

Photochemistry of Small Molecules

The classic text book in photochemistry is that of Noyes and Leighton, *The Photochemistry of Gases* published in 1941. In 1966, a comprehensive volume by Calvert and Pitts brought the field up to date, but it soon became obvious that the field of photochemistry was expanding too rapidly to be covered in a single comprehensive volume. In fact, in the latter part of the 20th century organic photochemistry and physical photochemistry existed as separate disciplines with largely separate constituencies. Organic photochemistry included such molecules as methane (CH_4), whereas NO and other oxides of nitrogen are inorganic. The book by Hideo Okabe, *Photochemistry of Small Molecules* [1], published in 1978, is so titled to convey the author's intent to include both organic and inorganic molecules, but to direct his attention to simple molecules of both genres. The author's definition of "small" as five or fewer atoms is arbitrary and, unfortunately, excludes much of his own seminal work on the photochemistry of ethane and propane, which contain eight and eleven atoms respectively.

In his *Photochemistry of Small Molecules* Okabe provides an elegant discussion of the spectroscopy of atoms and molecules as well as of the rotational, vibrational, and electronic energy states. In photochemical research, small molecules often have discrete electronic spectra, and any discussion of mechanisms of photochemical reactions must be consistent with these spectra. Accordingly, Okabe gives special attention to the details of what was known about the spectra. He systematically presents chapters on photochemistry and spectroscopy of diatomic, triatomic, and polyatomic molecules (i.e., four and five atom) in Chapters V, VI and VII of the book. His discussion of the basis of photochemical correlation rules and selection rules is very thoroughly presented. His knowledge of the relevant spectroscopy is at a very high level, and his incorporation of spectroscopic aspects into his discussion of the photochemistry, if not unique, is certainly extraordinary.

Okabe's subject, the photochemistry of small molecules, came into prominence in the 1960-1980 period just at the time when planetary modelers were struggling to provide a quantitative understanding of the chemistry of the atmospheres of the giant planets and their moons. The key molecules were methane and ammonia, and the electromagnetic radiation driving the chemistry was the Lyman alpha solar emission line in

the vacuum ultraviolet at 121.6 nm. It was Okabe and his NBS colleagues who provided much of the hard science in support of this objective. The table had been set for the writing of this scholarly book by the appearance in 1964 of a review of the field of vacuum ultraviolet (VUV) photochemistry by McNesby and Okabe [2]. The long term impact of Okabe's work is illustrated by Nobel Laureate Roald Hoffmann's devoting a chapter in his 1995 book [3] to Okabe's 1961 paper on the photolysis of ethane [4] ("a text book case for the application of the scientific method"). Another Nobel prize winner, Yuan T. Lee, published a paper in 1999 [5] with his colleagues in which testimony is given that Okabe was the discoverer of molecular elimination of hydrogen in VUV photolysis of hydrocarbons. The Lee paper was the first in which molecular elimination from propane was studied using very sophisticated techniques not even imagined at the time of Okabe's 1961 discovery. Lee and coworkers used 157 nm laser excitation of propane and employed photofragment translational spectroscopy to measure directly the site-specific molecular elimination of hydrogen. They determined that the elimination of molecular hydrogen from the central carbon atom was the dominant process. This is what Okabe concluded 37 years earlier on the basis of experiments with deuterated propanes [6,2].

As a result of the book and his series of research papers, Okabe became widely known as a leader in the field of vacuum ultraviolet photochemistry. There have been more than 600 (non-self) citations to *Photochemistry of Small Molecules*, and it continues to be regarded as the definitive text on this subject.

Prior to Okabe's work at NBS (which extended from 1959 to 1983), little attention was given to photochemical requirements for measurements in the vacuum ultraviolet, such as spectral purity of light sources, appropriate window materials, and the effect of temperature on the transmittance of these materials. When he first joined the photochemistry group at NBS, he was given the choice of a project to pursue, but was urged to consider photochemistry in the vacuum ultraviolet and soon made this commitment. He quickly recognized the necessity of establishing the purity and monochromaticity of his light sources. Early attempts to study VUV photochemistry with electroded resonance lamps were plagued by outgassed impurities which made it impossible to know the active wavelengths in the photolysis. Okabe's meticulous methods produced the first high

intensity rare gas resonance lamps with outputs of essentially pure wavelength. He achieved this by use of a scanning vacuum monochromator to establish the purity of the resonance lines of xenon, krypton, and argon, the first time this powerful technique was used by a photochemist. The simplicity of the design of the resonance lamps is illustrated in Fig. 1. By powering the light sources with a microwave generator and getting rid of the impurities, light sources of spectacular chromatic purity were produced (Fig. 2), which facilitated studies of the photolysis of small molecules in the vacuum ultraviolet.

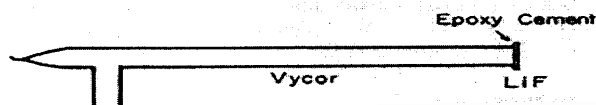


Fig. 1. Resonance lamp design.

