

Sensitization and Protection Observed in G-Value and Radiation Induced Luminescence

By

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(Received April 25, 1959)

From both the G-values and fluorescence intensity in organic two component systems, the direction of the excitation energy transfer may be determined. Agreement between the directions determined by these two methods, i. e., G-value and fluorescence intensity, is found to hold in most cases. But in the benzene-methyl acetate system, the directions determined are found to be opposite to each other.

It is found that the carbon-carbon double bond in vinyl monomers is able to quench the excited state of the saturated or unsaturated hydrocarbons.

It is concluded that with some exceptions, the excitation energy is transferred from saturated hydrocarbons to unsaturated hydrocarbons, vinyl monomers and halogenated compounds, and from unsaturated hydrocarbons to vinyl monomers and halogenated compounds, and also from vinyl monomers to halogenated compounds.

Some excitation energy transfer schemes are discussed quantitatively in comparison with experimental results, and some rate constants are determined. It is found that a constants referring to the energy transfer obtained in fluorescence experiments is much larger than that obtained in radical formation.

1. Introduction

In the radiation effects of organic systems, sensitization or protection have been already observed (1), (2), (3). These phenomena may be explained as the excitation energy transfer from one component to another. When it is transferred from the radiation chemically stable component to the unstable one, sensitization phenomena may be observed, and when it is transferred in the reverse direction, protection phenomena may be expected.

On the other hand, it has also been known that the luminescence of a liquid scintillator could be quenched by the addition of a quenching agent, carbon tetrachloride or oxygen for example (4), (5), and the quenching phenomenon might be due in part to the excitation energy transfer from the excited state of the solvent (6).

It is to be noted that in both cases, i. e., these of radiation chemical effects and radiation induced luminescence in organic systems, the excitation energy transfer plays an important role. The luminescence experiment is performed here especially in connection with radiation chemistry.

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2. Experiment

2.1) Experimental Arrangement

The experimental arrangement is the same as that of Kallman (7) and Burton (8), and here the radiation induced luminescence is measured as the anode current of a photomultiplier type EMI 6097 F which has a maximum sensitivity near $420 \text{ m}\mu$. This apparatus has a heat regulating jacket, but it is not used here. (Fig. 1)

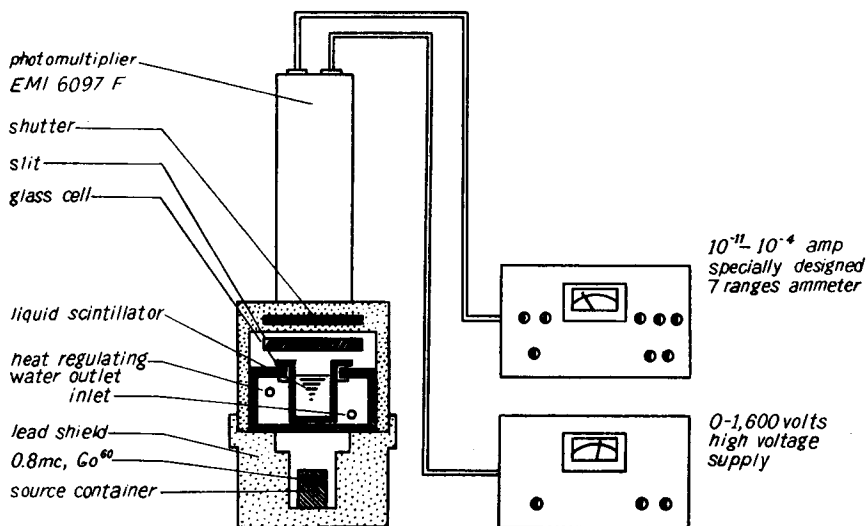


Fig. 1. Experimental arrangement.

2.2) Procedure

The volume of the samples used is 20 ml, and the sample is held in a glass cell. The experiment is performed at room temperature, in air or vacuum.

The anode potential is fixed at 680 volts, and the intensity of radiation induced luminescence is measured by the anode current of the photomultiplier. The anode current amounts to 95×10^{-11} amp in air saturated benzene solution of 1 g/l p-terphenyl. The back ground amounts to 5×10^{-11} amp. according to the luminescence of the solvent and glass cell, and to the direct effects by gamma radiation on the photomultiplier. The solvent luminescence is of Čerenkov radiation. p-terphenyl is used as the scintillating solute in this experiment. The fluorescence intensity of p-terphenyl may be obtained as the difference between the observed total luminescence and the back ground mentioned above.

2.3) Materials

The materials used are as follows:—

p-terphenyl	: Tracer Lab. Inc., scintillation grade
benzene	: Eastman Kodak Co., spectro grade Nakarai & Co., Ltd., analytically guaranteed reagent

toluene	: Hayashi Pure Chemical Industries, Ltd., analytically guaranteed reagent
cyclohexane	: Eastman Kodak Co., spectro grade
carbon tetrachloride	: Eastman Kodak Co., spectro grade Nakarai & Co., Ltd., analytically guaranteed reagent
chloroform	: Eastman Kodak Co., spectro grade
carbon tetrabromide	: Tokyo Kasei Kogyo Co., Ltd., analytically guaranteed reagent
methyl acetate	: Nakarai & Co., Ltd., analytically guaranteed reagent
ethyl acetate	: Hayashi Pure Chemical Industries, Ltd., analytically guaranteed reagent
ethyl benzene	: Tokyo Kasei Kogyo Co., Ltd., analytically guaranteed reagent
methyl propionate	: Tokyo Kasei Kogyo Co., Ltd.
ethyl propionate	: Wako Pure Chemicals, Ltd.
vinyl monomers	: Purified by ordinary method for polymerization
vinyl polymers	: Polymerized by radical or thermal polymerization

These samples employed do not show the marked absorption of the fluorescence of *p*-terphenyl at the concentrations examined in the spectral range (320–420 m μ).

3. Results on the G-Value and Fluorescence Intensity in Two Component Systems

The typical features of the G-value and the fluorescence intensity in two component systems are represented in the following figures. (Figs. 2-7). In these systems, the linear additivity rule referring to the components is not established.

