U.D.C. 541.515

The Chemistry of Acyl Radicals in Solution

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The available methods for the generation of acyl radicals and their reactions in solutions are reviewed. The effect of stabilising and polar factors on the reactivity of acyl radicals and the mode of their addition to unsaturated molecules are discussed. The characteristics of the reactions involving acyl radicals, initiated by various methods (by peroxides, ultraviolet light, γ-irradiation, etc.) have been examined. Much attention has been devoted to the role of acyl radicals in chain processes constituting the basis of new methods for the synthesis of carbonyl compounds.
The bibliography includes 266 references.

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I. INTRODUCTION

Acyl radicals are some of the simplest carbonium radicals. In 1949 Kharasch et al.[1] proposed a method for their preparation from aldehydes with the aid of peroxides and ultraviolet light. In the next 20 years numerous studies were made on the reactivity of acyl radicals and their role in liquid-phase homolytic processes was investigated. Owing to the ease of formation of acyl radicals in solution, they are finding increasing application in organic synthesis.

At the present time there are six main methods for the generation of acyl radicals in solution:

1. Homolytic removal of hydrogen from aldehydes:

$$R-C\overset{H}{\underset{O}{<}} + A\cdot \rightarrow R-\dot{C}=O+AH\,.$$

2. Homolytic removal of a halogen from acid halides:

$$R-C\overset{X}{\underset{O}{<}} + A\cdot \rightarrow R-\dot{C}=O+AX\,.$$

3. Thermal, photolytic, or radiolytic dissociation of ketones and carboxylic acid derivatives:

$$R-C\overset{Y}{\underset{O}{<}} \rightarrow R-\dot{C}=O+Y$$

(Y = alkyl or a functional group).

4. One-electron oxidation of aldehydes:

$$R-C\overset{H}{\underset{O}{<}} + M^{n} \rightarrow R-\dot{C}=O + M^{n-1} + H^{+} \quad (M\text{—metal})\,.$$

5. Addition of carbon monoxide to alkyl radicals:

$$R^{\cdot} + CO \rightarrow R-\dot{C}=O\,.$$

6. Decomposition of more complex radicals, for example:

$$R-\underset{R'}{\overset{\dot{O}}{\underset{|}{C}}}-\overset{O}{\overset{\|}{C}}-R'' \rightarrow R''\dot{C}=O + R-\overset{O}{\overset{\|}{C}}-R'\,.$$

The radicals R–Ċ=O readily add to multiple carbon–carbon bonds and also to the bonds >C=O, >C=N–, –N=N–, etc. At elevated temperatures they lose carbon monoxide and are converted into alkyl radicals. Many photochemical rearrangements and decompositions of aldehydes, ketones, and carboxylic acid derivatives involve acyl radicals.

The radicals R–Ċ=O generated in solution are usually identified on the basis of the products of their further reactions. Owing to the short lifetime of acyl radicals in the liquid phase, their ESR spectra[2–5] can be obtained only at low temperatures (in the frozen state).

The present review deals with studies on the methods of generation and reactions of acyl radicals published up to 1970.

II. METHODS OF GENERATION OF ACYL RADICALS

1. FORMATION OF ACYL RADICALS FROM ALDEHYDES

In the generation of acyl radicals from aldehydes, compounds which readily undergo thermal dissociation (organic peroxides, azo-compounds, etc.), oxygen, and variable-valence metal salts are most often employed. Acyl radicals are also obtained by allowing ultraviolet light or γ-rays to act directly on aldehydes.

The relative reactivities of various aldehydes in reactions involving the removal of a hydrogen atom by t-butoxy-radicals have been investigated[6–8]. The t-butoxy radicals were obtained from t-butyl hypochlorite. The reaction has a chain mechanism, the chain being probably initiated as a result of the trimolecular reaction

$$2\,(CH_3)_3COCl + RCHO \rightarrow 2\,(CH_3)_3C-O\cdot + HCl + RCOCl\,.$$

The removal of a hydrogen atom by the $(CH_3)_3CO\cdot$ radical from CH_3CHO and from C_6H_5CHO is faster by a factor of 4.3 and 3.4 respectively than from cyclohexane[6]. *m* and *p*-Nitrobenzaldehydes do not react with $(CH_3)_3COCl$[7] owing to the electrophilic properties of t-butoxy-radicals. In this case the polar factor promotes an increase of activation energy, which hinders the removal of a hydrogen atom[6]. Probably this is why the removal of hydrogen from n-butyraldehyde by perbenzoate radicals is much easier than from benzaldehyde[9].

The relative reactivities of substituted benzaldehydes in the reaction with sulphuryl chloride initiated by benzoyl peroxide have been investigated by the method of competing reactions. Aroyl radicals are generated as a result of an attack on the aldehyde by the $\cdot SO_2Cl$ radical[10-12]. The values obtained are correlated in terms of the Hammett equation ($\rho = -0.48$). The effect of substituents is determined by the role of polar factors in the transition state[12]:

$$RC\overset{O}{\underset{H}{\diagup\diagdown}} + \cdot SO_2Cl \rightarrow RC\overset{\delta+}{\underset{O}{\diagup\diagdown}} \cdots H \cdots \overset{\delta-}{SO_2Cl} \rightarrow R-\dot{C}=O + SO_2 + HCl\,.$$

The relative reactivities of substituted benzaldehydes in the reaction with $\cdot CCl_3$ radicals were determined by Lee[13]. In this case $\rho = -0.74$. When C_6H_5CHO is replaced by C_6H_5CDO, the kinetic isotope effect is 2.4 at 80°C. $BrCCl_3$ was used as a source of $\cdot CCl_3$ radicals. The reactivities of C_6H_5CHO and other hydrogen donors with respect to the trichloromethyl ($\cdot CCl_3$)[14] and phenyl ($\cdot C_6H_5$)[15] radicals have been compared[14,15]. Table 1 lists the reactivities of C–H bonds in reactions involving the removal of hydrogen by certain radicals.

Table 1. Relative reactivities of various C–H bonds in reactions involving the abstraction of a hydrogen atom.

Radical	Compound				References
	$C_6H_5CH_3$	C_6H_5CHO	CH_3CHO	cyclohexane	
$(CH_3)_3C-O\cdot$	1	12.8	16.1	0.16	6
$\cdot SO_2Cl$	1	9.7	—	2.9	11
$\cdot CCl_3$	1	58	—	—	14

$\alpha\alpha'$-Azobisisobutyrate, a widely used initiator of many homolytic processes, has proved relatively ineffective for the generation of acyl radicals from aliphatic aldehyde[16]: only 15–20% of the total amount of $\cdot C(CH_3)_2-COO-CH_3$ radicals formed in the decomposition of the azo-compound removed hydrogen from the aldehyde, while the remainder recombined or added to the azo-group of the initiator.

When acrolein is attacked by t-butoxy-radicals, the reaction involving the removal of hydrogen from the aldehyde group predominates ($K_{rem}/K_{add} \geqslant 18$):[8]

$$(CH_3)_3COCl \xrightarrow{h\nu} (CH_3)_3C-O\cdot + Cl\cdot$$

$$(CH_3)_3C-O\cdot + CH_2=CHCHO \begin{cases} \xrightarrow{K_{rem}} CH_2=CH-\dot{C}=O + (CH_3)_3COH \\ \xrightarrow{K_{add}} (CH_3)_3COCH_2-\dot{C}H-CHO\,. \end{cases}$$

Acetyl radicals are generated in the catalytic chain oxidation of acetaldehyde by oxygen (catalysed by a cobalt salt)[17-19]. At an advanced stage of the reaction, the following elementary steps play a decisive role in chain initiation[19]:

$$CH_3CHO + Co^{III} \rightarrow CH_3-\dot{C}=O + Co^{II} + H^+\,,$$

$$CH_3\overset{O}{\overset{\|}{C}}-OO-\overset{OH}{\overset{|}{C}}HCH_3 + Co^{II} \rightarrow CH_3COO^- + Co^{III} + \cdot O-\overset{OH}{\overset{|}{C}}HCH_3\,.$$

Subsequently the $CH_3CH(OH)O\cdot$ radical removes hydrogen from the aldehyde, as a result of which $CH_3-\dot{C}=O$ is formed.

From a study of the kinetics of the oxidation of aromatic aldehydes by hydrated cobalt ions in aqueous acetonitrile, a mechanism was proposed for this reaction with intermediate formation of aroyl radicals[20]:

$$ArCHO + Co^{III} \rightarrow Ar-\dot{C}=O + Co^{II} + H^+\,.$$

A kinetic isotope effect of 2.3 at 10°C was observed in the oxidation of ArCDO. Consequently the rate-limiting stage of the process is the dissociation of the C–H(D) bond in the aldehyde group[20].

The $C_6H_5-\dot{C}=O$ radicals were obtained by the oxidation of C_6H_5CHO with cerium(IV) perchlorate in 85% acetic acid[21]. Acrylonitrile was used as the $C_6H_5-\dot{C}=O$ acceptor. Each molecule of polyacrylonitrile formed contained one benzoyl group.

Free radicals, most probably $C_6H_5-\dot{C}=O$, are generated in the oxidation of benzaldehyde by chromic acid[22] and chromyl acetate[23]. In the first case the radicals arise only after the appearance in the solution of chromium(IV), which is evidently responsible for their formation.

