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The Migration of the Exciton in the Radiolysis of Alkanes

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A number of studies of the exciton migration in molecular crystals have been mostly concerned with aromatic crystals. Though the energy transfer in the γ-irradiated aromatic crystal has been interpreted in terms of the excitation transfer,[1] the possibility of the excitation transfer in the solid alkane has been ignored in radiation chemistry; only the energy transfer *via* an ionic process, such as a charge transfer, an ion-molecular reaction, or an electron capture, has been emphasized. Recently, however, Miyazaki *et al.* have found phenomena which suggest the migration of the exciton in the radiolysis of isobutane,[2] neopentane,[3] and 2,3-dimethylbutane.[4]

The theoretical treatment of the migration of the exciton in the alkanes has not been undertaken previously. In order to obtain some information on whether or not the electronic excitation transfer is possible in solid alkane, the theoretical treatment of irradiated aromatic materials[5] will be applied here to alkanes.

In order to occur at all, excitation transfer requires some interaction between excited and unexcited molecules. The interaction energy (u) can be approximated as the interaction between the transition dipoles of molecules. Since the transition dipoles can be represented by the experimentally-available oscillator strength (f), the interaction energy is given by:

$$u = -3f(ea_0)^2 \frac{R}{\Delta E} \frac{\Omega}{r} \tag{1}$$

where a_0 is the first Bohr radius; R, the Rydberg energy; ΔE, the excitation energy; Ω, the geometric factor, depending upon the orientation of the transition dipole moments, and r, the distance between nearest neighboring molecules.

The oscillator strengths (f) of isobutane, neopentane, and 2,3-dimethylbutane were obtained by the integration of the absorption spectra;[6] they are shown in Table 1. The distances (r) between adjacent molecules of isobutane, neopentane, and 2,3-dimethylbutane were obtained from the densities at 77K; they are 5.3, 6.7, and 6.7 Å respectively. As for the geometric factor of transition dipole moments (Ω), the optimum condition is here considered to be that in which the transition dipoles are directed along the line joining the molecular centers. In this case, $\Omega=2$. The interaction energies calculated from Eq. (1) are shown in Table 1.

One can estimate roughly the migration distance of the exciton from the interaction energy by means of the following equation:[7]

$$u \simeq \frac{h\Delta n}{t}$$

where h denotes Planck's constant and Δn, the number of molecules through which the exciton migrates during its lifetime (t). The calculated distances of the exciton migration are shown in Table 1.

The interaction energies of isobutane, neopentane, and 2,3-dimethylbutane range from 0.01 to 0.1 eV (Table 1). These values are not small as compared with those of benzene calculated by Voltz.[5]

TABLE 1. CALCULATED VALUES OF THE TRANSITION DIPOLE-DIPOLE INTERACTION ENERGIES AND THE DISTANCES OF EXCITON MIGRATION IN IRRADIATED ALKANES

Compound	Excitation energy ΔE eV	Oscillator strength f	Interaction energy u, eV	Distance corresponding to different lifetimes, Δn[a]	
				10^{-8}—10^{-9} sec	10^{-11}—10^{-13} sec
Isobutane	(1st) 7.7	0.03			
	8.7	0.37	0.094	2.3×10^4—2.3×10^4	230—2
	9.4	0.13	0.031	7.5×10^4—7.5×10^3	75—1
Neopentane	(1st) 7.9	0.14	0.019	4.6×10^4—4.6×10^3	46—0
	8.4	0.04			
	9.0	0.47	0.075	1.4×10^4—1.4×10^3	140—1
2,3-Dimethylbutane	(1st) 7.9	0.08	0.011	2.7×10^4—2.7×10^3	27—0
	8.2	0.03			
	8.8	0.45	0.056	1.4×10^5—1.4×10^4	140—1

a) Unit is the number of molecules through which exciton migrates.

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Table 2. Experimental values of distances of exciton migration in irradiated alkanes

Host	Guest	Distance of exciton migration, Δn^{a}	Reference
Isobutane	Carbontetrachloride	7	2), 3)
Isobutane	Propane	8	2), 3)
Neopentane	Cyclopentane	40	3), b)
Neopentane	Cyclohexane	85	3), b)
2,3-Dimethylbutane	Toluene	1.3×10^3	4)

a) Unit is the number of molecules through which exciton migrates.

b) M. Kato, T. Miyazaki, Y. Saitake, and Z. Kuri, to be presented at the 15th Japanese Conference of Radiation Chemistry, Oct. 1972, Osaka, Japan.

From the measurements of the fluorescence of liquid alkanes, the lifetimes of the lowest singlet-excited states were obtained: *n*-hexane (2×10^{-9} sec), cyclohexane (7×10^{-9} sec), *etc.*[8] Therefore, the lifetimes of the lowest singlet-excited state of neopentane and 2,3-dimethylbutane are probably 10^{-8}—10^{-9} sec. It is expected from the calculated values shown in Table 1 that the excitons of these alkanes in the lowest excited states can migrate through 10^4—10^3 molecules during their lifetimes. It is interesting to note that the distance obtained experimentally by the measurements of luminescence from solid 2,3-dimethylbutane containing toluene lies in the range expected from this calculation (Table 2).

In the solid-radiolysis of isobutane or neopentane containing other alkanes, it was suggested that the excitation transfer may occur *via* highly excited states.[3] Since the internal conversion from the highly excited states occurs very fast, the lifetime of the highly excited state may be extremely small as compared with that of the lowest singlet-excited state. An exact estimation of the lifetime of the highly excited state is currently impossible; from indirect theoretical and experimental evidence, however, it may be expected to lie between 10^{-11}—10^{-13} sec.[5,9] The calculated results in Table 1 show that the excitons in the highly-excited states of isobutane and neopentane migrate through 200—1 molecules during their lifetimes. It is interesting to note that the distances obtained experimentally in the radiolysis of isobutane and neopentane are 7—8 and 40—85 molecules respectively, which lie in the range expected from this calculation.

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