3.1) Cyclohexane-Benzene System (Figs. 2-3)

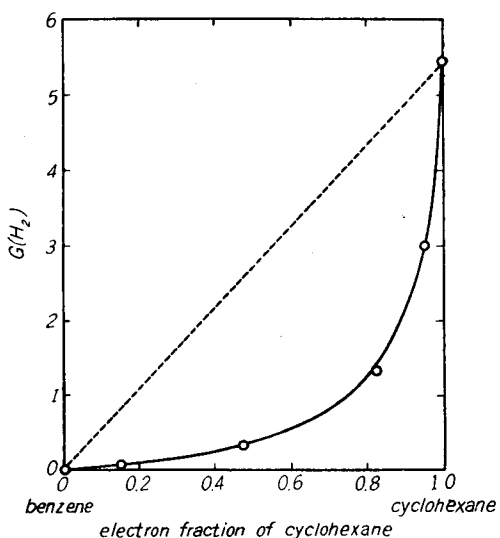


Fig. 2. $G(H_2)$ in benzene-cyclohexane system. (in vacuum)
Manion & Burton (2).

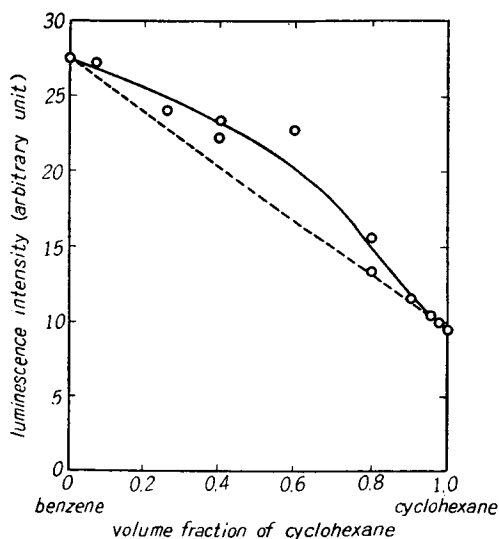


Fig. 3. Luminescence intensity in benzene-cyclohexane system. (in vacuum, *p*-terphenyl concentration = 1.58 g/l)
Burton, Berry & Lipsky (8).

3.2) Benzene-Carbon Tetrachloride System (Figs. 4-5)

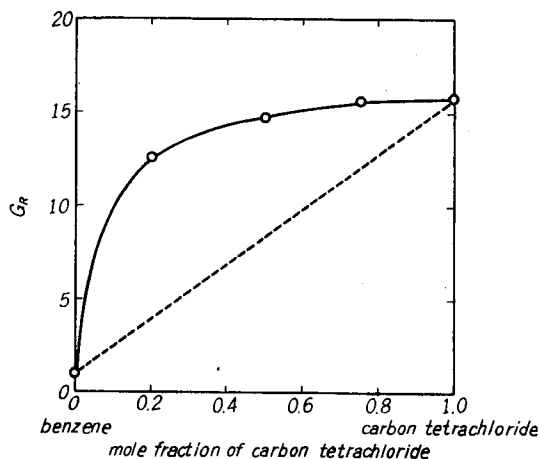


Fig. 4. G_R in benzene-carbon tetrachloride system. (in vacuum) Okamura & Futami (3).

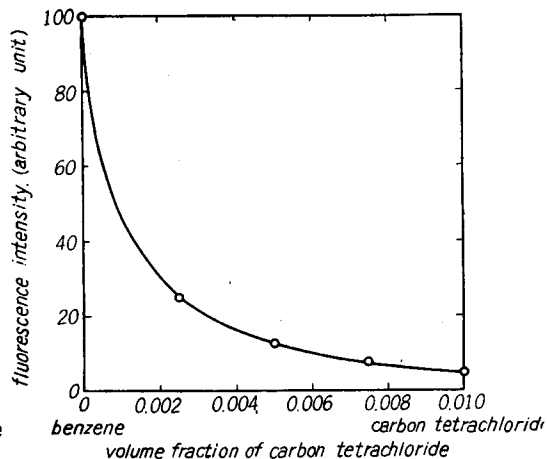


Fig. 5. Fluorescence intensity in benzene-carbon tetrachloride system. (in vacuum, *p*-terphenyl concentration=1 g/l)

3.3) Benzene-Methyl Acetate System (Figs. 6-7)

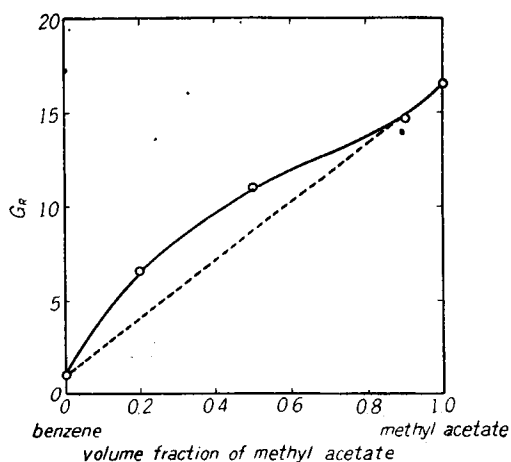


Fig. 6. G_R in benzene-methyl acetate system. (in air) Bouby & Chapiro (9).

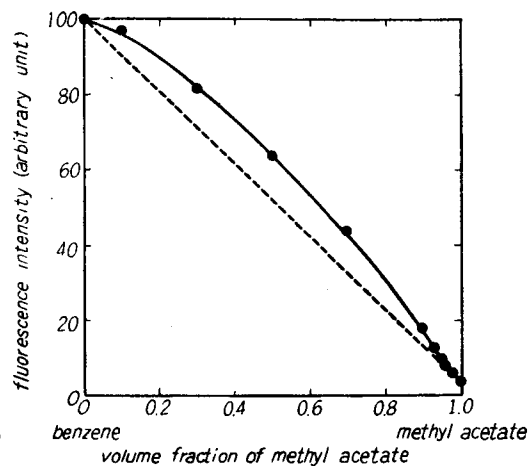


Fig. 7. Fluorescence intensity in benzene-methyl acetate system. (in air, *p*-terphenyl concentration=1 g/l)

4. Discussion on the Direction of Excitation Energy Transfer Observed in G-Value or Radiation Induced Fluorescence

It may be reasonable to assume that quenching is a kind of excitation energy transfer. When the addition of a quenching agent causes a drop in fluorescence intensity in liquid scintillators, solvent- or solute-quenching or both may be considered.

