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# Tetrachloroethylene from methane and carbon tetrachloride: a new approach to the utilization of toxic organochlorine waste

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**A new method of $CCl_4$ utilization by a catalytic reaction with methane at 250–400 °C is proposed.**

Carbon tetrachloride is harmful to the ozone layer. According to the programme of UNO Environmental Programmer and international ozone layer protection agreements (the Montreal Protocol),[1,2] the manufacture of $CCl_4$ and its usage in industry is almost prohibited nowadays. However, large quantities of $CCl_4$ are formed as a by-product in the manufacture of important organochlorine products (tetrachloroethylene, chloromethanes, *etc*.). It would be much more expedient, if instead of destroying carbon tetrachloride by incineration, it could be transformed into some useful products. Hydrogenation of $CCl_4$ with molecular hydrogen is known to produce chloroform,[3,4] while its reaction with *n*-alkanes in the presence of copper-containing catalysts allows one to obtain chloroform and chloroalkanes:[5,6]

$$RH + CCl_4 \rightarrow RCl + CHCl_3. \qquad (1)$$

Using methane as hydrogen stuff in the reaction with $CCl_4$ looks especially attractive and is the subject matter of this study.

One might expect that carrying out the reaction in the presence of copper catalysts analogous to those used in the reaction with alkanes would also give methyl chloride and chloroform according to reaction (1). It turned out, however, that $CHCl_3$ is formed only in very small quantities, and the main product of $CCl_4$ transformation under the reaction conditions (250–350 °C; catalyst, 0.5–2% Cu on silica) is tetrachloroethylene:

$$2CCl_4 + 2CH_4 \rightarrow Cl_2C{=}CCl_2 + 2CH_3Cl + 2HCl. \qquad (2)$$

The $CH_3Cl$ formed in the reaction can also react with $CCl_4$ to give methylene chloride:

$$2CCl_4 + 2CH_3Cl \rightarrow Cl_2C{=}CCl_2 + 2CH_2Cl_2 + 2HCl. \qquad (3)$$

The data on product yields and reaction selectivity are given in Table 1. As can be seen, the formation of tetrachloroethylene proceeds with high selectivity (up to 90%). The $CCl_4$ conversion rapidly increases with temperature approaching quantitative at 350 °C and varies only slightly with increasing copper content of the catalyst. The yield of tetrachloroethylene is not far from a theoretical value (100% from theory corresponds to 50 mol% of the $CCl_4$ consumed in the reaction). The total yield of methyl and methylene chlorides relative to the methane consumed approaches 100%.

There is no further chlorine redistribution by the reaction of $CH_2Cl_2$ with $CCl_4$, as shown in a control experiment. Small amounts of chloroform resulted from reaction (1); chloroform is inert under the reaction conditions and does practically not react with methane: the conversion of chloroform under conditions analogous to entry 3 in Table 1 is below 0.5%. The possible impurity in $CCl_4$ ($CHCl_3$, $CH_2Cl_2$) does not influence offered process.

**Table 1** Interaction of methane with $CCl_4$: product yields and reaction conditions.[a]

| Entry | Catalyst | $T$/°C | Conversion of $CCl_4$ (%) | Yield (%) relative to the feed $CCl_4$ | | Yield (%) relative to the reacted $CH_4$ | |
|---|---|---|---|---|---|---|---|
| | | | | $C_2Cl_4$ | $CHCl_3$ | $CH_3Cl$ | $CH_2Cl_2$ |
| 1 | 0.5% Cu/$SiO_2$ | 250 | 35 | 25 | 3.1 | 61 | 39 |
| 2 | 0.5% Cu/$SiO_2$ | 300 | 58 | 45 | 2.8 | 49 | 51 |
| 3 | 0.5% Cu/$SiO_2$ | 350 | 90 | 74 | 2.8 | 41 | 59 |
| 4 | 2.0% Cu/$SiO_2$ | 250 | 47 | 34 | 4.2 | 59 | 41 |
| 5 | 2.0% Cu/$SiO_2$ | 300 | 64 | 52.5 | 3.5 | 46 | 54 |
| 6 | 2.0% Cu/$SiO_2$ | 350 | **94** | **81** | **2.2** | 37 | 63 |

[a]Reactions were carried out at the molar ratio $CH_4$:$CCl_4$ = 1.5 and a contact time of 47 s.