In contrast to aromatic aldehydes, aliphatic aldehydes are oxidised by transition metal ions in an aqueous medium in the hydrated[24,25] or enolic[26] forms. One may expect that alkoxy-radicals are generated in such cases. Recently a method has been proposed for the preparation of acyl radicals by the reaction of aliphatic aldehydes with manganese triacetate in the absence of a solvent of in glacial acetic acid[27]. The authors believe that this reaction proceeds via a stage involving the intermediate formation of a radical-cation[28]:

$$RCHO + Mn(OAc)_3 \rightarrow R-\overset{+}{\underset{H}{\overset{O}{\diagup\diagdown}}}C\,[Mn(OAc)_3]^- \rightarrow R-\dot{C}=O + AcOH + Mn(OAc)_2\,.$$

When aldehydes are irradiated with ultraviolet light, acyl radicals are generated as a result of the secondary reactions of the excited molecules. The primary processes occurring in the photolysis of aldehydes have been fairly thoroughly investigated[29]. For the majority of aldehydes, the lowest excited state corresponds to an $n-\pi^*$ transition (i.e. the transition of one of the non-bonding $2p$ electrons of the oxygen atom to an antibonding π^* orbital of the carbonyl group). Since in the $n-\pi^*$ excited state aldehydes, like ketones, exhibit the properties of free radicals with an unpaired electron at the oxygen atom[30], they can remove hydrogen from other aldehyde molecules with formation of acyl free radicals:

$$RCHO \xrightarrow{h\nu} RCHO^*\,,$$

$$RCHO^* + RCHO \rightarrow R-\dot{C}H-OH + R-\dot{C}=O\,.$$

Although the decomposition of excited aldehyde molecules into $R-\dot{C}=O$ and a hydrogen atom has been observed under the condition of flash photolysis, nevertheless it does not play a significant role in photolytic reactions[29].

It is noteworthy that the use of ultraviolet light for the generation of $R-\dot{C}=O$ radicals from aldehydes frequently involves undesirable side processes, for example the cleavage of the aldehyde molecule with formation of an olefin (a Norrish type II cleavage)[29] or the polymerisation of the aldehyde to a cyclic trimer[31,32].

γ-Irradiation has been used to generate acyl radicals in free-radical reactions involving the addition of aldehydes to alk-1-enes (Section III). The study of γ-radiolysis of propionaldehyde showed that this process has a chain mechanism[33].

2. Formation of Acyl Radicals from Ketones

The most widely used method of generation of acyl radicals from ketones involves ultraviolet irradiation. Many studies have been made on the photolysis of ketones [29,34-38]. The mode of photolytic decomposition of ketones, like that of aldehydes, is greatly influenced by their structure. n-Alkyl methyl ketones, such as methyl propyl ketone and butyl methyl ketone undergo exclusively a type II decomposition on ultraviolet irradiation in the liquid phase, i.e. they decompose into acetone and an olefin (ethylene and propene respectively) [39]. Such decomposition (via a cyclic transition state) is readily undergone also by other ketones with hydrogen atoms in the γ-position. Acyl radicals are formed preferentially on ultravilet irradiation of aliphatic ketones without hydrogen atoms in the γ-position, for example, alkyl t-butyl ketones [39,40]. They are cleaved in accordance with the rule governing the formation of the most stable alkyl radical (in this case the t-butyl radical):

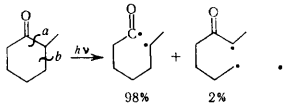
$$(CH_3)_3C-\overset{O}{\overset{\|}{C}}-R \xrightarrow{h\nu} (CH_3)_3C\cdot + O{=}\dot{C}-R.$$

Cis-trans isomerisation of hex-4-en-2-one also takes place with homolytic dissociation of the C–C bond adjoining the carbonyl group [41]. The $CH_3-\dot{C}{=}O$ radicals generated in this process add to the multiple bond (if the photolysis is carried out in the presence of an alkene) and butenyl radicals recombine to isomeric octadienes.

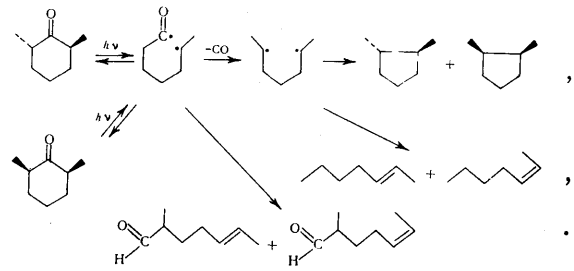
It has been shown that acyl radicals are obtained together with hydrogen and alkyl and α-oxoalkyl radicals in the liquid-phase radiolysis of simple aliphatic ketones (acetone [42], ethyl methyl ketone [43], and diethyl ketone [43]).

Many reactions are known in which cyclic ketones are photochemically cleaved with formation of an unsaturated aldehyde or ketone, which are formally products of an intramolecular disproportionation of intermediate acyl–alkyl biradicals. Nevertheless the problem of whether or not free radicals are really formed in the photolysis of cyclic ketones was regarded as controversial until recently [29]. In contrast to the free-radical mechanism, a hypothesis was put forward according to which the C–C bond of the cyclic ketone is dissociated and new bonds are formed by a synchronous mechanism, i.e. without the involvement of the radical pair [36,44].

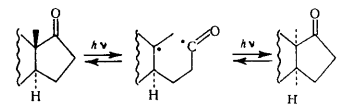
Nowadays the formation of an acyl–alkyl biradical on ultraviolet radiation should probably be regarded as proved, at least for simple cyclic ketones. Important studies designed to confirm this view have been made by Pritchard, Rickdorn, and others [45,46]. They found that the opening of the 2-methylcyclohexanone ring takes place to the extent of 98% at *a* and only to the extent of 2% at *b*. Such high process selectivity is due to the greater stability of a secondary alkyl radical compared with a primary radical:



As a result of the intramolecular disproportionation of the intermediate acyl–alkyl biradical, a mixture of *cis*- and *trans*-isomers of 5-heptenal is obtained (under the reaction conditions, these isomers are not interconverted) [49]. The photochemical cleavage of 2,6-dimethylcyclohexanone takes place similarly [45]. Ultraviolet irradiation of both the *cis*- and *trans*-isomer of this ketone leads to the same mixture of *cis*- and *trans*-1,2-dimethylcyclopentanones, *cis*- and *trans*-hept-2-enes, and *cis*- and *trans*-2-methylhept-5-enals with the same component ratio, which unambiguously demonstrates a free-radical mechanism:



2,3-Dimethylcyclopentanone is also cleaved by ultraviolet light with formation of an acyl-alkyl biradical, because the reaction products are a mixture of *cis*- and *trans*-1,2-dimethylcyclobutanes [47]. Homolytic dissociation of the C–C bond takes place also in the photolysis of bicyclic ketones, since examples of their photochemical epimerisation are known [48]:



Section V deals with examples of the migration of acyl groups, which confirm the free-radical mechanism of the photochemical cleavage of cyclic ketones. It should be noted that in some cases steric factors can favour the preferential occurrence of the reaction involving a molecular (synchronous) mechanism [49].

Radiolysis of cyclopentanone [50] leads to ring opening, probably via the same mechanism as in the photolysis of cyclic ketones, i.e. with intermediate formation of an acyl–alkyl biradical, but in this process side hydrogenation–dehydrogenation reactions play a significant role (the radiolysis products contain appreciable amounts of cyclopenten-2-one and cyclopentanol).

α-Diketones can also be used for the generation of acyl radicals. Thus diacetyl undergoes thermal dissociation into acetyl radicals with a 50% decomposition time of about 17 h at 145 °C [21]. Acetyl radicals are obtained from diacetyl also under milder conditions—when it is attacked by the alkyl radicals generated from the solvent by peroxides or ultraviolet irradiation [52,53]. In both cases intermediate α-oxoalkoxy-radicals are formed and are readily decomposed:

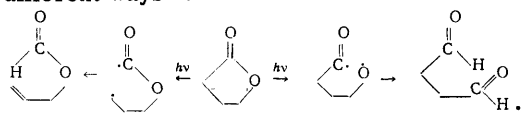
$$R\cdot + CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \rightleftarrows CH_3-\overset{O\cdot}{\underset{R}{\overset{|}{C}}}-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow$$

$$\rightarrow CH_3-\overset{O}{\overset{\|}{C}}-R + CH_3-\dot{C}{=}O.$$

Photolysis of dibenzoyl leads to $C_6H_5-\dot{C}{=}O$ with a quantum yield of 0.25 on irradiation with light at a wavelength of 366 nm. [64] The photochemical cleavage of other α-diketones has also been investigated [55].

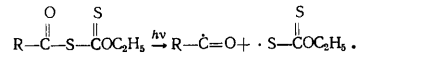
3. Formation of Acyl Radicals from Carboxylic Acid Derivatives

Irradiation of α-butyrolactone with light at a wavelength of 253.7 nm leads to the cleavage of the lactone ring in two different ways [56]:

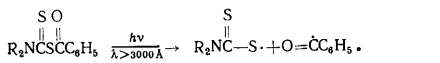


The quantum yields of succinaldehyde and allyl formate are respectively 0.06 and 0.23 at 25°C. As a result of the photolysis of carboxylic α-ketoacids, carbon monoxide is evolved with formation of acyl and alkoxy-radicals [57].

A convenient method for the preparation of acyl radicals is based on the photolysis of *S*-acyl and *O*-alkyl xanthates [58]:

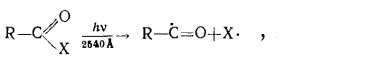


Mixed benzoic and dithiocarbamic acid anhydrides can serve as a source of benzoyl radicals [59]:



In contrast to *N*-disubstituted anhydrides, *N*-monosubstituted mixed anhydrides undergo photochemical dissociation in two ways [60]: with the scission of both $C_6H_5-\dot{C}=O$ and $C_6H_5C(O)\dot{S}$.

