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Study of the Mechanism of Homolytic Reactions in Solution by a Combination of Isotopic and Mass-spectrometric Methods

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The use of mass spectrometry for the isotopic analysis of the products of homolytic reactions in deuterated solvents has made is possible to find the ratio of all isotopic forms of the substances studied and has opened up new possibilities in the study of the mechanism of homolytic reactions.
The present review examines critically work carried out by this method. These studies have made it possible to investigate the properties and regular features of the behaviour of various kinds of hydrocarbon radical in various solvents; have led to the discovery of reliable criteria for distinguishing free-radical processes from homolytic reactions taking place in the reaction complex without the liberation of radicals; and have made possible a deeper study of the mechanism of a number of types of free-radical reaction—the photolysis of organic halides and their reactions with metals, the thermal decomposition of benzoyl peroxide, diazo-compounds, and azo-compounds, various reactions of organometallic compounds, and processes of hydrocarbon oxidation. The bibliography contains 144 references.

CONTENTS

I.	Introduction	626
II.	Thermal decomposition of benzoyl peroxide and the photolysis of iodobenzene. Properties of phenyl radicals	626
III.	Photolysis of organic halides and the properties of the corresponding radicals	628
IV.	Various reactions of organometallic compounds	630
V.	Reactions of diazo- and azo-compounds	631
VI.	Processes of hydrocarbon oxidation	632
VII.	Reactions of organic halides with metals	633
VIII.	Possibilities and limitations of the method	636

I. INTRODUCTION

Since 1960, studies of the mechanism of homolytic reactions in solution by means of deuterium have been combined, on an increasing scale, with analysis of the products by low-voltage mass spectrometry. In this method (see for example Refs. 1 and 2), the ionising voltage in the mass spectrometer is reduced, so that the minimal number of fragment ions is formed. In a number of instances it is possible to obtain mass spectra corresponding to the molecular ions of isotopic forms of the compounds being analysed and to find the ratio of these forms directly from the ratio of the intensities of the corresponding peaks. These data have proved to be more valuable for an understanding of reaction mechanisms than previously available information on only the total concentration of deuterium in the products.

The considerable volume of work which has now been carried out by means of a combination of the isotopic and mass-spectrometric methods, and the importance of the results, have stimulated the publication of this review. The work examined in it has been directed towards the study of the properties of radicals with different structures, the investigation of the mechanism of a number of specific reactions with the intermediate formation (or assumed formation) of radicals, and the discovery of new criteria for distinguishing reactions involving free radicals from homolytic reactions taking place in the reactive complex. This last requires some explanation.

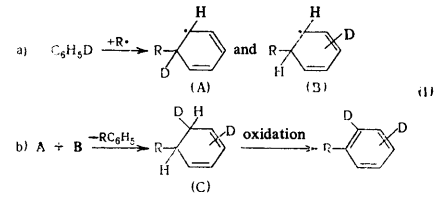
For any homolytic reaction in solution, mechanisms of two types are possible a priori—a free-radical mechanism and a mechanism which does not involve free radicals but which involves the redistribution of the bonds in an intramolecular or intermolecular reactive complex without the liberation of radicals (see for example, Refs. 3–5). It is obvious that the choice between these two possibilities is extremely important for an understanding of the mechanism. It is not always a simple matter to make this choice, however, since the two reaction paths may lead to the same products, and direct methods for detecting radicals are usually insufficiently sensitive, particularly in the most important case of highly reactive radicals. These difficulties have been responsible for a number of errors and contradictions in published data on the mechanism of homolytic reactions in solution and emphasise the importance of the discovery of reliable criteria for distinguishing a free-radical mechanism.

In this review, the results of studies carried out by means of deuterium and mass spectrometry are examined critically and compared with data obtained by other methods.

II. THERMAL DECOMPOSITION OF BENZOYL PEROXIDE AND THE PHOTOLYSIS OF IODOBENZENE. PROPERTIES OF PHENYL RADICALS

The first paper in this field, published by Eliel and coworkers[6], described the thermal decomposition of acyl peroxides. It was found in particular that benzoyl and acetyl peroxides in a solution of benzene C_6H_5D give, among other products, biphenyl and toluene containing the d_2 isotopic forms. This observation provided further confirmation of the processes, established a short time earlier[7], involving the disproportionation of radicals formed by the attachment of phenyl radicals to benzene,

and also proved the analogous reactions with methyl radicals [see scheme (1)]†:



(1)

The origin of the products of the reaction of R· radicals with benzene is now explained on the basis of the disproportionation and also the dehydrogenation and dimerisation of radicals of type (A). It was suggested[6] that the first two of these reactions take place with a kinetic isotopic effect, determining the isotopic effect for the formation of diaryls or alkylaryls (the differences between their isotopic composition and the composition calculated from the original benzene). The existence of this last effect, the presence of the isotopic forms d_2 in the diaryls or alkylaryls obtained in benzene-d_1, and the formation of dihydrodiaryls or dihydroalkylaryls (C) in an inert atmosphere were regarded by Eliel and coworkers[8] as indications that free radicals R· take part in the reactions. We shall return to these indications later, but meantime we would point out that the authors cited were unable to explain the isotopic composition of the biphenyl obtained in experiments with benzoyl peroxide. This was done later (see below).

In subsequent work[9-12], the decomposition of benzoyl peroxide and the photolysis of iodobenzene were studied in benzene C_6D_6 (also containing the d_5, d_4, and d_3 forms), in benzene ($C_6D_6 + C_6H_6$), or in cyclohexane ($C_6D_{12} + C_6H_{12}$). The solvents after the experiments, the biphenyls obtained, and the unreacted iodobenzene were subjected to mass-spectrometric analysis.

It was found that the benzenes C_6H_5D and C_6H_6 are formed in the reactions; the ratio of the other forms of benzene remains unchanged; the cyclohexane is enriched in deuterium, but new isotopic forms are not produced; the iodobenzene does not contain the form C_6D_5I and other deuterated forms; the isotopic composition of the biphenyls from the experiments in benzene exhibit characteristic features, which are discussed in detail below.

The thermal decomposition of benzoyl peroxide[6,7,13,14] and the photolysis of iodobenzene[15-18] undoubtedly take place with the intermediate formation of free phenyl radicals. The observations listed above make it possible to reach a number of conclusions regarding the properties of these radicals and the mechanism of the reactions being considered, and to formulate the indications of the participation of free phenyl radicals in homolytic reactions.

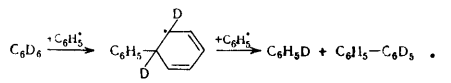
It has often been suggested (see for example Refs. 15, 16, 19–21), that phenyl radicals are capable of removing deuterium from heavy benzene:

$$C_6H_5^{\cdot} + C_6D_6 \rightarrow C_6H_5D + C_6D_5^{\cdot} \quad . \qquad (2)$$

Considerable importance was attributed to this process of "chain transfer" since it was assumed that it increases the "lifetime" of the phenyl radicals and the possibility of their reaction. A consequence of reaction (2) would be the formation of products containing C_6D_5 residues, namely C_6D_5I, $C_6D_5-C_6D_5$, $C_6D_5-C_6D_4H$, etc., formed by the recombination of $C_6D_5^{\cdot}$ with atomic iodine or by attachment to benzene from the medium. The iodobenzene after the experiments did not contain deuterium (see above), however, and the biphenyls did not contain forms with more than five deuterium atoms, and all the deuterium was present in one of the rings. Another consequence of reaction (2) with different isotopic forms of benzene from the medium should have been a change in the ratio of the quantities of these forms (as a result of the kinetic isotopic effect). In actual fact, however, the ratio does not change.

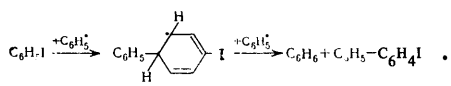
For these reasons it was concluded that "chain transfer" by the phenyl radicals does not take place to a significant extent either in its simplest form (2) or in a later version[20,22,23] involving a π complex of a radical and benzene. An analogous conclusion was reached on the basis of less direct data[24,25].

The formation of benzenes d_1 and d_0 in these experiments was attributed to reactions of type (3) with different isotopic forms of benzene from the medium:



This suggestion agrees with all the observations, since reactions (3) cannot lead to the formation of C_6D_5I or $C_6D_5-C_6D_5$ and should not lead to a change in the ratio of the heavy forms of benzene, since we should not expect significant kinetic isotopic effects in processes involving attachment to different isotopic forms of benzene.