If a reagent quenches the solvent, the excitation energy is removed from the solvent. Here, for the sake of convenience, only solvent quenching will be considered, and the quenching will be assumed to be an excitation energy transfer from solvent to quencher. According to the opinion of Furst and Kallman (4), excitation energy transfer from a poor solvent to an effective solvent is also assumed. On these points of view, the direction of excitation energy transfer observed in radiation induced fluorescence may be determined. From the sensitization and the protection observed in the G-values in organic two component systems, the direction of energy transfer may also be determined. The direction of energy transfer thus determined may be summarized as the following two cases.

4.1) Same Direction Cases

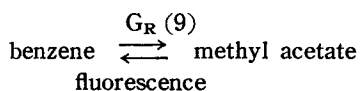
In the following systems, the directions of excitation energy transfer determined by the two methods mentioned above, G-value and fluorescence, are found to agree.

			G-value	fluorescence
cyclohexane	→ Benzene	$G(H_2)$	(2)	(8)
benzene	→ carbon tetrachloride	G_R	(3)	(6)
benzene	↔ chloroform	G_R	(9)	(6)
benzene	→ toluene	$G(H_2)$	(2)	unpublished data
styrene	→ carbon tetrachloride	G_R	(1)	„
styrene	→ carbon tetrabromide	G_R	(3), (10)	„

In the benzene-chloroform system, an excitation energy exchange is observed, the case of which may be discussed later. In the benzene-toluene system, the addition rule is found to hold true.

4.2) Opposite Direction Cases

The agreement between the directions determined by these two methods may be observed in most cases, but in the following system, the directions determined are found to be opposite to each other.



5. Quenching of the Radiation Induced Fluorescence by Carbon-Carbon Double Bond

It was found that vinyl acetate would quench effectively the radiation induced fluorescence of the benzene-p-terphenyl mixture, but, it was not so with ethyl acetate (6), the saturated compound corresponding to vinyl acetate. On the other hand, the quenching cross sections of various unsaturated hydrocarbons for mercury, cadmium

and sodium resonance radiation are about 100 times larger than for the corresponding saturated hydrocarbons (11). These facts suggest the quenching ability of the carbon-carbon double bond. Several vinyl monomers, polymers and the corresponding saturated compounds are examined here as the quenching agents. The experiments are performed at room temperature and in air saturated solution, and the concentration of *p*-terphenyl is fixed at 1 g/l.

5.1) Quenching of the *p*-Terphenyl Fluorescence in Benzene Solution by Vinyl Monomers

The results obtained for vinyl monomers and the corresponding saturated compounds are shown in Fig. 8.

From the results shown in Fig. 8, it is found that vinyl monomers are able to quench the *p*-terphenyl fluorescence in benzene solution, but the saturated compounds corresponding to vinyl monomers have no such ability at all. Thus it may be reasonable to conclude that the quenching ability of these vinyl monomers is due mainly to the carbon-carbon double bond.

The less effective quenching ability of vinyl acetate compared to other monomers examined suggests a relationship between the quenching ability and the chemical structure. The carbon-carbon double bond C=C in vinyl acetate is not in conjugation, but in other

monomers, there is a conjugated double bond $\text{C}=\text{C}$, $\text{C}=\text{C}$, $\text{C}=\text{C}$.

$$\begin{array}{c} \text{O} \\ | \\ \text{C}=\text{C} \\ | \\ \text{C}=\text{O} \end{array}, \quad \begin{array}{c} \text{C}=\text{C} \\ | \\ \text{C} \\ | \\ \text{C}_6\text{H}_4 \end{array}, \quad \begin{array}{c} \text{C}=\text{C} \\ | \\ \text{C}\equiv\text{N} \end{array}$$

The mechanism of the quenching, whether it is of solvent quenching or of solute quenching, is not clarified here. If vinyl monomers quench the excited benzene, the excitation energy transfer from benzene to vinyl monomers may be expected. But this expectation contradicts the conclusions of Nikitina and Bagdasaryan (12) who have already assumed in their experiments on the radiation solution polymerization that the excitation energy might be transferred from methyl methacrylate to benzene.

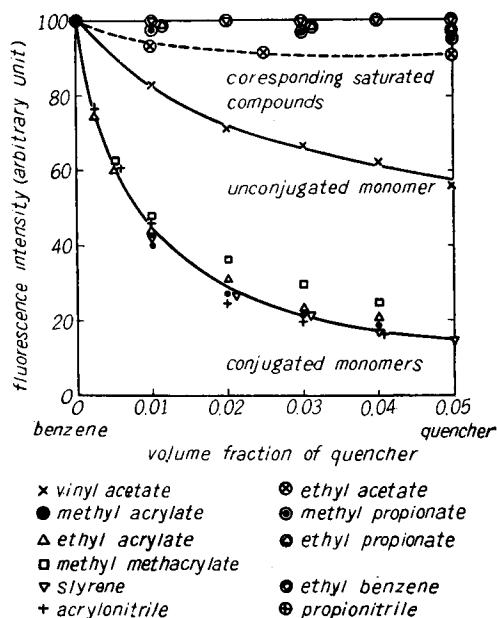


Fig. 8. Quenching of the *p*-terphenyl fluorescence in benzene solution by vinyl monomers and the corresponding saturated compounds. (in air, *p*-terphenyl concentration=1 g/l)

On the other hand, as the difference between Chapiro's theory (1) and their experimental results is found to be rather small, the discrepancy between the theory and the experiments may perhaps be due to the dilution effect of the monomer.

5.2) Quenching of the *p*-Terphenyl Fluorescence in Benzene Solution by Polymers

Further experiments on vinyl polymers are made here to confirm the nature of the quenching ability of vinyl monomers as discussed above. The results obtained are shown in Fig. 9.

