SOME ORGANIC REACTIONS INVOLVING THE OCCURRENCE OF FREE RADICALS IN SOLUTION

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CONTENTS

I. General introduction 169
II. Decomposition of aryl organometallic compounds 173
III. Decomposition of carbonyl compounds 173
IV. Decomposition of azo and diazo compounds 175
V. Reactions of diazo hydroxides 178
VI. Reactions of nitrosoacylarylamines 179
VII. Reactions of arylazotriarylmethanes 183
VIII. Reactions of diacyl peroxides 186
IX. Properties of free aryl radicals 193
X. Diradicals 194
XI. Electrode reactions 197
XII. Free radicals from reactions involving metals 200
XIII. Reactions due to free halogen atoms 201
XIV. Conclusions and summary 203
XV. References 204

I. GENERAL INTRODUCTION

It has become quite evident today that there are two ways in which a covalent molecule may be disrupted during the course of a chemical change (151). *Either* the covalent bond is broken symmetrically

$$A{:}B \rightarrow A\cdot + \cdot B$$

to yield two *neutral* atoms or radicals, each possessing an unpaired electron,[1] e.g.,

$$Br_2 + h\nu \rightarrow 2Br\cdot$$

$$(C_6H_5)_3CC(C_6H_5)_3 \rightarrow 2(C_6H_5)_3C\cdot$$

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[1] Throughout this article a single dot, e.g., A·, represents one unshared electron; where specifically indicated a chemical bond, i.e., an electron duplet, is denoted by a dash.

or the covalent bond is broken unsymmetrically

$$A:B \rightarrow A: + B$$

to yield two *ions* of opposite charge, A^- and B^+, e.g.,

$$HCN \rightleftharpoons H^+ + CN^-$$

$$(C_6H_5)_3CC(C_6H_5)_3 \rightleftharpoons (C_6H_5)_3\overset{+}{C} + \overset{-}{C}(C_6H_5)_3$$

Subsequently, these initially formed activated radicals or ions interact with other similarly activated fragments, or with neutral molecules, to yield eventually stable molecular reaction products.

For reactions in the gaseous phase the former, or *atomic*, mode of dissociation is almost universal, and the neutral radicals produced by the initial decomposition of a reactant molecule either combine with each other upon collison, or, quite frequently, initiate a chain reaction which is consequent upon their collision with neutral molecules. This is typified by the reactions of atomic sodium in the vapor phase:

$$Na\cdot + CH_3Cl \rightarrow NaCl + CH_3\cdot$$

$$CH_3\cdot + H_2 \rightarrow CH_4 + H\cdot$$

$$CH_3\cdot + H\cdot \rightarrow CH_4, \text{ etc.}$$

The investigations of Polanyi and others (24, 119, 111, 71, 135, 70, 80) of reactions initiated by free atoms in the gaseous phase have shown that in many cases a chemical change ensues *immediately* a free atom or radical collides with another molecule, and no extra "energy of activation" may be needed. Even with such stable organic vapors as those of methyl chloride or chlorobenzene the critical energy increment for reaction with a sodium atom is no more than 7000 to 9000 cal., which is very much less than the activation energy usually needed to bring about a chemical reaction between two molecules.

Since 1929, when Paneth and Hofeditz (114) first prepared the free radical *methyl*, $CH_3\cdot$, by heating lead tetramethyl in a rapid current of hydrogen at a pressure of 1 to 2 mm., and showed it to have a half-life period of 6×10^{-3} sec. by measuring the gradual decay of its reactivity with metallic lead or zinc,

$$4CH_3\cdot + Pb \rightleftharpoons Pb(CH_3)_4$$

it has been shown that the thermal decomposition of organic substances is a quite general process for the production of neutral radicals (125, 128). Thus Rice and his colleagues have shown that at a temperature of 800–1000°C. most organic substances can be broken down in the vapor phase by a "cracking" process, in which simple aliphatic radicals such as methyl or ethyl are produced. Moreover, the requisite energy of activation is 75,000 to 85,000 cal., which is approximately the calculated value of the heat of formation of a carbon-to-carbon single covalent linkage.

Photochemical activation appears to be another general process for free radical formation. It has been studied most extensively with the vapors of aldehydes and ketones (see section III), which usually, but not invariably, eliminate the stable molecule, carbon monoxide, and yield free hydrocarbon radicals. Alkyl halides and the aliphatic azo compounds have also been shown to give free radicals by photochemical decomposition (7, 96), and research work in this field is developing with great rapidity at the present time.

Whenever free radicals have been produced by the decomposition of the vapors of organic substances they have proved to be exceedingly reactive bodies. Not only do they combine instantly with metals such as lead, zinc, antimony, and mercury, and with non-metallic elements such as iodine and tellurium, but they will combine with each other on collision, even if cooled to the temperature of liquid air. Also, as previously mentioned, collision with a stable molecule will easily lead to chemical reaction, and the probability that an encounter with a molecule will occur with sufficient activation energy for chemical change is rarely less than one in ten thousand.

In view of this intense reactivity of the simple free organic radicals it is not surprising that their existence is hard to prove in any reactions occurring in the liquid phase, since a molecule in a liquid may undergo quite 10^{14} collisions per second. Without exception the free neutral radicals, such as triphenylmethyl, which have been proved to exist for any appreciable time in solution, are complicated molecules in which the energy normally associated with the presence of a single unshared electron has been stabilized by resonance within the molecule. Thus Hückel (82) has calculated that in hexaphenylethane, $(C_6H_5)_3CC(C_6H_5)_3$, the binding energy between the two triphenylmethyl radicals is only about 13,000 cal. instead of the normal value of 79,500 cal. for the carbon-to-carbon link in ethane. Triphenylmethyl is in consequence a relatively stable compound, but its rapid reactions with sodium, iodine, and oxygen are nevertheless typical of a neutral radical possessing an unshared electron. For lack of experimental evidence one cannot dismiss as impossible the transient formation in solution of much simpler unstabilized free neutral radicals of high energy content, since quite a complicated sequence of chemical changes could occur in the short time interval of 10^{-10} sec. or less, which is a maximum estimate for their mean free life. It is undoubtedly true, however, that free radicals are only produced in a small minority of reactions in solution, for in most of the reactions of organic chemistry one can demonstrate that *ions* must intervene (151). The use of ionic reagents and of ionizing solvents is the rule and not the exception in organic chemistry, and indeed the whole theory of "polarity" for predicting and accounting for the courses and the relative rates of organic reactions can be built up on the hypothesis that the reactions of covalent molecules in solution normally involve the unsymmetrical ionic fission of a covalent link.

There is little doubt that a purely ionic fission of a covalent link,

$$A{:}B \rightarrow [A{:}]^{-} + [B]^{+}$$

involves more energy than a non-ionic fission,

$$A{:}B \rightarrow A\cdot + \cdot B$$

since (*a*) an extra amount of coulombic energy must be required to separate the oppositely charged ions from an initial close proximity, and (*b*) gaseous molecules scarcely ever dissociate into charged ions (in the absence of electrons, α-rays, or the like). In solution, however, every molecule is associated with the many others in its vicinity, and there is a mutual perturbation of the electronic fields. Both on account of the high dielectric constant of the solvent medium, and on account of the ease of formation of an electrical circuit of polar molecules, the energy required for the ionic fission of a covalent link in a dissolved substance may easily become much less than that required for the formation of neutral radicals. One has therefore to seek abnormal reactions of organic compounds in solution in order to discover any which might conceivably involve the transient formation of unstabilized free neutral radicals.

In the following sections a number of such reactions are discussed, and more of a similar type may be proved to exist in the future. From the foregoing introduction, however, it would appear probable (i) that neutral radicals are likely to be formed from those molecules which readily tend to undergo thermal self-decomposition at comparatively low temperatures, (e.g. explosives, endothermic compounds, etc.); (ii) that photochemical reactions are likely to involve free radical formation; (iii) that reactions in solvents containing ions or dipoles, or of high dielectric constant, are unlikely to proceed via neutral radicals, whilst reactions in non-polar solvents of low dielectric constant, such as benzene, carbon tetrachloride, or carbon disulfide, may do so; (iv) that a non-ionic fission of a covalent link will be improbable if the electrical dissymmetry (i.e., the dipole moment) of that link be large.

Molecules which readily undergo thermal self-decomposition at comparatively low temperatures have one structural characteristic in common. The heat of formation of certain of the covalent bonds must be small, and one finds almost invariably that there can be eliminated either the stable atom of an element with a monatomic vapor, such as lead or mercury, or a simple molecule of high stability, such as nitrogen, carbon monoxide, or carbon dioxide.

II. DECOMPOSITION OF ARYL ORGANOMETALLIC COMPOUNDS

With few exceptions the decomposition of organometallic compounds has been studied only in the vapor phase. Just as lead tetramethyl on heating yields lead and free methyl, so lead tetraphenyl yields the free phenyl radical. Dull and Simons (30) refluxed lead tetraphenyl with mercury and obtained some mercury diphenyl. Free phenyl may also be formed in the liquid phase from lead tetraphenyl, tin tetraphenyl, and mercury diphenyl, for on heating these substances in paraffin oil containing sulfur Razuviev and Koton (121) obtained diphenyl disulfide, $C_6H_5SSC_6H_5$, and inferred that free phenyl must have been produced. Hein and others (72, 74, 75) have also suggested that pentaphenylchromium hydroxide, $(C_6H_5)_5CrOH$, can eliminate a neutral phenyl radical in certain of its reactions.

III. DECOMPOSITION OF CARBONYL COMPOUNDS

Since 1932 the photochemical decomposition of aldehydes and ketones has been studied by Norrish and his collaborators at Cambridge (110, 108, 109, 106, 133, 6), who have concluded that the primary photochemical decomposition is the elimination of carbon monoxide with the production of neutral hydrocarbon radicals,

$$R_1COR_2 \rightarrow R_1\cdot + R_2\cdot + CO$$

The presence of free neutral radicals in these photochemical processes has been established beyond doubt by the work of Pearson (115) and of Pearson and Purcell (116, 117), who have shown that the primary decomposition products were able to combine with metallic mirrors.

In the case of aldehydes, the final reaction is almost exactly represented by the equation,

$$RCHO \rightarrow RH + CO$$

and it appears that the free alkyl radical, R·, and the free hydrogen atom, H·, do not have any appreciable free existence. Norrish (105) has suggested that the two stages of the photochemical decomposition process

$$RCHO + h\nu \rightarrow R\cdot + HCO\cdot \quad - 89.5 \text{ Cal.}$$

and

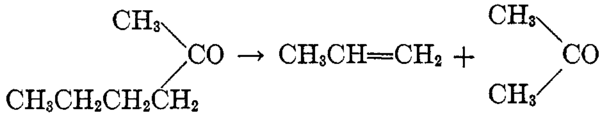
$$HCO\cdot \rightarrow H\cdot + CO \qquad \text{(thermoneutral)}$$

occur in such rapid succession that the R· radicals and the H· atoms never get free of one another's sphere of influence and are therefore eliminated as the single hydrocarbon RH.