The formation of benzene-d_0, however, cannot be attributed entirely to reactions (3), since in experiments in which the original benzene contained 95% deuterium, this reaction, for all possible values of the kinetic isotopic effect of its second stage, should give more benzene-d_1 than benzene-d_0, whereas the opposite was observed. Thus the formation of benzene C_6H_6 was attributed not only to process (3) but also to an analogous reaction of type (4) or, in the experiments with benzoyl peroxide, to processes of the same kind involving, instead of C_6H_5I, the peroxide or other aromatic compounds not containing deuterium.



(4)

This treatment, in particular, attributed the increase in the ratio C_6H_5D/C_6H_6 with decrease in the concentration of C_6H_5I or peroxide in benzene to the fact that the decrease leads to a decrease in the extent to which reaction (4) takes place. We shall see below that reactions of type (4) must be assumed in order to explain the isotopic composition of the biphenyls formed. It should also be noted that in the photolysis of iodobenzene, iodobiphenyl is in fact obtained[18].

In a medium of cyclohexane, benzenes-d_1 and -d_0 are formed by reactions (5), taking place with a kinetic isotopic effect, which explains the enrichment of the cyclohexane in deuterium after the experiments:

$$C_6H_5^{\cdot} + C_6D_{12} \rightarrow C_6H_5 + C_6D_{11}^{\cdot};\ C_6H_5^{\cdot} + C_6H_{12} \rightarrow C_6H_6 + C_6H_{11}^{\cdot} \quad . \qquad (5)$$

The magnitude of this effect was found to be 9. It was measured[26] relative to the quantities of C_6H_5D and C_6H_6 formed in the photolysis of C_6H_5I, since it was shown that in a medium of cyclohexane, reaction (5) is the only source of benzenes-d_1 and -d_0.

The behaviour of phenyl radicals in toluene $C_6H_5CD_3$ has not been studied by this method. It will be shown in the next section, however, that a number of radicals which are less reactive than $C_6H_5^{\cdot}$ remove hydrogen from the methyl

†Here and subsequently, one of the possible formulae for cyclohexadienyl radicals is given.

group of toluene. It may therefore be assumed that hydrogen is also removed by phenyl radicals, and that published data [27] which deny this removal are in this respect erroneous.

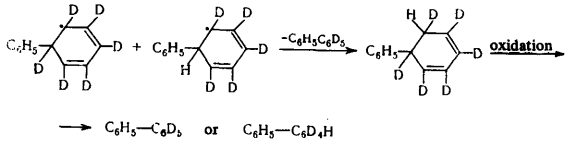
The reaction of the cyclohexyl radicals formed by reaction (5) was not specially studied in the works cited. From this work it followed, however, that C_6H_{11} radicals are not significantly capable of undergoing disproportionation and chain transfer:

$$C_6H_{11}^{\cdot} + C_6D_{11}^{\cdot} \rightarrow C_6H_{11}D + C_6D_{10}$$

$$C_6H_{11}^{\cdot} + C_6D_{12} \rightarrow C_6H_{11}D + C_6D_{11}^{\cdot} \qquad (6)$$

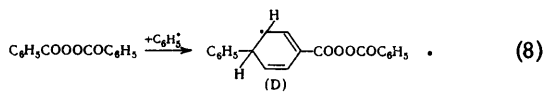
since the cyclohexane after the experiments did not contain the form $C_6H_{11}D$. This conclusion was later confirmed (see section III).

The isotopic composition of the biphenyls from these experiments shows that these substances are formed not only by the previously accepted schemes of types (3) and (7) involving various isotopic forms of benzene, but also by other paths. This followed from the results of a calculation which showed that the isotopic composition of the biphenyls obtained by schemes (3) and (7) or their combination differs from that observed experimentally: in the biphenyls the proportion of the d_0, d_1, and d_2 forms is higher, and among the other forms the proportion of d_5 is lower than that given by calculation. Allowance for kinetic isotopic effects does not give agreement between the calculated and experimental results.



$$\rightarrow C_6H_5{-}C_6D_5 \quad \text{or} \quad C_6H_5{-}C_6D_4H \qquad (7)$$

The experimental results can be explained, however, if it is assumed that in addition to reactions (3) and (7), the photolysis of C_6H_5I involves the disproportionation of iodohydrobiphenyl radicals, formed according to scheme (4), with isotopic forms of hydrobiphenyl radicals, formed by reaction (3). Calculation shows that this process leads to a decrease in the proportion of the biphenyl-d_5 in the biphenyls-d_3, -d_4, and -d_5. Moreover, it leads to the formation of the iodobiphenyl-d_1. The latter, and also the iodobiphenyl-d_0, give on photolysis the radicals $C_6H_5C_6H_3D^{\cdot}$ and $C_6H_5C_6H_4^{\cdot}$, which, like phenyl radicals, remove hydrogen and deuterium from the medium, giving the biphenyls-d_0, -d_1, and -d_2. In the experiments with benzoyl peroxide, the isotopic composition of biphenyl is explained analogously: in addition to reactions (3) and (7), the process involves attack by the phenyl radicals on the peroxide (and other aromatic compounds present), for example:



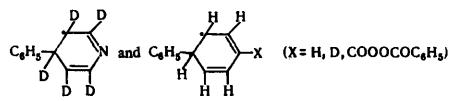
(8)

The radicals (D) after dehydrogenation and disproportionation give phenyl-substituted benzoyl peroxides-d_0 and -d_1, decomposition of which leads to the formation of $C_6H_5C_6H_4^{\cdot}$ and $C_6H_5C_6H_3D^{\cdot}$ radicals, which remove hydrogen and deuterium from the medium with the formation of the biphenyls-d_0, -d_1, and -d_2.

It will be shown below that the isotopic composition of the products of many reactions involving $C_6H_5^{\cdot}$ radicals in benzene are explained analogously.

Thus the isotopic composition of biphenyl results from the reactions of free radicals of various types. In biphenyl there is an increase in the concentration of the d_0, d_1, and d_2 forms, and a decrease in the concentration of the d_5 form. There characteristic features of the isotopic composition, as shown by Gragerov and coworkers (see for example, Refs. 10, 11, 27, 38, 74, 112), can be used to distinguish reactions involving $C_6H_5^{\cdot}$ free radicals in benzene from reactions taking place in the reactive complex. Another indication, as is clear from above, is the appearance of the benzenes-d_1 and -d_0 in benzene and cyclohexane after the experiments. It will be shown below that reactions which do not involve free radicals do not lead to the formation of the benzene-d_1 and -d_0 and give biphenyl with composition corresponding to that of the benzene solvent.

The thermal decomposition of benzoyl peroxide in heavy pyridine was studied recently [28] and it was shown that there is an extensive analogy in the reaction mechanisms in pyridine and in benzene. As in a medium of C_6D_6, the reaction gave the benzenes-d_1 and -d_0 and the products of the reaction of the C_6H_5 residues with the solvent—phenylpyridines, and also biphenyl. These results were attributed to the free-radical mechanism of the process. It was confirmed by the isotopic composition of the phenylpyridine and biphenyl, which could be explained only by assuming reactions, similar to those examined above, undergone by radicals of type (9), formed by the attachment of C_6H_5 to the isotopic forms of pyridine and the aromatic compounds present in the system



(9)

The experiments showed that the benzenes-d_1 and -d_0 are not formed by direct removal of hydrogen from pyridine:

$$C_6H_5^{\cdot} + NC_5D_5 \rightarrow C_6H_5D + NC_5D_4^{\cdot} \qquad (10)$$

since the reaction was not accompanied by a change in the ratio of the quantities of its isotopic forms and did not give heavy bipyridyls (the probable products of the attachment of pyridyl radicals to pyridine). The formation of the benzenes-d_1 and -d_0 was attributed to the dehydrogenation of radicals (9) by phenyl radicals.

III. PHOTOLYSIS OF ORGANIC HALIDES AND THE PROPERTIES OF THE CORRESPONDING RADICALS

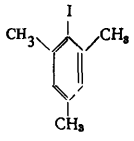
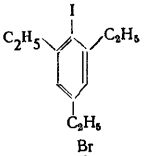
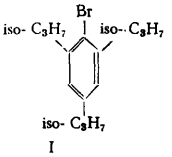
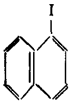
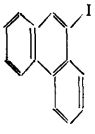
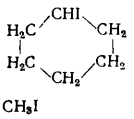
The free-radical mechanism of the photolysis of organic halides is firmly established [11,16,18,29,30], and this reaction provides a convenient and general source of free radicals. It is used in studies carried out by means of deuterium and mass spectrometry to investigate the properties and the mechanism of the reactions of hydrocarbon radicals. Simple aliphatic, substituted phenyl, aryl, and arylalkyl radicals and various radicals stabilised by conjugation have been studied in various solvents. A summary of the reactions studied and references to the corresponding literature are given in the Table.

