraction of the gas to escape and to be mass spectrometrically examined, simply replacing the concept of an optical window by that of a molecular leak. The use of molecular beam techniques associated with modulating and chopping of the neutral beam eluted from the radical source (furnace, plasma, or flame) has greatly favored the investigation of such radical sources by mass spectrometry (see above Part II. B. Brief Survey of the First Instrumental Developments for Radical Studies). And threshold ionization at or below the appearance energy value of the radical investigated is currently employed for radical detection.<sup>411</sup> Among the numerous studies devoted to radical detection must be mentioned the pioneering work of a few laboratories,<sup>46,47,49,53</sup> mainly encompassing the application of direct sampling techniques subsequently completed with dry ice trapping methods for the investigation of plasma components.<sup>412</sup> Following this, technical developments have led to reinvestigate older works conducted to study reactions of ionic precursor species in electrical discharges as the main subject of analysis.<sup>413–415</sup> But some time passed before the development of experimental techniques allowing one to probe both neutral and ionic species in the same experiments.<sup>416,78</sup>

From the mid 1970s, improved experiments have been proposed to increase the sensitivity for radical detection, trying to reconcile the necessity to work at a low electron energy current to reduce the weight of interfering molecules in the acquired mass spectra, and to work with sufficient sensitivity for the detection of low-concentration radicals. Most of the sampling systems proposed consisted of a discharge flow system with a global working pressure of ca.  $10^{-2}$  Torr and an intermediate flow regime expected to minimize collisions before sampling. Such a system based on free radical sources has been proposed by Clyne and Watson<sup>417</sup> to sample halogen monoxide radical  $XO\cdot$ , generated by atom reactions with ozone, exploiting fully the sensitivity of mass spectrometry for the detection of free radicals in avoiding the presence of interfering molecules. Remaining difficulties resided in the calibration of ion currents as a function of radical concentration, which is neverthe-

less required for quantitative kinetic studies. Usually, just like the example of  $XO\cdot$  radicals with a correlated  $XO^+$  ion current, the decay of the investigated radicals along the reaction zone is related to the measurement of the decay of corresponding ion currents. Nevertheless, this correlation can be complicated by the absence of an effective method to calibrate the ionic current with the radical concentration, as exemplified by the case of  $FO\cdot$  radicals.<sup>417,418</sup>

With the purpose of going further than elucidating the ion–molecule reactions involved in plasma processes, Vasile and Smolinsky<sup>416,419</sup> introduced a procedure for reactive plasma diagnosis, including either ionic or neutrals, later extended to radicals.<sup>420,421</sup> These experiments at that time were primarily conducted with the aim of completing reported speculations on polymerization mechanisms observed under radio frequency glow discharge conditions at low pressure (0.1–1 Torr) with saturated or unsaturated hydrocarbon gases.<sup>422,423</sup> Their first reported study on ionic and neutral species produced in a methane radio frequency discharge monitored at low pressures and long residence times led to the conclusion that electron impact processes on methane were responsible for the formation of monocarbon ions and radicals ( $CH_3^+$ ,  $CH_4^+$ ,  $CH_5^+$ , and  $CH_3\cdot$ ) which were shown to subsequently react with methane to produce  $C_2$  ions and radicals.<sup>420</sup> The general trends of the steady-state discharge mechanisms responsible for the detected products were first described by an electron interaction with methane to generate primary ions in quantities proportional to the electron ionization cross-sections, and second by ion–molecule reactions with neutral molecules to produce higher-order ions ( $C_2H_3^+$ ,  $C_2H_5^+$ ,  $C_3H_5^+$ ,  $C_3H_7^+$ ) or neutrals ( $C_2H_2$ ,  $C_2H_4$ ,  $C_2H_6$ ). However, the extent of radical participation in polymerization processes could not be drawn clearly. A complementary study on a methane plasma conducted under several discharge conditions (axial or radial sampling, capacitively, or inductively coupled discharge) confirmed the role of a primary ionization, followed by secondary ion–molecule reactions,<sup>421</sup> in accounting for the formation of detected products. Axial and radial samplings of the species generated in the core of the plasma were shown to result in noticeable differences in the content of detected species, the former configuration of sampling yielding dominant ions with a low carbon content, namely,  $C_1$  to  $C_2$ , while the latter configuration provided a significant fraction of species  $C_4$  and  $C_6$  ions. The difference in ion distribution has been attributed to the difference in electron energy acting in the ionization processes and to the difference in the kinetic energy of primary ions, favoring in the latter radial sampling configuration ion–molecule reactions with an increased probability for condensation reactions. Polymerization reactions in pure methane discharge were investigated by Marcus and Platzner,<sup>424</sup> using microwave irradiation and higher pressure conditions (0.5–5 Torr) compared to Vasile and Smolinsky, and confirmed the observance of condensation reactions of  $C_2$  ions, mainly  $C_2H_2^+$  and  $C_2H_3^+$ , with methane and  $C_2$  neutrals. However,



radical species with the methylene radical  $\text{CH}_2$  as the dominant reactant, and hydrogen-deficient ions  $\text{CH}_2^+$  and  $\text{CH}^+$  were proposed to intervene in primary processes which lead to the formation of the previously detected  $\text{C}_2$  precursor ions. Adding a rare gas, argon or krypton, to the methane was shown to contribute to a higher rate of polymerization, attributed to efficient primary dissociation processes of methane molecules through collisions with excited rare-gas species. Methyl radicals were not included as a major component in the previous modeling of methane plasma processes. However, they were detected in radio frequency discharge in pure methane but at lower pressure (0.5–20 mTorr) by Toyoda and co-workers using the threshold ionization technique.<sup>425</sup> These authors reported the first mass spectrometric evaluation of the methyl radical density with a deduced value of  $3.1 \times 10^{11}$  radicals/ $\text{cm}^3$  for a methane pressure of 10 mTorr. The methyl radical density was shown to increase monotonically with the methane pressure for a fixed irradiation power.  $\text{CH}_5^+$  and  $\text{C}_2\text{H}_5^+$  were found as dominant ionic species in accordance with previous results<sup>420</sup> and the role of ion–molecule reactions in the variation of the methyl radical density with the pressure was confirmed. In the course of these investigations, a methyl radical recombination rate of  $4.3 \times 10^{-11}$   $\text{cm}^3$  radical<sup>-1</sup> was evaluated which corresponds to a low sticking probability evaluated at a value below  $10^{-3}$ . Spatial distributions of methyl radicals and methylene  $\text{CH}_2$  were similarly measured in methane discharge<sup>426</sup> and modeled with predominant ion–molecule reactions for the formation of the  $\text{CH}_3^+$  species at the higher pressures, while direct electron impact ionization was proposed to account for the formation of detected methylene. Similarly, differences were proposed in the processes leading to the loss of the two radicals with a predominance of recombination phenomenon for the decrease of  $\text{CH}_3^+$  and a predominance of radical–molecule reactions to account for the loss of  $\text{CH}_2$ . Rudolph and Moore<sup>427</sup> reported observations of the ions and neutrals generated in a microwave discharge in methane with various contents of argon or hydrogen as well as species formed from ablation of an amorphous C:H film by discharge in hydrogen. Large polymeric species of both ions and radicals have been observed and shown to depend on the flow rates, percent of methane, and nature of the carrier gas used. Discharges in a methane–argon mixture appeared to favor the production of highly unsaturated molecules with prominent linear polyalkyne molecules and a few radicals, while discharges in methane–hydrogen mixtures appeared to favor the formation of more saturated compounds with distribution continuing out to the  $\text{C}_{21}$  species.<sup>427</sup> The details of radical contents in each case are not provided, but analysis of the discharge mechanisms lead to the dramatic influence of the argon content in the mixture of gases to favor radical formation through bond breaking processes resulting from energy transfer by metastable argon. Methylene is proposed as a key participant in the plasma polymerization processes and methyl radicals are thought to account for the formation of observed hydrocarbons with either