From Fig. 9, it is clear that the quenching efficiency of vinyl polymers is less effective as compared with vinyl monomers. But some vinyl polymers, such as polystyrene and poly-(vinyl acetate), also seem to quench, though the efficiency may be lower. Generally speaking, in the case of polymers, the viscosity effects on the efficiency may have to be considered. If the excitation energy transfer from solvent to scintillating solute is caused by the collision between molecules (13), the high viscosity of the polymer solution may hinder the energy transfer resulting in the reduction of the fluorescence intensity. On the other hand, in the viscous medium, the fluorescence efficiency of the scintillating solute becomes in itself relatively high (14).

Thus the viscosity effects on fluorescence intensity seem to be very complex. The effects of side chains in a vinyl polymer are not yet made clear in this report,

The quenching ability of the carbon-carbon double bond may be a means for the determination of both the quantity and quality of the double bond.

5.3) Quenching of the *p*-Terphenyl Fluorescence in Cyclohexane Solution by Vinyl Monomers and the Corresponding Saturated Compounds

Contrary to the case of benzene, the saturated compounds corresponding to these monomers seem to quench as effectively as the monomers themselves in the case of

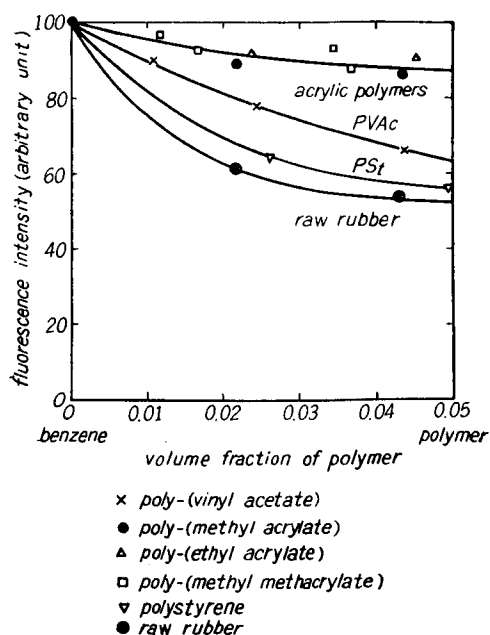


Fig. 9. Quenching of the *p*-terphenyl fluorescence in benzene solution by polymers. (in air, *p*-terphenyl concentration=1 g/l)

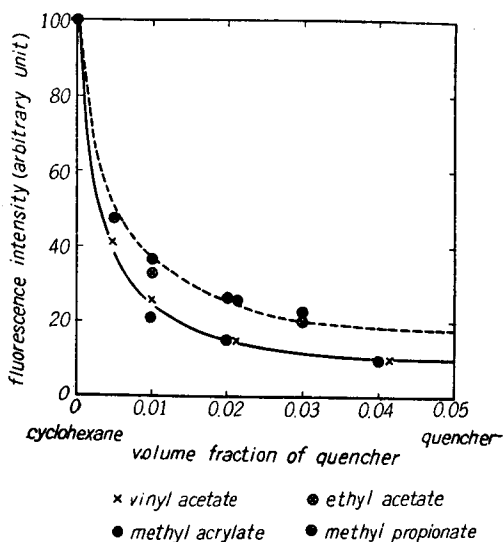


Fig. 10. Quenching of the *p*-terphenyl fluorescence in cyclohexane solution by vinyl monomers and the corresponding saturated compounds. (in air, *p*-terphenyl concentration=1 g/l)

cyclohexane. (Fig. 10). But the solubility of *p*-terphenyl in cyclohexane is much smaller than in benzene, and so the sedimentation of dissolved *p*-terphenyl by the addition of a quencher is observed sometimes in the case of cyclohexane. Thus further studies may be necessary.

6. General Scheme of the Energy Transfer Direction and the Sensitization or Protection in the Organic Two Component Systems

From the experiments on radiation induced fluorescence in cyclohexane-benzene mixtures, Burton et al concluded that the excitation energy might be transferred from cyclohexane to benzene (8). The experiment on *n*-hexane- or paraffin-xylene mixtures by Furst and Kallman suggested that an energy transfer from *n*-hexane or paraffin to xylene might be expected (4). At the same time, $G(H_2)$ in cyclohexane-benzene mixtures suggests an energy transfer from cyclohexane to benzene (2), and $G(H_2 + CH_4)$ in triacontane ($C_{30}H_{62}$)-benzene mixtures suggests an energy transfer from triacontane to benzene (15). And also $G(H_2)$ in cyclohexane-cyclooctatetraene (C_8H_8) mixtures suggests an energy transfer from cyclohexane to cyclooctatetraene (15). From these results, it may be concluded that the excitation energy may be transferred from the saturated hydrocarbons such as cyclohexane, *n*-hexane and paraffin to unsaturated hydrocarbons such as benzene, xylene, terphenyl and cyclooctatetraene.

The excitation energy transfer from aromatic compounds to halogenated compounds may be confirmed by various experiments (1), (3), (4), (5), (6), (10), (12).

The excitation energy transfer from aromatic compounds to vinyl monomers may be assumed on the basis of the quenching ability of the vinyl monomers already mentioned above.

The excitation energy transfer from vinyl monomers to halogenated compounds may be expected from the solution polymerization in styrene-carbon tetrachloride (1), (12), styrene-carbon tetrabromide (10) and methyl methacrylate-carbon tetrachloride (12) mixtures.

The stability to irradiation may be ranked as follows:—unsaturated hydrocarbons > saturated hydrocarbons > halogenated compounds. Thus, the general scheme of the energy transfer direction and the sensitization or protection in the organic two component systems may be summarized as shown in the following figure. (Fig. 11).