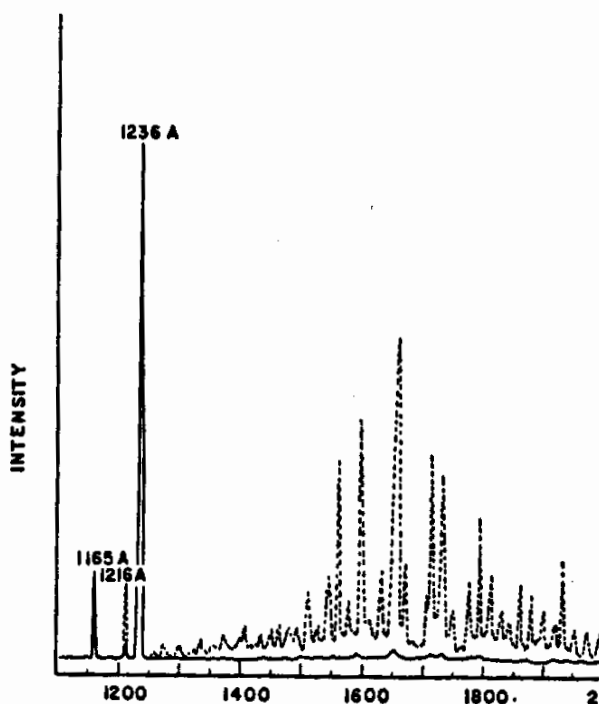


Fig. 2. Krypton resonance lamp with and without (----) getter.

There was particular interest in the NBS group in studying the kinetics of the reactions of methyl (CH_3) radicals. Virtually all such studies had been done by producing CH_3 by near ultraviolet photolysis of such large molecules as acetone. The difficulty always was the concurrent formation of large organic fragments accompanying the methyl radicals and the complications

attending the resulting chemistry. The simple solution to these problems seemed rather obvious—to photolyse ethane ($\text{CH}_3\text{-CH}_3$) since the conventional wisdom was that the weaker C-C bond would break, producing nothing but methyl radicals. What Okabe learned very quickly came as a tremendous surprise to him and to his colleagues. The conventional wisdom was wrong: the reaction product was almost entirely hydrogen rather than the expected methane. Further experiments with deuterium strategically placed at various locations in the molecule gave still more surprising results—that the molecular hydrogen produced came nearly exclusively by molecular elimination from one end of the molecule, not one hydrogen atom from each carbon atom.

This result was to change everyone's thinking about VUV photochemistry of ethane and other simple hydrocarbons of planetary interest, because the major planetary light source, Lyman alpha at 121.6 nm, had nearly the same frequency as the krypton resonance line at 123.6 nm. The extension of this research to methane photolysis, where H_2 was also found to be ejected, caused modelers of atmospheric dynamics of the giant planets, which are rich in methane, to alter their models. This result attracted the attention of NASA, which then partially supported the NBS work for a number of years, with the objective not only to understand planetary atmospheric dynamics but also to satisfy their well known interest in the origin of life in the solar system. In all cases the key molecules are water, methane, ammonia, and carbon dioxide (all "small molecules") and ethane.

Hideo Okabe was born 13 December 1923 in Nagano-ken, Japan. During World War II he was an undergraduate at the University of Tokyo; he was deferred from military service because he was a science student. Needless to say, these were trying times for him as bombs fell all around on a regular basis. As a student he was twice bombed out of his rooming house. After a protracted course of study during these ordeals, Okabe completed the requirements for an undergraduate degree in engineering in 1947. The idea of coming to the United States seemed attractive in a milieu that was driven by the devastation of Japan, resulting in its inability to support graduate education adequately. He had developed an interest in photochemistry during these years and ultimately applied for admission to the University of Rochester to work with the dean of academic photochemists, W. Albert Noyes, Jr. Hideo was awarded the Ph.D. from the University of Rochester in 1957, after which he received a post-doctoral appointment at the National Research Council of Canada with E. W. R. Steacie. Both Noyes and Steacie endorsed Okabe as one of their better students, and he was offered and accepted an NBS staff position in 1959. Shortly

after joining NBS he was granted a leave of absence to return to Japan for a short stay for the purpose of marrying his bride, Tomoko Shoji. The newlyweds returned to the United States and eventually he and Tomoko had three children. Okabe was a Visiting Scholar at Bonn University in 1963 and a Visiting Professor at Tokyo Institute of Technology in 1978, the year recognition came in the form of a Gold Medal from the U.S. Department of Commerce and the publication of *Photochemistry of Small Molecules* [1]. In 1983 Okabe's position at NBS was eliminated in a reorganization and he opted for early retirement, although he remained active at NBS as a consultant for a number of years. A colleague, then at Howard University in Washington but a former member of the NBS group, William M. Jackson, took him on as a senior researcher in his laboratory. Okabe still works at Howard as Research Professor of Chemistry in the Institute of Atmospheric Research and has two remaining graduate students.

Prepared by James R. McNesby with assistance from Ralph Klein.

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