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THE INTERMOLECULAR TRANSFER OF ENERGY DURING THE RADIOLYSIS OF SOLUTIONS OF ORGANIC SUBSTANCES

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CONTENTS

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1. TRANSFER OF ENERGY DURING THE RADIOLYSIS OF LIQUID MIXTURES

In the chemical action of ionising radiation on a substance the absorption of the energy of the radiation leads to the formation of ions and excited molecules capable of further chemical changes. The decomposition of, or any other change in the ions and excited molecules, taking place with the rupture or formation of a new chemical bond, is called the "primary" radiochemical process, and the resulting products (for example ions, free radicals, or molecules) are called primary radiolysis products. The primary radiolysis products may react with one another or with other molecules to give secondary products.

Unlike light, ionising radiation is not absorbed selectively by substances, since the absorbing power of the latter with respect to radiation is determined by their electron density, *i.e.* by the number of electrons in unit volume. It is therefore usually assumed that when ionising radiation acts on a multicomponent system, the radiation energy absorbed by each component is proportional to its electronic fraction in the mixture. The electronic fraction of a given component (ϵ_i) is defined by the expression

$$\varepsilon_i = \frac{n_i e_i}{\sum_i n_i e_i}, \qquad (1)$$

where n_i is the mole fraction of the i-th component in the mixture and e_i the number of electrons in the molecule of this component.

Accordingly, we can formulate an additivity (averaging) rule, for the radiolysis of multicomponent mixtures, according to which the yield of the primary products of the radiochemical change for each component of the mixture should be proportional to the electronic fraction of the component.

The additivity rule has been confirmed in the study of the radiolysis of binary mixtures of certain organic liquids (benzene–toluene[1], methyl methacrylate–ethyl acetate[2], methyl methacrylate–styrene[3], cyclopentane–cyclohexane[4], etc.).

Muccini and Schuler[4] studied the radiolysis of cyclopentane–cyclohexane mixtures and showed that in the presence of iodine, which reacts with the cyclopentyl and cyclohexyl radicals formed during the radiolysis, the yields of cyclopentyl iodide and cyclohexyl iodide are proportional to the electronic fractions of the corresponding hydrocarbons. At a high dose rate ($\sim 2 \times 10^5$ r sec^{-1}) the yields of cyclopentylcyclopentane, cyclohexylcyclopentane,

and cyclohexylcyclohexane correspond to the additivity rule if it is assumed that at this dose rate the recombination of the radicals formed initially is more rapid than their reaction with hydrocarbon molecules.

However, it has been shown that the additivity rule is not obeyed during the radiolysis of many binary mixtures. Thus Manion and Burton[1], who studied the dependence of the radiation yield† of hydrogen $G(H_2)$ on the composition of a cyclohexane–benzene mixture, found that $G(H_2)$ decreases sharply with increase in the proportion of benzene in the solution. If it is assumed that the hydrogen evolved during the radiolysis of a cyclohexane–benzene mixture is formed either by the primary decomposition of excited molecules, for example

$$C_6H_{12}^* \rightarrow C_6H_{10} + H_2, \qquad (2)$$

or by the reaction of the atomic hydrogen, formed during the primary decomposition, with hydrocarbon molecules, then the yield of hydrogen is equal to the yield of excited hydrocarbon molecules decomposing with the formation of H_2 and H. Thus according to the additivity rule it would be expected that $G(H_2)$ would decrease linearly with increase in the electronic fraction of the component most stable to radiation, *i.e.* benzene. The more rapid decrease in $G(H_2)$ than expected from the additive scheme was attributed by the authors to the fact that radiation energy, absorbed initially by the cyclohexane, is later transferred to the benzene, whose molecules have a higher probability of deactivation.

Generally speaking, the transfer of energy from a component less stable to radiation to a more stable component usually leads to an increase in the stability to radiation of the whole system, the so-called "sponge type protection", and the dependence of the yield of primary radiolysis products on the composition of the mixture should then be described by a curve of type *II* in Fig.1. Curve *III* corresponds to the transfer of energy from a component more stable to radiation to a less stable component A. Sometimes, in addition to sensitisation of the decomposition of A, a decrease in the decomposition yield of B takes place – "sacrificial protection"[1].

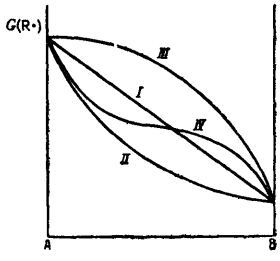


Fig.1. Typical curves for the dependence of the yield of primary radiolysis products on the composition of binary mixtures.

† The radiation yield is the number of molecules of substance formed, or decomposed for the absorption of 100 eV of energy by the starting material.

Since radiolysis yields ions and excited molecules, the transfer of energy may take place either by transfer of charge or by transfer of the energy of electronic excitation from the molecules of one component to the molecules of another according to the scheme

$$A^+ + B \rightarrow A + B^+,$$
$$A^* + B \rightarrow A + B^*. \qquad (3)$$

It is usually assumed that a necessary condition for the transfer of energy is that $E_A \geq E_B$, where E_A and E_B are the lowest electronic excitation levels of the molecules of the energy donor and acceptor. Transfer of charge can take place only when the corresponding relationship holds for the ionisation potentials.

Since the yield of hydrogen formed during the radiolysis of cyclohexane–benzene mixtures may be influenced by various secondary reactions, in particular by the reaction

$$H^\cdot + C_6H_6 \rightarrow C_6H_7^\cdot, \qquad (4)$$

the data obtained are to some extent ambiguous. To elucidate the role of secondary chemical processes in the decrease in the yield of hydrogen, Burton and Patrick[6,7] studied the radiolysis of cyclohexane–[D_6]-benzene mixtures. It was shown that even if allowance is made for reaction (4), the dependence of $G(H_2)$ on the composition of the cyclohexane–benzene mixture does not change significantly.

Freeman[8] determined the yields of cyclohexene, bicyclohexyl, cyclohexylcyclohexadiene, and other products of the radiolysis of the cyclohexane–benzene mixture in addition to the yield of hydrogen. The yields of all the products determined, with the exception of cyclohexylcyclohexadiene, decreased with increase in the electronic fraction of the benzene much more rapidly than expected from the linear law. In an examination of the possible reactions involved in the formation of these products from the primary radiolysis products Freeman also concluded that the excited molecules of cyclohexane may be deactivated by transfer of energy to the benzene. Some of the excited cyclohexane molecules, which decompose to radicals with the subsequent formation of cyclohexylcyclohexadiene, however, are apparently not deactivated by benzene, since in the case of this product a linear dependence on the composition of the mixture is observed. The author concludes that two types of excited cyclohexane molecule exist. This suggestion appears to be confirmed by the data of Gäumann[9], who found that, when the electronic fraction of benzene in the mixture is increased from 0.1 to 1, the yield of phenylcyclohexane decreases linearly from 0.2 to 0.