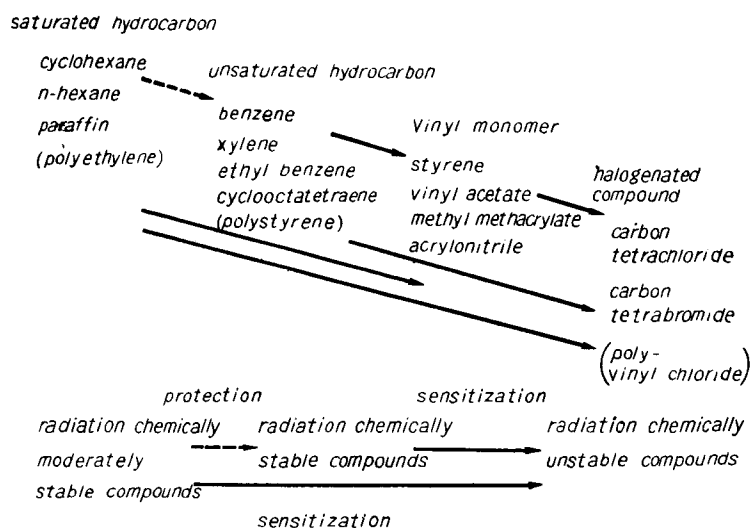
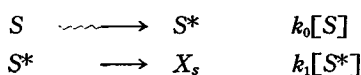
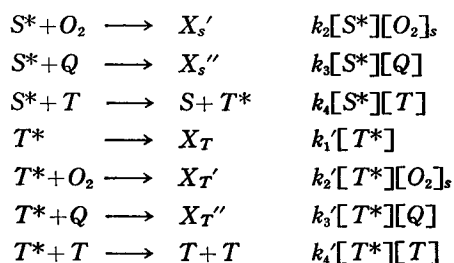


Fig. 11. General scheme of the energy transfer direction and the sensitization and protection in the organic two component systems.

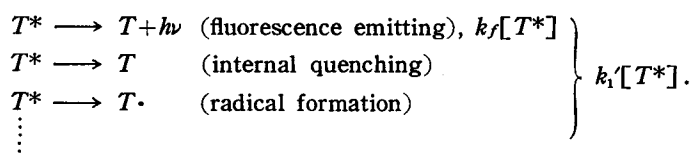
7. Quenching Mechanism and its Examples in the Liquid Scintillators

Burton et al have considered the quenching mechanism of liquid scintillator as the following (5), where S is the solvent, T , the scintillating solute (p-terphenyl), Q , the quenching material and O_2 is the dissolved oxygen.





where the process $T^* \rightarrow X_T$ represents the following various processes.



From the above kinetic analysis, fluorescence intensity I becomes

$$I = k_f[T^*] = \frac{k_f k_4 k_0 [S][T]}{(k_1 + k_2[O_2]_s + k_3[Q] + k_4[T])(k_1' + k_2'[O_2]_s + k_3'[Q] + k_4'[T])}. \quad (1)$$

Defining $I = I_0$, $[S] = [S]_0$ at $[Q] = 0$, and $[Q] = [Q]_0$ at $[S] = 0$, the following equation is obtained from Eq. (1).

$$\frac{I_0/I}{[S]_0/[S]} = \left(1 + \frac{k_3[Q]_0}{k_1 + k_2[O_2]_s + k_4[T]} \frac{[Q]}{[Q]_0}\right) \left(1 + \frac{k_3'[Q]_0}{k_1' + k_2'[O_2]_s + k_4'[T]} \frac{[Q]}{[Q]_0}\right). \quad (2)$$

Defining γ and γ' as follows;

$$\left. \begin{array}{l}
\gamma = \frac{k_3[Q]_0}{k_1 + k_2[O_2]_s + k_4[T]} \\
\gamma' = \frac{k_3'[Q]_0}{k_1' + k_2'[O_2]_s + k_4'[T]}
\end{array} \right\} \quad (3)$$

and if

$$[S]/[S]_0 \rightleftharpoons 1$$

or

$$[Q]/[Q]_0 \rightleftharpoons 0$$

the following equations are obtained.

$$\frac{I_0}{I} = \left(1 + \gamma \frac{[Q]}{[Q]_0}\right) \left(1 + \gamma' \frac{[Q]}{[Q]_0}\right) \quad (4)$$

$$(I_0/I - 1) / ([Q]/[Q]_0) = \gamma + \gamma' + \gamma\gamma' ([Q]/[Q]_0) \quad (5)$$

$[Q]/[Q]_0$ is considered to stand for the volume fraction of the quenching material.

From Eq. (4), it is understood that the I_0/I vs. $[Q]/[Q]_0$ relationship is linear when solvent quenching or solute quenching alone exists. And it is also clear that I_0/I shows a positive deflection from linearity with increasing $[Q]/[Q]_0$ when both solvent- and solute-quenching exist.

In Figs. 12 and 13, the results obtained in carbon tetrachloride and chloroform are shown.

From comparing Figs. 12 and 13 with the theory expressed in Eqs. (4) and (5), it may be understood that the theory may be correct in the case of carbon tetrachloride but not so in the case of chloroform. It is also clarified that the theory is correct in the case of carbon tetrabromide.

Burton et al have attributed the downward deflection from linearity in the I_0/I vs. $[Q]/[Q]_0$ relationship to Čerenkov radiation (5). Here, however, as the effect of Čerenkov radiation is already set aside from I and I_0 , the reason for the deflection is

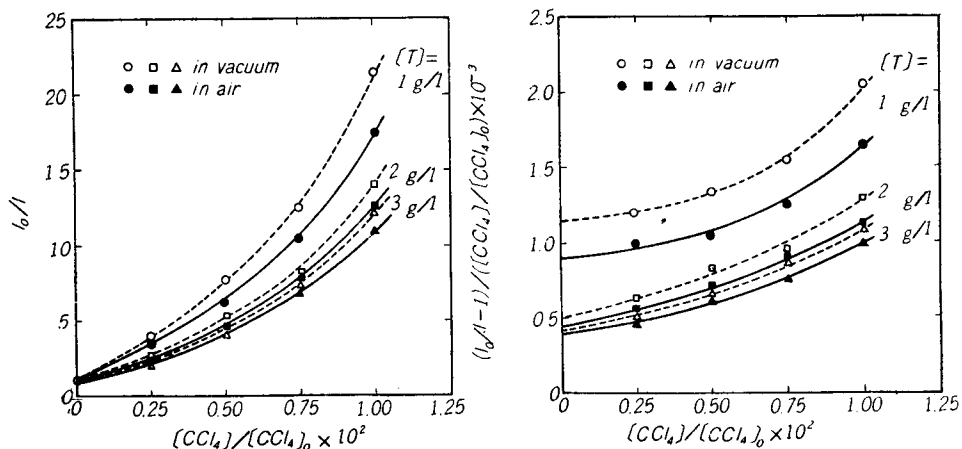


Fig. 12. Quenching of the radiation induced fluorescence by carbon tetrachloride in benzene solution of *p*-terphenyl.

