ESR Study on Free Radicals Produced from Hexane by Vacuum-Ultraviolet Photolysis, Sensitized Photolysis, and γ-Radiolysis

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Synopsis. The free radicals generated from polycrystalline hexane at 77 K by photolysis with vacuum-ultraviolet light, sensitized photolysis, and γ-radiolysis were compared with each others using the ESR method. The selectivity of radical formation was found to depend on the excitation method.

Although the free radicals produced from saturated hydrocarbons have been extensively studied using ionizing radiation combined with ESR measurements, the mechanism for radical formation has not yet been fully understood.[1,2] Ionizing radiation generates primarily electrons, ions, and excited states, and possibly initiates several reaction channels which produce free radicals; thus, elucidating the reaction mechanism may be both complex and difficult. It seems to be helpful to produce free radicals with different excitation methods in order to obtain a deeper insight into the mechanism of free-radical formation.

In the present investigation free radicals generated from polycrystalline hexane by different methods were compared. The methods of radical generation used were direct photolysis with vacuum-ultraviolet (VUV) light from a Xe resonance lamp, sensitized photolysis with benzene and biphenyl as sensitizers, and radiolysis with ^{60}Co γ-rays. Direct photolysis with a proper wavelength of VUV-light brings hexane molecules to selected excited states either below or above the ionization threshold, from which radical formation proceeds. Although VUV-photolysis combined with ESR spectroscopy is expected to help elucidate the mechanism of radical formation, the reported studies have been scanty[3-6] because of experimental difficulties. Sensitized photolysis results in radical formation from hexane, either through energy transfer from the excited sensitizer or abstraction of an H atom by the excited sensitizer.

Experimental

All chemicals were of spectroscopic grade from Wako Pure Chemical Ind., Ltd. and were used without further purification after deaerating by freezing-thawing-pumping cycles. All irradiations and ESR measurements with an X-band spectrometer (Varian, Model E109) were made at 77 K.

A Xe electrodeless lamp constructed according to a method described in the literature[7] was used as the source of VUV light. Hexane was slowly condensed on the cold finger under vacuum of 10^{-5} Torr for one hour and then irradiated with VUV light. The irradiated sample was protected by covering with further condensation and was quickly transferred into a quartz Dewar vessel for ESR measurements.

For the sensitized photolysis, hexane with dissolved benzene (0.01—1 mol dm^{-3}) or biphenyl (0.1—1 mol dm^{-3}) was deaerated, sealed in a quartz ESR tube, and frozen at 77 K. The samples were irradiated with light from a Xe-Hg lamp through a Toshiba UV-D33S filter (250—400 nm) for one hour.

The γ-radiolysis was made with a ^{60}Co source with a dose of 1—4 kGy for hexane both in the sample tube and on the cold finger.

Results and Discussion

Typical examples of ESR spectra observed for the various radical generation methods are shown in Fig. 1. The spectra are generally a superposition of component spectra due to the hexyl, 1-methylpentyl, and 1-ethylbutyl radicals generated by the loss of an H atom from hexane. The component spectrum due to the hexyl radical is weak, since it is unstable and readily transforms into the 1-methylpentyl radical.[8]

For sensitized photolysis, the observed spectra is partly due to cyclohexadienyl-type and/or phenyl-type radicals originating from sensitizer molecules. However, the component spectra of these radicals are confined to the central, narrow region of the total spectral patterns. The yield of the sensitizer radicals was found to decrease with a decrease in the sensitizer concentration, and to be less for biphenyl than for benzene. Actually, the radicals from sensitizer benzene at 1 mmol dm^{-3} were almost ignored, compared to those from solvent hexane. These results indicate that the formation of radicals from hexane is not due to the hydrogen abstraction by the excited sensitizer but, rather, to the scission of a C–H bond of hexane caused by an energy transfer from the excited sensitizer. The formation of sensitizer radicals (cyclohexadienyl-type and phenyl-type) is due to a reaction between excited and ground-state sensitizer molecules, which can occur due to the heterogeneous dissolution at high sensitizer concentration.

