

Charge Transfer in Binary Organic Liquid Mixtures of Cyclohexane and Methyl-substituted Benzenes

Shozo HORIKIRI*, Toshifumi SAIGUSA** and Kazutoshi MORITA***

Takarazuka Radiation Laboratory, Sumitomo Atomic Energy Industries, Ltd., Takarazuka

Received January 11, 1967

The radiation-induced light emission from binary liquid mixtures of cyclohexane and various methyl-substituted benzenes has been measured. The kinetic equation of Stern-Volmer type can not explain the variation of the emission intensities from each component. The kinetic equation derived under the assumption that energy transfer is possible only within the region of influence around excited cyclohexane gives a satisfactory explanation of the variation. The results obtained suggest that the energy transfer between cyclohexane and methyl-substituted benzene is considered to be due to charge transfer mechanism, and give the charge transfer distances and the life times of the charge transfer pairs.

I. INTRODUCTION

In the radiolysis of binary organic mixtures, there are many cases where one component in some manner protects the radiolysis of another component. It is well known that the radiolysis of excited cyclohexane is protected by benzene. As the results of this protection, the yield of hydrogen from cyclohexane is much less than that predicted by the assumption that radiation energy absorbed by each component is proportional to its mole or electron fraction.

The mechanisms proposed for this protection have included excitation transfer from one component to another, negative ion formation, and charge transfer. Burton and Lipsky¹⁾ have given an excellent review of these mechanisms.

Hardwick²⁾ and Dyne *et al.*^{3,4)} have recently reported that in radiolysis of binary liquid mixtures of saturated hydrocarbons charge transfer mechanism played a dominant role. Ramaradhya and Freeman⁵⁾ have also reported the evidence that charge transfer took place in gas phase radiolysis of cyclohexane and benzene mixture.

In the previous paper⁶⁾ we reported the new method to investigate energy transfer in binary organic liquid mixtures. This method depends on the measurement of the radiation-induced light emission from organic liquids. Since the light emission is considered to be due to directly or indirectly excited molecules, ions, and radicals, the possibility of hydrogen atom scavenging and uncertainty in

* 堀切 尚三

** 三枝 利文, Also at Shimizu Laboratory, Institute for Chemical Research, Kyoto University. Present address: Health Physics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

*** 森田 和俊

reaction mechanism to explain the change of radiolytic yields by protection are excluded from the result obtained by this method.

We have investigated the energy transfer between cyclohexane and methyl-substituted benzenes using this method. Here we report the possibility that energy transfer in these systems are also considered to be due to charge transfer mechanism.

II. EXPERIMENTAL

All measurements reported in this paper were done with degassed solutions. Ten ml portions of solutions being investigated were placed in part *A* of special Pyrex cells shown in Fig. 1. These cells were then attached to a vacuum line and the solutions were degassed by the freeze-pump-thaw technique. Liquid nitrogen was used to freeze the solutions. After degassing the cell was sealed off at part *C*. After the contents of the cell had equilibrated at room temperature the solution in part *A* was transferred to part *B* of the cell. The solution thickness in part *B* was 1 cm. The cell was placed with reproducible geometry above a 2 mC Co⁶⁰ source and below the window of a Toshiba type MS-9SY photomultiplier. The experimental arrangement is shown schematically in Fig. 2.

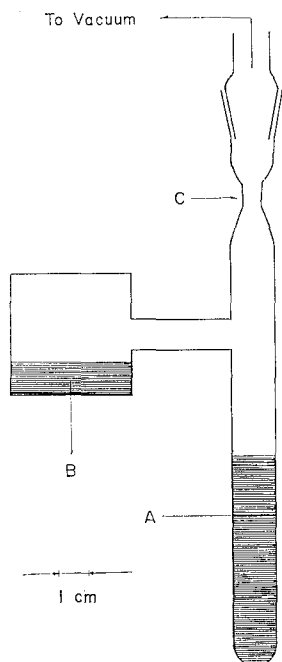


Fig. 1. The glass cell used for the measurement of γ -ray induced-emission from organic liquids.

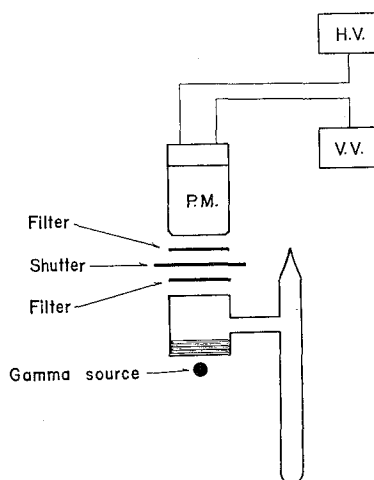


Fig. 2. Scheme of experimental apparatus for the study of γ -ray induced emission from organic liquids.