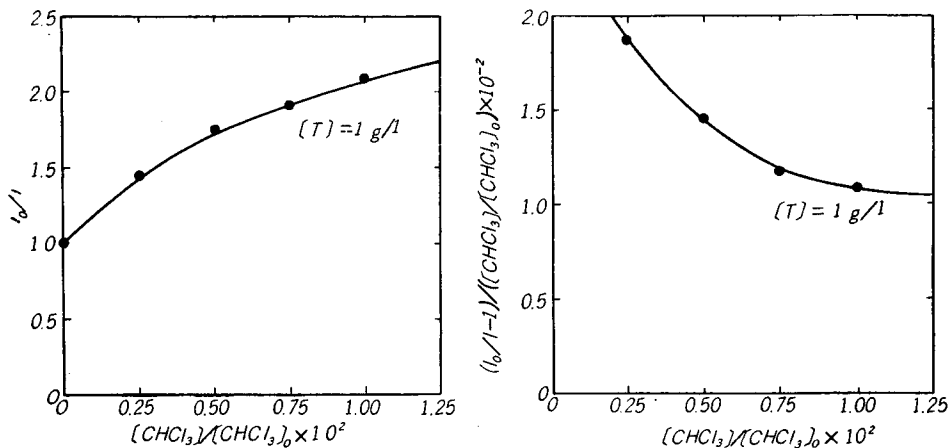
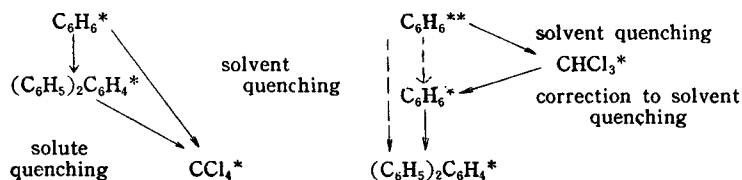


Fig. 13. Quenching of the radiation induced fluorescence by chloroform in benzene solution of *p*-terphenyl. (in air)

to be sought elsewhere. And thus, the following excitation energy exchange mechanism is proposed in the case of chloroform.



In the case of vinyl acetate, the results obtained are shown in Fig. 14. The special feature may be illustrated elsewhere.

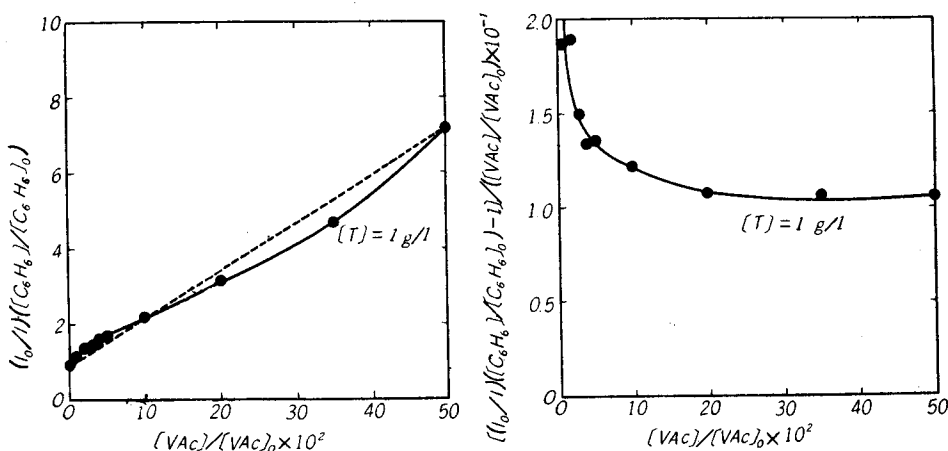


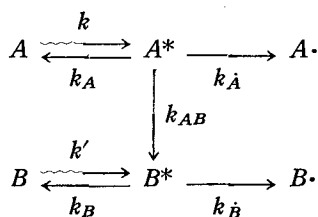
Fig. 14. Quenching of the radiation induced fluorescence by vinyl acetate in benzene solution of *p*-terphenyl. (in air)

8. Some Excitation Energy Transfer Mechanisms and G_R in Two Component Systems

The excitation energy transfer processes have been discussed quantitatively by several authors, for example, by Burton et al in cyclohexane-benzene system (2), Nikitina and Bagdasaryan in styrene-carbon tetrachloride system (12), and by Magat et al in benzene-chloroform system (16). The theoretical calculations made by Nikitina and Bagdasaryan are, however, approximate, and the results obtained by Magat et al are not considered to be easily comparable with the experiments. Several types of excitation energy transfer mechanism are represented here in comparison with the experiments.

8.1) One Way Excitation Energy Transfer (a)

In the following mechanism (3), the fundamental equations are as follows;



$$kI[A] = k_A[A^*] + k_{A'}[A^*] + k_{AB}[A^*][B] \quad (6)$$

$$k'I[B] + k_{AB}[A^*][B] = k_B[B^*] + k_{B'}[B^*] \quad (7)$$

$$V_R = k_{A'}[A^*] + k_{B'}[B^*] \quad (8)$$

where I is the radiation intensity and V_R is the rate of radical formation.

