Russian Chemical Reviews **63**(3) 269–277 (1994)
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UDC 547.539:66.095.21:541.127:541.515

The synthesis and reactivity of organobromine compounds in homolytic addition and telomerisation processes

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Abstract. Studies carried out in recent years on the radical chemistry of organobromine compounds, primarily on their application as addends in addition and telomerisation reactions, are surveyed. The use of metal complex initiating systems based on iron pentacarbonyl, together with traditional peroxide initiators, is described. This made it possible to expand significantly the synthetic possibilities of these reactions in view of their highly selective course involving the C–Br bond, and the involvement in the reaction of organic monobromo- and dibromo-compounds which hardly react under the conditions of peroxide initiation. The first examples of the stereocontrolled occurrence of the radical addition of organobromine addends to chiral monomers, leading to one of the stereoisomers, are presented. The bibliography includes 36 references.

I. Introduction

The radical reactions occurring with dissociation of the C–Br bond have been investigated to a lesser extent than the analogous processes with organochlorine compounds, but the greater ease of the dissociation of the C–Br bond as well as the high reactivity of even single bromine atoms activated by neighbouring groups lead to extensive possibilities for the synthesis of a wide variety of polyfunctional organic compounds. Organic bromo-derivatives readily enter into radical addition and telomerisation reactions; in the initiation stage, they actively generate radicals as a consequence of the dissociation of the C–Br bond, while in the chain-transfer stage their reactivity is caused by the greater ease (than for the chloro-derivatives) of electron transfer in the transition state as a consequence of the ready polarisability of the C–Br bond. This determines also the wide range of initiators and initiating influences which may be used—peroxides, azo-compounds, irradiation, oxidation–reduction systems, and, in certain cases, also ordinary illumination.

The significant difference in the chemical behaviour of chloro- and bromo-derivatives as telogens (addends) can be clearly seen on comparing the reactions of chloro- and bromoacetic acid esters: the esters of monochloroacetic acid react under radical conditions exclusively via a C–H bond, while monobromoacetic acid esters react via the C–Br bond. Experimental results have shown that the greater the number of halogen atoms at the carbon atom to which bromine is attached, the greater the reactivity of such a compound in addition and telomerisation reactions both in the initiation and chain-transfer stages. The C–Br bond is also activated by electron-accepting substituents in the α-position, for example by ester groups.

Among the bromine-containing compounds investigated, CBr_4 and CCl_3Br are the most reactive. When suitable initiators are used, the reactions involving them proceed at 50–70 °C, which is close to the optimum temperatures.

Dibromodichloromethane is fairly reactive in radical reactions. Among hydrogen-containing polybromomethanes, bromoform is outstanding. In contrast to chloroform, it reacts exclusively with dissociation of the C–Br bond regardless of the initiation conditions. However, the nature of the secondary and side reactions occurring is determined primarily by the nature of the initiating system (see below). Methylene bromide, which also reacts predominantly via the C–Br bond although isolated instances of reactions proceeding via the dissociation of a C–H bond are known,[1] is less effective.

Nonactivated α-alkyl bromides react nonselectively under radical conditions because the radicals formed in the chain propagation stage actively abstract hydrogen atoms from the alkyl chain of the bromoalkane. On the other hand, organic monobromo-compounds with functional group substituents enter readily into addition and telomerisation reactions exclusively via the C–Br bond.

The high effectiveness of bromine-containing compounds in homolytic processes makes it possible to involve readily polymerising monomers—vinyl chloride, acrylic esters, and styrene—in reactions with them. This affords individual adducts or, in isolated instances, mixtures of lower telomers. The first examples of stereocontrolled radical reactions with participation of chiral monomers, which make it possible to drive the process towards the formation of only one of the stereoisomers, have been described. The reaction of bromomethanes with vinyl carbonate provides a simple path to the synthesis of carbohydrates.[2]

The use of monomers with functional group substituents in addition and telomerisation reactions with organobromine compounds, taking into account the possibility of the successive replacement of bromine atoms by other groups, leads to polyfunctional compounds with different lengths of the main chain.

Acetylenes are not very promising in these reactions because they require fairly severe conditions which are incompatible with their explosive nature. The reactions with dienes frequently

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Received 14 December 1993
Uspekhi Khimii **63**(3) 280–288 (1994); translated by A K Grzybowski

proceed in different ways (1,2- and 1,4-addition), which hinders the isolation of individual compounds.

The comparatively high reactivity of even a single bromine atom in the adduct and telomers determines the possibility of the occurrence of secondary processes. The adducts formed may react with a new monomer molecule, affording stepwise telomerisation products. The presence of a bromine atom next to the radical centre leads to the probability of fragmentation with ejection of a bromine atom, which initiates a new reaction chain. Finally, under the conditions of metal complex initiation in the presence of a hydrogen donor, there is a possibility of the reduction of the tri- and di-halomethyl groups in the adduct and also of chain transfer via a C–H bond.

In the present review, we shall consider the literature data obtained during the last 6–7 years; earlier studies have been surveyed fairly completely in a monograph[3] (in the chapter devoted to organobromine compounds). The earlier data will be included when necessary.

II. Reactions of bromine-containing addends

1. Polybromomethanes

a. Reactions of carbon tetrabromide

A series of interesting features have appeared in recent years in reactions involving CBr_4. They are associated with the use of initiators, which are new for reactions of the given type, and also with the expansion of the range of monomers employed.

