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# Copper-catalyzed chlorination and condensation of acetylene and dichloroacetylene

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## Abstract

The chlorination and condensation of acetylene at low temperatures is demonstrated using copper chlorides as chlorinated agents coated to model borosilicate surfaces. Experiments with and without both a chlorine source and borosilicate surfaces indicate the absence of gas-phase and gas-surface reactions. Chlorination and condensation occur only in the presence of the copper catalyst. $C_2$ through $C_8$ organic products were observed in the effluent; PCDD/F were only observed from extraction of the borosilicate surfaces. A global reaction model is proposed that is consistent with the observed product distributions. Similar experiments with dichloroacetylene indicate greater reactivity in the absence of the copper catalyst. Reaction is observed in the gas-phase and in the presence of borosilicate surfaces at low temperatures. The formation of hexachlorobenzene is only observed in the presence of a copper catalyst. PCDD/F were only observed from extraction of the borosilicate surfaces. A global reaction model is proposed for the formation of hexachlorobenzene from dichloroacetylene. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Acetylene; Dichloroacetylene; Chlorination; Condensation; Hexachlorobenzene; PCDD/F

## 1. Introduction

Recent studies indicate that copper species play an important role in the thermal formation of chlorinated combustion by-products and in thermal condensation reactions of aliphatic compounds (Froese and Hutzinger, 1994, 1996a,b). Copper chlorides have been shown to play a predominant role in surface-catalyzed chlorination reactions. In the Deacon reaction, HCl is oxidized in the presence of copper salts to molecular chlorine ($Cl_2$). Chlorine reacts with acetylene at temperatures above 450°C to yield tetrachloroethylene (Chloberag, 1950; Fruhwirth and Walla, 1940). Cupric chloride ($CuCl_2$) can act directly as a chlorinating agent by a ligand-transfer-oxidation mechanism (Nonhebel, 1970). In gas-surface reactions copper species are considered among the most effective catalysts in thermal formation of chlorinated combustion by-products, e.g., polychlorinated dibenzo-p-dioxins (PCDD) and -furans (PCDF) (Addink and Olie, 1995 and references therein). Froese and Hutzinger (1996b) have shown that acetylene in the presence of cupric oxide (CuO) and HCl forms chlorinated benzenes, phenols and PCDD/F at 600°C.

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The objectives of this study were investigations of the role of $CuCl_2$ and CuO in molecular growth reactions of acetylene and dichloroacetylene using model borosilicate surfaces. It is shown that these surfaces reduce the temperature required for chlorination and/or condensation from 700°C (gas-phase) to temperatures as low as 150°C. The formation of PCDD/F from both $C_2H_2$ and $C_2Cl_2$ is also indicated from HRGC/MS analyses of surface extracts. Global reaction mechanisms for both acetylene and dichloroacetylene involving $CuCl_2$ and cuprous chloride (CuCl) intermediates are presented.

## 2. Experimental

All experiments were conducted using an isothermal, fused silica gas–solid flow reactor equipped with an in-line GC–MS analytical system for analysis of stable reaction products. The experimental approach has been described previously (Wehrmeier et al., 1998). A brief summary is presented here.

A cylindrical borosilicate foam (1.5–2.0% $Na_2O$, 1.0–1.5% $K_2O$, 9.5–10.0% $B_2O_3$, 9.0–9.5% $Al_2O_3$, 77–80% $SiO_2$), with a length of 5 cm, a diameter of 7 mm, and a pore size of 200 μm was used as the catalyst support. Studies were performed with two different copper catalysts, $CuCl_2$ and CuO. $CuCl_2$ was applied to the support by impregnation with a 20% aqueous solution of $CuCl_2$ followed by drying at 120°C for 1 h (Bond et al., 1991). The CuO-coated foam was prepared by calcining an impregnated $Cu(NO_3)_2$ foam at 480°C for 16 h in air. Cupric chloride was thermally treated at 250°C for four days in a flow of oxygen-free helium to remove substantial amounts of chlorinated compounds, especially hexachlorobenzene. Technical grade acetylene was obtained from a local compressed gas supplier (Air Products). Acetylene was withdrawn from the cylinder under sub-ambient temperatures to minimize the amount of acetone impurity (~1%). Dichloroacetylene was synthesized using methods reported in the literature (Pielichowski and Popielarz, 1984).