In the case of ketones, the free radicals mainly escape separately from the decomposing molecule, and in consequence can intermingle and form mixed products;

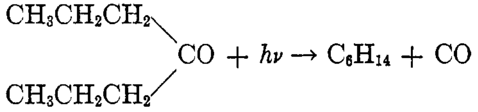
$$\mathrm{R_1COR_2} \rightarrow \mathrm{R_1\cdot} + \mathrm{R_2\cdot} + \mathrm{CO} \rightarrow \mathrm{R_1R_1} + \mathrm{R_1R_2} + \mathrm{R_2R_2}$$

Higher aldehydes and ketones, however, tend to decompose differently (106, 6);

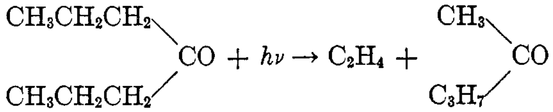


$$\begin{matrix}\mathrm{CH_3}\diagdown \\ \mathrm{CH_3CH_2CH_2CH_2}\diagup\end{matrix}\mathrm{CO} \rightarrow \mathrm{CH_3CH{=}CH_2} + \begin{matrix}\mathrm{CH_3}\diagdown \\ \mathrm{CH_3}\diagup\end{matrix}\mathrm{CO}$$

Quite recently the photochemical decomposition of ketones has been extended to the liquid state. Even in an inert solvent, such as hexane or cyclohexane, the photochemical decomposition of acetone will occur if the temperature is sufficiently high, but the free radical reacts with the solvent, as Bowen and Horton have shown (25). Norrish and Bamford (107) have shown that in the liquid state the decomposition of ketones with formation of carbon monoxide, which involves the production of free radicals (reaction a), is completely suppressed at low temperatures, but the decomposition by rupture of the hydrocarbon chain with liberation of an olefin (reaction b) can still occur.



$$\begin{matrix}\mathrm{CH_3CH_2CH_2}\diagdown \\ \mathrm{CH_3CH_2CH_2}\diagup\end{matrix}\mathrm{CO} + h\nu \rightarrow \mathrm{C_6H_{14}} + \mathrm{CO} \qquad \text{(a)}$$



$$\begin{matrix}\mathrm{CH_3CH_2CH_2}\diagdown \\ \mathrm{CH_3CH_2CH_2}\diagup\end{matrix}\mathrm{CO} + h\nu \rightarrow \mathrm{C_2H_4} + \begin{matrix}\mathrm{CH_3}\diagdown \\ \mathrm{C_3H_7}\diagup\end{matrix}\mathrm{CO} \qquad \text{(b)}$$

In a still more recent communication Norrish and Bamford (107a) have extended their study of the photodecomposition of ketones in solution, and disclose the interesting result that the free alkyl radicals disengaged in the photolysis do not combine together, as in the gaseous phase, but mainly react with molecules of the paraffin solvent by abstraction of hydrogen, R· + R′H → RH. The paraffin solvent then shows unsaturation. It is suggested that these results may indicate the occurrence of a continuous interchange of hydrogen atoms between paraffin molecules and free alkyl radicals, until two such radicals meet and react to give an olefin and a paraffin by disproportionation.

This property of alkyl radicals in solution is in striking agreement with the observations set out in this review of the characteristic properties of aryl radicals in solution, as revealed in reactions of the diazo compounds, nitrosoacylarylamines, arylazotriarylmethanes, and diacyl peroxides. Thus, it is repeatedly shown that the phenyl radicals react mainly with the solvent and do not combine together.

Quite definitely, therefore, one can state that if free radicals are formed in solutions they do not have a sufficiently long free life to intermingle and combine with each other, but must react almost immediately with adjacent solvent molecules.

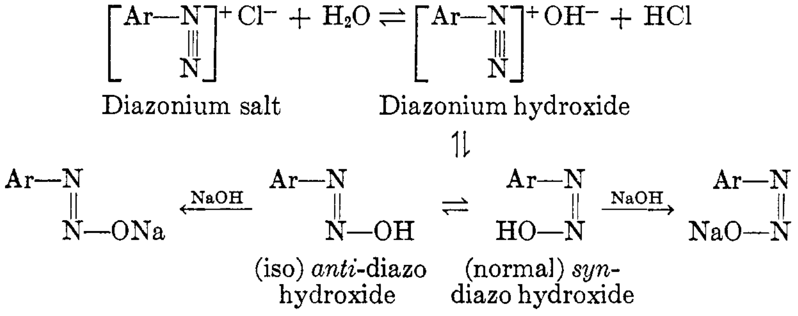
IV. DECOMPOSITION OF AZO AND DIAZO COMPOUNDS

In 1919 Langmuir (95) pointed out that carbon monoxide, $:\overset{-}{C}\equiv\overset{+}{O}:$, is isosteric with nitrogen gas, $:N\equiv N:$, and hence it is not at all unlikely that nitrogen should be eliminated from azo compounds just as carbon monoxide can be eliminated from carbonyl compounds. The ease of fission of nitrogen is, however, much greater, for azomethane, $CH_3N{=}NCH_3$, and diazomethane $CH_2{=}N_2$ (the analogue of ketene) are both explosive gases. The former decomposes thermally at 400°C. to give free methyl radicals (96, 126), whilst for acetone a temperature of over 600°C. is required.

Not only do purely aliphatic azo compounds decompose into free radicals, but also compounds containing one aryl group, $ArN{=}NX$. The evidence for the production of free radicals from the decomposition of compounds containing the azo grouping $N{=}N$, by fission of nitrogen, is discussed below and in sections V, VI, and VII.

The readiness with which nitrogen is eliminated both from the diazonium salts, $[ArN\equiv N]^+X^-$, and from the diazotates, $ArN{=}NOX$, makes both classes of compound possible sources for the production of free aryl radicals, but it would be in those reactions which take place in non-dissociating organic solvents of low dielectric constant that the formation of free radicals would be most likely.

According to Hantzsch (64, 65, 66, 67), diazonium salts in solution are in tautomeric equilibrium with derivatives of benzenediazo hydroxide, which are capable of existing in two geometrically isomeric forms:



$$\begin{bmatrix}\mathrm{Ar{-}N}\\ \|\!| \\ \mathrm{N}\end{bmatrix}^+ \mathrm{Cl}^- + H_2O \rightleftharpoons \begin{bmatrix}\mathrm{Ar{-}N}\\ \|\!| \\ \mathrm{N}\end{bmatrix}^+ \mathrm{OH}^- + \mathrm{HCl}$$

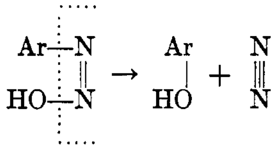
Diazonium salt Diazonium hydroxide

$$\rightleftharpoons$$

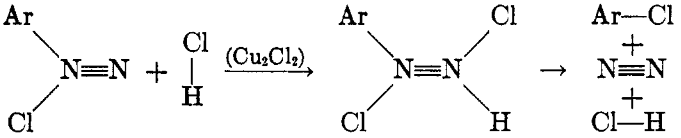
$$\begin{matrix}\mathrm{Ar{-}N}\\ \| \\ \mathrm{N{-}ONa}\end{matrix} \xleftarrow{NaOH} \begin{matrix}\mathrm{Ar{-}N}\\ \| \\ \mathrm{N{-}OH}\end{matrix} \rightleftharpoons \begin{matrix}\mathrm{Ar{-}N}\\ \| \\ \mathrm{HO{-}N}\end{matrix} \xrightarrow{NaOH} \begin{matrix}\mathrm{Ar{-}N}\\ \| \\ \mathrm{NaO{-}N}\end{matrix}$$

(iso) *anti*-diazo hydroxide (normal) *syn*-diazo hydroxide

Of these diazo hydroxides (which are weak acids capable of forming easily hydrolyzed salts, the diazotates, with alkali metals) the compound with the *syn*-diazo structure was supposed to be unstable, owing to the ease with which it might eliminate a molecule of nitrogen, thus:



and in all decomposition reactions of diazo compounds it was suggested that the *syn*-diazo structure must have been formed, either by a tautomeric change, as depicted above, or by an addition reaction, represented as follows:



In addition to the fact that the geometrical structures assigned to the isomeric diazo hydroxides and their derivatives have not been confirmed experimentally, reaction velocity measurements have shown that this view is no longer tenable in all cases. For example Pray (120) has studied the decomposition of dry benzenediazonium chloride in a series of aliphatic alcohols and acids. It was found that for a series of aliphatic alcohols the reaction velocities, as measured by the rate of evolution of nitrogen, were all of the same order and in the case of the lower members of the series were practically identical (see table 1). Similar results were obtained with a series of aliphatic acids. Particular attention may be directed to the results obtained with methyl and ethyl alcohols, for although the reactions of benzenediazonium chloride with these two alcohols are to an appreciable extent qualitatively different, as shown by Hantzsch and Jochem (68),

$$C_6H_5N_2Cl + CH_3OH \rightarrow C_6H_5OCH_3 + N_2 + HCl$$

$$C_6H_5N_2Cl + CH_3CH_2OH \rightarrow C_6H_6 + CH_3CHO + N_2 + HCl$$

yet the observed rate of reaction was identical in the two cases. The initial rate-determining process cannot therefore be, as Hantzsch imagined, the rate of decomposition of the addition compound with the *syn*-diazo structure, for this would depend on the nature of the alcohol ROH. These results, however, may be incorporated satisfactorily into a reaction mechanism involving the slow formation of free aryl radicals from the diazo compound, or, more probably, from its wholly covalent tautomer. Under these circumstances the reaction velocity, measured by the rate of evolution of nitrogen, becomes the rate of formation of free aryl radicals, and this would be a unimolecular reaction, independent or practically independent of the second component, which is present in large excess and merely acts as a medium for the decomposition. The subsequent fate of the phenyl radical, whether it is converted into benzene, a phenyl alkyl ether, or some more complicated molecule, will have no bearing on the initial rate-determining stage.

Attention may also be directed here to the observation made by Möhlau and Berger (102) that 2- and 4-phenylpyridines are formed when dry benzenediazonium chloride decomposes in pyridine solution. This reaction seems to involve a non-ionic mechanism, probably through the agency of a free phenyl radical, since attack by phenyl cation and chloride anion would have resulted in the formation of phenylpyridinium chloride.

TABLE 1

The rate of decomposition of benzenediazonium chloride in various alcohols and organic acids (Pray)

$k' = 0.4343\, k \times 10^4$

SOLVENT	k' AT 20°C.	k' AT 30°C.	k' AT 40°C.
Methyl alcohol	11.3	53.5	227
Ethyl alcohol	11.3	53.5	218
n-Propyl alcohol		52.0	204.2
n-Butyl alcohol		50.0	201
Isobutyl alcohol		54.0	208
Amyl alcohol		46.3	
Formic acid		18.6	73.1
Acetic acid		18.7	82.0
Propionic acid		18.9	82.0
Butyric acid		23.0	102.0
Water		25.0	107.0

Quite recently Waters (153a) has found that when benzenediazonium chloride decomposes under acetone the metals antimony, bismuth, lead, and mercury are attacked even though the mixture is kept neutral with calcium carbonate. This experimental evidence affords strong support for the view, mentioned above, that free neutral radicals may also be produced in certain of the decomposition reactions of benzenediazonium chloride. Neutral radicals would not be produced from a diazonium salt, such as $[C_6H_5N_2]^+Cl^-$, unless the latter were converted into a covalent molecule, such as $C_6H_5—N═N—Cl$, before the fission of the nitrogen occurs. Otherwise the stable chloride anion would remain unchanged throughout the whole of the decomposition process. The chloride anion does not attack the metals mentioned above and yet this decomposition reaction sets in at room temperature. Moreover, the principal reaction, in neutral conditions, between benzenediazonium chloride and acetone is

$$C_6H_5N_2Cl + CH_3COCH_3 \rightarrow C_6H_6 + ClCH_2COCH_3 + N_2$$

and the substitution of a hydrogen atom in the acetone molecule by one of chlorine again indicates that a reactive form of chlorine must be produced during the decomposition. The reaction between benzenediazonium chloride and acetone is quite evidently of the same type as the well-known reduction of a diazonium salt by an alcohol, for example:

$$C_6H_5N_2Cl + CH_3CH_2OH \rightarrow C_6H_6 + CH_3CHO + HCl + N_2$$

After consideration of the newer experimental evidence set out in this review, there can be little doubt that the forty-year old theories of Hantzsch regarding the structural changes and decomposition reactions of the diazo compounds now need a thorough reëxamination, although as yet the newer hypotheses are only addenda to his general conceptions and do not conflict with them on any vital point.

