IDENTITY REACTIONS, INVOLVING THE TRANSFER OF IDENTICAL RADICALS IN SOLUTIONS (THE STEPWISE TRANSFER OF RADICALS)

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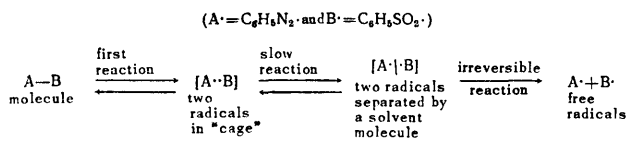
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I. INTRODUCTION

Many important chemical processes in gases and in solutions involve the formation and the reactions of free radicals, several radical reactions being known which are common to both states of aggregation. Liquid–phase reactions, however, have some additional features: thus, in solutions, each individual solute particle is surrounded by a "cage" of solvent molecules. This impedes the breakdown of the solute molecules into free radicals, since, owing to the slow diffusion of the latter in liquids, most of those which are formed recombine immediately. This primary recombination lowers the initial yield of formation reactions in solutions as compared with gases. When, however, the free radicals are able to escape from the "cage", the surrounding layer of solvent molecules now prevents their recombination and favours reaction between the radical and a solvent molecule.

With the thermal decomposition of phenylphenylsulphonyl diimide (A–B) in benzene as example, Rosenthal and Overberger[1] illustrate the mechanism of formation of free radicals, and their escape from the "cage", by the following scheme



The principle of the primary recombination of free radicals, put forward earlier by Franck and Rabinowitch[2], is valid only for inert solvents[3], *i.e.* those in which the escape of the radicals from the "cage" into the "bulk" of the solvent takes place by diffusion.

When a free radical R· is able to abstract an X atom from a solvent molecule RX, escape of radicals from the "cage" into the bulk can occur by stepwise radical transfer in addition to diffusion. The transfer of one atom from a reactant molecule to the free radical leads to the production of a new radical and molecule which are identical with the previous ones

$$R\cdot + RX \rightleftarrows RX + R\cdot \qquad (1)$$

Thus the transfer of identical radicals, or the so-called stepwise radical transfer, means the reaction of a molecule RX with the corresponding radical R· according to Eqn.(1). The regeneration of radicals by the solvent molecules can be repeated many times. The result is that the free valence moves in a stepwise manner from one molecule to the next, as illustrated by the collision of a moving sphere with a stationary row of spheres, when the motion of the first sphere is transferred to the last sphere of the row.

These considerations are inadequate for a complete description of the effect of the solvent on the course of radical reactions. Recent work indicates that free radicals can interact with solvent molecules to give unstable intermediate complexes, which then form the active centres between which reaction takes place.

Russell[4] points out that the course of the photochemical chlorination of 2,3-dimethylbutane is changed by introducing an aromatic compound into the reaction medium. The effect of the solvent is explained by the chlorine atom forming a π complex with the aromatic nucleus. The complex is less reactive, and hence a more selective chlorinating agent, than free atomic chlorine. A similar phenomenon has been observed by Walling and others in the photochemical chlorination of some hydrocarbons[5]. The marked influence of solvents (benzene, carbon disulphide, chlorobenzene) on the relative ease with which hydrogen atoms attached to primary, secondary, and tertiary carbon atoms can be replaced by chlorine is due to the formation of relatively stable π complexes.

In the photolysis of iodobenzene, diphenylmercury, and tetraphenyl-lead in cumene, Bryce-Smith *et al.*[6] observed a difference in the composition of the isomeric reaction products, and concluded that phenyl radicals give intermediate compounds with the solvent during photolysis.

It is now firmly established that the phenylation of aromatic compounds by phenyl radicals takes place via π and σ complexes. The view that complexes are formed between the radicals and the solvent is not incompatible with reaction (1).

The heat ΔH of transfer of identical radicals (R′ = R) is zero. In the case of different radicals (R′ ≠ R) ΔH differs slightly from zero[7]. The rate of stepwise transfer of a free radical depends on the activation energy of the process. Semenov showed by a simple calculation that this type of radical transfer often predominates over diffusion in solutions[3]. Assuming an activation energy of 5 kcal, the stepwise transfer of radicals at 400°K is 60 times as rapid as diffusional transfer. With large activation energies, on the other hand, the rate of diffusion will exceed that of estafette radical transfer. With an activation energy of 10 kcal, for example, the velocity ratio will be 10, diffusion being predominant.

The reaction between the CH_3· radical and CH_4 in the gas phase has an activation energy[8] of ~ 11.2 kcal mole^{-1}. Unfortunately, no experimental data have been published on the activation energy of liquid-phase stepwise reactions.

Although the estafette transfer of radicals is relatively unimportant in most of the cases investigated, some authors ascribe to it a great part in radical processes.

The opinion is held that exchange between radicals and the solvent may increase the life of the free radicals. Thus, Waters[9] and Semenov[3] consider that, when acetyl peroxide is boiled in acetic acid, the $CH_3COO\cdot$ radical may possess an abnormally long life as a result of regeneration by exchange with the solvent.

However, Fry *et al.*[10] have shown that the decomposition of acetyl peroxide in acetic acid $^{14}CH_3COOH$ is accompanied by hardly any stepwise transfer of acetoxy radicals, for the methane evolved in the reaction contains no more than 1% of radioactive carbon. Analogous results have recently been obtained by Razuvaev *et al.*[11] for the decomposition of acetyl benzoyl peroxide in acetic acid $CH_3.^{14}COOH$. The transfer of acetoxy radicals was determined from the radioactive $^{14}CO_2$ obtained by decarboxylation of $CH_3.^{14}COO\cdot$ radicals.

Many workers have investigated reactions of this type, but a detailed study has been made only of those involving the splitting off of hydrogen from hydrocarbons by methyl radicals in the gas phase. Little research has been done on the stepwise transfer of radicals in the liquid phase, and most of this work is confined to a qualitative assessment of the reaction; quite often contradictory views are encountered. The results of work in this field have not yet been systematised.

In the foreign literature, reactions involving the transfer of identical radicals have been called "identity reactions"[12].

The present paper is concerned mainly with an examination of liquid-phase identity reactions. For purposes of comparison, reactions involving the transfer of methyl radicals are considered first, as they have been studied in the gas phase.

The stepwise transfer of radicals is accompanied not only by purely chemical changes, but can be followed from the change in optical activity of the molecule involved. If RX is an optically active molecule, in which the activity is due to the asymmetry of R·, this optical activity is not retained when X is split off[13]. Thus the stepwise transfer will result in a racemisation of RX.

The transfer of identical radicals can be monitored much more simply and more accurately by means of labelled atoms. Various isotopes of carbon and hydrogen can be used for this purpose, but hydrogen isotopes introduce a large isotope effect[14]. Either the solvent or the source of free radicals can be labelled. In the former case, interaction between radicals and solvent is determined from the isotopic composition of the products formed by combination of the radicals, and in the latter case from the change in isotopic composition of the solvent. Most of the work has been carried out by the first method.