In separate experiments, acetylene or dichloroacetylene ($1100 \pm 200$ ppm in 4% $O_2$ in helium, 167 micromoles total) was flowed over borosilicate (BS) impregnated with $300 \pm 75$ μmol of CuO or $350 \pm 80$ μmol of $CuCl_2$. In the $C_2H_2$ CuO experiments, the reaction gas also contained $1100 \pm 200$ ppm HCl to provide a chlorine source. Fuel-lean conditions were maintained to prevent soot formation which was reported to be problematic in previous studies (Froese and Hutzinger, 1996a,b). Experiments were conducted over a temperature range of 150–500°C, with a gas-phase residence time over the support of 1–10 s and a total reaction time of 60 min. Gas-phase products were analyzed using both in-line and off-line GC-MS; the catalyst foam was subjected to off-line HRGC-MS analysis for trace PCDD/F. The procedures for the analysis of the $C_2$–$C_8$ organics in the reactor effluent have been described in detail in a prior publication (Wehrmeier et al., 1998).

For PCDD/F analysis (Schramm et al., 1995), the borosilicate foam was removed and then spiked with $^{13}C$ internal standards prior to 24 h soxhlet extraction in toluene. High resolution open column chromatography was used to separate the compounds of interest from interferences. A small quantity of the sample, between 1 and 3 μl, was injected into a high resolution GC-MS (Finnigan MAT 95, resolution = 10 000). The injector was programmed as follows: 120°C, 12°C/s to 280°C (10 min hold), then heat at 12°C/s to 300°C (10 min hold). The transfer line temperature was 260°C. The following GC column was used: Rtx 2330 (60 m, 0.25 mm ID, 0.1 μ film thickness). The GC temperature program was as follows: 90°C (hold 15 min), 25°C/min – 180°C, then 2°C/min to 260°C (30 min hold). The column head pressure was 24 psi. Analysis of PCDD/F was conducted in the SIM mode. The MSD scanned for the parent ion ($M$) and the parent ion plus 2 ($M + 2$) of the compounds of interest. Assumptions for quantification of PCDD/F include that: (i) response factors and recoveries of $^{12}C$ and $^{13}C$-labeled congeners are equal; (ii) response factors and recoveries within a certain isomer group are equal; (iii) response factors and recoveries of mixed PCDD/Fs are equal to those of their fully chlorinated analogs.

## 3. Results

Reactions of acetylene on $CuCl_2$-impregnated borosilicate foams produced a variety for chlorinated organic compounds. This system was able to chlorinate acetylene to form chlorinated $C_2$ compounds. Even carbon numbered condensed products up to $C_8$ were observed in the gas-phase (Fig. 1). The most striking feature in the distribution of reaction products was the high degree of chlorination. A majority of products were perchlorinated. A surprising observation was the lack of unchlorinated acetylene polymerization products, e.g., vinylacetylene, benzene, ethynylbenzene and naphthalene. Furthermore, cracking products and compounds with an odd number of carbon atoms were not detected.

CuO was also tested for its catalytic activity towards acetylene condensation and chlorination in the acetylene–CuO/BS and acetylene/HCl–CuO/BS system, respectively. Gas-phase reaction products formed in the acetylene/HCl–CuO/BS system were observed in similar amounts as in the acetylene–$CuCl_2$/BS system at comparable temperatures at and above 300°C. In contrast to the acetylene–$CuCl_2$/BS system, no reaction products were detected at temperatures below 300°C. The two systems investigated without adding copper species, acetylene–BS and acetylene/HCl–BS, did not result in any reaction products at temperatures up to 500°C.

