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Role of Copper Species in Chlorination and Condensation Reactions of Acetylene

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We examined the thermally induced acetylene chlorination and condensation reactions on different types of copper salt impregnated surfaces. The System for Thermal Diagnostic Studies provided a powerful tool to study these reactions under defined reaction conditions, which were related to typical conditions in postcombustion incineration processes. Experiments were conducted with acetylene or acetylene/HCl mixtures in a quartz reactor filled with a borosilicate foam of known pore size at temperatures between 150 and 500 °C. Borosilicate was also used as the catalytic support for gas−solid reactions of acetylene and acetylene/HCl mixtures with $CuCl_2$ and CuO. Reaction products were trapped in-line and analyzed by GC/MS. It was shown that borosilicate is not able to catalyze acetylene condensation reactions. $CuCl_2$-impregnated borosilicate was a highly effective catalyst for acetylene chlorination/condensation reactions at temperatures above 150 °C. The same behavior was found for CuO-impregnated borosilicate in the presence of HCl. However, temperatures above 300 °C were required for this catalytic system. Mainly perchlorinated C-2 to C-8 hydrocarbons were trapped as reaction products in the gas phase. Maximum yields for acetylene chlorination/condensation reactions in each related catalytic system were found at temperatures between 300 and 400 °C. Results of the surface-catalyzed acetylene chlorination and condensation reactions were summarized in a global mechanism. A ligand transfer oxidative chlorination of acetylene with $CuCl_2$ was proposed to be the initiating step. Chlorinated acetylene then condenses to higher molecular weight compounds, catalyzed by CuCl in metallacyclization reactions.

Introduction

Recent studies indicate that copper species play an important role in the thermal formation of chlorinated combustion byproducts and in thermal condensation reactions of aliphatic compounds (*1*−*3*). Acetylene (C_2H_2) is known to be a major precursor in the thermal formation of condensed hydrocarbons including aromatic structures and soot. Gas-phase condensation reactions of acetylene have been studied extensively since the beginning of this century and have recently been reviewed (*4*, *5*). These reviews concluded that condensation of acetylene in the gas phase initiated at temperatures above 700 °C and led to condensation products including vinylacetylene, benzene, styrene, etc. but also gave pyrolysis products such as vinylidene (*6*). Condensation reactions in solutions of monosubstituted acetylenes were investigated leading to the respective substituted benzenes (*7*, *8*). Studies of chlorinated analogues indicated that dichloroacetylene dissolved in ether condensed to hexachlorobenzene (*9*). The temperature for condensation of chlorinated acetylenes in solutions was reported to be below 130 °C (*10*). However, recent investigations of other C-2 aliphatic compounds such as trichloroethylene and tetrachloroethylene reported gas-phase condensation temperatures above 700 °C and chlorinated products analogous to those observed in acetylene condensation (*11*−*13*).

Historically, acetylene has been an important starting material in the industrial synthesis of chemical compounds (*14*). Since the early twentieth century a variety of catalysts for acetylene condensation reactions were investigated; in solution chemistry the synthesis of Reppe is of particular significance (*15*). In the presence of carbonyl−nickel−phosphine complexes acetylene condenses, forming cyclooctatetraene and benzene at temperatures below 100 °C. Cuprous chloride (CuCl) dissolved in polar solvents is used for coupling of acetylenes in preparative chemistry. These reactions are known as the Glaser reaction for coupling of symmetrically substituted acetylenes and Cadiot−Chodkiewicz coupling for unsymmetric ones (*16*).

Copper chlorides also play a predominant role in surface-catalyzed chlorination reactions. In the Deacon reaction, HCl is oxidized with oxygen in the presence of copper salts to chlorine (Cl_2). Chlorine reacts with acetylene at temperatures above 450 °C to yield tetrachloroethylene (*17*, *18*). Cupric chloride ($CuCl_2$) can act directly as a chlorinating agent by a ligand transfer oxidation mechanism (*19*). In gas−surface reactions copper species are considered among the most effective catalysts in thermal formation of chlorinated combustion byproducts, e.g., polychlorinated dibenzo-*p*-dioxins (PCDD) and -furans (PCDF) (*20* and references therein). Froese and Hutzinger (*3*) have shown that acetylene in the presence of cupric oxide (CuO) and HCl forms chlorinated benzenes, phenols, and PCDD/F at 600 °C. They have also shown that condensation of trichloroethylene (TCE) was not catalyzed by CuO (*1*).

The objectives of this study were to investigate the role of $CuCl_2$ and CuO in thermal molecular growth reactions of acetylene in gas−surface reactions using model borosilicate surfaces under controlled experimental conditions. It is shown that these surfaces reduce the reaction temperature of acetylene to chlorinated and condensed products from 700 °C in the gas phase to 150 °C. The nature of this catalytic reaction is discussed. A global reaction mechanism consistent with observed gas-phase products is proposed based on metallacyclization reactions involving cuprous chloride (CuCl) intermediates.

Experimental Section

Surface-catalyzed chlorination and condensation reactions of acetylene with copper species were performed using the System for Thermal Diagnostic Studies (STDS) (Figure 1).