Neither method is reliable with all radicals. As will be shown below, participation of the solvent in the formation of a dimer is not always a proof of the stepwise transfer of radicals. The appearance of activity in the solvent can also result from intramolecular splitting off of an atom from a solute molecule by the labelled radical. More trustworthy evidence of stepwise radical transfer is obtained by using both methods, which makes it possible to check and compare results obtained in different ways.

II. REACTIONS INVOLVING THE TRANSFER OF METHYL RADICALS IN THE GAS PHASE

The simplest example of radical transfer is the interaction between hydrogen atoms and the hydrogen molecule H_2. This is accompanied by the interconversion of ortho and para forms of hydrogen, caused by the magnetic field of the free radical[15]

$$H\cdot + H_2\ (\text{para}) \rightleftarrows H_2\ (\text{ortho}) + H\cdot$$

Other radical-transfer reactions are the reversible reaction of atomic hydrogen with a hydrocarbon molecule[16] and of alkyl radicals with molecular hydrogen[17].

During the past decade a detailed quantitative investigation has been made of the transfer of methyl radicals in the gas phase. A reaction of this type is the splitting off of a hydrogen atom from a methane molecule by a methyl radical:

$$CH_3^{\cdot} + CH_4 \rightleftarrows CH_4 + CH_3^{\cdot}$$

A competing reaction in this case is the dimerisation of the radicals. The gas-phase transfer of methyl radicals has been studied during the photolysis of acetone in the presence of methane. Different workers have employed compounds labelled with deuterium or radiocarbon ^{14}C for this purpose.

Photolysis of a mixture of acetone and deuteromethane at 354° gives[18] CH_3D, CD_3H, $C_2H_3D_3$, and C_2D_6. Irradiation of this mixture is stated to induce the following basic reactions

$$\begin{aligned} CH_3COCH_3 &\xrightarrow{h\nu} 2CH_3^{\cdot} + CO\ , \\ CH_3^{\cdot} + CD_4 &\xrightarrow{k_1} CH_3D + CD_3^{\cdot}\ . \qquad (2a) \\ CH_3^{\cdot} + CH_3COCH_3 &\xrightarrow{k_2} CH_4 + \cdot CH_2COCH_3\ , \qquad (2b) \\ CD_3^{\cdot} + CH_3^{\cdot} &\rightarrow C_2H_3D_3\ , \\ 2CD_3^{\cdot} &\rightarrow C_2D_6\ . \end{aligned}$$

The ratio of the rate constants k_1/k_2 was found from a mass-spectrographic determination of the 17/16 mass ratio (CH_3D/CH_4). The velocity constant k_1 was calculated as

$$1.8 \times 10^8 \exp(-\ 12.93 \pm 0.65\ \text{kcal}/RT)\ \text{litres mole}^{-1}\ \text{sec}^{-1}\ .$$

The activation energy of reaction (2a) is $E_{2a} = 12.9 \pm \pm 0.65$ kcal mole^{-1}. It was proved in separate experiments that no deuterium exchange takes place between CD_4 and CH_3COCH_3. No methane was formed when acetone was heated to 354° in the absence of u.v. irradiation.

Other investigators[19] used a mixture of deuteroacetone and methane, which also was subjected to photolysis at 360°–428°

$$\begin{aligned} CD_3COCD_3 &\xrightarrow{h\nu} 2CD_3^{\cdot} + CO\ , \\ CD_3^{\cdot} + CH_4 &\xrightarrow{k_1} CD_3H + CH_3^{\cdot}\ , \qquad (3) \\ CD_3^{\cdot} + CD_3COCD_3 &\xrightarrow{k_2} CD_4 + \cdot CD_2COCD_3\ . \end{aligned}$$

Mass-spectrographic determination of the 19/20 mass ratio (CD_3H/CD_4) yielded the ratio of the velocity constants k_1/k_2.

The rate constant was calculated[18] as $k_1 = 0.17 \times \times 10^3$ litres mole^{-1} sec^{-1} at 180°. The activation energy of reaction (3) was $E_3 = 14.1$ kcal mole^{-1}. The slight difference in activation energy (1.15 kcal mole^{-1}) between reactions (3) and (2a) is ascribed to the isotope effect in the splitting off of deuterium.

In order to eliminate the isotope effect in this reaction, radiocarbon ^{14}C was also used

$$CH_3^{\cdot} + {}^{14}CH_4 \rightarrow CH_4 + {}^{14}CH_3^{\cdot}. \quad (4)$$

The reaction was carried out by exposing to u.v. radiation a mixture of acetone and radioactive methane at partial pressures of 50 and 62–425 mm Hg respectively. The reaction velocity was determined from the radioactivity of the ethane formed by recombination of the free methyl radicals [20]. The rate constant of reaction (4) was found to be

$$\log k_1 \text{ (litres mole}^{-1} \text{ sec}^{-1}) = 8.83 - (14.65 \text{ kcal})/2.303\,RT.$$

This value is very close to that obtained previously for reaction (3).

The ratio of the velocity constants of the reactions

$$^{14}CH_3^{\cdot} + CH_3COCH_3 \xrightarrow{k_1} CH_3^{\cdot} + {}^{14}CH_3COCH_3, \quad (5a)$$

$$^{14}CH_3^{\cdot} + CH_3COCH_3 \xrightarrow{k_2} {}^{14}CH_4 + \cdot CH_2COCH_3, \quad (5b)$$

was found to be $k_1/k_2 = 0.036$ at 350°. In this case the extent to which the exchange of methyl radicals [reaction (5a)] occurs is about 3% of the abstraction of hydrogen by these radicals according to reaction (5b).

The exchange of methyl radicals with ethane, methyl ether, acetone, and propene (CH_3R) has also been investigated [21]. The compound was heated at 550°–575° with deuteroacetaldehyde CD_3CDO, the thermal decomposition of which yields $CD_3^{\cdot}$ radicals, which interact with the CH_3R

$$CD_3^{\cdot} + CH_3R \xrightarrow{k_1} CD_3R + CH_3^{\cdot}, \quad (6a)$$

$$CD_3^{\cdot} + CH_3R \xrightarrow{k_2} CD_3H + CH_2R^{\cdot}. \quad (6b)$$

The ratios of the velocity constants for reactions (6a) and (6b) (k_1 for the exchange reaction and k_2 for the splitting off of hydrogen) were found from mass-spectrographic determinations of the CD_3R/CD_3H ratios: for ethane the CD_3CH_3/CD_3H ratio is 1/1500, for methyl ether CD_3OCH_3/CD_3H = 1/2800, for acetone CD_3COCH_3/CD_3H = = 1/90, and for propene $CD_3.CH:CH_2/CD_3H$ = 1/19.

Comparison of the ratio found for acetone (CD_3COCH_3/CD_3H = 1/90) with the ratio of the velocity constants for the analogous reactions (5a) and (5b) (k_1/k_2 = = 0.036) shows that, although the values obtained by different workers differ, they are of the same order of magnitude.

The decomposition of acetyl peroxide was investigated in toluene medium [22] in order to study the possible liquid-phase exchange of methyl radicals. As expected, no exchange took place between methyl radicals of the peroxide and the methyl group of the toluene. The decomposition of acetyl peroxide in $C_6H_5CD_3$ does not lead to the formation of CHD_3 or CD_4, and also no toluene $C_6H_5CH_3$ was detected after the reaction.