The chief result of these studies is the establishment of the extensive similarity between a number of radicals and phenyl radicals and the discovery of the general regular features of their behaviour and of criteria which make it possible to detect the participation of free hydrocarbon radicals in reactions whose mechanism has not been established. Specific properties have been found only for the

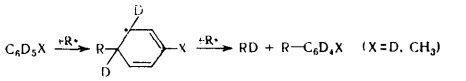
benzyl and cyclohexyl radicals, which will be examined separately.

The R' radicals studied (with the exception of the benzyl and cyclohexyl radicals), in the reactions given in the Table, give the hydrocarbons RD and RH. As with the phenyl radicals, the isotopic composition of the benzene, toluene with deuterium in the ring, and naphthalene after the experiments remains the same as that for the original solvents, whereas cyclohexane and toluene with deuterium in the methyl group are usually enriched in deuterium. The products of the direct removal of hydrogen from benzene by R' radicals are not obtained.

Reactions involving the photolysis of organic halides (the symbol + denotes that the reaction has been studied).

Halides	Heavy solvents: benzene	cyclohexane	deuteromethyltoluene	toluene with deuterium in the ring	naphthalene	triphenyldeuteromethane	References
p-$C_6H_5C_6H_4I$	+	+	+	–	–	–	31–33
	+	+	+	+	–	–	34
	+	+	+	+	–	–	34
	+	+	+	–	–	–	34
	+	+	+	+	+	–	31–33
	+	–	–	–	–	–	35
$C_6H_5CH_2I$	+	+	+	+	–	+	32,33,36
$(C_6H_5)_2CHBr$	+	–	–	–	–	–	35
$CH_2{=}CH{-}CH_2I$	+	+	+	–	–	–	35
	+	+	+	–	+	+	32,33,36
CH_3I	+	+	–	–	–	–	12,37–39
C_2H_5I	+	+	–	–	–	–	12,37–39

These facts were interpreted by assuming that the radicals R', like phenyl radicals, remove hydrogen directly from cyclohexane and the methyl group of toluene, but not from benzene, the toluene ring, or naphthalene. They add on to the latter and remove hydrogen from the resulting radicals of the cyclohexadienyl type, according to a scheme analogous to (3), for example:



(11)

This course of the reactions is confirmed by the fact that in a number of instances, products of the type RC_6D_4X have been isolated or their formation established from the mass spectra. Their isotopic composition, like the composition of the biphenyl formed by the reaction of phenyl radicals with benzene (section II), usually differed from that calculated entirely according to a scheme of type (11): the products contained less than the calculated quantity of the d_4 form and more than the calculated quantities of the d_0 and d_1 forms [12,34,37–39]. These characteristic features of the isotopic composition were explained by assuming that the formation of these substances, in addition to reactions of type (11), also involves processes of type (1b) including a disproportionation stage.

The hydrocarbons (RH + RD) obtained in these reactions contain much more of the d_0 than d_1 form even in experiments with highly deuterated solvents. As with the phenyl radicals, this was explained by assuming that the hydrocarbons RH are obtained not only by the above reactions with heavy solvents, which give the compounds RD and RH, but also by the reaction of the R' radicals with the original aromatic halides and other light aromatic compounds [according to a scheme analogous to (4)] or by the direct removal of hydrogen from aliphatic halides, other aliphatic compounds present in the system, and aliphatic substituents in the aromatic rings.

These data made it possible to formulate criteria for the participation of R' free radicals in reactions whose mechanisms have not been established. These are: 1) the appearance of the hydrocarbons RD and RH in reactions in a medium of heavy benzene, cyclohexane, toluenes with deuterium in the ring or in the methyl group, and naphthalene; 2) the presence in the products of the type $R{-}C_6H_5$, obtained in heavy benzene, of larger quantities of the isotopic d_0 and d_1 forms and smaller quantities of the d_5 form than expected by calculation according to a scheme of type (11).

Benzyl radicals in aromatic media behave like the other radicals examined above. Unlike the latter, however, they do not remove hydrogen at 30–40° from the methyl group of toluene or from cyclohexane (but they remove it from the C–H group of triphenylmethane). Thus not all of the critieria for a free-radical mechanism, formulated above, apply to benzyl radicals.

It was found that cyclohexyl radicals cannot remove hydrogen at 30–40°C from benzene, toluene, cyclohexane, naphthalene, or the CH groups of triphenylmethane, either directly or through intermediate attachment to aromatic rings. Thus the method examined here cannot be used to indicate these radicals.

It should be noted, however, that the properties of cyclohexyl radicals raise a number of problems. For example, the reason for their low reactivity compared with benzyl radicals, and the mechanism of formation of light cyclohexane and cyclohexene obtained by photolysis of iodocyclohexane in heavy media [33,36], are not understood. This makes it uncertain whether the photolysis of $C_6H_{11}I$ does in fact give free radicals C_6H_{11}, particularly in view of the recent report [40,41] that the cyclohexyl radicals obtained by the photolysis and thermal decomposition of $Pb(C_6H_{11})_4$ and $Pb_2(C_6H_{11})_6$ in benzene remove hydrogen from the medium. It should be remembered, however,

that the $C_6H_{11}^{\cdot}$ radicals formed by the removal of hydrogen from cyclohexane under the influence of phenyl radicals do not disproportionate and do not remove hydrogen from cyclohexane [12]. The same was found for the $C_6H_{11}^{\cdot}$ radicals produced by the action of naphthyl radicals on cyclohexane [31-33]. Thus the properties of cyclohexyl radicals require further study.

Some other remarks and comparisons may be made regarding these data.

The study of 2,4,6-trialkylphenyl radicals was of interest in connection with the fact that steric hindrance can alter the properties of radicals considerably. The data show, however, that the properties of these radicals are qualitatively analogous to the properties of $C_6H_5^{\cdot}$ radicals.

Allyl radicals, as expected (but contrary to certain published work [42]), are much more reactive than benzyl radicals. It is difficult to reconcile their ability to remove hydrogen from cyclohexane with the data in Ref. 43 and with some of the data in Ref. 42.

The reaction of diphenylmethyl radicals with benzene contradicts the data of Ref. 44, which are apparently erroneous in this respect. It must be assumed that these radicals, like benzyl radicals, do not react at low temperatures with cyclohexane and the methyl group of toluene.

IV. VARIOUS REACTIONS OF ORGANOMETALLIC COMPOUNDS

The mechanism of the photolysis of diphenylmercury was not elucidated completely by a large number of studies, carried out in particular by the isotopic method. Thus in Refs. 15, 19, 21, 22 it was concluded that this reaction in benzene takes place by a free-radical mechanism, whereas in Refs. 45 and 46 it was concluded that the reaction takes place in the reactive complex, without the liberation of radicals. The photolysis in cyclohexane and cyclohexene was explained by means of a free-radical scheme [46,47].

The use of a combination of the isotopic and mass-spectrometric methods showed [12,37-39] that the photolysis in benzene or in cyclohexane takes place by a free-radical mechanism, and also made it possible to determine various details of the mechanism.

In heavy solvents it was established that the benzenes-d_1 and -d_0 are formed, and this provided proof that $C_6H_5^{\cdot}$ radicals take part in the reaction. The fact that the form C_6H_6 predominates in the experiments in benzene was attributed, as with the photolysis of iodobenzene and the decomposition of benzoyl peroxide, to the fact that this form, unlike C_6H_5D, is obtained not only by a reaction of type (3) with the forms of benzene from the medium, but also by a reaction analogous to (4), involving diphenylmercury:

$$(C_6H_5)_2Hg \xrightarrow{+C_6H_5^{\cdot}} \underset{(E)}{C_6H_5\text{-}C_6H_6\text{-}HgC_6H_5} \xrightarrow{+C_6H_5^{\cdot}} C_6H_6 + C_6H_5C_6H_4HgC_6H_5. \quad (12)$$

Further proof of the free-radical mechanism of the photolysis of diphenylmercury in benzene is provided by the characteristic features of the isotopic composition of the biphenyl produced. This does not contain biphenyls with more than five deuterium atoms and contains more of the d_0, d_1, and d_2 forms, and less of the d_5 form, than required by calculation according to reactions (3), (7), or their combinations, with any possible kinetic isotopic effects. This observation was attributed to the fact that the disproportionation of type (7) involves the radicals (E), which do not contain deuterium, and this leads to a decrease in the concentration of the d_5 form in the biphenyl obtained and to the appearance of $C_6H_5C_6H_4HgC_6H_5$ and $C_6H_5C_6H_3DHgC_6H_5$ molecules, which on photolysis give $C_6H_5C_6H_4^{\cdot}$ and $C_6H_5C_6H_3^{\cdot}$ radicals; the latter remove hydrogen and deuterium from the medium, with the formation of the biphenyls-d_0, -d_1, and -d_2.

