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Catalysis Today 27 (1996) 159–166

CATALYSIS TODAY

Catalytic reduction of polyhalogenated aromatic hydrocarbons by Cu(I) under Dow-Phenol conditions

W. Buijs [1]

DSM Research, P.O. Box 18, 6160 MD Geleen, Netherlands

Abstract

Poly chlorinated and brominated aromatic hydrocarbons and ethers are catalytically reduced by Cu(I)benzoate under Dow-Phenol conditions in the absence of air. This homogeneous catalytic reaction is very robust and can be transformed into a promising future environmental technology for some specific halogenated waste streams.

Keywords: Reduction; Polyhalogenated aromatic hydrocarbons; Copper(I); Dow-Phenol conditions

1. Introduction

Halogenated hydrocarbons have found widespread use in all parts of the society, due to its well established excellent physical and chemical properties [1,2]. Unfortunately these properties also lead to severe adverse effects, ranging from enhancing the greenhouse effect to toxicological effects of mutagenicity and (co)carcinogenicity [3,4].

Though progress is being made in various areas dealing with specific parts of the overall problem, there is still a need for an economically feasible process for the conversion of halogenated hydrocarbons into harmless compounds.

During research on the thermal decomposition of Cu(II) aryl carboxylates, anomalous behaviour of Cu(II) 3-chloro benzoate, lead to the discovery of a new reaction: the reduction of 3-chloro benzoic acid to benzoic acid and inorganic chloride by Cu(I) under Dow-Phenol conditions.

This paper deals with the results of chemical and technological research to determine the scope of this new reaction and its potential as an environmental technology to detoxify halogenated waste.

2. Experimental

All experiments have been conducted in an oil heated, double walled reactor, having an effective volume of about 250 ml. The reactor was equipped with a controlled stirrer, gas inlet, gas outlet via a distillation setup, sampling point and a reactor mass tapping point. The offgas was sent to a cold trap (−78°C) to remove condensables, and thereafter analyzed for CO_2. CO_2 was analyzed as cumulative amount absorbed in a washing column (250 mM NaOH) vs. time, by a simple titration using a (fresh) 100 mM HCl solution. Specific attention was given to the residence time distribution of this offgas system since this can be a

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[1] Fax: +31 46 4767603

SSDI 0920-5861(95)00184-0

serious source of errors in the interpretation of kinetic data. Plug-flow behaviour of the offgas stream could be established.

Liquid samples of reactor mass, and condensables of the cold trap were analyzed using (standard) reverse phase HPLC and GC-MS.

All starting materials were obtained from regular suppliers, and were of a purity >98%.

3. Results and discussion

3.1. Dow-Phenol chemistry

In the Dow-Phenol Process, molten pure benzoic acid is oxidized at $T > 180°C$ with air to yield eventually phenol and CO_2 [5,6]. The catalytic role of Cu-ions is visualized in the next simplified scheme, coupling the redox reactions (Eq. (1–2)) and the hydrolysis of phenyl benzoate (Eq. (3)) to give the net overall reaction (Eq. (4)).

$$2Cu(II) + 2ArCOOH \rightarrow 2Cu(I) + 2H^+ + ArCO_2Ar + CO_2 \quad (1)$$

$$2Cu(I) + 1/2O_2 \rightarrow 2Cu(II) + H_2O \quad (2)$$

$$ArCO_2Ar + H_2O \rightarrow ArOH + ArCOOH \quad (3)$$

Overall:

$$ArCOOH + 1/2O_2 \rightarrow ArOH + CO_2 \quad (4)$$

Thermal decomposition of Cu(II) benzoate is a main reaction in this overall catalytic process (Eq. (1)). This reaction, often referred to as an oxidative decarboxylation, leads to the formation of phenyl benzoate and CO_2 via ortho benzoyl salicylic acid, as outlined in Fig. 1. The reaction is general for Cu(II) aryl carboxylates with at least one hydrogen in the 2 or 6 position on the aromatic nucleus.

To enable close mechanistic research on thermal decomposition of Cu(II) aryl carboxylates, the reaction was made stoichiometric, replacing the air feed by a N_2 feed. Now its kinetics can be measured by the formation of CO_2 vs. time, which is stripped off with the N_2, and analyzed in the (dried) offgas. From Eq. (1), it is clear that the amount of CO_2 produced in the stoichiometric thermal decomposition, is directly proportional to the amount of Cu(II) reacted and thus the conversion of the reaction. In the absence of air, Cu(II) is introduced as either Cu(II)O or Cu(II) benzoate, prepared by standard methods.

The research showed that thermal decomposition of Cu(II) aryl carboxylates is very complex and highly sensitive to all kinds of medium effects [7].

3.2. Discovery of the reduction

The cumulative CO_2 formation vs. time from the thermal decomposition of Cu(II) benzoate follows a normal pattern, reaching a stable value of about 70% of the theoretical maximum, based on the starting amount of Cu(II). At this time the conversion is almost complete however, due to selectivity loss under these conditions, the CO_2 production will not reach the theoretical value of 100%.