The absence of an exchange reaction in this case can be explained by the fact that methyl radicals do not form intermediate complexes with aromatic compounds. This is consistent with Antonovskii and Berezin's observation [23] that, when acetyl peroxide undergoes decomposition in tritiobenzene, the resulting methyl radicals split off the benzene hydrogen atoms more readily than the tritium atom. The large isotope effect (6.02 ± 0.07) indicates that the methyl radicals capture the hydrogen atoms, not in an intermediate complex, but by directly attacking the benzene ring.

In the gas phase, as several workers have suggested [7], the regenerative exchange of methyl radicals takes place *via* a transition state, involving a "coupling" of the bond system

$$H_3C\cdots\cdots H\cdots\cdots CH_3,$$

with three delocalised electrons. The energy of this system can be defined as the energy required to remove the hydrogen atom to infinity. If a methyl radical reacts with a more complex paraffin hydrocarbon molecule HR, the energy required to split off a hydrogen atom in the initial and final states is decreased by the coupling energy. In this respect Polanyi's rule is valid for the reaction

$$CH_3^{\cdot} + HR \rightleftarrows CH_4 + R^{\cdot},$$

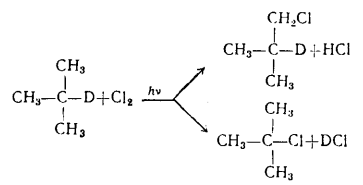
with few exceptions: the activation energy of the reaction and the bonding energy D(R–H) are linearly related. These quantities decrease as the radical becomes more complex. This question has been discussed in detail by Bagdasar'yan [7].

A considerable amount of work has been published on the stepwise transfer of other, more complex radicals in various solvents. The reactions of t-butyl, cyanoisopropyl, and trichloromethyl radicals will be examined in section III; those of radicals such as benzyl, diphenylmethyl, and 2-phenylbutyl in section IV. The stepwise transfer of phenyl and acyloxy radicals will be discussed separately because these groups have several peculiar features.

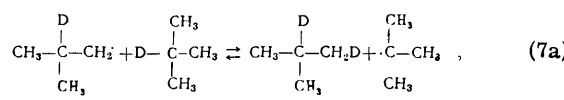
III. REACTIONS INVOLVING THE TRANSFER OF ALIPHATIC RADICALS

The stepwise transfer of t-butyl, cyanoisopropyl, and trichloromethyl radicals in the liquid phase has been investigated.

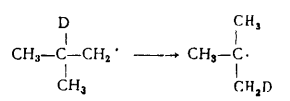
Brown and Russell [24] investigated the possibility of t-butyl radical transfer during the photochemical chlorination of 2-deutero-2-methylpropane in the liquid phase, and found that exchange does not occur between this radical and the corresponding hydrocarbon under the conditions indicated below. The photochemical chlorination of 2-deutero-2-methylpropane in the liquid phase at -15° involves the replacement of hydrogen by chlorine both in the methyl group and at the tertiary carbon atom



It is quite possible that chlorination is accompanied by the formation of free radicals, which can undergo either exchange or rearrangement. If such exchange (7a) or rearrangement (7b) takes place during the photochemical chlorination



(7a)

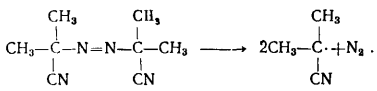


(7b)

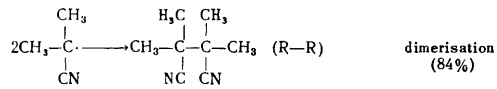
the relation between the quantities of deuterium chloride and the tertiary chloride formed will be complicated. It was established that equimolecular amounts of these compounds were formed. It would appear, therefore, that neither hydrogen exchange between the radicals and the hydrocarbon (7a) nor rearrangement of the free radical (7b) takes place during photochemical chlorination. The obvious explanation was that reaction between chlorine and the radical takes place considerably more rapidly than exchange or displacement of hydrogen atoms. Thus the presence of three methyl groups in the t-butyl radical $(CH_3)_3C\cdot$ does not increase the ability of the radical to split off hydrogen by stepwise transfer.

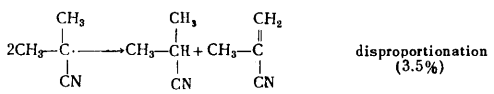
It is interesting to compare these results with those obtained with the cyanoisopropyl radical[25], which is extremely reactive and acts as an initiator for the polymerisation of many vinyl monomers. It might be supposed that the presence of the cyano group in the $CN.C(CH_3)_2^{\cdot}$ radical would have a definite effect, which could be observed from the exchange reaction.

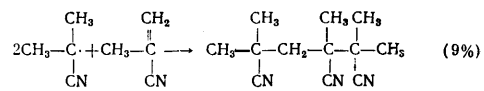
Cyanoisopropyl radicals are easily obtained by the decomposition of azo-2, 2′-di-isobutyronitrile



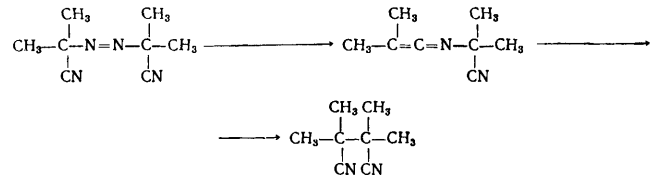
Studies of the decomposition products of this compound in various solvents showed that the main reaction undergone by the resulting radicals is dimerisation[26]. In toluene, for example, the decomposition is represented by the scheme





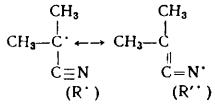


Actually, the interaction of the cyanoisopropyl radicals is more complicated than this. In the decomposition of azo-2, 2′-di-isobutyronitrile (RN.NR) the dimer tetramethylsuccinonitrile (R.R) can be obtained[27] by isomerisation of the less stable intermediate compound, dimethyl-*N*-(2-cyano-2-propyl)ketenimine (R.R′)



i.e. RN = NR → R—R′ → R—R.

The formation of the intermediate compound (R.R′) indicates that the radicals can rearrange and interact during the course of this reaction



Hammond *et al.*[27] point out that dimethyl-*N*-(2-cyano-2-propyl)ketenimine polymerises styrene considerably more slowly than does azo-2, 2′-di-isobutyronitrile. This is explained by the primary decomposition of the compound R.R′ occurring *via* an intermediate complex of the radicals with the solvent or the monomer

$$R{-}R' \rightarrow \overline{2R^{\cdot}}\,,$$

$$\overline{2R^{\cdot}} + C_6H_6 \rightarrow R^{\cdot} + [C_6H_6 \rightarrow R^{\cdot}]\,,$$

$$[C_6H_6 \rightarrow R^{\cdot}] \rightleftarrows C_6H_6 + R^{\cdot}$$

They point out that the cyanoisopropyl radical (R·) can behave as an electron acceptor, and will therefore give complexes with aromatic compounds.