From Eqs. (6), (7) and (8), the following equation is obtained.

$$V_R = kIW_A[A] + k'IW_B[B] + \frac{\alpha_{AB}(W_B - W_A)}{1 + \alpha_{AB}[B]} kI[A][B] \quad (9)$$

where

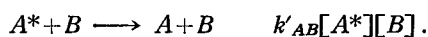
$$\left. \begin{array}{l}
 W_A = \frac{k_{A'}}{k_A + k_{A'}} \\
 W_B = \frac{k_{B'}}{k_B + k_{B'}} \\
 \alpha_{AB} = \frac{k_{AB}}{k_A + k_{A'}}
 \end{array} \right\} \quad (10)$$

8.2) One Way Excitation Energy Transfer (b)

There is another type of quenching A^* by B besides



That is (2)



In considering also the second type of quenching, the rate of radical formation is found to be

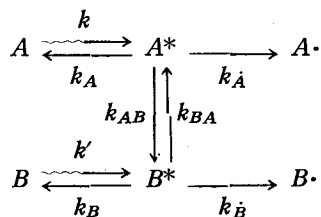
$$V_R = kIW_A[A] + k'IW_B[B] + \frac{\alpha_{AB}(W_B - W_A) - \alpha'_{AB}W_B}{1 + (\alpha_{AB} + \alpha'_{AB})[B]} kI[A][B] \quad (11)$$

where

$$\alpha'_{AB} = \frac{k'_{AB}}{k_A + k_{A'}} \quad (12)$$

8.3) Excitation Energy Exchange (a)

Nikitina and Bagdasaryan proposed the following excitation energy transfer scheme (12), where the excitation levels of A and B are in near approximation.



In this case, the rate of radical formation is found to be

$$V_R = kIW_A[A] + k'IW_B[B] + \frac{(k\alpha_{AB} - k'\alpha_{BA})(W_B - W_A)}{1 + \alpha_{AB}[B] + \alpha_{BA}[A]} I[A][B] \quad (13)$$

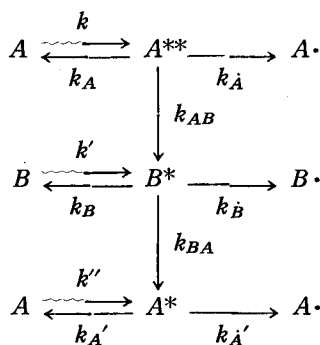
where

$$\alpha_{BA} = \frac{k_{BA}}{k_B + k_B'} \quad (14)$$

8.4) Excitation Energy Exchange (b)

In the G_R of benzene-chloroform mixtures, both sensitization and protection were observed in ref. (9). In the region rich with benzene the sensitization effect of chloroform by benzene is observed, and the protection effect of chloroform by benzene is also observed in the region rich with chloroform. The fluorescence experiment already mentioned above may have some relation with G_R .

Magat et al proposed the following scheme to explain the special feature in benzene-chloroform mixtures (16).



The rate of radical formation may be obtained as the following.

$$V_R = kIW_A[A] + k'IW_A'[A] + k'IW_B[B] + a \frac{A-d}{(b+A)(1+C-A)} A(1-A) \quad (15)$$

where, A is the volume fraction of the component A , and

$$W_{A'} = \frac{k_{A'}}{k_{A'} + k_{A'}} \quad (16)$$

$$\left. \begin{aligned}
 a &= kI[A]_0(W_{A'} - W_A) + k'I[B]_0(W_B - W_{A'}) \\
 b &= 1/\alpha_{BA}[A]_0 > 0 \\
 c &= 1/\alpha_{AB}[B]_0 > 0 \\
 d &= \frac{1 + \frac{1}{\alpha_{AB}[B]_0} \frac{k[A]_0(W_B - W_A)}{k'[B]_0(W_B - W_{A'})}}{1 + \frac{k[A]_0(W_{A'} - W_A)}{k'[B]_0(W_B - W_{A'})}} \frac{1}{\alpha_{BA}[A]_0}
 \end{aligned} \right\} \quad (17)$$

and $[A]=[A]_0$ at $[B]=0$, $[B]=[B]_0$ at $[A]=0$.

9. Determination of the Rate Constants

From the fluorescence experiment and the measurement of the G-value, the rate constants concerned with the primary processes may be determined. The discussions are made here on benzene-carbon tetrachloride system and benzene-chloroform system.

9.1) Benzene-Carbon Tetrachloride System

Defining $I=I_0$ at $[Q]=0$, $[O_2]_s=0$, following equation is obtained from Eq. (1).

$$\frac{I_0}{I_0} = \left(1 + \frac{k_2[O_2]_s}{k_1 + k_4[T]}\right) \left(1 + \frac{k_2'[O_2]_s}{k_1' + k_4'[T]}\right).$$

In consideration of the discussions made by Burton et al (5), the effect of solute quenching may be neglected, so that the following equation is obtained.

$$\frac{I_0}{I_0 - I_0} = \frac{k_1}{k_2[O_2]_s} + \frac{k_4}{k_2[O_2]_s} [T].$$

From the linear relationship in $I_0/(I_0 - I_0)$ vs. $[T]$, k_2/k_1 may be obtained as follows;

$$k_2/k_1 = 500 \text{ l/mole}$$

where

$$[O_2]_s = 1.43 \times 10^{-3} \text{ mole/l (5)}.$$

γ and γ' in Eq. (3) are found to be of the same order of magnitude in the case of benzene-carbon tetrachloride-p-terphenyl mixture. The individual determination of γ and γ' by $(I_0/I - 1)/([CCl_4]/[CCl_4]_0)$ vs. $[CCl_4]/[CCl_4]_0$ relationship is impossible in reference to the accuracy of the experiment. And thus γ is determined from $\gamma + \gamma'$ on the assumption of equality of γ and γ' .

Defining $\gamma = \gamma_0$ at $[O_2]_s = 0$, following equation may be obtained from Eq. (3).

$$\gamma_0 = [\gamma]_{[O_2]_s=0} = \frac{k_3[Q]_0}{k_1 + k_4[T]}.$$

From the linear relationship in $1/\gamma_0$ vs. $[T]$, k_3/k_1 may be obtained as follows;

$$k_3/k_1 = 190 \text{ l/mole}$$

k_4/k_1 may be obtained from the $I_0/(I_0 - I_0)$ vs. $[T]$ relationship as follows;

$$k_4/k_1 = 120 \text{ l/mole}$$

and may also be obtained from the $1/\gamma_0$ vs. $[T]$ relationship as follows;

$$k_4/k_1 = 740 \text{ l/mole.}$$

From these results the following range for k_4/k_2 is obtained

$$k_4/k_2 = 0.24 - 1.48.$$

On the other hand, Burton et al obtained for the same quantity the following range (5);

$$k_4/k_2 = 0.18 - 0.80.$$

9.2) Benzene-Chloroform System

As previously discussed, chloroform was found to quench the radiation induced fluorescence of benzene-p-terphenyl mixtures, and the mechanism of the quenching was different from that of carbon tetrachloride. In the region extremely rich in benzene, the linear relationship between I_0/I and the concentration of chloroform appears to be established. Then considering the quenching mechanism proposed already, it may be reasonable to assume that only the usual solvent quenching is active in that region. From these points of view, the following equation may be obtained

$$\frac{I_0}{I} = 1 + \frac{k_3[Q]_0}{k_1 + k_2[O_2]_s + k_4[T]} \frac{[Q]}{[Q]_0}.$$