V. REACTIONS OF DIAZO HYDROXIDES

The reactions between the diazo hydroxides (or diazo anhydrides) and neutral aromatic liquids have been studied by Gomberg and Bachmann (56) and by Gomberg and Pernert (58), who have developed thereby a useful method for the preparation of unsymmetrically substituted biaryls. According to these workers a moderately concentrated aqueous solution of the sodium diazotate is stirred vigorously in the cold with a neutral aromatic liquid. Nitrogen is evolved and a biaryl is formed in yields usually varying from about 5 to 40 per cent.

$$ArN_2OH + C_6H_5R \rightarrow ArC_6H_4R + N_2 + H_2O$$

There is ample evidence to indicate that, as suggested by Gomberg and Pernert, the essential reaction of biaryl formation takes place in the non-aqueous medium. The diazo hydroxides being in general weak acids, their salts will suffer considerable hydrolysis in aqueous solution, and, according to these authors, "the success of the reaction is seen at once to lie in the ability of the non-aqueous liquid to extract from the aqueous layer the reactive diazo compound as fast as it is formed." The most characteristic feature of the reaction under discussion is the fact that in the formation of the biaryl the ordinary laws which govern aromatic substitution are not obeyed.

Aromatic substitution reactions are generally regarded as belonging to one of two types. In the case of normal substitution by a cationoid reagent (e.g., nitric acid) groups such as the halogens, methyl, hydroxyl, and amino are said to be ortho-para directive, while groups such as nitro, carboxyl, aldehydo, and nitrile are said to be meta directive. On the other hand, for substituting agents which are anionoid in type (e.g. ammonia, potassium hydroxide) the normal orientation laws are reversed and the nitro group, for example, now becomes ortho-para directive (152). In the reactions studied by Gomberg, however, a third type of reaction is revealed, which will fit into neither of these categories and which appears to give rise to ortho-para substitution *irrespective of the nature of the so-called directing group*. For example, it was shown that from diazotized aniline and toluene, bromobenzene, benzonitrile, and nitrobenzene one obtained, respectively, 2- and 4-methylbiphenyl, 2- and 4-bromobiphenyl, 4-cyanobiphenyl, and 4-nitrobiphenyl. This remarkable feature, noted by Gomberg and Pernert, was encountered many years earlier by Kühling (93, 94), who from the sodium salt of diazotized *p*-nitroaniline and toluene obtained a compound proved by Kliegl and Huber (90) to be 4-nitro-2′-methylbiphenyl, while with nitrobenzene the product consisted of 4,4′-dinitrobiphenyl and 4,2′-dinitrobiphenyl. Further examples of this reaction have been recorded by Grieve and Hey (59, 60, 61), by Hey (77), and also by Cook and Cook (27).

The reactions which embrace aromatic substitution by either cationoid or anionoid reagents are clearly polar in type, whereas the formation of biaryls from the diazo hydroxides in all probability involves a non-polar mechanism. This conclusion is supported by a recognition of the conditions under which the reaction is effected and also by the unique characteristic of invariable ortho-para substitution, which would be difficult to explain on any polar basis.

A further reaction of benzenediazo hydroxide, which is of particular interest in connection with the reactions discussed in the later sections, is that in which carbon tetrachloride is used in place of the aromatic liquid as used by Gomberg. In this case an appreciable quantity of *chlorobenzene* is formed.[2] Another characteristic feature of these reactions is the frequent replacement of the diazo group by hydrogen. Reference to this property is made in later sections.

VI. REACTIONS OF NITROSOACYLARYLAMINES

Closely related to the diazo hydroxides are the *N*-nitrosoacylarylamines formed by the action of nitrous fumes on an acetic acid solution of an anilide. From acetanilide Fischer (37) obtained in this way nitroso-

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[2] Unpublished observation by D. H. Hey.

acetanilide, which was later used by Bamberger (5), who showed that in benzene solution nitrogen was evolved and biphenyl was formed:

$$C_6H_5N(NO)COCH_3 + C_6H_6 \rightarrow C_6H_5C_6H_5 + N_2 + CH_3COOH$$

Bamberger (4), v. Pechmann and Frobenius (118), and Hantzsch and Wechsler (69) claim to have shown that nitrosoacetanilide is probably tautomeric with benzene *iso*(*anti*)-diazoacetate,

$$C_6H_5N(NO)COCH_3 \rightleftharpoons C_6H_5N{=}NOCOCH_3$$

since it can also be obtained by acetylating sodium benzene diazotate with acetic anhydride. A close correspondence would therefore be expected between the reactions of the diazo hydroxides studied by Gomberg and the reactions of nitrosoacylarylamines.

Such a correspondence has in fact been revealed by Grieve and Hey (61), who have shown that when nitrosoacetanilide reacts in turn with toluene, chlorobenzene, nitrobenzene, and benzaldehyde, 4-methylbiphenyl, 4-chlorobiphenyl, 4-nitrobiphenyl, and biphenyl-4-aldehyde, respectively, are formed. The phenyl group enters the aromatic nucleus at the para-position in each case.

The reactions with nitrosoacetanilide lend themselves more readily to critical study than do those using diazo hydroxides, since they take place wholly in a homogeneous organic medium. If, as in the case of the diazo hydroxide reactions, the formation of the biaryl is dependent upon the production of a free phenyl radical as the first stage in the reaction mechanism, then the rate of evolution of nitrogen should be practically independent of R in the equation:

$$C_6H_5N(NO)COCH_3 + C_6H_5R \rightarrow p\text{-}C_6H_5C_6H_4R + N_2 + CH_3COOH$$

Measurements of the rate of evolution of nitrogen were made in benzene, toluene, *m*-xylene, mesitylene, chlorobenzene, anisole, and nitrobenzene, and it was shown that good unimolecular velocity constants were obtained, which varied but little from case to case (61). This is illustrated in figures 1 and 2, in which log $[V_\infty/(V_\infty - V_t)]$ is plotted against t, where V_∞ is the final observed volume of nitrogen, V_t the volume at time t, and k the unimolecular velocity constant. The reaction with the second component C_6H_5R (solvent) is thus secondary, involving one of the products, namely the free phenyl radical, of the primary unimolecular rate-determining stage. The reaction may therefore be more correctly written thus:

$$C_6H_5N(NO)COCH_3 \rightarrow C_6H_5\cdot + N_2 + CH_3COO\cdot \qquad (a)$$

$$C_6H_5\cdot + C_6H_5R \rightarrow p\text{-}C_6H_5C_6H_4R + H\cdot \qquad (b)$$

$$CH_3COO\cdot + H\cdot \rightarrow CH_3COOH \qquad (c)$$

Significant also is the fact that the rate of evolution of nitrogen from nitrosoacetanilide in carbon tetrachloride solution is also of the same order,

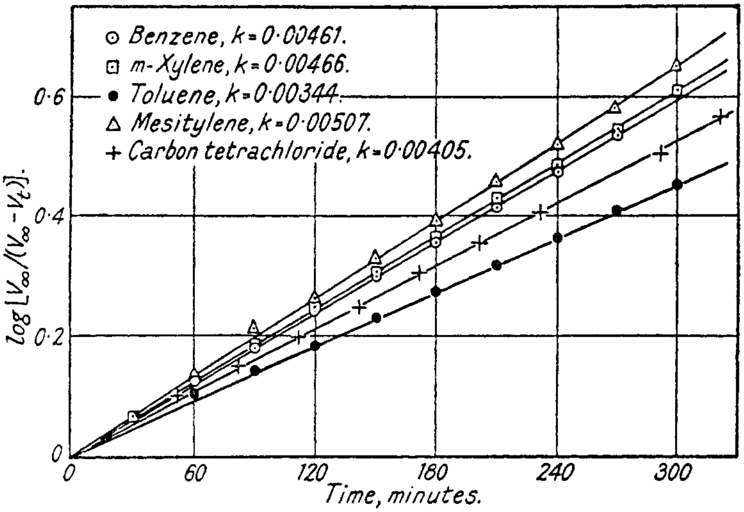

FIG. 1. Rate of decomposition of nitrosoacetanilide in various solvents. (From Grieve and Hey: J. Chem. Soc. **1934**, 1800).

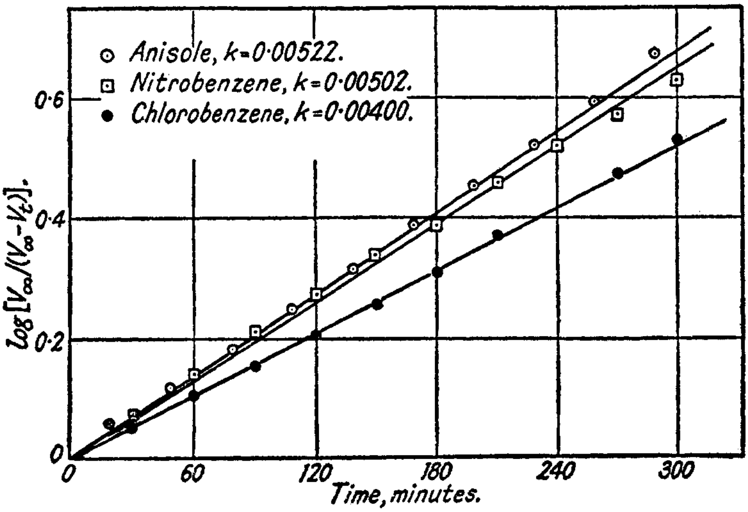

FIG. 2. Rate of decomposition of nitrosoacetanilide in various solvents. (From Grieve and Hey: J. Chem. Soc. **1934**, 1800).

being practically identical with that in chlorobenzene solution. The qualitative nature of this reaction must of course be vastly different from those in which biaryl formation results, but the final products are independent of the rate-determining reaction (reaction a), which seems to take place in all neutral media.

Further evidence for the non-ionic nature of the nitrosoacetanilide reactions has been provided by Waters (153), who allowed dry nitrosoacetanilide to decompose in a number of varied anhydrous solvents at room temperature. From reaction in *n*-hexane, cyclohexane, diethyl ether, dioxane, acetone, ethyl acetate, acetonitrile, and acetic anhydride, benzene was produced in each case, thus indicating the regular occurrence in non-aromatic hydrogen-containing solvents of the reaction:

$$C_6H_5\cdot + RH \rightarrow C_6H_6$$

This reaction recalls the formation of benzene by the decomposition of a benzenediazonium salt in ethyl alcoholic solution, which is customarily regarded as due to the action of a reducing agent. Further, with both methyl and ethyl iodides there was produced iodobenzene; with ethyl bromide and with bromoform there was produced bromobenzene; and with chloroform and carbon tetrachloride there was produced chlorobenzene. Thus in non-aromatic halogen-containing solvents the reaction may be represented:

$$C_6H_5\cdot + RHal \rightarrow C_6H_5Hal$$

The reaction with carbon tetrachloride recalls that previously recorded with benzenediazo hydroxide (p. 179).

Attention has also been directed by Waters to the other products which may be formed during the initial decomposition of nitrosoacetanilide into phenyl radicals and nitrogen gas. As represented above (reaction a) a neutral acetate radical is formed, which finally appears as acetic acid (reaction c). While it is true that acetic acid is formed in most cases, it has been known for some time that the amount formed is always somewhat less than that corresponding to the quantity of nitrogen evolved, as expressed in the simple equation. It was shown by Waters that in many cases carbon dioxide is also liberated. This confirms the transient existence of the neutral acetate radical,

$$CH_3COO\cdot \rightarrow CO_2 + \cdot CH_3 \; (\rightarrow CH_3CH_3)$$

since an acetate anion never loses carbon dioxide at room temperature, except on discharge at an anode. Strong confirmatory evidence for the production of the acetate radical has been found in the fact that when nitrosoacetanilide decomposes in carbon disulfide or carbon tetrachloride solution metals, such as zinc, iron, copper, tin, lead, mercury, and antimony, may be attacked, giving rise to the formation of salts, principally the acetates. The metals are attacked even in the presence of an excess of calcium carbonate, so that the solution of the metal is not to be attributed to an attack by acetic acid molecules in presence of air. When the decomposition in presence of mercury was carried out in carbon tetrachloride solution mercuricphenyl chloride, C_6H_5HgCl, was also found as a reaction product; in benzene solution some mercurous acetate was formed.[3] These reactions with metals, many of which are normally inert, recall in striking manner the tests used by Paneth for free alkyl radicals. The reactions with mercury are particularly significant in this respect.