The addition of CBr_4 to a series of monomers, including monomers with functional group substituents (hept-1-ene, oct-1-ene, styrene, methyl acrylate) has been achieved in the presence of divalent samarium iodide under mild conditions; the yield of the adducts reaches 80% under these conditions.[4] The reaction is carried out in the presence of 5%–10% SmI_2 in solution in acetonitrile at 60 °C. The overall reaction mechanism described by the authors[4] includes the formation of an intermediate initiating complex **A** and subsequent chain transfer by the radical-adduct **B** to the initial polyhalomethane.

$$YCX_3 + SmI_2 \longrightarrow \underset{\mathbf{A}}{(YCX_3)^{-\cdot}SmI_2^{+}}$$

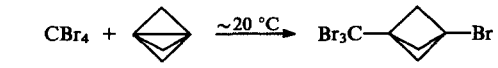
$$\mathbf{A} \longrightarrow SmI_2Y + \dot{C}X_3$$

$$\dot{C}X_3 + CH_2{=}CHR \longrightarrow \underset{\mathbf{B}}{CX_3CH_2\dot{C}HR}$$

$$\mathbf{B} + YCX_3 \longrightarrow CX_3CH_2CHYR$$

Trivalent samarium compounds do not participate in the chain transfer; the reconversion of Sm^{3+} into Sm^{2+} apparently requires a fairly powerful reductant. This constitutes a significant difference between the given reaction and the analogous processes initiated by systems based on $Fe(CO)_5$, where the halogen-containing iron carbonyl complex formed as an intermediate participates in the chain-transfer stage (the halogen passes from the complex to the radical-adduct), after which a zerovalent iron species, capable of propagating the reaction, is regenerated.[3]

The reaction of carbon tetrabromide with 1,1,1-propellane proceeds almost instantaneously, affording the corresponding adduct in a high yield.[5]



The process does not require illumination and proceeds at room temperature. The radical nature of the process has been confirmed by the presence of the corresponding signals in the EPR spectrum.

The ready homolysis of the C–Br bond in CBr_4 made it possible to carry out under the usual conditions (with benzoyl peroxide as the initiator) a radical chain reaction between carbon tetrabromide and 3,3,3-trifluoropropene, although in this instance highly electrophilic compounds function as the reactants (the addend and the monomer), i.e. a combination of polar factors highly unfavourable for the reaction is present.[6]

$$CBr_4 \xrightarrow{(C_6H_5CO)_2O_2} \dot{C}Br_3$$

$$\dot{C}Br_3 + CH_2{=}CHCF_3 \longrightarrow CBr_3CH_2\dot{C}HCF_3$$

The presence of the CF_3 group next to the radical centre imparts to the radical a highly electrophilic character and only the low dissociation energy of the C–Br bond makes it possible to achieve the subsequent process as a chain reaction.

$$CBr_3CH_2\dot{C}HCF_3 + CBr_4 \longrightarrow \underset{\mathbf{T_1}}{CBr_3CH_2CHBrCF_3} + \dot{C}Br_3$$

However, the unfavourable combination of polar factors renders this stage less effective, as a result of which the radical-adduct also participates in the competing chain propagation reaction with formation of the telomer $\mathbf{T_2}$, which is in principle atypical for reactions with carbon tetrabromide.

$$CBr_3CH_2\dot{C}HCF_3 + CH_2{=}CHCF_3 \xrightarrow{CBr_4} \underset{\mathbf{T_2}}{CBr_3CH_2CH(CF_3)CH_2CHBrCF_3}$$

The partial chain transfer constants $C_n = k_{tr}/k_p$ (k_{tr} is the transfer rate constant and k_p the chain propagation rate constants) have been estimated for this reaction involving the first three growing radicals ($C_1 = 15$, $C_2 = 64$, $C_3 = 60$), their values indicating in this case that chain transfer by the growing radicals is appreciably more effective than chain propagation. Similar values of the constants were obtained earlier also for the reaction with vinyl chloride,[7] although the properties of this monomer differ significantly from those of trifluoropropene (vinyl chloride readily polymerises, whereas this is not a characteristic feature of trifluoropropene).

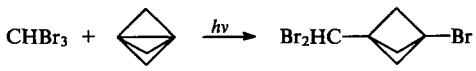
From the subsequent exposition, it will be clear that a less effective addend (for example, $CHBr_3$) reacts differently with these monomers. This applies to both chemical and kinetic results. The reaction of CBr_4 with vinyl chloride proceeds under the usual conditions as telomerisation mainly with formation of the first two telomers having the structure $CBr_3(CH_2CHCl)_nBr$, an appreciable amount (up to 10%) of the third telomer being formed only for high monomer : telogen ratios.[7]

Asahara and Chou[8] estimated the quantitative composition of the mixture of telomers by thin-layer chromatography and obtained values of C_n significantly less than unity (0.33), which is unlikely bearing in mind the high effectiveness of the telogen. The results were subsequently checked using gas–liquid chromatography.[7] In this case $C_1 = 14.6$ and $C_2 = 73.5$ were obtained, these values being in better agreement with the real reactivities of the reactants.

b. Reactions of bromoform

The C–Br bond in bromoform undergoes homolysis with greater difficulty than in CBr_4, which is the reason for a number of characteristic features of the reactions involving it: the use of effective initiation methods (up to the metal complex method) and comparatively severe reaction conditions. Relatively small differences in the nature of the reactants have a more marked effect on the results. Thus, in contrast to CBr_4, the reactions with $CH_2{=}CHCl$ and $CH_2{=}CHCF_3$ proceed differently; in certain cases, nonselective processes are observed under the conditions of peroxide initiation.

The reaction of bromoform with 1,1,1-propellane requires irradiation.[5]



The adduct is formed in a high yield (88%) and the process is not accompanied by the formation of telomers. The presence of a bromine atom at a tertiary carbon atom in the adduct molecule makes these compounds promising synthons for further chemical reactions.

As mentioned above, because of the smaller effectiveness of bromoform, compared with CBr_4, as a reaction chain-transfer agent, the intermediate radicals begin to participate also in competing reactions.