an odd or even number of hydrogens. Similarly, preliminary experiments on methane discharges conducted by Fujii and Syouji<sup>428</sup> using ion attachment mass spectrometry (IAMS) to detect radicals generated under similar plasma conditions confirmed the drastic influence of hydrogen addition on the radical content of a methane-based plasma. All the radical peaks observed by IAMS in a pure methane discharge were almost completely depleted after hydrogen addition to the methane gas. However, methyl radicals were not detected under pure methane discharge conditions using IAMS nor during the former experiments of Rudolph and Moore.<sup>427</sup> The observed appearance of polymer hydrocarbons by lithium ion attachment acts in favor of radical–molecule reactions in expected chain initiation processes even if ion–molecule reactions are known to appear typically at faster rates than radical–molecule reactions. Obtaining information on neutral products from ion–molecule reactions would be beneficial for definite identification of the involved precursors in such mechanisms. Such studies are still lacking even if some experiments have been recently attempted for this purpose, using laser single-photon ionization for the direct detection of the radical products generated during ion–molecule processes.<sup>429,430</sup> For example, direct detection of methyl radicals in a flowing afterglow apparatus by single-photon ionization has been reported recently<sup>430</sup> from gas-phase reaction studies of  $\text{CO}^+$  and  $\text{N}_2\text{O}^+$  ions with  $\text{CH}_4$ . Nevertheless, complementary works on a methane discharge using IAMS with lithium ions<sup>431</sup> confirmed the results reported previously<sup>428</sup> as well as the efficiency of the method,<sup>78</sup> since experiments and theoretical calculations<sup>80,81</sup> are in accordance with the fact that the  $\text{Li}^+$  affinity of the detected  $\text{C}_n\text{H}_{2n-1}$ ,  $\text{C}_n\text{H}_{2n+1}$  hydrocarbon radicals is large enough that the radicals react with  $\text{Li}^+$  ions at nearly gas-kinetic collision rates with little if any mass discrimination.<sup>431</sup>

Using  $\text{Li}^+$  IAMS, Fujii and Syouji<sup>432,433</sup> reported investigations of both ions and radicals emanating from  $\text{CH}_4/\text{O}_2$  plasmas. The presence of various O-containing ionic species,  $\text{C}_n\text{H}_{2n+2}\text{OH}^+$ ,  $\text{C}_n\text{H}_{2n+2}\text{O}_2\text{H}^+$ ,  $\text{C}_n\text{H}_{2n}\text{OH}^+$ ,  $\text{C}_n\text{H}_{2n-1}\text{O}^+$ , as well as several neutrals,  $\text{C}_n\text{H}_{2n+2}\text{O}$ ,  $\text{C}_n\text{H}_{2n+2}\text{O}_2$ ,  $\text{C}_n\text{H}_{2n}\text{O}$ ,  $\text{C}_n\text{H}_{2n}\text{O}_2$  were observed, emphasizing the influence of proton-transfer reactions for the observance of the former species with  $\text{CH}_5^+$  or  $\text{C}_2\text{H}_5^+$  as suggested proton-transfer reagents to model the chemistry of the  $\text{CH}_4/\text{O}_2$  plasmas. Similarly, products resulting from proton transfer reactions, presumably,  $\text{CH}_5^+$  or  $\text{C}_2\text{H}_5^+$ , too have been detected from the study of a  $\text{CH}_4/\text{N}_2$  discharge,<sup>434</sup> besides primary electron ionization products. The features of the ion chemistry in  $\text{CH}_4/\text{N}_2$  discharge appear to be related to excited nitrogen molecules or nitrogen atoms interactions with the hydrocarbon species to produce nitrogen-bearing polymer hydrocarbons,  $\text{C}_m\text{H}_n\text{CN}$ ,  $\text{NC}(\text{CH}_2)\text{CN}$ ,  $\text{C}_m\text{H}_n\text{NH}_2$ ,  $\text{C}_m\text{H}_n\text{N}_2\text{H}_3$ , in addition to the above-mentioned proton-transfer reactions. Various kinds of chemical species have been effectively demonstrated to appear in microwave  $\text{CH}_4/\text{N}_2$  discharge since over 50 N-bearing products have been identified.

Smolinsky and Vasile<sup>435</sup> reported on a mass spectrometric study of the ionic and neutral species generated in a low pressure (0.1–1.0 Torr) ethylene discharge and confirmed the necessity of sampling the discharge at different locations to obtain an accurate representation of the plasma chemistry since the observed chemistry can significantly differ depending on whether the discharge is sampled axially or radially from the core of the plasma. In fact, the appearance of abstraction reactions responsible for the formation of intermediate radical species such as vinyl radicals requires the presence of “hot” hydrogen atoms to compete with the formation of ethyl radicals through addition reactions to the parent ethylene molecules to rationalize the expected reaction pathways of the ethylene discharge. Production of energetic hydrogen atoms were then proposed to be limited to the rf sheath of the plasma and accounting for the predominance of the vinyl radicals when the discharge is sampled in this part of the plasma, namely axially. On the contrary, radial sampling did not show any noticeable vinyl radical flux. Similar measurements were carried out for the ethyl radicals resulting in a deduced balance between ethyl and vinyl radicals of 1.3 in favor of vinyl radicals to account for the conversion of precursor ethylene molecules to acetylene molecules. In addition to the radical chemistry of the plasma, the ion chemistry also differs from the place of sampling in accordance with previous results reported for methane<sup>420,421</sup> or ethane<sup>436</sup> discharges. And the dominant proposed mechanism for ion formation was ionization of radicals in the rf sheath of the plasma as was the case for the methane and ethane systems. However, no gaseous products containing more than two carbon atoms were detected.<sup>435</sup> On the contrary, identification of an unfamiliar neutral species, carbon carbenes up to  $C_9H_2$ , and hydrocarbon polymer radicals,  $C_nH_3^*$ ,  $C_nH_5^*$ ,  $C_nH_7^*$ , was reported by Fujii and Kim<sup>437</sup> using  $Li^+$  IAMS to probe a microwave discharge in pure ethylene. Larger hydrocarbon compounds are thought to result from the initial formation of ethyl radicals through ethylene dissociation reaction, followed by successive condensation reactions of this radical with other hydrocarbon compounds. The formation of higher carbene compounds are accounted for by the formation of a linear cumulene backbone with successive additions of carbon atoms with acetylene as a neutral intermediate species. The observation of  $C_4H_3^*$  suggested either the reaction of acetylene with an ethynyl radical or the abstraction reaction of molecular hydrogen with acetylene by a vinyl radical to explain its presence.<sup>437</sup>

