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Structural features and reactivity of tetrahalomethanes

B V Timokhin
Irkutsk State University

ABSTRACT. It is shown from an analysis of data on the structure and properties of tetrahalomethanes CX_4, where X = Cl, Br, I, that their chemical behaviour in many respects depends on the energy accessibility of the lowest unoccupied molecular orbital, which is the antibonding analogue of a bonding orbital of σ-type. This characteristic is responsible for, on the one hand, the occurrence of intramolecular interactions between halogen atoms and, on the other hand, their electrophilic properties in reactions with electron donors.

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I. Introduction

The problem of nucleophilic substitution in alkyl halides is one of the most frequently studied in theoretical organic chemistry. Up to the present time the structural factors that determine the reactivity of the substrate and nucleophile are generally apparent, the stereochemical characteristics of these processes are clear, and there exists the possibility of controlling a reaction using the solvent.[1,2] However, it has been observed for a long time that as the degree of halogenation of CH_nX_{4-n} molecules increases, the rate of reaction of bimolecular nucleophilic substitution usually decreases despite the increase in electron-withdrawing action of the substituents. Tetrahalomethane molecules, which are the limiting case of this type of α-substitution, react very sluggishly with nucleophiles. The reactions only take place under much more severe conditions and their results are ambiguous.[3] The nature of this type of α-effect is not at all clear up to the present time. Different explanations of this phenomenon have been put forward both in terms of the valence bond approach[4] and the molecular orbital approach.[5–7]

In recent times tetrahalomethanes, principally carbon tetrachloride and carbon tetrabromide, have started to be used effectively in different syntheses, especially those involving phosphorus-containing nucleophiles,[8] to give products whose formation cannot be accounted for on the basis of substitution reactions on the carbon atom.

Recently the concept of so-called "X-philic reactions" was developed.[9] It accounts for this and other similar reactions that take place by attacking a peripheral site rather than the central carbon atom on the basis of the theory of the perturbation of molecular orbitals. Ligand transfer to the nucleophile results from such reactions. By solving this problem in a general form and not solely for halogen-containing substrates, the authors who developed this concept did not set themselves the task of trying to find the structural causes through which a tetrahalomethane becomes the source of a "positive" halogen. Moreover, being clearly aware of the possibility of an alternative to the mechanism of an X-philic reaction, they confined their study solely to a theoretical approach. Meanwhile, there is a variety of information on the use of carbon tetrahalides in different chemical reactions related to halogenation of a nucleophile, in which the existence of radical intermediates have been recorded. The lack of correspondence that occurs, in our opinion, can be resolved by establishing the structural features and reactivity of polyhalomethanes from the available information, which, despite its considerable volume, has not been correlated to date. What has been stated above, together with the possibility of the future use of the conclusions obtained to interpret similar reactions of tetrahalides of other elements such as phosphorus,[10] constituted the reason for writing this review.

II. Structural features of polyhalomethanes

The properties of polyhalomethanes are determined in many respects by the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO).

According to nonempirical calculations the electronic configuration of tetrahalomethanes can be represented by the following MO sequence:[11,12]

$$(1a_1)^2\,(1t_2)^6\,(2a_1)^2\,(2t_2)^6\,(1e)^4\,(3t_2)^6\,(1t_1)^6\,(3a_1)^0\,(4t_2)^0.$$

The orbitals with e, $3t_2$, and t_1 symmetry are classed as π-type group orbitals formed from the p_z and p_y atomic orbitals (AO) of the unshared electron pairs (UEP) of the halogen atom. The $3a_1$ and $4t_2$ orbitals are classed as antibonding analogues of the $2a_1$ and $2t_2$ σ-type bonding orbitals.

Localisation of the upper occupied levels and their composition have been demonstrated by X-ray and photoelectron spectra, a detailed discussion of which is conducted in a recently published monograph.[13] In this case the first ionisation potential (IP) of halomethanes can be related to the HOMO energy, and the energy of the LUMO can be obtained by comparing these values and the energies of the $p \rightarrow \sigma^*$ transitions in UV spectra,[14,15] which generally correspond to the difference in energy between HOMO and LUMO.

In contrast to alkyl fluorides CH_nF_{4-n}, in which the energy levels of the UEP of the fluorine atoms lie below the bonding energy levels of the σ bonds, which are most apparent in the far UV region,[15] their analogues with heavier halogen atoms have certain characteristics.

Thus, the first IP in these derivatives correspond to the UEP of the halogen. It is clear that on increasing the degree of halogenation and also on replacing Cl by Br, the magnitudes of the first IP decrease (Table 1), which is probably due to a decrease in orbital energy of the ligand atoms on changing from Cl to Br and a decrease in effective charge on the carbon atom.[13]

Table 1. First ionisation potentials (IP, eV) and energies of the $p \rightarrow \sigma^*$ transition (E, eV) for halomethanes.[13,14]

Compound	F		Cl		Br		I	
	IP	E	IP	E	IP	E	IP	E
CH_3X	13.1	—	11.29	7.3	10.54	6.20	9.54	4.77
CH_2X_2	11.29	—	11.10	7.29	10.61	5.64	9.52	—
CHX_3	14.28	—	11.48	7.09	10.47	5.10	9.21	—
CX_4	16.30	—	11.69	7.08	10.39	4.90	9.10	3.20

When the energies of the $p \rightarrow \sigma^*$ transitions in the UV spectra of alkyl halides CH_nX_{4-n}, X = Cl, Br, I, n = 0–3 are examined and compared with the ionisation potentials, it can be seen that the energy gap between the HOMO and LUMO in this series of compounds decreases since the energy of the LUMO successively decreases on replacing chlorine with bromine and iodine and by increasing the degree of halogenation of methane.[16] These changes in the HOMO and LUMO should apparently assist both intra- and intermolecular interactions which depend on the energy of the frontier orbitals. For example, as the degree of halogenation of methane increases, the electron affinity should increase.[17] This conclusion is supported by the decrease in the values of the half-wave potential of polarographic reduction on increasing the number of bromine atoms in a methane molecule,[18] since it is known that its value is proportional to the energy of the LUMO.[19] This is also convincingly shown by the spectroscopic data of dissociative attachment of electrons to halomethane molecules.[20–23] The results obtained by different authors suggest that when an electron interacts with a halomethane molecule it is placed in its σ^* orbital with t_2 symmetry to form a temporary anionic state. This is very unstable and decomposes almost immediately. A quantum-chemical calculation with a CNDO/2 approximation on an *sp* and *spd* basis was used to analyse the different ways for the decomposition of such CX_4^- intermediates when X = Cl, Br, I:[24]

$$CX_4^- \rightarrow CX_4 + e^-, \quad CX_4^- \rightarrow CX_3^- + X^-, \quad CX_4^- \rightarrow CX_3^- + X^\cdot.$$

It transpired that the route leading to a halogen anion and trihalomethane radical has the least energy. Consequently, this route is predominant in the dissociative attachment of an electron. In this case the maximum yield of halogen will occur at the absorption energy of the electron. It is possible thus to determine the electron affinity in CH_nX_{4-n} molecules, which increases as the number of halogen atoms increases and on going from chloromethanes to their bromine analogues,[22,23] which accords with the direction of change in energy of the LUMO in these molecules.