The isotopic composition of the undecomposed biphenylmercury residue was also studied, and it was found that it does not contain deuterium. These results are of interest in connection with the fact that the introduction of tracer from the benzene into the diphenylmercury during photolysis was considered [15,21,22] to be one of the most important proofs of the existence of "chain transfer" of phenyl radicals (see section II). The introduction was not confirmed in subsequent work by the same authors [45,46].

Recently, they returned again [41,48] to the study of the photolysis and thermal decomposition of diphenylmercury, and also the photolysis and thermal decomposition of tetraphenyl-lead and hexaphenyldilead in heavy benzene, this time using the isotopic and mass-spectrometric methods. It was established that the reactions give the benzenes-d_1 and -d_0 and biphenyls of three kinds: unlabelled—A, labelled in one ring—B, and labelled in two rings—C. The mechanism of these reactions was examined for the example of the photolysis of diphenylmercury. The biphenyl A, in the opinion of the authors cited, is obtained as a result of the intramolecular decomposition, catalysed by mercury, of part of the diphenylmercury, with recombination of the radicals on the metal surface. We have seen, however, that another explanation for the appearance of this biphenyl is possible.

The formation of the biphenyl B was attributed to two mechanisms—decomposition in the reactive complex and free-radical reaction according to schemes (3) and (7)—and the production of the biphenyl C was attributed to free-radical "chain transfer" (2) and attachment of the radicals $C_6D_5^{\cdot}$, $C_6D_4H^{\cdot}$, etc., formed according to scheme 2, to the isotopic forms making up the heavy benzene.

It was later shown [49] that the biphenyls A, B, and C are also obtained in the photolysis and thermal decomposition of triphenylbismuth in heavy benzene, and the same explanations were put forward.

The formation of the biphenyl C in photolysis at low temperatures and the conclusion, on this basis, that "chain transfer" of phenyl radicals takes place do not agree with the work on the photolysis of diphenylmercury [11,37-39] or with other data on the behaviour of phenyl radicals in heavy benzene (see section II). The following considerations also cast doubt on the correctness of this observation. The isotopic composition of the biphenyl C can readily be calculated from the composition of the benzene solvent. The results of the calculation, however, show a marked lack of correspondence with the composition found in the works cited. It may therefore be assumed that that part of the work which refers to the production of the biphenyl C and the "chain transfer" in the photolysis is erroneous. It is not excluded, however, that "chain transfer" is observed at high temperatures, under the conditions of the thermal decomposition.

The decomposition and oxidation of diphenylzinc in heavy benzene have been studied [50,51]. Both reactions led to the appearance of the benzenes-d_1 and -d_0 and gave the biphenyls A and B, together with a small quantity of C in the thermal decomposition. The formation of the biphenyl A was attributed to intramolecular decomposition or oxidation of $Zn(C_6H_5)_2$, and the formation of the biphenyl B was attributed to reaction between the solvent and $C_6H_5^{\cdot}$ radicals

formed on decomposition or oxidation. Under the conditions of the thermal decomposition, the diphenylzinc underwent isotopic exchange with benzene. It must therefore be assumed that the biphenyl C was obtained by reaction between the solvent and labelled phenyl radicals from the organometallic compound, which had undergone partial exchange.

It was recently established[28] that the photolysis of diphenylmercury in heavy pyridine takes place by a free-radical mechanism. All that has been said regarding the decomposition of benzoyl peroxide in pyridine (section II) applies to the mechanism of this reaction.

V. REACTIONS OF DIAZO- AND AZO-COMPOUNDS

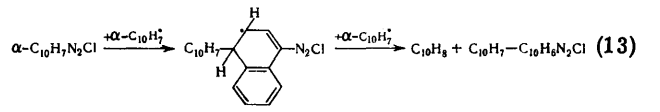
Despite extensive published material[3,14,30,52-55], the participation of free radicals in the thermal decomposition of diazonium salts was disputed—evidence was published for[30,56,57] and against[58] this suggestion. The same is true of the thermal decomposition of nitrosoacetanilide (NAA)[14,30,53,55] and phenylazotriphenylmethane (PAT)[59]: evidence has been put forward for[60-70] and against[8,22,58] a free-radical mechanism. Confirmation was also required for the free-radical mechanism of the Gomberg–Bachmann reaction[14,30,52,53,55,71,72]. The mechanism of the arylation of benzene by aromatic amines under the influence of isopentyl nitrite in neutral medium[73] was not studied. Studies of these reactions by a combination of the isotopic and mass-spectrometric methods are discussed below.

The decomposition of phenyldiazonium fluoroborate and chloride was studied in various deuterated solvents[9,10,12,38,39,74,75]. In benzene, cyclohexane, toluene $C_6D_5CH_3$, bromobenzene, and chloroform, the fluoroborate did not give the benzenes-d_1 and -d_0, and the biphenyl obtained in a medium of benzene had an isotopic composition corresponding to the combination of the C_6H_5 residues from the salt and from the solvent. Thus $C_6H_5^{\cdot}$ radicals do not take part in the decomposition of $C_6H_5N_2BF_4$. $C_6H_5^{+}$ ions (whose reactions were detected in some examples of the decomposition of the fluoroborate[76,77]) apparently do not take part in the decomposition either, since it may be assumed that these ions, like Alk^+ ions, which remove hydrogen from Alk–H molecules[78,79], react with the solvents to give the benzenes-d_1 and -d_0. The decomposition of $C_6H_5N_2BF_4$ takes place in the reactive complex.

The decomposition of $C_6H_5N_2Cl$ in the same solvents, on the other hand, gave the benzenes-d_1 and -d_0, and the biphenyl obtained in a medium of benzene had the isotopic composition characteristic of free-radical reactions. Thus $C_6H_5^{\cdot}$ free radicals take part in this reaction. Their yield, however, is much less than that in the other reactions examined, since the yield of benzenes-$(d_1 + d_0)$ is unusually small. The process probably takes place in two directions—by the free-radical mechanism and in the reactive complex—with the latter direction predominating.

In the decomposition of $C_6H_5N_2BF_4$ in heavy pyridine and α- and β-picolines with deuterium in the methyl group, all the indications of the participation of $C_6H_5^{\cdot}$ free radicals were observed (the formation of the benzenes-d_1 and -d_0, and the characteristic isotopic composition of the phenylpyridine), whereas in the decomposition of $C_6H_5N_2Cl$ they were observed only in a medium of picolines. The fluorobenzene and chlorobenzene formed in these reactions did not contain deuterium.

The intermediate formation of free radicals was established in the thermal decomposition of α-naphthyldiazonium chloride[32,33,80] in heavy benzene, cyclohexane, and naphthalene. The reaction led to the formation of the naphthalenes-d_1 and -d_0, obtained by direct removal of hydrogen from cyclohexane and according to schemes of types (11) and (13):



$$\alpha\text{-}C_{10}H_7N_2Cl \xrightarrow{+\alpha\text{-}C_{10}H_7^{\cdot}} C_{10}H_7\text{–}N_2Cl \xrightarrow{+\alpha\text{-}C_{10}H_7^{\cdot}} C_{10}H_8 + C_{10}H_7\text{–}C_{10}H_6N_2Cl \quad (13)$$

The last reaction is analogous to scheme (4).

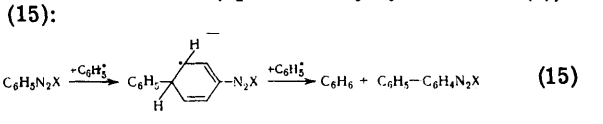
The chloronaphthalene from these experiments did not contain deuterium, so that it was not formed by chlorination of the naphthalene by atomic chlorine. The chloronaphthalene was possibly obtained in the "solvent cage":

$$\alpha\text{-}C_{10}H_7N_2Cl \xrightarrow{-N_2} (\alpha\text{-}C_{10}H_7^{\cdot} + Cl^{\cdot}) \rightarrow \alpha\text{-}C_{10}H_7Cl \quad (14)$$

and the low yields may be due to the fact that most of the radicals leave the "cage" and do not give this substance. It is not excluded that some chloronaphthalene is obtained by a reaction which does not involve free radicals, as with the halogenobenzenes.