The variation of the spectral shape of the solvent radicals depending on the generation method, as shown in Fig. 1, was found to be essentially due to the varying ratio of the 1-methylpentyl radical to the 1-ethylbutyl radical: the observed spectral shapes could be reproduced by superposing the theoretical shapes simulated for the 1-methylpentyl and 2-ethylbutyl radicals[8,9] and a broad spectrum due to radical pairs.[9] The 1-methylpentyl/2-ethylbutyl yield ratio was determined to be 3/2, 4/1, and 9/1 for VUV photolysis, biphenyl-sensitized photolysis, and γ-radiolysis, respectively.

The spectral shape observed for benzene-sensitized photolysis (Fig. 1d) comprises eight equally-spaced

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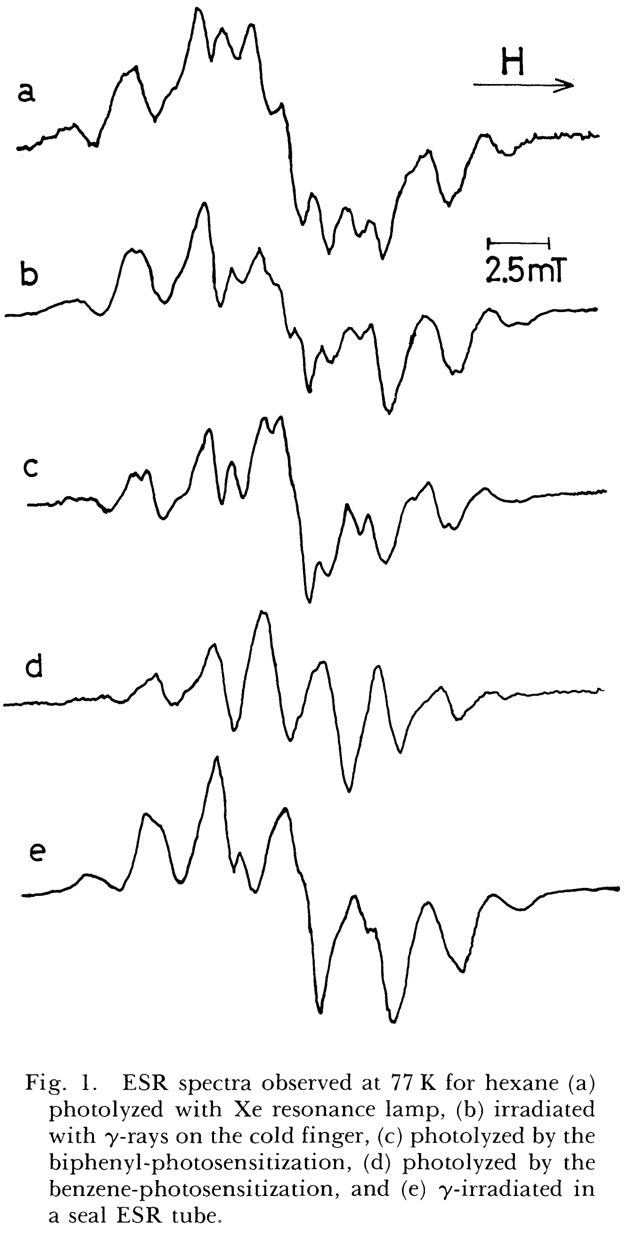

Fig. 1. ESR spectra observed at 77 K for hexane (a) photolyzed with Xe resonance lamp, (b) irradiated with γ-rays on the cold finger, (c) photolyzed by the biphenyl-photosensitization, (d) photolyzed by the benzene-photosensitization, and (e) γ-irradiated in a seal ESR tube.

hyperfine lines. This cannot be reproduced by any ratio of the 1-methylpentyl to 2-ethylbutyl radicals with normal conformation. Based on the McConell's relation, $a_\beta(\theta)=B\ cos^2\ \theta$,[10] the distortion of the conformation by rotating about the C_α–C_β bond by 20° changes the hyperfine coupling constants of the β-CH_2 protons to 4.27 and 1.82 mT. These coupling constants well reproduce the observed spectral shape. Therefore, the free radicals generated by the benzene-sensitized photolysis are attributable to the 1-methylpentyl radicals with a distorted conformation.