From the results obtained in Fig. 13, and also the values of k_2/k_1 and k_4/k_1 discussed above, k_3/k_1 may be obtained as the following;

$$k_3/k_1 = 40 \text{ l/mole.}$$

9.3) Comparison of the Rate Constants Obtained in Fluorescence with that of G_R

As previously noticed, the same excitation energy transfer direction was recognized in almost all cases. The rate constants obtained in fluorescence are compared here with those of G_R .

a) benzene-carbon tetrachloride system

The results on G_R obtained in benzene-carbon tetrachloride system are unified by the scheme already proposed in section 8.1, and a constant is obtained on the assumption that A represents benzene and B represents carbon tetrachloride (3).

$$\frac{k_{AB}}{k_A + k_{\dot{A}}} \sim 1 \text{ l/mole.}$$

In comparing the scheme with that proposed in the section 7, it may be understood that $k_A + k_{\dot{A}}$ corresponds to k_1 and k_{AB} corresponds to k_3 . k_3/k_1 was obtained already in section 9.1 as the following;

$$k_3/k_1 = 190 \text{ l/mole.}$$

From these results, it may be understood that the constant referring to the energy transfer obtained in the fluorescence experiment is much larger than that obtained in G_R .

b) benzene-chloroform system

The results on G_R obtained by Bouby and Chapiro in the benzene-chloroform system (9) are adjusted by the scheme represented in section 8.4, in assuming that A represents benzene and B represents chloroform, while Magat et al assumes that A stands for chloroform (15). In this system the constant C may be obtained as follows ;

$$C = 0.04 .$$

Considering Eqs. (10) and (17), a constant may be obtained as follow ;

$$\frac{k_{AB}}{k_A + k_A} = 2 \text{ l/mole} .$$

In comparing the constant with that obtained in section 9.2, that is ;

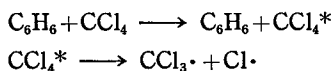
$$k_3/k_1 = 40 \text{ l/mole} ,$$

it may be concluded as it was in the benzene-carbon tetrachloride system that the constant referring to energy transfer obtained in the fluorescence experiment is much larger than that obtained in G_R .

10. Excitation State of Benzene Referring to the Radical Formation or Fluorescence

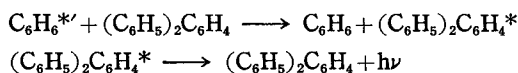
It is found that there is a wide discrepancy between these constants referring to radical formation and those referring to fluorescence. The very fact may suggest the distinction of the excitation state of benzene referring to the radical formation from that of fluorescence. An estimation will be made here to determine the excitation levels.

In the sensitization of carbon tetrachloride by benzene, the following primary processes may be considered.



The excitation level of carbon tetrachloride may be located near that of benzene because a high efficiency of energy transfer is expected. Thus, the excitation level of benzene may be estimated from the dissociation energy of C-Cl. As the energy is 69 Kcal/mole, the excitation level of benzene referred to the sensitization of carbon tetrachloride may be 3.0 ev or more.

On the other hand, the excitation level of benzene referred to the quenching by carbon tetrachloride may be estimated from the wave length of the p-terphenyl fluorescence.



As the wave length of the p-terphenyl fluorescence extends from 320 m μ to 420 m μ , the excitation level of benzene referred to the quenching by carbon tetrachloride may be 3.0-3.9 ev.

Thus it may be concluded that there is no clear distinction between these excitation levels of benzene. Further consideration of these points will be given later.

References

- 1) A. Chapiro; J. Chim. Phys., **47**, 747-763 (1950).
- 2) J. P. Manion and M. Burton; J. Phys. Chem., **56**, 560-569 (1952).
- 3) I. Sakurada, S. Okamura and H. Inagaki; Paper reported at the second international conference on peaceful uses of atomic energy in Geneva. 1958-Sept.
- 4) M. Furst and H. Kallmann; J. Chem Phys., **23** 607-612 (1955).
- 5) P. J. Berry, S. Lipsky and M. Burton; Trans. Faraday Soc., **52**, 311-320 (1956).
- 6) S. Okamura, T. Manabe and T. Motoyama; Isotopes and Radiation (Tokyo), **1**, 95-102 (1958).
- 7) H. Kallmann and M. Furst; Phys. Rev., **79**, 857-870 (1950).
- 8) M. Burton, P. J. Berry et S. Lipsky; J. Chim. Phys; **52**, 657-666 (1955).
- 9) L. Bouby et A. Chapiro; J. Chim. Phys., **52**, 645-656 (1955).
- 10) S. Okamura and T. Manabe; Chem. High Polymer, Japan. **15**, 688-694 (1958).
- 11) P. Pringsheim; "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, p. 111, 113, 117, (1949).
- 12) T. S. Nikitina and Kh. S. Bagdasaryan; Symposium on Radiation Chemistry, Academy of Sciences of the USSR, Moscow. (1955). in English translation, p. 153-164, Consultants Bureau, Inc., New York, copyright 1956.
- 13) M. Furst and H. Kallmann; Phys. Rev., **94**, 503-507 (1954).
- 14) G. Oster and Y. Nishijima; J. Am. Chem. Soc., **78**, 1581-1584 (1956).
- 15) S. Shida, H. Yamazaki, S. Arai, Y. Kawai, S. Arai and Z. Kuri; Symposium on Radiation Chemistry at Tokyo Institute of Technology, Tokyo, Japan. 1958-Nov.
- 16) M. Magat, L. Bouby, A. Chapiro et N. Gislou; Electrochem., **62**, 307-311 (1958).