The interaction of bromoform with 3,3,3-trifluoropropene, in which the nature of the products and the composition of the reaction mixtures depend significantly on the method of initiation, is instructive in this respect.[9] Investigation showed that, in the presence of benzoyl peroxide, the reaction proceeds in a complex manner with formation of a mixture of compounds containing from two to four bromine atoms in the molecule. Together with telomers with the normal structure, the reaction mixture contains substances formed as a result of the involvement of the intermediate radical in rearrangements, hydrogen-transfer reactions, successive addition of a new monomer molecule, etc. This reaction was carried out selectively[9] using the $Fe(CO)_5$+DMF system. In this case, the reaction proceeds exclusively via the C–Br bond with formation of only one series of telomers containing three bromine atoms in the molecule.

$$CHBr_3 \xrightarrow{Fe(CO)_5+DMF} \dot{C}HBr_2$$

$$\dot{C}HBr_2 + CH_2{=}CHCF_3 \longrightarrow CHBr_2(CH_2CHCF_3)_n^{\cdot}$$

$$CHBr_2(CH_2CHCF_3)_n^{\cdot} \xrightarrow{DBr} CHBr_2(CH_2CHCF_3)_nBr$$

(DBr = bromine donor)

Telomers with $n = 1-3$ have been isolated in a pure form. The nature of the activity of metal complex initiating systems in radical reactions of polyhalomethanes with unsaturated compounds has been examined in detail in a monograph.[3] Their employment proved particularly promising when the reactions were carried out with readily polymerising acrylic monomers when initiation by peroxides is ruled out. The $Fe(CO)_5$+DMF system made it possible to achieve selective homolytic addition of bromoform to acrylic monomers at the C–Br bond without significant polymerisation.[10]

$$CHBr_3 + CH_2{=}CRX \xrightarrow{Fe(CO)_5+DMF} CHBr_2CH_2CRBrX$$

R = H; X = CN, CO_2CH_3;
R = CH_3; X = CO_2CH_3.

The radical nature of the process is confirmed in this instance by the structure of the adducts obtained (addition as a result of the dissociation of the C–Br bond). Haloforms are known to undergo ionic addition to a C–H bond, which leads to adducts with a CX_3 group at the end of the chain.[11] The best yield of the adduct with bromoform has been noted for methyl acrylate (78% relative to the unreacted $CHBr_3$); for acrylonitrile and methyl methacrylate, the yields are significantly lower (25% and 15% respectively).

The radical addition of bromoform to ketene silyl acetals, initiated by azobisisobutyronitrile (AIBN) or $B(C_2H_5)_3$, has been described.[12] Polyfunctional silicon-containing complexes of the type $CHBr_2CR^1R^2CBr(OR^3)OSiR_3^4$ or the products of their chemical reactions (hydrolysis, fragmentation, etc.) have been obtained as a result of such addition.

c. Reactions of methylene bromide

Methylene bromide is much less effective as a chain-transfer agent for the reaction via the C–Br bond than other polybromomethanes and the reaction with this compound is therefore as a rule nonselective and involves a low conversion of the addend. The reaction requires more severe conditions in this case. Thus the telomerisation of methylene bromide with 3,3,3-trifluoropropene has been carried out at 140–145 °C using the $Fe(CO)_5$+DMF initiating system. Telomers having the general formula $CH_2Br(CH_2CHCF_3)_nBr$ are the main but by no means the only reaction products.[9] The first two telomers (n = 1, 2) were isolated in a pure form. The reactions of methylene bromide with other monomers had been investigated earlier.[3]

2. Bromochloromethanes

The reactivity of polyhalomethanes in the reactions with the same monomer depends mainly on the number of halogen atoms in the polyhalomethane, while the nature of the halogen (chlorine or bromine) has much less influence. Comparison of relative kinetic data for the reactions of a series of polyhalomethanes with vinyl chloride makes it possible to arrange the addends investigated in the following series:[7] $CBr_4 > CCl_2Br_2 > CCl_3Br \gg CHBr_3$. Evidently, bromochloromethanes with two C–Br bonds and even one such bond in the molecule are more effective as reaction chain-transfer agents than bromoform.

a. Reactions of bromotrichloromethane

Among the mixed bromochloromethanes reacting via the C–Br bond, bromotrichloromethane has been most widely investigated. Monomers of different nature have been involved in the reaction with this compound and a wide variety of initiation procedures have been used.[3]

The employment of divalent samarium salts, which actively initiated these reactions under mild conditions, is fundamentally new, as for CBr_4.[4]

$$CCl_3Br + CH_2{=}CHR \xrightarrow[60\ ^\circ C,\ 10\ h]{SmI_2,\ CH_3CN} CCl_3CH_2CHBrR$$

R = C_4H_9, C_6H_{13}, C_6H_5, CO_2CH_3.

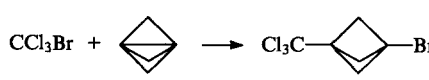
The authors suggest that one-electron transfer takes place with participation of the $(BrCCl_3)^{-\cdot}/SmI_2^+$ species (possibly a charge-transfer complex), which generates the chain-propagating $\dot{C}Cl_3$ radical.

Despite the high effectiveness of bromotrichloromethane as a chain-transfer agent, its reactions with the readily polymerising methacrylic acid esters are accompanied by the formation of telomers with two and three monomer units in an expectedly large amount.[13]

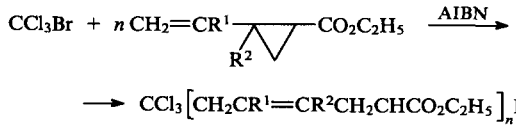
$$CCl_3Br + CH_2{=}C(CH_3)CO_2R \longrightarrow CCl_3\left[CH_2C(CH_3)CO_2R\right]_nBr$$

n = 1–3; R = *iso*-C_3H_7, *tert*-C_4H_9.