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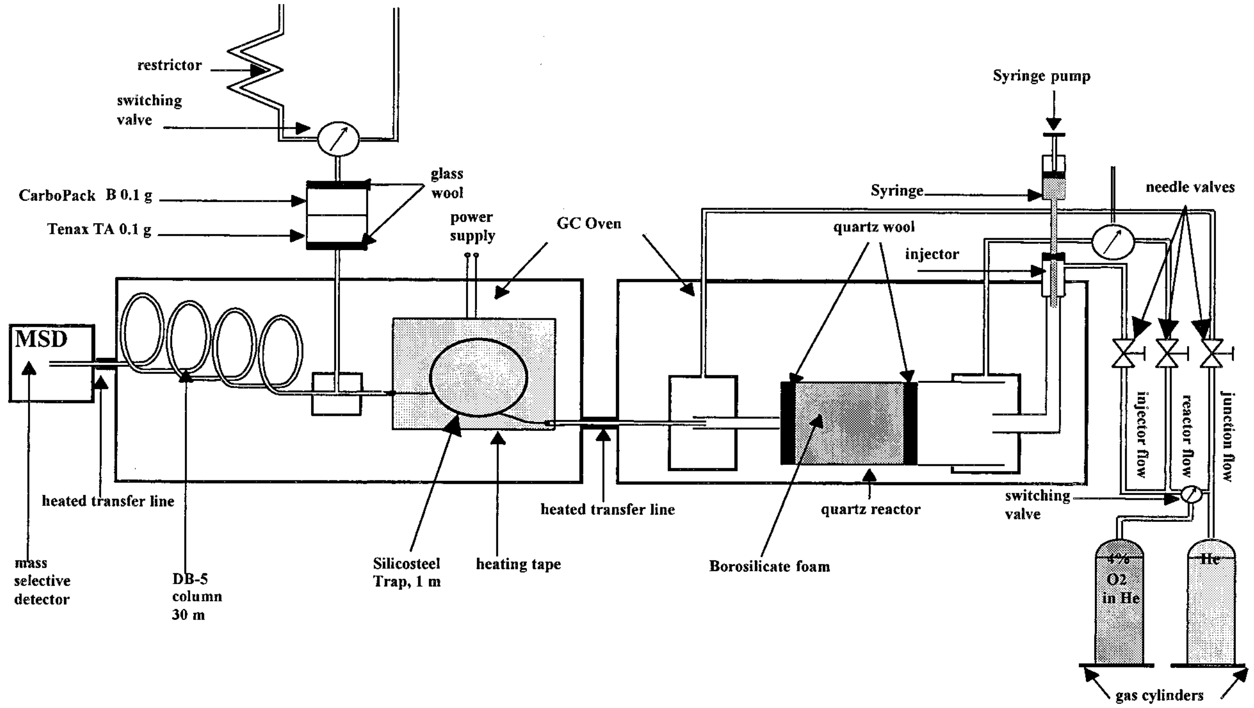

FIGURE 1. Schematic of the System for Thermal Diagnostic Studies (STDS) as modified for this heterogeneous combustion study.

The STDS is a high-temperature flow reactor coupled with an in-line gas chromatograph/mass spectrometer (GC/MS) system designed to simulate the reaction conditions in a combustor postflame zone. The setup is described in detail elsewhere (*21*). Briefly, the STDS consists of four integrated units: (1) a control console for precise adjustment of temperature, pressure, residence time, and the respective gas flows; (2) a thermal reactor compartment containing a high-temperature furnace (Lindberg) housed within a gas chromatograph (HP 5890) to allow precise sample introduction into and out of a quartz reactor; (3) a gas chromatographic oven (HP 5890) containing a silicosteel trap and a capillary column (DB-5, J & W Scientific) for separation of organic reaction products; and (4) a mass spectrometer (HP 5970B MSD) for product identification and quantification.

A cylindrical borosilicate (BS) 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 0.7 cm, and a pore size of 200 μm, was purchased from Cercona of America, Inc., and used as the catalytic support. The support was coated with different catalysts. Cupric chloride ($CuCl_2$, 99.999% Aldrich) and cupric nitrate ($Cu(NO_3)_2$, 99.999% Aldrich), respectively, were applied to the borosilicate by impregnation to incipient wetness (*22*). The borosilicate was impregnated with the respective cupric salt by dipping it into an ~20% aqueous solution of $CuCl_2$ or $CuNO_3$. Foams were dried at 120 °C for 1 h. The cupric oxide (CuO)-coated foam was prepared from the $Cu(NO_3)_2$ foam by calcinating at 480 °C for 16 h in air. Amounts of CuO and $CuCl_2$ on the borosilicate varied between 1 and 9%, respectively. It should be noted that $CuCl_2$ needed prior cleaning because of the presence of substantial amounts of chlorinated compounds, especially hexachlorobenzene. Hence, powdered $CuCl_2$ was thermally treated at 250 °C for 4 days in a flow of oxygen-free helium to remove all organic contaminants.

The borosilicate foams were positioned inside a quartz reactor, held in place with quartz wool, and heated to furnace temperatures of 150, 200, 250, 300, 400, and 500 °C, respectively. A mixture of 4% oxygen in helium was used as reaction atmosphere. The gas flow rate for the injector was 5 mL/min. The reactor gas flow was adjusted to an average residence time inside the catalytic foam of 2.0 s (±0.06 s), depending on the reaction volume inside the foam and the temperature and pressure inside and outside the reactor. Hence, reactor gas flow rates varied with temperature from 18 to 36 mL/min. Acetylene containing an impurity of 2% acetone (technical grade, Air Products) or acetylene and HCl (technical grade, Air Products) were injected directly into the reactor using a syringe pump. Flow rates of 0.065 mL/min (1100 ppm) were used for both reagents resulting in very fuel-lean reaction conditions for acetylene according to relative stoichiometric oxidation. Soot formation from acetylene was prevented. All experiments were conducted for 1 h. Semivolatile reaction products were trapped on a 1 m long silicosteel trap positioned inside a gas chromatographic oven held at 40 °C. Volatile reaction products which were not trapped on the silicosteel were collected through a split outside the GC oven on a Carbopack B (0.2 g, mesh 60/80)/Tenax TA (0.2 g, mesh 60/80) trap, with the Tenax-end connected to the silicosteel trap. This setup provided a tool to measure the volatile reaction products, which were expected to be formed in higher amounts with higher split values than the semivolatile reaction products.

