

PHOTOIONIZATION OF ALKANES IN THE RIGID PHASE  
AS STUDIED BY ELECTRON SPIN RESONANCE

Keiji Kuwata and Koji Inada  
Department of Chemistry, Faculty of Science,  
Osaka University,  
Toyonaka, Osaka, Japan

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Recently photochemical reactions of alkanes in vacuum ultraviolet region have been extensively studied (1). In this new field, special attention has been paid to photoionization of these compounds because of its close relation to the primary process postulated in radiation chemistry of organic compounds.

In primary process of radiation chemistry, the formation of ionic species through ionization by the scattered electrons has been postulated, and experimental efforts to investigate these ionic intermediates have been made through optical (2) and electron spin resonance techniques (3).

Electron spin resonance technique has been applied to the experimental study on photoionization and photolysis of alkanes through irradiation of vacuum ultraviolet light, and we wish to report here some interesting results of trapped electron in some alkanes of rigid state and its conversion to alkyl radicals through irradiation of ultraviolet of

longer wavelength, and photodecomposition of alkanes to alkyl radicals.

n-Heptane, n-octane, iso-octane, cyclohexane, cycloheptane, and cyclooctane were irradiated by ultraviolet light from a Wood type hydrogen discharge lamp with LiF window, which mainly emits ultraviolet light of 1200 to 1600Å wavelength, at the liquid nitrogen temperature in vacuum. Spin resonance spectra were observed at the same temperature.

In the case of cycloheptane a narrow line spectrum was observed after irradiation of vacuum ultraviolet light for one hour, and this spectrum changed quickly to a sextet spectrum through irradiation of ultraviolet light of 2000 to 3000Å wavelength from the filtered low pressure mercury lamp for a period of 10 seconds or so.

The similar singlet spectrum was observed in the case of n-octane, and doublet lines of hydrogen atom were also observed. After bleaching with ultraviolet light of 2000 to 3000Å wavelength a sextet spectrum became dominant as shown in Fig. 2.

In the case of iso-octane, after bleaching of longer period of two minutes or more, formation of methyl radical was recognized by appearance of its characteristic quartet spectrum.

The characteristics of the singlet spectra of alkanes and the hyperfine structures of alkyl radicals appeared

after bleaching, were summarized in Table 1 and 2.

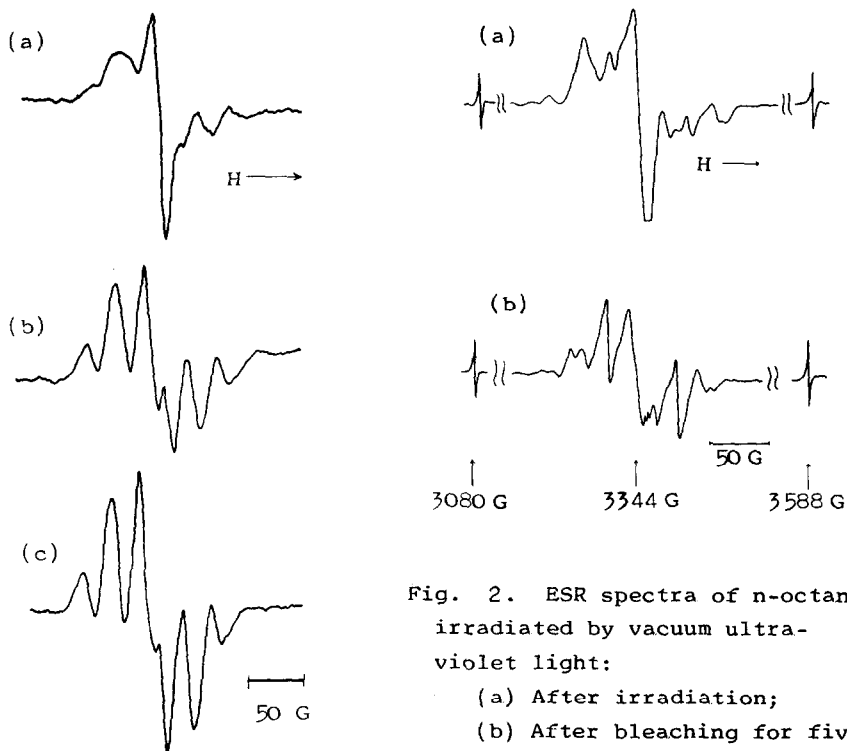


Fig. 2. ESR spectra of n-octane irradiated by vacuum ultraviolet light:  
 (a) After irradiation;  
 (b) After bleaching for five minutes.