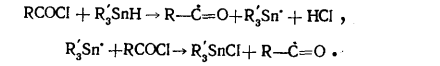
There are preliminary data [61] showing the formation of $R-\dot{C}=O$ on heating acid anhydrides with activated charcoal above 200°C. Schmidt [3,4,62,63] showed that acyl radicals are generated on ultraviolet irradiation of aliphatic and aromatic carboxylic acid halides:



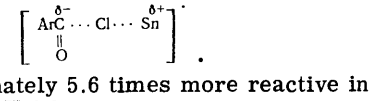
where X = Br or Cl.

In contrast to the above reaction, when carboxylic acid halides react with peroxides, only the hydrogen atoms linked to the α-carbon atom of the acid halide are attacked; acyl radicals are not then formed [63,94].

Metal hydrides or carbonyls can be used successfully for the generation of acyl radicals from acid halides. For example, trialkyl- and triphenyl-tin hydrides readily react with acyl halides according to the mechanism [65]:

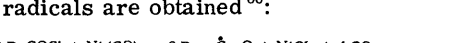


The relative reactivities of substituted aroyl halides in the reaction with tributyltin hydride have been determined [65]. The observed effect of substituents on the rate of removal of chlorine from the acid chloride is evidence of the important role of polar factors in the transition state



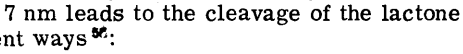
C_2H_5COCl is approximately 5.6 times more reactive in the above reaction than C_6H_5COCl.

When perfluoroacyl chlorides react with nickel carbonyl, perfluoroacyl radicals are obtained [66]:



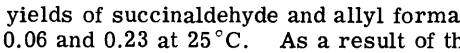
The reaction is catalysed by benzonitrile, the use of which as a solvent makes it possible to lower the temperature from 150° to 20°C.

Carboxylic acid chlorides are readily reduced to the corresponding aldehydes in the presence of palladium (Rosenmund reaction). Although the mechanism of this catalytic process is not altogether clear, it is quite likely that acyl radicals are formed in the first stage [67]:



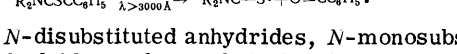
4. Formation of Acyl Radicals from Other Compounds

Acyl radicals can be obtained by the addition of carbon monoxide to alkyl radicals generated by the usual methods from saturated and unsaturated hydrocarbons [68-72] or from tetra-alkyl-lead [73]:



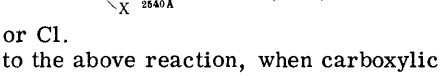
Since the reaction is reversible, the process is usually carried out under a pressure in excess of 500 atm in order to displace the equilibrium towards the formation of $R-\dot{C}=O$ and also to suppose the side reaction of R· with the solvent.

Thermolysis of α-acyl-t-alkyl hypochlorites leads to unstable α-acyl-t-alkoxy-radicals which are readily decomposed with elimination of $R-\dot{C}=O$:



Subsequently the reaction develops as a chain process. The decomposition of α-acetyl-s-butyl hypochlorite results in a quantitative yield of 2-butanone and acetyl chloride [74].

Acyl radicals are obtained by the reaction of di-t-butyl peroxide with three-five-membered cyclic ethers, for example tetrahydrofuran (THF). [75] The reaction is remarkable because acyl radicals are generated as a result of an intramolecular rearrangement of the alkyl radicals formed initially [75]:

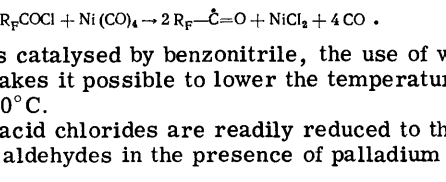


Attempts have been made to generate $R-\dot{C}=O$ radicals by the thermal decomposition of acyl and aroyl di-imides (RCO–N=N–COR). However, this process apparently has a complex mechanism, since propionyl di-imide initiates the polymerisation of olefins (acrylonitrile, styrene, etc.) only very slightly [73] and the thermal decomposition products of benzoyl di-imide contain only an insignificant amount of dibenzoyl [76]. More definite data supporting the formation of $C_6H_5-\dot{C}=O$ from benzoyl di-imide were obtained in a study of its photolytic cleavage [76].

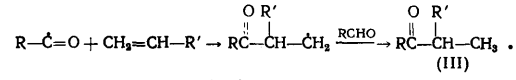
III. ADDITION OF ACYL RADICALS TO MULTIPLE BONDS

1. GENERAL RELATIONS

The free-radical addition of aldehydes to α-olefins was described for the first time by Kharasch et al. [1] The process has a chain mechanism:



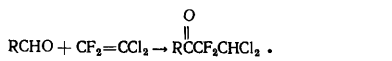
A detailed study of the products of the reaction initiated by peroxides [32,77], ultraviolet light [32], and γ-radiation [78,79] showed that acyl radicals attack not only the terminal but partly also the β-carbon atom of the vinyl group in the α-olefin:



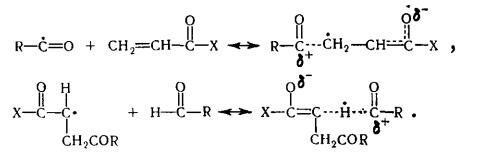
The content of compound (III) in a mixture of compounds (II) and (III) is 5–10%. The composition of the mixture of isomeric ketones is independent of the method of initiation of the reaction and of the reactant ratio [32].

As in other free-radical reactions, the mode of addition of R–Ċ=O to olefins is determined in the first place by the degree of stabilisation of the intermediate alkyl radical. The addition to isobutene [32] and 2-methylbut-2-ene [80] takes place almost exclusively at the least substituted carbon atom of the C=C group and the addition to straight-chain alk-2-enes takes place approximately equally at both carbon atoms linked by the double bond [80].

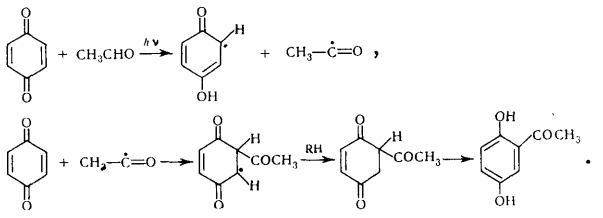
The radical additionof aldehydes to norbornene and camphene takes place stereoselectively with formation of ketones having the *exo*- and *endo*-configurations respectively [81,82]. When acyl radicals react with $\alpha\beta$-unsaturated acids, their esters, and nitriles, the β-carbon atom of the above compounds is also attacked preferentially. The reaction of aliphatic aldehydes with asymmetric dichlorodifluoroethylene gives only one isomer [83]:



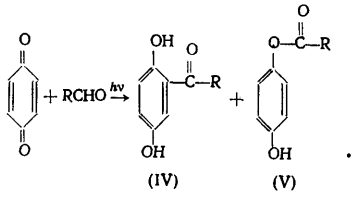
Although the reactivities of acyl radicals with respect to different types of double bond have not been estimated quantitatively, it has been shown in many cases that they add most readily to >C=C< or >C=O bonds with a reduced electron density. The radical addition of aldehydes to $\alpha\beta$-unsaturated carbonyl compounds and nitriles, perfluoro-olefins, and hexafluoroacetone takes place with a high yield and without the formation of an appreciable amount of telomers. According to Walling's hypothesis [84], the nucleophilic properties of acyl radicals are due to the effect of their electron-donating properties in the transition state in stages involving addition and chain transfer:



The role of polar factors in the attack by acyl radicals on multiple bonds is shown most strikingly in the photoinitiated reaction of aldehydes with quinones. When a solution of 1,4-benzoquinone in acetaldehyde is illuminated, hydroquinone (15%), acetylhydroquinone (67%), and an insignificant amount (0.6%) of *p*-hydroxyphenyl acetate are obtained [85]. The mechanism of the formation of acetylhydroquinone may be as follows:

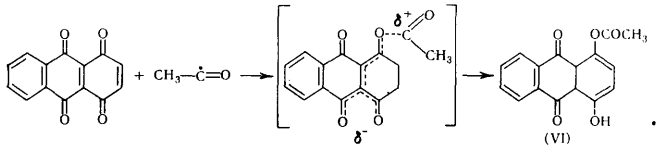


The products of the addition of benzaldehyde to benzoquinone contain benzoylhydroquinone (49%) and hydroquinone monobenzoate (15%), i.e. benzoyl radicals add not only to the carbon–carbon double bond but also attack to an appreciable extent the carbonyl group of the quinone [86]. The lower selectivity of the addition of benzaldehyde compared with acetaldehyde is probably associated with the fact that C_6H_5–Ċ=O is less nucleophilic than CH_3–Ċ=O owing to the conjugation of the unpaired electron with the benzene ring. The ratio of the products of the addition of substituted benzaldehydes to the >C=C< and >C=O bonds of benzoquinone depends greatly on the nature of the substituent:



The (V) : (IV) ratio increases as the R–Ċ=O radical becomes less nucleophilic, *p*-nitrobenzaldehyde and cinnamaldehyde adding exclusively to the carbonyl group of benzoquinone [86].

When a solution of quinizarinquinone in acetaldehyde is illuminated, only the monoester is obtained [86], which can be explained by the ease of formation of the transitional dipolar structure promoting attack on the oxygen atom of the carbonyl group by the acetyl radical:



In contrast to the reaction of acetaldehyde with unsubstituted *p*-benzoquinone, its addition to chloranil takes place almost exclusively at the carbonyl group [87], owing to steric hindrance in the attack on the C=C bond of chloranil.