After each combustion experiment, the injector and reactor flow was reduced to negligible values and the junction flow of helium was increased. The semivolatile reaction products were then released by heating of the silicosteel trap to 300 °C. Separation of semivolatile gas-phase products was achieved using a DB-5 capillary column (30 m, i.d. 0.25 mm, film thickness 0.25 μm, J & W Scientific) and the following temperature program: 40 °C // 10 °C/min // 290 °C // 5 min. The mass selective detector (HP 5970B MSD) was operated in the electron ionization mode, scanning all masses from 40 to 500 amu. Higher volatile reaction products trapped on the Carbopack/Tenax trap were analyzed in a similar system. Products were thermally desorbed in reverse flow using oxygen-free helium as carrier gas. The temperature program for desorption was 35 °C // 25 °C/min // 300 °C // 15 min. Compounds were then trapped on a DB-1 capillary column (30 m, i.d. 0.32 mm, film thickness 0.32 μm, J & W Scientific), held at −60 °C. Gas chromatographic separation was done using a linear temperature program: −60 °C // 10 °C/min //

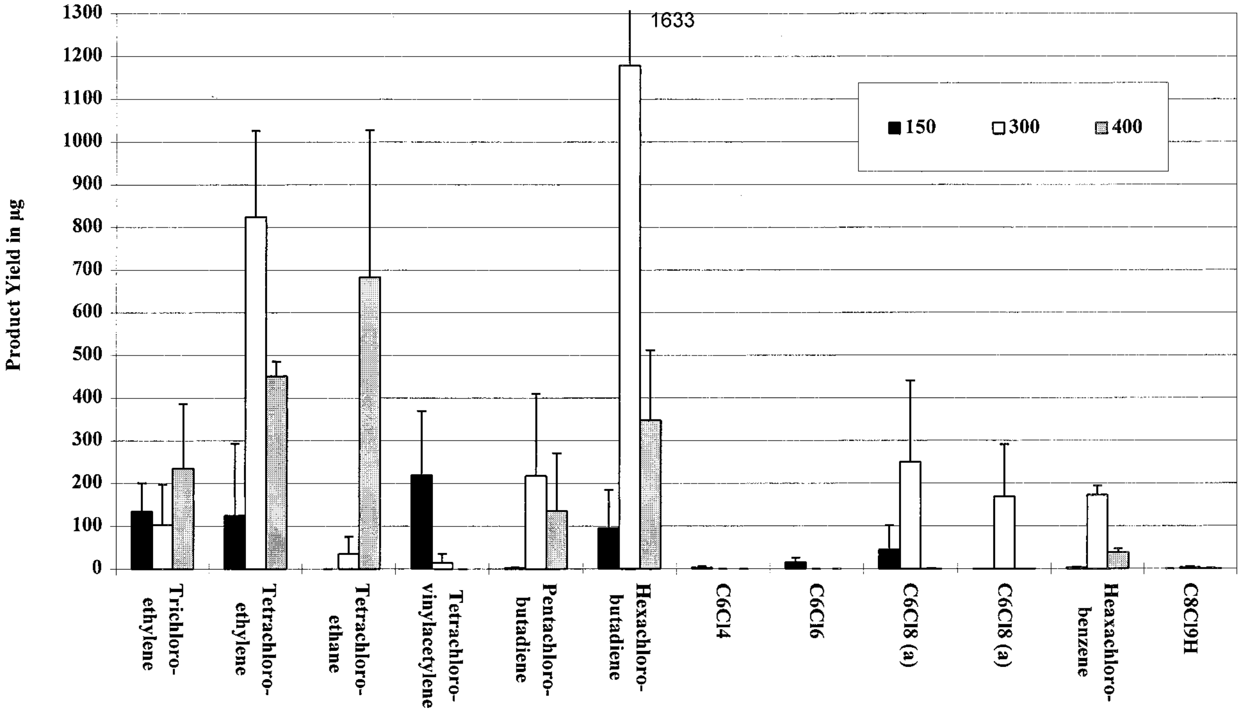

FIGURE 2. Predominant gas-phase products for the reaction of acetylene on $CuCl_2$/BS at 150, 300, and 400 °C, respectively. $[C_2H_2]_{total} = 4.35$ mg, $[CuCl_2]_0 = 58 \pm 11$ mg, $t_r = 2.0$ s, reactor gas: 4% O_2 in He.

280 °C // 1 min. Products were analyzed by means of a mass selective detector (HP 5970B MSD) operating in scan mode from 15 to 300 amu. Quantification for both volatile and semivolatile reaction products was accomplished using external standard calibration curves for the respective analyzed product or chemically similar compounds in cases where standards were not available.

Results

Reactions of acetylene in a very fuel-lean atmosphere (fuel–air equivalence ratio ~0.06) on $CuCl_2$-impregnated borosilicate foams produced a variety of chlorinated organic compounds. This system was able to chlorinate acetylene to form chlorinated C-2 compounds. Besides these, condensed products up to C-8 chloroorganics were analyzed in the gas phase; higher molecular weight compounds (*23*) were adsorbed on the borosilicate surface. The most striking feature in the distribution of reaction products was the high degree of chlorination of the organic moiety. A majority of products were perchlorinated. An interesting observation was the lack of unchlorinated acetylene polymerization products. Furthermore, cracking products and compounds with an odd number of carbon atoms were not detected under these reaction conditions. Besides hexachloropropane-2-one, which was formed in a few experiments in very small amounts, no oxygenated reaction products were trapped from the gas phase. Hexachloropropane-2-one was probably the chlorination product of acetone, a 2% impurity in the technical grade acetylene (selected experiments were conducted where the acetone impurity was reduced to less than 1%). The main reaction products formed in the acetylene–$CuCl_2$/BS system were as follows (Figure 2): tetrachloroethylene (C_2Cl_4) > hexachlorobutadiene (C_4Cl_6) > trichloroethylene (C_2HCl_3) > pentachlorobutadiene (C_4HCl_5) > tetrachlorovinylacetylene (C_4Cl_4) > hexachlorobenzene (C_6Cl_6) > tetrachloroethane > C_6Cl_8 (two different isomers) > pentachlorobenzene (C_6HCl_5) > C_6Cl_6 (isomer of hexachlorobenzene) > C_6Cl_4 > C_8Cl_9H.

Reaction products with a lower degree of chlorination (e.g. pentachlorobutadiene) were predominately formed at higher temperatures. The compounds C_6Cl_4 and the isomer of hexachlorobenzene were only detected at 150 °C. Maximum product yields were typically produced at 300 °C.