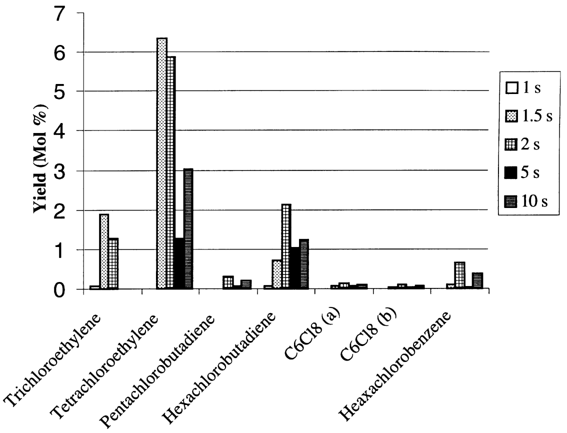


Fig. 1. Major gas-phase products (mol%) for the reaction of acetylene on $CuCl_2$/BS at different residence times. $[C_2H_2]_{total} = 167$ μmol; $[HCl]_{total} = 167$ μmol; $[CuCl_2]_0 = 344 \pm 80$ μmol; $[C_2Cl_2]_{total} = 167$ μmol; $T = 300°C$; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He.

Acetylene was unreactive in the gas phase at temperatures between 200°C and 500°C.

The total yield of reaction products was a function of both temperature and residence time. For the acetylene–$CuCl_2$/BS system, reaction started at temperatures below 150°C and rose to maximum yields at about 300°C (Wehrmeier et al., 1998). Yields decreased at higher temperatures. No reaction products were produced at 500°C. Reaction products for the acetylene/HCl–CuO/BS system were only found at and above 300°C with maximum yields at 400°C. In contrast to the acetylene–$CuCl_2$/BS system, significant amounts of reaction products were formed at 500°C. Approximately 9 mol% of acetylene was transformed to chlorinated and condensed reaction products in the presence of a $CuCl_2$-impregnated borosilicate foam at 300°C. In the presence of 1100 ppm HCl, yields rose to just over 10 mol%.

The time-dependent studies indicated that chlorination and condensation reactions are fast processes, which readily occur at $t_r = 1.0$ s and achieve their maximum rate at $t_r = 1.5$–$2.0$ s. Product yields for $C_2$ and $C_4$ species generally decreased for residence times greater than 2 s. Yields of $C_6$ species achieved a steady-state or decreased with increasing reaction time. The expected shift in molecular weight distribution of reaction products with increasing residence time was not observed.

The main reaction products formed in the acetylene–$CuCl_2$/BS system at 300°C are illustrated in Fig. 2. Reaction products with a lower degree of chlorination (e.g., trichloroethylene) were predominantly formed at higher temperatures. Maximum product yields were typically produced at 300°C. Adding HCl to the acetylene-$CuCl_2$/BS system increased the total product yield. The same reaction products were formed, but the distribution was shifted towards higher chlorinated compounds, i.e., trichloroethylene was not detected. A few minor reaction products were not quantified; these products are not included in summation of product yields. These products included tetrachloromethane, pentachloroethane, and mono- through pentachlorobenzene.

Changes in product yields for the two systems corresponded to changes of the surface. The color of dry $CuCl_2$ is yellow–brown and it did not change when it was loaded onto the borosilicate. Heating this system to 300°C did not show any changes in color, but $CuCl_2$ started to sublime from the foam above 300°C and the loaded borosilicate reverted back to its original white color when it was heated to 500°C. This effect indicated a loss of $CuCl_2$ from the borosilicate at elevated temperatures. The CuO-mediated borosilicate was black. This appearance did not change upon heating to 500°C. However, upon addition of HCl, the color of the foam turned yellow–brown at temperatures above 300°C, indicating that CuO started to react with HCl at 300°C, which resulted in formation of $CuCl_2$.