The reactivities of chloroperfluoro-olefins in the homolytic reaction with aldehydes decrease in the sequence $CFCl{=}CCl_2 > CF_2{=}CCl_2 > CFCl{=}CFCl$. [88]

The relative reactivities of cyclic olefins in their radical reaction with acetaldehydes initiated by γ-radiation have been determined [89]: cyclo-octene > cyclopentene > cycloheptene > cyclohexene.

2. ADDITION TO THE CARBON–CARBON DOUBLE BOND

In recent years the addition of aldehydes to olefins has come to be very widely used, since it permits the ready synthesis of a wide variety of organic compounds containing the keto-group [18,90,91]. It is usually initiated by organic peroxides, ultraviolet light, or γ-radiation. It has been shown recently that oxygen and variable-valence metal salts can also be employed as initiators. Each of the above methods of initiation has its characteristics, which have a specific effect on the process. Therefore the examples of the addition of R–Ċ=O to the carbon–carbon double bond will be classified on the basis of the methods of initiation of the reaction.

a. Reactions Initiated by Peroxides

The addition of aldehydes to olefins is usually initiated by benzoyl and acetyl peroxides, which undergo thermal decomposition at 80–100°C. It is undesirable to carry out the reaction above 100°C since decarbonylation of acyl radicals begins to play an important role under these conditions (Section IV). In order to suppress the telomerisation side reaction, a three–five-fold excess of the aldehyde is employed.

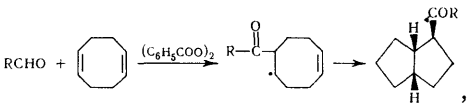
The free-radical addition of aldehydes to ethylene [92], alk-1-enes [1,32,77,93–95], α-pinene [97], β-pinene [77,97], camphene [81,97], norbornene [81,82], (+)-limonene [97], cyclohexene [93], crotonic [98] and substituted acrylic [99] acids and their esters [98,100] and nitriles [99,101], the nitrile of cinnamic acid [98,102], the esters of maleic [98,100,103–105], fumaric [103], itaconic [103], aconitic [108], and undeconoic [100,106–108] acids, αβ-unsaturated ketones [109,110], allyl acetate [111,112], and other esters of allyl alcohols [112,113], allyl ethers [112], acetals of acrolein [112,114], dichlorodifluoroethylenes [83], perfluoro-olefins [115,116], and unsaturated silicon-containing compounds [117–119] has been described.

The radical addition of butyraldehyde to 3,3-diphenylbut-1-ene is accompanied by a rearrangement with migration of the phenyl group [120]:

$$R\dot{C}{=}O + CH_3C(C_6H_5)_2CH{=}CH_2 \longrightarrow$$

$$CH_3C(C_6H_5)_2\dot{C}HCH_2COR \xrightarrow{O} CH_3\dot{C}(C_6H_5)CH(C_6H_5)CH_2COR$$

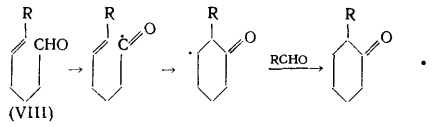
In the presence of benzoyl peroxide a bicyclic ketone is formed from aliphatic aldehydes and *cis-cis*-cyclo-octa-1,5-diene by an intramolecular interaction in the intermediate cycloalkyl radical with the second double bond [121]:



where R = CH_3 or C_3H_7.

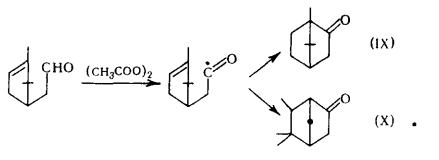
According to patent data, acetaldehyde adds to hexa-1,5-diene [93] and isoprene [122] (in both cases to one double bond).

The acyl radicals generated from unsaturated aldehydes of type (VIII) add intramolecularly to the double bond, forming a six-membered cyclic ketone (yield 40 to 50%):[123]



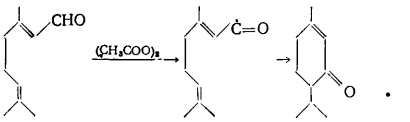
(VIII)

The free-radical cyclisation of α-campholenic aldehyde [124] takes place in two ways:



The reaction products consist of a mixture of 95% of camphor (IX) and 5% of dihydrocamphenone (X).

Similar results were obtained in a study of the radical cyclisation of apocampholenic aldehyde, citronellal, and citral [125]. For the last aldehyde, the reaction is complicated by the simultaneously occurring thermal isomerisation processes, but on rapid decomposition of acetyl peroxide in citral an αβ-unsaturated cyclic ketone is the main product:

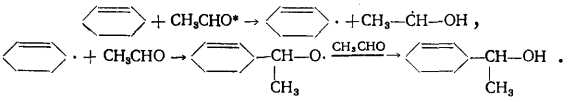


In contrast to the reactions described above, the interaction of 4-formylcyclohexene and *endo*-5-formylbicyclo-[2,2,2]oct-2-ene with di-t-butyl peroxide leads to dimeric products [126].

b. Reactions Initiated by Ultraviolet Light, γ-Radiation, and β-Radiation

The radiation and photochemical methods for the initiation of the reactions of aldehydes with olefins have been fairly well investigated. The addition of aldehydes to ethylene [127,128], propene [78,127], isobutene [127,129], alk-1-enes [79,80,127], alk-2-enes [80,127], cyclohexene [79,130,131], other cyclic mono-olefins [85], chlorotrifluoroethylenes [84,132], perfluorocyclobutene [116], and dimethyl esters of maleic and fumaric acids [133] has been achieved under the influence of γ-radiation.

In the reaction of aldehydes with olefins initiated by ultraviolet light the main process is often accompanied by side reactions, which as a rule play a significant role. Thus the photochemical addition of butyraldehyde to hept-1-ene proved to be relatively ineffective owing to the formation of a considerable amount of parabutyraldehyde [32]. The photochemical reaction of aliphatic aldehydes with cycloalkenes also does not take place unambiguously [130]: a considerable amount of acetoin was obtained together with cyclohexyl methyl ketone from a mixture of acetaldehyde and cyclohexane. According to the data of other workers [134], cyclohexylmethylmethanol is also formed in the above reaction, probably according to the following mechanism:



Illumination of an equimolar mixture of methylenecyclohexane and n-butyraldehyde gives four products, one of which is cyclohexylmethyl ethyl ketone [135].

A preparative method of synthesising γ-silylketones by the photochemical addition of aldehydes to vinylsilanes has been proposed [136]:

$$R_3SiCH{=}CH_2 + R'CHO \xrightarrow{h\nu} R_3SiCH_2CH_2\overset{O}{\overset{\|}{C}}R' ,$$

where R = CH_3, C_2H_5, or OC_2H_5 and R′ = CH_3, C_2H_5, iso-C_4H_9, etc. Benzaldehyde does not react with vinylsilanes [136].

Only one example of the initiation of the addition reaction by a beam of electrons has been described. When a mixture of acetaldehyde and cyclohexene was exposed to β-radiation, cyclohexyl methyl ketone and a considerable amount of side products—acetoin and 1-acetyl-2-(2′-cyclohexenyl)cyclohexene—were obtained [130].

c. Reactions Initiated by Oxygen and (or) Variable-valence Metal Salts

The effectiveness of oxygen as an initiator of the addition of aldehydes to a multiple bond depends on the structure of the olefin. The reaction takes place most readily with olefins having an electrophilic multiple bond. Thus the ester of butyrylsuccinic acid was obtained from butyraldehyde and dimethyl maleate in a quantitative yield[137]. The process is interesting because acyl radicals are generated directly in the reaction between the aldehyde and oxygen (the intermediate peroxides do not play a significant role in this case):

$$RCHO + O_2 \rightarrow R-\dot{C}=O + HO\dot{O} \text{ or}$$

$$2\,RCHO + O_2 \rightarrow 2R-\dot{C}=O + H_2O_2\ ,$$

$$R-\dot{C}=O + CH_3OOCCH=CHCOOCH_3 \xrightarrow{RCHO} H_3COOC\dot{C}HCH_2COOCH_3\ .$$
$$\quad\quad\quad

of tributyltin hydride was proposed recently. The reaction takes place at room temperature via a chain mechanism:

$$RCOCl \xrightarrow{Bu_3SnH} R-\dot{C}=O\,,$$

$$R-\dot{C}=O + R'R''C=O \rightarrow RCOO-\dot{C}R'-R''\,,$$

$$RCOO-\dot{C}R'-R'' + Bu_3SnH \rightarrow RCOOCHR'R'' + Bu_3Sn\cdot\,,$$

$$Bu_3Sn\cdot + RCOCl \rightarrow Bu_3SnCl + R-\dot{C}=O \quad \text{etc.}\,.$$

The relative reactivities of various aldehydes and ketones with respect to the propionyl radical have been determined. It was found that n-heptanal is more reactive than benzaldehyde and the rate of addition of $CH_3CH_2-\dot{C}=O$ to cyclohexanone is about 20 times faster than the rate of addition of cyclopentanone [151].

The relative reactivities of substituted benzaldehydes in the above reaction are correlated with the σ^+ constants [151]. Electron-accepting substituents accelerate and electron-donating substituents retard the reaction (ρ = 0.43), which is consistent with the hypothesis that acyl radicals have nucleophilic properties.