Fig. 1. ESR spectra of cycloheptane irradiated by vacuum ultraviolet light:  
 (a) After irradiation;  
 (b) After bleaching for two minutes;  
 (c) After bleaching for five minutes.

Exceptionally a weak singlet signal or none was observed in the cases of cyclohexane and n-heptane though just after irradiation of vacuum ultraviolet, and alternatively, the

TABLE 1  
 Characteristics of Singlet Spectra  
 Observed for Alkanes

Alkanes	g-Factors	Linewidth; $\Delta H_{msl}$ (in Gauss)	Relative intensity
n-Heptane	$2.0021 \pm 0.0005$	10	weak
n-Octane	$2.0024 \pm 0.0006$	9	strong
iso-Octane	—	12	strong
Cycloheptane	$2.0022 \pm 0.0005$	11	strong
Cyclooctane	$2.0021 \pm 0.0005$	11	strong

TABLE 2  
 Characteristics of Hyperfine Structure  
 Observed for Alkanes

Alkanes	Hyperfine structure	Hyperfine coupling constant (in Gauss)
n-Heptane	6 lines	$A_{\alpha}^H \simeq A_{\beta}^H = 22$
n-Octane	6 lines	$A_{\alpha}^H \simeq A_{\beta}^H = 20$
Cyclohexane	6 lines	$A_{\alpha}^H = 22, A_{\beta}^H = 41$
Cycloheptane	6 lines	$A_{\alpha}^H = A_{\beta_1}^H = 25, A_{\beta_2}^H = 16$
Cyclooctane	5 lines	$A_{\alpha}^H = A_{\beta_1}^H = 21, A_{\beta_2}^H = 2 \cdot A_{\beta_1}^H$

hyperfine structures of alkyl radicals appeared already without bleaching.

Because the ionization potentials of these alkanes in gas phase are ranged from 10.2ev to 10.4ev, and considerable lowering of these values in condensed phase seems to be possible, it is reasonable to expect that these alkanes are photoionized through irradiation of vacuum ultraviolet light of 1200 to 1600Å wavelength, energies of photo-quanta of which are 10.3 to 7.8ev.

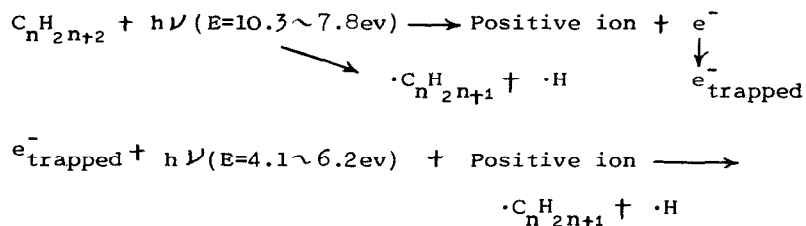
The narrow line spectra observed in alkanes were assigned to a kind of "trapped" electron in rigid media because of their low values of g-factor, the lack of hyperfine structure, the microwave saturation behavior, the sensitivity toward the irradiation of light of longer wavelength, and the strong luminescence after bleaching.

There is considerable evidence now that possible electron trapping sites are the impurities of greater electron affinity and "lattice imperfections" or "cavities" in rigid state. Recent investigation to characterize the "trapped" electron in rigid organic solvents has given an evidence to assign the narrow singlet spectrum to the carbon dioxide radical anion (4). Such narrow singlet spectrum was previously assigned tentatively to the "solvated" electron.

With caution against the contamination with oxygen or carbon dioxide as an impurity of possible electron trapping site, some of the samples for irradiation were repeatedly

purified through vacuum distillation over freshly evaporated sodium film. For the samples purified on such a way, however, no difference in spectra was observed.

There seems to be a limit in explanation of the nature of the electron trapping site in alkanes as far as our experimental knowledge is concerned, so we would like to suggest here only the overall reaction schemes for the photochemical processes of alkanes with undefined nature of the ionic species.



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#### References

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