The initial state of copper in the catalyst is zero valent. However, CuCl is formed almost immediately on the copper surface on contact with $CCl_4$.[7] It can also interact with $CCl_4$ with the formation of the $CCl_3^{\bullet}$ radical.[8] This is the first stage of the $CCl_4$ reaction with alkanes studied earlier.[5,6]

In view of the high energy of C–H bond in methane (at least 8.5 kcal mol$^{-1}$ stronger than C–H bonds in $CH_2$ groups in *n*-alkanes[9]), the trichloromethyl radical thus formed, in contrast to the reaction with paraffins, reacts only to a small extent with methane, but mainly gives hexachloroethane $C_2Cl_6$. The latter also reacts with CuCl to give the $C_2Cl_5^{\bullet}$ radical, which is unstable under the reaction conditions. Its rate constant of dissociation to $C_2Cl_4$ and the chlorine atom is ~$10^7$ s$^{-1}$ at 350 °C.[10] The resulting scheme of tetrachloroethylene formation may be drawn as follows:

$$(Cu)_s + CCl_4 \rightarrow (CuCl)_s + CCl_3^{\bullet}, \qquad (4)$$

$$2(CuCl)_s + 2CCl_4 \rightarrow 2(CuCl_2)_s + 2CCl_3^{\bullet}, \qquad (4a)$$

$$2CCl_3^{\bullet} \rightarrow C_2Cl_6, \qquad (5)$$

$$C_2Cl_6 + (CuCl)_s \rightarrow C_2Cl_5^{\bullet} + (CuCl_2)_s, \qquad (6)$$

$$C_2Cl_5^{\bullet} \rightarrow C_2Cl_4 + Cl^{\bullet}. \qquad (7)$$

The proposed scheme is confirmed by published data and our experimental results. Reactions (4) and (4a) have already been discussed above. The low yield of chloroform indicates that it is recombination (5) rather than reaction with methane that is the main depletion pathway of the trichloromethyl radicals. Reaction stages (6) and (7) are proved primarily by the fact that hexachloroethane is virtually absent from the reaction products. Furthermore, passing $C_2Cl_6$ vapour together with methane over a copper-containing catalyst leads to its complete consumption even under relatively mild conditions and gives the same products as the reaction with carbon tetrachloride. At 350 °C and the molar ratio $CH_4$:$C_2Cl_6$ = 5, the conversion of $C_2Cl_6$ is 100%, the yield of $C_2Cl_4$ is 90% (the rest being hexachlorobutadiene and hexachlorobenzene), and $CH_2Cl_2$ and $CH_3Cl$ are obtained from methane. Passing $C_2Cl_6$ over CuCl on silica under the same conditions gives tetrachloroethylene with a quantitative yield until all CuCl is converted to $CuCl_2$.

For the reaction as a whole to run in a catalytic mode the regeneration of the active form of the catalyst containing Cu$^{I}$ is required. The only reducing agent present in the system from the outset is methane, and we have to assume its interaction with copper(II) chloride formed on the catalyst surface:

$$2(CuCl_2)_s + CH_4 \rightarrow 2(CuCl)_s + CH_3Cl + HCl. \qquad (8)$$

This process was not described previously. In order to make sure of its feasibility, we performed special control runs, in which methane was passed over 0.5 wt% copper(II) chloride on silica under conditions analogous to those used in the reaction with $CCl_4$. At 350 °C, $CuCl_2$ is almost entirely reduced to CuCl and methane is chlorinated to $CH_3Cl$. This allows us to complete the process scheme with reaction (8).