The mass spectra together with possible molecular structures of the unidentified compounds C_6Cl_4, C_6Cl_8 (two isomers with identical mass fragmentation), and C_8Cl_9H are shown in Figure 3. The C_6Cl_6 isomer and hexachlorobenzene has identical mass spectra, but are eluted at different retention times. The reaction products C_6Cl_4, the two isomers of C_6Cl_8, and hexachlorobenzene all show similar mass fragmentation. They just differ by two chlorine atoms more (C_6Cl_8) or less (C_6Cl_4) than hexachlorobenzene. The molecular mass for the predominant molecule isotope is 214 amu for C_6Cl_4 and 354/356 amu (similar heights) for C_6Cl_8. The predominant molecule isotope of C_8Cl_9H has a mass of 414 amu. Its mass fragmentation pattern is not related to hexachlorobenzene. Figure 3 shows only a choice of possible molecular structures of these unidentified reaction products, other structures are as likely, e.g., besides octachlorocyclohexa-1,4-diene, another cyclic C_6Cl_8 isomer, octachlorocyclo-1,3-diene, can be formed.

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 toward higher chlorinated compounds, e.g., trichloroethylene was not detected.

CuO was tested for its catalytic activity toward 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 formed in amounts similar to those 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. Figure 4 gives the total gas-phase product yields at 300 °C for the respective surfaces and reaction gas mixtures.

A few minor reaction products were not quantified, and hence, these products are not included in sum of product

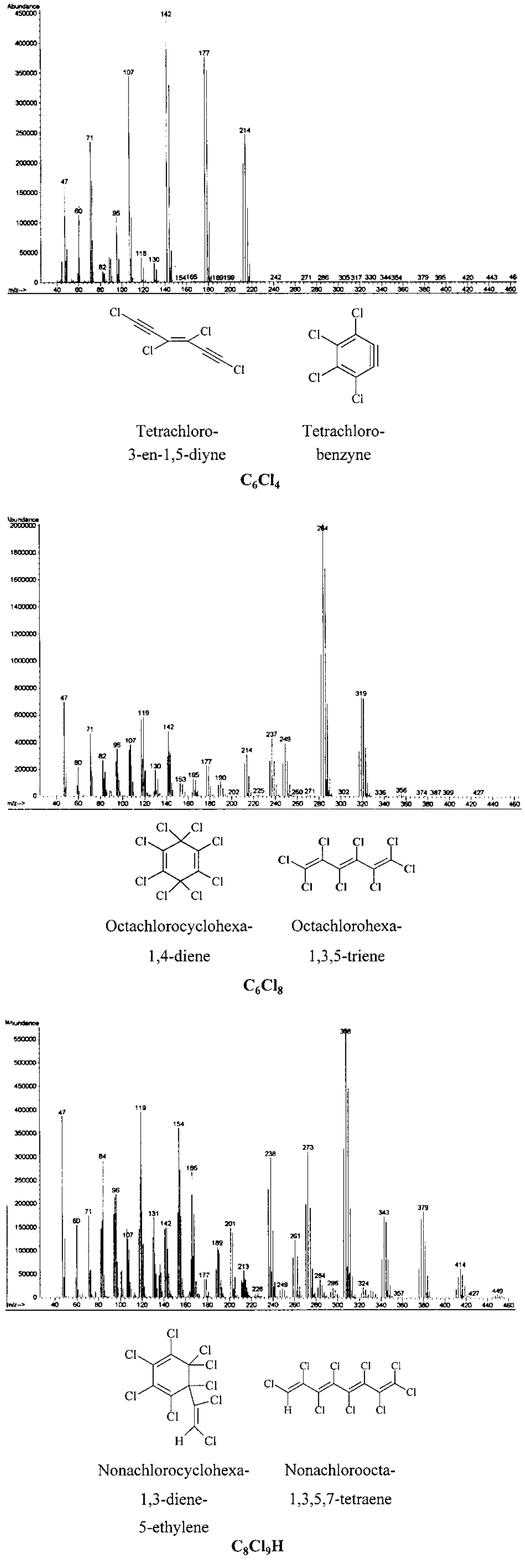

FIGURE 3. Mass spectra and some possible structures of the unidentified gas-phase products C_6Cl_4, C_6Cl_8, and C_8Cl_9H.

yields. Approximately 6 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 9.5 mol %.

The total yield of reaction products was a strong function of temperature. For the acetylene−$CuCl_2$/BS system, reaction started at temperatures below 150 °C and rose to maximum yields at about 300 °C. 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 (Figure 5).

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 up to 300 °C did not produce 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 $CuCl_2$.

Discussion

The condensation of acetylene in the presence of HCl has recently been studied in a fixed bed reactor on different kinds of surfaces (*1*−*3*). Fly ash mediated reaction started at 400 °C, and gas-phase product yields rose in general up to 600 °C. Different kinds of chlorinated reaction products including benzenes, phenols, dibenzo-*p*-dioxins, and -furans were formed. Metal oxide mixtures with SiO_2 were also tested for their catalytic behavior at 600 °C. At this temperature, chlorinated and condensed reaction products were formed with different kinds of surfaces, including SiO_2 and a SiO_2/CuO mixture.

We did not investigate acetylene chlorination and condensation above 500 °C, because both reaction types are known to occur in the gas phase at elevated temperatures (see Introduction). Our goal was to study the catalytic activity of $CuCl_2$ and CuO for these reactions. The catalytic support, borosilicate, did not show any catalytic activity for the acetylene reactions below 500 °C. Hence, in the study of Froese and Hutzinger (*1*−*3*), reaction products found with SiO_2 as support at 600 °C may have involved a gas-phase reaction, mediated by the surface. Furthermore, many reaction products formed at 600 °C with CuO/SiO_2 may have also formed by a surface-mediated, not catalyzed, gas-phase reaction. An increase in product yields by adding CuO to SiO_2 at 600 °C was only observed for highly chlorinated compounds. However, in our study, CuO-impregnated borosilicate in the presence of HCl did result in acetylene chlorination/condensation reactions at temperatures below 600 °C. Therefore, these reactions were indeed catalyzed by copper species.