A mechanism for radical formation from γ-irradiated *n*-alkanes has previously been proposed by Iwasaki et al.,[9]

$$RH \longrightarrow (RH^+)^* + e^-, \tag{1}$$

$$(RH^+)^* \longrightarrow R_I^+ + H \xrightarrow{+e^-} R_I + H, \tag{2}$$

$$(RH^+)^* \xrightarrow{+e^-} RH^* \longrightarrow R_I + H, \tag{3}$$

$$(RH^+)^* \xrightarrow{+RH} RH_2^+ + R_I \xrightarrow{+e^-} 2R_I + H_2 \text{ or } RH + H + R_I, \tag{4}$$

and

$$H + RH \longrightarrow R_{II},\ R_{III} + H_2. \tag{5}$$

They claimed that C–H bond scission by ionizing radiations occurs primarily at the chain-end, forming the terminal alkyl radical (R_I, $\dot{C}H_2CH_2$–) and a hydrogen atom, by one of the charge recombinantion processes: (2), (3), or (4). The terminal alkyl radical readily abstracts a hydrogen atom from a neighboring molecule to form a penultimate alkyl radical (R_{II}, $CH_3\dot{C}HCH_2$–) at 77 K in triclinic crystals of linear hydrocarbons with an even number of carbon atoms. The liberated H atom abstracts a hydrogen atom from a nearby molecule to form either R_{II} or an internal radical (R_{III}, –$CH_2\dot{C}HCH_2$–) secondarily (reaction 5).

In contrast, the present VUV-photolysis is a nonionic process, since the photon energy from the Xe resonance lamp (8.43 eV) is lower than the ionization threshold of hexane (10.06 eV in gas phase). The formation of hexyl radicals originates from the excitation:

$$RH + h\nu \longrightarrow RH^* \longrightarrow R + H. \tag{6}$$

Subsequent hydrogen abstraction (reaction 5) is also a possible source of hexyl radicals in VUV-photolysis. Assuming that the excited states in γ-radiolysis and VUV-photolysis (RH^* in reaction paths (3) and (6)) are identical, the smaller R_{II}/R_{III} radical yield ratio for VUV-photolysis than for γ-radiolysis seems to results from a comparatively efficient formation of R_{III} through reaction path (3), compared with paths (2) and (4) for radiolysis. Iwasaki et al presumed that all of the reaction paths ((2),(3), and (4)) result in the formation of R_I, which then transforms into R_{II} at 77 K.[9] The present results, however, indicate that the dissociation of excited hexane into R_{III} cannot be ignored.

Kuwata et al.[4] previously reported that the VUV-photolysis of *n*-alkanes (C_5—C_8) with the Lyman-α line from a hydrogen discharge lamp gives ESR spectra with six hyperfine lines due to R_{III}. Their result is essentially consistent with the present result that the R_{II}/R_{III} yield ratio is comparatively low for VUV-photolysis, compared with γ-radiolysis.

In sensitized photolysis as well, radical formation occurs nonionically through reaction (7), followed by reaction (5),

$$RH + S^* \longrightarrow RH^* + S \longrightarrow R + H + S. \tag{7}$$

It was previously reported that an energy transfer from a benzene or biphenyl molecule occurs from its second or higher triplet state created by T–T absorption.[12] In benzene-sensitized photolysis, the influence of energydonating benzene causes a selective formation of R_{II} with a distorted conformation. Takeshita and Tsuji previously observed the selective formation of the 1-methylpentyl radical from hexane by photolysis with benzoic acid used as sensitizer.[13]

In conclusion, the selectivity in radical formation from polycrystalline solid hexane depends on the excitation method used, VUV-photolysis, sensitized photolysis, or γ-radiolysis. This is in contrast with the absence of selectivity reported for 3-methylpentane in the amorphous state.[12,14–17] It is not presently known whether the difference observed between hexane and 3-methylpentane can be attributed to differences in molecular structure or differences in the aggregation state.

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