Cu (I) and Cu (II) species were identified from post-experiment XPS analysis of the borosilicate surfaces. The fraction of Cu (I) species increased from 30% at 150°C to 40% at 350°C. Cu (I) and Cu (II) species containing chlorine were identified from XPS analysis of the acetylene/HCl-CuO/BS experiments, lending credibility to the hypothesis that CuCl/$CuCl_2$ is the dominant chlorinating system in these experiments.

A series of experiments with dichloroacetylene were conducted to determine if the major reaction products were similar to the acetylene–$CuCl_2$/BS system. As illustrated in Fig. 3, a distinct similarity was observed. Gas-phase experiments with $C_2Cl_2$ at 300°C indicated significant dimerization of the starting material (~8 mol% $C_2Cl_2$ conversion) with tetrachlorovinylacetylene the major product. In the presence of the catalyst support, significant changes in reactivity were observed with tetrachloroethylene, tetrachlorovinylacetylene, and hexachlorobutadiene the major products (~15 mol% $C_2Cl_2$ conversion). Addition of CuO to the surface resulted in further changes in reactivity with tetrachloroethylene, tetrachlorovinylacetylene, hexachlorobutadiene, and hexachlorobenzene as the major products (~9 mol% $C_2Cl_2$ conversion). The presence of CuO resulted in increased yields of hexachlorobenzene at the expense of the other products. These experiments demonstrate that condensation of dichloroacetylene (beyond dimerization) does not readily occur in the absence of the copper catalyst. The acetylene and dichloroacetylene experiments clearly indicate that chlorination and formation of $C_6$ and other chlorinated aromatic compounds at these low temperatures requires the copper catalyst.

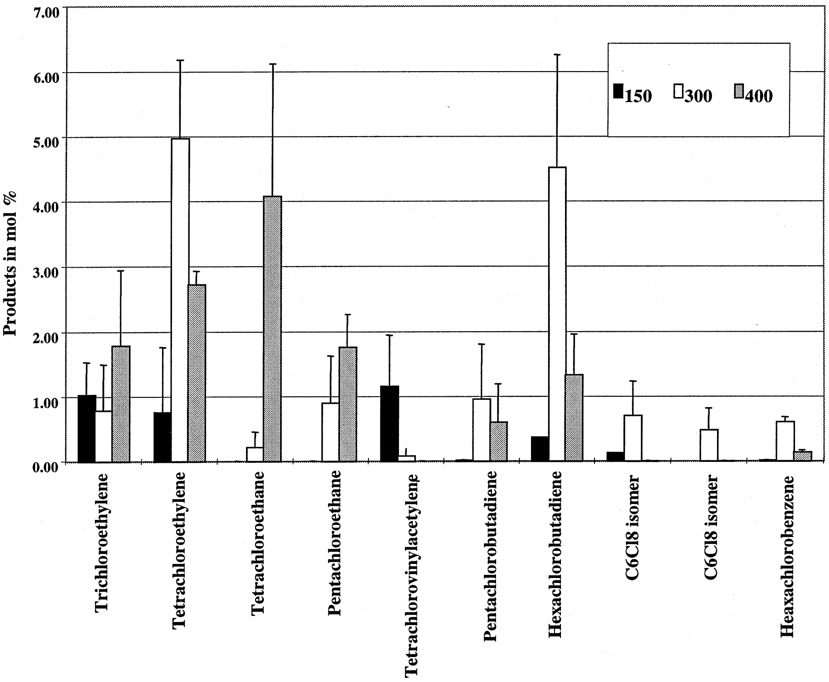


Fig. 2. Major gas-phase products (mol%) for the reaction of acetylene on $CuCl_2$/BS at 150°C, 300°C and 400°C, respectively. $[C_2H_2]_{total} = 167$ μmol; $[CuCl_2]_0 = 344 \pm 80$ μmol; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He. Error bars represent relative standard deviations in the product measurements.