An ester can be synthesised also by the direct interaction of an acid chloride or bromide with a substituted tin hydride [151,153]. Benzyl benzoate was obtained by this method in 87% yield from benzoyl chloride and triphenyltin hydride at room temperature in the absence of a solvent [153]:

$$2\,C_6H_5COCl + 2\,(C_6H_5)_3SnH \rightarrow C_6H_5COOCH_2C_6H_5 + 2\,(C_6H_5)_3SnCl\,.$$

It has been suggested that in this case an aldehyde formed as an intermediate in the reduction of the acid chloride is acylated [151]. This explanation is consistent with the finding that an aldehyde is present in the reaction product and the aldehyde : ester ratio varies from 9 to 0.25, depending on the nature of the reactants and the experimental conditions [151]. The ester is probably formed by the radical-chain mechanism described above, since the reaction is sensitive to inhibitors and is accelerated by azobisisobutyronitrile [153].

Esters of enediols have been synthesised by the reaction of perfluoroacyl chlorides with nickel carbonyl in benzonitrile:

$$R_FCOCl \xrightarrow{Ni(CO)_4} 2\,R_F-\dot{C}=O \rightarrow R_F-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_F;$$

$$R_F-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-R_F + R_F-\dot{C}=O \rightarrow R_F\overset{O}{\overset{\|}{C}}O-\overset{R_F}{\overset{|}{C}}=\overset{R_F}{\overset{|}{C}}-O\cdot \xrightarrow{R_F-\dot{C}=O} R_F\overset{O}{\overset{\|}{C}}O\overset{R_F}{\overset{|}{C}}=\overset{R_F}{\overset{|}{C}}\overset{O}{\overset{\|}{C}}O-R_F.$$

The addition of an acyl radical to the carbonyl group probably takes place as one of the stages in the original method for the preparation of substituted propiolactones by the condensation of aldehydes with keten under the influence of benzoyl peroxide [154]:

$$R-\dot{C}=O + CH_2=C=O \rightarrow \overset{R-C=O}{\underset{CH_2-\dot{C}=O}{|}} \rightarrow \overset{\dot{R}-C-O}{\underset{CH_2-C=O}{|}} \xrightarrow{RCHO} \overset{R-CH-O}{\underset{CH_2-C=O}{|}}.$$

9-Benzoyloxy-10-hydroxyphenanthrene was obtained by a photochemical reaction of benzaldehyde with phenanthrenequinone [155]:

$$C_{14}H_8\overset{O}{\underset{O}{<}} \xrightarrow{h\nu} C_{14}H_8\overset{O\cdot}{\underset{O\cdot}{<}}\,,$$

$$C_{14}H_8\overset{O\cdot}{\underset{O\cdot}{<}} + C_6H_5CHO \rightarrow C_{14}H_8\overset{OH}{\underset{O\cdot}{<}} + C_6H_5-\dot{C}=O\,,$$

$$C_6H_5\dot{C}=O + C_{14}H_8\overset{O}{\underset{O}{<}} \rightarrow C_{14}H_8\overset{O\cdot}{\underset{OCOC_6H_5}{<}} \xrightarrow{C_6H_5CHO} C_{14}H_8\overset{OH}{\underset{OCOC_6H_5}{<}}\,.$$

5. Addition to N=O and N=N Bonds

The addition of acyl radicals to N=O and N=N bonds has been much less investigated than the addition to C=C and C=O bonds.

The reaction of acyl radicals with nitroso-compounds [156] is of interest as a convenient method for the synthesis of stable nitroxy-radicals:

$$R-\dot{C}=O + O=N-R' \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}-O\,.$$

t-Butyl peroxide and also nitrosoalkanes, which readily decompose into NO and alkyl radicals under the influence of heat or ultraviolet light, were used to generate $R-\dot{C}=O$ radicals in this process. Stable acylnitroxy-radicals were obtained also by another method [156]—by decomposing alkyl nitrites in hydrocarbons. The aldehydes and nitroso-compounds formed as intermediates react further with one another as described above.

A radical-chain addition of aldehydes to certain azo-compounds (azobenzene, azodibenzoyl, and azodicarboxylic acid esters) has been described:

$$RCHO + R'-N=N-R' \rightarrow R-\overset{O}{\overset{\|}{C}}-\overset{R'}{\overset{|}{N}}-NH-R'\,,$$

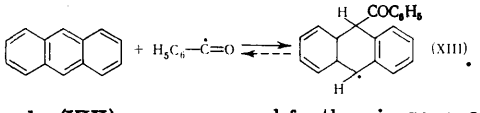
where R = C_6H_5CO, CH_3CO, etc. and R' = C_6H_5, C_6H_5CO, or R''OCO. Di-t-butyl peroxide [157], azobisisobutyronitrile [158], and atmospheric oxygen [159,160] were used as initiators. The reaction is of preparative interest for the synthesis of acylated hydrazine derivatives (yields up to 90%).

In its thermal and photolytic decomposition in organic solvents, azodibenzoyl undergoes radical benzoylation [79], which leads to tribenzoylhydrazine and diphenyloxadiazole. The same compounds were isolated in the oxidation of benzoylhydrazine by silver oxide [76]. Both reactions probably have similar mechanisms. It has been suggested [76] that in the latter case benzoyl radicals add to the benzoylhydrazine formed.

Benzoyl radicals can also attack the azo-group of azobisisobutyronitrile [157].

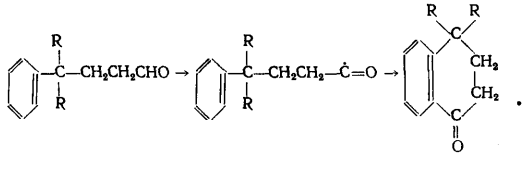
6. ADDITION TO AROMATIC SYSTEMS

Very little is still known about the addition of acyl radicals to aromatic systems. The addition of the benzoyl radical to anthracene has been investigated [161]. The first stage of this process is probably reversible:



The radicals (XIII) are consumed further in several ways: they recombine with one another or with $C_6H_5-\dot{C}=O$; also they lose hydrogen atoms and are converted into benzoylanthracene.

When a peroxide is allowed to react with aliphatic aldehydes containing a phenyl substituent in the γ-position, the benzene ring undergoes intramolecular acylation [149]:



The oxidation of benzoylhydrazine by silver(II) oxide in the presence of ferrocene leads to benzoylferrocene. It is most likely that ferrocene is acylated by a free-radical mechanism [161,162].

The possibility of the free-radical acylation of heterocyclic bases (pyridine, acridine, isoquinoline, etc.) by aldehydes in an acid aqueous medium has been demonstrated [163]. The reaction is initiated by redox systems. Owing to the nucleophilic properties of acyl radicals, they readily attack the electrophilic centres in the rings of the above bases.

IV. DECARBONYLATION

Decarbonylation is the reverse process in relation to the addition of carbon monoxide to alkyl radicals described in Section II:

$$R-\dot{C}=O \rightleftarrows R' + CO.$$

At a pressure close to atmospheric R–Ċ=O decomposes almost irreversibly and therefore such decomposition is often used as a method for the generation of free alkyl radicals [26]. Acyl radicals are usually obtained from aldehydes. The decarbonylation of aldehydes is a chain process:

$$RCHO + Z\cdot \rightarrow R-\dot{C}=O+ZH,$$

$$R-\dot{C}=O \rightarrow R' + CO,$$

$$RCHO + R\cdot \rightarrow RH + R-\dot{C}=O \text{ etc.}$$

The ease of removal of CO from R–Ċ=O depends significantly on the nature of R· (Table 2). It has been firmly established in a number of cases that the decomposition of R–Ċ=O takes place more readily the more stable is R. [16,126,164,165] However, this rule is valid only for aliphatic and alicyclic acyl radicals (benzoyl radicals do not show any capacity for the removal of CO) [4,16,58].

Table 2. Relative reactivities of certain aldehydes in the decarbonylation reaction [164].

R in RCHO	Reactivity	R in RCHO	Reactivity
$CH_3CH_2CH_2$	1	1-norbornyl	0.6
$(CH_3)_2CH$	8.3	1-bicyclo[2,2,2]octyl	110
$(CH_3)_3C$	90	1-adamantyl	175

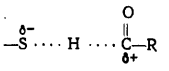
The rate of decarbonylation of the first three aldehydes depends linearly on the R–H bond energy in the hydrocarbon formed. The C–H bond energies in norbornane, bicyclo[2,2,2]octane, and adamantane have been estimated by extrapolation on the basis of the above relation [164].

The stability of the intermediate alkyl radical evidently plays a decisive role also in the decarbonylation of cyclopropanealdehyde [165] (Table 3).

The decarbonylation of the optically active bicyclo[2,2,2]octanealdehyde gave a racemic mixture of bicyclooctanes [166].

In a series of bicyclic aldehydes with similar structures, *endo*-bicyclo[2,2,2]oct-2-ene-5-aldehyde is decarbonylated most readily owing to the formation, following the removal of CO, of a stable non-classical alkyl radical [126]. The reactivities of alicyclic [167,168] and bicyclic [126] aldehydes are in many cases significantly influenced by steric factors.

The dependence of the decarbonylation chain length on the proportions of the aldehyde and di-t-butyl peroxide [169], usually employed as an initiator, has been investigated. In the presence of small amounts of mercaptans the chain length increases appreciably [170–172]. The explanation is that the formation of the transition state S...H...C requires a lower activation energy than the formation of the transition state C...H...C, owing to the ease of formation of the acylated complex



Thus mercaptans play the role of chain-transfer agents in the decarbonylation of aldehydes.