The catalyzed chlorination/condensation reaction of acetylene on CuO/BS in the presence of HCl started at 300 °C with maximum yield at 400 °C. The color of the CuO-impregnated borosilicate in the presence of HCl changed with rising catalytic reactivity from black to yellow-brown. No change in the color of the foam and no reaction products were observed for the CuO/BS system, without adding HCl. Hence, the reaction product of CuO and HCl was likely the effective catalyst. This reaction is known to take part in the

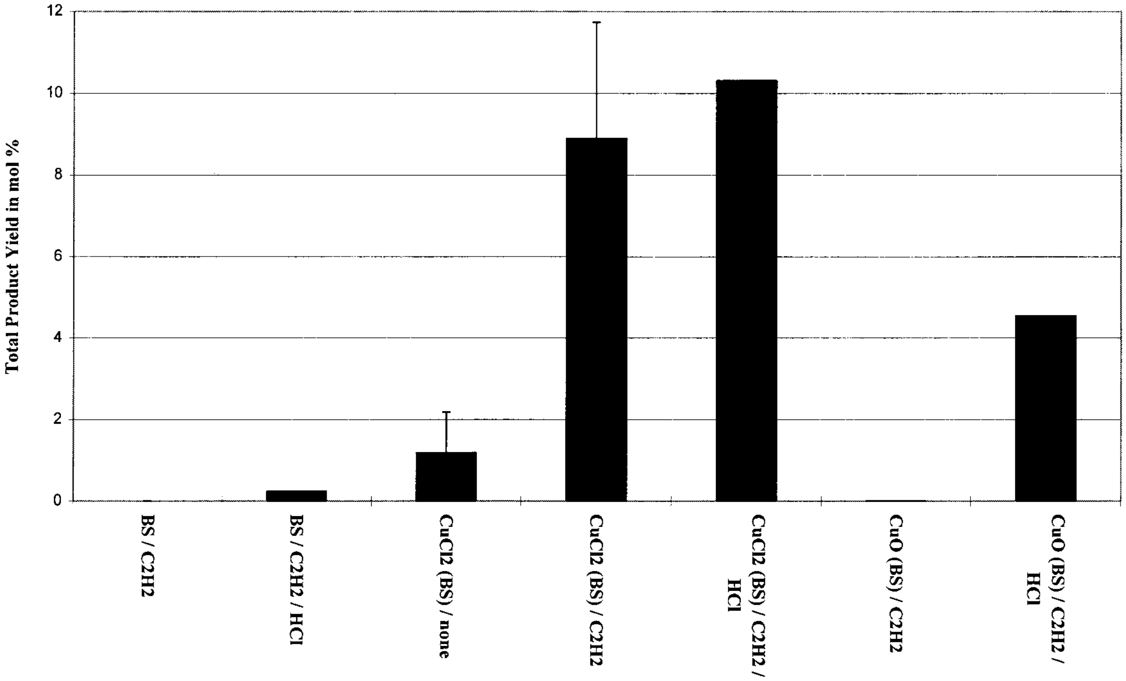

FIGURE 4. Total gas-phase product yields in mole percent according to acetylene injection to the respective surfaces at 300 °C. $[C_2H_2]_{total} = 167\ \mu mol$, $[HCl]_{total} = 167\ \mu mol$, $[CuCl_2]_0 = 344 \pm 80\ \mu mol$, $[CuO]_0 = 302\ \mu mol$, $t_r = 2.0$ s, reactor gas: 4% O_2 in He.

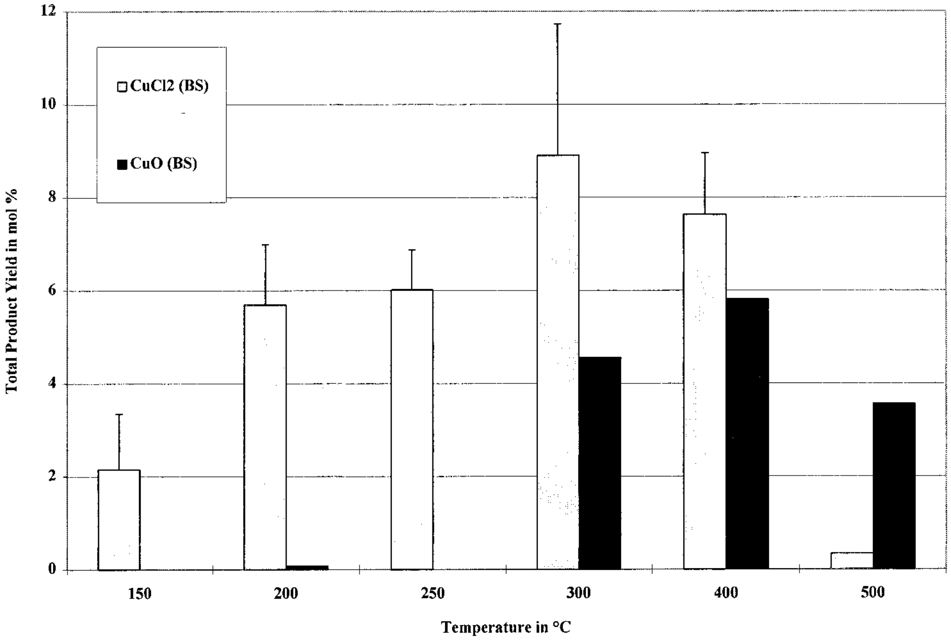

FIGURE 5. Total gas-phase product yields for the reaction of acetylene on $CuCl_2$-mediated borosilicate (gray bars) and acetylene/HCl mixture on CuO-mediated borosilicate (black bars) at different temperatures. $[C_2H_2]_{total} = 167\ \mu mol$, $[HCl]_{total} = 167\ \mu mol$, $[CuCl_2]_0 = 344 \pm 80\ \mu mol$, $[CuO]_0 = 302\ \mu mol$, $t_r = 2.0$ s, reactor gas: 4% O_2 in He.