In other mixtures the additivity rule is again observed for some products and not for others: in a toluene–benzene mixture[1] the yield is linearly dependent on the composition for H_2 and CH_4, whereas the additivity rule is not observed for acetylene and ethylene. Manion and Burton, who studied this mixture, attributed this result to the fact that the first two substances are formed by the decomposition of excited molecules and the second two by the decomposition of ionised molecules. During the radiolysis transfer of charge apparently takes place from the benzene to the toluene, but there is no transfer of excitation energy.

Analogous results were obtained at the same time for the cyclohexane–benzene system. In propionaldehyde–[D_6]-benzene[6] mixtures, a linear relationship is observed for products such as CH_4 and C_2H_4 but not for C_2H_6.

Schuler *et al.*[10] determined the yields of primary free radicals from a cyclohexane–benzene mixture. Iodine was used as the radical acceptor. The yield of radicals was determined from the consumption of iodine, which reacts with radicals according to the scheme $R\cdot + I_2 \rightarrow RI + I\cdot$. They obtained for the free radicals a curve of type *II*, in accordance with Burton's data.

It is interesting to estimate the efficiency of the transfer of energy from cyclohexane to benzene. Let us consider the following kinetic scheme for the formation of radicals or other primary products during the radiolysis of a two-component mixture‡:

$$\begin{array}{ccc} A \underset{k_A}{\overset{k_{A^*}}{\rightleftarrows}} A^* \xrightarrow{k_{\dot{A}}} 2R\cdot & & \\ \Big\downarrow k_{AB} & & (5) \\ B \underset{k_B}{\overset{k_{B^*}}{\rightleftarrows}} B^* \xrightarrow{k_{\dot{B}}} 2R\cdot . & & \end{array}$$

From the steady-state condition for radiolysis, we can write

$$\begin{aligned} I k_{A^*} e_A &= k_A [A^*] + k_{\dot{A}} [A^*] + k_{AB} [A^*] [B], \\ I k_{B^*} e_B &= k_B [B^*] + k_{\dot{B}} [B^*] - k_{AB} [A^*] [B]. \end{aligned} \qquad (6)$$

The left-hand sides of Eqns.(6) give the rates of formation of excited molecules A* and B* (in mole litre^{-1} sec^{-1}) by the direct action of radiation at a dose rate of I eV litre^{-1} × × sec^{-1}. The rates of the elementary reactions in which these excited molecules take part are summed on the right-hand sides of the equations.

From this, we readily obtain

$$\frac{G_a(A)}{G_a(A) + G_a(B) - G(R\cdot)} = \frac{1}{1-\nu}\left(1 + \frac{k_A + k_{\dot{A}}}{k_{AB}} \frac{1}{[B]}\right), \qquad (7)$$

where $G_a(A) = \dfrac{100 k_{A^*} k_{\dot{A}} e_A N}{k_A + k_{\dot{A}}}$ and $G_a(B) = \dfrac{100 k_{\dot{B}^*} e_B N}{k_B + k_{\dot{B}}}$

are the radiation yields of radicals during the radiolytic decomposition of the components A and B, calculated from the additivity rule (N is Avogadro's number); $G(\dot{R})$ is the yield of radicals determined experimentally, and

$$\nu = \frac{k_{\dot{B}}}{k_{\dot{B}} + k_B} \Big/ \frac{k_{\dot{A}}}{k_{\dot{A}} + k_A}$$

is the ratio of the probability of decomposition of the excited molecules of B to the corresponding quantity for the excited molecules of A. The quantity defined by the left-hand side of Eqn.(7) should be linearly dependent on 1/[B].

Fig.2 shows the corresponding linear relationships, constructed on the basis of the yield of free radicals[10] and the yield of hydrogen[6] from a benzene–cyclohexane mixture. The ratios $k_{AB}/(k_{\dot{A}} + k_A)$ and ν, which can be determined graphically, characterise the efficiency of the transfer of energy from the excited molecules of cyclohexane to benzene and the relative probability of the decomposition of excited molecules of benzene compared with cyclohexane.

‡ A number of assumptions have been made to simplify the proposed scheme. In particular, it is assumed that the excited molecules formed by energy transfer from A to B are kinetically identical to those formed by the direct action of radiation. Analogous considerations are applicable to processes involving charge transfer.

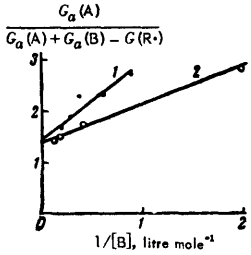


Fig.2. Variation of the radiochemical yields with the reciprocal of the benzene concentration in benzene–cyclohexane mixtures.

It follows from the data of Schuler *et al.* that $k_{AB}/(k_{\dot{A}} + k_A) = 1$ litre mole^{-1} and $\nu = 0.3$; from Burton and Patrick's data $(k_{AB}/(k_{\dot{A}} + k_A) = 2$ litre mole^{-1} and $\nu = 0.3$. Freeman[8] obtained $k_{AB}/(k_{\dot{A}} + k_A) = 0.78$. It is important to note that part of the hydrogen evolved during the radiolysis of cyclohexane is formed independently of the radical stage, for example by reaction (2)[11,12]. On the other hand, the decomposition of excited molecules at the C–C bond to form radicals does not as a rule lead to the subsequent formation of hydrogen. The fact that the values of ν and $k_{AB}/(k_{\dot{A}} + k_A)$ determined by two different methods (from the yield of radicals and from the yield of H_2) are similar probably indicates that cyclohexane molecules in the same excited state can decompose either with the formation of radicals or by a non-radical method.

Despite the fact that the cyclohexane–benzene mixture has been studied in most detail and is the "classical" example of a system in which sponge-type protection takes place, it is not even clear if the additivity rule applies to this system. Recently Lamborn and Swallow[13] suggested that the absorption of the energy of the fast electrons and δ electrons formed as a result of the Compton scattering of γ-rays depends on the structure of the hydrocarbons. They consider that the excitation cross-section of the π electrons of the benzene is about 10 times greater than that of the δ electrons in benzene and cyclohexane. Thus the protective action of benzene is attributed to the greater probability of primary absorption of radiation energy by the benzene molecules.

Determination of the radiation yield of the primary free radicals appears to be one of the most convenient and unambiguous methods of studying energy transfer during the radiolysis of liquid mixtures. The yields of radicals during the radiolysis of liquids are usually determined from the consumption of solutes which react with free radicals[14].

Free-radical acceptors which have been used include iodine, αα-diphenyl-β-picrylhydrazine (DPPH)[15,16], ferric chloride[17,18], benzoquinone[18,19], and other substances[20,21] which react effectively with free radicals. The concentration of these acceptors should be high enough to ensure that all the radicals formed during the radiolysis of the liquid are able to react with the acceptor before recombination with one another. This concentration should remain fairly low (usually less than 0.1 M), however, so that the direct action of radiation on the acceptor can be neglected[16].