The reactions of nitrosoacetanilide thus enumerated are typical of free neutral radicals and cannot be satisfactorily explained through the agency of phenyl cations or anions.

VII. REACTIONS OF ARYLAZOTRIARYLMETHANES

The reactions of phenylazotriphenylmethane, $C_6H_5N{=}NC(C_6H_5)_3$, and of similar compounds have been studied by Gomberg and his coworkers (54, 57, 55) and more recently by Wieland and his coworkers (162, 157). Gomberg showed that when phenylazotriphenylmethane was heated above its melting point (111°C.) alone, admixed with sand, or in toluene or xylene solution, nitrogen was evolved and tetraphenylmethane was formed, but only in small yield:

$$C_6H_5N{=}NC(C_6H_5)_3 \rightarrow N_2 + C(C_6H_5)_4$$

Wieland and his coworkers studied the same reaction in greater detail and found that solutions of phenylazotriphenylmethane in specially purified light petroleum, xylene, or ethyl benzoate evolved nitrogen at about 80°C. with liberation of free triphenylmethyl radicals, which were identified spectrographically. The greater part of the free triphenylmethyl was isolated as the peroxide. In this reaction it is difficult and unreasonable not to admit, with the authors, the production of free phenyl radicals at the same time, thus:

$$C_6H_5N{=}NC(C_6H_5)_3 \rightarrow C_6H_5\cdot + N_2 + \cdot C(C_6H_5)_3$$

The fate of the phenyl radical, however, remained obscure. Exhaustive search was made for biphenyl, which, it was supposed, would be formed from two phenyl radicals by polymerization, but none could be found. It was established that the phenyl radical was partly converted into benzene, which was isolated from the product when the reaction was carried out in highly purified light petroleum free from all aromatic hydrocarbons. The exact source which supplied the hydrogen remained unknown. The product also contained triphenylmethane and some

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[3] Unpublished observation by J. W. Haworth and D. H. Hey.

tetraphenylmethane, the formation of the latter accounting for the destination of part of the free phenyl. The isolation of benzene in this reaction is very significant and is in agreement with the results obtained by Waters (153) in the reactions of nitrosoacetanilide with non-aromatic hydrogen-containing solvents described in the previous section. In similar manner the naphthylazotriphenylmethanes in *n*-hexane give rise to the production of naphthalene.

In order to make more complete the correspondence between the reactions of phenylazotriphenylmethane and nitrosoacetanilide, reactions of phenylazotriphenylmethane in aromatic solvents have been carried out by Hey (78). If the suggested free radical mechanism is common to the reactions of both types of compound, then in neutral aromatic solvents reaction should ensue between the phenyl radical and the solvent to give a biaryl compound. As predicted, when phenylazotriphenylmethane was allowed to decompose in benzene solution some biphenyl was formed, while in chlorobenzene solution some 4-chlorobiphenyl was formed. In an endeavor to extend the correspondence to include the reaction in nitrobenzene solution, only triphenylmethane could be identified in the product.

These results on the interaction of phenylazotriphenylmethane with aromatic solvents have since been confirmed and extended by Wieland and his collaborators (157). Thus, in reaction with toluene they obtained 2- and 4-methylbiphenyl, while with pyridine they obtained a mixture of phenylpyridines regarded as consisting of 2- and 4-phenylpyridine. The reaction with pyridine recalls that of Möhlau and Berger (102) using dry benzenediazonium chloride (see section IV). Further, Wieland showed that in carbon tetrachloride solution phenylazotriphenylmethane gave rise to chlorobenzene and triphenyltrichloroethane. The formation of chlorobenzene here is an exact reproduction of the result obtained by Waters with nitrosoacetanilide described above (section VI) and also of the reaction between benzenediazo hydroxide and carbon tetrachloride (section V). Similarly α- and β-naphthylazotriphenylmethane in carbon tetrachloride give rise to some α- and β-chloronaphthalene, respectively.

Among the more remarkable features of these reactions are the persistence with which the phenyl radical removes hydrogen from all non-aromatic hydrogen-containing solvents and itself becomes converted into benzene and, secondly and in contrast, the readiness with which biaryls are formed with aromatic solvents; the latter change involves the replacement and expulsion of a hydrogen atom. Wieland (157) has shown that when phenylazotriphenylmethane, admixed with sand only, is heated at 105–115°C. in a high vacuum some benzene is formed, together with tetraphenylmethane and triphenylmethane. One can only suppose here that part of the compound undergoes disruptive decomposition in order to supply the hydrogen required. Again, in the thermal decomposition of *m*-phenylenebisazotriphenylmethane the bivalent phenylene radical also yields benzene. It is not certain, however, whether in this case the bivalent radical is formed as such, or whether the two molecules of nitrogen are eliminated successively. With regard to the replacement and expulsion of aromatically bound hydrogen, part of it becomes associated with triphenylmethyl as triphenylmethane, but it has also been shown that if phenylazotriphenylmethane is allowed to decompose in benzene solution containing some benzoquinone, in an atmosphere of nitrogen, there is formed, in addition to some phenylbenzoquinone and the di(triphenylmethyl) ether of hydroquinone, some quinhydrone, thus indicating the production of active hydrogen during the reaction. Further examples to illustrate these points are included in Wieland's communication, and from these it may be noted that, in general, as the complexity of the arylazotriarylmethane increases there is a tendency in the reactions with benzene or toluene for the latter to serve merely as sources of hydrogen, in much the same way as the aliphatic hydrocarbons, and biaryl formation is less prevalent. This may be attributed partly to the greater difficulty attendant on the isolation of compounds of higher molecular weight which might be formed.

Wieland and his coworkers have also studied the reactions of acylazotriphenylmethanes (159, 158). They showed, for example, that when benzoylazotriphenylmethane was heated in xylene solution nitrogen was evolved and some benzoyltriphenylmethane was formed, probably through the agency of free radicals:

$$C_6H_5CON{=}NC(C_6H_5)_3 \rightarrow N_2 + C_6H_5COC(C_6H_5)_3$$

When the same decomposition was carried out in carbon tetrachloride solution the free benzoyl radical removed chlorine from the solvent, with formation of benzoyl chloride. Similar reactions were carried out with acetylazotriphenylmethane and other acylazotriphenylmethanes and, when effected in an atmosphere of oxygen, peroxides were formed from the triphenylmethyl radicals and in some cases from the acyl radicals also. It is interesting to note that as the hydrogen in the acetyl radical is successively replaced by phenyl there is an increasing tendency for the loss of carbon monoxide to occur (compare section III), according to the following equations:

$$C_6H_5CH_2CON{=}NC(C_6H_5)_3 \rightarrow C_6H_5CH_2C(C_6H_5)_3 + CO + N_2$$

$$(C_6H_5)_2CHCON{=}NC(C_6H_5)_3 \rightarrow (C_6H_5)_2CHC(C_6H_5)_3 + CO + N_2$$

$$(C_6H_5)_3CCON{=}NC(C_6H_5)_3 \rightarrow (C_6H_5)_3CC(C_6H_5)_3 + CO + N_2$$

The greater yield in which benzoyltriphenylmethane is formed from benzoylazotriphenylmethane compared with the small yield of tetraphenylmethane obtained from phenylazotriphenylmethane, and other cognate facts, led Wieland to consider the possibility of a step-wise decomposition thus:

$$(C_6H_5)_3CN{=}NR \rightarrow (C_6H_5)_3C\cdot + \cdot N{=}NR$$

$$\cdot N{=}NR \rightarrow N_2 + R\cdot$$

where R may be aryl or acyl. This may be equally possible in decomposition reactions of the diazonium salts and of the diazotates, since small yields of azo compounds are found as by-products in many of the reactions of these compounds (58, 31, 97, 23).

VIII. REACTIONS OF DIACYL PEROXIDES

When a solution of dibenzoyl peroxide in benzene is heated, carbon dioxide is evolved and biphenyl is formed, thus:

$$C_6H_5COO{-}OCOC_6H_5 + C_6H_6 \rightarrow C_6H_5C_6H_5 + CO_2 + C_6H_5COOH$$

The participation of the solvent in this reaction is proved by the fact that di-*p*-chlorobenzoyl peroxide with benzene gives 4-chlorobiphenyl and not 4,4′-dichlorobiphenyl, and that in similar manner di-*m*-nitrobenzoyl peroxide with benzene gives 3-nitrobiphenyl and not 3,3′-dinitrobiphenyl (40). With dibenzoyl peroxide and toluene a mixture of the 2- and 4-methylbiphenyls is obtained (41). The reactions of the diacyl peroxides, however, are more complicated than the above simple equation would imply, and have been studied in great detail.

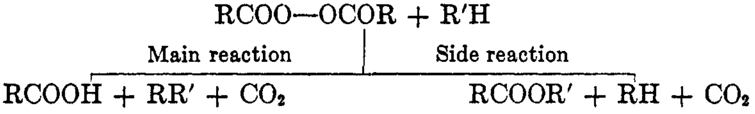
The fact that dibenzoyl peroxide is itself thermally unstable and can undergo reaction in an aromatic solvent to yield a derivative of biphenyl suggests that the reactions of the diacyl peroxides may have much in common with those of the diazo hydroxides, nitrosoacylarylamines, and arylazotriarylmethanes, and may decompose, with the elimination of the stable molecule carbon dioxide and production of free radicals, just as the diazo and azo compounds decompose with the elimination of the stable molecule nitrogen. In order to find out how far the resemblance extends, reactions were carried out by Hey (78) in which dibenzoyl peroxide was allowed to decompose in solution in chlorobenzene, nitrobenzene, and ethyl benzoate in turn. In chlorobenzene solution 4-chlorobiphenyl was formed, and with nitrobenzene both 2- and 4-nitrobiphenyl were isolated from the reaction product. The experiment with nitrobenzene is confirmed by Wieland, Schapiro, and Metzger (165). The phenomenon of *invariable ortho-para substitution* is therefore also a characteristic of the reactions of the diacyl peroxides. This receives further confirmation from the observation, due to Overhoff and Tilman (113), that 2- and 4-phenylpyridine are formed during the decomposition of dibenzoyl peroxide in pyridine solution. It will be recalled that a similar reaction with pyridine has been observed with dry benzenediazonium chloride (see p. 177) and with phenylazotriphenylmethane (see p. 184).

When dibenzoyl peroxide undergoes decomposition in solution in ethyl benzoate, ethyl biphenyl-4-carboxylate is formed, together with some ethyl biphenyl-3-carboxylate (78). The isolation of the latter led to a more detailed examination of the product of the reaction between sodium benzenediazotate and ethyl benzoate, which revealed that, while the main product was ethyl biphenyl-4-carboxylate, smaller quantities of both the corresponding 2- and 3-carboxylic esters were also formed at the same time. The differences in reactivity usually shown between the ortho- and meta-positions in ethyl benzoate have not the clear demarcation found, for example, between the corresponding positions in nitrobenzene. The isolation of all three isomerides in the reaction with ethyl benzoate may be correlated with this fact, but it is not clear why, in general, reaction at the ortho- and para-positions should take precedence over reaction at the meta-positions in the reactions under discussion, and it might well be that a more exhaustive examination of the products in these reactions would reveal in every case the presence of all three isomerides. It is quite definitely established that in aromatic substitution both by cationoid and anionoid reagents the ortho- and para-positions are the most reactive, but when substitution is brought about through the agency of a free radical, as is here supposed, the position is not so clear. It has been pointed out, however, that the phenyl, or substituted phenyl group, which enters the aromatic nucleus has unique properties in that it is able to compensate electrostatic disturbances of either sign (83, 84). This amphoteric characteristic enables the group to function *as if it were* a potential cationoid or anionoid reagent, as occasion demands, and may be an important factor in influencing the course of the reaction. Further, mesomeric changes within any aromatic ring are confined to resonance structures in which the ortho- and para-positions, but not the meta-positions, have variable energy levels. The isolation of all three isomerides in these reactions, however, even if it proves to be general, in no way invalidates the argument put forward, the essential feature of which is a characteristic departure from the laws governing normal aromatic substitution.