Chemical changes of this type undergone by cyanoisopropyl radicals may have prevented Fedotova and Lazaris[25] obtaining definite evidence for the occurrence of stepwise transfer of this radical in the decomposition of azo-2, 2′-di-isobutyronitrile (labelled with ^{14}C in the nitrile group) dissolved in isobutyronitrile at 102°. The activity shown by the solvent should be a measure of the nitrile obtained by stepwise transfer and by disproportionation of the cyanoisopropyl radical. On dilution of the solution the percentage activity corresponding to disproportionation should remain constant, while stepwise transfer should increase with dilution. The molar ratio of the reactants was varied between wide limits (from 1 : 57 to 1 : 510), but no substantial change was observed in the activity in the isobutyronitrile (from 6.1 to 9.2%).

These workers consider that stepwise transfer of the cyanoisopropyl radical is absent owing to the large stabilisation energy of this radical. The appearance of activity (6.1—8.1%) in the isobutyronitrile is ascribed wholly to disproportionation, but some increase in activity (by 2—3%) with dilution is ascribed to experimental error. No other results have been published on the abstraction of hydrogen atoms from other organic molecules by the cyanoisopropyl radical.

Razuvaev *et al.* have investigated the possibility of the stepwise transfer of the trichloromethyl radical with displacement of hydrogen or chlorine[28]

$$CCl_3^{\cdot} + {}^{14}CCl_4 \rightleftarrows CCl_4 + {}^{14}CCl_3^{\cdot}\,, \qquad (8a)$$

and

$$CCl_3^{\cdot} + {}^{14}CHCl_3 \rightleftarrows CHCl_3 + {}^{14}CCl_3^{\cdot}\,. \qquad (8b)$$

A mixture of CCl_4 and $^{14}CHCl_3$ was therefore heated in the presence of Raney nickel in a stream of nitrogen at 80° for 10 h. In this case the primary reaction in the formation of CCl_3 radicals can only be the interaction of CCl_4 and Ni. If the resulting CCl_3 radicals then reacted according to Eqn. (8a), the C_2Cl_6 obtained would be active. The C_2Cl_6 and CCl_4 isolated from the reaction were not active, indicating that reactions (8a) and (8b) had not occurred.

The absence of reaction (8b) has been demonstrated also in the u.v. irradiation of a mixture of CCl_4 and $^{14}CHCl_3$: the CCl_4 isolated after exposure was inactive, although the C_2Cl_6 did show activity. The CCl_4 and C_2Cl_6 isolated after exposure of a mixture of CCl_4, CH_3OH, and $^{14}CHCl_3$ to u.v. radiation contained hardly any activity, showing that the CCl_3 radical does not abstract hydrogen from the alcohol. These workers explain the impossibility of abstracting hydrogen from the alcohol or from chloroform and the absence of stepwise transfer with the CCl_3 radical by the considerable stabilisation energy of this radical, which is estimated as 12 or 19 kcal mole^{-1} by Schumacher and Wolf[29] and by Miller and Willard[30] respectively.

A postulated stepwise transfer of the CCl_3 radical of only 2–3% could have remained unnoticed, since the original $^{14}CHCl_3$ was feebly active (with a count of 900 min^{-1}).

No other work has been published on the transfer of the CCl_3 radical. The reactivity of the trichloromethyl radical has been investigated by Kharasch *et al.*[31]

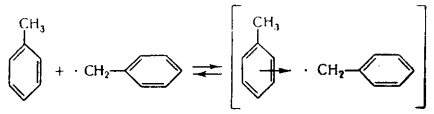
Thus the work which has been considered shows that – (1) the t-butyl, cyanoisopropyl, and trichloromethyl radicals undergo little or no exchange by estafette transfer in the liquid phase; (2) the presence of functional groups in these radicals has practically no effect on the rate of exchange.

IV. REACTIONS INVOLVING THE TRANSFER OF ARYL RADICALS

The liquid-phase stepwise transfer of the phenyl, benzyl, methylbenzyl, diphenylmethyl, and 2-phenylbutyl radicals has been investigated. Results obtained for the phenyl radical will be discussed separately in the next section.

The transfer of benzyl radicals has been investigated by several workers. Benzyl radicals are not very reactive, their stabilisation energy being[32] 21.5 kcal $mole^{-1}$, and they hardly undergo any exchange with toluene. In fact, u.v. irradiation of dibenzylmercury in deuterotoluene yielded 1, 2-diphenylethane containing $< 1\%$ of the deuterium in the original toluene[33]. Similar results were obtained for the thermal decomposition of dibenzylmercury in [1-^{14}C] toluene. The 1, 2-diphenylethane which was isolated contained only 1.5% of active carbon.

These data agree well with interesting observations by Cassidy and coworkers[34] who showed that the pyrolysis of toluene vapour at low pressures followed by rapid cooling to -78° yields a pyrolytic mixture containing benzyl radicals, which exist for $1\frac{1}{2}$ h. During this period the radicals can be easily titrated with iodine to benzyl iodide. These workers point out that the radicals exist in the form of a complex in the toluene solution



Furthermore, stepwise transfer of the benzyl radical does not occur[24,35] in the liquid-phase photochemical chlorination of $C_6H_5CH_2D$ at 80°. Substitution of a methyl hydrogen could be accompanied by the formation of benzyl radicals of the types $C_6H_5CH_2^{\cdot}$ and $C_6H_5CHD^{\cdot}$. It was possible that the benzyl radicals might exchange with the toluene according to the following scheme

$$C_6H_5CHD^{\cdot} + C_6H_5CH_2D \rightleftharpoons \begin{matrix} C_6H_5CHD_2 + C_6H_5CH_2^{\cdot} \\ C_6H_5CH_2D + C_6H_5CHD^{\cdot} \end{matrix} \quad (A)$$

$$C_6H_5CH_2^{\cdot} + C_6H_5CH_2D \rightleftharpoons \begin{matrix} C_6H_5CH_3 + C_6H_5CHD^{\cdot} \\ C_6H_5CH_2D + C_6H_5CH_2^{\cdot} \end{matrix} \quad (B)$$

The exchange of the radicals with the hydrocarbon could be detected from the formation of $C_6H_5CHD_2$, Eqn. (A), or, less reliably, from the formation of non-deuterated toluene Eqn. (B).

An experimental test showed that $C_6H_5CHD_2$, Eqn. (A), is formed only in small amounts, which is explained by the considerably higher speed of the interaction of the radicals with chlorine than the abstraction of hydrogen from the toluene.

There are indications that, in contrast to the benzyl radical, the *p*-methylbenzyl radical exchanges readily with *p*-xylene. Cadogan *et al.*[36] conclude from an investigation of the reaction of benzoyl peroxide with α-deutero-*p*-xylene that transfer of *p*-methylbenzyl radicals

$$CH_3C_6H_4CH_2^{\cdot} + CH_3C_6H_4CH_2D \rightarrow CH_3C_6H_4CH_3 + CH_3C_6H_4CHD^{\cdot} \quad (9a)$$

occurs to a greater extent than their dimerisation

$$2CH_3C_6H_4CH_2^{\cdot} \rightarrow CH_3C_6H_4CH_2CH_2C_6H_4CH_3.$$

This conclusion is based on the fact that the deuterium content of the 1, 2-di-*p*-tolylethane isolated is greater than that of the xylene taken. If this reaction product had been formed by the recombination of radicals produced initially, its deuterium content should have been the same as that of the radicals, *i.e.* as that of the solvent. This discrepancy is explained by the occurrence of reaction (9a) with preferential displacement of hydrogen.