The principle of our technique has been discussed in the previous paper⁶⁾ but here will be briefly described again.

We let *A* and *B* be the components which compose a mixture. I_{A_0} and I_{B_0} are the respective emission intensities from each component under irradiation.

Charge Transfer in Binary Organic Liquid Mixtures

When I_{A_0} and I_{B_0} are measured through a filter, these intensities will be reduced by factors α and β , respectively. As the emission intensity from the mixture, I_{A+B} , consists of the emission intensities from each component I_A and I_B , it follows that

$$I_{A+B} = I_A + I_B. \quad (1)$$

When this emission intensity is measured through the filter used to determine α and β , then emission intensity from the mixture, I'_{A+B} , will be expressed as follows:

$$I'_{A+B} = \alpha I_A + \beta I_B. \quad (2)$$

As I_{A+B} , I'_{A+B} , α , and β are the values obtained experimentally, it follows from Eqs. (1) and (2) that

$$I_A = \frac{I'_{A+B} - \beta I_{A+B}}{\alpha - \beta}, \quad (3)$$

$$I_B = \frac{\alpha I_{A+B} - I'_{A+B}}{\alpha - \beta}. \quad (4)$$

All chemicals in present experiments were of guaranteed reagent grade from Nakarai Chemical Co. and were distilled through a 30-theoretical-plate column without further treatment.

The purity of distillate was analyzed at several stages of distillation by the gas chromatography, and the distillates whose purity were 99.99% or more were used for the present experiment.

III. RESULTS AND DISCUSSION

III. 1. Theoretical Consideration

Figures 3(a), (b), (c), (d), (e), and (f) give the variation of the γ -induced

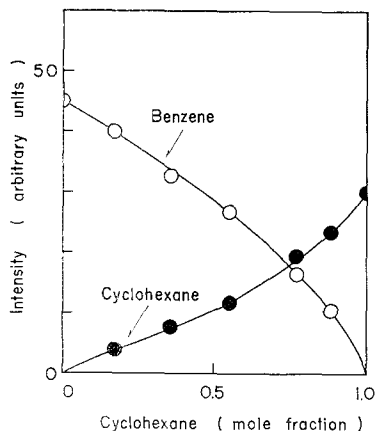


Fig. 3(a). Variation of emission intensities from benzene and cyclohexane in their mixture with its composition.

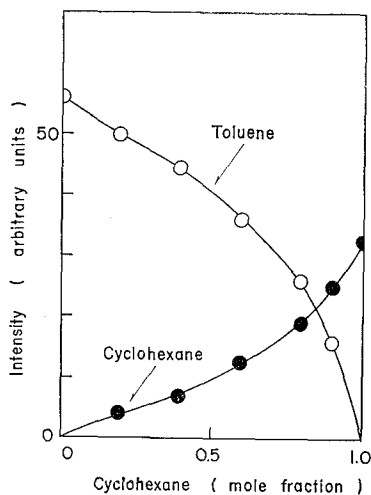


Fig. 3(b). Variation of emission intensities from toluene and cyclohexane in their mixture with its composition.

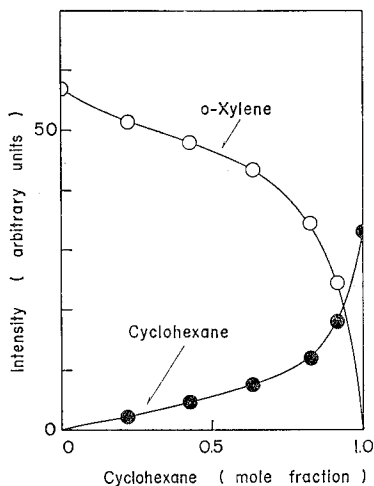


Fig. 3(c). Variation of emission intensities from o-xylene and cyclohexane in their mixture with its composition.

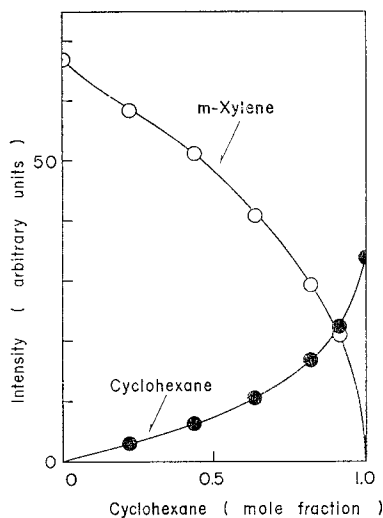


Fig. 3(d). Variation of emission intensities from m-xylene and cyclohexane in their mixture with its composition.