This method (with DPPH as the radical acceptor) has been used to study a number of binary mixtures[2,22,23], particularly systems in which one or both components are chlorinated hydrocarbons[22,23]. The yields of primary free radicals of all the mixtures studied, containing halogenated hydrocarbons, showed deviation from the additive values (Table 1)§.

As a rule, the addition of even small quantities of alkyl chlorides to hydrocarbons and esters leads to a considerable positive deviation from the additivity rule (curve of type *III* in Fig. 1), but in some cases, at higher alkyl chloride concentrations, the $G(R^{\cdot})$–composition curves show an inflection (curve *IV* in Fig. 1). Table 1 shows that this S-shaped curve is characteristic of mixtures of alkyl halides with aromatic hydrocarbons. It may be that when the alkyl chloride content of the mixture is high, processes involving energy transfer from the alkyl chloride to the aromatic hydrocarbon predominate and that at low alkyl chloride concentrations the energy transfer takes place in the opposite direction. An interesting features is that chlorobenzene shows a protective action with respect to chloroform (curve of type *II*) but gives a relationship of type *III* in mixtures with benzene.

The efficiency of the energy transfer $k_{AB}/(k_A + k_A)$ during the radiolysis of mixtures containing alkyl halides, calculated from formula (7), lies in the range 1–5 litre × × mole^{-1}.

TABLE 1. Nature of the dependence of the yield of primary radiolysis products on the composition for different binary mixtures.

Linear relation	Positive deviation from linear relation	Negative deviation from linear relation	S-shaped curve
Cyclohexene – benzene		cyclohexane – cyclohexene [1,26]	
Benzene – toluene [1]	methyl acetate – benzene [22]	cyclohexane – benzene [1,6-8]	CCl_4 – benzene [24,25]
Propionaldehyde – [D_6] benzene [6]	vinyl acetate – benzene [2]		
Methyl methacrylate – ethyl acetate [2]	CCl_4 – methyl acrylate [24,25]	$CHCl_3$ – chlorobenzene [23]	CCl_4 – styrene [2]
Methyl methacrylate – styrene [3]	CCl_4 – methyl methacrylate [2]	methyl methacrylate – benzene [29]	$CHCl_3$ – benzene [22]
	$CHCl_3$ – methyl acetate [22]	octane – benzene [27] $CHCl_3$ – CCl_4 [28]	
	CCl_4 – vinyl acetate [26]		
	chlorobenzene – benzene [23]		

§ Analysis of the products of the radiolysis of dilute solutions of DPPH in CCl_4 and $CHCl_3$ by Chapiro *et al.*[29] showed that these products are extremely varied and of complex composition. DPPH apparently reacts not only with the primary products but also with secondary intermediate products. Nevertheless, the authors consider that the consumption of DPPH during radiolysis gives unambiguous information on the yield of free radicals. Dainton *et al.*[30], on the basis of a study of the kinetics of the decoloration of solutions of DPPH in CCl_4 and $CHCl_3$ under the influence of γ-rays, suggested that DPPH reacts not only with free radicals but also with excited molecules.

When one of the components of the mixture is a monomer capable of undergoing radical polymerisation, the yield of radicals during radiolysis of the mixture can be determined from the kinetics of the polymerisation of the monomer[31]. This method has been used by Chapiro[32], and later by Nikitina and Bagdasar'yan[33], who studied the radiolysis of CCl_4–styrene and CCl_4–methyl methacrylate mixtures. The relationships for the yield of radicals initiating polymerisation are described by an S-shaped curve for the first mixture and by a curve of type *III* for the second. (The yield of radicals from pure CCl_4 or at very low concentrations of monomer cannot be determined by the polymerisation method.) Nikitina and Bagdasar'yan were the first to explain the sensitising action of CCl_4 on the basis of a theory of redistribution of the initially absorbed energy between the components of the mixture and they put forward a phenomenological theory to describe quantitatively the experimental data[2,23]. They suggest that the rate of energy transfer is much greater than the rates of deactivation and decomposition of the excited molecules, from which

$$\frac{[B^*]}{[A^*]} = \alpha \frac{[B]}{[A]}, \qquad (8)$$

where α is a coefficient characterising the redistribution of the absorbed energy.

If $\alpha > 1$, then for equal concentrations of A and B the energy is transferred from A to B; when $\alpha < 1$ energy transfer occurs in the opposite direction.

Using Eqn. (8), and remembering that the sum $[A^*] + [B^*]$ is proportional to the dose rate (I_{abs}) and that the rate of initiation is

$$V_R = [A^*]\frac{k_{\dot{A}}}{k_A + k_{\dot{A}}} + [B^*]\frac{k_{\dot{B}}}{k_B + k_{\dot{B}}}, \qquad (9)$$

we obtain

$$G(R\cdot) = \frac{kV_R}{I_{abs}} = k\frac{k_{\dot{A}}}{k_A + k_{\dot{A}}}\frac{1 + \alpha\,[B]/[A]\,\nu}{1 + \alpha\,[B]/[A]}. \qquad (10)$$

Table 2 gives the values of α and ν for the mixtures studied by Nikitina and Bagdasar'yan[2]. Table 3 gives the values of $G(R\cdot)$ calculated by Nikitina and Bagdasar'yan on the assumption that $\nu = G_B(R\cdot)/G_A(R\cdot)$ and that $G(R\cdot)$ for benzene is equal to 0.7. Table 3 also gives for comparison the values of $G(R\cdot)$ for the same liquids, determined by means of DPPH. The two methods give similar results.

Of particular interest is the idea of using protective action of the sponge type to retard the radiolytic decomposition of substances which can be used as organic heat-carriers and retarding agents in nuclear reactors. Colichman and Fish[35] studied the radiolysis of terphenyls at 400°–450°. The stability of the isomers to radiation

TABLE 2. Values of α and ν for some two-component systems (A = monomer).

System	α	ν
Methyl methacrylate – ethyl acetate	1.0	1.0
Methyl methacrylate – benzene	1.5	9.1
Methyl methacrylate – CCl_4	45.0	0.42
Styrene – CCl_4	30.0	0.053

TABLE 3. Yields of radicals for some liquids.

Substance	From polymerisation[2]	By means of DPPH
Benzene	0.7	0.7[34]
Styrene	0.8	0.6[3]
Methyl methacrylate	6.3	5; 6.7[3,24]
Ethyl acetate	6.3	7[34]
Carbon tetrachloride	15.4	19; 18; 3[24,25]

was compared from the yield of polymers. *p*-Terphenyl had the highest stability. The decrease in the yield of polymer by 30% when 4.5% of *p*-terphenyl was added to *m*-terphenyl was attributed by the authors to the redistribution of the absorbed energy between the components of the mixture.