The steric structure of halomethanes with a varying degree of substitution has been studied in detail in both the gas phase and crystalline state. Extensive tables of data on interatomic distances are available in a monograph[25] and booklets.[26,27] Data obtained by the same or comparable methods are given in Table 2.

Table 2. Carbon–halogen bond lengths in CH_nX_{4-n} molecules, Å.[25–27]

Compound	F		Cl		Br		I	
	g	c	g	c	g	c	g	c
CH_3X	1.383	—	1.781	1.805	1.939	1.863	2.133	2.134
CH_2X_2	1.357	—	1.767	1.768	1.925	1.91	—	2.12
CHX_3	1.332	—	1.758	1.750	1.930	—	2.12	2.18
CX_4	1.319	—	1.767	1.751	1.942	—	2.18	—

Note: g—gas phase; c—crystalline state.

Despite the fact that the absolute values of the C–X interatomic distances obtained for the different phase states are not the same, their patterns of change with a successive build-up of halogen atoms as well as when changing the nature of the halogen atom are clearly visible. On the one hand, there is an evident tendency of the C–X bond length to decrease with an increase in the number of halogen atoms in halomethanes in the case of the relatively compact fluorine and chlorine atoms. This can be followed most clearly in fluoromethanes. This would appear to result from the increase in effective electronegativity of the carbon-centred fragment, so that there is a reduction in polarity of the bond and as a result a reduction of the interatomic distance.[28] This is also indicated by the decrease in dipole moment of the C–X bond as the degree of halogenation of methane increases[29] and also by the occurrence of the shortest recorded carbon–halogen bond in the case of tetrahedral chlorides and bromides in chloro- and bromotrinitromethanes (1.712 and 1.885 Å respectively).[25]

On the other hand, on going to the more diffuse, bulky bromine and iodine atoms a tendency for the C–X bond to lengthen becomes apparent. This effect may be due to the steric interactions of the neighbouring halogen atoms, which is suggested, for instance, by the unusual intramolecular distances of X...X in the dihalomethanes CH_2Br_2 and CH_2I_2 [30,31] and in CCl_4.[32] In these molecules they are noticeably less than the sum of the van der Waals radii of the halogen atoms. It is also thought that these interactions reduce the energy of dissociation of the C–X bond, where X = Cl, Br, I, as the methane is halogenated, which does not occur for fluorination. It is possible that for this reason the valence force constants of this bond are reduced.[34]

It appears that the interactions of the geminal halogen atoms also have an effect on the enthalpy of formation of halomethanes. It has been observed that when there is a build-up of halogen atoms, this function increases nonlinearly.[37]

Another interesting feature of these alkyl halides CH_nX_{4-n}, X = Cl, Br, I, is the effect of the decrease in halogen–halogen intermolecular distances in the crystalline state.[30,31] It is thought

that this occurs as a result of charge transfer from a halogen atom to the σ^* orbital of a C–X bond in neighbouring molecules. This results in a decrease in the magnitude of halogen-halogen intermolecular contacts and consequently to underestimated values of the van der Waals radii.[38,39] It is therefore thought that the very concept of a radius for halogens is only significant when applied to contacts with atoms that do not have unshared electron pairs.

Table 3. Dissociation energy of the C–X bond in halomethanes CH_nX_{4-n}.[35,36]

Compound	Dissociation energy, kcal mol^{-1}			
	F	Cl	Br	I
CH_3X	112	83.6	69.7±1	54
CH_2X_2	114.5	81±3	62.7±5	45.5
CHX_3	128±5	77.2±5	56.7±5	37
CX_4	92.0±4	73.3±2	49.7±5	28.5

It cannot be excluded that this intermolecular charge transfer has an effect on the length of the C–X bond in tetrahalomethanes that is determined in the crystalline state. It should also be mentioned that a similar but solely intramolecular interaction is quite likely to occur between geminal halogen atoms, making it possible for them to converge to distances less than the sum of the van der Waals radii.

Table 4. Dipole moments of CH_nX_{4-n} molecules (μ), the C–X bond (μ_{C-X}), and the charges on the halogen atom (q_X).[40–42]

Compound	F			Cl			Br		
	μ, D	μ_{C-X}, D	q_X, e	μ, D	μ_{C-X}, D	q_X, e	μ, D	μ_{C-X}, D	q_X, e
CH_3X	1.87	—	0.2083	1.861	1.59	0.0850	1.86	1.52	0.0237
CH_2X_2	1.96	—	0.1983	1.57	1.05	0.0738	1.42	1.03	0.0176
CHX_3	1.62	—	0.1967	1.01	0.55	0.0659	0.99	0.54	0.0190
CH_4	0	—	0.1980	0	0.08	0.0664	0	0.05	0.0208

An increase in the effective electronegativity of the CR_3 fragment in an R_3C-X molecule on increasing the degree of methane halogenation should lead to a reduction in negative charge on the halogen atom through its transfer to the bond. A consequence of this should be a reduction in dipole moment of the C–X bond, as has been mentioned above. In fact, a comparison of the dipole moment of halomethane molecules (the dipole moments are determined in the gas phase in order to exclude intermolecular interactions) with the value of the group dipole moment of the C–X bond [40,41] and the magnitude of the charge on the halogen atom (obtained by calculation using the modified CNDO/2 method[42]) supports this conclusion (Table 4).