Deacon reaction, where HCl is oxidized to Cl_2 in the presence of a copper(II) catalyst:

$$CuCl_2 + {}^1/_2\, O_2 \rightarrow CuO + Cl_2$$

$$CuO + 2HCl \rightarrow CuCl_2 + H_2O$$

$$2HCl + {}^1/_2 O_2 \rightarrow H_2O + Cl_2$$

With $CuCl_2$ as catalyst the Cl_2 liberation starts at 375 °C and gives significant yields of chlorine above 420 °C (*24*). However, reaction temperatures can be reduced down to 350 °C by adding a silicate support (*25*). This process probably occurs in the acetylene/HCl–CuO/BS system. CuO and HCl react at a temperature above 300 °C supported by borosilicate to $CuCl_2$, which itself reacts as the catalytic agent.

The experiments with the $CuCl_2$-impregnated borosilicate showed catalytic activity for the acetylene chlorination/condensation reactions above 150 °C. The maximum product yields for this system were found at 300 °C, but in contrast to the CuO/HCl system, no reaction products were formed at 500 °C. The lack of product formation at elevated temperatures is due to sublimation of $CuCl_2$ from the support. $CuCl_2$ begins to sublime at 300 °C and was completely sublimed from the borosilicate at 500 °C, as indicated by the white color of the foam at this temperature. Hence, no catalyst was involved in the 500 °C acetylene reaction. However, $CuCl_2$ was formed as an intermediate in the CuO/HCl system at 500 °C and was then able to act as a catalyst, leading to significant yields of reaction products. The distribution of reaction products at 300 and 400 °C was the same for the acetylene−$CuCl_2$/BS and the acetylene/HCl−CuO/BS system. This finding is another indication that copper chlorides are the catalytic compounds in the acetylene chlorination/condensation reaction.

$CuCl_2$ is known to be a very effective chlorinating agent (*26*). Most products found in our experiments were perchlorinated; partially chlorinated reaction products were more predominant at elevated temperatures. The degree of chlorination increased by adding HCl. This indicates that $CuCl_2$ is consumed in the reaction to CuO, like the first step of the Deacon reaction, or reduced to CuCl, in the presence of acetylene as the reducing agent. According to the second step of the Deacon reaction, CuO can react with HCl to reform $CuCl_2$. On the other hand, CuCl in the presence of HCl can be oxidized by air to $CuCl_2$.

The chlorination of acetylene is usually electrophilic in nature (*27*) but may also occur by a free-radical mechanism in cases where free-radical initiators, UV-radiation, or high temperatures are present (*28*). $CuCl_2$ and CuCl may be involved in both mechanisms. They catalyze the formation of Cl_2 in the Deacon reaction. In a radical mechanism, Cl_2 is then able to chlorinate acetylene at temperatures above 450 °C (*17, 18*). In addition, $CuCl_2$ and CuCl react as Lewis acids, which support a heterolytic Cl_2 bond cleavage. In our case, chlorination occurred at temperatures below 150 °C, temperatures too low for the thermal dissociation of Cl_2 and the initiation of free radical reactions. Assuming that free-radical initiators and UV-radiation did not play a role, free-radical reactions are unlikely under our reaction conditions. A direct transfer of chlorine in a ligand transfer oxidation mechanism, like that proposed by Nonhebel for aromatic compounds (ArH), appears more plausible (*19*):

$$\mathrm{ArH} + \mathrm{CuCl_2} \rightarrow \mathrm{ArHCl^{\bullet}} + \mathrm{CuCl}$$

$$\mathrm{ArHCl^{\bullet}} + \mathrm{CuCl_2} \rightarrow \mathrm{ArCl} + \mathrm{CuCl} + \mathrm{HCl}$$

$CuCl_2$ is then regenerated from CuCl with oxygen and HCl:

$$\mathrm{CuCl} + 2\mathrm{HCl} + {}^{1}/{}_{2}\mathrm{O_2} \rightarrow \mathrm{CuCl_2} + \mathrm{H_2O}$$

Tetrachloroethane was formed as the only saturated C-2 reaction product of Cl-addition to acetylene. Even higher yields were detected for the C-2 compounds trichloroethylene and tetrachloroethylene. This indicates that besides Cl-addition to acetylene HCl-elimination also occurs at the temperatures investigated. However, no chlorinated acetylenes were detected. This might be due to their high reactivity. Dichloroacetylene is known to condense, when dissolved in ether at temperatures below 130 °C, to a variety of chlorinated organic compounds including hexachlorobenzene as the main reaction product (*9, 10*). Hexachlorobenzene was detected as the main C-6 reaction product in our experiments. Other reaction products formed in our experiments including perchlorinated vinylacetylene, highly chlorinated butadienes, pentachlorobenzene, and compounds with the formula C_6Cl_8 and C_8Cl_9H may be the result of a condensation of mono- or dichloroacetylene. Because of the high reactivity of chlorinated acetylenes, catalytic surfaces are not required for their low-temperature condensation in solutions of chlorinated acetylene. However, in the gas-phase kinetic modeling of C_2Cl_2 formation from C_2HCl_3, C_2Cl_4, and C_4Cl_6, temperatures in excess of 700 °C were necessary for C_2Cl_2 condensation reactions to occur (*11−13*).

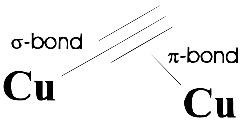

FIGURE 6. Structure of copper−acetylene complexes.

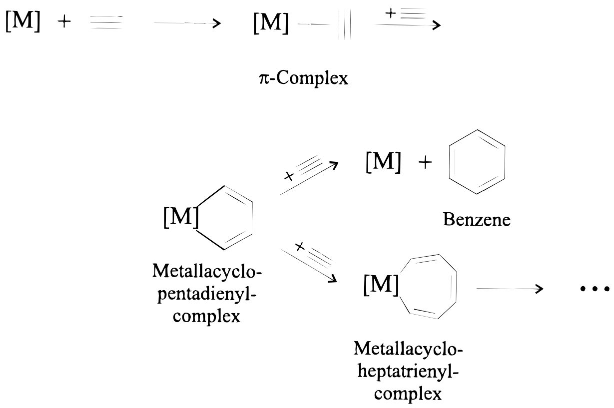

FIGURE 7. Metallacyclization reaction of acetylene and formation of cyclooligomers.