There is no direct experimental indication of the mechanism of the transfer of energy from one component to another. According to Burton *et al.*[36-38], the transfer of charge from one component to another in mixtures of liquid hydrocarbons is unlikely, since the probability of formation of negative ions as a result of the attachment of a thermal electron to a neutral molecule is small in this case, and the neutralisation of the initially formed positive ions by thermal electrons takes place in $< 10^{-13}$ sec. It may be assumed that, in mixtures of the benzene–cyclohexane type, the energy of electronic excitation is transferred from cyclohexane to benzene. Freeman[39] has recently cast doubts on this suggestion.

In mixtures containing halogenated hydrocarbons the capture of thermal electrons by the molecules of the latter is possible, due to the high electron affinity of these substances. The resulting negative ions may decompose, leading to an increase in the yield of radicals in these mixtures, for example

$$C_nH_{2n+2} \rightsquigarrow C_nH_{2n+2}^{+} + e\,,$$
$$e + RCl \rightarrow RCl^{-} \rightarrow R + Cl^{-}. \qquad (11)$$

This process involves essentially the transfer of charge from the hydrocarbons to the halogen derivatives. Since the latter are less stable to radiolysis, the total yield of radicals in such mixtures is higher than expected from the additivity rule.

The S-shaped curves obtained for mixtures of alkyl halides and aromatic hydrocarbons can be explained if it is assumed that the excited molecules of the alkyl halides can transfer electronic excitation energy to the aromatic hydrocarbons and at the same time act as electron acceptors for the transfer of charge from the aromatic hydrocarbons. In this case, at low concentrations of the aromatic hydrocarbons, the processes of excitation-energy transfer predominate and the total yield of radicals is smaller than the averaged value. On the other hand, the addition of alkyl halides to aromatic hydrocarbons leads to a sharp increase in the yield of radicals, as a result of the transfer of charge to the molecules of the additive, which are less stable to radiation.

This scheme cannot, however, explain the fact that the addition of CCl_4 to styrene leads to a sharp increase in the rate of initiation of polymerisation, not only under the influence of ionising radiation, but also under the influence of ultra-violet light, which is absorbed chiefly by the monomer[35]. No ionisation takes place during photo-initiation, so that the transfer of charge according to scheme (11) should not take place.

Chapiro *et al.*[23] attribute the S-shaped curves to the fact that the processes of energy transfer involve excited molecules of the halogen derivatives in two different electronic levels, for example singlet and triplet. Here the energy transfer takes place in the direction: alkyl halide (singlet level) → aromatic hydrocarbon → alkyl halide (triplet level).

A more general explanation, covering the behaviour of mixtures containing halogenated hydrocarbons under the influence of ionising radiation and light, is the suggestion that intermediate complexes of excited molecules (which are electron donors) with the molecules of acceptors are formed, with subsequent decomposition to positive and negative ions or radicals:

$$A^{*} + B \rightarrow (A^{-}B^{+})^{*} \rightarrow A^{-} + B^{+}. \qquad (12)$$

This mechanism of charge transfer was considered by Weiss[41,42] to explain the quenching of the fluorescence of dyes by oxygen, Fe^{3+}, I^{-}, Br^{-}, etc. The quenching of fluorescence by these substances is attributed to redox reactions of type (12), leading to the non-radiative deactivation of the excited molecules A*. Reaction (12) can take place if

$$E_A + h\nu \geqslant E_B + X, \qquad (13)$$

where E_A and E_B represent the electron affinities of the molecules of A and B, $h\nu$ the energy of electronic excitation of A, and X the change in the potential energy of the components in the process of electron transfer, *i.e.* the rate of energy transfer is higher, the greater the electron affinity of the luminescent material and the lower that of the quenching agent. It is obvious that in the case of the reaction

$$A^{*} + B \rightarrow (A^{+}B^{-}) \rightarrow A^{+} + B^{-}, \qquad (14)$$

E_A and E_B should appear in Eqn.(13) with opposite signs.

An even more general explanation of the deviation of binary mixtures from the additivity rule was given by Bagdasar'yan[43], who considers that it is always necessary to make allowance for the reaction of the excited molecules with the surrounding molecules of liquid, irrespective of whether the latter are individual liquids or mixtures. Formally this interaction can be regarded as the formation of binary complexes as a result of exchange and donor–acceptor forces. In a pure liquid complexes of the type (AA)* are formed, and in mixtures also complexes (AB)*. If the energy of the excited states of A and B differ considerably, the exchange interaction is small. The formation of a complex can be expected only if the conditions favour donor–acceptor bonds $(A^{-}B^{+})^{*}$ or $(A^{+}B^{-})^{*}$ (see for example Eqn.(13)].

Thus the radiolysis of a two-component mixture involves formation, deactivation, and decomposition of excited complexes to radiolysis products:

$$A^{*} + A \xrightarrow{k_{AA}} (AA)^{*} \nearrow^{A+A}_{\searrow 2R\cdot \text{ (or } 2R\cdot + A),}$$
$$A^{*} + B \xrightarrow{k_{AB}} (AB)^{*} \nearrow^{A+B}_{\searrow 2R \text{ (or } 2R\cdot + A, \text{ or } 2R + B).} \qquad (15)$$

Analogous processes take place during the interaction of B* with A and with B. If the probability of decomposition of (AB)* with the formation of radicals or other products is greater than that for (AA)*, the addition of B to A leads to

a positive deviation from additivity, and if the probability is smaller it leads to a negative deviation. From this viewpoint, when the additivity rule is observed, we have a particular case, where $k_{AB}/k_{AA} = 0$ and $k_{BA}/k_{BB} = 0$, *i.e.* the probabilities of decomposition of the complexes (AB)*, (AA)*, and (BA)* and (BB)* are respectively equal. The scheme suggested by Bagdasar'yan explains from a single viewpoint the different cases where the additivity rule is not observed during the radiolysis of binary mixtures.

The lifetime (τ) of the excited molecules of the energy donor can be estimated from Smolukhovskii's formula for calculating the number of collisions (Z) between these molecules and acceptor molecules[44]

$$Z = 4\pi DRN, \qquad (16)$$

where D is the diffusion coefficient, R the radius of interaction, and N Avogadro's number.

Assuming that the probability of energy transfer when the molecules approach to the interaction distances is equal to 1, *i.e.* $k_{AB} = 4\pi DRN$, and making allowance for the fact that $1/(k_A^* + k_A) = \tau$, we have

$$\frac{k_{AB}}{k_A^* + k_A} = 4\pi DRN\tau. \qquad (17)$$

Since the transfer of energy by the above mechanism requires the overlap of the electronic orbitals of the interacting molecules, *i.e.* it requires their approach to a distance not exceeding the kinetic radii of the molecules, $R = 2-5$ Å. For liquids such as cyclohexane, benzene, and CCl_4, $D \simeq 10^{-5}$ cm^2 sec^{-1}. Since $k_{AB}/(k_A^* + k_A) = 1$, we obtain from Eqn.(17) $\tau = 5 \times 10^{-10}$ sec.