To explain these results, it was suggested[75] that the free-radical mechanism of decomposition of diazonium salts plays a greater role, the more stable the radicals formed, and that this stability is determined not only by their chemical character but also by solvation. It was still not clear, however, why the decomposition of $C_6H_5N_2Cl$ in pyridine takes place by a reaction which does not involve free radicals.

The decomposition of NAA and PAT in heavy benzene or cyclohexane[81] takes place by a free-radical mechanism. It gave benzenes-d_1 and -d_0, presumably by reactions (3), (5), and (15):



$$C_6H_5N_2X \xrightarrow{+C_6H_5^{\cdot}} C_6H_5\text{–}N_2X \xrightarrow{+C_6H_5^{\cdot}} C_6H_6 + C_6H_5\text{–}C_6H_4N_2X \quad (15)$$

$X = -OCOCH_3$ or $-C(C_6H_5)_3$

to which, in the case of PAT, was added reaction with the triphenylmethanes formed in the experiments:

$$C_6H_5^{\cdot} + (C_6H_5)_3CH \text{ (or } (C_6H_5)_3CD) \rightarrow C_6H_6 \text{ (or } C_6H_5D) + (C_6H_5)_3C^{\cdot} \quad (16)$$

The latter were evidently obtained by the removal of hydrogen or deuterium from radicals of the cyclohexadienyl type by $(C_6H_5)_3C^{\cdot}$ radicals according to schemes of types (3) and (15) with $(C_6H_5)_3C^{\cdot}$ instead of $C_6H_5^{\cdot}$ in the second stages. The formation of triphenylmethanes confirmed indirectly the free-radical mechanism of the decomposition of PAT. Direct confirmation was obtained by the EPR method, which made it possible to identify the triphenylmethyl radicals.

Eliel and coworkers[8] found, however, that in the decomposition of NAA and PAT in benzene-d_1, biphenyl is obtained without a kinetic isotopic effect and does not contain the d_2 form, and the products of the reactions in an inert atmosphere do not contain dihydrobiphenyl. This absence of the "indications of the participation of free radicals in the reactions" (see section II) was interpreted as proof that the decomposition of NAA and PAT takes place by a mechanism which does not involve free radicals.

We cannot agree with this intrepretation. It has been correctly noted[64] that all the above "indications" of Eliel and coworkers are the result of disproportionation of radicals of the cyclohexadienyl type (see section II). Their presence proves that the reactions take place by a free-radical mechanism, but their absence merely indicates that disproportionation does not take place.

It has also been demonstrated[81] that disproportionation does not take place, since the biphenyls obtained in the work cited contained the forms from d_5 to d_2 in the ratio corresponding to that calculated according to scheme (3).

Disproportionation of radicals of the cyclohexadienyl type is apparently suppressed by more rapid reactions involving dehydrogenation and combination with $(C_6H_5)_3C^\cdot$ or $C_6H_5-N=N-O^\cdot$ radicals, which are formed in appreciable concentrations, because of their relative stability[64,68].

The biphenyls in the experiments being discussed[81] contained larger quantities of d_1 and d_0 forms relative to those calculated according to scheme (3), and a source of these forms, in addition to reactions (3), is provided by the thermal decomposition of $C_6H_5C_6H_4N_2X$ molecules formed according to scheme (15), and the removal of hydrogen and deuterium from the medium by the $C_6H_5C_6H_4^\cdot$ radicals produced (see section II). Thus the isotopic composition of the biphenyls also indicates that the thermal decomposition of NAA and PAT takes place by a free-radical mechanism.

Of the Gomberg–Bachmann reactions, the reactions of $C_6H_5N_2Cl$, α-$C_{10}H_7N_2Cl$, and p-$C_6H_5C_6H_4N_2Cl$ with aqueous alkali in benzene and cyclohexane have been studied[10,12,38,39,74] and the free-radical mechanism of these reactions has been proved. Like other free-radical processes, the reactions led to the formation of the benzenes-d_1 and -d_0, the naphthalenes-d_1 and -d_0, and the biphenyls-d_1 and -d_0 respectively, obtained by the direct removal of hydrogen from cyclohexane by the radicals according to schemes of types (3) and (11) and by reactions analogous to reactions (13) and (15). The biphenyl from the experiments with $C_6H_5N_2Cl$ in benzene contained smaller quantities of the d_5 form and larger quantities of the d_0, d_1, and d_2 forms relative to those calculated according to scheme (3), and this again indicated that the reaction takes place by a free-radical mechanism. In the experiment with $C_6H_5C_6H_4N_2Cl$, in accordance with the free-radical scheme, one of the products was terphenyl.

The reaction of aromatic amines $ArNH_2$ with isopentyl nitrite was studied in heavy benzene, cyclohexane, or naphthalene[82] with the compounds aniline, p-nitroaniline, p-anisidine, α-, and β-naphthylamines, p-aminobiphenyl, and γ-aminopyridine. A free-radical mechanism was found for all these reactions: the products contained the compounds ArD and ArH, formed, as usual, by the removal of hydrogen from cyclohexane by Ar$^\cdot$ radicals according to reactions of type (11) with benzene or naphthalene and also ArH formed by the removal of hydrogem from isopentyl nitrite and its reaction products by the radicals, and also by a reaction analogous to reaction (11), but with the original amines instead of benzene or naphthalene. The last reaction, in the case of aniline, should give aminobiphenyl, which, by reacting with isopentyl nitrite, leads to the formation of the biphenyls-d_1 and -d_0. These were in fact found in the experiment with aniline in benzene in quantities greater than that calculated according to scheme (11). In the other experiments the isotopic composition of the products of the arylation of benzene coincided with that calculated according to this scheme. Thus in this instance, as in the decomposition of NAA and PAT, the disproportionation of radicals of the cyclohexadienyl type is not significant. This reaction is apparently suppressed by the more rapid dehydrogenation, possibly under the influence of isopentyl nitrite or its decomposition products.

The radicals β-$C_{10}H_7^\cdot$, p-$O_2NC_6H_4^\cdot$, p-$CH_3OC_6H_4^\cdot$, and γ-$NC_5H_4^\cdot$, obtained by the reaction of the corresponding amines with isopentyl nitrite, were first studied in the work cited by means of a combination of isotopic and mass-spectrometric methods. From the foregoing it follows that their behaviour in benzene, cyclohexane, and naphthalene does not differ from that of other aryl or simple alkyl radicals.

In the work cited it was suggested that diazo-hydroxides are formed in intermediate stages:

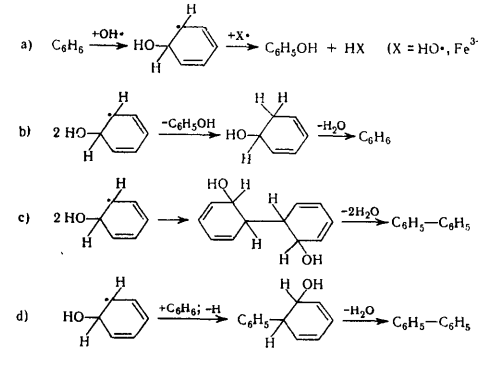
$$ArNH_2 + C_6H_{11}ONO \xrightarrow{-C_6H_{11}OH} ArNHNO \rightarrow Ar-N=N-OH \quad . \qquad (17)$$

The same substances are obtained in the first stages of the Gomberg–Bachmann reaction. The similarity in the mechanisms of the two reactions was recently confirmed[83] by the fact that in the reaction of aniline with isopentyl nitrite in benzene the EPR method established the existence of the same radicals $C_6H_5-N=N-O$, which were recently assumed[72] to be intermediate products of the Gomberg–Bachmann reaction.

VI. PROCESSES OF HYDROCARBON OXIDATION

It has been shown by isotopic and mass-spectrometric methods[12,38,84,85] that in the oxidation of a mixture of benzenes C_6D_6 and C_6H_6 by potassium permanganate in acid medium or by ammonium peroxosulphate catalysed by Ag^+ ions, the unreacted hydrocarbon residue does not contain the benzene-d_1. It was assumed that radicals are formed in the intermediate stages of the oxidation of organic compounds by permanganate (for example Refs. 86 and 87) and by peroxosulphate (for example Ref. 88). The results given above show that in the examples being considered these radicals cannot be $C_6H_5^\cdot$ radicals. On the other hand, the radiolysis of dry benzene (C_6D_6 + C_6H_6) gave biphenyl with the isotopic composition corresponding to a free-radical scheme of formation, confirming the previously assumed (for example Ref. 89) participation of $C_6H_5^\cdot$ radicals in this reaction.