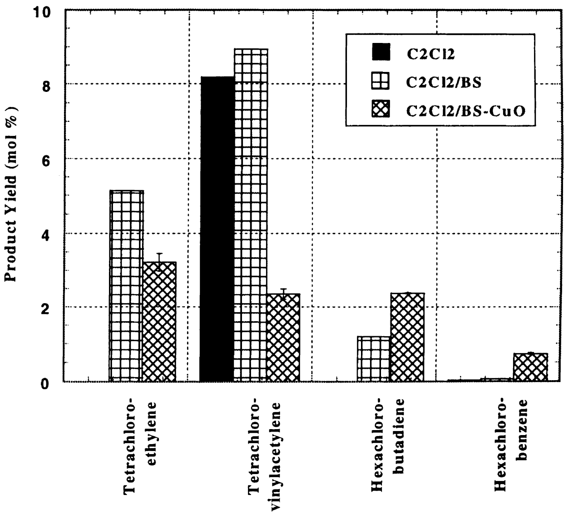


Fig. 3. Major gas-phase products (mol%) for the reaction of dichloroacetylene on CuO/BS at 300°C. $[C_2Cl_2]_{total} = 167$ μmol; $[CuO]_0 = 300 \pm 75$ μmol; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He. Error bars represent relative standard deviations in the product measurements.

Chlorophenols and PCDD/F were not observed in the reactor effluent. However, significant levels of many PCDD/F congeners were observed from subsequent extraction of the catalyst surface as illustrated in Figs. 4 and 5 for acetylene and dichloroacetylene, respectively. The high yields of PCDD/F extracted from the surface suggests that significant levels, i.e., ~10%, should have been observed in the gas-phase. This expectation is derived from results of municipal waste incinerators. The ratio of PCDD/F remaining on fly ash and further transferred by the flue gas at the ESP unit at 300°C is estimated in the range of 10:1 (Hutzinger and Fiedler, 1993). The lack of gas-phase detection of PCDD/F suggests that copper-coated borosilicate surfaces may not be a good model for fly ash-mediated formation of PCDD/F from the perspective of gas–solid partitioning. The lack of gas-phase detection of chlorophenols is also consistent with this observation.

For the acetylene experiments, the pattern of isomers of tetra- to heptachloro dibenzo-p-dioxins, the PCDD/PCDF ratio (<1), and the temperature of maximum yields (300–400°C) are consistent with published data from various full-scale combustors (Lenoir et al., 1998; Wehrmeier et al., 1998). The data for the tetrachlorodibenzo-p-dioxin isomers obtained at a factor of 9 higher initial acetylene concentration is shown in Fig. 6. This result demonstrates the relevance of these experiments to full-scale incineration systems. It should also be mentioned that the residence times examined in our experiments are in the same range as observed by

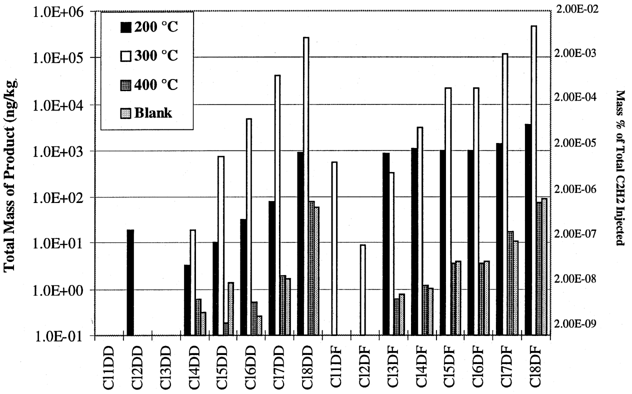


Fig. 4. Homologue profile for surface-bound PCDD/F following acetylene experiments at 200°C, 300°C, and 400°C. Also shown is the result for a blank borosilicate surface. $[C_2H_2]_{total} = 167$ μmol; $[CuCl_2]_0 = 344 \pm 80$ μmol; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He.