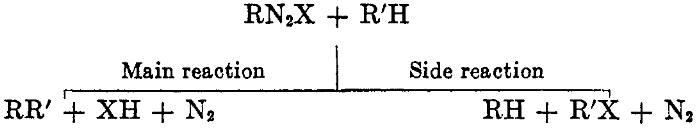
Gelissen and Hermans (40) have shown that the action of dibenzoyl peroxide on boiling benzene gives, in addition to biphenyl, carbon dioxide, and benzoic acid, smaller quantities of phenyl benzoate, terphenyl, and quaterphenyl. The formation of the latter hydrocarbons is a general feature of the reactions under discussion and has already been encountered by Gomberg and his coworkers (56, 58) in their reactions with the diazo hydroxides. The presence of these polyphenyls must be attributed to the successive action of the peroxide or diazo hydroxide on the hydrocarbons initially formed. The same phenomenon was observed by Gerngross and Dunkel (47) and by Gerngross, Schachnow, and Jonas (48) in a study of the formation of biphenyl from diazotized aniline in the presence of copper by the method of Gattermann (39).

The reactions of dibenzoyl peroxide show further characteristics which simulate very closely those exhibited by the diazo hydroxides, the nitrosoacylarylamines, and the arylazotriarylmethanes. For example, Gelissen and Hermans (42, 43, 45, 46) have shown that in ethyl alcohol, isobutyl alcohol, acetic acid, 2-pentene, and cyclohexane, dibenzoyl peroxide decomposes to give benzene. Similar results were obtained by Böeseken and Gaster (20) from the action of dibenzoyl peroxide on light petroleum and on *n*-octane. These reactions constitute further examples of the removal of hydrogen from an aliphatic solvent by the phenyl radical. Again, Böeseken and Gelissen (21) showed that the action of dibenzoyl peroxide on carbon tetrachloride yields chlorobenzene, and a similar reaction has been observed by Reynhart (124) using tetrachloroethylene.

A remarkable correspondence between the reactions of the diacyl peroxides and the diazonium compounds formed the subject of a communication of Gelissen and Hermans (44), who suggested that an addition compound was formed between the peroxide and the hydrocarbon, which then decomposed with evolution of carbon dioxide. This mechanism is similar to that proposed by Hantzsch (see p. 176) for the decomposition reactions of diazonium salts with evolution of nitrogen. The reactions were represented thus:



$$\begin{array}{cc} \multicolumn{2}{c}{\mathrm{RCOO{-}OCOR + R'H}} \\ \text{Main reaction} & \text{Side reaction} \\ \mathrm{RCOOH + RR' + CO_2} & \mathrm{RCOOR' + RH + CO_2} \end{array}$$



$$\begin{array}{cc} \multicolumn{2}{c}{\mathrm{RN_2X + R'H}} \\ \text{Main reaction} & \text{Side reaction} \\ \mathrm{RR' + XH + N_2} & \mathrm{RH + R'X + N_2} \end{array}$$

Examples are quoted in which the compound R′H may be a hydrocarbon, an alcohol, or water. It may be noted that several cases are known in which a diazonium salt decomposes in water with replacement of the diazo group by hydrogen without recourse to the use of a reducing agent (168, 101, 112). Further, Gomberg and Pernert (58) have drawn special attention to examples of the replacement of the diazo group by hydrogen in the reactions of the diazo hydroxides, where the addition of a reducing agent is not necessary. These reactions show a close correspondence to the reactions of nitrosoacetanilide with aliphatic hydrogen-containing solvents recently carried out by Waters (153) and described in section VI.

In summarizing the reactions of the diacyl peroxides Gelissen and Hermans (46) distinguished between the thermal decomposition, which takes place on heating above the melting point, and in which two molecules of carbon dioxide are evolved, thus:

$$\mathrm{RCOO{—}OCOR \rightarrow RR + 2CO_2}$$

and the reaction with a solvent R'H, in which only one molecule of carbon dioxide is evolved, but which could proceed in two ways as shown above. The formation of biphenyl on the thermal decomposition of dibenzoyl peroxide, however, takes place only to a limited extent unless a catalyst is present (40) or unless a high temperature is used (123). Biphenyl is also formed by the action of ultra-violet light on dibenzoyl peroxide (35). In more recent surveys of the problem by Böeseken and Hermans (22) and by Hermans (76), the reactions of the diacyl peroxides have been represented in a new manner. It is held that when heated, either alone or with a solvent, they react according to one or more of the following equations:

$$\mathrm{RCOO{—}OCOR \rightarrow RR + 2CO_2} \tag{1}$$

$$\mathrm{RCOO{—}OCOR \rightarrow RCOOR + CO_2} \tag{2}$$

$$\mathrm{C_6H_5COO{—}OCOR \rightarrow RC_6H_4COOH + CO_2} \tag{3}$$

$$\mathrm{RCOO{—}OCOR + R'H \rightarrow R'COO{—}OCOR + RH} \tag{4}$$

$$\mathrm{RCOO{—}OCOR + R'H \rightarrow \underset{\substack{\downarrow \\ RCOOH\ +\ CO_2}}{[RCOO{—}OCOH]} + RR'} \tag{5}$$

Reactions 1 and 2 represent the main courses followed on thermal decomposition, whereas the reaction with a solvent, R'H, is now represented as a type of "double decomposition" (reactions 4 and 5), as the result of which two new peroxides are formed, each of which is capable of subsequent reactions as represented in the equations 1 to 5.

Although this scheme embraces in an apparently satisfactory manner the great variety of products which may be formed when a diacyl peroxide undergoes decomposition alone or in solution, yet it is difficult to find direct evidence to support the "double decomposition" reactions (4 and 5), which in many cases imply the formation, from a thermally unstable compound, of a new compound of similar constitution yet less stable. The participation of free radicals in these reactions is not considered by Böeseken and Hermans to be an essential feature, and the implication is drawn that the formation of free radicals is improbable. Reynhart (123) also considers the formation of free phenyl radicals in the thermal decomposition of dibenzoyl peroxide improbable, since when the decomposition was carried out in an atmosphere of bromine at 210°C. no bromobenzene was formed; similarly in the presence of iodine no iodobenzene was formed. This evidence, however, is not conclusive, for in an analogous reaction, the photochemical decomposition of aldehydes (compare p. 173), there is no mixed product, i.e.,

$$\mathrm{RCHO} \rightarrow \mathrm{RH} + \mathrm{CO}$$

only, for the two free radicals, produced in close proximity, unite at once, before any other molecule can intervene (110, 6).

An extensive investigation into the reactions of the diacyl peroxides was also made by Wieland and Razubaiev (163), which included the reactions of many unsymmetrical diacyl peroxides, $\mathrm{RCOO{-}OCOR'}$. With aromatic peroxides of the type $\mathrm{C_6H_5COO{-}OCOC_6H_4R}$ decomposition in benzene solution gave rise to two biaryls, namely $\mathrm{C_6H_5C_6H_5}$ and p-$\mathrm{C_6H_5C_6H_4R}$, whereas in the case of benzoyl acetyl peroxide, biphenyl and methane were produced in addition to benzoic and acetic acids:

$$\mathrm{C_6H_5COO{-}OCOCH_3 + C_6H_6 \rightarrow C_6H_5C_6H_5 + 2CO_2 + CH_4}$$

The fate of the acetate radical in this reaction resembles closely that of the acetate radical in the reactions of nitrosoacetanilide. Wieland, Schapiro, and Metzger (165) extended the investigations to include the thermal decomposition of a number of new symmetrical and unsymmetrical diacyl peroxides. In the thermal decomposition of dihydrocinnamoyl peroxide, diluted with sand, at 70°C. approximately 1.5 moles of carbon dioxide were evolved and the main reactions were represented thus:

$$(a)\ \mathrm{C_6H_5CH_2CH_2COO{-}OCOCH_2CH_2C_6H_5 \rightarrow 2CO_2 + 2C_6H_5CH_2CH_2\cdot}$$
$$\text{and } \mathrm{2C_6H_5CH_2CH_2\cdot \rightarrow C_6H_5CH_2CH_2CH_2CH_2C_6H_5}$$

$$(b)\ \mathrm{C_6H_5CH_2CH_2COO{-}OCOCH_2CH_2C_6H_5 \rightarrow}$$
$$\mathrm{CO_2 + C_6H_5CH_2CH_2COO\cdot + C_6H_5CH_2CH_2\cdot}$$
$$\text{and } \mathrm{C_6H_5CH_2CH_2COO\cdot + H\cdot \rightarrow C_6H_5CH_2CH_2COOH}$$

$$(c)\ \mathrm{C_6H_5CH_2CH_2COO{-}OCOCH_2CH_2C_6H_5 \rightarrow}$$
$$\mathrm{CO_2 + C_6H_5CH_2CH_2COOCH_2CH_2C_6H_5}$$

The greater part of the reaction proceeds according to equation *a*, but it is pointed out that the subsequent changes in the radical $C_6H_5CH_2CH_2\cdot$ are not completely disclosed. Both 1,4-diphenylbutane and ethylbenzene were isolated, but no styrene was found. The source of the hydrogen in reaction *b* is not revealed. To account for the minor reactions which occur with the formation of ethylbenzene and compounds of higher molecular weight, it is held that the 1,4-diphenylbutane first formed may then react with more unchanged peroxide, as in the decomposition reactions carried out in solution. It is stated, however, that in none of these reactions is it necessary to assume the intermediate formation of free radicals, and that the reaction in solution is more likely to be one between peroxide molecules and solvent molecules. In the case of mixed aliphatic-aromatic peroxides it was established that it is the aliphatically bound carbon dioxide which is eliminated to a preponderating extent. A further example studied was the thermal decomposition of benzoyl *o*-chlorobenzoyl peroxide. It was argued that if free aryl radicals were formed the product should contain, not only 2-chlorobiphenyl, but also biphenyl itself and 2,2′-dichlorobiphenyl. No biphenyl was detected in the product, however. Against this argument must be brought the evidence from the thermal decomposition of phenylazotriphenylmethane, in which case the formation of a phenyl radical is highly probable, yet no biphenyl is formed.

Wieland and his coworkers regard the correspondence between the reactions of the diacyl peroxides and those of the arylazotriarylmethanes, both with and without solvents, as superficial only. The difference, it is claimed, is illustrated best in the thermal decomposition in absence of solvent, for while phenylazotriphenylmethane yields some benzene and no biphenyl, dibenzoyl peroxide yields biphenyl and no benzene. This argument is, however, discounted, since Erlenmeyer and Schoenauer (32) have shown that benzene *is* formed when dibenzoyl peroxide suffers decomposition. There is also an important difference between the two cases, since in the phenylazotriphenylmethane molecule there is only one phenyl group, whereas in the dibenzoyl peroxide molecule there are two. The life of the free aryl radical is essentially very short and biphenyl formation, as opposed to benzene formation, is therefore likely to be far more probable in the case of the peroxide reaction in which the two free phenyl radicals would probably be produced simultaneously and in close proximity by the elimination of carbon dioxide from the symmetrical starting product. The decomposition of the diacyl peroxides seems to bear a similar relationship to the decomposition of the arylazotriarylmethanes as does the photochemical decomposition of aldehydes to that of ketones. It is a difference of degree rather than of kind.

