

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

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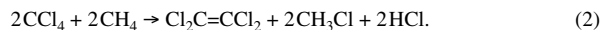
A new method of CCl₄ utilization by a catalytic reaction with methane at 250–400 °C is proposed.

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 CCl₄ and its usage in industry is almost prohibited nowadays. However, large quantities of CCl₄ 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 CCl₄ 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}

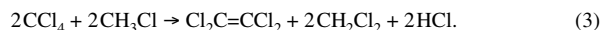


Using methane as hydrogen stuff in the reaction with CCl₄ looks especially attractive and is the subject matter of this study.

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 CHCl₃ is formed only in very small quantities, and the main product of CCl₄ transformation under the reaction conditions (250–350 °C; catalyst, 0.5–2% Cu on silica) is tetrachloroethylene:



The CH₃Cl formed in the reaction can also react with CCl₄ to give methylene chloride:



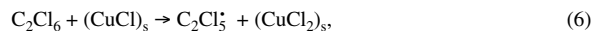
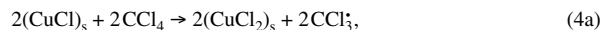
The data on product yields and reaction selectivity are given in Table 1. As can be seen, the formation of tetrachloroethylene proceeds with high selectivity (up to 90%). The CCl₄ conversion rapidly increases with temperature approaching quantitative at 350 °C and varies only slightly with increasing 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 CCl₄ 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 CH₂Cl₂ with CCl₄, 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 CCl₄ (CHCl₃, CH₂Cl₂) does not influence offered process.

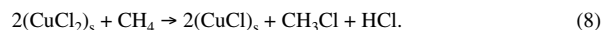
The initial state of copper in the catalyst is zero valent. However, CuCl is formed almost immediately on the copper surface on contact with CCl₄.⁷ It can also interact with CCl₄ with the formation of the CCl₃• radical.⁸ This is the first stage of the CCl₄ reaction with alkanes studied earlier.^{5,6}

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 CH₂ groups in *n*-alkanes⁹), the trichloromethyl radical thus formed, in contrast to the reaction with paraffins, reacts only to a small extent with methane, but mainly gives hexachloroethane C₂Cl₆. The latter also reacts with CuCl to give the C₂Cl₅• radical, which is unstable under the reaction conditions. Its rate constant of dissociation to C₂Cl₄ and the chlorine atom is ~10⁷ s^{–1} at 350 °C.¹⁰ The resulting scheme of tetrachloroethylene formation may be drawn as follows:



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 C₂Cl₆ 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 CH₄:C₂Cl₆ = 5, the conversion of C₂Cl₆ is 100%, the yield of C₂Cl₄ is 90% (the rest being hexachlorobutadiene and hexachlorobenzene), and CH₂Cl₂ and CH₃Cl are obtained from methane. Passing C₂Cl₆ over CuCl on silica under the same conditions gives tetrachloroethylene with a quantitative yield until all CuCl is converted to CuCl₂.

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:



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 CCl₄. At 350 °C, CuCl₂ is almost entirely reduced to CuCl and methane is chlorinated to CH₃Cl. This allows us to complete the process scheme with reaction (8).

Table 1 Interaction of methane with CCl₄: product yields and reaction conditions.^a

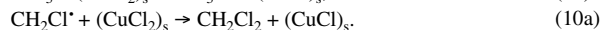
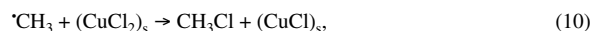
Entry	Catalyst	T/°C	Conversion of CCl ₄ (%)	Yield (%) relative to the feed CCl ₄		Yield (%) relative to the reacted CH ₄	
				C ₂ Cl ₄	CHCl ₃	CH ₃ Cl	CH ₂ Cl ₂
1	0.5% Cu/SiO ₂	250	35	25	3.1	61	39
2	0.5% Cu/SiO ₂	300	58	45	2.8	49	51
3	0.5% Cu/SiO ₂	350	90	74	2.8	41	59
4	2.0% Cu/SiO ₂	250	47	34	4.2	59	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

^aReactions were carried out at the molar ratio CH₄:CCl₄ = 1.5 and a contact time of 47 s.

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



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



Changing Cu or CuCl in the catalyst formula to CuCl₂ leads to a sharp drop in CCl₄ conversion. In the presence of the catalyst based on CuCl₂, the conversion of CCl₄ 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 CCl₄, and starting the process with the CuCl catalyst should not make much difference. On the other hand, if the catalyst initially contains only CuCl₂, 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 CuCl₂. 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 CCl₄ 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 P₂O₅ at atmospheric pressure before the experiments.

Catalysts were prepared by incipient wetness impregnation. SiO₂ (surface area of 250 m² g⁻¹) was used as a support. For the preparation of Cu/SiO₂ 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 CuCl₂/SiO₂ 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/SiO₂ 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. CCl₄ 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 cm³ 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*_{col} = 50–140 °C, programmed heating). Liquid products were separated on a column with SE-30 (*l* = 3 m, *d* = 3 mm, *T*_{col} = 70–240 °C, programmed heating) using a flame ionization detector.