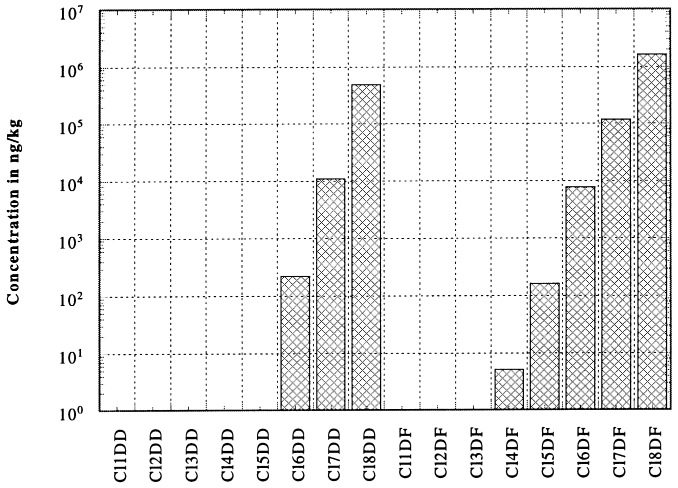


Fig. 5. Homologue profile for surface-bound PCDD/F following dichloroacetylene experiments at 300°C. $[C_2Cl_2]_{total} = 167$ μmol; $[CuO]_0 = 300 \pm 75$ μmol; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He.

Faengmark et al. (1994) for PCDD/F formation in a pilot-plant burning municipal waste.

Comparison of the acetylene and dichloroacetylene-derived PCDD/F homologue profiles, cf. Fig. 7, indicates substantial differences. Dichloroacetylene preferentially forms OCDF. Yields of OCDF were more than a factor of 2–3 larger for dichloroacetylene than acetylene and acetylene/HCl. However, as the level of chlorination decreased, relative PCDD/F yields become increasingly larger from acetylene. PCDD/F dechlorination reactions have been offered as an important mechanism in rationalizing PCDD/F homologue profiles from both laboratory experiments using actual fly ashes and full-scale data. The results presented here appear inconsistent with this mechanism. The dichloroacetylene data do not support the contention that significant dechlorination of PCDD/F occurs on the surface, based on surface retention times of up to 60 min. In fact, one can rationalize the larger yields of less chlorinated PCDD/F from acetylene with the observation of partially chlorinated aromatic intermediates, e.g., mono- through pentachlorobenzene. This may be followed by the dissociative adsorption of these compounds with the formation of surface-bound partially chlorinated phenols.

## 4. Discussion

The following experimental observations indicate that acetylene is chlorinated prior to surface-catalyzed condensation:

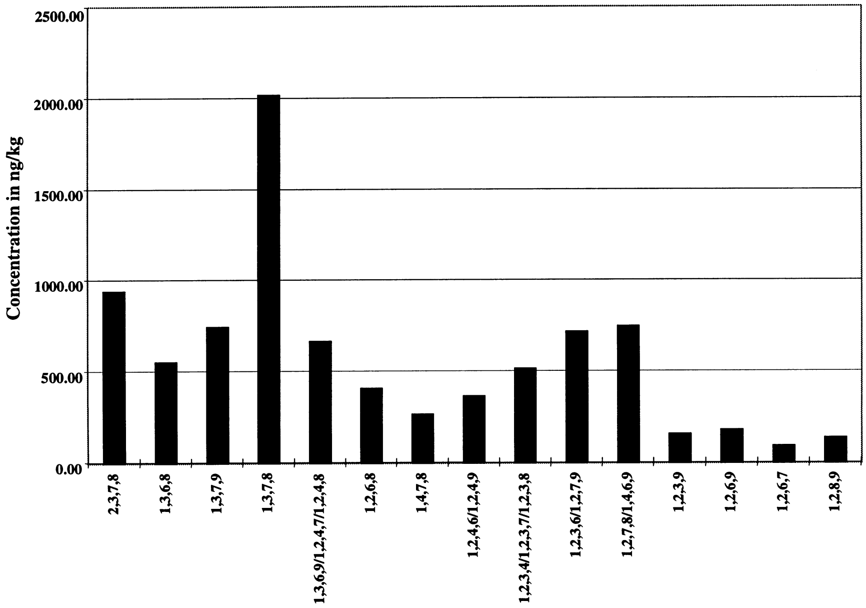


Fig. 6. Concentrations of tetrachlorodibenzo-p-dioxin isomers following acetylene experiments at 300°C. $[C_2H_2]_{total} = 1510$ μmol; $[CuCl_2]_0 = 344 \pm 80$ μmol; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He.