Discharges in acetylene present the disadvantages of rapidly generating deposits on the walls of the discharge tube, making the tube opaque and plugging the orifice. Conversion to a polymer occurs at a rapid rate, which makes the control of the steady-state conditions of the discharge difficult and limits the experimental investigation. However, Vasile and Smolinsky<sup>438</sup> characterized the acetylene rf discharge using direct axial and radial samplings of ions and neutrals. The principal ionic condensation reaction was summarized in a reaction sequence involving

$C_2H_x^+$  ionic species that successively react with neutral acetylene to generate higher-order ionic products,  $C_4H_2^+$ ,  $C_4H_3^+$ ,  $C_6H_2^+$ , etc. As observed in the preceding studies,<sup>420,421,435,436</sup> axially sampled ions appeared to be characteristic of more energetic ionization processes compared to radially sampled ions, and in the latter case, these ions are presented as resulting from more abundant ion–molecule condensation reactions. The reported nonionic products were hydrogen and acetylene.<sup>438</sup> The state of excitation of reactant ions was believed to be correlated with the resulting degree of unsaturation in the corresponding condensation products and no evidence appeared for the alteration of the observed chemistry by diluting the gas mixture with rare gas. Only xenon showed evidence for excess energy reaction. Platzner and Marcus<sup>439</sup> confirmed later the noninfluence of the admixture of argon in a microwave discharge in acetylene. Operating with a higher pressure value than in the preceding case (namely, ca. 2 Torr vs 0.1–0.4 Torr), only polyacetylene of general formula  $H(C\equiv C)_nH$  was identified in pure acetylene plasma. The ethynyl radical was proposed as a major reactant for the condensation of the acetylene molecule to a  $C_4H_2$  product, which further reacts with acetylene to generate higher carbon-content neutrals. As no species with an odd number of carbon atoms were detected during the experiments, the authors concluded that radicals, or ions, with one carbon atom were not generated directly in the plasma, the microwave energy is assumed to preferentially conduct to a C–H bond breaking rather than a  $C\equiv C$  triple bond breaking in accordance with the energy requirements for such dissociations.<sup>439</sup> Nevertheless, this preference is altered when adding oxygen or nitrogen to the acetylene discharge. In the presence of oxygen and nitrogen, oxidation products and nitrogen-containing species (mainly cyanoacetylenes  $H(C\equiv C)_nCN$ ) are generated in addition to polyacetylenes, and methylene or  $CN^*$  radicals are presented as the major radical intermediates. Among the two major reaction channels proposed for the observation of condensation products formed from acetylene plasmas,<sup>440</sup> the ion–molecule reaction channel involving  $C_2H_2^+$  ions was preferred to the radical–molecule reaction channel involving the ethynyl radical. The above suggestion that ions are the major reactive species for the observed condensation reactions is in disaccord with the assumption presented by Koyabashi and co-workers<sup>422</sup> who proposed that free radicals are more likely responsible for the glow-discharge polymerization processes on the basis of their higher expected density compared to ionic species.

The determination of ionic and neutral components of a microwave discharge in pure acetylene has been performed by  $Li^+$  IAMS conducted in investigating the various parameters which influence the plasma composition, flow rate (pressure), microwave-induced power input, and microwave cavity position.<sup>441</sup> An attempt to make the link between the ionic and neutral species involved in the condensation processes led to a model for the reaction sequences implicating both ions and radicals in relation to the

corresponding species detected in these experiments. The principal ionic condensation reaction was proposed to result from the condensation of ionized acetylene  $C_2H_2^+$  with neutral acetylene to generate the  $C_{n+2}H_2^+$  species, while hydrogen atoms were proposed to account for the formation of the  $C_mH_n$  neutral species ( $n > m$ ). The lack of neutral and ionic species with odd-numbered carbons was interpreted by the unfavorable cleavage of acetylene to CH radicals to a significant extent, in agreement with the conclusion drawn earlier.<sup>439</sup> Analysis of a dilute mixture of acetylene with nitrogen was reported later by Fujii,<sup>443</sup> with the observed production of derived nitriles, amines and hydrazines. The mechanisms for generation of these species are supposed to involve active nitrogen atoms as the primary radical product, with likely exothermic interactions between  $N^*$  and acetylene or other hydrocarbon species suggesting the production of N-bearing hydrocarbon products. The  $C_2H_2/N_2$  microwave discharge effectively led to the detection of over 70 N-bearing products of formulas  $C_mH_nCN$ ,  $NC(CH_2)_nCN$ ,  $NC(C)_nCN$ ,  $C_mH_nNH_2$ ,  $C_mH_nN_2H_3$  with  $m$  and  $n$  continuing on to 8 and 15, respectively. These results suggested that nitriles, amines, and hydrazines of higher molecular weight as well as their derivatives may have been synthesized under similar processes implying energy delivery through a plasma medium and could be considered for the modeling of primary planetary processes.

In addition to simulation experiments of primary planetary atmospheres, MS analysis of plasmas generated from electrical discharges presents advantages as a tool for investigating the role of radicals in chemical vapor deposition processes and for developing plasma processing methods. For this purpose, Weimer and Johnson<sup>444</sup> reported the use of a microwave plasma-enhanced chemical vapor deposition system to characterize reactive species of plasmas generated from methane, acetylene, ethylene, and carbon monoxide as carbon-source gases. Emission of CH was observed from the different plasmas but using optical emission spectroscopy to complement mass spectrometry. This study confirmed the emission of a  $C_2$  species in an acetylene plasma mixed with hydrogen gas as previously reported for microwave discharge in pure acetylene,<sup>441,442</sup> and molecular oxygen was shown to drastically affect the product composition mainly converting the carbon source to carbon monoxide. Among the methods used, molecular beam mass spectrometry<sup>445</sup> has been employed for the specific purpose of measuring the gaseous composition of the vapor environment during chemical vapor deposition of diamond. In principle, this type of experiment has been revealed to be adaptable to a broad range of other applications that rely either on thermal- or plasma-induced chemical kinetics. Examples of applications have been provided with the detection of H,  $H_2$ ,  $CH_3$ ,  $CH_4$ , and  $C_2H_2$  during diamond growth.