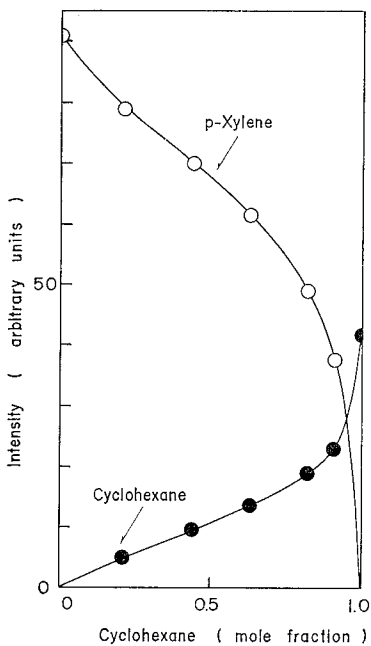


Fig. 3(e). Variation of emission intensities from p-xylene and cyclohexane in their mixture with its composition.

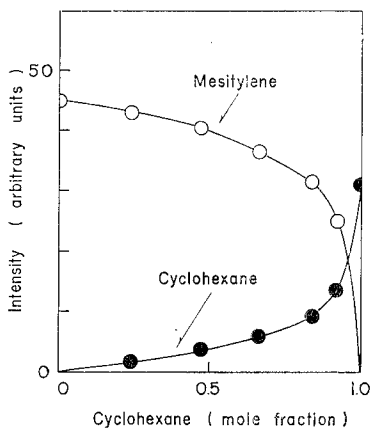


Fig. 3(f). Variation of emission intensities from mesitylene and cyclohexane in their mixture with its composition.

emission intensities from each component with its composition in the following liquid mixtures, respectively: benzene, toluene, o-xylene, m-xylene, p-xylene, and mesitylene, all with cyclohexane. In these systems, cyclohexane acts always as donor and methyl-substituted benzenes as acceptor.

Charge Transfer in Binary Organic Liquid Mixtures

If we write quite formally $D^* + A \rightarrow D + A^*$ as the reaction scheme of energy transfer, the kinetic equation can be expressed as follows:

$$\frac{d[D^*]}{dt} = k_1[D] - k_2[D^*] - k_3[A][D^*], \quad (5)$$

where $[D^*]$ and $[A]$ represent the molar concentration of excited donor and acceptor molecules, respectively, and k_1 , k_2 , and k_3 are the respective rate constants of production of D^* , of disappearance of D^* , and of energy transfer from D^* to A . Throughout this paper we have assumed that radiation energy is absorbed by each component in proportion to its relative molar concentration.

As the γ -induced emission intensities I_D and I_A are proportional to $[D^*]$ and $[A^*]^{\text{6}}$, respectively, Eq. (6) is derived from Eq. (5) under stationary condition.

$$\frac{I_{D_0}}{I_D} \cdot \frac{[D]}{[D_0]} = 1 + \frac{k_3}{k_2}[A], \quad (6)$$

where I_{D_0} and $[D_0]$ represent I_D and $[D]$ when $[A]$ is zero.

Equation (6) shows that $\frac{I_{D_0}}{I_D} \cdot \frac{[D]}{[D_0]}$ vs. $[A]$ should be linear. The experimental results, however, does not follow this linearity law as shown in Fig. 4, where a strong deviation from linearity law occurs at higher acceptor concentration. In Fig. 4, in stead of $[A]$ its mole fraction, m_A , is used as abscissa. This gives no difference in the above statement.