The chlorine atoms formed according to reaction (7) must rapidly react with methane, as well as with methyl chloride formed in the reaction, abstracting hydrogen atoms, as expected for gas-phase chlorination of hydrocarbons:[11]

$$\mathrm{Cl^{\bullet} + CH_4 \rightarrow {}^{\bullet}CH_3 + HCl,} \qquad (9)$$

$$\mathrm{Cl^{\bullet} + CH_3Cl \rightarrow CH_2Cl^{\bullet} + HCl.} \qquad (9a)$$

The alkyl and chloroalkyl radicals thus formed are known to react with copper(II) chloride at diffusion-limited rates.[12]

$$\mathrm{{}^{\bullet}CH_3 + (CuCl_2)_s \rightarrow CH_3Cl + (CuCl)_s,} \qquad (10)$$

$$\mathrm{CH_2Cl^{\bullet} + (CuCl_2)_s \rightarrow CH_2Cl_2 + (CuCl)_s.} \qquad (10a)$$

Changing Cu or CuCl in the catalyst formula to $CuCl_2$ leads to a sharp drop in $CCl_4$ conversion. In the presence of the catalyst based on $CuCl_2$, the conversion of $CCl_4$ is 17% during the initial time, while in the presence of CuCl, it is 50% for same time under the same conditions. This is only to be expected, since in the catalyst initially containing zero-valent copper, CuCl is almost immediately formed on contact with $CCl_4$, and starting the process with the CuCl catalyst should not make much difference. On the other hand, if the catalyst initially contains only $CuCl_2$, the efficient generation of radicals becomes impossible, chlorine atoms and/or organic radicals are formed at a low rate, possibly, by various side reactions, such as thermal dissociation of $CuCl_2$. Later on, with the accumulation of one-valent copper on the catalyst surface, the reaction rate should increase, which is actually observed.

In summary, the results obtained in this work show that the interaction of $CCl_4$ with methane in the presence of copper-containing catalysts is a promising technique to convert carbon tetrachloride into valuable products. A minimum cost of the starting material (methane), high yields of valuable chlorocarbons (tetrachloroethylene, methylene and methyl chloride), and a low amount of by-products make this process highly attractive from technological and ecological points of view.[†]

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[†] Methane containing no less than 99.9% of the base material and less than 0.004% of water vapour was used without further purification. Carbon tetrachloride was distilled from $P_2O_5$ at atmospheric pressure before the experiments.

Catalysts were prepared by incipient wetness impregnation. $SiO_2$ (surface area of 250 $m^2\,g^{-1}$) was used as a support. For the preparation of $Cu/SiO_2$ the support calcined at 500 °C for 0.5 h was impregnated with an appropriate aqueous solution of copper nitrate. The catalysts were dried at 150 °C for 16 h and heated at 300 °C in a flow of hydrogen for 2 h. Samples of $CuCl_2/SiO_2$ were prepared by wet-impregnation of the calcined support with an aqueous solution of copper(II) chloride, whose concentration was selected in order to achieve 2 wt% Cu content in the final preparation. The catalysts were dried at 150 °C for 16 h. The $CuCl/SiO_2$ catalyst was prepared as follows. The calcinated silica gel was placed in a Schlenk vessel and evacuated at 50 °C for 3 h; then, the solution of CuCl in acetonitrile was added and the obtained solution was stirred for 30 min. The solvent and absorbed gases were pumped off. The catalyst thus prepared was put into the reactor under argon.

The reaction of carbon tetrachloride with methane was carried out in a fixed-bed flow reactor at atmospheric pressure and 250–350 °C with contact times from 5 to 47 s. The methane flow passed through a needle valve from the cylinder to the evaporator. $CCl_4$ was pumped to the same evaporator, evaporated and mixed with methane. The obtained gas mixture entered into the quartz reactor disposed in the electric furnace. The reactor was filled with the catalyst. The catalyst volume was 15 $cm^3$ in typical experiments. The reactor temperature was maintained constant to ±1 °C. At the outlet of the reactor, the products were cooled in a water cooler and condensed in a trap cooled to –40 °C. The gaseous products were collected in a gas burette.

The reaction products were analysed by gas-liquid chromatography on a Crystal Luxe 4000 chromatograph. The gaseous products were analysed by chromatography with a thermal conductivity detector. The column packed with Porapak Q was 2 m long ($T_{\mathrm{col}}$ = 50–140 °C, programmed heating). Liquid products were separated on a column with SE-30 ($l$ = 3 m, $d$ = 3 mm, $T_{\mathrm{col}}$ = 70–240 °C, programmed heating) using a flame ionization detector.