The remarkable correspondence now revealed between the reactions of the diazo hydroxides, the nitrosoacylarylamines, the arylazotriarylmethanes, and the diacyl peroxides demands that the possibility of the participation of free radicals in the reactions of the latter class of compounds should be reconsidered. The available evidence points strongly to a specific reaction mechanism common to all four cases. The various reactions which the diacyl peroxides can undergo, both on thermal decomposition alone and on decomposition in solution, can all be accounted for satisfactorily by the initial formation of free radicals thus:

$$\mathrm{RCOO{-}OCOR} \rightarrow \mathrm{R\cdot} + \mathrm{RCOO\cdot} + \mathrm{CO_2}$$
$$\mathrm{C_6H_5COO{-}OCOR} \rightarrow \mathrm{C_6H_5\cdot} + \mathrm{RCOO\cdot} + \mathrm{CO_2}$$
$$\mathrm{C_6H_5COO{-}OCOR} \rightarrow \mathrm{R\cdot} + \mathrm{C_6H_5COO\cdot} + \mathrm{CO_2}$$

The free radicals thus produced, by further action with themselves or with other molecules, can then give rise to the various hydrocarbons, acids, and esters which are formed. Thus:

$$\mathrm{R\cdot} + \mathrm{R'H} \rightarrow \mathrm{RR'} + \mathrm{H\cdot}$$
$$\mathrm{R\cdot} + \mathrm{R'H} \rightarrow \mathrm{RH} + \mathrm{R'\cdot}$$
$$\mathrm{RCOO\cdot} + \mathrm{H\cdot} \rightarrow \mathrm{RCOOH}$$
$$\mathrm{RCOO\cdot} + \mathrm{R\cdot} \rightarrow \mathrm{RCOOR}$$
$$\mathrm{RCOO\cdot} + \mathrm{R'\cdot} \rightarrow \mathrm{RCOOR'}$$
$$\mathrm{C_6H_5\cdot} + \mathrm{R'H} \rightarrow \mathrm{C_6H_5R'} + \mathrm{H\cdot}$$
$$\mathrm{C_6H_5\cdot} + \mathrm{R'H} \rightarrow \mathrm{C_6H_6} + \mathrm{R'\cdot}$$
$$\mathrm{C_6H_5COO\cdot} + \mathrm{H\cdot} \rightarrow \mathrm{C_6H_5COOH}$$
$$\mathrm{C_6H_5COOH} + \mathrm{R\cdot} \rightarrow \mathrm{RC_6H_4COOH} + \mathrm{H\cdot}$$
$$\mathrm{C_6H_5COOH} + \mathrm{R'\cdot} \rightarrow \mathrm{R'C_6H_4COOH} + \mathrm{H\cdot}$$
$$\mathrm{C_6H_5\cdot} + \mathrm{C_6H_5R'} \rightarrow \mathrm{C_6H_5C_6H_4R'} + \mathrm{H\cdot}$$
$$\mathrm{C_6H_5\cdot} + \mathrm{C_6H_5R'} \rightarrow \mathrm{C_6H_6} + \mathrm{R'C_6H_4\cdot}$$
$$\mathrm{C_6H_5COOH} + \mathrm{R'C_6H_4\cdot} \rightarrow \mathrm{R'C_6H_4C_6H_4COOH} + \mathrm{H\cdot}\text{, etc., etc.}$$

The intermediate formation of new unstable diacyl and acyl formyl peroxides by double decomposition, as assumed by Böeseken and Hermans (22), is no longer required.

More recently the thermal and photochemical decomposition of diacetyl peroxide in solution has been studied by Walker and Wild (150a), who have shown (*a*) that the reaction in solution is complex, (*b*) that in an excess of solvent (toluene) the thermal reaction is of the first order with respect to diacetyl peroxide, and (*c*) that in the decomposition in solution (cyclohexane or ethyl alcohol) less ethane and more methane is obtained than from the photodecomposition in absence of a solvent. Hence Walker and

Wild suggest that the primary process may consist of a dissociation into free acetate radicals, which decompose further into carbon dioxide and methyl radicals, which could combine together to form ethane or react with surrounding solvent molecules to give methane. These results again are in complete agreement with the properties of free radicals in solution as presented in this review.

IX. PROPERTIES OF FREE ARYL RADICALS

Although it has been shown above that the arguments brought by Wieland and others, which tend to weigh against a free radical mechanism, are not insuperable, it should be emphasized that all the reactions of the diacyl peroxides may not involve the formation of free radicals. The same proviso must be applied to the reactions of the azo and diazo compounds.

The free radicals can at most have only a transient existence and one can only postulate their production in thermal or photochemical self-decompositions, or in reactions of the same type occurring in neutral non-ionizing solvents.

The marked differences between the reactions of the free substances in the vapor phase and their reactions in solvents have already been stressed, and it has been pointed out that in the latter reactions the free radical invariably reacts with the solvent molecule. This indeed is a marked characteristic of the phenyl radical.

In opposition to the views set forth above, it might be contended that in every case some polymerization should be evident with formation of biphenyl, quite irrespective of the nature and presence of any second component or solvent. It is known that free phenyl radicals formed in the gaseous phase at relatively high temperatures and low pressures, as, for example, in the thermal decomposition of lead tetraphenyl (30) or from the action of sodium vapor on bromobenzene (79) give rise to biphenyl. In the reactions carried out in solution, however, polymerization to biphenyl does *not* take place (162, 157). Biphenyl formation only occurs when benzene is present,

$$C_6H_5\cdot + C_6H_6 \rightarrow C_6H_5C_6H_5 + H\cdot$$

and the isolation of ter-, quater- and even quinque-phenyl in smaller quantities, which is characteristic of these reactions, also indicates a reaction between the radical and a hydrocarbon molecule,

$$C_6H_5\cdot + C_6H_5C_6H_5 \rightarrow C_6H_5C_6H_4C_6H_5 + H\cdot$$

$$C_6H_5\cdot + C_6H_5C_6H_4C_6H_5 \rightarrow C_6H_5C_6H_4C_6H_4C_6H_5 + H\cdot, \text{ etc.}$$

rather than reaction between two phenyl radicals, which can result in the formation of the binuclear hydrocarbon only,

$$C_6H_5\cdot + C_6H_5\cdot \rightarrow C_6H_5C_6H_5$$

The formation of a substituted diphenyl $C_6H_5C_6H_4R$, when reaction is carried out in a benzene derivative, C_6H_5R, also illustrates the same point.

Thus, the main characteristics of the phenyl radical, when formed in the presence of a solvent, may be summarized as follows: (*1*) The free phenyl radical is an extremely reactive substance of short life, able to interact with and decompose almost the first molecule of any type which it encounters. (*2*) Polymerization to biphenyl is not encountered. (*3*) Reaction with non-aromatic hydrogen-containing solvents gives rise to the formation of benzene:

$$C_6H_5\cdot + RH \rightarrow C_6H_6$$

(*4*) Reaction with non-aromatic halogen-containing solvents gives rise to the formation of halogeno-benzene:

$$C_6H_5\cdot + RHal \rightarrow C_6H_5Hal$$

(*5*) Reaction with neutral aromatic liquids gives rise to the formation of biphenyl derivatives, in which the radical enters the nucleus at the ortho- and para-positions, irrespective of the nature of any so-called directing group which may be present:

$$C_6H_5\cdot + C_6H_5R \rightarrow o\text{- and } p\text{-}C_6H_5C_6H_4R$$

These properties are entirely consistent with those of the free alkyl radicals. Thus the free methyl radical will abstract hydrogen from practically any other organic molecule with formation of methane (129),

$$CH_3\cdot + RH \rightarrow CH_4$$

in both the gaseous and liquid phases (compare section III).

X. DIRADICALS

Just as azomethane on heating gives nitrogen and free methyl radicals, so diazomethane, $CH_2{=}N_2$, decomposes into nitrogen and the free methylene radical CH_2: at a temperature of 350–600°C. The latter was conclusively identified by its reaction with tellurium, when telluro-formaldehyde, $(CH_2Te)_n$, was produced (127). As long ago as 1912, however, Staudinger and Kupfer (146) had shown that on heating in carbon monoxide diazomethane yielded a little ketene:

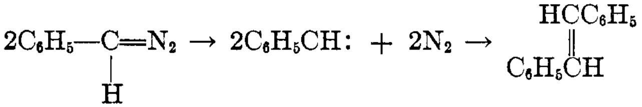
$$CH_2{=}N_2 + CO \rightarrow CH_2{=}CO + N_2$$

and suggested that free methylene was a transient product.

In 1916 Staudinger put forward the view that free divalent radicals were possible initial decomposition products of all aliphatic diazenes (aliphatic diazo compounds) (142, 143, 144, 145). On standing alone, or in inert solvents such as ether or hydrocarbons, diazenes gradually evolve nitrogen and a ketazine is produced or, in a few cases, an olefin, e.g.,

$$(C_6H_5)_2C{=}N_2 \rightarrow (C_6H_5)_2C\colon + N_2$$

$$(C_6H_5)_2C\colon + N_2{=}C(C_6H_5)_2 \rightarrow (C_6H_5)_2C{=}N{-}N{=}C(C_6H_5)_2$$



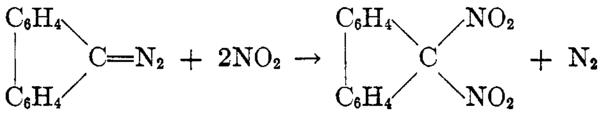
$$2C_6H_5{-}\underset{\displaystyle H}{\underset{|}{C}}{=}N_2 \rightarrow 2C_6H_5CH\colon + 2N_2 \rightarrow \begin{array}{c} HCC_6H_5 \\ \| \\ C_6H_5CH \end{array}$$

This reaction is promoted by ultra-violet light and is catalyzed by both iodine and oxygen.

Iodine itself reacts as follows:

$$CH_2{=}N_2 + I_2 \rightarrow CH_2I_2 + N_2$$

and, as Wieland and Reisenegger (164) showed, nitrogen peroxide can replace the nitrogen by two NO_2 groups, as, for example, in diazofluorene:



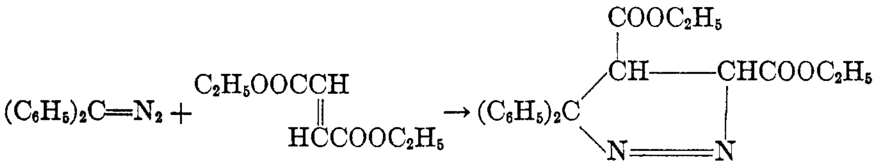
$$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>C{=}N_2 + 2NO_2 \rightarrow \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>C<\!\!\begin{array}{l} NO_2 \\ NO_2 \end{array} + N_2$$

These reactions are reminiscent of those of triphenylmethyl and afford strong support to the hypothesis of fission into a neutral free diradical.