On this evidence, the increased reactivity of the *p*-methylbenzyl radical compared with the benzyl radical can be ascribed only to the influence of the methyl group. No quantitative assessment of the reactivity of the methylbenzyl radical is given in the paper.

Insignificant radical exchange is observed in the decomposition of various peroxides in aromatic hydrocarbons[37], but the stepwise transfer of methylbenzyl radicals has not been investigated in this connection. Wang and Cohen[38] investigated the stepwise transfer of the diphenylmethyl radical $(C_6H_5)_2CH^{\cdot}$ in diphenylmethane. This radical, like benzyl, is unreactive and stabilised, so that its stepwise transfer is improbable. When azobisdiphenylmethane $(C_6H_5)_2CH.N:N.CH(C_6H_5)_2$ decomposes in diphenylmethane $(C_6H_5)_2{}^{14}CH_2$ at 60°, the resulting $(C_6H_5)_2CH.CH(C_6H_5)_2$ contains only 1.5% of the total activity.

The stepwise transfer of the 2-phenylbutyl radical has been investigated in the decomposition of acetyl peroxide in optically active 2-phenylbutane[22].

Decomposition of the peroxide yields methyl radicals, which remove the hydrogen from the tertiary carbon atom of the 2-phenylbutane

$$CH_3^{\cdot} + CH_3{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}C_2H_5 \rightarrow CH_4 + CH_3{-}\underset{\displaystyle C_6H_5}{\overset{}{\underset{|}{\overset{|}{C^{\cdot}}}}}{-}C_2H_5 \quad (A)$$

The radicals thus produced (A) can then undergo stepwise transfer with a solvent molecule or may dimerise

$$CH_3{-}\underset{\displaystyle C_6H_5}{\overset{}{\underset{|}{\overset{|}{C^{\cdot}}}}}{-}C_2H_5 + CH_3{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}C_2H_5 \rightleftharpoons CH_3{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle H}{\underset{|}{\overset{|}{C}}}}{-}C_2H_5 + CH_3{-}\underset{\displaystyle C_6H_5}{\overset{}{\underset{|}{\overset{|}{C^{\cdot}}}}}{-}C_2H_5 \quad (9b)$$

$$2CH_3{-}\underset{\displaystyle C_6H_5}{\overset{}{\underset{|}{\overset{|}{C^{\cdot}}}}}{-}C_2H_5 \rightarrow C_2H_5{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}\underset{\displaystyle C_6H_5}{\overset{\displaystyle CH_3}{\underset{|}{\overset{|}{C}}}}{-}C_2H_5 \quad (B)$$

Free 2-phenylbutyl radicals (A) cannot maintain optical activity[13], so that, if reaction (9b) takes place, the optical activity of the 2-phenylbutane should fall. It has been found experimentally that the decomposition of acetyl peroxide in optically active 2-phenylbutane is accompanied by the formation of the inactive 3, 4-dimethyl-3, 4-diphenylhexane (B), while the 2-phenylbutane isolated from the reaction was only slightly racemised[22]. This shows that stepwise transfer might occur but only to a slight extent.

These workers remark that, although the results showed the absence of radical transfer on a large scale, it does not necessarily follow that transfer is entirely absent. If it is postulated that the extent of the reaction is slight, it is possible that in many cases the transfer of radicals could have remained unnoticed.

Thus the above data on the regenerative exchange of some aryl radicals indicate that benzyl and diphenylmethyl radicals react by a stepwise mechanism to only a very slight extent, not exceeding 1.5–2%. The exchange of methylbenzyl radicals has not been assessed quantitatively.

V. REACTIONS INVOLVING THE TRANSFER OF PHENYL RADICALS

The exchange reaction has been investigated in greatest detail in the case of phenyl radicals. This is because the transfer of radicals in aromatic compounds is accompanied by homolytic (amphoteric) substitution. The mechanism of homolytic substitution has been studied in detail by many workers, and fully described by Hey[39]; therefore it will be mentioned only briefly here when the need arises.

Ideas on the mechanism of the reaction between phenyl radicals and benzene have greatly changed during the development of the chemistry of free radicals. Until recently it was considered that phenyl radicals could react with benzene in three ways

$$C_6H_5^{\cdot} + C_6H_6 \rightarrow C_6H_5{-}C_6H_5 + (H\ ), \qquad (10a)$$

$$C_6H_5^{\cdot} + C_6H_6 \rightarrow C_6H_6 + C_6H_5^{\cdot}, \qquad (10b)$$

$$C_6H_5^{\cdot} + C_6H_6 \rightarrow \text{(A)}. \qquad (10c)$$

The three reactions were considered independently and serious objections were raised to each in turn. Reaction (10a) is considered improbable, since the evolution of atomic hydrogen is energetically unfavourable[40]. Besides, repeated attempts to confirm the formation of atomic hydrogen during the reaction were not successful. Rafikov and Kudinova's results[41] for the determination of the very small amounts of hydrogen formed cannot be accepted as conclusive, which these workers admit.

It is doubtful whether a hydrogen atom in benzene could be directly replaced by a phenyl radical. A more probable situation is one in which the hydrogen atom is removed by means of another radical, so that any overall assessment of the energy involved will include the energy of formation of a new bond with the hydrogen atom. In such a situation the removal of a hydrogen atom will be energetically feasible[42]. Originally, however, reaction (10b), the transfer of radicals, was regarded as the direct removal of a benzene hydrogen by phenyl radicals.

In fact, such a view is not confirmed by an experimental determination of the isotope effect. In the opinion of several investigators[23], as noted above, the direct removal of hydrogen atoms by radicals according to reaction (10a) is characteristic only of reactive radicals such as $CH_3^{\cdot}$ and $\cdot OH$. More complicated radicals are able to yield complexes with solvent molecules, a process favoured by the presence of substituents.

This hypothesis has recently been confirmed experimentally by Hey *et al.*[43] in the case of phenyl radicals. They found no isotope effect for the abstraction of hydrogen during the phenylation of tritiobenzene with benzoyl peroxide. This fact indicates the formation of a complex between the radical and the benzene, but does not suggest a mechanism involving the direct capture of hydrogen by phenyl radicals.

As already pointed out, the formation of complexes between radicals and solvent molecules does not exclude stepwise radical transfer: on the contrary, it is a necessary stage in the latter. Exchange occurs between the component parts of the complex, within the latter, in the course of reaction (10c). The result of this reaction is an unstable complex compound for which there is very convincing experimental evidence. In a recent investigation of the polymerisation of styrene and its benzene solutions in the presence of various peroxides, Dannley *et al.*[44] noted that the quantity of initiator fragments incorporated is greatly dependent on the presence of the solvent. They point out that polystyrene obtained in the absence of solvent contains 88–95% of all the aroyloxy groups of the peroxides, including *p*-nitrobenzoyl peroxide. In contrast to this, polymers obtained in benzene solution had a far lower content of ArCOO groups, and in the case of this latter initiator no *p*-nitrobenzoyloxy groups were detected at all. The phenomenon is explained by the ability of benzene to capture these free radicals.