The electric polarisability of the molecules may serve as a qualitative measure of the mobility of the electrons and hence may also reflect the intramolecular interactions. In this case the anisotropy of bond polarisability calculated from the molecular anisotropy and the Kerr constants serves as a specific test for such effects.[43,44] For example, in a determination of the ellipsoids of polarisability for molecules of the type CH_2X_2, X = Cl, Br, I, for all three axes and when comparing the results with monohalogen derivatives, it was concluded that the significant experimental deviations from additivity in dihalomethanes are due to the interaction of the neighbouring C–X bonds through space.[45] Since the values of polarisability of the valence MOs decrease with an increase in the number of halogen atoms,[46] it may be assumed that the main contribution to polarisability is provided by the UEP of the halogen atom.

Table 5. Chemical shifts (δ, ppm) of ^1H, ^{13}C, ^{19}F, and ^{35}Cl atoms in halomethane molecules.

Compound	F			Cl			Br		I	
	δ^1H	$\delta^{13}C$	$\delta^{19}F$	δ^1H	$\delta^{13}C$	$\delta^{35}Cl$	δ^1H	$\delta^{13}C$	δ^1H	$\delta^{13}C$
CH_3X	7.1	75.5	271.9	7.1	25.1	40	7.3	10.2	7.6	−23.5
CH_2X_2	8.8	112.2	143.4	9.9	54.2	230	10.1	21.6	9.8	−61.1
CHX_3	10.3	118.8	78.6	11.8	77.7	410	12.4	12.3	6.5	−139.7
CX_4	—	119.9	63.3	—	96.7	560	—	−28.5	—	−229.1

Note. Chemical shifts of the ^1H atoms were measured relative to methane,[47] ^{13}C atoms relative to tetramethylsilane,[48,53] ^{19}F atoms relative to fluorotrichloromethane,[49] and ^{35}Cl atoms relative to an aqueous solution of sodium chloride.[50]

Haloalkanes have been studied repeatedly using radiospectroscopic methods and almost always the relationship between the changes in the spectroscopic characteristics of the indicator atom and the number of halogen atoms on the carbon atom has been investigated. As a rule a build-up of electronegative geminal substituents on carbon in halomethanes results in nonadditive effects which distort the dependences of the spectroscopic properties of these compounds on the structure. The chemical shifts in the spectra of halomethanes in relation to the number and nature of the halogen atoms can be given as such an example (Table 5).

It is clear from Table 5 that with an increase in the number of halogens the ^1H chemical shift is displaced downfield. This type of deshielding conforms to the increased electronegativity of the halomethyl residue and is likely to correspond to a reduction in electron density on the hydrogen atoms. However, it is noticeable that the contribution of a halogen in shielding the proton is not additive, as is indicated, for example, by the unsatisfactory value of the ^1H chemical shift in haloforms using Shoolery constants.[51]

A study of intramolecular interactions in halomethanes using ^{13}C NMR spectroscopy has been undertaken by different authors.[48,52–55]

By treating the chemical shifts of the ^{13}C nuclei in these compounds as the sum of mono-, di-, and tri-atomic increments that take into account interactions along the C–X bond as well as those through space,[48,52] it was possible to make quite an accurate prediction of their value. However, in considering this approach limited, Dostovalova et al.[54] gave greater consideration to the reasons for the nonoadditivity of the changes in this spectroscopic parameter and made an attempt to represent it through the bond increments $\Delta\delta_{C-X}$.[55] These values occur as the ratio of the difference between the chemical shifts of the halohydrocarbon in question and unsubstituted methane to the degree of substitution. The nonlinear change in these values is due to nonbonded interactions between the geminal halogen atoms, which lead to a distortion of their electron shell and consequently to an alteration in the charge on the C–X bond. The nature of such nonbonded interactions is probably similar to that which has been put forward to explain the changes in chemical shifts of ^{13}C and ^{19}F atoms in a number of substituted fluorochloromethanes.[56] In this case overlap of the UEP orbitals of the halogen with the virtual orbitals of the neighbouring carbon–halogen bond is thought to be most likely. This approach is confirmed by quantum-chemical calculations with the CNDO/2 approximation and by the good correlation of the ^{13}C chemical shift with the charge on this atom.

In the opinion of Cheremischin and Schastnev,[57] another reason for the nonadditive changes in chemical shifts of carbon that increase as the number of substituents in halomethanes increases is the occurrence of spin-orbit interaction. It has been observed that this effect is small for chloro derivatives but is substantial for the bromine- and iodine-containing analogues.

NMR spectroscopy of halogen nuclei has, with the exception of fluorine, not been used much for the study of halomethanes.[50,58] This is mainly because of the limitations arising as a result of broadening of the resonance line. Thus, for example, in the ^{35}Cl NMR spectrum of CCl_4 its width is equal to 15 kHz. Nevertheless it can be seen that the stepwise change from methyl chloride to carbon tetrachloride leads to deshielding of the nucleus of the chlorine atom.[50] The linear relationship between the chemical shifts of the ^{35}Cl and ^{19}F atoms indicates that there is a uniform structural effect on the shielding of both nuclei.[58]

An interpretation of the spectroscopic data of nuclear quadrupole resonance (NQR) of the nuclei of halogen atoms using the Townes–Dailey approximation can be used to determine the spatial distribution of electron density around these nuclei, and it has therefore been widely used to study organohalogen compounds, in particular halomethanes.[59]

It can be observed here that as the number of halogen atoms in the methane molecule increases, the NQR frequencies increase, which is interpreted as a consequence of the decrease in ionic nature of the C–X bond. However, it can be seen that the change in frequency is nonadditive.[60]

Introduction of substituents that are electron-donating relative to the halogen into the CX_4 molecule reduces the frequency of ^{35}Cl NQR, while electron-withdrawing substituents increase it. However, the change in frequencies in this case is determined by the inductive effect only to a first approximation. For example, for RCH_2Cl derivatives in which substituent R has unshared electron pairs (X = RO, F, Cl, Br) there are appreciable deviations from a linear dependence, which is due to conjugation of $p \rightarrow \sigma^*$-type.[61,62]

Thus, a study of intramolecular interactions in polyhalomethanes using radiospectroscopic methods shows that the change in spectroscopic characteristics is subject to the effect of the geminal halogen atoms, which in all probability is due to overlap of the orbitals of the unshared electron pairs of the halogen with the low-energy antibonding orbital of the neighbouring C–X bond. This effect is likely to determine the overall specific nature of intramolecular interactions in tetrahalomethanes. The energy availability of the antibonding orbitals of the C–X bond enables CX_4 molecules (X = Cl, Br, I) to exhibit electrophilic properties which give rise to reactions with certain types of charged and neutral nucleophiles as well as with free radicals.