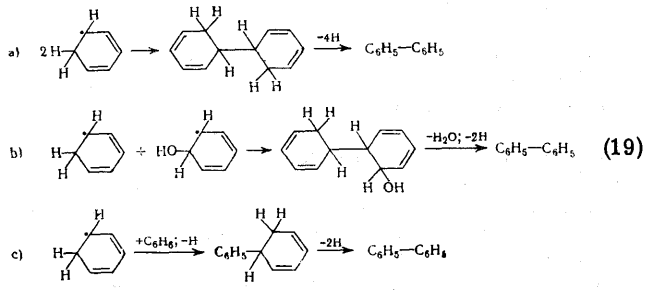
$C_6H_5^\cdot$ radicals are not obtained in the oxidation of heavy benzene by Fenton's reagent or pernitrous acid or in the radiolysis of a degassed water–benzene mixture[12,84,85,90]. These data refuted the commonly encountered schemes for radiolysis and oxidation by Fenton's reagent involving the participation of phenyl radicals (for example Refs. 91–94), assumed to be produced by the removal of hydrogen from benzene by OH$^\cdot$ radicals. We give below alternative schemes (for example Refs. 93–96) in which OH$^\cdot$, like other radicals, do not remove hydrogen from benzene, but add on to it:



(18)

The isotopic composition of the products of these reactions made it possible to refine these schemes and to obtain new data on the mechanism.

The composition of the biphenyls concided with that calculated for reactions (18*c*) or (18*d*). For the radiolysis, it made it possible to reject another possible mechanism—the formation of biphenyl from $C_6H_7^{\cdot}$ ($C_6D_7^{\cdot}$) radicals, assumed to be formed [97,98] by the attachment of hydrogen atoms from the water to benzene:

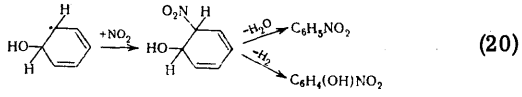


(19)

since the isotopic composition of the biphenyl differed sharply from that calculated according to schemes (19). Disproportionation of the radicals $C_6H_7^{\cdot}$ and $C_6D_7^{\cdot}$ does not take place either. This would have given (after dehydrogenation of the C_6H_7D disproportionation product) the benzene-d_1, which was not detected.

The phenol obtained in oxidation with Fenton's reagent had an isotopic composition close to that calculated according to scheme (18*a*) but markedly different from that corresponding to scheme (18*b*) with allowance for the dehydrogenation of dihydrophenol. Thus disproportionation of the hydrophenol radicals (18*b*), if it takes place at all, does not take place to a significant extent. This is apparently related to the high concentration of oxidising agents (Fe^{3+}, H_2O_2) in the reaction system; these rapidly dehydrogenate the radicals according to reaction (18*a*). The results obtained confirm schemes (18*a*), (18*c*), and (18*d*).

It has been suggested [99] that in the reaction of benzene with pernitrous acid, nitrobenzene and nitrophenol are formed according to the scheme:

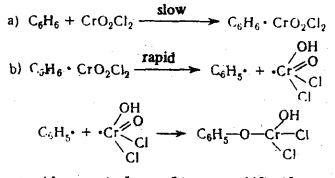


(20)

The isotopic composition of the reaction products showed that the removal of water and hydrogen takes place with a kinetic isotopic effect and therefore takes place in the slow stages of reactions (20). Another possible mechanism for the formation of nitrophenol—hydroxylation of nitrobenzene—cannot be distinguished from mechanism (20) on the basis of the results being discussed. It should be noted that a mechanism which does not involve free radicals is also possible for oxidation by pernitrous acid [12] and that the results being discussed do not make it possible to choose between this and scheme (20).

In the mechanism of the oxidation of hydrocarbons by chromyl chloride (Etard's reaction), the problem of the nature of the first, most important, oxidative stage, which is complete with the formation of an insoluble complex of the hydrocarbon and CrO_2Cl_2, was unresolved. Ionic (for example Ref. 100), radical [101-103], and molecular [104] mechanisms were proposed for this stage. It was recently shown [103] that the free-radical scheme agrees with all published data, but direct confirmation was given only in Refs. 9, 10, 12, 32, 38, 105. In these experiments, mixtures of light and heavy benzene, toluene, and naphthalene or solutions of toluene, diphenylmethane, biphenyl, naphthalene, anthracene, and phenanthrene in heavy benzene or in heavy cyclohexane were subjected to incomplete oxidation. It was found that the unreacted residues of the oxidised hydrocarbons contained their d_1 isotopic forms, indicating the intermediate formation of the radicals corresponding to the hydrocarbons. The oxidation of toluene and diphenylmethane in benzene gave further proof of the intermediate formation of benzyl and diphenylmethyl radicals—the isolation of benzophenone and triphenylcarbinol, which are products of the oxidation of diphenylmethane and triphenylmethane, formed by the addition of the $C_6H_5CH_2^{\cdot}$ or $(C_6H_5)_2CH^{\cdot}$ radicals to benzene according to scheme (11).

In the works cited and in Ref. 106 it was established that a kinetic isotopic effect is not observed in the oxidation of benzene and naphthalene by CrO_2Cl_2, but that this effect is observed in the oxidation of toluene and triphenylmethane. The reaction scheme finally proposed is given below for the example of benzene:



(21)

(22)

Analogous reactions take place with the second molecule of the oxidising agent. Reaction (22) competes with the usual reactions of $C_6H_5^{\cdot}$ radicals in benzene—reaction (3), which gives benzene-d_1, and reaction (7). In some instances, for example in the oxidation of toluene and triphenylmethane, the slow stage is stage (21*b*), and this leads to a kinetic isotopic effect.

The participation of free radicals in Etard's reaction was recently confirmed directly by the EPR method [107].

VII. REACTIONS OF ORGANIC HALIDES WITH METALS

The participation of free radicals in the mechanism of the reactions of organic halides with metals is often assumed, but it has been demonstrated convincingly in only a few studies. Studies of the reactions of magnesium, lithium, sodium, potassium, and copper with organic halides by a combination of isotopic and mass-spectrometric methods are discussed below. These studies not only proved that these reactions involve free radicals, but also revealed many aspects of their mechanisms.

A number of authors (for example Refs. 108 and 109) assumed on the basis of indirect data that reactions of this kind involving magnesium take place by a free-radical mechanism. This was subsequently confirmed more convincingly [110,111], but it was still not clear whether this mechanism was general and whether it still holds in the presence of ether, in which preparative syntheses are usually carried out.

In the study of the reaction of magnesium with iodobenzene in heavy benzene or cyclohexane [9,10,12,38,39,112], the substances A isolated directly from the reaction mixture and the substances B obtained by the action of water on the residue from the complete separation of compounds A were analysed separately. Benzenes-d_0 and -d_1 were found in the compounds A, indicating that the free radicals $C_6H_5^{\cdot}$ take part in the reactions. The formation of the radicals was explained by the scheme:

$$C_6H_5I + Mg \rightarrow C_6H_5^{\cdot} + MgI^{\cdot} \rightarrow C_6H_5MgI \qquad (23)$$

and the formation of the benzenes-d_1 and -d_0 was explained by the usual schemes (3), (4), and (5). In the biphenyl A from the experiments in benzene, the proportions of the

forms from d_5 to d_2 corresponded to those calculated according to scheme (3), whereas the proportions of the d_1 and d_0 forms were found to be much greater. Thus reactions of type (3) provide the main source of the biphenyls from d_5 to d_2, and the disproportionation (7) is not significant. The formation of the biphenyl-d_0 was attributed to the reaction:

$$C_6H_5MgI + C_6H_5I \rightarrow C_6H_5{-}C_6H_5 + MgI_2 \quad (24)$$

and the formation of the biphenyls-d_1 and some -d_0, as in other examples of reactions involving phenyl radicals in benzene, was attributed to the removal of hydrogen or deuterium from the medium by $C_6H_5C_6H_4^{\cdot}$ radicals. The latter were produced from iodobiphenyl [formed by reaction (4)] by a scheme similar to schemes (23) or (26) (see below).

The benzene B was formed by the reaction

$$C_6H_5MgI + H_2O \rightarrow C_6H_6 + MgIOH \quad . \quad (25)$$

It did not contain deuterium, indicating the absence of isotopic exchange between C_6H_5MgI and benzene (discovered earlier [113]). The biphenyl B from the experiment in benzene was apparently obtained analogously from $C_6H_5C_6H_4MgI$. It contained a small quantity of deuterium, probably as a result of isotopic exchange between $C_6H_5C_6H_4MgI$ and biphenyl A under the severe conditions of the separation of the latter. The compounds B obtained in benzene or cyclohexane included hydrogen (H_2 + HD). The formation of HD molecules was attributed to the dehydrogenation of radicals of the hydrobiphenyl type by the species $MgI^{\cdot}$ or to the removal of hydrogen from cyclohexane by these species and reaction of the resulting MgID molecules with water. The existence of compounds of the type MgIH was recently confirmed [114]. The biphenyls A and B from the experiments in cyclohexane did not contain deuterium, since they were formed by reaction (24) and by the reaction of $C_6H_5C_6H_4MgI$ with water.

