The Vacuum Ultraviolet Photolysis of Liquid *n*-Hexane in the Presence of SF_6

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The photolysis of liquid *n*-hexane has been studied at room temperature and at −78°C by using the resonance lines of Xe and Kr. The main process is hydrogen detachment, giving the same amount of hydrogen and of hexenes; relatively small amounts of the decomposition and dimer products were also formed. Upon the addition of SF_6, the yield of the hydrogen detachment decreased strongly with an increase in the concentration of SF_6, and then approached a constant value of 0.65 relative to that in pure *n*-hexane. The total amount of fluorine-containing products detected in the presence of SF_6 was relatively small compared with the amount of the decrease in the hydrogen detachment. As another electron scavenger, $C_6H_{13}F$ was also tested; here, the decrease in the hydrogen detachment was quite small.

The ionic process in the radiolysis of hydrocarbons is one of the most important problems in radiation chemistry; as chemical approaches to this problem, various charge scavengers are used to elucidate the reaction mechanism.[1,2] By using this technique, a number of interesting results, such as the existence of ion-molecule reactions in liquid hydrocarbons,[3] have been obtained. However, the charge scavengers added may possibly react as radical scavengers or as deactivators of the excited states.[4] For quantitative experiments, the suitability of the charge scavenger should, therefore, be tested by using various methods. Along those lines, Holroyd[5,6] examined the energy-transfer process by using vacuum ultraviolet light in the system of liquid cyclohexane with N_2O; he observed a marked decrease in the photoproducts upon the deactivation of the solute. Lipsky and Hirayama[7-10] found that the donor fluorescence state in a hydrocarbon solution of the scintillator was deactivated by the addition of various electron scavengers, such as O_2, SF_6, N_2O, and CO_2. These experiments seem to indicate that the excited states of hydrocarbons can be quenched by electron scavengers. However, the details of this process are still unknown, so the present experiment was undertaken in order to clarify this process and to find ideal electron scavengers.

Experimental

The Xe and Kr lamps were constructed by the usual method.[11] The LiF window of the lamps was jointed with Araldite, and a Ba getter was used to obtain an intense resonance line by the removing impurity lines. The Xe and Kr lamps were operated with a microwave generator of 2450 MHz and 200 W made by the Ito Chotanpa Co. The intensities of the lamps were about $10^{15}-5\times10^{14}$ photon/sec, depending on the diameter of the lamps.

A sample of *n*-hexane (99.99% purity) was obtained from the Phillips Co.; it was purified by passing it through $Mg(ClO_4)_2$ and NaOH column to remove any CO_2 and H_2O and then led into the reaction vessel through a greaseless stopcock. SF_6 of a spectroscopic purity obtained from the Takachiho Co. and $C_6H_{13}F$ (purum) obtained from the Fluka A. G. Co. were used as electron scavengers without any further purification. The concentrations of SF_6 in the liquid *n*-hexane in the samples were determined by means of the partition ratios of SF_6 between the gas and liquid phases at room temperature and at −78°C, as measured by the use of a large amount of *n*-hexane.

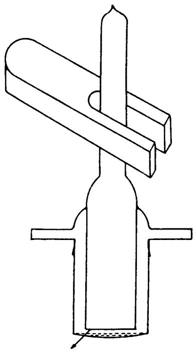

Fig. 1. Apparatus of photolysis in liquid phase.

The apparatus for the photolysis of liquid *n*-hexane is shown in Fig. 1. In the present experiment, the distance between the outer surface of the LiF window and the liquid surface was maintained at about 1 mm. Some experiments were also carried out by placing the LiF window in contact with the liquid surface. In the former case, the temperature of the reaction system was kept at −78°C to prevent direct photolysis in the gas phase. The intensity of light absorbed in the case of −78°C was fairly constant compared with that in the latter case.

After each run, the reactant and the products were condensed in a liquid-nitrogen trap. The noncondensable gases were gathered and measured by means of a Teopler-McLeod

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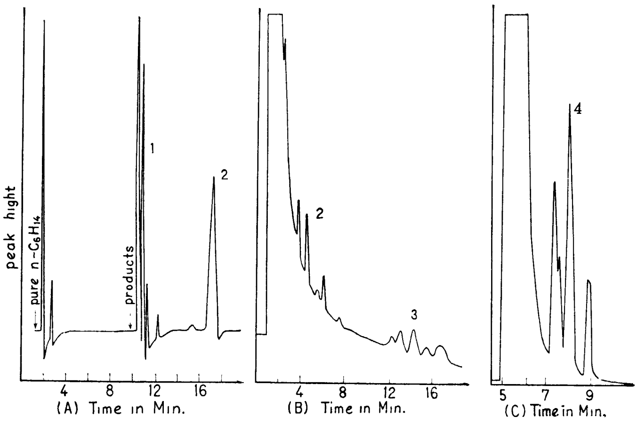

Fig. 2. Gas chromatogram of condensable products.

system. The noncondensable gases were mainly hydrogen. The condensable products, such as olefins and dimers, were analyzed by means of a Shimadzu gas chromatograph (Silicone D.C. 550, 5 m at 140°C and dimethyl sulpholane (10 m) at room temperature), equipped with a flame ionization detector. A Shimadzu electron-capture gas chromatograph was also used to detect the fluorine-containing products. The gas chromatograms of the condensable products are shown in Fig. 2, where (A) stands for the electron-capture detector, and where (B) and (C) indicate the flame-ionozation detector. The two peaks, Peak 1 and Peak 2, of the fluorine-containing products are magnified by the use of the electron-capture detector.

