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Carbon Tetrabromide—A New Brominating Agent for Alkanes and Arylalkanes*

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Abstract—Quantitative catalytic bromination of alkanes, cycloalkanes, and arylalkanes with carbon tetrabromide as brominating agent was accomplished for the first time.

The present communication describes catalytic bromination of alkanes (decane and dodecane), cycloalkanes (cyclohexane and adamantane), haloalkanes (butyl chloride) and arylalkanes (toluene, *p*- and *m*-xylenes, and mesitylene) by the action of CBr_4 in the presence of metal-complex catalyst. The process follows the equation

$$CBr_4 + RH \longrightarrow CHBr_3 + RBr \qquad (1)$$

This reaction can be regarded as metathesis of $C-H$ and $C-Br$ bonds in saturated compounds. Reaction (1) in the presence of transition metal complexes has not been studied previously. We showed in [1] the possibility for preparation of bromo derivatives of aromatic hydrocarbons by heating the corresponding arenes with CBr_4 for a long time at 150–180°C in the absence of a catalyst and solvent. The yield of the products was 30–70%, but our attempts to use CBr_4 as brominating agent for alkanes was unsuccessful. Schreiner *et al.* [2] reported on the bromination of alkanes and cycloalkanes with carbon tetrabromide in combination with sodium hydroxide in a two-phase system in the presence of phase-transfer catalyst [2]. However, this process is low effective: the reaction time is as long as 90 h, and the yield of the products does not exceed 30–70%. Vol'pin *et al.* [3] used carbon tetrabromide in the form of a catalytic complex with $AlBr_3$ to brominate alkanes and cycloalkanes; the complex $CBr_4–2AlBr_3$ itself can act as brominating agent in the absence of

molecular bromine [4]. Synthetic utilization of this procedure is complicated by the necessity of using twofold excess of aluminum bromide and by sensitivity of the brominating agent to moisture. Likewise, the bromination of alkanes with methylene bromide in the presence of SbF_5 [5] requires relatively large amounts of metal halide (molar ratio of CH_2Br_2 to SbF_5 is about 2). Presumably, a high concentration of catalyst is a general feature of the halogenation of alkanes in the presence of Lewis acids; this makes such processes less attractive from the preparative viewpoint. The goal of the present study was to effect selective bromination of alkanes and arylalkanes with CBr_4 in the presence of a catalytic amount of transition metals.

As catalysts we used copper complexes formed by reaction of $CuBr$ or $CuBr_2$ with quatenary ammonium bromides, e.g., $CuBr–Bu_4NBr$ (1:1) (**Ia**), $CuBr_2–Bu_3(PhCH_2)NBr$ (1:4) (**Ib**), polymetalphenylsiloxanes of the general formula $\{[PhSiO_{1.5}]_2CuO\}_n$ (**IIa**, metal concentration in the heterogeneous catalyst 0.11%), and $\{[PhSiO]_6CuO]\}_n$ (**IIb**, metal concentration 0.3%), as well as related nickel derivative $\{[H_2N(CH_2)_3SiO_{1.5}]_2NiO\}_n$ (**III**, 0.16% of Ni). Previously, copper chloride complexes analogous to **I** and silica-immobilized polymetalorganosiloxanes (PMOS) with phenyl, alkyl, and aminoalkyl substituents on the silicon (analogous to catalysts **II** and **III**) were examined as catalysts of $C-Cl$ and $C-H$ bond metathesis in the systems CCl_4–alkane [6–8]. These catalytic systems are advantageous due to their stability, high activity, and simplicity of the synthetic procedure. Reactions with CCl_4 in the presence of such catalysts ensured preparation of chloroform and monochloroalkanes with a selectivity of 98–99%, the conversion of the initial alkane being 50–80%.