2. TRANSFER OF ENERGY DURING THE RADIOLYSIS OF DILUTE SOLUTIONS

a. Liquid phase. In the radiolysis of some solutions containing small quantities of acceptors (< 0.1 M), the deviation of the yields of radiolysis products from the values corresponding to the additivity rule are often found to be greater than those at high acceptor concentrations.

Krongauz and Bagdasar'yan[45] found that in the radiolysis of solutions of benzoyl peroxide in benzene the yield for the decomposition of benzoyl peroxide at concentrations < 0.01 M is greater by at least one and a half powers of ten than the yield corresponding to the direct action of radiation on the solute.

Study of the radiolysis of such solutions in the presence of DPPH showed that the high decomposition yield is not related either to reaction with the radicals formed from the solvent or to chain decomposition of the peroxide. It was suggested that decomposition of the peroxide in dilute solutions is due to the transfer of excitation energy from the solvent to the solute.

Later, studies were made of the radiolysis of solutions of a number of other substances, which decompose readily to form radicals (peroxides, azo-compounds, disulphides), in different solvents (toluene, cyclohexane, ethyl acetate, styrene, etc.). It was shown that effective sensitisation of the decomposition of the solutes takes place only when both the solvent and the solute are aromatic compounds. The yield for the decomposition of the acceptors at first increases sharply with concentration and then, from a concentration ~ 0.01 M, the yield increases less rapidly and follows a linear relation (Fig.3).

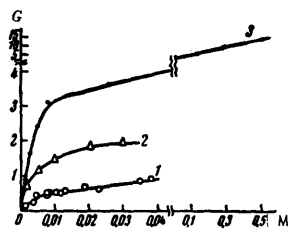


Fig. 3. Variation of the radiochemical yield for the decomposition of solutes with their concentration in benzene:
1) $C_6H_5-N=N-C(C_6H_5)_3$;
2) $C_6H_5-S-S-C_6H_5$;
3) $C_6H_5-\overset{\overset{O}{\|}}{C}-O-O-\overset{\overset{O}{\|}}{C}-C_6H_5$.

In accordance with reaction scheme (5), we can obtain, for the yield for the decomposition of the solute $G(-B)$, the relation

$$G(-B) = \frac{100Ne_A k_A^* k_{AB} k_B [B]}{(k_A^* + k_A + k_{AB}[B])(k_B + k_B^*)} + \frac{100Ne_B k_B^* k_B^*}{k_B^* + k_B}, \qquad (18)$$

where N is Avogadro's number.

At low concentrations the direct action of radiation on the solute is small and the second term in Eqn.(18) can be neglected. $1/G(-B)$ should then be linearly dependent on $1/[B]$ and for the benzene solutions studied, at concentrations < 0.01 M, a linear relation does hold. This makes it possible to determine the ratio $k_{AB}/(k_A^* + k_A)$, characterising the efficiency of the transfer of energy from the solvent to the solute and the ratio $k_A^* k_B^*/(k_B^* + k_B)$, characterising the probability of decomposition of the resulting excited acceptor molecules.

The corresponding values for dilute solutions of some substances in benzene are compared in Table 4 which shows that the efficiency of the transfer of energy in dilute solutions of these substances is greater by about two powers of ten than that in the binary systems described in the preceding section. As already mentioned, this efficiency is observed only when both components are aromatic. The difference in the yields for the decomposition of solutions of the substances listed in Table 4 is due chiefly to the difference in the probabilities of decomposition of the excited molecules. An interesting feature is that the probability of decomposition of the excited molecules of these compounds is not directly related to the dissociation energy, which is approximately the same for all of them (~ 30 kcal mole^{-1}).

TABLE 4.

Acceptor	$\frac{k_{AB}}{k_A^* + k_A}$, litre mole^{-1}	$\frac{100\,k_A^* k_B^* N}{k_B^* + k_B}$
Benzoyl peroxide	380	3
Phenylazotriphenylmethane	430	0.35
Diphenyl disulphide	370	1.4

It may be suggested that the slower increase in $G(-B)$ at acceptor concentrations > 0.01 M arises because all the excited benzene molecules are able to transfer energy to the acceptor molecules before their deactivation and that the subsequent increase in $G(-B)$ is due to the direct action of radiation. A more detailed examination[34] shows, however, that at higher concentrations transfer of energy from another type of excited molecule is also possible and this takes place with a much lower efficiency.

Let us try to estimate the interaction distance for the interaction of excited molecules of the solvent with acceptor molecules R assuming that at concentrations 0.01 M all the excited molecules are able to transfer energy to the acceptor. Inside the sphere of radius R described around each excited solvent molecule taking part in the effective transfer of energy there is at least one molecule of solute. Since the average distance between the solute molecules at a concentration 0.01 M is

$$\left(\frac{3.2\times10^{-21}}{0.01}\right)^{1/3} \simeq 70\times10^{-8} \text{ cm},$$

we have $R \simeq 35$ Å. The value of R obtained in this way shows that the energy transfer takes place at a distance about 10 times greater than the kinetic radii of the molecules. This "long-range action" in the non-radiative transfer of energy from some molecules to others was first detected in a study of luminescence in multicomponent systems. As early as 1922, Frank and Cario[49] showed that the irradiation of a mixture of mercury and thallium vapour by light corresponding to the resonance line of mercury leads to the emission of fluorescent light whose spectrum contains, in addition to the mercury lines, lines characteristic of thallium. The authors showed that this phenomenon cannot be attributed to the trivial reabsorption, by the thallium atoms, of light emitted by the mercury; therefore this sensitisation of the luminescence was interpreted as the result of the non-radiative transfer of the energy of electronic excitation from the mercury atoms to the thallium atoms.

Sensitised fluorescence was later detected in solutions of a number of organic dyes[50,51].

Studies of the concentration dependence of the yield or the intensity of fluorescence, together with fluorometric measurements of the lifetime of the excited molecules, have indicated that in the sensitisation of the fluorescence the transfer of energy takes place at a distance considerably greater than the effective kinetic radii of the molecules. To explain the long-range action in the transfer of excitation energy in solutions, the theory of the so-called resonance transfer of excitation energy has been developed[52]. Förster[52], considering the resonance transfer of energy as the result of the dipole–dipole interaction of excited and unexcited molecules, obtained for the probability of energy transfer (n) from donor to acceptor the following dependence on the distance between the molecules (R):

$$n = \frac{1}{\tau}\left(\frac{R_0}{R}\right)^6, \qquad (19)$$

where τ is the average life time of the excited molecules of the energy donor and R_0 the critical distance at which the probability of energy transfer is equal to the probability of spontaneous deactivation of the excited molecules of the donor. The theory makes it possible to calculate R_0, which is greater, the greater the overlap of the fluorescence spectrum of the energy donor and the absorption spectrum of the energy acceptor. For solutions, R_0 is usually 20–80 Å.