The plasma-etching processes of silicon and silicon dioxide with perfluorocarbon gases have received a great deal of attention in relation to their industrial interest. Mass spectrometry and optical emission spectroscopy have been complementarily used in the

diagnosis of such plasmas. Due to the different conditions under which each technique is used, reported results, however, can be sometimes so different if not even conflicting and, consequently, several chemical and physical mechanisms have been suggested to model the etching processes. The chemical pathways that lead to film growth in silicon chemical vapor deposition processes are diverse and complicated enough to justify a need for further investigations even if some aspects of these mechanisms have already been revealed in detail.<sup>446</sup>

Smolinski and Flamm<sup>447</sup> reported a mass spectrometric analysis of the plasma reactions observed from  $CF_4$  and  $CF_4/O_2$  discharges as functions of several experimental parameters (pressure, flow rate, oxygen contents). The observed products from pure tetrafluoromethane discharge were the fluorine atom, molecular fluorine and hexafluoroethane. Although no direct evidence for the presence of trifluoromethyl radicals could be found downstream from the discharge, they have been inferred from the detection of  $C_2F_6$  as a product. In the presence of Si crystals, the discharge composition evolved with a noticeable decrease of the fluorine atom concentration and the presence of  $SiF_4$ , proposed to result from the reaction of trifluorosilyl radicals with molecular fluorine.  $CF_4/O_2$  discharges showed a marked change in product formation, with an increase of the concentration of fluorine atoms and fluorine molecules, the vanishing of  $C_2F_6$  molecules and the appearance of new carbonyl products, COF,  $COF_2$ , and CO. In presence of Si crystals, product analysis suggested recombination of  $F_2$  with  $SiF_x$  intermediates characterized by the detection of  $SiF_4$ . In both cases, in adding molecular oxygen to the gas, evidence was presented that carbon monoxide forms in an early stage of an oxidation process and is subsequently oxidized to the  $CO_2$  and  $COF_2$  observed products detected at longer residence times of the experiments. In the course of the previous study, the effect of added hydrogen on a rf discharge in  $CF_4$ ,  $CF_3H$ ,  $C_2F_6$  was reported.<sup>448</sup> Observed products from the  $CF_4$  discharge were F,  $F_2$ , and  $C_2F_6$  in accordance with previous experiments. In the case of the  $CF_3H$  discharge, products were HF,  $CF_4$ ,  $C_2F_4$ ,  $C_2F_6$ ,  $C_2HF$ , and  $C_2H_2$  and the presence of  $CF_2$  intermediates was postulated. The  $C_2F_6$  discharge provided essentially  $CF_4$  and  $C_2F_4$  as products. On adding molecular hydrogen to the feed gas, both  $CF_4$  and  $C_2F_6$  gave the same products as the  $CF_3H$  discharge with distributions correlated to the  $H_2$  concentration. Rationalization of the mechanisms led these authors to consider that the chemistry of the  $CF_4$  and  $C_2F_6$  discharges was primarily that of trifluoromethyl radicals with successive fluorine atom abstraction reactions to involve the lower-order intermediates in the reaction scheme. Hydrogen addition was revealed to trap radical intermediates at low concentration when a change of the nature of the discharge was observed at higher concentration.

Ionic and neutral species eluting from a radio frequency discharge in tetrafluoroethylene have been investigated by Vasile and Smolinsky<sup>449</sup> and chemistry of this plasma has shown dominant gas-phase

neutral production as well as polymeric species deposition. Ionic species are reported as characteristics of electron impact ionization on tetrafluoroethylene and neutral products containing three or four carbon atoms usually not observed under the same conditions in hydrocarbon discharges.<sup>420,435,436</sup> Using appearance energy measurements for the characterization of the radical species, experiments gave evidence for the effusion of  $\text{CF}_2$  but not for  $\text{CF}^\bullet$  or  $\text{CF}_3^\bullet$  radicals from the tetrafluoroethylene discharge.<sup>449</sup> The effect of added acetylene on the radio frequency discharge chemistry of  $\text{C}_2\text{F}_6$  has been studied as a function of acetylene concentration.<sup>450</sup> Detected products were similar to those observed in  $\text{C}_2\text{F}_6/\text{H}_2$  discharge. A large amount of polymeric products with a  $(\text{CF})_n$  composition was generated in the discharge zone and  $\text{CF}_2$  was readily observed in the effluent gas. Under etching conditions, introducing  $\text{SiO}_2$  in the discharge zone, the level of difluorocarbene was observed to diminish, suggesting an active role for the etching processes involving both  $\text{CF}_2$  and  $\text{SiO}_2$ . The resulting chemical model to account for the discharge composition finally assumed an equilibrium between dissociation and recombination reactions of fluorocarbon fragments and fluorine atoms, whereas the addition of oxygen to the feed gas was shown to scavenge low valent carbon species, making more fluorine atoms available for etching processes.

Development of predictive models for chemical vapor deposition processes has led to the use of mass spectrometry techniques for obtaining physical constants directly involved in these processes. Jasinski<sup>451</sup> reported direct loss measurements for the heterogeneous reaction of silyl radical  $\text{SiH}_3^\bullet$  in a discharge flow reactor coupled to a mass spectrometer in order to follow the radical concentration, and total surface loss coefficients for the silyl on two different surfaces were then determined, confirming the lower reactivity of the silyl radical compared to silylidene  $\text{SiH}^\bullet$  and silylene  $\text{SiH}_2^\bullet$  in qualitative consistency with reported hydride bond values for these species.<sup>446</sup> These values must be correlated to the sticking coefficients of  $\text{SiH}_x^\bullet$  radicals measured from real-time detection in a low-pressure Knudsen cell using the REMPI technique.<sup>452,453</sup>

Similarly, appearance mass spectrometry has been applied to high-sensitivity space-resolved measurements of the number density of neutral free radicals in reactive plasmas including methane and  $\text{CF}_4$ .<sup>454</sup> The influence of excited parent molecules and radical sticking could be probed and spatial distributions of the neutral radical could be measured. Koshi and co-workers<sup>455,456</sup> performed kinetic studies of  $\text{SiH}_3^\bullet + \text{SiH}_3^\bullet$  and  $\text{SiH}_3^\bullet + \text{O}_2$  reactions using the near-threshold electron impact ionization method and measured the related rate constants through the first-order decay rate of the silyl precursors generated from laser photolysis of a mixture of  $\text{CCl}_4/\text{SiH}_4/\text{He}$  and  $\text{CCl}_4/\text{SiH}_4/\text{O}_2/\text{He}$ , respectively. Robertson et al.<sup>457</sup> measured the  $\text{SiH}_n^\bullet$  radical density at the deposition surface of a radio frequency discharge using low-energy electron ionization for the detection of corresponding  $\text{SiH}_n^+$  ions. The principal radical detected

in proximity of the discharge was  $\text{SiH}_3^\bullet$ , whereas the silylene radical  $\text{SiH}_2^\bullet$  was proposed as a nondominant species suggesting a reduced role for this latter radical in film growth processes. Mayo and co-workers<sup>458</sup> reported on their dissociation study of tetrachlorosilicon to silicon and hydrogen chloride in a microwave plasma of argon or argon/hydrogen. While mass spectrometry was used in conjunction with the electron-spin resonance and electrostatic double-floating probe system for evaluating electron energy and ion density, kinetic studies of the system indicated different dissociation mechanisms involving predominance of ion-molecule or radical-molecule reactions, depending on the plasma compositions and the presence of hydrogen in the initial gas mixture, with  $\text{SiCl}_3^\bullet$  and  $\text{SiCl}_2^\bullet$  as the major radical species. As quoted above, for the analysis of processes leading to the formation of diamond-like films,<sup>427</sup> the determination of active species, ions or radicals, is essential for the understanding of deposition mechanisms and, for this purpose, Erhardt and co-workers<sup>459</sup> used secondary ion mass spectrometry to investigate hydrogenated C:H films under a wide range of pressures and ion-energy conditions in determining the composition of carbon clusters observed in the bulk material of these films. The threshold ionization technique was utilized by Robertson and Gallagher<sup>460</sup> for the determination of relative densities of  $\text{SiH}_n/\text{SiH}_3$  silicon radicals in silane/argon mixtures under the most appropriate conditions for the formation of high-quality amorphous Si:H films.  $\text{SiH}_3^\bullet$  was reported as the dominant monosilicon radical under studied conditions, whereas  $\text{Si}_2\text{H}_2^\bullet$  was the prominent disilicon radical detected. The general high-disilicon radical densities suggested the presence of higher homologues,  $\text{Si}_x\text{H}_n^\bullet$  ( $x > 2$ ), for those authors who considered these species to be involved in processes of nucleation and dust formation. Hayashi and co-workers<sup>461</sup> coupled a radio frequency plasma chamber to a field ionization mass spectrometer for the purpose of detecting neutral species generated in discharge plasmas. They applied this technique to the analysis of radio frequency silane and silane/nitrogen plasmas.<sup>462</sup>  $\text{SiH}_3^\bullet$  was also suggested as the dominant  $\text{SiH}_n^\bullet$  monosilicon radical species and responsible for the growth of amorphous Si:H films. The silane plasma was shown to contain  $\text{Si}_2\text{H}_n^\bullet$  radicals, presumably resulting from chemical reactions of atomic hydrogen present in the plasma with film surfaces. For silane/nitrogen plasmas, the growth of the SiN films was suggested to result from reactions between atomic nitrogen and deposited  $\text{SiH}_n^\bullet$  radicals.