III. Reactions of tetrahalomethanes with free radicals

It was noted earlier that when the number of halogen atoms on carbon is increased, the capacity of halomethanes for dissociative attachment of an electron increases. In this case temporary anionic states are formed, readily decomposing in the case of tetrahalides to a trihalomethyl radical and a halogen anion. Acceptance of an electron into an antibonding orbital accounts for the instability of the intermediate, which, however, decreases with an increase in the number of halogen atoms. This is indicated by a quantum-chemical calculation using the MINDO/3 approximation.[63]

Free radicals, as real electron carriers, should also in principle cause a similar dissociation of a halomethane. In fact, elimination reactions of a halogen from polyhalomethanes by the action of free radicals are well known. It has been shown by a large number of experiments that the energy of activation of the chain-transfer reaction

$$R^{\cdot} + CH_nX_{4-n} \rightarrow RX + \dot{C}H_nX_{3-n}$$

decreases as the number of halogen atoms in polyhalomethanes is increased, and when chlorine is replaced by bromine and then by iodine.[64] It should be emphasised here that such reactions are not typical for fluoromethanes.

Studies of a model chain-transfer reaction in the polymerisation of alkenes showed that in the reaction of the hydrocarbon radicals $(CH_3)_2C^{\cdot}R$, where R = PhO, MeCOO, PhS, Ph, with CBr_4, CCl_3Br, and CCl_4, there is electron transfer from the radical to the polyhalomethane. In this case the rate of reaction decreases in the series $CBr_4 > CCl_3Br > CCl_4$.[65]

Free-radical donor properties relative to tetrahalomethanes have been found in the case of the formation of adducts between 2,2,6,6-tetramethylpiperidine *N*-oxide and carbon tetrachloride.[66] At the same time paramagnetic shifts were detected in the ^1H NMR spectra of chlorine-containing molecules without α-hydrogen atoms in the presence of stable nitroxyl radicals. An analysis of the concentration dependence of these shifts showed that in this case weak complexes are formed between the components.[67] Morishima et al.[68,69] also found a downfield shift of the resonance signal in the ^1H and ^{13}C NMR spectra in the reaction of halomethanes with di(t-butyl)nitroxyl. They relate this phenomenon to the formation of short-lived complexes. The linear dependence between the observed contact shift and the half-wave potential of polarographic reduction of halomethanes serves as evidence of the donor-acceptor nature of these interactions involving a σ^*-type LUMO of the halomethanes. This is suggested by the appearance of a new absorption band in the region 310–370 nm in a solution of the same stable radical in carbon tetrachloride. It is thought that for carbon halides containing hydrogen, a complex is formed through hydrogen bonding,[70] while for tetrahalides the acceptance of electron density may only occur via the antibonding orbital of the C–X bond.

IV. Reactions with charged nucleophiles

During the last fifteen years attempts have been made to obtain carbon compounds with a coordination number greater than four. The highest expectations in this area relate to stabilisation of this unusual state by electron-withdrawing substituents. Hence the pentahalocarbonate anion CX_5^- has attracted a considerable amount of attention from research workers. The most promising method of obtaining this is the reaction of carbon tetrachloride or tetrabromide with phosphonium or tetraorganylammonium halides[71] as halide anion donors. Thus, it was possible to obtain complex compounds, but when they were studied by IR and Raman spectroscopy and X-ray diffraction analysis it was shown[72] that in the crystalline state carbon is not pentacoordinate in these compounds. In this case there is the formation of a complex ion in which a halogen anion is surrounded by four tetrahalomethane molecules with coordination via the halogen atoms (the three-membered fragment C—X—X is linear).

The formation of complex compounds with a $Br_3C-Br..Br^-$ fragment can be accounted for using the following two models. On the one hand, it is possible to form a donor-acceptor complex whose existence is achieved through charge transfer from the halogen anion to an antibonding orbital of the C—X bond or using a vacant 3*d* orbital of the halogen in the carbon halide. On the other hand, it may be assumed that because of the high polarisability of the CX_4 molecule, an electrostatic interaction of the type ion—induced dipole can occur.

An analysis of the X-ray diffraction data showed that the X...X distance in these complexes is considerably less than the sum of the van der Waals radii.[72] It was found for complexes of $R_4N^+Hal^-$ (R = Me, Et; Hal = Cl, Br, I) with CX_4 (X = Cl, Br, I) that the X...X distance increases (for a given halomethane) as a function of the halogen anion in the series $Cl^- < Br^- < I^-$, and it increases as a function of the acceptor molecule (for a given anion) in the series $CCl_4 < CBr_4 < CI_4$. The data obtained provide a basis for classing these complexes as donor-acceptor types. In the opinion of Creighton and Thomas,[72] the acceptor orbital in these complexes is a σ^*-type LUMO.

Recently a nonempirical calculation of the structure and stability of pentahalocarbonate anions CX_5^- (X = F, Cl, Br, I) was carried out. The formation energies of the three most probable structures were compared in this case. One of them has D_{3h} symmetry and two have C_{3v} symmetry. They differ in that the incoming anion coordinates either on the side or the top of the CX_4 tetrahedron.[73] It transpired that a pentahalocarbonate anion with a trigonal bipyramidal structure is unstable for any type of halogen. When the symmetry is reduced to C_{3v} the result is that such structures for X = F, whatever the approach of the incoming anion, are energetically unfavourable and the anion is unstable both in the gas phase and crystalline state. However, for X = Cl, Br, I, the coordination of the incoming anion to the halogen atom situated at the top of the tetrahedron always requires 25—45 kJ mol^{-1} less energy than when approach is made to the side, namely, to the carbon atom. In other words, according to the nonempirical quantum-chemical calculation, attack by the halogen anion on to the tetrahalomethane molecule occurs via a halogen atom, which is in complete agreement with the findings of X-ray structural analysis as given above.