Fission of nitrogen also occurs, however, when aliphatic diazenes interact with polar reagents such as alcohols, acids, bases, and acyl halides, and it has been suggested that in these cases the nitrogen elimination follows a polar addition process, which yields a transient aliphatic diazonium ion (26):

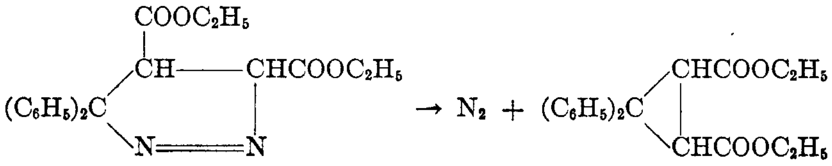
$$XH + CH_2{=}N_2 \rightarrow X^-[HCH_2N{=}N]^+ \rightarrow XCH_3 + N_2$$

With olefins undoubtedly an addition reaction occurs initially, for pyrazole ring compounds can easily be isolated:



$$(C_6H_5)_2C{=}N_2 + \begin{array}{c} C_2H_5OOCCH \\ \| \\ HCCOOC_2H_5 \end{array} \rightarrow (C_6H_5)_2C<\!\!\begin{array}{l} \overset{\displaystyle COOC_2H_5}{\overset{|}{C}}H{-}{-}CHCOOC_2H_5 \\ \qquad\qquad\quad | \\ N{=}{=}{=}N \end{array}$$

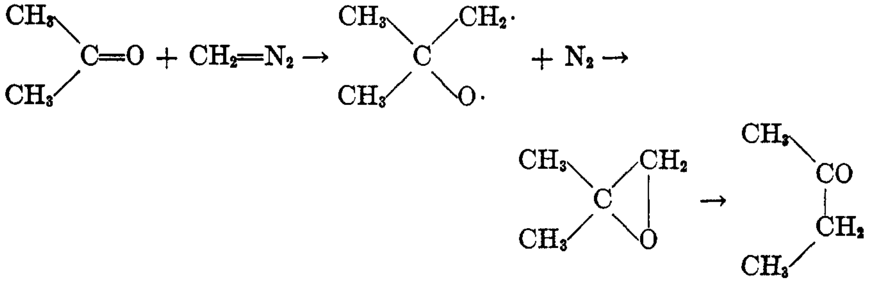
On heating, however, these cyclic azo compounds invariably lose nitrogen and give trimethylene ring derivatives.



$$(C_6H_5)_2C<\!\!\begin{array}{l} \overset{\displaystyle COOC_2H_5}{\overset{|}{C}}H{-}{-}CHCOOC_2H_5 \\ \qquad\qquad\quad | \\ N{=}{=}{=}N \end{array} \rightarrow N_2 + (C_6H_5)_2C<\!\!\begin{array}{l} CHCOOC_2H_5 \\ | \\ CHCOOC_2H_5 \end{array}$$

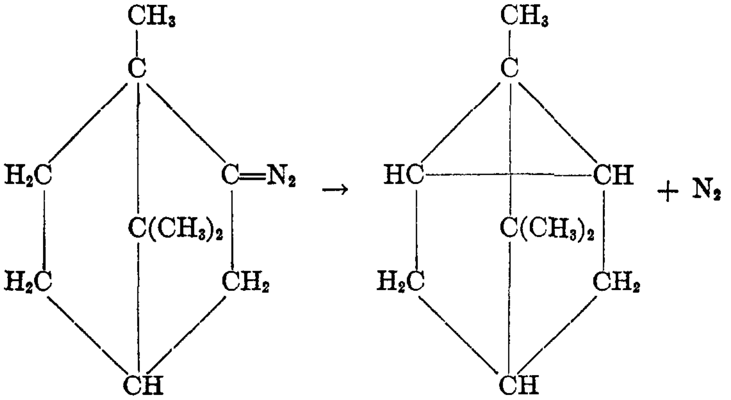
This final decomposition may well give rise to transient free radicals, just as in the case of the azo compounds considered in section IV. In some cases it takes place spontaneously, but in others heating alone, or in an inert solvent, is needed.

Similar circumstances have been recorded for the Schlotterbeck reaction between diazomethane and acetone (138, 2). Meerwein (98, 99) represents this reaction as follows:



and has established the fact that dimethylethylene oxide is an intermediate product. However, whilst Meerwein and also Mosettig and Burger (104) favor the free radical mechanism as depicted above, Robinson and Smith (132) consider that the whole process is polar in type.

The decomposition of diazocamphane (100) is another reaction which is possibly of non-ionic type; it yields tricyclene and not bornylene or camphene, which are products of ionic changes. Thus:



The decomposition of diazocamphor is similar.

In a very similar manner the azides may possibly yield a diradical with univalent nitrogen. Thus when phenyl azide is heated in benzene in a sealed tube at 150–160°C. azobenzene is produced (9, 10).

$$C_6H_5N_3 \rightarrow N_2 + C_6H_5N: \rightarrow C_6H_5N{=}NC_6H_5$$

With *p*-xylene, however, the free radical, $C_6H_5N:$, reacts to give *p,p'*-ditolylethane and aniline, the free radical thus reacting with an aliphatic side chain in the usual manner by abstracting hydrogen:

$$C_6H_5N: + 2CH_3C_6H_4CH_3 \rightarrow C_6H_5NH_2 + CH_3C_6H_4CH_2CH_2C_6H_4CH_3$$

Schmidt (140) also suggested that hydrazoic acid yields the radical HN: when treated with sulfuric acid:

$$HN_3 \rightarrow HN: + N_2$$

Goldschmidt and his coworkers (51, 52, 53) have suggested that the free radical $C_6H_5N:$ is also produced when phenyldichloroamine, $C_6H_5NCl_2$, decomposes, or when aniline is oxidized in non-ionizing solvents. Further, Goldschmidt and Wurzschmitt (52) oxidized aniline with lead peroxide, in dry ether containing hexaphenylethane, using anhydrous sodium sulfate to remove the water as it was produced, and obtained anilinotriphenylmethane in good yield.

They represent the reaction as follows:

$$2C_6H_5NH_2 + PbO_2 \rightarrow 2C_6H_5NH\cdot + PbO + H_2O$$

$$C_6H_5NH\cdot + \cdot C(C_6H_5)_3 \rightarrow C_6H_5NHC(C_6H_5)_3$$

Evidence for the existence of the analogous free radical diphenyl nitrogen, $(C_6H_5)_2N\cdot$, which is produced by the dissociation of tetraphenylhydrazine,

$$(C_6H_5)_2NN(C_6H_5)_2 \rightarrow 2(C_6H_5)_2N\cdot$$

just as hexaphenylethane dissociates into triphenylmethyl, has been brought forward by Wieland (154, 161, 155), but its participation in certain reactions of the tetraarylhydrazines is regarded as unlikely (156).

The carbonyl compounds analogous to the aliphatic diazenes are the ketenes, and these substances will, on heating to a high temperature, eliminate carbon monoxide (compare the reactions of the ketones, section III):

$$2CH_2{=}CO \rightarrow C_2H_4 + 2CO$$

The most characteristic properties of the ketenes are their additive reactions, which take place at a double bond (141). It has been suggested, therefore that the ketenes might be regarded as diradicals (160, 81).

XI. ELECTRODE REACTIONS

A neutral radical must obviously be produced whenever an ion is discharged at an electrode, but the liberated radicals then promptly react either with each other or with other adjacent ions or neutral molecules. Thus in the electrolysis of dilute sulfuric acid there occurs:

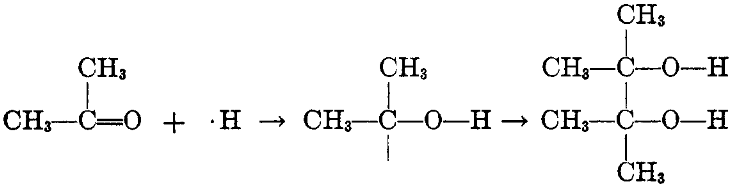
at the cathode:
(i) $H^+ + e \rightarrow H\cdot$
(ii) $2H\cdot \rightarrow H_2$

at the anode:
(i) $OH^- \rightarrow \cdot OH + e$
(ii) $2\ \cdot OH \rightarrow H_2O_2$
(iii) $2\ \cdot OH \rightarrow H_2O + O \quad (\rightarrow O_2)$

Hence free neutral radicals may be involved in many of the electrolytic reactions that are used in practical organic chemistry. However, an exact study of each reaction is required before its precise mechanism can be established, for it has been shown that many reactions which were once formulated as unions of ions upon discharge are in reality much more complicated, and involve purely chemical reactions brought about by reactive molecular products (such as hydrogen peroxide) formed in the immediate vicinity of the electrode (50).

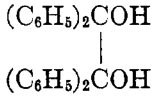
A. Cathode reactions

A wide range of organic compounds can be reduced, either in acid or in alkaline solution, if placed in the cathode compartment of an electrolytic cell; the nature and yield of the reaction product depend mainly upon the electrode potential and the current density employed. The reduction of all covalent organic compounds at a cathode is of course brought about by the hydrogen liberated at the electrode, but it is rarely possible to decide whether it is the initially produced hydrogen atoms or the hydrogen molecules which attack the organic compound. The reduction of an organic compound at a metallic cathode may be catalyzed by the electrode, and metals are powerful catalysts for reduction by hydrogen gas. A few of the experimental observations of electrolytic reduction, however, are explicable most easily upon the free radical hypothesis. By the electrolytic reduction of ketones, pinacones are produced, whilst aldehydes can yield glycols (166, 148, 136). Pinacone (pinacol) formation can be explained most simply as due to combination of two free ketyl radicals:



$$CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}O + \cdot H \rightarrow CH_3{-}\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}{-}O{-}H \rightarrow \begin{array}{c} CH_3 \\ | \\ CH_3{-}C{-}O{-}H \\ | \\ CH_3{-}C{-}O{-}H \\ | \\ CH_3 \end{array}$$

In the same way sodium benzophenone, $(C_6H_5)_2CONa$, yields benzopinacol,



$$\begin{array}{c}(C_6H_5)_2COH\\ |\\ (C_6H_5)_2COH\end{array}$$

on treatment with water. This hypothesis receives further confirmation from the fact that, in warm acid solutions, ketones on electrolysis at mercury cathodes yield mercury dialkyls, and at lead cathodes, lead tetraalkyls (147, 149, 122, 134, 63).

B. Anode reactions

Many inorganic anode reactions have been considered to involve a combination reaction of free neutral radicals, e.g.,

$$I^- \rightarrow I\cdot + e; \qquad 2I\cdot \rightarrow I_2 \tag{a}$$

$$[HSO_4]^- \rightarrow [HSO_4]\cdot + e; \qquad 2[HSO_4]\cdot \rightarrow H_2S_2O_8 \tag{b}$$

It has been demonstrated that when solutions of zinc ethyl or of ethyl magnesium bromide are electrolyzed the free ethyl radical is liberated at the anode (73, 91, 92). If this is composed of a metal like lead, antimony, or bismuth, it is attacked with formation of the corresponding organometallic compound. At an inert electrode a mixture of hydrocarbon gases is liberated.

Kolbe's reaction, the formation of carbon dioxide and a hydrocarbon upon electrolysis of a salt of an aliphatic acid, was represented by Crum Brown and Walker (29) as follows:

$$[CH_3COO]^- \rightarrow e + CH_3COO\cdot \rightarrow CO_2 + \cdot CH_3 \rightarrow C_2H_6$$

On the other hand Fichter and his coworkers (34, 33, 36) considered that an organic peroxide or per acid was first formed at the anode, and that this, like any other organic peroxide, then decomposed to give carbon dioxide and a mixture of hydrocarbons. From a detailed investigation of the electrolysis of acetates, however, Glasstone and Hickling (49, 50) have come to the conclusion that in aqueous solution the acetate anion is not discharged to any appreciable extent, but that hydroxyl anions are discharged preferentially, and unite in pairs to form hydrogen peroxide. The hydrogen peroxide, formed in high local concentration and in the presence of a catalyst (the electrode material), is then presumably able to oxidize acetate anions to ethane and carbon dioxide.

$$2[CH_3COO]^- + H_2O_2 \rightarrow C_2H_6 + 2CO_2 + 2OH^-$$

This oxidation possibly takes place with the intermediate formation of diacetyl peroxide. In non-aqueous solutions, such as glacial acetic acid, in which hydrogen peroxide cannot be formed, the acetate anions may be discharged, and under these circumstances the mechanism of Crum Brown and Walker would be valid.