Among the radical species that have retained the particular attention of the experimentalists for a long period, the hydroperoxy radical,  $\text{HO}_2^\bullet$ , is one such radical due to its importance as intermediate in most combustion chain reactions involving hydrogen and oxygen, from the early stage of radical MS experiments.<sup>34,43,53</sup> First detection of the  $\text{HO}_2^\bullet$  species was reported unequivocally by Foner and Hudson<sup>463</sup> from the gas-phase reaction of hydrogen atoms with oxygen molecules. The lack of direct spectroscopic evidence of its presence in trapping experiments<sup>464</sup> as well as the absence of the characterization of other

potential compounds to explain the reducing properties of isolated condensation products, suggesting higher-order hydrogen superoxides,<sup>465,466</sup> have given impetus to thorough investigations on the detection of HO<sub>2</sub><sup>•</sup> radicals. Characterization of HO<sub>2</sub><sup>•</sup> radicals by mass spectrometry opened the way to experimental measurements of related thermochemical quantities<sup>467,468</sup> as well as preliminary studies on hydrogen/oxygen<sup>469,470</sup> or methane/oxygen reactions,<sup>471</sup> which in turn opened the way to experiments later developed in the field of kinetic chemistry.

## 2. Flame Analysis

A flame is a complex reacting chemical system which contains many interfering species, and is also a flow system with steep gradients of reactive species that can result in substantial concentration differences between different locations of sampling involving the necessity to associate a composition with a precise position in the system. Consequently, the central problem for flame analysis by mass spectrometry lies in obtaining a representative sample and an accurate interpretation of the sample qualitatively and quantitatively within the experimental procedure.<sup>472</sup> Justifiable concerns about the ways of probing the sampled system and the consequent credibility of mass spectrometric data have appeared in the literature.<sup>473</sup> If the objective is the identification of occurring species and the determination of appearance energies, flame disturbance becomes less important. If the aim is to analyze the processes involved, the sampling operation must not disturb the flame and the quantitative nature of the sampling must be scrupulously established. As a matter of fact, and from an experimental point of view, molecular beam mass spectrometry has been revealed to be particularly well-suited for such investigations<sup>46,53</sup> as a technique allowing the study of both stable and unstable species using the same experimental procedure.<sup>474</sup> The difficulty of flame sampling is related to the complexity of observed processes and the production of nonequilibrium excited species: atoms, ionic, and radical species.<sup>472</sup> The important reaction intermediates in flames are atomic and radical species and these include principally H<sup>•</sup>, OH<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, and HO<sub>2</sub><sup>•</sup>,<sup>472–474</sup> as quoted in most of the available mass spectrometric studies mainly devoted to hydrocarbon flame analysis (Table 5). However, these investigations are generally conducted with the aim of validating hydrocarbon combustion mechanisms rather than to characterize a particular radical species and, consequently, are more relevant to the field of chemical kinetics than the field of mass spectrometry investigations.<sup>475</sup> Among the above radicals, the hydroxyl and hydroperoxo radicals are particularly well-documented in kinetic studies often using mass spectrometry as a complementary tool, even if MS has been particularly useful for the determination of quantities such as in particular, IEs<sup>476–481</sup> and EAs.<sup>482–484,308,310</sup>

Homann and co-workers<sup>485–487</sup> introduced a radical scavenging method for the identification of hydrocarbon radicals by supersonic nozzle-freezing combined with a reaction with dimethyl disulfide on a

liquid nitrogen cooled trap followed by subsequent characterization using GC/MS after warming-up. This method has been applied to radicals generated from electrical discharges or flames and shown to allow a quantitative analysis of the effluent content. The scavenging reactions, addition or displacement, and related rate constants in the gas-phase are reported to be of minor importance for the scavenging efficiencies<sup>485</sup> after investigation of the various parameters—radical concentration, flow of scavenger molecules, pressure in the vacuum chamber, and flow through the sampling nozzle, which influence the processes. It was concluded from these testing experiments<sup>485</sup> that the method should be more efficient for heavier radicals in lowering the large scattering effects observed for light species, like hydrogen atoms, and for the investigation of higher-mass radicals would avoid the production of very volatile products more difficult to analyze through GC/MS. Applied to acetylene/oxygen flame, the method permitted one to characterize the methylene, phenyl, and C<sub>3</sub>H<sub>2</sub><sup>•</sup> radicals besides the H<sup>•</sup> and O<sup>•</sup> atoms, while an analysis of the same mixture submitted to a microwave discharge lead to the detection of the C<sub>2</sub>H<sup>•</sup>, C<sub>4</sub>H<sup>•</sup>, C<sub>6</sub>H<sup>•</sup>, C<sub>3</sub>H<sub>2</sub><sup>•</sup>, C<sub>2</sub><sup>•</sup> radicals besides H<sup>•</sup> atoms.<sup>486</sup> The original trapping device was later modified to improve the quantification of the radical species.<sup>487</sup> Large hydrocarbon radicals, usually difficult to detect by the only optical methods have been characterized by this method of radical scavenging with dimethyl disulfide. Further sampling of acetylene/oxygen flames<sup>488</sup> lead to the characterization of large C<sub>x</sub>H<sub>y</sub> radicals ( $x = 4$ ), as well as H<sup>•</sup>, CH<sub>3</sub><sup>•</sup>, C<sub>4</sub>H<sub>3</sub><sup>•</sup>, and C<sub>6</sub>H<sub>5</sub><sup>•</sup> radicals scavenged as monomethylthio compounds. The observed bis(methylthio) compounds were attributed to carbene precursor species that can be assigned to reaction with dimethyl disulfide proceeding via a transient ylide intermediate with a subsequent insertion into a C–S bond or preferentially into a weaker S–S bond. An unusual scavenging product, tris(methylthio)ethane (CH<sub>3</sub>S)<sub>3</sub>C<sub>2</sub>H<sub>3</sub>, was obtained and attributed to a multiple addition of methylthio radicals (with a bis(methylthio)ethane radical intermediate) even though similar precursors, C<sub>4</sub>H<sub>3</sub><sup>•</sup>, C<sub>2</sub><sup>•</sup>, C<sub>3</sub>H<sup>•</sup>, did not yield the same scavenging products through a possible analogous chain reaction. A further unresolved question concerned the origin of scavenging products of general formula, C<sub>2n</sub>H<sub>2</sub>(SCH<sub>3</sub>)<sub>2</sub> ( $n = 1–4$ ), for which a similar chain reaction involved thioethyne radical intermediates; their observation might give first evidence for the presence of excited acetylene or excited polyynes in the acetylene/oxygen flame. Consecutive reactions of radicals with stable products in the flame as well as their recombinations in the cold trap were considered to be suppressed by the scavenging reactions. Preliminary comparisons with reported hydrocarbon mole fractions confirmed that condensing efficiencies for mono and polycyclic aromatic hydrocarbons was nearly 100%, leading to a resulting similar assumption for the phenyl, C<sub>4</sub>, and C<sub>5</sub> radicals. This technique of radical scavenging with dimethyl disulfide has been used for the investigation of pyrolysis products of several hydrocarbons—ethene, acetylene,