On the other hand, the reaction with propellane leads to the formation mainly of an adduct even in an excess of propellane.[14]



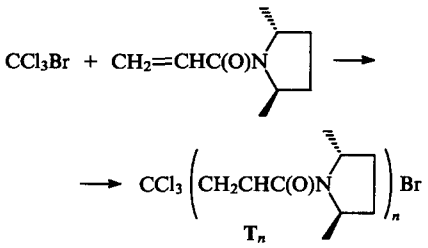
From the standpoint of the synthesis of polyfunctional compounds, the reaction of bromotrichloromethane with alkenylcyclopropanes is of interest.[15]



R^1, R^2 = H, CH_3; n = 1–7.

Telomers are formed mainly in the (*E*)-form and the partial chain transfer constants C_n for the growing radicals are close to unity and hardly change with increase in the chain length of the radical. This is quite reasonable because, even in the first growing radical ($n = 1$) the CCl_3 group is fairly remote from the radical centre and hardly affects its reactivity, which is determined for all the growing radicals mainly by the presence of ethoxycarbonyl groups in the neighbouring positions. The closeness to unity of the partial constants reflects the equal probability of the involvement of the growing radical in the chain-transfer and propagation stages.

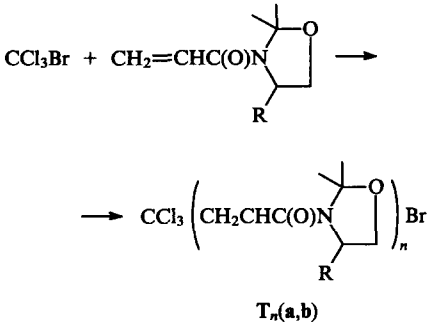
Several studies demonstrating the possibility, in principle, of stereocontrol in radical addition and telomerisation processes have been published recently.[16-18] In particular, the photochemical telomerisation of bromotrichloromethane with the chiral *N*-acryloyl-2,5-dimethylpyrrolidine has been described.[16]



T_n

The first five members of the series ($n = 1-5$) have been isolated and identified. It has been shown that the telomers T_2 and T_3 are formed predominantly in one stereoisomeric form (in the presence of small amounts of other possible stereoisomers), i.e. the radical addition reaction permits asymmetric control in the addition and chain transfer stages. The partial constants C_n are also given in the above communication, their values lying in the range 0.3–0.5. These quantities are not very reliable because, judging from the chromatograms presented in the communication (liquid and gel chromatography), the telomer ratio can be estimated quantitatively only very approximately.

The addition of bromotrichloromethane to substituted *N*-acryloyloxazolidines also proceeds with stereochemical selectivity.[17]

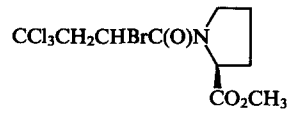


T_n(a,b)

R = C_6H_5 (**a**), *iso*-C_3H_7 (**b**).

The stereospecificity of this reaction for the telomer T_3^a reaches 15:1. The telomer T_3^a proved to be crystalline; this made it possible to use X-ray diffraction to investigate its stereochemistry. The stereoselectivity of the formation of T_3^a demonstrates that stereochemical control is achieved both in the addition stage and in the stage involving the transfer of the halogen to the growing radical.

Yet another example of this type of reaction is the addition of CCl_3Br to (*S*)-1-acryloyl-2-methoxycarbonylpyrrolidine catalysed by the $Fe(CO)_5 + P(C_6H_5)_3$ system.[18] In this case, it proved possible to achieve the virtually complete exclusion of the formation of telomers and to obtain the adduct



in 80% yield. It is one of the two possible diastereoisomers. This first example of the stereoselective occurrence of radical reactions initiated by $Fe(CO)_5$-based metal carbonyl complexes demonstrates the possibility and likely usefulness of metal complex initiators in the synthesis of stereoisomerically pure adducts.

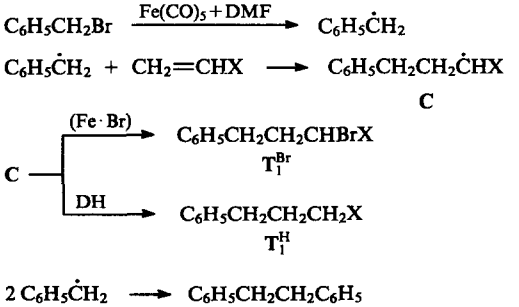
b. Reactions of dibromodichloromethane

The reaction of dibromodichloromethane with vinyl chloride under the usual conditions proceeds as telomerisation[7] and, when the monomer : telogen ratio is varied from 1.5 to 15, the content of the adduct in the reaction mixture falls from 80% to 30%. The first three telomers $CCl_2Br(CH_2CHCl)_nBr$ ($n = 1-3$) were isolated in a pure form. The values of C_n obtained ($C_1 = 7.7$; $C_2 = 54.3$) indicate a high effectiveness of dibromodichloromethane as a chain-transfer agent, comparable with the effectiveness of CBr_4 ($C_2 = 74.2$) in the analogous process with vinyl chloride.[7]

3. Benzyl bromide

Organic monobromo-compounds which have not been activated by functional groups do not enter as a rule into radical reactions under the conditions of peroxide initiation. The selective homolysis of the C–Br bond with a satisfactory yield of the adducts can be achieved under these conditions only when metal complex initiators are employed. Benzyl bromide has been most widely investigated among the monobromo-derivatives. Studies have shown that $Fe(CO)_5$-based initiating systems are most promising for its reactions with unsaturated compounds. Thus, in the presence of the $Fe(CO)_5$ + DMF(HMPA) (HMPA = hexamethylphosphoramide) system, the reactions of benzyl bromide with a wide range of monomers, differing significantly from one another by the polar characteristics of their substituents and by their capacity for polymerisation, have been achieved.[19,20] The addition of $C_6H_5CH_2Br$ to monomers with functional group substituents constitutes a promising method of synthesis of polyfunctional aliphatic–aromatic compounds. This reaction is a model for the study of the reactivity of benzyl radicals.