The luminescence of liquid organic scintillators under the action of ionising radiation is evidently also related to the resonance transfer of energy[53]. These scintillators consist of dilute solutions of aromatic compounds with condensed nuclei (anthracene, p-terphenyl, 2,5-diphenyloxazole, etc.) in organic solvents[54]. The applied ionising radiation is absorbed almost completely by the solvent, which transfers the energy to the molecules of the solute, which is an efficient phosphor. Furst and Kallmann[55] determined the dependence of the intensity of fluorescence of various liquid scintillators on the concentration of the solutions and estimated the efficiency of the energy transfer from the solvent to the phosphor (Table 5).

Table 5 shows that the efficiency of the energy transfer, determined by the fluorescence method, is of the same order of magnitude as the efficiency of the transfer in the radiolysis of the dilute solutions considered above (Table 4). It may be that resonance transfer of energy also takes place in the sensitised radiolysis of dilute solutions.

As a rule, the highest luminescence yield is given by scintillators in aromatic solvents[56]. This is apparently related to the overlap of the spectra of the components being a maximum, which may also explain the fact that effective transfer of energy in radiolytic reactions is observed only when both components of the solution are aromatic.

To confirm the suggestion that the mechanisms of the transfer of energy in the case of fluorescence excited by ionising radiation and in the sensitised radiolysis of dilute solutions are similar, a study was made of the radiolysis of three-component benzene–benzoyl chloride–phosphor solutions[57]. It was shown that small quantities of added organic phosphors (anthracene and phenanthrene) protect the benzoyl peroxide from decomposition. This appears to indicate that the benzoyl peroxide and the phosphor compete for the same excited solvent molecules in the process of energy transfer. Taking this into account, let us try to estimate by a somewhat different method the distance for the transfer of energy in the radiolysis of solutions.

Let us assume that the transfer of energy from an excited solvent molecule to a molecule of solute requires that they approach to a certain distance (irrespective of whether the energy transfer takes place as a result of the collision of molecules or at much greater distances). This suggestion was put forward by Galanin *et al.*[58], who showed that in ordinary aromatic solvents (benzene, toluene, xylene, etc.) the diffusion displacement during the lifetime of the excited molecules of the solvent may be commensurate with and even greater than the critical distance of resonance interaction R_0. As a result, the

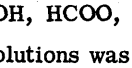
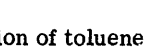
TABLE 5. Values of $k_{AB}/(k_A + k_A)$ litre mole^{-1} for liquid solutions of luminescent materials.

Luminescent material	Solvents				
	benzene	toluene	xylene	cumene	p-dioxane
Anthracene	425	318	336	254	89
Anthranilic acid	260	228	182	125	76
Diphenylbutadiene	550	443	330	166	102
Phenyl-α-naphthylamine	550	447	365	115	54
p-Terphenyl	380	280	384	190	41

transfer takes place with a much greater probability than would be expected on the assumption that the molecules are immobile during the transfer. Calculating the probability of energy transfer as the probability of the "collisions" whose effective cross-section is determined by the distance for resonance transfer, Galanin obtained satisfactory agreement with experiment. The suggestion that approach by diffusion to the distance of "long-range action" is necessary also agrees with the hypothesis of Burton *et al.*[59], of the excited molecules of solvent forming characteristic "aggregates" with the surrounding solvent molecules. A characteristic feature of these aggregates is that the collision of the molecules of an acceptor with any of the molecules in the aggregate is equivalent to collision with the initially-excited molecule. It is therefore possible to use Eqn.(17) to estimate the interaction distance.

The value of τ for excited benzene molecules was estimated by Burton and Dreeskamp[60], who studied the concentration dependence of the time required for quenching of the fluorescence, initiated by X-rays, of *p*-terphenyl dissolved in benzene. By extrapolating the observed values of the time required for quenching to zero concentration, these authors found for the characteristic lifetime of the excited benzene molecules taking part in the energy transfer the value $\tau = 2 \times 10^{-8}$ sec. A similar value of τ was obtained by Knau[61] in a study of the photo- and radio-luminescence of solutions of anthracene in benzene.

Assuming $k_{AB}/k'_{\dot{A}} + k_A = 380$ (Table 4), we obtain from Eqn.(17) $R \simeq 30$ Å, which agrees with the value estimated above by a different method.

The sensitised radiolytic decomposition of substances of the type X–CH_2–, where X is Cl, OH, HCOO, CH_3COO, H, –CH_2, in cyclohexane solutions was studied by McLachlan[62]. With the exception of toluene and dibenzyl, all the above substances decompose in 0.1 M solutions with a radiochemical yield, $G(C_6H_5CH_2X) \simeq 4$, which is much greater than the maximum possible yield due to the direct action of radiation. Taking into account the fact that $G(-C_6H_5CH_2Cl)$ is independent of the concentration of the solute (in the range 0.05–0.5 M) and dose rate, the author concludes that the radiolytic decomposition of this compound does not take place by a chain mechanism. Radiolysis of the solutions in the presence of radical acceptors such as cyclohexene and iodine decreases considerably the yield for the decomposition of solutes but does not suppress it completely. From this it is concluded that the high yield for the decomposition of $C_6H_5CH_2Cl$ cannot be due entirely to reaction with radicals formed from the solvent but is to a considerable extent related to the transfer of energy from the solvent. The fact that $G(-C_6H_5CH_2Cl)$ is independent of the concentration appears to indicate that at concentrations > 0.05 M, the reaction of a solute with the species transferring the energy reaches saturation. The absence of data on the radiolysis of more dilute solutions where saturation is not reached makes it impossible to determine the efficiency of the energy transfer.

Schuler and Burton *et al.*[63–65] showed that the addition of small quantities of I_2, CH_3I, C_2H_5I, CH_3Br, bromobenzene and cyclohexylbenzene (10^{-2}–10^{-3} M) decreases sharply the yield of hydrogen in the radiolysis of cyclohexane. In the radiolysis of solutions of iodine in cyclohexane the quantity of HI formed is much less than the corresponding decrease in $G(H_2)$. They therefore consider that the protective action of iodine and alkyl halides is not related to the capture by the solutes, of the H· atoms formed in the radiolysis of hexane, but is due to the deactivation of the excited or ionised cyclohexane molecules by the molecules of the additive, *i.e.* by the transfer of energy from the solvent to the solutes.