Chlorinated condensed reaction products could be formed in a competitive way at temperatures below gas-phase reaction temperatures. Dimerization of acetylene or substituted acetylenes are catalyzed by CuCl in the Glaser or the respective Cadiot−Chodikiewicz reaction. According to Clifford and Waters (*29*), the mechanism starts with the loss of a proton:

$$\mathrm{C_2H_2} \xrightarrow{\text{base}} \mathrm{C_2H^-} + \mathrm{H^+}$$

Subsequently, the chloride in CuCl reacts with the acetylide as the nucleophile by a S_N2 reaction:

$$\mathrm{C_2H^-} + \mathrm{CuCl} \rightarrow \mathrm{Cu(C_2H)} + \mathrm{Cl^-}$$

In the following step, the acetylide is oxidized by $CuCl_2$ to a C_2H radical:

$$\mathrm{Cu(C_2H)} + \mathrm{CuCl_2} \rightarrow \mathrm{C_2H^{\bullet}} + 2\mathrm{CuCl}$$

The acetylene dimer is then rapidly formed from two C_2H radicals:

$$2\mathrm{C_2H^{\bullet}} \rightarrow \mathrm{HC_2{-}C_2H}$$

The Glaser and the Cadiot−Chodikiewicz reactions were elucidated for acetylene coupling in dissolved liquid phases. Hence, a base-catalyzed loss of a proton as the initiating step is conceivable. In our case of a gas−surface reaction heterolytic bond cleavages are very unlikely. However, the mechanism proposed by Clifford and Waters can be extended to a surface-catalyzed mechanism, in which only single-electron processes proceed. Solid-state CuCl is known to react with gaseous acetylene or substituted acetylenes to give complexes of the following composition (*30*):

$$n\mathrm{CuCl} + \mathrm{C_2H_2} \rightarrow [(\mathrm{CuCl})_n(\mathrm{C_2H_2})]$$

Copper forms relative weak acetylene complexes with a copper/acetylene ratio below 1. These complexes contain

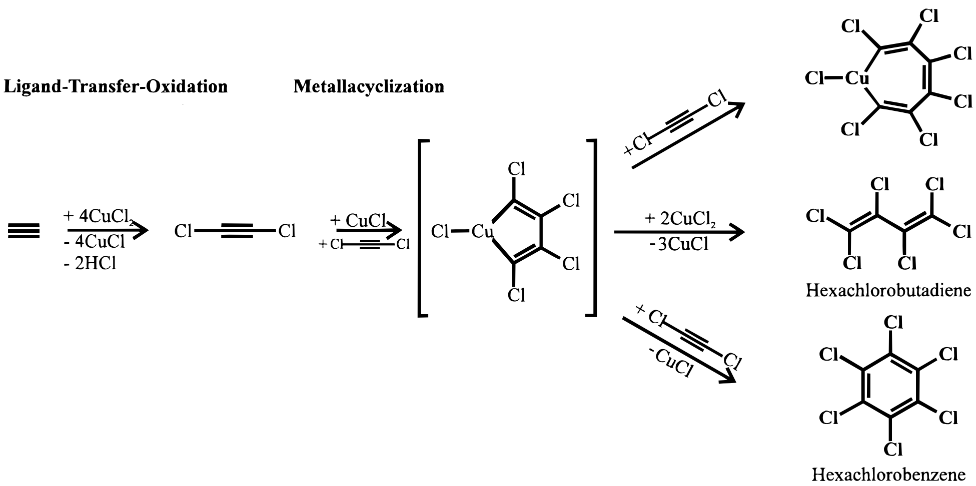

FIGURE 8. Global acetylene chlorination/condensation mechanism.

acetylene as well in σ-metal−carbon bonds, in which copper is bonded to an acetylide, as in π-metal−carbon bonds (*31*) (Figure 6).

These relatively weak complexes thermally decompose and may lead to release of the acetylene or, most frequently in reaction with acetylene, to formation of oligomers and cyclooligomers. The reaction starts with the formation of a metal ([M])−acetylene π-complex. Acetylene may react with this complex to form metallacyclic compounds. These complexes are able to react with additional acetylene to give metallacycloheptatrienyl complexes or release benzene (Figure 7) (*32*).

Metallacyclization reactions occur most readily in complexes in which metals possess d^8−d^{10} electron configurations (e.g., Cu^+ in d^{10} configuration). The formation of cyclooctatetraene and other cyclic hydrocarbons is well known as one of the Reppe-synthesis reactions with Ni(0) complexes as catalysts (*15*).

This type of gas−surface reaction may occur in our experiments since observed products are analogous to those found in acetylene condensation reactions (*4*, *5*). However, the following experimental observations indicate that acetylene is chlorinated prior to surface-catalyzed condensation: (1) no acetylene polymerization products were found with either catalyst investigated, including CuO/borosilicate; (2) condensed reaction products were only found with a chlorine source present; (3) yields of reaction products increased with additional chlorine; (4) reaction products were predominantly perchlorinated.

A third type of reaction, which is known in solution chemistry and may be involved in the acetylene condensation reaction, is the [4+2] cycloaddition or Diels−Alder reaction. Electron-rich 4π-systems, the diene, and electron-poor 2π-systems, the dienophile, are required for this reaction to take part readily. However, recent results indicate that this reaction can be catalyzed by Lewis acids such as Li^+ and transition metal complexes such as $cp(CO)_2Fe(THF)^+$ (*33*). The Lewis acids CuCl or $CuCl_2$ are then able to catalyze the [4+2] cycloaddition of, e.g., hexachlorobutadiene, one major reaction product with electron-poor dienophile, or dichloroacetylene to hexachlorobenzene, another major reaction product.

Consistent with our experimental results and in analogy with mechanisms found in solution chemistry, we propose the following global reaction mechanism for the gas−surface chlorination/condensation reaction of acetylene on copper species (Figure 8): 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 can then form oligomers in a surface-catalyzed reaction. It was shown by Stahl et al. that reactive dichloroacetylene is stabilized in metal complexes (*34*). These metal−dichloroacetylene complexes react with additional dichloroacetylene to form chlorinated metallacyclopentadienes (*35*, *36*), which can be intermediates in dichloroacetylene condensation reactions. According to the Glaser and Cadiot−Chodikiewicz reaction, Cu^+ complexes are possible catalysts (*16*). Chlorinated metallacyclopentadiene can form chlorinated butadienes in oxidative chlorination reaction with $CuCl_2$ or react with dichloroacetylene in an insertion or Diels−Alder type reaction to form chlorinated benzenes (*35*, *36*).