The addition of $C_6H_5CH_2Br$ to the $CH_2=CHX$ [X = H, C_4H_9, $Si(CH_3)_3$, Cl, CF_3, CO_2CH_3, CN] monomers using $Fe(CO)_5$ (up to 10%) combined with DMF or HMPA as the reaction initiator has been investigated under comparable conditions.[19,20] The reactions proceed in accordance with the general mechanism



The authors suggest that the radical-adduct **C** transfers the chain as a result of the abstraction of a bromine atom from the bromine-containing iron carbonyl complex whereupon the adduct T_1^{Br} is formed. The stabilisation of the radical **C** by the abstraction of hydrogen leads to the formation of the adduct T_1^H.

The identification of bibenzyl in the reaction mixture constitutes, according to the authors, one of the pieces of evidence in support of the radical nature of the reaction. It was noted that the amount of bibenzyl in the reaction mixture decreases with increase in the monomer concentration. For all the monomers, the main reaction product is T_1^{Br}. From the standpoint of the reactivity of the monomers, it was noted that the best results have been obtained with trimethylvinylsilane and somewhat worse ones with hex-1-ene. In the reaction with hex-1-ene using DMF and HMPA as initiators, an appreciable difference was observed between the yields of the adducts—in the case of HMPA the yield of the adduct increases by a factor of 2.5 for virtually the same degree of conversion of the telogen, i.e. the $Fe(CO)_5$+HMPA system is more effective as a complex initiator of the reaction. When the reaction is carried out with CH_2=CHX monomers containing electron-accepting groups (Cl, CF_3, CO_2CH_3, CN), the yield of the adducts is lower while the degree of conversion of benzyl bromide is high. 3,3,3-Trifluoropropene is of special interest in the above series of monomers. A multiplicity of reactions of the intermediate telomeric radicals have been noted for this compound, which stimulated a more detailed study of this process. Together with telomers having the structure $C_6H_5CH_2(CH_2CHCF_3)_nBr$ (n = 1, 2), the compound $C_6H_5CH{=}CHCH(CF_3)CH_2CH_2CF_3$ was detected in the reaction mixture. The authors explain its formation by a rearrangement of the radical with two monomer units and its subsequent ready dehydrobromination:

$$C_6H_5CH_2CH_2CH(CF_3)CH_2\dot{C}HCF_3 \xrightarrow[k_{re}]{1.5\text{-H}} \longrightarrow C_6H_5\dot{C}HCH_2CH(CF_3)CH_2CH_2CF_3,$$

where k_{re} is the rearrangement rate constant.

The intramolecular mechanism of the rearrangement was demonstrated and the rearrangement rate constant was determined [$k_{re} = (5.0 \pm 0.3) \times 10^4\,s^{-1}$] at 22 °C on model radicals, generated by abstracting a bromine atom from T_2^{Br}, in a special EPR investigation.[21,22] In addition, the fragmentation of the radical $C_6H_5CH_2CH_2\dot{C}HCF_3$ was observed for the first time by the EPR method, i.e. a third process—fragmentation which introduces certain corrections to the kinetic process parameters—is added to the two competing processes with participation of the radical (chain transfer and propagation).[23]

$$C_6H_5CH_2CH_2\dot{C}HCF_3 \longrightarrow C_6H_5\dot{C}H_2 + CH_2{=}CHCF_3$$

A similar process has been detected by the EPR method also for the $C_6H_5CH_2CH_2\dot{C}H_2$ radical (the reaction of benzyl bromide with ethylene), whereas fragmentation is not observed under similar conditions for the radicals $C_6H_5CH_2CH_2\dot{C}HX$ [X = Cl, $Si(CH_3)_3$]. Concerning the kinetics of the addition reactions, the rate constants $k_{add}(X)$ for the addition of the radical $C_6H_5\dot{C}H_2$ to the unsaturated compounds listed above were estimated under the conditions of metal complex initiation using the method of competitive kinetics;[24] the addition of the benzyl radical to trimethylvinylsilane was adopted as the standard: $k_{add}[Si(CH_3)_3]$.

X	$k_{add}(X)/k_{add}[Si(CH_3)_3]$
C_4H_9	0.29
CF_3	0.22
$Si(CH_3)_3$	1
Cl	1.02
CO_2CH_3	11.9
CN	24.0

It is seen from these data that the benzyl radical adds much more readily to the electrophilic methyl acrylate and acrylonitrile than to the relatively nucleophilic hex-1-ene. This is one of the pieces of evidence for the nucleophilic nature of the benzyl radical. Judging from the ratios $k_{add}(CN)/k_{add}(C_4H_9)$ = 83 and $k_{add}(CO_2CH_3)/k_{add}(C_4H_9)$ = 41, the polar effect influences significantly the kinetic parameters of the processes. In the study of the kinetics of the addition of the nucleophilic cyclohexyl radical to the monomers $CH_2=CXC_6H_5$, for which the decisive influence of the polar factor on the rate of addition has been established,[25] the ratio $k_{add}(CO_2C_2H_5)/k_{add}(CH_3)$ = 46, i.e. of the same order of magnitude as that obtained for $C_6H_5\dot{C}H_2$, was found.

The authors also drew attention to a fairly unexpected result—the ratio $k_{add}(CF_3)/k_{add}[Si(CH_3)_3]$ is close to that for hex-1-ene but not for methyl acrylate. One of the possible explanations is the fragmentation of the radical-adduct mentioned above, which ultimately decreases the content in the reaction mixture of the adduct whose concentration is used in the calculation. The same feature has been noted also for the reaction of benzyl bromide with vinyl chloride: $k_{add}(Cl)/k_{add}[Si(CH_3)_3]$ = 1. Although fragmentation was not observed in the EPR study of the $C_6H_5CH_2CH_2\dot{C}HCl$ radical, under real conditions (140 °C) it may play a decisive role. This appears particularly likely, since calculation of the activation energy[20] for the stage involving the addition of $C_6H_5\dot{C}H_2$ to vinyl chloride yielded a significantly lower value (by 7 kcal mol^{-1}) than that for the reaction of trimethylvinylsilane, i.e. there are no anomalies whatever in the addition stage. For vinyl chloride, this stage is more favourable in energy terms than for trimethylvinylsilane.