Table 1. Bromination of alkanes with carbon tetrabromide

Run no.	Alkane (RH)	Molar ratio $RH:CBr_4$	Catalyst	Time, h	Temperature, °C	Yield of RBr, % (with respect to CBr_4)
1	$C_{12}H_{26}$	10:1	**Ia**[a]	2.5	180	67
2	$C_{10}H_{22}$	5:1	**Ia**	8	160	93
3	$C_{12}H_{26}$	10:1	**Ia**	5	180	95
4	$cyclo$-C_6H_{12}	10:1	**Ia**	10	180	86
5	$C_{10}H_{22}$	10:1	**Ib**[a]	0.5	150	62
6	$C_{10}H_{22}$	10:1	**Ib**	1	150	88
7	$C_{10}H_{22}$	10:1	**Ib**	2	150	98
8	$C_{12}H_{26}$	10:1	**IIa**[b]	2.5	160	130[c]
9	$C_{12}H_{26}$	10:1	**IIa**	5	150	68
10	$C_{12}H_{26}$	2.2:1	**IIa**	5	150	61
11	$C_{12}H_{26}$	10:1	**IIa**	10	130	55
12	$C_{12}H_{26}$	10:1	**IIa**	10	98	28
13	$C_{10}H_{22}$	10:1	**IIa**	5	150	60
14	$cyclo$-C_6H_{12}	10:1	**IIa**	8	150	48
15	$PhCH_3$	10:1	**IIa**	1.5	150	99
16	m-$(CH_3)_2C_6H_4$	10:1	**IIb**	1	150	87
17	m-$(CH_3)_2C_6H_4$	10:1	**IIb**	2	150	110[c]
18	Adamantane	4:1[d]	**IIb**	1.5	150	95 (all isomers)
19	Mesitylene	10:1	**IIb**	1	150	91
20	$C_{12}H_{26}$	10:1	**III**[e]	2.5	150	155[c]
21	$cyclo$-C_6H_{12}	10:1	**III**	10	150	67
22	$PhCH_3$	10:1	**III**	10	150	160[c]
23	$PhCH_3$	5:1	**III**	10	150	145[c]
24	p-$(CH_3)_2C_6H_4$	10:1	**III**	5	150	135[c]

[a] Equimolar mixture of CuBr (or $CuBr_2$) + Bu_4NBr [or $Bu_3(PhCH_2)NBr$], 10 wt % relative to the reactants.

[b] Polycopperphenylsiloxane on Silochrome, 1 g per 10 ml of solution; copper concentration in the catalyst 0.11 wt % (**IIa**) or 0.3%.

[c] Yields greater than 100% arise from participation of more than one bromine atom from CBr_4 molecule.

[d] In chlorobenzene at a dilution of 1:10.

[e] Polynickelsiloxane on Silochrome (**III**, 0.16% of Ni), 10 wt % relative to the reactants.

Reactions of carbon tetrabromide with alkanes and cycloalkanes. Reactions of CBr_4 with alkanes and cycloalkanes in the presence of catalysts **I**–**III** occur in the temperature range from 150 to 180°C and give the corresponding monobromo derivatives in quantitative or nearly quantitative yield (calculated on the initial CBr_4). No induction period is observed. Table 1 contains the yields of the products obtained under various conditions. The reaction is highly selective: cyclohexane gives rise exclusively to cyclohexyl bromide; secondary bromoalkanes are formed from decane and dodecane; neither 1-bromoalkanes nor dibromo derivatives were detected (or they were present in trace amounts). The mass spectra of isomeric linear secondary bromoalkanes are similar; therefore, we failed to assign ion peaks to particular

isomers while analyzing the GC–MS data. We can only state that the yields of all secondary bromoalkanes are comparable. For example, the bromination of dodecane at 150°C in the presence of catalyst **Ia** yields five isomeric secondary bromododecanes at a ratio of 1.3:1.2:1.0:1.4:0.9 (±0.1); this means that the selectivity with respect to particular isomers ranges from 16 to 24% (±2%), no 1-bromododecane being formed. In the reaction with adamantane, the bromination occurs mainly at position *1*, and the ratio of 1- and 2-bromoadamantanes at 150°C is 9.5:1. Quantitative yields of bromoalkanes above 150°C are attained in several hours; the conversion of CBr_4 in the reaction with adamantane is complete in 1.5–2 h. At 98–130°C, the reaction rate falls down but remains measurable (Table 1, run nos. 11 and 12). This is

a distinctive feature of the reaction under study, in contrast to analogous processes with participation of carbon tetrachloride, which proceed very slowly at temperatures below 150°C. As follows from the data in Table 1 (run nos. 9, 10, 23, and 24), initial reactant ratio has no significant effect on the product yield.