Results and Discussion

In the photolysis of liquid *n*-hexane, the main products were hydrogen and hexenes in almost identical amounts; small amounts of dimers and the decomposition products were also found. This means that the molecular detachment of hydrogen is the main process, unlike the radiolysis, where the hydrogen-atom splitting is the more important process. No difference was observed in the products between the Xe and Kr resonance lines. Holroyd⁶⁾ obtained almost the same results in his photolysis of liquid cyclohexane.

In the presence of SF_6, the relative yields of the major products, *i.e.* hydrogen and hexenes, decrease greatly, as is shown in Fig. 3. For sufficiently high concentrations of SF_6, the yields of hydrogen and the total hexenes approach a constant value (*ca.* 0.65 relative to that of pure hexane), irrespective of the Kr and Xe resonance lines; a preliminary experiment with the Br resonance line showed the same tendency. The photolysis of *n*-hexane in the gas phase was also carried out, but no decrease in the relative yield was observed upon the addition of SF_6. As one possible mechanism, the energy transfer between *n*-hexane molecules may occur faster in the liquid phase than in the gas phase, and then the energy may be trapped by SF_6. The energies of the Kr (1236 Å), Xe (1470 Å), and Br (1634 Å) resonance lines are 0.4, 2.0, and 2.8 eV below the ionization potential of *n*-hexane. The Xe and Kr resonance lines may be able to excite the *n*-hexane molecule in the semi-ionized states or in locally-ionized states.12)

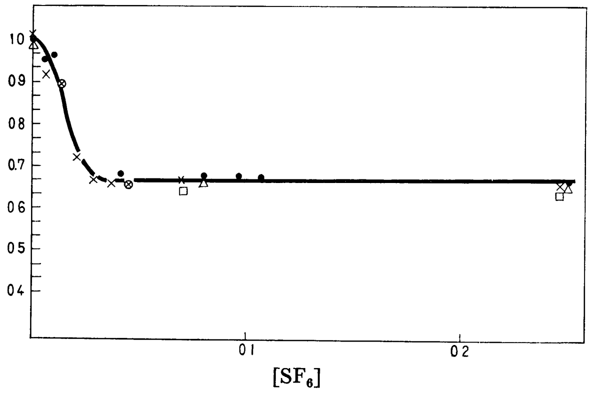

Fig. 3. The relative yields of hydrogen (●1470 Å, × 1236 Å) and hexenes (△1470 Å, □1236 Å) as a function of concentration of SF_6.

The experimental results are quite similar for both the Xe and Kr resonance lines, indicating that the main process is the molecular detachment of hydrogen, which was often observed in the lower excitation of paraffins in the gas phase. As a general rule in the photolysis of paraffins, it was observed that the ratio of the atomic and molecular detachments of hydrogen increased with an increase in the photon energy.14) Slightly below the ionization potential, the radius of the wave function of the excited electron is quite large; for example, the maximum of the radial-distribution function of the hydrogenic 2*s* orbital is five times larger than that of the 1*s* orbital. In liquid paraffin, the Onsager radius is several hundreds Ångstrom, so that within this radius the probability of geminate recombination is larger than that of free-ion formation. The states in which electrons reside between the Onsager radius and a radius several times larger than the radius of the ground state of a molecule may be called semi-ionized or locally ionized states, and a number of molecule may be present inside the orbital. When an electron approaches the positive ion, thus decreasing the radius of the orbital and the kinetic energy, the electron may enter into the lower excited state of the neutral molecule, where the molecular detachment of hydrogen, then takes place, as in the case of the photolysis of the gas phase.14) Since the photolysis products in the liquid phase were quite similar to those in the gas phase, the same precursor of the reaction can be expected in both phases, as in the case of cyclohexane.⁶⁾ The preliminary experiment on the Br resonance line also shows the same dependence of the hydrogen-molecule splitting on the concentration of SF_6. The absorption coefficient of hexane is quite large at 1470 and 1236 Å, while that of SF_6 is relatively small.15,16) Therefore,

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12) The Br resonance line excites the *n*-hexane molecule to the first singlet excited state (8.2 eV (calcd), 8.3 eV (obsd)).13)