1,3-butadiene, and benzene.<sup>489</sup> Compared to molecular beam mass spectrometry that uses sampling through a nozzle probe, the free jet condensation scavenging method does not present the problems associated with product ion fragmentations<sup>490</sup> and, in addition, calibration for quantitative analysis can be done with stable products in solution for the GC/MS detection procedure rather than with radicals in the gas-phase. Quantitative analysis of hydrocarbon radicals and carbenes in flat premixed low-pressure flames of acetylene, 1,3-butadiene, ethylene, and methane burned in a fuel-rich mixture with pure oxygen were reported by Hausmann and Homann<sup>490</sup> with the derived profiles for the mole fractions of observed radicals. Qualitatively, the flame composition was shown to be similar for the four cases, but quantitatively large differences were observed. Methyl radicals were found as the most abundant hydrocarbon radical in all flames studied, even though its quantitative characterization was not possible. The methane flame showed the largest concentration of methylene, with a little higher hydrocarbon content, suggesting that methylene is not an important growth species for the formation of large aromatics. Observed scavenging products were attributed to dicarbon ( $C_2^*$ ), unsaturated or aromatic hydrocarbon radicals ( $C_2H^*$ ,  $C_3H^*$ ,  $C_4H^*$ ,  $C_6H_5^*$ ,  $C_{2n}H_3^*$ ), alkyl radicals ( $CH_3^*$ ,  $C_2H_5^*$ ) and carbenes ( $C_3H_2$ ,  $C_5H_2$ ), while methoxy was found only in methane flame as well as oxygenated products in the 1,3-butadiene flame. Discussion on the results focused on the compatibility between observed products and published mechanisms for combustion processes. Satisfactory agreement was observed for stable (nonradical) components of the flames, while less agreement was obtained for the radical species. However, this new scavenging technique, particularly useful for the modeling of hydrocarbon chemistry in flames, might be more oriented to experimental radical concentrations than provided before by other techniques, resulting in proposals for the mechanism of formation, as exemplified in the case of ethynyl- or vinyl-type radicals.<sup>490</sup> Recently, radical detection by the free jet condensation scavenging method was extended to REMPI mass spectrometry for the analysis of large flame polycyclic aromatic hydrocarbon radicals.<sup>491,492</sup> The two photons-REMPI technique associated with high-resolution time-of-flight mass spectrometry was proposed as a means to analyze a wide variety of PAHs-derived compounds in low-pressure flames.<sup>491</sup> Among these, a wide range of  $C_xH_y^*$  radicals ( $x = \text{even, odd number, } x = 18-70, y = \text{odd number}$ ) was observed. The results obtained on large PAH radicals lead the authors to reconsider the mechanism for their formation. The model in which PAHs appear to be too inert for adding smaller unsaturated hydrocarbon molecules (acetylene) for the growth processes, and which necessitates that free H atoms are abstracted from PAHs to generate  $\sigma$ -radicals was cast in doubt. On the contrary, rather than the radical or nonradical character of the intermediates, their structures were considered to have more influence in forming reactive structures with a decisive role for the hydrogen-rich PAHs with respect to growth and consumption.

## C. Miscellaneous

Interest in elusive species is, to a large extent, due to the role these species are supposed to play as intermediates in the chemistry of interstellar media or gaseous mixtures assumed to model primary atmosphere conditions. However, the execution of simulation experiments of planetary atmospheres is a challenging laboratory task since sensitive detection and isolation of reactive species must be conducted during the same experiments. Experiments illustrative of mass spectrometry studies of free radicals have however been reported in this domain and will be touched on here.

Production of gaseous hydrocarbons, nitriles, and amines in a continuous-flow microwave plasma discharge of a 10%CH<sub>4</sub>/90%N<sub>2</sub> mixture was reported by Fujii and Arai.<sup>493</sup> During these experiments potentially relevant to the atmospheric chemistry in Titan's atmosphere, more than 70 gaseous products were detected and compared to the species detected by the Voyager spacecraft. As a consequence of the good correlation between simulation and compiled space data, microwave discharge plasma was proposed as a valid simulation of processes suspected to occur under various atmospheric conditions relevant to interstellar media. Unfamiliar polycarbon nitriles  $C_nN^*$  ( $n = 2-5$ ) of interstellar importance were revealed to be accessible and characterized in the gas-phase by neutralization-reionization mass spectrometry (NRMS) by primary electron impact ionization of the dicyanoacetylene  $NC(C\equiv C)CN$  and the dicyanodiacetylene  $NC(C\equiv C)_2CN$  neutral precursors, followed by a direct cleavage process which affords the complete series of the corresponding  $C_nN^+$  ions.<sup>494</sup> These mass-selected ions subsequently submitted to an NRMS experiment provided abundant recovery signals attributed to the corresponding polycarbon nitrile radicals, obtained either directly through reionization or alternatively by fragmentation of the precursor ion prior to reionization. More recently, again under NRMS conditions, it was the small unsaturated  $NCN^*$  radical which has been unequivocally generated by charge-stripping experiments of the  $NCN^*$  precursor anion for which the structure was assigned by charge reversal experiments.<sup>332</sup>

In the domain of interstellar chemistry, the chemistry of silicon compounds has focused a particular attention on the understanding of chemical pathways permitting one to assert mechanisms involved in the pathways from cationic silicon precursors to neutral silicon-containing homologues. With such a purpose in mind, the silicon acetylide  $SiC_2H^*$  radical<sup>495</sup> and hydrogenated silicon carbides  $SiC_xH^*$ <sup>496</sup> have been generated and characterized by NRMS experiments. In the latter case, investigations on the structural characterization of the  $SiC_xH^*$  series, reflecting indeed the stability of such silicon carbide derivatives in the gas-phase, have confirmed the accessibility to the  $SiC_4H^*$  and  $SiC_6H^*$  radicals through neutralization-reionization of the precursors cations  $SiC_xH^+$  directly generated from electron impact ionization of the  $C_6H_5SiH_3$  neutral precursor.<sup>496</sup> Interest in elusive silicon-containing species has not weakened over the

years since the silicon radical cation might be involved in the formation of Si–N bonds in the chemistry of interstellar clouds.<sup>497</sup> Mass spectrometric studies have demonstrated that the hydrogensilacyanid radical HNSi• could be observed in neutralization experiments of HNSi<sup>+</sup> cations generated by electron bombardment of a mixture of nitrogen and iodosilane.<sup>498</sup> If there is still a doubt about the structure of this radical since the silacyanic acid NSiH• cannot be completely ruled out, in view of corroborating experimental data and theoretical calculations, the HNSi• structure is more probable. In a paper reporting combined collisional activation and neutralization–reionization experiments, Goldberg and co-workers<sup>497</sup> compiled detailed theoretical and experimental investigations of various isomeric structures of the [H<sub>2</sub>SiN]<sup>+</sup> cations with circumstantial evidence for the existence of the SiNH<sub>2</sub>• radical.