The compounds C_6Cl_8 and C_8Cl_9H can be formed from the respective chlorinated metallacycloheptatrienes or metallacyclononatetraenes by similar oxidative chlorination reaction with $CuCl_2$ (for a detailed discussion of these pathways see ref *37*).

The toxic compounds formed in our experiments are usually unwanted combustion byproducts in applied incineration techniques such as municipal waste incineration. Our mechanisms of chlorination and condensation reaction therefore provide a tool toward minimizing these compounds in the effluents of incinerators. Since copper in incineration processes is mostly present as CuO, in addition to the reduction of the copper feed, temperatures in the cooling zone should be quenched immediately below 300 °C to prevent a $CuCl_2$ formation, which according to our model is responsible for the formation of these toxic combustion byproducts.

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Literature Cited

(1) Froese, K. L.; Hutzinger, O. *Chemosphere* **1994**, *28*, 1977−1987.
(2) Froese, K. L.; Hutzinger, O. *Environ. Sci. Technol.* **1996**, *30*, 998−1008.
(3) Froese, K. L.; Hutzinger, O. *Environ. Sci. Technol.* **1996**, *30*, 1009−1013.
(4) Kiefer, J. H.; Von Drasek, W. A. *Int. J. Chem. Kinet.* **1990**, *22*, 747−786.
(5) Kiefer, J. H.; Sidhu, S. S.; Kern, R. D.; Xie, K.; Chen, H.; Harding, L. B. *Combust. Sci. Technol.* **1992**, *82*, 101−130.
(6) Duran, R. P.; Amorebieta, V. T.; Colussi, A. J. *J. Am. Chem. Soc.* **1987**, *109*, 3154−3155.
(7) Breitkopf, V.; Hopf, H.; Klärner, F.-G.; Witulski, B.; Zimmy, B. *Liebigs Ann.* **1995**, 613−617.

(8) Smirnov, K. M.; Tomilov, A. P.; Shchekotikhin, A. I. *Russ. Chem. Rev.* **1967**, *36*, 326−338.
(9) Ott, E.; Dittus, G. *Chem. Ber.* **1943**, *76*, 80−84.
(10) Riemschneider, R.; Brendel, K. *Liebigs Ann.* **1960**, *640*, 1−15.
(11) Taylor, P. H.; Tirey, D. A.; Rubey, W. A.; Dellinger, B.; *Combust. Sci. Technol.* **1994**, *101*, 75−102.
(12) Taylor, P. H.; Tirey, D. A.; Dellinger, B. *Combust. Flame* **1996**, *104*, 260−271.
(13) Taylor, P. H.; Tirey, D. A.; Dellinger, B. *Combust. Flame* **1996**, *106*, 1−10.
(14) Parshall, G. W. Wiley: New York, 1980, p 223.
(15) Reppe, W.; v. Kutepow, N.; Magin, A.; *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 727−766.
(16) Chodikiewicz, W. *Ann. Chim.* (*Paris*) **1957**, *13*, 819−869.
(17) Chloberag; Chlorbetrieb Reinfelden; DBP. 868294, 1950.
(18) Fruhwirth, O.; Walla, H.; Donau Chemie AG.; Erf.; DBP. 734024, 1940.
(19) Nonhebel, D. C. *J. Chem. Soc. Special Publication* **1970**, *24*, 409.
(20) Addink, R.; Olie, K. *Environ. Sci. Technol.* **1995**, *29*, 1425−1435.
(21) Rubey, W. A.; Grant, R. A. *Rev. Sci. Instrum.* **1988**, *59*, 265.
(22) Bond, G. C.; Namijo, S. N.; Wakeman, J. S. *J. Mol. Catal.* **1991**, *64*, 305.
(23) Wehrmeier, A.; Lenoir, D.; Schramm, K.-W.; Taylor, P. H.; Sidhu, S. Unpublished data.
(24) Hisham, M. W. M.; Benson, S. W. *J. Phys. Chem.* **1995**, *99*, 6194−6198.
(25) Hardie, D. W. F. *Ind. Chemist* **1951**, *27*, 502.
(26) Olah, G. A. *Friedel−Crafts and related Reactions*; Interscience: New York, 1965; Vol. 4, p 127−183.
(27) de la Mare, P. B. D. *Electrophilic Additions to Unsaturated Systems*, 2nd ed.; Elsevier: New York, 1982.
(28) March, J. *Advanced Organic Chemistry. Reactions, Mechanisms and Structures*, 3rd ed.; Wiley: New York, 1985; p 725.
(29) Clifford, A. A.; Waters, W. A. *J. Chem. Soc.* **1963**, 3056−3062.
(30) Pruchnik, F. P. *Organometallic Chemistry of the Transition Elements*; Plenum Press: New York, 1990; p 389−412.
(31) Lang, H.; Köhler, K.; Blau, S. *Coordination Chem. Rev.* **1995**, *143*, 113−168.
(32) Peter, K.; Vollhardt, C. *Acc. Chem. Res.* **1977**, *10*, 1−8.
(33) Bonnesen, P. V.; Puckett, C. L.; Honeycuck, R. V.; Hersh, W. H. *J. Am. Chem. Soc.* **1989**, *111*, 6070−6081.
(34) Stahl, K.; Weller, F.; Dehnicke, K.; *Z. Anorg. All. Chem.* **1986**, *533*, 73−82.
(35) Sünkel, K. *J. Organomet. Chem.* **1990**, *391*, 247−257.
(36) Sünkel, K. *Chem. Ber.* **1991**, *124*, 2449−2451.
(37) Taylor, P. H.; Sidhu, S. S.; Rubey, W. A.; Dellinger, B.; Wehrmeier, A.; Lenoir, D.; Schramm, K.-W. 27th Symposium on Combustion; The Combustion Institute: Pittsburgh, PA, 1998, in press.

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