It may be noted that the possibility of formation of radicals by reactions of type (23) has been doubted (see for example Refs. 109 and 110) and it has been suggested that the radicals are obtained in processes described by overall equations of type (24). Special experiments [115] confirmed that reaction (24) takes place by a free-radical mechanism. This does not alter the essential features of the interpretation given for the mechanism of reaction of iodobenzene with magnesium, but only modifies stage (24), interpreting it as a radical reaction:

$$C_6H_5MgI + C_6H_5I \rightarrow MgI_2 + 2C_6H_5^{\cdot} \quad (26)$$

It must be assumed that most of the $C_6H_5^{\cdot}$ radicals formed according to this scheme combine in a "solvent cage", and this explains the high percentage of the d_0 form in the biphenyl obtained in benzene C_6D_6 according to reaction (26) and in the biphenyl A.

Returning to process (23) and the analogous reaction of $C_6H_5C_6H_4I$, we may note that their free-radical mechanism was assumed [12] because it was impossible to explain the formation of hydrogen HD without assuming the participation of $MgI^{\cdot}$ radicals. $MgI^{\cdot}$ radicals may also be obtained, however, by the thermal decomposition of organomagnesium compounds (see below and Ref. 116). Thus the free-radical nature of reaction (23) and its analogues has not yet been proved.

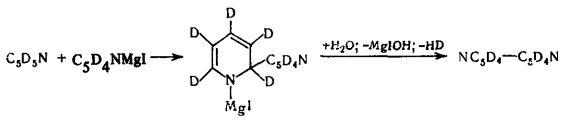
It has been shown [33, 115] that the free-radical mechanism of the reaction of magnesium with iodobenzene is preserved in the presence of ether. Free-radical mechanisms were also found for the reactions of magnesium with α-iodonaphthalene in heavy benzene, with p-iodobiphenyl in heavy benzene mixed with ether and in heavy cyclohexane mixed with ether, and with benzyl chloride in heavy benzene mixed with ether. These reactions gave naphthalenes-d_1 and -d_0, biphenyls-d_1 and -d_0, and toluenes-d_1 and -d_0 respectively. Moreover, terphenyl was obtained in the experiments with iodobiphenyl in benzene/ether, and diphenylmethane and bibenzyl were obtained in the experiments with benzyl chloride.

The mechanism of these reactions is analogous to that examined above: the hydrocarbons RD and RH were obtained according to schemes (11), (5), and (4) with light aromatic compounds and by removal of hydrogen from ether by the radicals. Terphenyl and diphenylmethane were formed according to schemes of type (11), and bibenzyl was formed by the combination of benzyl radicals. The radicals were apparently produced by reactions analogous to reactions (26) and possibly (23).

The reaction of iodobenzene with magnesium in heavy pyridine takes place in unique fashion [28]. At 60° the isotopic composition of its products and its mechanism are analogous to the composition of the products and the mechanism of the decomposition of benzoyl peroxide and the photolysis of diphenylmercury in pyridine (sections II and IV). At 120°, the ratio of the isotopic forms in the solvent changes, and phenylpyridines containing more than four deuterium atoms, and heavy bipyridyls, are formed. These characteristic features were attributed to processes which begin on heating and which involve and exchange of MgI residues from the organomagnesium compounds for the hydrogen of the pyridine and phenylpyridine:

$$C_6H_5MgI + C_5D_5N \rightarrow C_6H_5D + C_5D_4NMgI$$
$$C_5D_4NMgI + C_6H_5C_5D_4N \rightleftarrows C_5D_4HN + IMgC_6H_4C_5D_4N$$

and the formation of the bipyridyls was attributed to the reaction:



or to the addition of pyridyl radicals of thermal origin to pyridine.

These explanations were confirmed by the fact that the reaction between C_6H_5MgI and heavy pyridine at 120° gave the same products and isotopic compositions with the same characteristic features as in the reaction of C_6H_5I with magnesium.

The reactions of C_6H_5MgBr with $CoCl_2$, AgBr, $CuCl_2$, $PtCl_4$, $HgBr_2$, $FeCl_3$, $SnCl_4$, and $CrCl_3$ in a medium of heavy benzene mixed with ether were studied [117]. The published data on the mechanism of reactions of this type (for example Refs. 118–124) contain a number of contradictions. It was moreover not clear whether free radicals take part in the reactions.

The formation of free radicals was established in all these reactions, since they gave the benzenes-d_1 and -d_0 and biphenyls containing deuterium. Most of the biphenyls consisted of the d_0 form. In a number of instances their isotopic composition could not be explained without assuming the disproportionation of radicals of the hydrobiphenyl type, produced in intermediate stages of the formation of the biphenyls.

The source of the radicals was detected in experiments with $HgBr_2$ and $SnCl_4$, where the chief products were stable diphenylmercury and tetraphenyltin. It must be assumed that the radicals were obtained at the stage involving the formation of these organometallic compounds, since their decomposition did not take place. It is possible

that other organometallic compounds, which are assumed to be intermediate products of these reactions [118], are obtained by a free-radical mechanism. The decomposition of at least some of them [119-121,125] also probably involves radicals.

The fact that the d_0 form predominates in the biphenyls obtained in these experiments can be attributed to the fact that most of the biphenyls are obtained from phenyl residues which have not become free radicals. These radicals have combined in the reactive complex, in a "solvent cage" or on the surface of the metals. Only a small percentage of C_6H_5 residues were liberated, and these gave the deuterated biphenyls.

In the work cited it was also shown that the benzenes-d_1 and -d_0 are formed when a solution of C_6H_5MgBr in a mixture of heavy benzene and ether is heated to 50° or oxidised with atmospheric oxygen.

The participation of free radicals in the reactions of organic halides with alkali metals has not been extensively studied. The recently proposed [126] simple radical scheme:

$$ArX + M \rightarrow Ar^{\cdot} + MX;\ 2Ar^{\cdot} \rightarrow Ar - Ar \qquad (27)$$

cannot now be accepted, since it has been established that organometallic compounds are formed in intermediate stages of the Fittig reaction. The alternative scheme [127,128]

$$\text{a) } ArX + 2M \rightarrow ArM + MX$$
$$\text{b) } ArM + ArX \rightarrow Ar{-}Ar + MX \qquad (28)$$

does not exclude the production of radicals in the formation of organometallic compounds or in their reaction with the aryl halides [129]. Radicals were found in various examples of the Wurtz reaction [130,131], but not in the Fittig reaction [9,112].

The study of the reaction of lithium with fluorobenzene in heavy benzene [132,133] showed that the reaction gives the benzenes-d_1 and -d_0, and the ratio of the other forms of benzene remains unchanged. This proved the participation and reaction of $C_6H_5^{\cdot}$ radicals, since phenyl-lithium does not undergo isotopic exchange with benzene [134]. The participation of radicals was confirmed by the isotopic composition of the biphenyl, which was found to be characteristic for the free-radical mechanism (see sections II–IV). In heavy cyclohexane with heating, the benzenes-d_1 and -d_0, and biphenyl, are formed. Biphenyl is not obtained at 20°, so that the process stops at the stage of C_6H_5Li formation. Under these conditions also, the benzene-d_1 was not obtained.

These results show that $C_6H_5^{\cdot}$ radicals are produced by the reaction of C_6H_5Li with C_6H_5F, giving biphenyl, and not in the formation of C_6H_5Li.

The course of this reaction was represented by schemes (28*a*), of form (26) with the participation of C_6H_5Li and C_6H_5F, by the reaction:

$$2C_6H_5^{\cdot} \rightarrow C_6H_5{-}C_6H_5 \qquad (29)$$

and by schemes (3), (5), and (4), and also by analogous reactions of fluorobiphenyl, formed according to the last scheme.

The $C_6H_5^{\cdot}$ radicals obtained by a reaction of type (26), apparently recombine chiefly in a "solvent cage". Thus most of the biphenyl is of the d_0 form.