The cumulative CO_2 formation vs. time from the thermal decomposition of Cu(II) 3-chloro benzoate shows an anomalous behaviour. The reaction seems to be almost zero-order until 100% conversion. Than it starts to slow down, eventually reaching a maximum value of approximately 130%, related to the starting amount of Cu(II).

A control experiment, using the same amount of Cu(I) 3-chloro benzoate, instead of Cu(II) 3-chloro benzoate, lead to the formation of about 60% CO_2. Cu(I) 3-chloro benzoate was prepared in situ from $Cu(I)_2O$ and 3-chloro benzoic acid.

HPLC analysis of the final reaction mass of the experiments with 3-chloro benzoic acid, showed

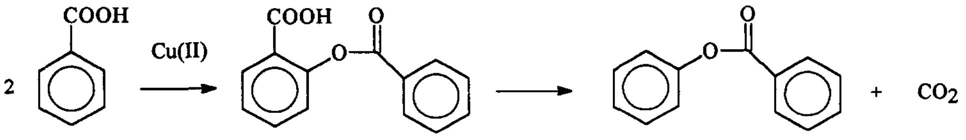

Fig. 1. The regiochemistry of the thermal decomposition of Cu(II) benzoate.

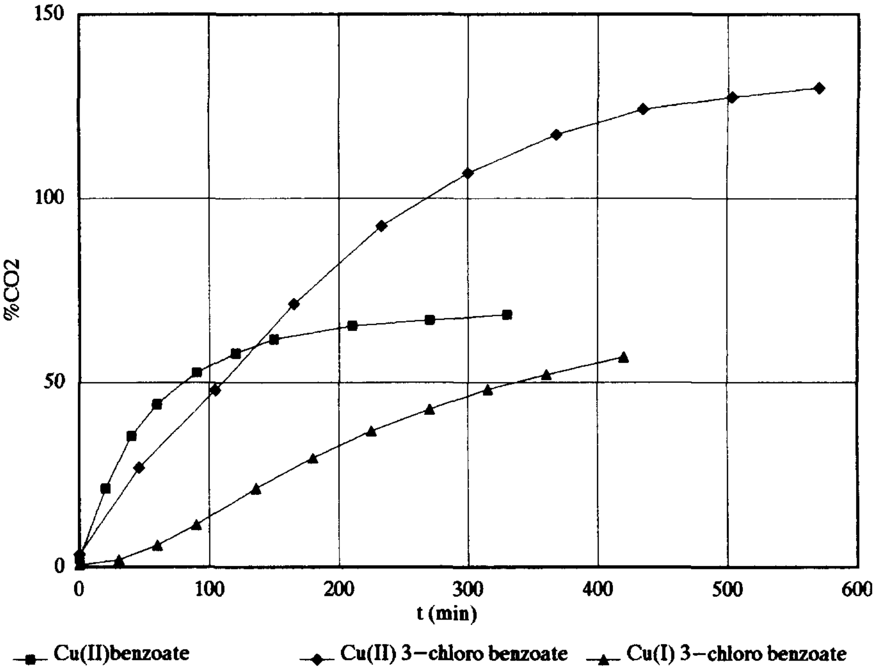

Fig. 2. Cumulative CO_2 formation vs. time from thermal decomposition of Cu(II) benzoate, Cu(II) 3-chloro benzoate and Cu(I) 3-chloro benzoate.

that the ortho selectivity of the thermal decomposition of Cu(II) 3-chloro benzoate is about 100%. With ortho selectivity is meant the sum of 2-chloro phenyl 3-chloro benzoate and 4-chloro phenyl 3-chloro benzoate. See also Fig. 2 on the regiochemistry of thermal decomposition of Cu(II) benzoate. Furthermore, benzoic acid was detected unambiguously. The reaction mass of the experiment with Cu(I) 3-chloro benzoate showed a white precipitate which eventually turned out to be Cu(I)Cl.

It is important to note that no metallic Cu was detected, since this would be another plausible explanation for the anomalous yield of 130% in the Cu(II) case and of 60% in the Cu(I) case. Disproportionation of Cu(I) leads to Cu(0) and Cu(II) and thus should lead to an additional CO_2 production.

From the experimental data it was concluded that the anomalous behaviour of 3-chloro benzoic acid could be explained by the assumption that Cu(I) was reoxidized to Cu(II) by the Ar–Cl bond, which in turn was reduced to a Ar–H bond. The Cu(II) 3-chloro benzoate thus formed, gives rise to normal thermal decomposition, turning a reaction which was meant to be stoichiometric, into a catalytic one.

To the authors best knowledge, this reaction has not been described sofar.

The reaction should not be confused with the copper catalysed dechlorination/ hydrogenation of polychlorinated dibenzo-p-dioxins, etc., described by H. Hagenmaier et al. [8], because these authors describe the heterogeneous reaction of chlorinated aromatic compounds with metallic copper powder.