If the decrease in the yield of hydrogen is related to the deactivation of the excited cyclohexane molecules by the additive, we have, according to scheme (5),

$$G(H_2) = G(-A) = \frac{100 N k_{\dot{A}} k_{A^*} e_A}{k_A + k_{\dot{A}} + k_{AB}[B]}. \qquad (20)$$

Using the data of Burton *et al.*[65] and Eqn.(20), it is possible to estimate the efficiency of the postulated energy transfer in dilute solutions of iodine and bromobenzene in cyclohexane, the values found being 70–100 litre $mole^{-1}$. This high efficiency of transfer of excitation energy is characteristic of solutions of "absorbing" acceptors, *i.e.* substances whose absorption spectra overlap the fluorescence spectrum of the solvent. In this case there is no such overlap of spectra. Burton *et al.* suggest that the transfer of energy takes place as a result of the capture, by the molecules of the additive, of the thermal electrons formed in the radiolysis.

Kolbanovskii *et al.*[66,67] consider that the action of small amounts of both absorbing and non-absorbing acceptors is based on the same mechanism. Their quantitative examination of the interaction of excited molecules of an energy donor with acceptor molecules shows that at low solution concentrations the protective action is proportional to the concentration of additive to the power 2/3.

It should be noted that these studies give no unambiguous proof that the decrease in the yield of hydrogen in the presence of iodine is related to the transfer of energy. Moreover, Dyne and Jenkinson's data[11] indicate that the decrease in $G(H_2)$ in the radiolysis of cyclohexane in the presence of iodine is due to the reaction of the iodine with atomic hydrogen. These authors measured the yield of D_2, HD, and H_2 from $C_6H_{12} + C_6D_{12}$ mixtures. Extrapolation of the dependence of $G(D_2)$ on the C_6D_{12} concentration in the mixture to zero C_6D_{12} concentration gives the yield of "molecular" D_2 formed, apparently, according to the scheme $C_6D_{12}^* \rightarrow C_6D_{10} + D_2$. The addition of I_2 decreases the total yield of hydrogen (D_2 + HD + H_2) but has almost no effect on the yield of molecular D_2. This is evidently because iodine is only a "trap" for radicals, particularly H· atoms, but is not an energy acceptor. That the yield of HI, measured by Schuler and Burton *et al.*[63,65], is much less than expected from the decrease in $G(H_2)$, is possibly due to secondary reactions such as R· + HI → RH + I.

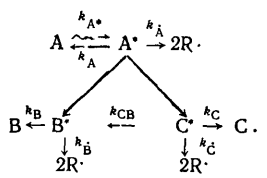
Of particular interest are the features of the redistribution of the initially absorbed energy in three-component systems containing two energy acceptors.

As already stated, the addition of small quantities of phenanthrene and anthracene to solutions of benzoyl peroxide in benzene decreases the yield for the decomposition of the peroxide. A similar effect is shown by other energy acceptors such as benzoic anhydride, aromatic azo-compounds, and disulphides[47,48]. The protective action of the second energy acceptor is apparently due to competition between the acceptor and the peroxide in the process of energy transfer from the solvent.

Increasing the concentration of the second acceptor in the solution sometimes enables the decomposition of the

peroxide to be almost completely suppressed, but in a number of cases (Fig.4) the yield for the decomposition of benzoyl peroxide reaches a limiting value and does not decrease further with increase in the concentration of the second acceptor[48,57]. In these solutions transfer of energy apparently also takes place from the second acceptor to the peroxide, and at sufficiently high concentrations of the second acceptor this compensates for its protective action.

For processes taking place in the radiolysis of three-component systems, we may then write the following kinetic scheme¶:



(21)

The steady-state equations have the form

$$I k_{A^\bullet} = k_A [A^\bullet] + k_{\dot{A}} [A^\bullet] + k_{AB} [A^\bullet][B] + k_{AC} [A^\bullet][C],$$
$$k_{AB} [A^\bullet][B] = k_B [B^\bullet] + k_{\dot{B}} [B^\bullet] - k_{CB} [C^\bullet][B], \quad (22)$$
$$k_{AC} [A^\bullet][C] = k_C [C^\bullet] + k_C [C^\bullet] + k_{CB} [C^\bullet][B],$$

from which

$$\frac{G(-B)}{G^0(-B)} = \frac{1 + k_{AC}/k_{AB}[C]/[B]\ \alpha}{k_{AC}/k_{AB} \cdot [C]/[B]} \quad (23)$$
$$\frac{1 + k_{\dot{A}} + k_A \cdot k_{AB}}{1/[B]+1},$$

where $G^0(-B)$ and $G(-B)$ are the yields for the decomposition of component B in the absence and in the presence of the component C, and $\alpha = \frac{k_{CB}[B]}{k_C + k_C^\bullet + k_{CB}[B]}$. When [B] = const, Eqn.(23) can be rearranged to a form convenient for the determination of α and $k_{AC}/k_{\dot{A}} + k_A$, if $k_{AB}k_{\dot{A}} + k_A$ is known[43,48].

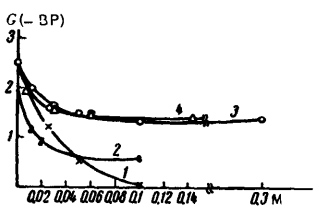
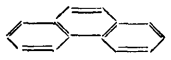


Fig. 4. Variation of the radiochemical yield for the decomposition of benzoyl peroxide with the concentration of protective additives at a constant concentration of the peroxide in benzene of ~ 0.05 M:
1) $C_6H_5-HN-N=N-C_6H_5$;
2) $C_6H_5-\overset{O}{\overset{\|}{C}}-S-S-\overset{O}{\overset{\|}{C}}-C_6H_5$;
3) $C_6H_5-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-C_6H_5$;
4) .

¶ For sufficiently dilute solutions, the direct action of radiation on the solutes can be neglected; $\epsilon_A \sim 1$.

When the direct exchange of energy between two acceptors does not take place, for example in the benzene–benzoyl peroxide–diazoaminobenzene system, *i.e.* when k_{CB} and α are zero, Eqn.(23) acquires the simpler form

$$\frac{G^0(-B)}{G(-B)} - 1 = \frac{(k_{AC}/k_{\dot{A}} + k_A)[C]}{1 + (k_{AB}/k_{\dot{A}} + k_A)[B]}. \quad (24)$$

The values of the efficiency of the transfer of energy from benzene to dibenzyl disulphide and phenylazotriphenylmethane, determined from their protective action [Eqns.(23) and (24)] and from the sensitised decomposition of these acceptors in solutions [Eqn.(18)]† show satisfactory agreement.

Thus in those cases where the energy acceptor does not fluoresce and does not undergo chemical change under the influence of the energy which it accepts, its efficiency can be estimated from its protective action in three-component solutions.

b. Solid phase. There are few radiochemical papers devoted to the intermolecular transfer of energy in glasses and polymers, although the analogous processes for the luminescence of scintillation plastics and glasses have been studied in considerable detail[68].