Undoubtedly, metathesis in the presence of copper complexes follows a radical mechanism. In keeping with the data of [6–10] on reactions involving CCl_4 and CCl_3Br, the process with participation of carbon tetrabromide may be represented by the following scheme:

$$\{Cu(I)\} + CBr_4 \longrightarrow \{Cu(II)Br\} + \overset{\cdot}{C}Br_3 \quad (2)$$

$$\overset{\cdot}{C}Br_3 + RH \longrightarrow CHBr_3 + R^{\cdot} \quad (3)$$

$$R^{\cdot} + CBr_4 \longrightarrow RBr + \overset{\cdot}{C}Br_3 \quad (4)$$
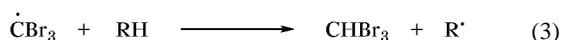
Here, {Cu(I)} and {Cu(II)Br} stand for bromide copper complexes. The mechanism of activation of halogen derivatives by nickel complexes remains unclear. The data of Gossage *et al.* [11] on related processes with participation of CCl_4 suggest that the reaction is accompanied by change of the metal valence [Ni(II) ↔ Ni(III)].

On the whole, the catalytic character of the reaction under study originates from reaction (5) which gives the final product and simultaneously regenerates the active form of the catalyst.

$$\{Cu(II)Br\} + R^{\cdot} \longrightarrow \{Cu(I)\} + RBr \quad (5)$$
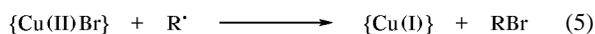
Reactions of carbon tetrabromide with aryl-alkanes. The bromination of arylalkanes, such as *p*- and *m*-xylenes, mesitylene, and ethylbenzene, proceeds at a high rate, and at 150°C carbon tetra-bromide is consumed almost completely in 1.5 h. However, the process is accompanied by alkylation. The role of CBr_4 itself as alkylating agent may be neglected in the first approximation (traces of tri-bromomethyl derivatives are usually present in the reaction mixtures), whereas the contribution of alkyla-tion of arylalkanes with monobromoalkyl derivatives is appreciable:

$$PhC(Br)R'R'' + PhCHR'R''$$
$$\longrightarrow PhCR'R''-C_6H_4-CHR'R''$$
$$R', R'' = CH_3, H.$$
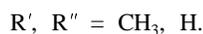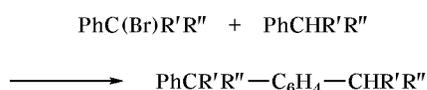
With *m*-xylene and ethylbenzene as examples, the data in Table 2 illustrate how the composition of the reaction mixture obtained in the present of catalyst **IIb** changes over a period of 10 h. It is seen that the alkylation of *m*-xylene becomes appreciable when the time of contact reaches 4 h and longer, i.e., after quantitative consumption of CBr_4. Analogous pattern was observed for toluene, *p*-xylene, and mesitylene. Therefore, preparative bromination of methylbenzene is not strongly hampered by the alkylation process due to a large difference in the rates of these reactions. Another situation is typical of compounds containing more active secondary or tertiary hydrogen atoms in the β-position relative to the aromatic ring. In this case the rate of alkylation is so high that the bromina-tion product could not be obtained in high yield (cf. data for ethylbenzene in Table 2). Likewise, carbon tetrabromide reacts with cumene.