The reaction of organometallic compounds (OMCs) with tetrahalomethanes has been studied for quite a long time and a considerable amount of information relating to this has been collected to date.[74] Information about the mechanisms of such reactions can be found in a monograph.[75]

Among OMCs of Group I metals, organolithium compounds are of the greatest interest. At very low temperatures (−115 to −100 °C) and in media with a high solvating capacity, such as in tetrahydrofuran or its mixtures with ether, a reaction that gives an organic halide and trichloromethyllithium readily occurs:[76—78]

$$R—Li + CHalCl_3 \rightarrow R—Hal + CCl_3Li,$$
$$R = Me, Et, n\text{-}Bu, Ph;\ Hal = Cl, Br, I.$$

However, when the temperature is increased, the reaction is different. It is frequently used as a source of dihalocarbenes. Thus, when ICF_3 [79] or CBr_2F_2 [80] is reacted with alkyllithium, difluorocarbene is formed and it is stabilised by alkene cyclopropanation. Reaction of methyl- and butyl-lithium under similar conditions with different tetrahalomethanes in the presence of cyclohexene gives dihalonorcarane in about 90% yield.[77] The change in the outcome of the reaction at an increased temperature is usually related to the ease of α-elimination of lithium halide from trihalomethyllithium. In fact, trichloromethyllithium which is obtained at a low temperature decomposes by 50% over a period of 30 min even at −65 °C according to the scheme

$$CCl_3Li \rightarrow LiCl + :CCl_2.$$

It should be mentioned here that there is no sign of a Wurtz type of condensation in these reactions.[74]

Among OMCs of Group II elements, organomagnesium compounds should first of all be mentioned. As a rule Grignard reagents react with CX_4 in different ways, in the case of alkylmagnesium halides forming complex mixtures of alkanes and olefins. However, it is thought that at low temperatures the reaction takes place via the formation of an organic halide and a trihalomethyl derivative of the metal.[81,82]

Comparatively recently a more detailed study of the reactions of organomagnesium compounds with tetrahalomethanes was made.[83—85] In this case chemically induced polarisation of ^1H nuclei was detected for the reaction between t-butylmagnesium chloride and carbon tetrachloride in bromotrichloromethane. Savin et al.[84] propose that the outcome of the reaction can be represented by a scheme that assumes single-electron transfer at the first stage:

$$(CH_3)_3CMgCl + CX_4 \rightarrow [(CH_3)_3\dot{C}MgCl^+ + C\dot{X}_4^-] \rightarrow (CH_3)_3\dot{C} + \dot{C}X_3 + MgClX.$$

The resulting radical pair disproportionates in two ways:

$$(CH_3)_3\dot{C} + \dot{C}X_3 \begin{cases} \rightarrow HCX_3 + (CH_3)_2C{=}CH_2 \\ \rightarrow (CH_3)_3CX + :CX_2 \end{cases}$$

as indicated by the ^1H polarisation phase in t-butyl chloride. In this case the high yield of products from the further reaction of dihalocarbene indicates that the reaction mainly occurs by the second route.

However, in the opinion of Davies et al.,[86] while the reaction of CCl_4 with EtMgBr occurs by a radical route (as is indicated by the formation of ethane and ethylene), the reaction of phenylmagnesium bromide, although giving 1,1-dihalonorcarane in the presence of cyclohexene, follows a heterolytic route via trichloromethylmagnesium bromide, which acts as a carbenoid. Thus, there is no common view about the mechanism of the

reactions of organic compounds of the most active metals of Groups I and II with halomethanes, but there is evidence to support radical processes which occur through the acceptance of electrons by tetrahalomethane.

A considerable number of reports on these types of reactions of carbon tetrahalides with OMCs relate to organomercury compounds. It is observed that in contrast to organolithium and organomagnesium compounds they generally react at higher temperatures. Thus, Ph_2Hg starts to react with CCl_4 at 200 °C, as a result of which phenylmercuric chloride, benzene, benzotrichloride, and hexachloroethane are formed.[87]

It is assumed that the initial stage of the reaction of organomercury compounds with CX_4 is dissociation of the OMC to radicals.[88-90] The free-radical pathway for the process has been confirmed by the inhibitor method.

Photolysis of organomercury compounds, which gives free radicals, assists the reaction, and in this situation it occurs even at room temperature.

Organic peroxides also have an initiating effect on the reaction between organomercury compounds and tetrahalomethanes.[91] A mechanism that includes a single-electron transfer stage has been proposed for reactions involving peroxides:[92]

$$\begin{matrix} R{-}Hg{-}OR \\ + \\ Cl{-}CCl_3 \end{matrix} \rightarrow \left[\begin{matrix} R{-}Hg^{+}\ \dot{O}R \\ Cl^{-}\ \dot{C}Cl_3 \end{matrix} \right] \rightarrow RHgCl + RO^{\cdot} + {}^{\cdot}CCl_3.$$

It is thought in this case that the catalytic effect of the peroxide consists essentially of forming a complex with the OMC, in which an additional polarisation of the carbon–metal bond occurs and hence the reactivity of the OMC towards the tetrahalomethane is increased. Strongly solvating media (dioxan, pyridine, hexamethylphosphotriamide) appear to have a similar effect.[93]

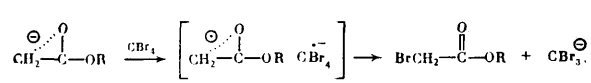
Tetrahalomethanes, in particular CCl_4, exhibit their electrophilic properties not only in the case of reactions with OMCs but also with other carbanion sources. These can be strong CH-acids which generate a carbanion *in situ* on treatment with different bases. The main course of the reactions, as in the case of OMCs, is halogenation of the carbanion. However, dimerisation can quite often be an alternative reaction.

Thus, by treatment with CCl_4 and lithium diisopropylamide or with alkali in alcohols it is possible to halogenate diarylmethanes,[94] ketones,[95,96] sulphones,[97,98] and saturated and unsaturated ethers.[99] Apart from CCl_4, CBr_4 or CCl_3Br can also act as halogenating agents.[99] It is interesting to note that in the latter case α-bromination of the carbanion mainly occurs, which is an indication of the greater ease of transfer of the bromine atom.