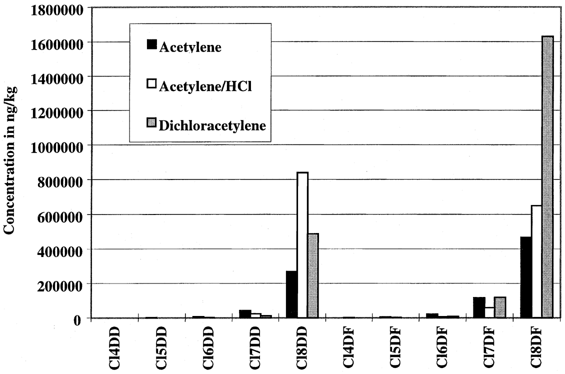
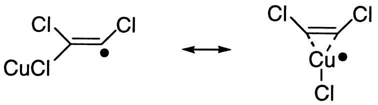


Fig. 7. Surface concentrations of $Cl_4$DD/F to $Cl_8$DD/F following acetylene, acetylene + HCl, and dichloroacetylene experiments at 300°C. $[C_2H_2]_{total} = 167$ μmol; $[HCl]_{total} = 167$ μmol; $[C_2Cl_2]_{total} = 167$ μmol; $[CuCl_2]_0 = 344 \pm 80$ μmol; $[CuO]_0 = 300 \pm 75$ μmol; $t_r = 2.0$ s. Reactor gas: 4% $O_2$ in He.

- No acetylene polymerization products were found with either catalyst investigated.
- Condensed reaction products were only found with a chlorine source present.
- Yields of reaction products increased with additional chlorine.
- Reaction products were predominantly perchlorinated.
- Major products from dichloroacetylene/BS/CuO were similar to those for acetylene/BS/$CuCl_2$.

Consistent with our experimental results and by analogy with mechanisms found in solution chemistry, we proposed the following global reaction mechanism for the gas-surface chlorination/condensation reaction of acetylene on copper species (Wehrmeier et al., 1998). Acetylene is chlorinated by $CuCl_2$ in a ligand transfer oxidation mechanism to mono- and dichloroacetylene and other less unsaturated chlorinated $C_2$ compounds. Chlorinated acetylenes then form oligomers in a surface-catalyzed reaction. Stahl et al. (1986) have shown that reactive dichloroacetylene is stabilized in metal complexes. These metal-dichloroacetylene complexes react with additional dichloroacetylene to form chlorinated metallacylopentadienes (Sünkel, 1990, 1991), known intermediates in dichloroacetylene condensation reaction. According to the Glaser and Cadiot–Chodikiewicz reaction, $Cu^+$ complexes are possible catalysts (Chodikiewicz, 1957). Chlorinated metallacylopentadiene then forms chlorinated butadienes in oxidative chlorination reaction with $CuCl_2$ or reacts with dichloroacetylene in an insertion or Diels–Alder type reaction to form chlorinated benzenes (Sünkel, 1990, 1991).

A similar mechanism involving CuCl can be envisioned for formation of hexachlorobenzene from dichloroacetylene, cf., Fig. 8. Interactions between the d orbitals of the Cu and the $\pi$ electrons of the dichloroacetylene result in the formation of chlorovinyl radical intermediates stabilized by the adjacent copper (see Scheme 1).



Scheme 1.