The reaction of benzyl bromide with trimethylvinylsilane has been used to investigate the overall kinetics of the addition reaction under the conditions of metal complex initiation.[26] One of the fundamental problems in this case is the mechanism of the chain transfer stage:

(a) 'purely' homolytic mechanism—via benzyl bromide:

$$C_6H_5CH_2(CH_2\dot{C}HX)_m + C_6H_5CH_2Br \longrightarrow C_6H_5CH_2(CH_2CHX)_mBr + C_6H_5\dot{C}H_2,$$

(b) redox-catalytic mechanism:

$$C_6H_5CH_2(CH_2\dot{C}HX)_m + [Fe(CO)_nL_{4-n}Br] \longrightarrow C_6H_5CH_2(CH_2CHX)_mBr + \left[Fe(CO)_nL_{4-n}\right].$$

Naturally, the overall kinetic equation is different in each case. For a radical process, we have

$$V(T_1^{Br}) = k_{rad}[Fe \cdot L]_0^{1/2}[S]_0^{1/2}[M]_0^{1/2},$$

where V is the rate, T_1^{Br} is the adduct, L is the ligand, S benzyl bromide, and M the monomer. For a redox process, we have

$$V(T_1^{Br}) = k_{red}[Fe \cdot L]_0[S]_0.$$

The study of the reaction order with respect to each reactant [for the 1 : 3 $Fe(CO)_5$ + DMF initiator] showed that in the given competitive case the radical mechanism of chain transfer is more likely. The authors believe that the mechanism may change in other reactions depending on the nature of the reactants and their capacity to form more or less stable complexes with $Fe(CO)_5$.

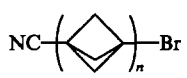
In the study of the competitive kinetics in the reaction of benzyl bromide with acrylonitrile and trimethylvinylsilane, modelling the cotelomerisation reaction of one telogen with two monomers,[27] an interesting feature was observed—the virtually complete alternation (rigorous alternation) of the monomer units under the conditions of the decisive influence of the polar factor. This reaction results in the formation of only one of the possible cotelomers

$$C_6H_5CH_2CH_2CH(CN)CH_2CHBrSi(CH_3)_3,$$

in which the nucleophilic benzyl radical adds effectively to acrylonitrile and the electrophilic radical $C_6H_5(CH_2)_2\dot{C}HCN$ formed adds to the relatively nucleophilic trimethylvinylsilane.

4. Reactions of functional bromine-containing compounds

The reaction of bromocyanogen with 1,1,1-propellane differs significantly from the reaction with bromotrichloromethane. In the case of BrCN, the telomers



are mainly formed,[14] but their proportions are unusual for telomerisation — the main reaction products are the second ($n = 2$) and third ($n = 3$) telomers in proportions of 4 : 1. It may be that their formation is a consequence of the secondary reaction of the adduct via the third bromine atom, i.e. stepwise telomerisation takes place.[3] Furthermore, bromocyanogen behaves in this reaction also as a brominating agent — the corresponding dibromo-derivative was detected among the products.

The photochemically initiated reaction of 1,2-dibromo-1-chlorotrifluoroethane with chlorotrifluoroethylene results in the formation of mainly the first two telomers.[28]

$$BrCFClCF_2Br + CClF{=}CF_2 \longrightarrow Br(CF_2CFCl)_n(CClFCF_2)_mBr$$

$n = 1$; $m = 1, 2$.

The general formula of the telomers adopted by the authors implies the possibility of the involvement of several molecules of not only the monomers but also of the telogen in the same molecular chain, although the corresponding compounds were not identified in the above investigation.

On irradiation or heating, *N*-bromodifluoromethyleneimine readily reacts with the fluoroolefins $CF_2{=}CFX$ (X = F, Br), affording the adducts $CF_2{=}NCF_2CFBrX$ in satisfactory yields (the yield is 82% for X = F and 67% for X = Br).[29]

The examples considered are summarised in Table 1.

III. Charge-transfer complexes as possible intermediates in radical processes

Complex systems based on $Fe(CO)_5$ combined with nucleophilic coinitiators (DMF, HMPA) are extremely effective as initiators of radical processes with participation of organic polybromo-compounds. Extensive experimental data indicate the existence of a relation between the effectiveness of the systems, the nature of the reactants, and the polar character of the intermediate radicals. Using UV spectroscopy, the nature of the transition state was discovered and the quantitative parameters correlated with the effectiveness of the system were found.[30,31] It was shown that charge-transfer complexes (CTC) are formed in many reactions with participation of organic bromo-compounds and that the quantitative characteristics of the charge-transfer band (CTB) (the intensity and the shift of the band in the spectrum compared with its position for the initial systems) are correlated with the effectiveness of the given metal complex system as the reaction initiator.

Selected data for the charge-transfer complexes of various metal carbonyls (MC) are presented in Table 2.[30-32] In the first place, one should note that a charge-transfer band whose position (λ_{max}) and intensity (I) differ significantly from the parameters for the initial compounds is observed in the metal carbonyl + CBr_4 system, i.e. a charge-transfer complex is indeed formed. In this connection, metal carbonyls can be clearly divided into two groups: for $Fe(CO)_5$ and $Mn_2(CO)_{10}$, there is a bathochromic shift of the charge-transfer band, whereas for the chromium, molybdenum, and tungsten carbonyls there is a hypsochromic shift. The same significant difference has been observed also between the initiating capacities of the systems based on the carbonyls: $Fe(CO)_5$ and $Mn_2(CO)_{10}$ are highly effective initiators of the reactions involving the dissociation of the C–halogen bond, while the remaining carbonyls are relatively ineffective as initiators.