In Eq. (5) we wrote formally $k_3[A][D^*]$ as energy transfer term. Is this expression correct? The life time of excited cyclohexane is considered to be the order of 10^{-13} sec. Thus, most of D^* molecules which can not find any acceptor mole-

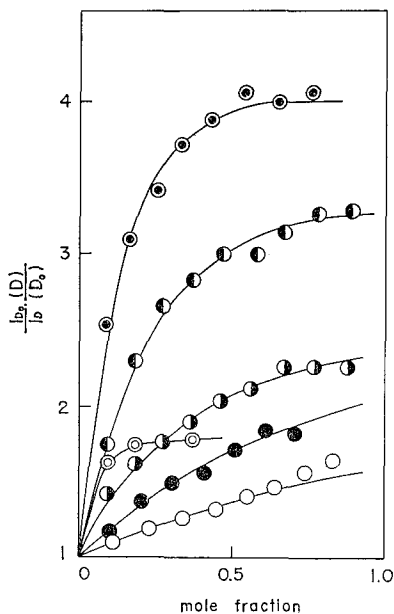


Fig. 4. Plots of $\frac{I_{D_0}}{I_D} \cdot \frac{[D]}{[D_0]}$ vs. mole fractions of benzene \circ , toluene \bullet , o-xylene \ominus , m-xylene \oplus , p-xylene \odot , and mesitylene \otimes in the mixtures with cyclohexane. Solid lines are calculated on the basis of Eq. (8) with appropriate parameter values.

cules in their vicinity at the moment of their creation will lose their excitation energy without transferring it to acceptor. Therefore, it is not suitable to express the energy transfer term as bimolecular reaction. It has already been known to be difficult to account for the magnitude of some energy transfer and quenching constants by diffusion theory⁷⁾. Their values appear to indicate that transfer to the quencher or acceptor occurs via another mechanism rather than by diffusion.

In the case where diffusion is insignificant, it may be suitable to consider the region of influence of the excited donor molecule; only the acceptor molecule within the region can receive excitation energy from the excited donor.

We let λ be the average number of acceptor molecule within the region and consider $N_0[D^*]$ excited donor molecules where N_0 is Avogadro's number. Then, $(1-e^{-\lambda})N_0[D^*]$ of these can transfer their excitation energy to acceptors.

Taking into account the fact that transfer in reality requires a certain time τ , Eq. (5) can be rewritten as follows:

$$\frac{dN_0[D^*]}{dt} = k_1N_0[D] - k_2N_0[D^*] - \kappa(1-e^{-\lambda})N_0[D^*], \quad (7)$$

where $\kappa=1/\tau$.

And, instead of Eq. (6), a following equation can be derived:

$$\frac{I_{D_0}}{I_D} \cdot \frac{[D]}{[D_0]} = 1 + \frac{\kappa}{k_2}(1-e^{-\lambda}). \quad (8)$$

Using suitable parameter values Eq. (8) can express satisfactorily the experimental result shown in Fig. 4.

Let v be the volume of the region of influence and V_A and V_D be the molar volume of acceptor and donor, respectively, then λ can be expressed as follows:

$$\lambda = N_0v \frac{[A]}{[A]V_A + [D]V_D}.$$

For the organic solvents we used in present study their molar volumes are almost same and approximately taken as 100 cm³ per mole. Therefore,

$$\lambda \simeq N_0 \frac{v}{V} m_A, \quad (9)$$

where $V \equiv V_A, V_D$, and

$$m_A = \frac{[A]}{[A] + [D]}.$$

In order to estimate the actual dimension of v , we change Eq. (8) into the following form:

$$\frac{\kappa}{k_2} \exp\left(-N_0 \frac{v}{V} m_A\right) = \left(1 + \frac{\kappa}{k_2}\right) - \frac{[D]}{[D_0]} \frac{I_{D_0}}{I_D}. \quad (10)$$

Equation (10) shows that on a semi-log paper the plots of the right side vs. m_A should yield a straight line, and its slope gives the actual value of $N_0 \frac{v}{V}$. The first term of the right side is also uncertain at present, but as this corresponds to the value of $\frac{[D]}{[D_0]} \cdot \frac{I_{D_0}}{I_D}$ for $\lambda \rightarrow \infty$, a suitable value can be obtained by visual inspection of Fig. 4. Table 1 summarizes the values of κ/k_2 thus obtained,

Charge Transfer in Binary Organic Liquid Mixtures

Table 1. Summary of R 's, κ/k_2 's, and the ionization potentials of the acceptors.

Acceptor	$R(\text{\AA})$	κ/k_2	I.P. (eV)
Benzene	3.3	1.0	9.245±0.01
Toluene	3.8	1.4	8.82 ±0.01
o-Xylene	5.7	2.3	8.56 ±0.01
m-Xylene	5.0	1.4	8.56 ±0.01
p-Xylene	5.7	0.8	8.445±0.01
Mesitylene	6.7	3.0	8.40 ±0.01
Cyclohexane	—	—	9.88 ±0.02

the radii, R , of the regions under the assumption that the regions of influence are spherical, and the ionization potentials of the acceptors and cyclohexane. We have here used photoionization potential data.