Phase-transfer catalysis is particularly promising for the halogenation of CH-acids with tetrahalomethanes. In the system concentrated alkali–triethylbenzylammonium chloride, halogenation of phenylacetylene,[100] 2-phenylalkyl nitriles,[101] and arylbenzyl ketones,[102] readily occurs. Dimerisation is possible as a side-reaction:[103]

$$PhCH_2CN + CCl_4 \rightarrow PhC(CN)=C(CN)Ph,$$
$$Ph_2CHCN + CCl_4 \rightarrow Ph_2C(CN)-C(CN)Ph_2.$$

It is assumed that halogenation of the carbanion occurs through the formation of a radical–radical anion pair as a result of discrete electron transfer,[96,99] for example:



It should be noted that a similar approach to the reactions of carbanions with alkyl halides has generally been actively discussed recently.[104]

V. Reactions with electron-neutral nucleophiles

The electrophilic properties of carbon tetrahalides are exhibited in the formation of complexes with different *n*- and π-donors. However, in this case also the coordination site is not carbon but a peripheral halogen atom. It is to be expected that this route is taken in the self-association of CX_4 molecules (X = Cl, Br, I),[105] which disappears on addition of cyclohexane,[106] if it is assumed that such an association occurs through the interaction of the UEP of the halogen atom (as an *n*-donor) with the antibonding orbital of the C–X bond of neighbouring molecules as occurs in intermolecular X...X contacts in these compounds in the crystalline state.[38,39]

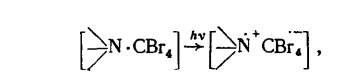
Interactions of a similar type apparently occur on mixing carbon tetrachloride with ethers, which act in this case as *n*-donors.[107]

It is well known that the π-electron properties of aromatic hydrocarbons have an effect on their ability to form complexes with various electron acceptors, including tetrahalomethanes. Thus, it has been known for quite some time that carbon tetrachloride and tetrabromide form crystalline complexes with benzene,[108,109] toluene,[109] and polymethylated benzenes.[110] X-Ray diffraction analysis of the complex between CBr_4 and *p*-xylene showed that in a crystal molecule of the partners alternate in small chains, in which each halide molecule is bonded to two molecules of aromatic compound via bromine atoms. In this case the distance between the bromine atom and the centre of the plane of the hydrocarbon ring is less than the sum of the van der Waals radii.[112] When the halogen nuclei were studied by NQR it was not possible to come to any conclusion about the nature of the bonding in these complexes,[113] but the data of IR spectroscopy suggest that in hydrocarbon–tetrahalomethane mixtures, complexes of composition 1:1 are apparently formed by charge transfer.[114,115] The changes in the Raman spectra of a solution of CCl_4 in benzene and mesitylene are interpreted as resulting from charge transfer from the π-donor to the chlorine atom.[116] It is thought in this case that an electron can be accepted either via the σ* orbital of the carbon–halogen bond[113] or via vacant 3*d* orbitals of the halogen atom.[116,117]

Reactions of tetrahalomethanes with neutral nucleophiles such as tricoordinate nitrogen or phosphorus compounds occupy a special place in terms of the quantity of information as well as the chemical effects. It is therefore worth examining them in greater detail.

The instability of solutions of amines in carbon tetrachloride was observed some time ago.[118-120] On standing in glass vessels, a precipitate is rapidly deposited from this mixture and chloroform is formed. It is thought that the cause of this instability is the formation of a charge-transfer complex between the reactants. The existence of such complexes has been confirmed by UV spectroscopy for the systems $NH_3 \cdot CCl_4$, $NH_3 \cdot CBr_4$,[121] $Et_3N \cdot CCl_4$, $Et_3N \cdot CBr_3Cl$,[120] and $Bu_3N \cdot CCl_4$.[122] Recently crystalline complexes of carbon tetrabromide with diazabicyclo[2.2.2]octane (DABCO) and quinuclidine were successfully isolated and studied using X-ray diffraction analysis.[123] It was shown that the molecular structure of the complex between CBr_4 and DABCO is in the form of sinuoidal chains in which the diamine is coordinated with the halogen atoms of two tetrahalide molecules, while quinuclidine forms discrete donor–acceptor pairs.

Since the formation of complexes in these cases, in the opinion of the authors, assumes that there is an interaction between the UEP of the donor and the σ^* orbital of the C–X bond, this transition to some extent neutralises the bonding due to the two electrons situated in the σ orbital. Therefore, on irradiation in the near-UV region dissociation of the complex can occur,[124] resulting in the formation of radical-ion pairs



whose reactions account for the photochemical instability of the solutions of amines and tetrahalomethanes. Thus, on irradiation of $RNH_2 \cdot CCl_4$ with visible light at $\lambda = 2537$ Å in the absence of oxygen, $R\overset{+}{N}H_3\ Cl^-$, $CHCl_3$, C_2Cl_6, $R'CH{=}NR$, and NH_3 are formed, with a quantum yield ranging from 1 to 100.[122] The formation of these compounds results from the following series of reactions:

$$RNH_2 \cdot CCl_4 \xrightarrow{h\nu} R\dot{\overset{+}{N}}H_2\ Cl^- + \dot{C}Cl_3,$$
$$R\dot{\overset{+}{N}}H_2\ Cl^- + RNH_2 \rightarrow R\overset{+}{N}H_3\ \bar{Cl} + R\dot{N}H,$$
$$\dot{C}Cl_3 + RNH_2 \rightarrow CHCl_3 + R\dot{N}H\ (\text{or}\ R'\dot{C}HNH_2),$$
$$R\dot{N}H\ (R'\dot{C}HNH_2) + RNH_2 \rightarrow R'CH{=}NH + R\overset{+}{N}H_3\ Cl^-,$$
$$R'CH{=}NH + RNH_2 \rightarrow R'CH{=}NR + NH_3,$$
$$2\dot{C}Cl_3 \rightarrow C_2Cl_6.$$

When the reaction is carried out in the presence of oxygen, the molar ratio of the reaction products varies and, moreover, *N,N'*-dialkylureas are formed, apparently by the reaction of the amine with phosgene that occurs as a result of the radical oxidation of CCl_4.