Table 1. Radical reactions of organobromine addends with unsaturated compounds.

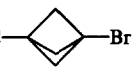
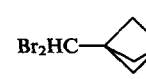
Addend	Monomer	Reaction conditions	Compounds identified [yield (%); C_n]	Ref.
CBr_4	$CH_2{=}CHCl$	$C_6H_5CO)_2O_2$	$CBr_3(CH_2CHCl)_nBr$; $n = 1-3$; $C_1 = 14.6$, $C_2 = 73.5$.	7
	$CH_2{=}CHCF_3$	$(C_6H_5CO)_2O_2$	$CBr_3(CH_2CHCF_3)_nBr$; $n = 1-3$; $C_1 = 15$, $C_2 = 64$, $C_3 = 60$.	6
	$CH_2{=}CHR$ R = C_4H_9, C_6H_{13}, C_6H_5, CO_2CH_3	SmI_2, 60°C	$CBr_3CH_2CH(R)Br$ (30–75)	4
		T_{room}	 (high yield)	3
$CHBr_3$	$CH_2{=}CHCN$	$Fe(CO)_5$ + DMF, 95–100 °C, 2 h	$CHBr_2CH_2CHBrCN$ (25)	10
	$CH_2{=}CHCO_2CH_3$	"	$CHBr_2CH_2CHBrCO_2CH_3$ (78)	10
	$CH_2{=}C(CH_3)CO_2CH_3$	"	$CHBr_2CH_2C(CH_3)BrCO_2CH_3$ (15)	10
	$CH_2{=}CHCF_3$	$(C_6H_5CO)_2O_2$	$CHBr_2[CH_2CH(CF_3)]_nBr$; $n = 1, 2$. $CBr_3CH_2CHBrCF_3$, $CBr_3CH_2CH(CF_3)CH_2CHBrCF_3$, $CHBr_2CH_2CH(CF_3)CH_2CH_2CF_3$, $CBr_3CH_2CH(CF_3)CH_2CH_2CF_3$	9
		$Fe(CO)_5$ + DMF, 100 °C	$CHBr_2[CH_2CH(CF_3)]_nBr$; $n = 1-3$.	9
		20–30 °C, 1.5 h	 (88)	5

Table 1 (continued)

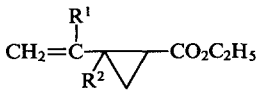
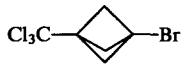
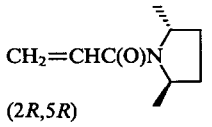
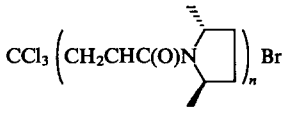
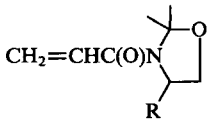
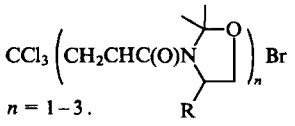
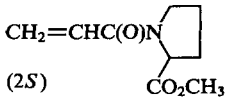
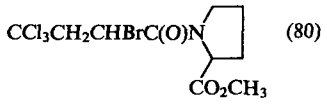
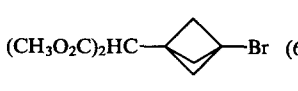
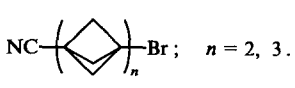
Addend	Monomer	Reaction conditions	Compounds identified [yield (%); C_n]	Ref.
CH_2Br_2	$CH_2{=}CHCF_3$	$Fe(CO)_5$ + DMF, 145 °C	$CH_2Br[CH_2CH(CF_3)]_nBr$; $n = 1, 2$.	9
CCl_2Br_2	$CH_2{=}CHCl$	$(C_6H_5CO)_2O_2$, 60 °C	$CCl_2Br(CH_2CHCl)_nBr$; $n = 1-3$; $C_1 = 7.7$, $C_2 = 54.3$.	7
CCl_3Br	$CH_2{=}C(CH_3)CO_2R$ R = *iso*-C_3H_7, *tert*-C_4H_9	50–90 °C	$CCl_3[CH_2C(CH_3)CO_2R]_nBr$; $n = 1-3$.	13
	$CH_2{=}CHR$ R = C_4H_9, C_6H_{13}, C_6H_5, CO_2CH_3	SmI_2, 60 °C	$CCl_3CH_2CH(R)Br$ (30–70)	4
	 $R^1 = R^2 = H$, CH_3	AIBN	$CCl_3(CH_2CR^1{=}CR^2CH_2CHCO_2C_2H_5)_nBr$; $n = 1-3$; $C_n \cong 1$.	15
		20 °C		14
	 (2*R*,5*R*)	*hv*	 $n = 1-5$; $C_2-C_5 \approx 0.3-0.5$.	16
	 R = C_6H_5, *iso*-C_3H_7	*hv*	 $n = 1-3$.	17
	 (2*S*)	$Fe(CO)_5 + P(C_6H_5)_3$, 75 °C, 2 h	 (80)	18
$C_6H_5CH_2Br$	$CH_2{=}CH_2$	$Fe(CO)_5$ + DMF(HMPA), 140 °C	$C_6H_5CH_2CH_2CH_2Br$	19
	$CH_2{=}CHC_4H_9$	"	$C_6H_5CH_2CH_2CHBrC_4H_9$	19
	$CH_2{=}CHSi(CH_3)_3$	"	$C_6H_5CH_2CH_2CHBrSi(CH_3)_3$	19
	$CH_2{=}CHCF_3$	"	$C_6H_5CH_2(CH_2CHCF_3)_nBr$; $n = 1, 2$.	19, 21, 22
	$CH_2{=}CHCO_2CH_3$	"	$C_6H_5CH_2CH_2CHBrCO_2CH_3$	19
	$CH_2{=}CHCN$	"	$C_6H_5CH_2CH_2CHBrCN$	19, 27
	$CH_2{=}CHCN$ + + $CH_2{=}CHSi(CH_3)_3$	"	$C_6H_5CH_2CH_2CHBrCN$, $C_6H_5CH_2CH_2CHBrSi(CH_3)_3$, $C_6H_5CH_2CH_2CH(CN)CH_2CHBrSi(CH_3)_3$	27
	$CH_2{=}CHCl$	"	$C_6H_5CH_2(CH_2CHCl)_nBr$; $n = 1, 2$.	20
$BrCH(CO_2CH_3)_2$		*hv*	 (69)	5
$BrCF_2CFClBr$	$CClF{=}CF_2$	UV	$Br(CF_2CClF)_n(CClFCF_2)_mBr$; $n = m = 1$; $n = 1$, $m = 2$; $n = m = 2$.	28
BrCN		*hv*	 $n = 2, 3$.	14
$CF_2{=}NBr$	$CF_2{=}CFX$, X = F, Br	*hv*	$CF_2{=}NCF_2CFBrX$ (82, 67)	29