Table 3.

Aldehyde	▷—CHO	▷(CH₃)—CHO	▷(C₆H₅)—CHO
Yield of CO, %	traces	50	90

The decomposition of acyl radicals is widely used for the investigation of various reactions of the radicals produced in this process. The following types of rearrangement of alkyl radicals have been observed in the decarbonylation of aldehydes: 1,2-C,C- [166,173–182] and 1,3-C,C-migration [149] of aryl groups, 1,2-C,C-migration of the acetoxy-group [183], allyl rearrangement [184], ring opening [182], and ring expansion [185,186]. Attempts have also been made to observe the 1,2-C,C-migration of methyl [187], benzyl [188], and phenoxy-groups [178] and 1,2-S,C-migration of the phenyl group [189], but these were unsuccessful.

The alkyl radicals formed in the decarbonylation of aldehydes are not only capable of removing hydrogen atoms but some can also add to the aldehyde groups:

$$RCHO \xrightarrow{-H\cdot} R-\dot{C}=O \xrightarrow{-CO} R,$$

$$R\cdot + RCHO \rightarrow R_2CH-O,$$

$$R_2CH-O\cdot + RCHO \rightarrow R_2CHOH + R-\dot{C}=O \text{ etc.}$$

The decomposition of di-t-butyl peroxide in n-butyraldehyde yields propane and dipropylmethanol in proportions of about 10 : 1. [190]

In the decarbonylation of aldehydes in the presence of olefins (alk-1-enes [191], chloropolyfluoroethylenes [83], and diethylmaleate [192]), the addition of alkyl radicals to the multiple bond was observed.

A convenient method has been proposed for the synthesis of ketones [193] by the oxidation of α-branched aldehydes with oxygen in a polar solvent (dimethylformamide, t-butyl alcohol). The ketone is formed as a result of the decomposition of the intermediate α-hydroperoxyacyl radical:

$$(CH_3)_2CHCHO \xrightarrow[\text{amine}]{-H^+} (CH_3)_2\overline{C}CHO \xrightarrow{Cu^{2+}} (CH_3)_2\dot{C}CHO \xrightarrow{O_2}$$

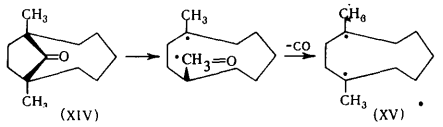
$$\rightarrow (CH_3)_2C(O-O\cdot)-C(=O)-H \rightarrow (CH_3)_2C(OOH)-C(=O)\cdot \xrightarrow[-CO,\,OH]{Cu^+} (CH_3)_2C=O.$$

The reaction is catalysed by copper salts and tertiary amines {amines with a sterically hindered electron pair

at the nitrogen atom, for example 1,4-diazabicyclo-[2,2,2]octane, are the most effective}.

The mechanism of the decarbonylation reactions of aldehydes and ketones initiated by ultraviolet radiation is frequently not susceptible to unambiguous interpretation, since the homolytic dissociation of the C–C bond and the removal of CO can occur as two consecutive stages or in a single photochemical step without the intermediate formation of an acyl radical. However, since the decarbonylation processes initiated by peroxides and ultraviolet radiation have many features in common, in many cases preference is given to the mechanism involving the R–Ċ=O radical. This hypothesis is valid at least for photochemical reactions of acyclic and simple cyclic ketones.

Since photolytic reactions in solution are usually carried out under mild conditions, only the least stable acyl radicals readily undergo photochemical decarbonylation. For example, acyl radicals with a quaternary α-carbon atom readily lose carbon monoxide [194,195]. Photolysis of the bicyclic ketone (XIV) [194] leads to three isomeric olefins as a result of an intramolecular disproportionation of the intermediate biradical (XV):



(XIV) (XV)

In the photolysis of dibenzyl ketone [196], carbon monoxide is split off and the benzyl radicals recombine quantitatively:

$$C_6H_5CH_2\overset{O}{\overset{\|}{C}}CH_2C_6H_5 \xrightarrow{h\nu} 2C_6H_5CH_2\cdot + CO,$$
$$2\,C_6H_5CH_2\cdot \rightarrow C_6H_5CH_2CH_2C_6H_5.$$

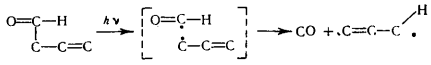
The free-radical mechanism of this reaction is confirmed by the fact that, when a mixture of dibenzyl ketone and 1,1,3,3-tetraphenylacetone is irradiated, two symmetrical and one asymmetric hydrocarbon are formed as a result of the recombination of the corresponding arylalkyl radicals.

In contrast to acetone, which hardly undergoes photolysis in the liquid phase [40,197], monochloropentafluoroacetone decomposes under the influence of ultraviolet light with liberation of carbon monoxide [198]. This is evidence of the instability of the CF_3–Ċ=O and CF_2Cl–Ċ=O radicals.

The liquid-phase photolysis of aldehydes, particularly those branched at the α-carbon atom, also gives rise to the elimination of carbon monoxide. Photochemical decarbonylation is inhibited by hydroquinone, which is evidence of a chain mechanism of the process [199]. The primary step in the photochemical decomposition of unsaturated aldehydes with a quaternary α-carbon atom yields formyl and alkyl radicals. The latter remove a hydrogen atom from the solvent and H–Ċ=O undergoes further decomposition [200]:

$$RCHO \xrightarrow{h\nu} RCHO^* \rightarrow R\cdot + H\text{–}\dot{C}=O$$
$$\text{solvent} \rightarrow RH \qquad \text{–H}\cdot \rightarrow CO.$$

The mechanism of the decarbonylation of $\beta\gamma$-unsaturated aldehydes differs from that described above. Hydrogen transfer in such aldehydes takes place intramolecularly via a stage involving the formation of a radical pair or via a synchronous mechanism [200,201]:



In the photolysis of benzaldehyde a certain amount of carbon monoxide is given off; however, this is not due to the decomposition of C_6H_5–Ċ=O, but is probably a result of the decomposition of the intermediate keten [4].

The irradiation of *O*-alkyl and *S*-acyl xanthates with visible or ultraviolet light [58] also leads to the liberation of carbon monoxide, which is believed to be caused by the decomposition of acyl radicals:

$$R\text{–}\overset{O}{\overset{\|}{C}}\text{–}S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5 \xrightarrow{h\nu} R\text{–}\dot{C}=O + \cdot S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5,$$
$$R\text{–}\dot{C}=O \xrightarrow{-CO} R\cdot;\ R\cdot + \cdot S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5 \rightarrow R\text{–}S\text{–}\overset{S}{\overset{\|}{C}}\text{–}OC_2H_5.$$

The reaction takes place smoothly when R = benzyl, s-alkyl, or t-alkyl, is more difficult with acyl xanthates where R is a primary alkyl, and does not occur in the photolysis of *S*-benzoyl xanthate.

Trimethylacetaldehyde undergoes a radical-chain decarbonylation in oxidation by manganese(III) acetate [27], as under the influence of peroxides or ultraviolet light. The intermediate t-butyl radicals remove hydrogen from the aldehyde and are also oxidised by the manganese(III) salt to isobutene:

$$(CH_3)_3CCHO \xrightarrow{Mn(OOCCH_3)_3} (CH_3)_3C\text{–}\dot{C}=O \rightarrow (CH_3)_3C\cdot + CO$$
$$\text{aldehyde} \rightarrow (CH_3)_3CH \qquad Mn^{III} \rightarrow CH_2=C(CH_3)_2.$$

In the oxidation of triphenylacetaldehyde with chromic acid [202], the evolution of carbon monoxide was also observed:

$$(C_6H_5)_3CCHO + Cr^{IV} \rightarrow (C_6H_5)_3C\text{–}\dot{C}=O + Cr^{III} + H^+,$$
$$(C_6H_5)_3C\text{–}\dot{C}=O \xrightarrow[H_2O]{Cr^{IV}(Cr^{VI})} (C_6H_5)_3COH + CO.$$

The reaction products contain (apart from triphenylmethanol) triphenylacetic acid, which may be formed as a result of the oxidation of the intermediate acyl radical with electron transfer or as a result of two-electron oxidation of the initial aldehyde. A more selective decarbonylation of $(C_6H_5)_3CCHO$ was observed when chromyl acetate or cerium(IV) salts were used as oxidising agents (in these cases the reaction products did not contain triphenylacetic acid) [202].

The decarbonylation of β-phylisovaleraldehyde catalysed by palladium [203] results in the formation of only an insignificant amount of the neophyl rearrangement products of this aldehyde. The authors believe that the decarbonylation may have a radical mechanism, but, as a result of the fixation of the radicals on the surface of the catalyst, the migration of the phenyl group in the 2-methyl-2-phenylpropyl radical is difficult.

V. PHOTOCHEMICAL ACYL RADICAL MIGRATION PROCESSES

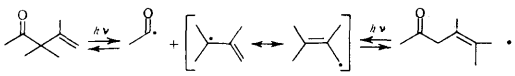
Many photochemical rearrangements of ketones, esters, and carboxylic acid amides involve the migration of acyl radicals. The rearrangements of ketones with

different structures (aliphatic, mono-, bi-, and polycyclic, $\beta\gamma$-unsaturated, etc.) have been thoroughly investigated.