Bagdasar'yan *et al.*[45] conclude from an investigation of radical phenylation using deuterated aromatic compounds that radical substitution takes place by reaction (10c), since changes in temperature and in the peroxide concentration have no effect on the deuterium content of the biaryls. The "cage effect" is also absent, since decomposition of *p*-nitrobenzoyl peroxide in benzene does not yield dinitrobiphenyls or biphenyl itself, but only nitrobiphenyls. The reaction between benzoyl peroxide and deuterobenzene produced biphenyl in which 45% of the phenyl radicals are derived from the solvent. These workers consider that formation of biphenyl has occurred *via* the complex A. The rather low content of deuterium in the biphenyl (45% instead of the calculated 50%) is explained by errors in the measurements.

The existence of an intermediate radical A has been established by DeTar and Long[46], who were able to isolate tetrahydroquaterphenyl and dihydrobiphenyl from the reaction between benzoyl peroxide and benzene, these products having been formed by dimerisation or the removal of hydrogen from the intermediate radical A.

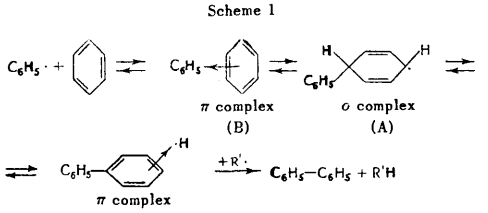
Thus, according to the latest results, the mechanism of homolytic arylation and the transfer of phenyl radicals in benzene are as follows. The first stage in the process is the direct addition of a phenyl radical to an aromatic nucleus to form the intermediate complex A (reaction 10c); the second stage is the transfer of a hydrogen atom to some radical fragment, this reaction taking place by the interaction of the complex A with another radical

$$\text{A} + R'\cdot \rightarrow R'H + C_6H_5C_6H_5. \qquad (10d)$$

The radical R′· may be of the same nature as R·. Razuvaev and his coworkers consider that exchange of phenyl radicals can continue to occur within the complex A until the complex undergoes the second stage in the reaction[47]. This

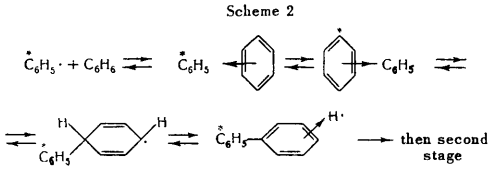
interpretation derives from the hypothesis[42] that reaction (10c) involves interconversion of the π and σ forms of the complex A (scheme 1).

Scheme 1



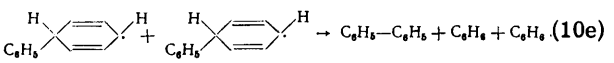
The exchange of phenyl radicals takes place, in Razuvaev's opinion, within the π complex (B). As can be seen from the scheme, this can pass into the σ complex (A) and enter the second stage of the reaction, or alternatively radical transfer can occur within (B) (scheme 2).

Scheme 2



If isomerisation of the π complex (B) and removal of a hydrogen atom by a second radical in the second stage are assumed to be fast, transfer of the phenyl radical will be determined by the presence of foreign radicals. In this way the regenerative exchange of radical fragments depends on the total concentration of radicals in the solution. This phenomenon has been observed in several experiments, which will be discussed below.

The discussion of reactions (10c) and (10d) shows some inconsistency. On the one hand, free radicals form complexes (A) with the aromatic compound (reaction 10c); and on the other, hydrogen is split off from this complex by free radicals (reaction 10d). In the writer's opinion, this discrepancy can be resolved by assuming that the removal of hydrogen from the complex (A) is effected by another complex radical. The first complex compound, by losing a hydrogen atom, is immediately converted into a biaryl. The other complex, by capturing a hydrogen atom, splits into two molecules



The aryl radicals taking part in some processes, such as the decomposition of peroxides into reactive complexes, may be different. The biaryls formed according to this scheme always consist of radicals from the substance which has decomposed and from a solvent molecule. Such a phenomenon is consistent with the experimental results, the solvent molecules acting in this case as "carriers" of free radicals.

Certain difficulties are involved in the detection and the quantitative determination of the transfer of phenyl radicals. Estimation of the stepwise reaction from the active benzene formed from phenyl radicals (by reaction 10b) is not always reliable. In the decomposition of labelled benzoyl peroxide, for example, active benzene can be obtained by another reaction occurring in parallel (see reactions 10d and 10e). A similar phenomenon is observed in the decomposition of pentaphenylphosphorus.

Unfortunately the second method – use of a labelled solvent and the estimation of radical transfer from the isotopic composition of the biphenyl – is also unjustified in the case of benzoyl peroxide. In several cases, therefore, the question of the occurrence of an identity exchange still remains unsettled.

In order to detect reaction (10b), the decomposition of many organic and organometallic compounds containing carbon and hydrogen isotopes has been investigated, a labelled solvent being used as well. These compounds used as sources of radicals included diphenylmercury, benzoyl peroxide, pentaphenylphosphorus, nitrosoacetanilide, lead tetrabenzoate, diphenyliodonium iodide, etc.

The first experimental data on the transfer of phenyl radicals in benzene were obtained by Razuvaev *et al.*[48] who showed that this reaction takes place during the decomposition of diphenylmercury in deuterobenzene. These results were later confirmed by Korshunov and Orlova[49] using benzene labelled with ^{14}C. Heating and u.v. irradiation of a solution of diphenylmercury in deuterobenzene yields biphenyl containing up to 14.5% of phenyl groups from the solvent. On the other hand, use of diphenylmercury labelled with ^{14}C and benzene in the molecular proportions 1 : 25 in this reaction enabled the escape of radicals from the organometallic compound into the solution to be determined as radioactive benzene. After the reaction, the benzene was found to contain 7.9% of the activity of the diphenylmercury[47]. The biphenyl obtained consisted of 61.5% of phenyl groups from the mercury compound and 38.5% from the solvent. The formation of active benzene (~ 7.9%) may perhaps be a quantitative indication of the transfer of phenyl radicals in the decomposition of diphenylmercury. In both cases, however, the biphenyl contains considerably more benzene rings from the solvent.

It is interesting that escape of phenyl radicals into the bulk of the solvent is not observed in the thermal decomposition of diphenylmercury in benzene containing finely divided metals such as platinum and copper[47]. Under these conditions biphenyl contains only phenyl radicals from the organometallic compound, the solvent taking practically no part (< 1.5%) in its formation. Almost all the phenyl radicals from the mercury compound recombined at the surface of the metals.

Bryce-Smith *et al.*[6] were able to isolate hydrobiphenyl from the photochemical decomposition of diphenylmercury in benzene in a current of nitrogen, but no mechanism for the formation of this compound is given.