III. 2. Charge Transfer

A criterion for charge transfer mechanism is that the acceptor molecule has a lower ionization potential than that of the donor molecule. If the energy transfer mechanism between cyclohexane and methyl-substituted benzenes is responsible for charge transfer mechanism, the protective efficiency in the radiolysis of cyclohexane by methyl-substituted benzenes would depend on their ionization potentials. As in our model the excited cyclohexane is protected by the acceptor molecules within the sphere of influence, the larger radius of the sphere results the larger protection. The magnitude of the radius of action shown in Table 1 is in the order benzene < toluene < xylene < mesitylene, which is also the order in which the ionization potential of the solvents decreases.

For tri-methyl-substituted benzenes, o-xylene slightly deviates from above order. This fact may be ascribed to the difference in their structures. At present time, therefore, we suggest that the energy transfer mechanism in these binary liquid systems is due to charge transfer and cyclohexane acts as electron acceptor and methyl-substituted benzenes as electron donor.

Further, as there is no indication of molecular complex formation between the donor and the acceptors at ground state, the charge transfer process takes place with the excited state of the donor molecule and should be of a contact type. In the charge transfer mechanism the donor molecule is not necessarily to be in its ionization state, because in an excited molecule an electron of which is excited to a higher molecular orbital, and its vacancy may generally act as an positive hole. Thus, an excited molecule may act as an electron acceptor. In contrast with this, an electron excited to a higher molecular orbital may easily escape from the parent molecule. Thus an excited molecule may also act as an electron acceptor. It depends on a partner molecule how an excited molecule behaves.

III. 3. Charge Transfer Distance

The radius of action shown in Table 1 is considered to correspond with the charge transfer distance. In order that a contact charge transfer complex is ef-

fectively formed, a donor and an acceptor molecule must be suitably oriented before any charge transfer takes place. The radius of action was obtained under the assumption that the region of influence is spherical. Thus, this assumption is approximate. The contact charge transfer complex is formed as a result of overlap of the donor molecular orbital with that of the acceptor. Thus, the charge transfer distance may be greater than the sum of the two van der Waals radii. Terenin and Ermolaev⁸⁾ have demonstrated the occurrence of energy transfer between triplet states, and found that the transfer distance was about 14 Å. As stated by them, an exchange mechanism should be considered in this case. This value, 14 Å, can be considered as the maximum estimate for the charge transfer distance. Thus, the magnitude of R' 's in Table 1, which was obtained under the the approximate assumption, may be to some extent smaller than that of true R but may not much differ from it.

III. 4. Life Time of Charge Transfer Complex

The κ was defined in Eq. (7) as the inverse of a time necessary for energy transfer. However, as the term $(1-e^{-\lambda})N_0[D^*]$ in Eq. (7) gives the number of charge transfer pair, $\tau(=1/\kappa)$ is unity may considered as the life time of charge transfer complex. The fact that the magnitude of κ/k_2 's is near unity may suggest that the life time of charge transfer complex has almost same magnitude as that of excited cyclohexane. Thus, we may conclude that the charge transfer complex has also the life time being of the order of 10^{-13} sec. This conclusion corresponds with that of Hardwick²⁾. He obtained 4×10^{-13} sec for the life time of the charge transfer pair in alkane solvents.

ACKNOWLEDGMENTS

The authors are very grateful to Dr. Kenji Fujimura, Director of their laboratory, and Professor Sakae Shimizu for their kind encouragement.

REFERENCES

- 1) M. Burton and S. Lipsky, *J. Phys. Chem.*, **61**, 1461 (1957).
- 2) T. J. Hardwick, *J. Phys. Chem.*, **66**, 2132 (1962).
- 3) P. J. Dyne, *Can. J. Chem.*, **43**, 1080 (1965).
- 4) P. J. Dyne, and W. M. Jenkinson, *Can. J. Chem.*, **38**, 539 (1960).
- 5) J. M. Ramaradhya and G. R. Freeman, *Can. J. Chem.*, **39**, 1795 (1961).
- 6) S. Horikiri and T. Saigusa, *Bull. Inst. Chem. Res., Kyoto Univ.*, **43**, 45 (1965).
- 7) C. R. Mullin, M. A. Dillon, and M. Burton, *J. Chem. Phys.* **40**, 3053 (1964).
- 8) A. N. Terenin, and V. L. Ermolaev, *Bull. Acad. Sci. USSR, Phys. Ser.* **26**, No. 1, 21 (1962).