Table 2. Charge-transfer complex formation data for various metal carbonyls.[30-32]

Compound	λ_{max}/nm	CTB for reaction with CBr_4	
		λ_{max}/nm	I
$Fe(CO)_5$	202.0	218.0	10200
DMF	204.0	221.0	3030
$Fe(CO)_5$ + DMF	224.0	221.0	11000
$Mn_2(CO)_{10}$	202.4	227.0	14390
$Cr(CO)_6$	227.0	217.0	4545
$Mo(CO)_6$	229.6	219.0	3800
$W(CO)_6$	226.0	218.4	3800

I is the relative intensity.[32]

The shift of the charge-transfer band in the reaction with CBr_4 is much smaller for $Fe(CO)_5$ than for $Mn_2(CO)_{10}$ and reaches approximately the same level only in the system containing DMF. There is a distinct correlation in this instance with chemical data—$Mn_2(CO)_{10}$ actively initiates the reactions without any additives, whereas $Fe(CO)_5$ initiates the reactions virtually only in the presence of additives (DMF, HMPA). Furthermore, $Mn_2(CO)_{10}$ is a much more effective initiator in the reaction with methyl bromoacetate than $Fe(CO)_5$ and the systems based on it.[33]

Analysis of data obtained when the reactants are added in succession suggests that the initial stage of the reactions with participation of organic bromo-compounds is the formation of an involved charge-transfer complex incorporating all the reactants. On the other hand, the study of the complexes formed in the case of simpler systems—binary, ternary, and finally quaternary [reaction components: $Fe(CO)_5$, DMF or HMPA, CBr_nH_{4-n}, CH_2=CHX]—enabled the authors to estimate fairly objectively the initiating activity of each complex system and its likely usefulness for initiation precisely for the given combination of reactants.[30]

In practice, this can facilitate significantly the choice of the initiating systems without carrying out a complex chemical experiment.

A similar study was later carried out also using chromium, molybdenum, and tungsten carbonyls.[32] Satisfactory quantitative correlations were obtained for these systems between the characteristics of the charge-transfer band and the effectiveness of the initiation of the homolytic addition and telomerisation proceeding with dissociation of the C–Br bond.

IV. Application of ^{13}C NMR spectroscopy in the establishment of the structures of organobromine compounds

Extensive and systematic study of radical reactions with participation of organobromine compounds led, as regards synthesis, to the formation of bromine-containing compounds with a fairly complex structure, sometimes including several different bromine-containing groups and functional groups. The ^{13}C NMR method proved to be one of the most promising for the study of their structures. The accumulated experimental data have been surveyed.[34] The tables in the above communication, in which the chemical shifts of carbon atoms involved in a C–Br bond and having different environments are compiled, are significantly helpful in the study of the structures of new compounds and in the determination of certain characteristics of the variation of the chemical shifts of the signals due to carbon atoms in particular groups as a function of the presence and nature of neighbouring substituents. Thus analysis of the spectra of 48 bromopolychloroalkanes showed that, in contrast to chlorine-containing groups for which the ^{13}C chemical shifts are usually in the range 38–105 ppm, the chemical shifts of the bromine-containing fragments (with the exception of $-CBr_2-$) are mainly in the range 25–50 ppm and are as a rule displaced upfield compared with the analogous organochlorine groups. These investigations showed[35] that the additivity of the influence of the α-, β-, and γ-halogen atoms on the ^{13}C chemical shifts frequently breaks down. Therefore the application of the usual additive schemes for calculations based on structural increments to organobromine compounds involves large discrepancies between the calculated ^{13}C chemical shifts and the experimental values.

The specific values of the α-, β-, and γ-effects have been obtained, taking into account the influence of the binary and ternary interactions of the halogen atoms, on the basis of ^{13}C NMR data for the most frequently encountered bromine-containing groups in 60 bromopolychloroalkanes. The increments reflecting the overall influence of the halogen atoms in *gem*-halogen-containing groups and also groups with a halogen atom attached to a secondary carbon atom on the ^{13}C shift in polyhaloalkanes were calculated. The increments obtained for the calculation of the chemical shifts of polyhaloalkanes make it possible to assign the ^{13}C signals of the isomers, their mixtures, and structurally similar compounds, when the differences between the chemical shifts of isotypical carbon atoms are small. A fairly detailed topological scheme for the empirical estimation of the ^{13}C NMR chemical shifts of polybromoalkanes, having definite predictive possibilities, was developed subsequently on the basis of these data.[35,36] An attempt was made in the above investigations to find an equation relating the topological image of the molecule to the experimental ^{13}C chemical shifts of polybromoalkanes taking into account the possibilities of interaction both through the chain and through space.

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