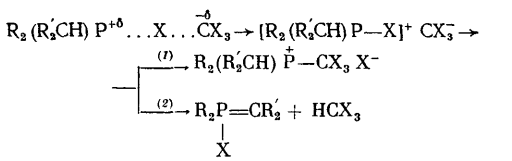
Recently the radical nature of the photochemical reaction of amines with carbon tetrachloride has been confirmed by the occurrence of the effect of chemically induced polarisation of the ^1H nuclei.[125]

The reaction with tetrahalomethanes in the dark and in the absence of oxygen can be initiated with Cu(I), Cu(II), Fe(II), and Fe(III) salts.[126] It is thought that in this case the reaction is radical in nature. In addition, the reaction mixture stimulates the addition of CCl_4 to olefins.[127]

The reactions of tetrahalomethanes, in particular CCl_4, with tricoordinate phosphorous derivatives have become quite widespread in recent times. The greatest attention of research workers has been given to the system Ph_3P-CCl_4, which is a mild selective reagent. This system has been applied most widely in the halogenation of alcohols with a very variable structure and also in reactions that accompany the dehydration and formation of the P–N bond.[128–130]

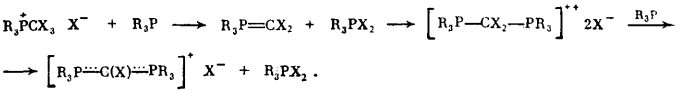
From the ideas about the electronic structure of tetrahalomethanes and their reactions with both charged and neutral nucleophiles, it is to be expected that the initial stage of the reaction involving the Ph_3P-CCl_4 system should be electron transfer from the phosphorus atom to the σ^* orbital of the C–Cl bond. But while in the case of the amine–tetrahalomethane system homolytic decomposition follows the transfer of electrons, in the case of tertiary phosphines there is heterolysis of the intermediate complex.[129] Nevertheless, it should be noted that on exposure of solutions of Ph_3P in carbon tetrachloride to light, photochemically induced homolytic reactions occur concurrently, as chemically induced polarisation of the ^{31}P nucleus occurs.[131]

Thus, a scheme involving nucleophilic attack by the phosphorus atom on a halogen atom in the tetrahalomethane has been proposed by many authors for reactions that take place in the absence of light and radical initiators:

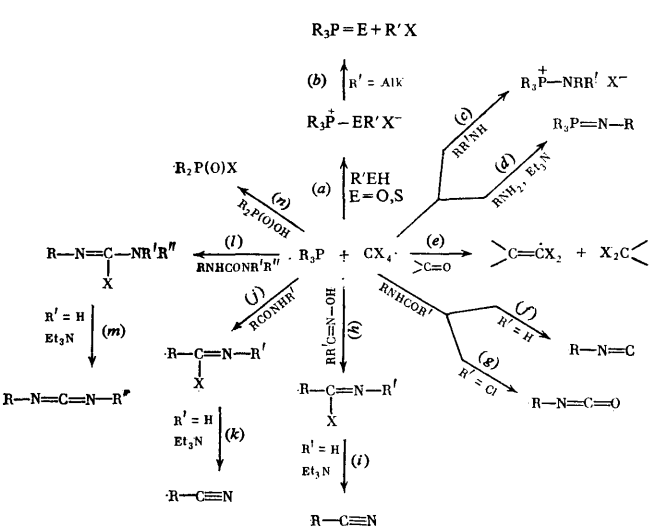


The resulting dipolar associate is converted to an ion pair with a trihalomethide anion, which, depending on the structure of the phosphorus-containing residue, is converted either to the corresponding phosphonium salt[132] or (when there is an active hydrogen on the α-carbon atom) to haloform and a *P*-halogen ylide by deprotonation.[130] The latter is stimulated on the one hand by an increased CH-acidity and on the other hand by steric shielding of the phosphorus atom. It is observed here that the reactivity of the tetrahalomethane increases on going from CCl_4 to CBr_4 and then CI_4.

Reactions of CX_4 with tertiary phosphines that take place by route (*1*) are not complete when the trihalomethyltriorganylphosphonium halide is formed. In the presence of excess phosphine these very active compounds react further:



It is assumed that the formation of triorganylhalophosphonium trihalomethide $R_3P^+Hal\ CHal_3^-$ at an intermediate stage of the reaction permits a considerable number of reactions involving tertiary phosphines and tetrahalomethanes to take place.[129]



The system tertiary phosphine–tetrahalomethane–hydrogen donor has been used successfully to obtain quasiphosphonium salts from phenols or thiophenols (*a*) and also alkyl halides from alcohols (*b*). By introducing secondary amines into the reaction it is

possible to obtain aminophosphonium salts (*c*). Phosphinic acids can readily be converted to their acid halides (*n*). For the purposes of organic synthesis an R_3P-CCl_4 mixture can be used for the preparation of chloroformamidines from trisubstituted ureas (*l*) or imidoyl halides from *N*-substituted carboxamides (*j*) and ketoximes (*h*). When carbamoyl halides are used it is possible to obtain isocyanates (*g*).

If the compound that acts as a hydrogen donor contains two active hydrogen atoms, conducting the reaction in the presence of triethylamine as a halogen halide acceptor has the result that dehydrohalogenation takes place by a route different from route (*c*) [reactions (*d*), (*f*), (*i*), (*k*), and (*m*)].

The use of the binary system R_3P-CX_4 to obtain 1,1-dihaloalkenes from aldehydes and ketones has been reported. Dihaloalkenes are probably obtained from an intermediate triorganylhalomethylenephosphorane as the result of a Wittig reaction (*e*).

The use of the system R_3P-CX_4 for halogenation of the hydroxyl group has been described in great detail.[128,129] However, during the time that has passed since these reviews were written, a large quantity of additional information has been published.

A considerable number of studies have been devoted to establishing the mechanism of this reaction. It has been shown conclusively that the reaction takes place via an intermediate alkoxyphosphonium salt, which then undergoes an S_N2 substitution.[133,134]

$$Ph_3P + CCl_4 \rightarrow Ph_3\overset{+}{P}-Cl\ CCl_3^- \xrightarrow{ROH} Ph_3\overset{+}{P}-OR\ Cl^- + HCCl_3,$$

$$Ph_3\overset{+}{P}-OR\ Cl^- \rightarrow Ph_3P{=}O + RCl.$$

Sometimes this salt can be separated as a stable hexafluorophosphorate.[135]

In recent times interest has mainly been directed towards using this sytem Ph_3P-CCl_4 for the halogenation of polyols.[136-140] It is observed that the reaction is selective, namely, only a primary hydroxyl group undergoes transformation. However, intramolecular cyclodehydration to an α-oxide can occur as a subsequent stage.[138,139]

There is continued interest in the use of systems containing CX_4 and diphenylphosphinated polymers for the halogenation of alcohols, giving higher yields of products than the binary system Ph_3P-CX_4.[141,142]