In a search of potential interstellar molecules, Peppe et al.<sup>499</sup> presented an investigation on C<sub>3</sub>HO• radicals generated from their charged precursors to assess their stability. HC<sub>3</sub>O• and •C<sub>2</sub>CHO radicals have been prepared under soft-ionization conditions, directly from the protonated methyl propionate for the former case and from a sequence of displacement reactions for the latter case. Theoretical calculations were shown to confirm that neutralization of HC<sub>3</sub>O<sup>+</sup> and •C<sub>2</sub>CHO ion precursors should produce the two former radicals. A combination of collisional activation and neutralization–reionization experiments has drawn the conclusion that the HCCCO• radical was stable within the neutralization–reionization experiment time scale. Charge-stripping of the precursor anion •C<sub>2</sub>CHO might produce predominantly the •C<sub>2</sub>CHO radical but isomeric rearrangement could appear with the HCCCO• structure as the most probable product.<sup>499</sup>

NRMS experiments devoted to radicals are by far not limited to the field of interstellar chemistry but have provided a wealth of data relevant to gas-phase chemistry in connection with atmospheric and combustion chemistries as well as mechanistic studies. In this regard, intermediates relevant to the oxygenated sulfur radical and molecule processes have been studied by combined high-level theoretical calculations and NRMS experiments by Frank and co-workers.<sup>500,501</sup> Preliminary experiments reported on the formation of the hydroxysulfinyl radical HOS•O from collisional reionization of the protonated sulfur dioxide cation HOSO<sup>+</sup>.<sup>500</sup> In subsequent experiments, hydroxysulfinyl HOS•O and hydrogensulfonyl HS(O)<sub>2</sub>• radicals were shown to be thermodynamically and kinetically stable with two evidenced rotamers for HOS•O.<sup>501</sup> However, it appeared that a major fraction of the hydroxysulfinyl HOS•O radicals was formed in an excited electronic state upon collisional electron transfer to account for the observed unimolecular dissociation processes under neutralization–reionization conditions. This observation provided additional evidence for the important role played by metastable excited states in the formation of transient species by fast collisional electron transfer. The capabilities of NRMS for studying unimolecular neutral dissociation have been extended recently by

the introduction of the variable-time method,<sup>502</sup> which uses different temporal profiles to scrutinize the dissociation processes. Methylsulfonyl CH<sub>3</sub>SO<sub>2</sub>• and methoxysulfinyl CH<sub>3</sub>OSO• radicals have been produced by femtosecond collisional electron transfer and studied by this method combined with fast-beam laser photoexcitation to probe ground and excited electronic states of these neutrals.<sup>503</sup> Both radicals are predicted to be stable in the gas-phase. Their counterpart cations were generated from dissociative ionization of methyl sulfone for the methylsulfonyl cation and from dimethyl sulfide for the methoxysulfinyl cation respectively, with a dissociation pathway greatly complicated by reaction energetics in the former case. The neutral and post-reionization ion dissociations were distinguished using variable-time experiments. The CH<sub>3</sub>SO<sub>2</sub>• radical was shown to dissociate to SO<sub>2</sub> and CH<sub>3</sub>• because of a large Franck–Condon energy associated with the neutralization whereas the CH<sub>3</sub>OSO• radical yielded the lowest dissociation pathway with the same products via an isomerization to its methylsulfonyl isomer.<sup>503</sup> The properties of the [C, H<sub>3</sub>, S, O<sub>2</sub>] ions and radicals paralleled those of the homologous [S, O<sub>2</sub>, H] species,<sup>501</sup> with comparable endothermic S–O bond cleavage, interpreted as occurring on the excited-state potential energy surfaces, generalizing the likely appearance of metastable excited electronic states under vertical electron transfer.

Sadilek and Tureček<sup>502</sup> addressed the question of the high-energy content of hydrochlorofluorocarbon radicals studying the dissociative processes of the •CHClF and •CHCl<sub>2</sub> radicals. Loss of the chlorine atom is revealed to be the major observed dissociation channel after collisional neutralization for both radicals. The direct bond cleavage processes (H• and Cl• atom formation) for the chlorofluoromethyl radical •CHClF are presented to surpass the HF elimination in dissociating •CHClF, making this radical an efficient source of chlorine atoms susceptible to contributing to ozone depletion if the radical possesses sufficient internal energy content.<sup>502</sup>

Tureček and co-workers<sup>504</sup> reported on the formation and unimolecular dissociation of the tetrahydroxyphosphoranyl radical P(OH)<sub>4</sub>• to scrutinize the intrinsic stabilities and Franck–Condon effects in collisional neutralization of this radical and its cationic homologue. Chemically, this radical can be viewed as a product of a hydrogen atom attachment to phosphoric acid or as an intermediate in hydroxyl radical attack on trihydroxyphosphine. In addition, such tetracoordinated oxygenated phosphorus radicals were prepared for the first time in the gas-phase. The P(OH)<sub>4</sub><sup>+</sup> cation, generated from dissociative ionization of triethyl phosphate, under vertical neutralization formed a tetrahydroxyphosphoranyl radical which appeared to dissociate by hydrogen loss to form phosphoric acid. Vertical neutralization of the P(OH)<sub>4</sub><sup>+</sup> cation is calculated to deposit 129 kJ/mol in the radical which agrees well with its observed unstability in the neutralization–reionization spectrum and, in regard to the hydrogen loss dissociation channel, is in agreement with the calculated energy requirement of 90 kJ/mol. The importance of the

Franck–Condon effect on vertical electron transfer in phosphorus oxo compounds is pointed out since large influences are expected from the differences in the P=O and P–O bond lengths as well as changes in electron distributions under ionization processes. Conversely, pathways from the cation to the radical can result in vibrational excitation that can drastically influence the unimolecular chemistry of the radical.

Application of a newly introduced method for sector mass spectrometry residing in the interpretation of differences observed in the fragmentation spectra of charged and neutral species (neutral and ion decomposition difference NIDD) has been demonstrated for investigation of the reactivity of alkoxy radicals in the gas-phase.<sup>505</sup> Two distinct reactivity patterns arose for the alkoxy radicals: (i) those with a short carbon chain, from C<sub>1</sub> to C<sub>3</sub>, showed a direct  $\alpha$ -cleavage resulting in the formation of corresponding carbonyl compounds, whereas (ii) those with side chains containing more than three carbon atoms showed a specific 1,5 hydrogen migration, namely, a Barton-type hydrogen migration. This rearrangement has been extensively investigated experimentally as well as theoretically in the case of *n*-pentyloxy radicals by the NIDD technique and completed by isotopic labelings. Identification of the stereoselectivity of the hydrogen migration has been done in the case of the 3-methylpentyloxy radicals, and these results are particularly promising for further developments of the technique in investigating gas-phase intramolecular reactions.