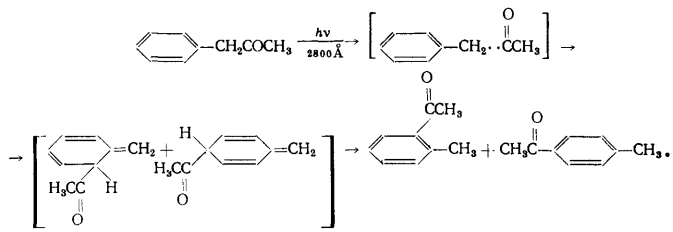
1. C,C-MIGRATION

a. Rearrangement of $\beta\gamma$-Unsaturated Acyclic Ketones

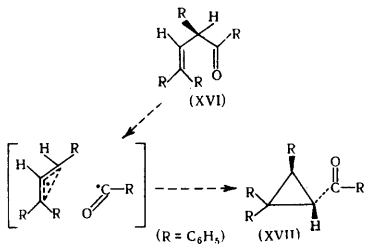
Kiefer and Carlson[204] observed the allyl rearrangement of 2,3,3-trimethylpent-1-en-4-one via a free-radical mechanism:



Irradiation of benzyl methyl ketone in t-butyl alcohol or n-hexane causes the formation of a mixture of *o*- and *p*-methylacetophenones[205]. The photolysis products also contain dibenzyl. The ratio of methylacetophenone and dibenzyl increases as the concentration of the ketone falls. The following mechanism has been proposed for this reaction:



When the ketone (XVI) is irradiated with ultraviolet light in benzene, the benzoyl group migrates with formation of the cyclopropane ring[206]. The reaction is stereospecific. However, cyclisation is not the main process in the photolysis of compound (XVI): it largely undergoes fragmentation to phenylallyl radicals, which then recombine, and benzoyl radicals, which probably behave as precursors of biphenyl. Compound (XVII) can be formally regarded as a product of the recombination of $C_6H_5-\dot{C}=O$ with the mesomeric cyclopropyl radical, but, in view of the stereospecificity of the process, the concerted mechanism involving the dissociation of compound (XVI) and the formation of a new bond must be regarded as more likely:

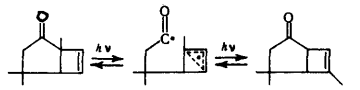


(XVI) (R = C_6H_5) (XVII)

b. Rearrangement of $\beta\gamma$-Unsaturated Cyclic Ketones

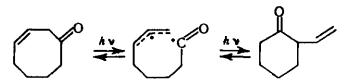
The allyl rearrangements of $\beta\gamma$-unsaturated cyclic ketones can take place with retention of the original number of carbon atoms in the ring (the position of the double bond or of substituents is altered) and with ring contraction or expansion. A characteristic feature of allyl rearrangements is their reversibility, i.e. the ratio of the isomeric ketones is independent of the isomer employed as the initial compound.

In 1960 Büchi and Burgess[207] described the rearrangement of a bicyclic $\beta\gamma$-unsaturated ketone, the mechanism of which can be represented as follows[208,209]:



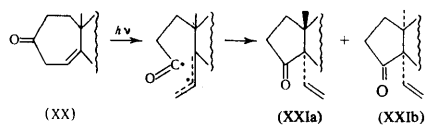
Subsequently a similar isomerisation was observed for other $\beta\gamma$-unsaturated bicyclic[208-210] and tricyclic[211] ketones.

One of the most typical examples of a rearrangement with a change in the number of carbon atoms in the ring is the conversion of cyclo-oct-3-en-1-one into 2-vinylcyclohexanone[212,213]:



(XVIII) (XIX)

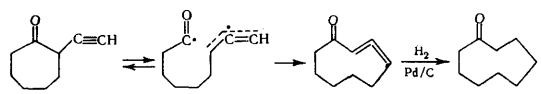
The ratio of compounds (XVIII) and (XIX) under the conditions of photoequilibrium is 7 : 40.[213] Ultraviolet irradiation of cyclodec-3-enone leads to a mixture of 2-vinylcyclo-octanone and the initial ketone in proportions of 2 : 5.[214] Similarly 2-isobutenylcyclopentanone was obtained from 2,2-dimethylcyclohepten-3-one[215]. A mixture of *cis*- and *trans*-isomers (XXI, a and b) was formed in the photolysis of the ketosteroid (XX), which is evidence of the intermediate formation of an acyl alkyl biradical[216]:



(XX) (XXIa) (XXIb)

Examples of the isomerisation of bicyclic ketones containing five-membered[217,218] and six-membered[210] rings to ketones with four-membered rings have been described.

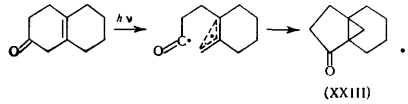
Acetylene—allene rearrangement. Carlson and Henton[219] described an interesting rearrangement of 2-ethnylcycloheptanone to a cyclic allene:



(XXII)

Compound (XXII) could not be isolated in a pure state, but its reduction gave a high yield of cyclononanone.

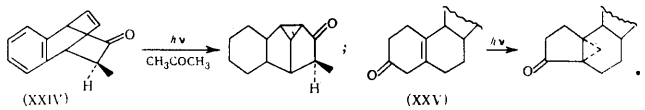
Rearrangements with formation and opening of rings are photochemical processes in which cyclopropane rings are mainly formed or cleaved. Ultraviolet irradiation of a solution of 2-oxo-1,2,3,4,5,6,7,8-octahydronaphthalene in t-butyl alcohol[220,221] gives the tricyclic ketone (XIII) in 60% yield:



(XXIII)

Cyclopropane hydrocarbons are obtained by the photolysis of six-membered $\beta\gamma$-unsaturated ketones only[220,221-224]. The solvent has a significant influence on the mode of photolysis. For example, when the ketone (XXIV)

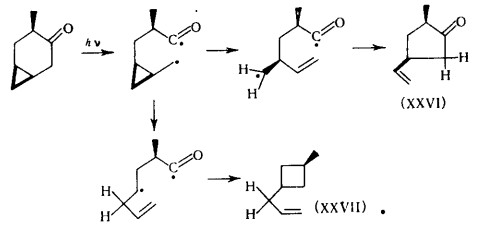
was irradiated in acetone, an isomeric ketone was obtained in 70% yield. In cyclohexanone solution only keten and naphthalene were obtained from compound (XXIV) [223]:



(XXIV) (XXV)

The photolysis of the $\beta\gamma$-unsaturated 3-oxosteroid (XXV), like that of compound (XXIV), is stereospecific and irreversible [221,222]. This is probably evidence that the dissociation of the C–C bond and the migration of the acyl group take place synchronously—a hypothesis which is consistent with conformation (XXV).

Irradiation of (–)-*cis*-4-caranone gives rise to C,C-migration of the acyl group and the opening of the cyclopropane ring [225]:

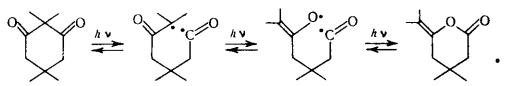


(XXVI) (XXVII)

The reaction is irreversible with (XXVI) : (XXVII) ≃ 3 : 1.

2. C,O-MIGRATION

Photolysis of compound (XXVIII) leads to the establishment in the solution of a photoequilibrium between compounds (XXVIII) and (XXIX) [229] with (XXIX) : (XXVIII) = 92 : 3.6:

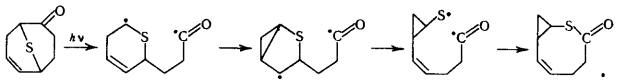


(XXVIII) (XXIX)

The rearrangement of other cyclic ketones containing two [227] or three [228] carbonyl groups in the β-positions relative to one another takes place similarly.

3. C,S-MIGRATION

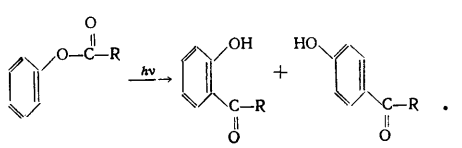
The recently described rearrangement of the thiaketone (XXX) belongs to this type of photochemical reactions [229]. One of the most likely mechanisms is



(XXX)

4. O,C-MIGRATION

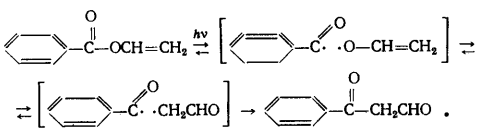
O,C-Migration of acyl groups has been observed in the photolysis of esters. The Fries photochemical rearrangement is best known:



Kobsa [230] proposed a free-radical mechanism for this reaction, according to which the bond between the carbonyl group and the ester oxygen atom is dissociated initially. The radical mechanism of the photochemical rearrangement of aryl esters has been fairly widely adopted, mainly because the reaction mixture always contains a phenol together with alkyl hydroxyphenyl ketones.

However, it has recently been shown [231] that the quantum yield of ketones is independent of the solvent, while the yield of the phenol decreases sharply as the viscosity of the medium increases. Consequently the formation of ketones takes place preferentially via a molecular mechanism and that of phenols via a free-radical mechanism.

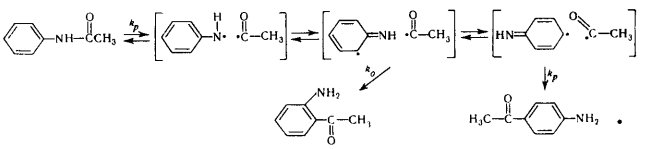
Ultraviolet irradiation of vinyl benzoate initiates the rearrangement according to the following probable mechanism [232]:



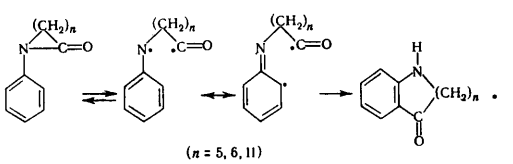
The intermediate formation of benzoyl radicals is also postulated in the photolysis of 1-cyclohexenyl benzoates [233].