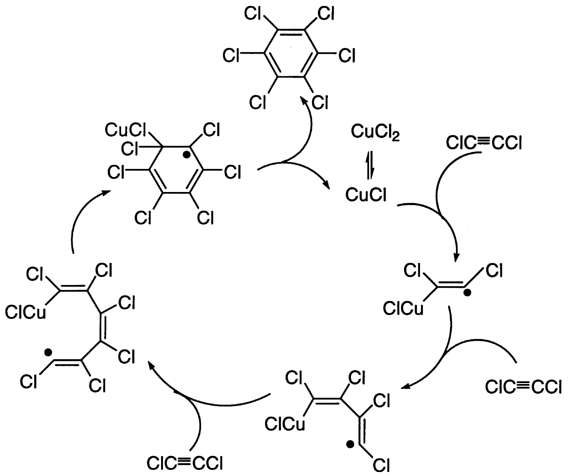


Fig. 8. Catalytic cycle for formation of hexachlorobenzene from dichloroacetylene via copper-stabilized chlorovinyl radicals.

A stable desorbed product, hexachlorobenzene, is formed by ring closure. The formation of hexachlorobenzene as the only $C_6$ product from dichloroacetylene reactions in the presence of the copper catalyst is experimental support for this mechanism.

## 5. Summary

Copper is mostly present in waste streams as CuO. Our results demonstrate that temperatures in the post-combustion zones should be quenched immediately below 300°C to prevent $CuCl/CuCl_2$ formation, an active catalyst system that may be in part responsible for the formation of these toxic combustion by-products. The mechanisms of chlorination and condensation discussed herein provide a tool towards minimization of these compounds in the effluents of incinerators. With government regulations constantly seeking lower emissions for these compounds, this method of preventing toxic combustion by-products from forming is an important step in reaching these goals.

## Acknowledgements

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## References

Addink, R., Olie, K., 1995. Environ. Sci. Technol. 29, 1425–1435.

Bond, G.C., Namijo, S.N., Wakeman, J.S., 1991. J. Molec. Catal. 64, 305–319.

Chloberag, 1950. Chlorbetrieb Reinfelden, DBP. 868294.

Chodikiewicz, W., 1957. Ann. Chim. (Paris) 13, 819–869.

Faengmark, I., Stroemberg, B., Berge, N., Rappe, C., 1994. Environ. Sci. Technol. 28, 624–632.

Froese, K.L., Hutzinger, O., 1994. Chemosphere 28, 1977–1987.

Froese, K.L., Hutzinger, O., 1996a. Environ. Sci. Technol. 30, 998–1008.

Froese, K.L., Hutzinger, O., 1996b. Environ. Sci. Technol. 30, 1009–1013.

Fruhwirth, O., Walla, H. 1940. Donau Chemie AG., Erf., DBP. 734024.

Hutzinger, O., Fiedler, H., 1993. Chemosphere 27, 121–129.

Lenoir, D., Wehrmeier, A., Kaune, A., Zimmermann, R., Taylor, P.H., Sidhu, S., 1998. Environ. Eng. Sci. 15, 37–48.

Nonhebel, D.C., 1970. J. Chem. Soc. (Special Publication.) 24, 409–437.

Pielichowski, J., Popielarz, R., 1984. Synthesis 5, 433–434.

Schramm, K.-W., Merk, M., Henkelmann, B., Kettrup, A., 1995. Chemosphere 30, 2249–2257.

Stahl, K., Weller, F., Dehnicke, K.Z., 1986. Anorg. All. Chem. 533, 73–82.

Sünkel, K., 1990. J. Organomet. Chem. 391, 247–257.

Sünkel, K., 1991. Chem. Ber. 124, 2449–2451.

Wehrmeier, A., Lenoir, D., Sidhu, S.S., Taylor, P.H., Rubey, W.A., Kettrup, A., Dellinger, B., 1998. Environ. Sci. Technol. 32, 2741–2748.

Wehrmeier, A., Lenoir, D., Schramm, K.-W., Zimmermann, R., Hahn, K., Henkelmann, B., Kettrup, A., 1998. Chemosphere 36, 2775–2801.