This latter example illustrates well the new fields of application opened up by making use of the general concept of NRMS. Species with missing (carbenes) or extrasubstituents (hypervalent species) can be conveniently formed in the gas-phase using the NRMS method since neutralization of a beam of a more stable ionic counterpart could be the easiest way of generating uncommon species. Reionization of the neutrals within an experimental time scale of a few microseconds permits testing of the stability of these neutrals, as well as to probing the unimolecular chemistry with a variable content of internal energy as a controlled parameter.<sup>29,31</sup> Although beyond the scope of this review, we should also mention the fact that recent NRMS experiments have been conducted on on hypervalent radicals including protonated hypervalent metastable ammonium radicals, hydrogentrimethylammonium (CH<sub>3</sub>)<sub>3</sub>NH<sup>•</sup>,<sup>506</sup> benzylammonium C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NH<sub>3</sub><sup>•</sup>,<sup>507</sup> dimethylammonium (CH<sub>3</sub>)<sub>2</sub>NH<sub>2</sub><sup>•</sup>,<sup>508</sup> various hexenylammonium radicals,<sup>509</sup> piperazine derivatives,<sup>510</sup> cyclic ammonium radicals,<sup>511</sup> or dimethylloxonium radicals,<sup>512</sup> and the  $\alpha$ -glycyl radical.<sup>513</sup>

Among the investigations on gas-phase intramolecular reactions and electron-transfer processes by MS techniques, studies on sulfur-containing species received detailed attention due to the possible links that could be established between gas-phase processes and those appearing in the condensed phase with molecules of biological interest. The question raised by the observation of preferential

cleavage of disulfide bonds in gaseous multiply protonated proteins has been addressed by the technique of electron capture dissociation with the investigation of cyclic and noncyclic-protein residues.<sup>514</sup> Electron-capture dissociation cleavage of the S–S bond appeared to be favored over fragmentation processes obtained by collisional activation methods and a mechanism including the formation of an intermediate hypervalent thiasulfonium radical was proposed for explaining the observed fragmentation. Release of an energetic hydrogen atom and involvement of an intramolecular mobile hydrogen atom associated with a nonreversible S–S capture was postulated in accordance with the high H atom affinity of the disulfide bond.<sup>514</sup> Transient hydrogen atom disulfide adducts were generated by NRMS experiments on precursor protonated dimethyl disulfide CH<sub>3</sub>SS(H)-CH<sub>3</sub><sup>+</sup> and protonated 1,2-dithiolan ions.<sup>515</sup> The corresponding radicals were observed to dissociate by cleavage of H–S, C–S, and S–S bonds adjacent to the hypervalent sulfur position differentiating the cleavage process from those observed in the case of multiply protonated proteins.<sup>514</sup> Although the exothermic character of the hydrogen atom capture by the disulfide bond was confirmed by theoretical calculations, two distinct stereochemical pathways were found for this addition in dimethyl disulfide with a kinetically preferred rear attack, the only observed reaction path in the 1,2-dithiolan. Stereoelectronic effects were conclusively predicted for the intramolecular hydrogen atom capture in the neutralized disulfide bond containing peptides.<sup>515</sup> Tureèek and Carpenter<sup>516</sup> reported on the unimolecular dissociation processes of the glycine-derived radicals, 2-glycyl, 2-glycyl methyl ester, and 2-glycyl *N*-methylamide radicals, as simple models of peptide containing glycyl radical residues. Simple bond cleavages, CO–X bonds (X = OH, OCH<sub>3</sub>, NHCH<sub>3</sub>) as well as C–CO bond, and rearrangements due to atom or methyl group migration were observed and correlated to ab initio calculations suggesting in turn high-energy processes for these unimolecular dissociations. These authors therefore concluded in favor of preferential bimolecular reactions for radicals in the condensed phase, like hydrogen abstraction from a suitable donor.

## V. Conclusion

In the past 60 years, a tremendous amount of experimental work has been published on free radical mass spectrometry studies. This review has attempted to provide an overview of this subject where mass spectrometry has been involved through its two complementary aspects: (i) its fundamental aspect for the study of structures and energetics of radicals, and (ii) its analytical aspect for the study and characterization of species emanating from plasmas, or flames. It is evident that in both aspects, mass spectrometry has made a large contribution to our understanding of fundamental processes involving radicals as well as the characteristics of involved elusive species, providing in addition information on reaction mechanisms that, most of the time, cannot be obtained by other techniques. These features obviously yield a



place of choice for mass spectrometry in the study of free radicals, placing it as the unavoidable and complementary technique for radical studies. The coverage of this review is tentatively as exhaustive as possible from 1960 up to approximately the beginning of 2002.

A wide variety of experimental techniques are available for examination of the characteristics of gas-phase radicals, and this review has attempted to introduce them to the reader in the first section. The investigations of free radicals by mass spectrometry has already afforded a wealth of data in the domain of thermochemistry where these mass spectrometry techniques can provide reliable determinations independent of traditional calorimetric and neutral kinetics methods. The major section of the review has been written with the purpose of quoting the literature available in this domain as well as to illustrate the complementary data on radical systems afforded by ionization energy, electron affinity and proton affinity determinations. In the latter section of the review, information on dynamic systems (plasmas and flames) is compiled, and we introduce some of the most recent results published on uncommon elusive species illustrative of the latest developments in the domain. However, a large body of work, especially that concerning data related to kinetic studies, could not be included here because it would have enlarged the scope of the review in an inefficient manner. Conversely, an implicit theme of radical studies, which encompasses theoretical analysis and predictive studies on chemical transient species, has only been tackled through the description of thermochemical studies. This must not diminish the role of such theoretical methods (of constantly increasing accuracy) that have revolutionized gas-phase thermochemistry of charged and uncharged species during the past decade and have proven their utility to complete experimental data, as exemplified in topical proton affinity determinations.

The activity in the field of mass spectrometry of free radicals is clearly illustrated through the work of laboratories that include gas-phase radical studies as a major subject of research. Given the continuing interest in the development and application of new techniques, it is probably appropriate to consider that the future of radical investigation by mass spectrometry methods is promising even if, unfortunately or fortunately, there is still a lot to be done. The examples provided by the advent of scrutinizing studies of uncommon species by neutralization-reionization mass spectrometry present, in the authors' opinion, a good illustration of what could be a future aspect of the mass spectrometry of free radicals. Similarly, the applications of ion-attachment mass spectrometry for the detection of radical intermediates in various systems due to its high sensitivity and its applicability to atmospheric pressure condition are promising in terms of developments and future prospects for the mass spectrometry of free radicals. Furthermore, new and original developments are expected from the mass spectrometry community which, and the authors live in the hope to faithfully express it in this review, has constantly

shown a great creativity in the domain of radical chemistry.

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