XII. FREE RADICALS FROM REACTIONS INVOLVING METALS

Polanyi and his coworkers have shown that in the vapor phase atoms of the alkali metals can undoubtedly decompose alkyl halides with production of free radicals (see section I),

$$Na\cdot + ICH_3 \rightarrow Na^+I^- + \cdot CH_3\,; \qquad 2CH_3\cdot \rightarrow CH_3CH_3$$

but it is doubtful whether this same mechanism can be applied to the hydrocarbon syntheses of Fittig, Wurtz, and Ullmann, which are usually carried out in inert solvents: e.g.,

$$2C_2H_5I + 2Na \rightarrow C_2H_5C_2H_5 + 2NaI$$

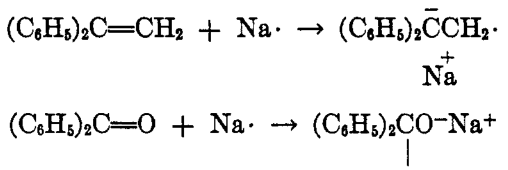
$$2C_6H_5I + 2Cu \rightarrow C_6H_5C_6H_5 + Cu_2I_2$$

since the reactions may proceed instead by means of the formation of organometallic compounds, e.g.,

$$C_2H_5Br + 2Na \rightarrow (C_2H_5)^-Na^+ + NaBr$$
$$C_2H_5Na + BrC_2H_5 \rightarrow C_2H_5C_2H_5 + NaBr$$

and evidence can be adduced in support of each theory (167, 3, 139, 169, 173, 103).

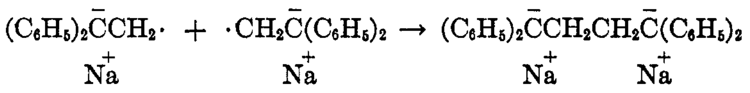
Transient free radicals may also be produced at one end of a double linkage when an alkali metal atom adds on to the other end, e.g.,



$$(C_6H_5)_2C{=}CH_2 + Na\cdot \rightarrow (C_6H_5)_2\underset{\overset{+}{Na}}{\bar{C}}CH_2\cdot$$

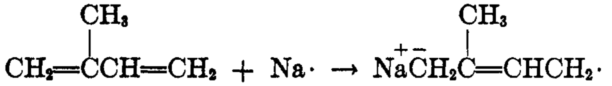
$$(C_6H_5)_2C{=}O + Na\cdot \rightarrow (C_6H_5)_2\underset{|}{C}O^-Na^+$$

These free radicals promptly unite to form double molecules (137), e.g.,



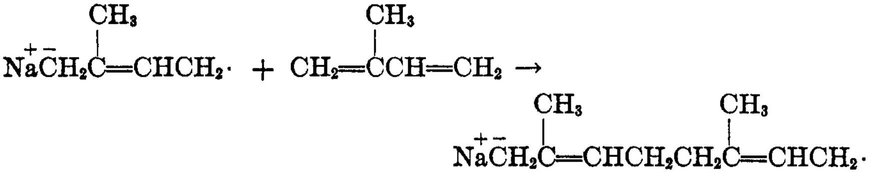
$$(C_6H_5)_2\underset{\overset{+}{Na}}{\bar{C}}CH_2\cdot + \cdot CH_2\underset{\overset{+}{Na}}{\bar{C}}(C_6H_5)_2 \rightarrow (C_6H_5)_2\underset{\overset{+}{Na}}{\bar{C}}CH_2CH_2\underset{\overset{+}{Na}}{\bar{C}}(C_6H_5)_2$$

but a chain polymerization process may also be initiated (8) and in this way one can explain in a simple manner the action of sodium metal in catalyzing the chain polymerization of styrene, isoprene, and analogous substances, though here again the mechanism of the reaction is not without doubt (1, 170, 171, 172). For example, if sodium metal adds on to isoprene as follows



$$\mathrm{CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH{=}CH_2 + Na\cdot \rightarrow \overset{+}{Na}\overset{-}{C}H_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2\cdot}$$

there would be produced a free radical which could unite with a second isoprene molecule to produce a dimeric free radical:



$$\mathrm{\overset{+}{Na}\overset{-}{C}H_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2\cdot + CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}CH{=}CH_2 \rightarrow \overset{+}{Na}\overset{-}{C}H_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2\cdot}$$

and by continuing this process a long-chain polymer might be formed.

Free radical formation may also explain the process of polymerization of these substances by ultra-violet light (38). It is also of interest to point out that the organic peroxides, such as dibenzoyl peroxide, are frequently employed as catalysts in bringing about the chain polymerization of olefins. From a consideration of the properties of these compounds (see section VIII), it can be seen that quite possibly they act by initiating free radical formation. In this connection too it may be mentioned that both in the gaseous phase (150) and in the liquid phase under high pressure (28, 131) it has been shown that the free methyl and ethyl radicals react with ethylene to form a hydrocarbon oil of high molecular weight.

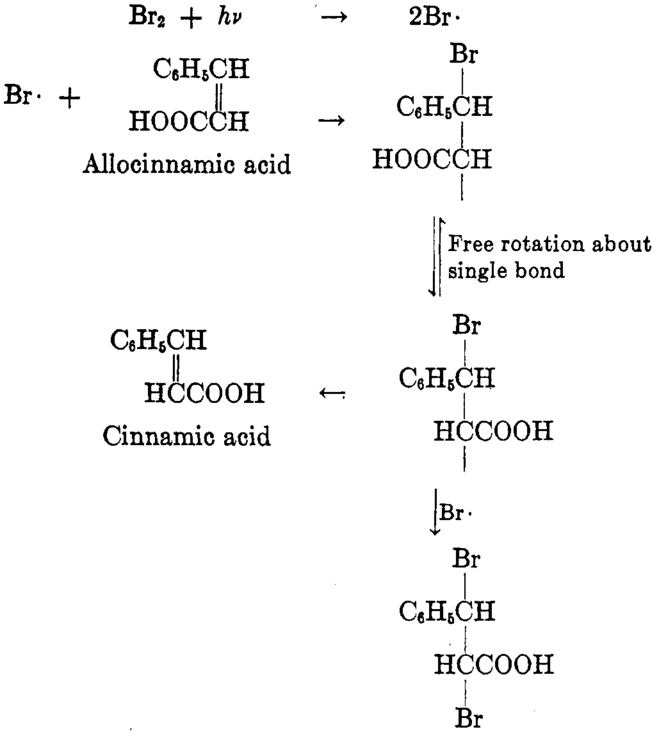
XIII. REACTIONS DUE TO FREE HALOGEN ATOMS

It is well known that halogen molecules are decomposed into neutral atoms by exposure to ultra-violet light, and many photochemical chain reactions of chlorine and bromine vapors are now believed to occur in consequence of the formation of these atoms. Thus the formation of phosgene is represented as follows (17, 19, 18):

$$Cl_2 + h\nu \rightarrow 2Cl\cdot$$

$$\left.\begin{aligned} Cl\cdot + CO &\rightarrow COCl\cdot \\ COCl\cdot + Cl_2 &\rightarrow COCl_2 + Cl\cdot \end{aligned}\right\}\ \text{chain process}$$

Berthoud (11, 13, 14, 15, 12, 16) and his colleagues have shown that the photochemical reactions between bromine and olefins in non-ionizing solvents are also due to the initial production of halogen atoms, since, with feeble illumination, the rate of reaction is proportional to the square root of the intensity of the light, indicating that each bromine molecule is split up into two reactive bromine atoms. The photochemical reactions between allocinnamic acid and bromine can thus be represented as follows:



$$Br_2 + h\nu \rightarrow 2Br\cdot \qquad (a)$$

$$Br\cdot + \begin{array}{c} C_6H_5CH \\ \| \\ HOOCCH \end{array} \rightarrow \begin{array}{c} Br \\ | \\ C_6H_5CH \\ | \\ HOOCCH \\ | \end{array} \qquad (b)$$

Allocinnamic acid

Free rotation about single bond

$$\begin{array}{c} C_6H_5CH \\ \| \\ HCCOOH \end{array} \leftarrow \begin{array}{c} Br \\ | \\ C_6H_5CH \\ | \\ HCCOOH \\ | \end{array} \qquad (c)$$

Cinnamic acid

$$\downarrow Br\cdot$$

$$\begin{array}{c} Br \\ | \\ C_6H_5CH \\ | \\ HCCOOH \\ | \\ Br \end{array} \qquad (d)$$

trans-Dibromocinnamic acid

In connection with this atomic mechanism for addition to olefins, recent observations of Kharasch and his coworkers (87, 88, 89, 85, 86) are of considerable interest. These investigators have shown that a pure olefin adds hydrogen bromide in the manner predicted by Markownikow's rule: e.g.,

$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CHBrCH_3 \qquad (a)$$

If the olefin has been exposed to the air, however, the hydrogen bromide tends to add on in the reverse manner:

$$CH_3CH{=}CH_2 + HBr \rightarrow CH_3CH_2CH_2Br \qquad (b)$$

This change is due to the presence of peroxides, and the addition of a little dibenzoyl peroxide to an olefin may completely reverse the mode of addition of hydrogen bromide from the normal type (a) to its converse (b). Since peroxides can be regarded as possible generators of neutral radicals it may be suggested that the addition process (b) is one requiring the transient production of neutral atoms of hydrogen and bromine from the hydrogen bromide.

After the manuscript of this review had been submitted for publication, Kharasch, Mansfield, and Mayo (86a) published a short communication in which they have put forward the same point of view as that given immediately above. In support of this theory they have shown that (*cis*)-isostilbene is not converted into (*trans*)-stilbene by the catalytic action of hydrogen bromide in the dark except in the presence of air or peroxidic substances, when the reaction becomes very rapid. The reaction initiated by peroxides is thus of exactly the same type as are the photochemical reactions of Berthoud. More recently still, Kharasch, Margolis, White, and Mayo (86b) have further extended the theory of reaction by atomic bromine in presence of peroxides to the halogenation of aromatic side chains in a way which had been very tentatively foreshadowed by Waters (152a). It has been shown that whereas the nuclear substitution of toluene is not catalyzed by peroxides, substitution in the side chain is very markedly affected. Thus when toluene is brominated in the dark at 25°C. in the presence of ascaridole, the reaction takes half an hour and the product is over 98 per cent benzyl bromide.

The peroxide effect discovered by Kharasch may be taken as an indication that olefins form addition compounds with neutral radicals, for oxygen gas is a paramagnetic molecule, which must therefore contain two uncoupled electrons and may be represented as a diradical $\cdot O—O\cdot$. It is beyond the scope of this review to discuss the reactions of oxygen gas, but it may be mentioned that Haber and Willstätter (62) have suggested that free radicals intervene in a large number of oxidation processes. The subject has been summarized recently by Rice and Rice (130) and is still speculative, for as yet no experimental evidence has been produced indicative of the independent existence of neutral radicals in any oxidation process.

XIV. CONCLUSIONS AND SUMMARY

The foregoing sections show that strong experimental evidence is available at the present time to substantiate the general statement made in the introduction to this review, that free neutral radicals may be formed by thermal or photochemical decompositions of organic molecules in the liquid phase as well as in the gaseous phase, and that these neutral radicals, when formed, have the properties of free atoms, or of the neutral entities discharged at electrodes in many electrolytic processes. It has been amply demonstrated, moreover, that the free neutral radicals are exceedingly reactive substances, and can therefore have only a transient existence.

So very reactive are they that they interact with and decompose practically the first molecule that they encounter, and, in consequence, the reactions which involve free radicals in solutions are almost without exception reactions between free radicals and solvent molecules. No solvent has yet been discovered which is inert to these free neutral radicals, and in this way the latter entities may be differentiated from free charged ions, which are often stable in solution.

The great reactivity of free neutral radicals, however, makes their experimental detection exceedingly difficult, and without the indubitable evidence of free radical reactions in the gaseous phase the analogous reactions in solution would have received but uncertain recognition.

The authors are well aware that the interpretation of the experimental evidence which they have set forward in this review may, in some cases, be open to criticism on theoretical grounds, for but few of the researches have yielded decisive results in themselves, although they accord with the general viewpoint which has been set forth. There may exist also several other reactions in organic chemistry in which transient free neutral radicals intervene, but it has been felt that, when the available experimental evidence is but fragmentary, theoretical speculation cannot be justified.

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