As already pointed out, Bagdasar'yan *et al.*[45] found that the biphenyl resulting from the reaction of benzoyl peroxide with deuterobenzene contained up to 45% of phenyl radicals from the solvent. Razuvaev *et al.*[47] used benzene labelled with ^{14}C in this reaction, and found the biphenyl to contain 42% of active benzene rings.

In order to obtain direct confirmation of radical transfer, use was made of benzoyl peroxide containing radiocarbon ^{14}C in the ring. Decomposition of this peroxide in benzene at a molecular ratio of 1 : 10 was accompanied by the formation of radioactive benzene containing ~ 9% of the total activity of the peroxide. When the molecular ratio was lower (1 : 13) the quantity of radioactive benzene increased to 12%. The biphenyl obtained in these experiments contained 63% of phenyl groups from the peroxide and 37% from the solvent.

The relatively high discharge of phenyl fragments from the peroxide into the solution suggests that part of the radioactive benzene is formed in the latter case not only by transfer (scheme 2) but also by reaction (10d) or (10e).

It is difficult to judge the relative importance of the different processes. The isotopic composition of the biphenyl obtained in this reaction evidently also gives no answer to this question. In order to obtain a more rigorous proof of radical transfer, an investigation was made of the decomposition of mercurous acetate initiated with benzoyl peroxide in ^{14}C-labelled benzene medium[50]. The phenylmercury chloride isolated on treatment of the reaction mixture contained 6.2–12% of active phenyl groups from the benzene. The formation of active phenylmercury acetate is explained by labelled phenyl radicals regenerated by a transfer reaction attacking the mercury salt. This hypothesis is confirmed by the fact that, in the decomposition of labelled benzoyl peroxide in the presence of a mercury salt in benzene solution, the solvent after the reaction also contains a certain number of active molecules[51]. Mercuration of the benzene by the mercury acetate is excluded under these conditions (heating at 80° for 2 h).[52]

The photochemical decomposition of benzoyl peroxide under the influence of u.v. radiation takes place by a different mechanism from that of the thermal decomposition. The biphenyl obtained in labelled benzene contains only 9% of phenyl groups from the solvent. It is interesting that regeneration of C_6H_5 radicals does not occur under these conditions. When benzoyl peroxide labelled with ^{14}C in the ring is decomposed in benzene, the latter remains inactive after the reaction. It is assumed that photolysis of the peroxide involves the participation of excited molecules but not of free radicals.

Razuvaev *et al.* have observed the participation of the solvent in the formation of biphenyl by the decomposition of pentaphenylphosphorus in benzene[53]. The biphenyl obtained in an experiment with deuterated benzene contained 18% of deuterated phenyl groups, whereas use of radioactive benzene yielded a biphenyl containing only 5% of labelled radicals from the solvent[54]. Decomposition of deuterated [1–5-D_5] pentaphenylphosphorus in ordinary benzene solution yielded 11.9% of deuterium which had passed into the solution in the form of benzene. The resulting biphenyl contained 83.0% of phenyl groups from the phosphorus compound. In the experiment with radioactive pentaphenylphosphorus, 16.5% of the original activity was found in the benzene, while the biphenyl contained 88.5% of phenyl fragments from the parent substance.

In many papers the participation of the solvent in the reaction, established from the composition of the dimer R–R, is regarded as proof of the transfer of identical radicals. However, the incorporation of part of the solvent molecule in the dimer is not always confirmation that stepwise transfer has taken place. This follows from the work of Razuvaev *et al.*[47] on the decomposition of lead tetrabenzoate and nitrosoacetanilide in benzene labelled with ^{14}C. They showed that the biphenyl obtained in these reactions contains equal quantities of phenyl groups from the benzene and from the above substances. Nevertheless, transfer of radicals definitely does not take place in this case.

Actually, no transfer of phenyl radicals from the lead salt to the benzene is observed in the decomposition in ordinary benzene of lead tetrabenzoate labelled in the nucleus with ^{14}C. The benzene isolated after the reaction has remained inactive[47]. Similar results were obtained for the decomposition of nitrosoacetanilide[51].

It is interesting that phenylmercury acetate obtained by the decomposition of nitrosoacetanilide in ^{14}C-labelled benzene in the presence of metallic mercury at 35°–40° showed no activity[55].

Finely divided metals have no influence on the mechanism of the decomposition of such compounds. This is evident from the fact that the isotopic composition of the biphenyl formed by the decomposition of nitrosoacetanilide in ^{14}C-labelled benzene does not change in the presence of freshly precipitated copper[55].

The reaction between diphenyliodonium iodide and labelled benzene in the presence of metallic mercury at 80° yields practically non-radioactive phenylmercury iodide and iodobenzene. Consequently, the solvent does not take part in the reaction.

The decomposition of the double diazonium salt $(C_6H_5N_2)_2ZnCl_4$ in labelled benzene at 80° also takes place without the formation of free radicals[55]. The main product of this reaction, chlorobenzene, is practically inactive.

The latter reactions are doubtless of homolytic type, but they proceed by a crypto-radical mechanism.

Thus the stepwise transfer of phenyl radicals is not characteristic of the decomposition of a number of "organo-elementary" compounds in benzene solution. The regenerative exchange of C_6H_5 radicals is completely absent in many of the reactions studied; it takes place to a slight extent (not exceeding 5–8%) in the thermal decomposition of diphenylmercury, benzoyl peroxide, and pentaphenylphosphorus.

VI. REACTIONS INVOLVING THE TRANSFER OF ACYLOXY RADICALS IN CARBOXYLIC ACIDS

It is sometimes suggested that regenerative exchange of acyloxy radicals can take place readily in carboxylic acids[3,9]

$$RCOO^{\cdot} + RCOOH \rightleftarrows RCOOH + RCOO^{\cdot}, \qquad (11a)$$

but such views are unfortunately expressed without experimental proof.

Most of the experiments on the transfer of acyloxy radicals have been carried out with acyl peroxides. The decomposition of many peroxides is accompanied by the formation of RCOO· and R· radicals

$$(RCOO)_2 \rightarrow 2RCOO^{\cdot}; \quad RCOO^{\cdot} \rightarrow R^{\cdot} + CO_2. \qquad (11b)$$

Both these radicals are able to split off the hydroxyl hydrogen in carboxylic acid medium, with regeneration of an acyloxy radical; in the case of the RCOO· radical this occurs by reaction (11a), and in the case of R· as follows

$$R^{\cdot} + RCOOH \rightarrow RH + RCOO^{\cdot}. \qquad (11c)$$

In many cases the decomposition of acyloxy radicals RCOO· into R· and CO_2 is an exothermic process, as shown by the heats of decomposition, which have been determined for several radicals. In the case of R = CH_3, C_2H_5, and n-C_3H_7 their values are 17, 14, and 13 kcal mole^{-1} respectively[56].

In contrast to the decomposition of these radicals, that of the benzoyloxy radical is thermoneutral, and therefore C_6H_5COO· can exist for a longer period and the possibility of its exchange with the solvent is increased.

Thus the concentration of R· radicals in the decomposition of peroxides is governed by the stability of the acyloxy radicals RCOO·, *i.e.* by the rate of decarboxylation (11b).