The system Ph_3P-CCl_4 has been used to obtain cyclic and acyclic 1,2-dichloroalkanes from α-oxides[143] and for the synthesis of 1,1-dichloroalkenes from the corresponding carbonyl compounds.[144,145]

In addition to the widely used carbon tetrachloride, other symmetric tetrahalomethanes have started to be used for halogenation of the OH group. It is observed in this case that CBr_4 and CI_4 react more readily than their chlorine analogue,[140,146-148] while in the case of CF_2Cl_2 only a chlorine atom participates in the reaction.[149]

The system CBr_4-PPh_3 has been quite widely used for the selective halogenation of primary hydroxyl groups in sugars and nucleosides.[140,146-147] It can be used to dehydrate amides, aldoximes, and ureas to the corresponding nitriles and carbodiimides after a shorter period of time and at a lower temperature than in the case of Ph_3P-CCl_4,[150] and there is a much greater ease in forming the ylide $Ph_3P{=}CBr_2$, which then either undergoes alkylation by alkyl halides to the corresponding phosphonium salts[151] or gives dibromoolefins by the Wittig reaction.[152,153] The quantitative polycondensation of *p*-aminobenzoic acid is achieved using the system CBr_4-PPh_3.[154]

The bromine atom in $BrCCl_3$ is attacked very readily by tertiary phosphines. This is suggested by the formation of only $Ph_3P{=}CCl_2$ [155,156] and also the preparation of bromophosphazo compounds from phosphinous acid anilides.[157]

The fluorine atom in fluorine-containing tetrahalomethanes CF_nX_{4-n} (X = Cl, Br, I; $n = 1-3$) is never attacked by tertiary phosphines. In all cases transfer of the more polarisable halogen occurs. This is suggested by the formation of $Ph_3P{=}CFX$ in the reaction of Ph_3P with CFX_nY_{3-n}, where X and Y = Cl, Br, I,[158] and by the trifluoromethylation of silicon chlorides R_nSiCl_{4-n} with the binary system $(Et_2N)_3P-CF_3Br$.[159]

$$(Et_2N)_3P + CF_3Br \rightarrow (Et_2N)_3\overset{+}{P}-Br\ CF_3^- \xrightarrow[-(Et_2N)_3PBrCl]{Me_3SiCl} Me_3SiCF_3.$$

It is thus possible to replace one or two chlorine atoms on silicon in organylchlorosilanes with the trifluoromethyl group. Similarly trifluoromethyl P(III) derivatives are formed if a tricoordinate phosphorus halide is introduced into the reaction as the third component.[160]

The stability of the C–F bond in tetrahalomethanes is confirmed by the formation of 1,1-difluoroolefins in the reaction of carbonyl compounds with a mixture of $(Me_2N)_3P-CF_2Br_2$ [161] or 1,1-difluorocyclopropanes as a result of the reaction of this system with disubstituted alkenes.[162]

1,1-Diiodoalkenes are formed in good yield when the binary system CI_4-Ph_3P is treated with aldehydes.[163]

The reaction of white phosphorus P_4 with CCl_4 may also be regarded as a process that involves reactions between tricoordinate phosphorus derivatives and tetrahalomethanes. Treatment of this reaction mixture with alcohols or phenols leads to the formation of phosphite esters[164,165] and treatment with thiols gives their thio analogues.[166]

Reactions of esters of tricoordinate phosphorus acids with tetrahalomethanes also play an important role in synthetic organophosphorus chemistry:

$$\rangle P-OR + CX_4 \rightarrow \rangle P\begin{matrix}O\\ \diagdown CX_3\end{matrix} + RX.$$

Those reactions with carbon tetrachloride are the most common. It reacts with phosphite,[128,167,168] phosphonite,[130,169,170] and phosphinite[171-174] esters and also with phosphorus acid ether amides.[175,176]

As a rule P(III) acid esters react with CBr_4 more readily than with CCl_4.[128,130] Among the other tetrahalomethanes that take part in reactions with phosphinites, mention should be made of $CBrCl_3$,[177,178] $CFBr_3$, and CF_2Br_2.[179]

As far as the mechanism of these reactions is concerned, at the present time the idea is becoming established that in the absence of radical initiators, in the dark, and when there is steric hindrance at the phosphorus atom, a heterolytic reaction takes place by means of attack by the phosphorus-containing nucleophile on a halogen atom:

$$\rangle P-OR + X-CX_3 \rightarrow RO-\overset{+}{P}\begin{matrix}X\\ \diagdown CX_3\end{matrix}\ CX_3^- \rightarrow$$

$$\rightarrow RO-\overset{+}{P}\begin{matrix}CX_3\\ \diagdown X\end{matrix}\ X^- \rightarrow \rangle P\begin{matrix}-CX_3\\ \| O\end{matrix} + R-X.$$

This relates to the reactions of $(RO)_3P$,[180] $RP(OR)_2$,[130,169] $(Me_2N)_2POR$,[176] R_2POR,[171,173] and $(R_2N)_2PSR$.[181]

It has been observed that the reactivity of P(III) acid esters towards CCl_4 varies in accordance with the following series:[176,182]

$$iso\text{-}PrO)_3P > (EtO)_3P > (MeO)_3P > (EtO)_2POPh > EtOP(OPh)_2 \gg P(OPh)_3.$$

This sequence matches the increase in the half-wave potential of the anodic oxidation of P(III) acid esters,[183] which is proportional to the HOMO energy. Thus, it may be assumed that these processes between CX_4 and tricoordinate phosphorus acid esters correspond to a donor-acceptor interaction between P(III) compounds and tetrahalomethanes and in this respect there is a perfect similarity between them and the reactions of tertiary phospines depicted above.

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The analysis carried out on the structural features and reactivity of carbon tetrahalides indicates that, in contrast to the widely known chemical inertness of CF_4, its analogues exhibit a large number of reactions on treatment with electron donors. These properties of CX_4 molecules, where X = Cl, Br, and I, are apparently due to the energy accessibility of σ-type antibonding molecular orbitals of the C–X bonds, which accounts for the coordination of the reactants on a peripheral halogen atom rather than on the carbon atom, resulting eventually in halogen transfer.

It cannot be excluded that similar reactions occur in the case of tetrahalides of other elements.

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