Chilton and Porter[69] studied the radiolysis of dilute solutions of triphenylmethane in organic glasses, for example a frozen mixture of methylcyclohexane and isopentane, at -196°. The yield of triphenylmethyl radicals was much higher than the value corresponding to the direct action of radiation. The efficiency of the energy transfer, determined from the dependence of the yield of radicals on the triphenylmethane concentration, was 830 litre mole^{-1}. The high efficiency of the energy transfer in glasses, observed by Chilton and Porter and by other workers[70,71], who studied sensitised fluorescence in polymers and glasses, does not agree with the theory of the ordinary resonance transfer of energy. Calculation shows[72] that the energy transfer takes place at distances much greater than the usual distances for resonance interaction between molecules (the probability of resonance transfer decreases sharply with distance and is inversely proportional to R^6). Since in glasses the approach of the excited donor molecules to the acceptor molecules by diffusion is excluded, it must be assumed that the energy migrates either in the form of excitons or in some other form not associated with spatial displacement of the molecules (for example the migration of holes or the resonance transfer of charge)[73]. In this case we may assume that the excitation is transferred from one molecule of solvent to another until an excited solvent molecule is found at the interaction distance from a solute molecule. If the "free path" of this excitation is much less than its total displacement, it may be assumed that in this case the migration of energy is diffusional in character[74]. We are then justified in using Eqn.(17) to calculate the radii of interaction in glasses, but in this case D is the diffusion coefficient of the excitation[72].

Since in Chilton and Porter's experiments the spectra of the substrate (solvent) and additive do not overlap, it

† Eqns.(22) and (23) appear to contain errors and are ambiguous. For a detailed treatment of this topic the interested reader is advised to consult A.J.Swallow, "The Radiation Chemistry of Organic Compounds", Pergamon, New York. 1960 [Ed. of Translation].

may be suggested that the transfer of energy from the excited molecules of the substrate to the molecules of the additive takes place at distances close to the molecular radii (R = 5 Å). In other words, for the transfer of energy, the electronic excitation in the substrate should be displaced from the molecule in which it originated to one lying close to molecules of the additive. Assuming that the lifetime of the excitation is of the same order of magnitude in the vitreous state as in the liquid state, we may assume that for methylcyclohexane $\tau = 5 \times 10^{-10}$ sec. Since $k_{AB}/k'_A + k_A$ = 830 litre mole^{-1}, the diffusion coefficient of the excitons, determined from Eqn.(17), is $D \simeq 4.5 \times 10^{-3}$ cm^2 sec^{-1}, from which the mean square displacement of the exciton, *i.e.* the distance at which the transfer of energy takes place in glasses during the lifetime of the excited state, is

$$\bar{x} = \sqrt{2D\tau} = 200\,\text{Å}. \qquad (25)$$

Intermolecular transfer of energy in solid mixtures of dicyclohexyldodecane and diphenyldodecane at -196° was observed by Voevodskii *et al.*[75]. Determination of the yield of radicals for each component separately and for their mixtures, by the EPR method, showed that the energy is transferred from the first component to the second.

The decrease in the radiochemical yield for the destruction or cross-linking of a number of polymers in the presence of small quantities of certain substances, so-called antirads, is apparently associated in many cases with the transfer of energy from the polymer to the antirad.

Alexander and Charlesby[76-78] studied the influence of the addition of various substances on the destruction, by radiation, of poly(methylmethacrylate) and found that the greatest protective action is shown by aromatic compounds (anthracene, naphthalene, benzophenone, 8-hydroxyquinoline, naphthylamine, etc.). Comparison of the protective action of 8-hydroxyquinoline and naphthalene showed that, whereas the efficiency of the former decreases during the radiolysis, the efficiency of the latter remains almost unchanged. Experiments with naphthalene labelled with ^{14}C showed that the quantity of naphthalene reacting with the polymeric molecules is too low for its action to be due to the combination of macroradicals, formed during radiolysis, *via* the naphthalene molecule. The protection of poly(methyl methacrylate) by naphthalene is evidently due chiefly to the transfer of energy from the polymer to the naphthalene molecules, which scatter it in the form of heat (sponge type protection).

The addition of small quantities (~ 0.2%) of a number of the aromatic amines and phenols normally used as antioxidants (phenyl-β-naphthylamine, di-β-naphthyl-*p*-phenylenediamine, di-t-butyl-4-methylphenol, etc.) decreases considerably the rate of cross-linking of polyethylene. Certain fatty acids, for example stearic acid, also prevent cross-linkage in polyethylene. Here it was found that the yield for the decomposition of the acid in the polymer, calculated for the direct action of the radiation, is 25 times greater than that in the pure acid. It may be assumed that in this case sacrificial protection of the polymer by the acid takes place. Salts of the acids do not exhibit the protective action, indicating the important part played by the mobile proton in the mechanism of protection. The part played by the transfer of energy in the prevention of cross-linking in polyethylene is not yet clear[79]. If the transfer of energy is significant, an important part is apparently played by the migration of energy along the hydrocarbon chains. It has been shown[27,75] that the energy taken up by molecules during radiolysis is readily transferred along aliphatic chains.

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The data at present available on the radiolysis of organic solutions are insufficient for a detailed examination of the mechanism of the intermolecular transfer of energy in radiochemical reactions. Nevertheless the study of the kinetics of these reactions enables systems to be differentiated according to the efficiency of the energy-transfer processes taking place in them. At high transfer efficiencies ($k_{AB}/k'_A + k_A = 10^2 - 10^3$ litre mole^{-1}), deviations from additivity are observed even at low acceptor concentrations (< 0.01 M), and at low efficiencies ($k_{AB}/k'_A + k_A \sim 1$) they are observed at higher concentrations (> 0.01 M). Sometimes, in the radiolysis of a given system in different ranges of acceptor concentration, the transfer of energy takes place with different efficiencies, indicating apparently that different excited or ionised states can take part in the energy transfer. This division of energy-transfer processes according to efficiency is not sharp and is to some extent arbitrary, since the efficiency of transfer depends both on the interaction cross-section of the molecules and on their lifetime in the excited state. However, it enables certain suggestions regarding the mechanism of energy transfer to be made.

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APPLICATION OF THE KINETIC ISOTOPE EFFECT OF TRITIUM TO THE INVESTIGATION OF THE MECHANISM OF HYDROGEN SUBSTITUTION AND TRANSFER REACTIONS

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I. INTRODUCTION

The velocity of a reaction is affected when the atom involved is replaced by its isotope in the molecule if the bond between this atom and another element is ruptured during the rate-determining stage of the reaction. The effect is expressed as the ratio of the rate constants for