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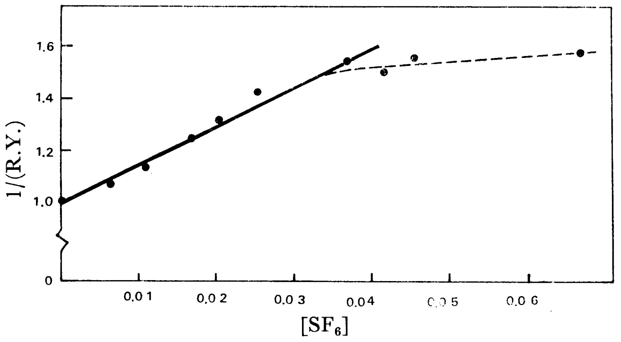

Fig. 4. The reciprocal plot of relative yields of hydrogen against concentration of SF_6.

the direct absorption of light by SF_6 is negligibly small.

In Fig. 4 the reciprocal relative yields (1/R.Y.) of the hydrogen detachment are plotted against the concentration of SF_6. A nearly straight line (solid line) is obtained for lower concentrations of SF_6. If the following reactions are postulated:

$$RH + h\nu \xrightarrow{k_1} RH^* \tag{1}$$

$$RH^* \xrightarrow{k_2} H_2 + R(-H) \tag{2}$$

$$RH^* + SF_6 \xrightarrow{k_3} \text{no hydrogen product} \tag{3}$$

$$RH^* + RH \longrightarrow RH + RH^* \tag{4}$$

where Eq. (4) shows the energy-transfer process to transport the excited state, RH*, to the vicinity of SF_6. Then, the steady-state treatment of the reaction yields the following relation:

$$1/\text{R.Y.} = 1 + k_3[SF_6]/k_2 \tag{5}$$

The k_3/k_2 ratio is obtained from the slope of the straight line extrapolated at the low concentration of SF_6. The value observed in this experiment is 15.0, while that of Holroyd was 4.5 in the photolysis of *n*-hexane in the presence of N_2O.5) SF_6 is, thus, an acceptor stronger than N_2O in the energy-transfer process. This tendency is consistent with the measurement7) of the fluorescence from the scintillator in a cyclohexane solution in the presence of various electron scavengers. The leveling-off at the higher concentrations of SF_6 (Fig. 3) was explained by the introduction of more than two excited states. Therefore, it may be considered that, in these excited states, only one excited state is responsible for discriminating the molecular detachment of hydrogen upon the addition of SF_6, as is shown in Eqs. (2) and (3), while the other excited states are not affected by the introduction of SF_6. The low-lying excited states of *n*-hexane were observed by the use of the electron reflection spectrum17) and the emission spectrum.18,19)

A prominent result is that the critical concentration of the scavenger is lower than that in the case of radiolysis. The reaction cross section calculated from the critical concentration of the scavenger is several hundred square Ångstrom. Such a large cross section was also observed in the energy-transfer process in a propane isobutane mixture at a low temperature using EPR measurements20) for isopropyl and isobutyl radicals; in this method, the effect of electron transfer is ruled out by the experimental condition that the ionization potential of the acceptor molecule is higher than that of the donor molecule. The large cross section may be explained by the fast movement of a pair of an electron and a positive ion. It is assumed that the excited state of hydrocarbon can react with SF_6 and form the state of charge separation20,21)

$$RH^* + SF_6 \longrightarrow RH^+ + SF_6^- \tag{6}$$

The neutralization between RH^+ and SF_6^- is expected to form fluorine-containing products. The sharp decrease in the yield of hydrogen molecular detachment upon the addition of SF_6 can be explained by assuming a fast energy transfer or charge transfer to produce RH^+ and SF_6^-.

In a recent study of the radiolysis of benzene in presence of N_2O and COS, Sato *et al.*,23) concluded that the energy transfer can take place neither through the superexcited state (20 eV) nor through the first excited state ($^1B_{2u}$), but must take place through some intermediate excited states between these states, although the details of energy transfer are not known.

Another possible explanation of the large reactive cross section is that a charge-transfer complex between *n*-hexane and SF_6 in either the ground or excited state may be formed and the detachment process may be perturbed by this complex formation. The weak interaction between the halogen molecule or halogen-containing compounds including SF_6 and paraffin was observed by the use of the spectroscopic method.24,25) The gas chromatographic measurement with an iodine column showed the existence of a weak interaction between iodine and paraffins.26) Therefore, the complex-formation mechanism appears to be a plausible explanation.

The quenching process by SF_6 may produce various fluorine-containing products. Several large peaks were detected in the electron-capture gas chromatogram (Fig. 1). One of the products was determined to be 1-fluorohexane (peak 1 in Fig. 2). These products increased with the increase in the concentration of SF_6. The total amount of these fluorine-containing products is smaller than that of the decrease in the hydrogen molecule.

To find an ideal electron scavenger without any deactivation by the energy-transfer process, 1-fluorohexane was tested. In the photolysis of liquid *n*-hexane,

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only a small decrease in the hydrogen yield was observed upon the addition of 1-fluorohexane.

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