Reaction of carbon tetrabromide with butyl chloride. Introduction of a halogen atom considerably reduces the reactivity of substrates in the bromination with CBr_4. Under the conditions described above for the bromination of alkanes and arylalkanes, the yield of the bromination products of butyl chloride in the presence of catalysts **IIa** and **III** was 28 and 22%, respectively (150°C, 10 h). The ratio of isomeric bromochlorobutanes almost does not depend on the catalyst and is as follows (the yield of 4-bromo-1-chlorobutane is assumed to be equal to unity):

4-Br-1-Cl	3-Br-1-Cl	2-Br-1-Cl	1-Br-1-Cl
1	10	6	4

Specific features of the reactions carried out in the presence of heterogeneous PMOS. Reactions of carbon tetrabromide with alkanes, adamantane, and methylbenzenes in the presence of homogeneous catalyst **I** exclusively follow Eq. (1) provided that the conversion does not exceed 50%. Presumably, heterogeneous catalysts **II** and **III** give rise to forma-tion of measarable amounts of hydrogen bromide (in some cases, up to 20–50% of the initial CBr_4) and (at higher conversion) of methylene bromide. In the reactions of active hydrocarbons (higher alkanes and alkylbenzenes) in the presence of catalysts **II** and **III** more than 1 mol of monobromoalkane can be obtained from 1 mol of the initial CBr_4 (runs nos. 5, 12, 14, 17, and 19–21; Table 1). This fact, as well as the formation of CH_2Br_2 and 10–20% excess of the yield of bromoalkanes over the yield of bromoform (which was observed in some experiments carried out with catalyst **I**), is explained by participation of $CHBr_3$ in the process. Presumably, the following

Table 2. Variation of the composition of the reaction mixture (% of the initial CBr_4) in the systems CBr_4–arylalkane–catalyst **IIb**; temperature 150°C, RH–CBr_4 ratio $10:1$[a]

Component	RH = m-Xylene				RH = Ethylbenzene			
	1 h	2 h	4 h	10 h	1 h	2 h	4 h	10 h
CBr_4	14	2	Traces	0	12	Traces	0	0
$CHBr_3$	86	99	75	70	85	11	8	Traces
RBr	87	110	90	82	55	48	29	17
R−R (alkylation product)	Traces	4.5	9.5	15	25	40	62	76

[a] Experimental values are given. The apparent disbalance with respect to bromine is likely to result from further transformations of the alkylation products and bromoform with formation of unidentified high-molecular-weight products.

reactions occur in the system containing CBr_4 and catalyst **II** or **III**:

$$R^\cdot + CHBr_3 \longrightarrow \overset{\cdot}{C}HBr_2 + RBr \quad (4a)$$

$$\overset{\cdot}{C}HBr_2 + RH \longrightarrow CH_2Br_2 + R^\cdot \quad (3a)$$

The contribution of reactions (4a) and (3a) rises as the conversion of CBr_4 and hence the $CHBr_3:CBr_4$ ratio increases. As a result, at high conversions the yield of bromoform over catalysts **II** and **III** is lower by 30–50% than the yield of monobromoalkane. Special experiments, in which a mixture of CBr_4 with $CHBr_3$ was used instead of CBr_4, showed that bromoform is in fact consumed in the presence of CBr_4. From a mixture of dodecane, $CHBr_3$, and CBr_4 at a molar ratio of $10:3.5:1$ (150°C, reaction time 1.5 h) we obtained a mixture of secondary monobromododecanes in 59% yield (calculated on the initial CBr_4), and the final $RH:CHBr_3:CBr_4$ ratio was $9.4:3.2:0.7$ instead of $9.4:3.5:0.4$ expected for the process involving no bromoform. Another proof for the participation of $CHBr_3$ in the reaction is that its concentration passes through a maximum during the process (see Table 2). In the absence of CBr_4 and brominated arylalkanes, i.e., compounds possessing weakened C−Br bonds and capable of chain initiating according to reaction (2), bromoform reacts with alkanes and arylalkanes very slowly. It should be noted that CBr_4 does not affect alkylation of arylalkanes by their bromination products.

One more specific feature of the reactions occurring in the presence of immobilized PMOS is formation of an unidentified polymeric product. Probably, a highly developed surface of the heterogeneous catalyst (about

80 m^2/g) favors the known disproportionation of tribromomethyl radicals [2] according to reaction (6):

$$2\overset{\cdot}{C}Br_3 \longrightarrow Br_2 + Br_2C{=}CBr_2 \quad (6)$$
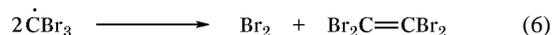
Polymerization of C_2Br_4 is a possible way of formation of the polymeric product. Thermal dissociation of bromine molecule could give rise to atomic bromine and hydrogen bromide:

$$Br_2 \longrightarrow 2Br^\cdot \quad (7)$$

$$Br^\cdot + RH \longrightarrow R^\cdot + HBr \quad (8)$$

Reactions (6)–(8) do not contribute much to the overall yield of RBr, for an equivalent amount of bromine atoms [and hence of molecules of the monobromo derivatives; reactions (4) and (8)] is formed by reaction (7) instead of those consumed by reaction (6) on the catalyst surface.