In the benzenes-($d_1 + d_0$) the proportion of the benzene-d_1 is much less than that in other reactions involving $C_6H_5^{\cdot}$ radicals. This was explained by assuming that in addition to the usual routes, the benzene-d_0 is obtained by the reaction:

$$C_6H_5F + C_6H_5Li \rightarrow \langle\bigcirc\rangle + C_6H_6 + LiF\ . \qquad (30)$$

The study of the mechanism of the reaction of iodobenzene with sodium is complicated by isotopic exchange of phenylsodium with benzene [19,112]:

$$C_6H_5Na + C_6D_6 \rightleftarrows C_6H_5D + C_6D_5Na \qquad (31)$$

which, like the reactions of phenyl radicals, gives the benzene d_1. Analogous processes involving biphenyl distort its isotopic composition.

It has been shown [132,133], however, that after several hours at room temperature, without mixing, exchange is not observed, but that under these conditions in benzene, the d_1 and d_0 forms appear, and the ratio of the other forms remains unchanged, and in the biphenyl obtained the ratio of the isotopic forms is that characteristic for a radical mechanism. All this shows that the reaction involves $C_6H_5^{\cdot}$ free radicals. This conclusion was confirmed by experiments in heavy cyclohexane.

The reaction mechanism must be represented by schemes analogous to that assumed for the reaction of fluorobenzene with lithium. As in the experiments with lithium, the proportion of the d_1 form is unusually low in the benzenes-($d_1 + d_0$) formed, and this was attributed to a reaction of type (30) involving iodobenzene and phenylsodium. The course of these processes has been convincingly proved [135].

These data show that the conclusion in Ref. 112 that the reaction of sodium with iodobenzene does not involve free radicals is incorrect.

It was stated above that the isotopic exchange of hydrogen between C_6H_5Na and C_6D_6 is not observed in the absence of mixing. This was attributed to the fact that benzene does not penetrate, or penetrates very slowly, into the thickness of the layer of phenylsodium and NaI surrounding the metal granules, or into the inner layers of the phenylsodium crystals. Thus exchange takes place only on the surface and remains insignificant. This interpretation is confirmed by the fact that mixing, which leads to mechanical breakdown of the above layer and to subdivision of the phenylsodium crystals, and also increase in the duration of contact between C_6H_5Na and C_6D_6, and heating, facilitate the exchange. The latter is observed from the appearance of deuterium in the benzoic acid obtained from phenylsodium and from the redistribution of deuterium (which often reaches random distribution) between the isotopic forms of benzene and biphenyl. The exchange of phenylsodium with benzene does not reach equilibrium, however, even under severe conditions, and part of the benzoic acid remains light. The other part consists of the set of isotopic forms corresponding to random distribution.

These observations confirmed the early assumptions [127,128,136,137] regarding the existence of the above layer, difficult to penetrate, on the surface of the sodium granules, and demonstrated the poor penetrability of the C_6H_5Na crystals with respect to benzene.

In the works cited [132,133], the reactions of fluorobenzene with sodium and potassium were also studied, and it was shown that they involve free radicals.

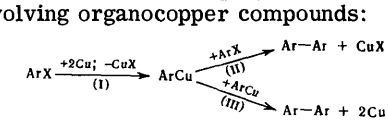
Subsequently, various examples of the Fittig and Wurtz reaction were studied [133-138] and it was found that a free-radical mechanism is extremely probable for the reaction of sodium with *p*-iodobiphenyl, α-iodonaphthalene, 9-iodophenanthrene, iodomesitylene, 2,4,6-triethyliodobenzene, 2,4,6-tri-isopropylbromobenzene, benzyl bromide, diphenylbromomethane, and triphenylchloromethane in heavy benzene or cyclohexane and for the reaction of sodium with ethyl iodide in a medium of heavy naphthalene. All these reactions gave hydrocarbons RD and RH corresponding to

the halides taken, and did not show signs of isotopic exchange between the compounds R–Na and the solvents; this exchange, like the reaction of R· radicals, might give RD molecules.

In the work cited it was also shown that the triphenylmethyl radicals, like many aryl and alkyl radicals, remove hydrogen from benzene. This reaction apparently involves an intermediate addition stage of the type corresponding to reactions (3).

In the interpretation of the mechanism of the reaction of aryl halides with copper (the Ulmann reaction) it was assumed that the halide forms on the metal surface a polar complex which attacks a second halide molecule [139,140], or that the reaction under the influence of copper gives free radicals, which react to give the final products [141,142], or, finally, that organocopper compounds are formed in some stages of the process [139]. Strong support was recently obtained for the last view.

The participation of radicals was proved [133,143] for the reaction of copper with iodobenzene, *p*-iodobiphenyl, and α-iodonaphthalene in a solution of heavy benzene or cyclohexane. The reactions gave benzenes, biphenyls, and naphthalenes-d_1 and -d_0, and the biphenyl isolated in the experiments with C_6H_5I in benzene had an isotopic composition corresponding to a free-radical mechanism of formation. The hydrocarbons (d_1 and d_0) obtained in benzene contained much more of the d_0 form than in other free-radical reactions. Here, as in the reaction of aryl halides with lithium or sodium, the hydrocarbons-d_0 are apparently formed not only from the usual sources of hydrocarbons-d_1 and -d_0 [reactions of types (3), (4), (5), and (11)], but also by reactions of type (30), which at the high temperature of the experiments (210–230°) become possible for organocopper compounds. The work cited adopted the scheme previously proposed [144] for the Ulmann reaction involving organocopper compounds:



(32)

with the refinement that stages I, II, or both involve the intermediate formation of aryl radicals. These processes apparently take place in such a way that only some of the radicals move from the surface into the solution. Thus the greater part of the diaryls formed does not contain deuterium. The reactions III probably take place in the reactive complex [144].

VIII. POSSIBILITIES AND LIMITATIONS OF THE METHOD

In conclusion we shall examine the extent to which the regular features of the behaviour of radicals and the criteria for a free-radical mechanism, discussed in this review, are of general importance.

These regular features and criteria were established for various hydrocarbon radicals—alkyl, aryl with different numbers of rings, arylalkyl (including such stable radicals as triphenylmethyl), and sterically hindered. It may be assumed that the great majority of hydrocarbon radicals show analogous behaviour. Differences in behaviour may be expected only for the radicals showing greatest steric hindrance (for example 2,4,6-tri-t-butylphenyl), since for these radicals, addition to aromatic rings and dehydrogenation and disproportionation of the addition products should be difficult. This is also to be expected for radicals which are unable to add on to aromatic systems for other reasons.

Dehydrogenation of type (11) may be brought about not only by R· radicals, but also by other radicals or oxidising agents X present in the system. As a result of this competition, the formation of the compounds RD may be suppressed by the preferential formation of the compounds XD, and one of the criteria for a free-radical mechanism is not observed. This possibility is apparently rarely realised, and was not observed in any of the works cited, even in the oxidation of hydrocarbons by chromyl chloride (section VI), when the concentration of the strong oxidising agent was high. The probability of complications of this kind is particularly great for R· radicals with low activity.

The formation of RD molecules may be prevented by the reaction of R· radicals with X· radicals produced simultaneously. This requires the collision of two short-lived species, however, and this process usually cannot compete with a reaction of type (11), in which R· adds on to the solvent, which is present in high concentration, and reacts with relatively stable radicals of the cyclohexadienyl type. The reaction of R· with X· (and the suppression of one of the criteria for a free-radical mechanism) may play a significant role in systems where the X· radicals have a low activity and their concentration is high.

Another complication is associated with the fact that disproportionation of type (1*b*) always competes with dehydrogenation of type (11) under the influence of R· radicals or other radicals or oxidising agents. A result of the competition may be the suppression of disproportionation. This leads to the non-observance of its consequences, for example a decrease in the concentration of d_5 form and an increase in the concentration of d_2 form in compounds of the type $R–C_6H_5$, formed by the reaction of R· radicals with benzene. Sections V and VII examined several examples of this kind, but it was shown that in these instances also, it is possible to reach reliable conclusions regarding the free-radical mechanism of reactions from the isotopic composition of the compounds of the form $R–C_6H_5$.

The suppression of disproportionation, as already noted, leads to the disappearance of the criteria for a free-radical mechanism proposed by Eliel and coworkers, since these are all consequences of the disproportionation.

It was shown above that most of the radicals which have been studied remove deuterium from heavy cyclohexane and the methyl group of heavy toluene, giving hydrocarbons RD (and RH). This criterion of a free-radical mechanism is convenient for the most reactive radicals, but not, for example, for benzyl radicals.

All the material of the present review shows that the method described for detecting free radicals and for studying the mechanism of free-radical reactions gives reliable results for a wide range of reactions with the participation of assumed participation of hydrocarbon radicals in solvents of different character. The applicability of this method to the study of radicals of other types has not yet been established.

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