5. N,C-MIGRATION

On ultraviolet irradiation, *N*-acylanilides isomerise in a manner similar to the rearrangement of aryl esters described above, with formation of a mixture of *o*- and *p*-acetanilides [234]. Shizuka [235] proposed a radical mechanism for this reaction:



The ratios of the rate constants for the recombination of the radicals $k_N : k_o : k_p = 1 : 0.35 : 0.6$ were calculated on the basis of the quantum yields of *o*- and *p*-acetanilides. The ratios are satisfactorily correlated with the "additional" π-electron density at the nitrogen atom and the carbon atoms of the benzene ring in the *o*- and *p*-positions: $\rho_N : \rho_o : \rho_p = 1 : 0.46 : 0.66$ (calculated ratios). The presence of an alkyl substituent at the nitrogen atom in acetanilide does not prevent the migration of the acyl group to the ring [236]. Consideration of the Fischer reaction [236] led to the development of a preparative synthesis of macrocyclic heterocycles:



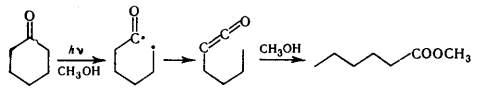
(n = 5, 6, 11)

VI. PHOTO-INITIATED DISPROPORTIONATION REACTIONS

1. REACTIONS WITH FORMATION OF UNSATURATED ALDEHYDES AND KETENS

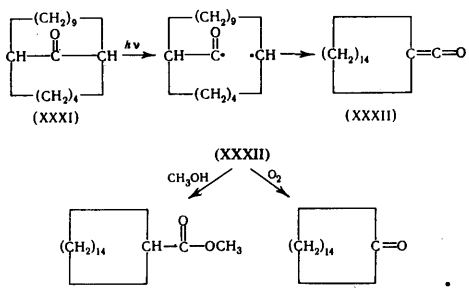
Many examples of the formation of unsaturated aldehydes in the photolysis of ketones in solution involving free radicals disproportionating in a solvent cage (Section II) are known. The reaction has been thoroughly described in monographs [29,34,35] and therefore will not be considered in detail in the present review.

The disproportionation of acylalkyl biradicals generated in the photolysis of cyclic ketones can result in the formation of a keten in addition to the unsaturated aldehyde. If the reaction is performed in the presence of water, an alcohol, or an amine, the keten is converted into an acid, an ester, or an amide [48,237]. For example, the main product of the photolysis of cyclohexanone in methanol is methyl caproate [237]:



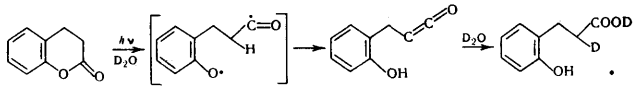
In contrast to cyclohexanone, in the photolysis of an alcoholic solution of cyclopentanone [237] only an insignificant amount of methyl valerate is obtained: in this case the second type of disproportionation of the acylalkyl biradical, leading to an unsaturated aldehyde, plays the main role.

Ketens are also formed when polycyclic ketones are irradiated with ultraviolet light [48,49,194,238-241]. Depending on the conditions, macrocyclic esters or ketones can be synthesised from bicyclic ketones of type (XXXI):



An ester is formed when the reaction is carried out in a carbon tetrachloride–methanol mixture and ketones are formed in carbon tetrachloride in the presence of oxygen [241].

An interesting rearrangement with ring opening was observed [231] when a cyclic lactone was irradiated in an aqueous dioxan solution:

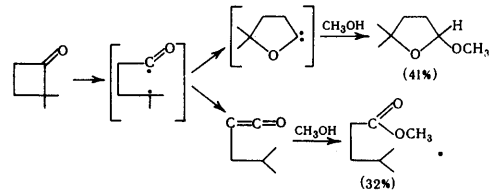


The intermediate formation of a keten was established by an isotope method [231-252].

2. REACTIONS WITH FORMATION OF OXACARBENES

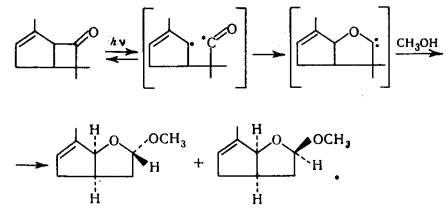
In a number of studies published in recent years [237,243-252] a new type of photochemical decomposition of cyclic ketones via a stage involving the generation of α-oxacarbenes was reported. The reaction takes place as a rule in the photolysis of alcoholic solutions of strained cyclic ketones [237]:

cyclobutanones [244,245,248,250], cyclobutanediones [246,247], camphor [252], and cyclocamphanone [243].



The photochemical reaction of *o*-phthalaldehyde probably also involves a carbene [251]. An oxacarbene is readily formed in the photolysis of aliphatic [249] and six-membered cyclic silaketones [237] in which the silicon atom is linked to the carbonyl group.

The involvement of acylalkyl biradicals in the formation of the oxacarbene was proved by Erman [253] by analysing the products of the photolysis of a bicyclic ketone:

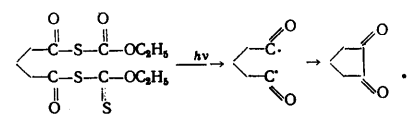


Identification in the reaction product of two epimeric bicyclic acetals is evidence that the dissociation of the carbon–carbon bond adjoining the carbonyl group precedes the formation of the oxacarbene.

Examples are known in which photolysis reactions of ketones involving a carbene take place stereospecifically [244,248,249]. In such cases the C–C bond probably dissociates via a concerted mechanism with formation of a carbene.

VII. OTHER REACTIONS

Acyl radicals are capable of dimerising to α-diketones. This reaction has been observed on ultraviolet irradiation of acetaldehyde [1], propionaldehyde [254], and isovaleraldehyde [254], on oxidation of acetaldehyde with oxygen [255] and manganese triacetate [27], on reaction of perfluoroacyl chlorides with nickel carbonyl [66], and on radiolysis of acetone [42]. An interesting example of an intramolecular recombination of acyl radicals as a result of the photochemical decomposition of a *cis*-*S*-acyl xanthate has been described [58]:



In the presence of hydrogen donors acyl radicals are converted into aldehydes [54,63,65].

When acyl radicals react with sulphuryl chloride [10-12,256], t-butyl hypochlorite [6-8], α-acyl-n-alkyl hypochlorites [74], carbon tetrachloride [16,63,69,173], bromotrichloromethane [13,14], and *N*-bromosuccinimide [14], they abstract a halogen atom forming acid halides. The preparation of acyl halides

from aldehydes using the above halogenating agents has a chain mechanism:

$$\left.\begin{matrix}RCHO\\XCl\end{matrix}\right\} \xrightarrow[(peroxide)]{\Delta} R-\dot{C}=O+X,$$

$$RCHO+X\cdot \rightarrow R-\dot{C}=O+HX,$$

$$R-\dot{C}=O+XCl \rightarrow RCOCl+X,$$

where $X\cdot$ = t-BuO·, $\cdot SO_2Cl$, $\cdot CCl_3$, etc.

Acyl radicals readily combine with oxygen and become converted into peroxy-radicals [257]:

$$R-\dot{C}=O+O_2 \rightarrow R-\overset{\overset{O}{\|}}{C}-OO\cdot$$

This reaction constitutes the basis of the industrial syntheses of acetic acid and acetic anhydride by the oxidation of acetaldehyde [255].

When di-t-butyl peroxide is decomposed in alcoholic or phenolic solutions of aldehydes in the presence of catalytic amounts (about 10^{-3} M) of variable-valence metal salts (Cu, Co, Fe, Mn), alkyl or phenyl benzoates are formed [258]. The formation of esters results from the one-electron oxidation of acyl radicals by the catalyst in the oxide form:

$$(CH_3)_3COOC(CH_3)_3+Cu^{I} \rightarrow (CH_3)_3CO\dot{C}u^{II}+(CH_3)_3C-O\cdot,$$

$$(CH_3)_3C-O\cdot+RCHO \rightarrow (CH_3)_3COH+R-\dot{C}=O,$$

$$(CH_3)_3COCu^{II}+R'OH \rightleftarrows R'OCu^{II}+(CH_3)_3COH,$$

$$R-\dot{C}=O+Cu^{II}OR' \rightarrow RCOOR'+Cu^{I}.$$

Acyl radicals give up an electron most readily in reactions with copper(II) and cobalt(III) salts.

Decomposition of aqueous hydrogen peroxide in the presence of carbon monoxide, iron salts, and various organic compounds leads to the formation of carboxylic acids [70]. It has been suggested that [70] the intermediate acyl radicals are converted in this process into acylium cations [70].

The oxidation of $CH_3-\dot{C}=O$ with electron transfer is postulated as one of the stages in the decarboxylation of pyruvic acid by manganese(III) [259] and cobalt(III) [260] ions.

One-electron oxidation of acyl radicals probably occurs also in the following processes catalysed by copper salts: decomposition of t-butyl perbenzoate in aldehydes [261,262], photolysis of diacetyl [263,264], radiolysis of acetone [265], and oxidation of aldehydes by Fenton's reagent [266].

Thus, owing to the simplicity of their preparation and the wide variety of their chemical properties, acyl radicals are finding increasing application in organic chemistry.

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