Our results show that the reaction with carbon tetrabromide provides an efficient and convenient method for functionalization of alkanes and arylalkanes. It is advantageous due to high conversion of initial CBr_4, high selectivity in the bromination of alkanes, cycloalkanes, and methylbenzenes, and no need of using hazardous and toxic reagents.

EXPERIMENTAL

Carbon tetrabromide of pure grade was thrice recrystallized from ethanol. Dodecane, decane, cyclohexane, bromoform, and dodecyl bromide were distilled and thoroughly dried. Copper(I) bromide of pure grade was used without additional purification.

Tetrabutylammonium bromide was synthesized from tributylamine and butyl bromide and was purified by azeotropic drying followed by double recrystallization from benzene. The catalytic complex was prepared from CuBr and Bu₄NBr by dissolving the components in the reaction mixture on heating to 40–50°C.

Oligomeric cage-like PMOS were synthesized as described in [12, 13]. Their structure was confirmed by the presence in their vibrational spectra of bands typical of $Si-O-Si$ (1030–1100 cm^{-1}; **II, III**), $Si-O-Cu$ (950–980 cm^{-1}, **II**), $Ph-Si$ (1130 cm^{-1}, **II**), and NH$_2$ groups (750, 3380 cm^{-1}; **III**); the electron absorption spectra of **IIa** and **IIb** contained a characteristic absorption at 750 nm due to d–d transitions in Cu(II) ion. The silicon-to-metal ratio in all compounds was close to 2, in keeping with the assumed structure; found for PMOS precursor of **IIa**: Cu 18.2%; Si 16.4%; C 45.3%; H 2.7%. $C_{12}H_{10}Si_2O_4Cu$. Calculated: Cu 18.8%; Si 16.6%; C 45.6%; H 3.0%; for precursor of **III**: Ni 19.0%; Si 18.5%; C 24.7%; H 5.0%. $C_6H_{16}N_2Si_2O_4Ni$. Calculated: Ni 19.9%; Si 18.9%; C 24.4%; H 5.4%. The silica-immobilized catalysts (silokhrom S-80) were prepared by adsorption of PMOS from a solution in toluene or toluene–DMF with subsequent separation by decanting, removal of the residual solvent by evacuation, and heating of the solid catalyst at 160°C under reduced pressure.

Alkanes were brominated with carbon tetrabromide in sealed ampules. An ampule was charged with required amounts of a solution of CBr$_4$ in alkane with a specified concentration and components of complex **I** (2 mol % with respect to the hydrocarbon) or heterogeneous catalyst (1 g per 10 ml of the reaction solution). The mixture was deoxygenated by repeated freezing–evacuation (to a residual pressure of 10^{-3} mm)–heating procedures. The ampule was then sealed and kept at a constant temperature as long as necessary. The thermostat was equipped with a setup for rotating an ampule at a variable rate in various directions. Samples were analyzed by GLC.

Isomeric composition of the bromination products (with dodecane as an example) was determined by gas chromatography–mass spectrometry using a Finnigan MAT-212 instrument coupled with a Varian 3740 chromatograph. The mass spectra of monobromododecanes characteristically contained peak of the $[M-Br]^+$ ion formed by elimination of bromine from the molecular ion (m/z 169) and a set of ion peaks typical of fragmentation of alkyl chain (m/z 43, 57,

71, 85, 113). The absence of 1-bromododecane among the products unambiguously follows from the lack of $C_4H_8Br^+$ ion peak (m/z 135, 137) which is typical of all 1-bromoalkanes [14].

The amount of hydrogen bromide liberated during the bromination process was determined by acid–base titration.

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