Under the same conditions, therefore, the extents to which reactions (11a) and (11c) take place will differ with different peroxides. The stepwise transfer (11a) may be expected to be considerably more marked with the more stable acyloxy radicals RCOO·.

Fry *et al.*[10] found that the methane evolved in the decomposition of acetyl peroxide in acetic acid $^{14}CH_3COOH$ contained ~1% of the activity of the acid. On this basis they assume that formation of $^{14}CH_4$ is due to decarboxylation of the acid radicals $^{14}CH_3COO·$, which could have been produced by reaction (11a) or (11b).

In Szwarc's opinion[57], acetoxy radicals are unstable and decompose almost completely. In many solvents they do not escape from the reaction "cage". In cyclohexane, however, the acetoxy radical does not exhibit its normal instability. Shine[58] points out that, when acetyl peroxide decomposes in cyclohexane, only 65–75% of CO_2 is evolved. The rest of the acetoxy radicals form esters with the cyclohexane. He considers that free acetoxy radicals are not formed in this reaction.

Results obtained by Szwarc and Smid[59] provide some confirmation that the more stable acyloxy radicals can undergo reaction (11a). Thus methane and ethane were detected among the products of the decomposition of benzoyl peroxide in acetic and propionic acids respectively. In contrast to this, methane and fluoroform are not formed in the analogous reactions of propionyl peroxide in acetic and trifluoroacetic acids respectively. The authors conclude that the ethyl radicals formed by decarboxylation of the unstable $C_2H_5COO·$ are incapable of splitting off carboxylic hydrogen from acetic and trifluoroacetic acids.

In the case of benzoyl peroxide, 3–7% of its radicals attack the bond between hydrogen and the acid radical (RCOO–H), but which of the two possible radicals ($C_6H_5COO·$ or $C_6H_5·$) abstracts the hydrogen has not been established. It is suggested that formation of a hydrogen bond between the stable $C_6H_5COO·$ radical and the carboxyl group of the acid is more probable.

In order to demonstrate the stepwise transfer of acyloxy radicals in carboxylic acids, Razuvaev *et al.*[11] have investigated the behaviour of benzoyloxy and *m*-nitrobenzoyloxy radicals, which are more stable than acetoxy radicals, in acetic and benzoic acids labelled with ^{14}C in the carboxyl group. The evolution of labelled $^{14}CO_2$ indicated that such exchange had occurred. When benzoyl, acetyl benzoyl, and *m*-nitrobenzoyl peroxides decompose in $CH_3{}^{14}COOH$ and $C_6H_5{}^{14}COOH$ media at 70°–100°, the carbon dioxide evolved contains 2–25% of $^{14}CO_2$.

When benzoyl and acetyl benzoyl peroxides decompose in benzoic acid (molecular ratios of 1 : 7.5–50) the activity increases to 6.4%. The increase in activity is especially marked in the decomposition of *m*-nitrobenzoyl peroxide in [α-^{14}C] benzoic acid, the quantity of active $^{14}CO_2$ increasing to 12.6% and 21.2% respectively.

The interaction of the R· radical of the peroxide with the carboxylic hydrogen of the acid according to reaction (11c) has been determined for the decomposition of benzoyl and *m*-nitrobenzoyl peroxides in CH_3COOD, dehydrogenation of the carboxyl being estimated from the isotopic composition of the RD formed. In the case of the phenyl radical, 3% of the deuterium is split off from the CH_3COOD, and 1.2% in the case of nitrophenyl. Thus the quantity of labelled $^{14}CO_2$ is by no means completely balanced by the deuterated benzene or nitrobenzene. For example, with *m*-nitrobenzoyl peroxide the ratio $NO_2C_6H_4D/{}^{14}CO_2$ is only 0.01.

Consequently the carboxylic hydrogen of the acid is split off mainly by the acyloxy radical of the peroxide according to Eqn. (11a)

$$RCOO· + R'{}^{14}COOH \rightleftarrows [RCOO'HOO{}^{14}CR'] \rightleftarrows RCOOH + R'{}^{14}COO·$$
$$R'{}^{14}COO· \rightarrow R'· + {}^{14}CO_2.$$

Stepwise transfer depends greatly on the temperature and the peroxide concentration, the amount of active $^{14}CO_2$ increasing as the concentration and the temperature fall. Thus lowering the temperature from 100° to 70° in the decomposition of *m*-nitrobenzoyl peroxide in acetic acid causes an increase in the activity of the $^{14}CO_2$ evolved from 21.2% to 24.6%. This fully agrees with the fact that the difference in stability between the $CH_3COO·$ and *m*-$NO_2C_6H_4COO·$ radicals is still greater at the lower temperature.

It is interesting that the $^{14}CO_2/CO_2$ (total) ratio obtained[11] in the decomposition of benzoyl peroxide in $CH_3{}^{14}COOH$ is 0.046, in good agreement with Szwarc's results (CH_4/CO_2 ratio = 0.044).[56]

Stepwise transfer of acyloxy radicals in carboxylic acids takes place *via* an intermediate complex of the radical with the acid [RCOOHOOCR']. The great ease with which the carboxylic hydrogen is split off by the acyloxy radical coincides with the possibility of its forming a hydrogen bond with the acid[59].

It is clear from the above that the transfer of identical radicals ($CH_3COO·$ radicals in acetic acid, and $C_6H_5COO·$ radicals in benzoic acid) takes place to the extent of 1–2.3%.

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On the whole, reactions involving the transfer of different radicals belong to a very widespread class of chemical changes. Many cases are known in which such changes take place at a fast rate and are clearly in the nature of chain reactions. The transfer of identical radicals considered here is a particular case of this general class of chemical reactions.

It might be expected at first glance that the regenerative exchange of identical radicals would take place just as readily as exchange reactions involving different radicals. The available experimental data, however, contradict such an assumption. In all the examples investigated, as has been pointed out, stepwise transfer of radicals of one kind has occurred to only a slight extent, not more than by 1–5%. Thus even in the case of methyl and phenyl radicals such an exchange must be regarded as a subsidiary process. The main reactions undergone by radicals generated under the conditions investigated are recombination and disproportionation at the sites at which they have been produced.

This conclusion is not unexpected in the case of the unreactive stabilised radicals which have been mainly studied. The transfer of reactive radicals has been investigated only in the cases of methyl and phenyl. The interaction between $CH_3^·$ and CH_4 has been investigated only in the gas phase, as it is impossible in the liquid phase. The reaction between $C_6H_5^·$ and benzene is complicated, owing to complex formation between the reactants. Although several aspects of this question still remain somewhat obscure, a number of facts confirm the occurrence of transfer with a small proportion (~5–8%) of the radicals.

With regard to the stepwise reaction as a whole, it must be recognised that the amount of work published on this question is very small. Therefore it does not appear possible at the present time to reach a definite conclusion concerning the role of stepwise transfer of identical radicals in the migration of reactive centres throughout the volume of a reacting system and in increasing the life of radicals as kinetically independent units in many processes. The latter is the main feature of all exchange reactions and is widespread in the chemistry of free radicals. The same cannot be said with regard to identical radicals.

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