3.3. Impression on the scope of the reduction

The new homogeneous reaction was explored to establish its scope, and to develop a mechanistic explanation. By the results of these experiments, its potential as a possible environmental technology was realised first. Fig. 3. shows typical results obtained with the different substrates. The activity of the substrates is still determined as the cumulative CO_2 production vs. time, however now

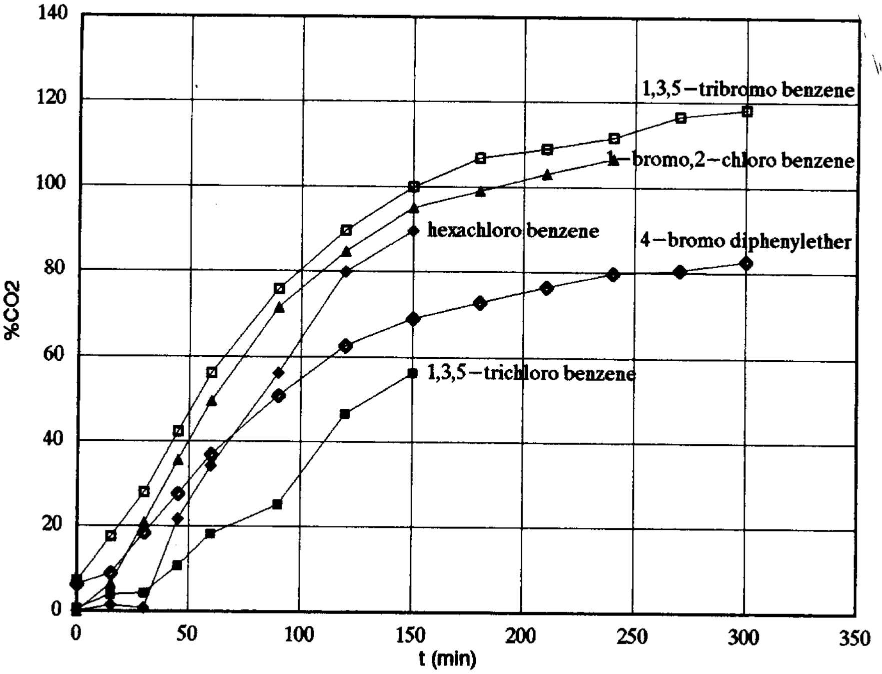

Fig. 3. Copper catalysed dehalogenation of several halogenated hydrocarbons in benzoic acid at 235°C, starting from $Cu(I)_2O$.

related to the starting amount of Cu(I), instead of Cu(II)!

From the substrates tested it is obvious that the reduction reaction is not limited to halogenated aryl carboxylic acids. The initial rates of CO_2 production are roughly the same for all substrates. Furthermore an increase in the temperature to 240°C, does not lead to a significant higher CO_2 production rate, indicating that really the reduction rates are reflected in the CO_2 production rates and not the thermal decomposition rates (results not shown).

1,3,5-tribromo benzene, 1-bromo, 2-chloro benzene and hexachloro benzene show the highest CO_2 production rate, while 4-bromo diphenylether and 1,3,5-trichloro benzene lead to a somewhat lower CO_2 production rate.

GC-MS analysis of the final reaction mass and the cold trap, of the experiment with 1,3,5-tribromo benzene, shows the presence of 1,3,5-tribromo benzene, 1,3-dibromo benzene, bromo benzene and benzene. The same analysis for the experiment with 1-bromo, 2-chloro benzene, shows the presence of chloro benzene, a significant amount of bromo benzene, benzene and a small amount of 1,2-dichloro benzene.

The reaction mass of the experiment with 4-bromo diphenylether shows the expected diphenylether and a small amount of 4-benzoato diphenylether.

The reaction mass of the experiment with hexachloro benzene shows mainly pentachloro benzene, together with almost equal amounts of hexachloro benzene and the isomeric tetrachloro benzenes, while the experiment starting from trichloro benzene, yields almost equal amounts of 1,3,5-trichloro benzene, 1,3-dichloro benzene and chloro benzene. Even benzene was detected in the latter case, but it cannot be excluded that this is due to simple decarboxylation of benzoic acid, also catalysed by Cu(I).

The decrease in CO_2 production rate is caused both by the decrease in substrate and the decrease in active catalyst, since Cu(I) halides do easily precipitate in benzoic acid.

So, it is concluded that the reaction is applicable to a wide range of poly chlorinated and brominated aromatic hydrocarbons and ethers. However the catalytic reaction is prohibited by the precipitation of Cu(I) halide. The limit of the number of carbon–halogen bonds per Cu, that can be reduced is close to one.

3.4. Speculative mechanism of the reduction

The reduction seems to be quite insensitive to either electronic effects of other substituents, or leaving group abilities. This is indicative for a reaction on a complex, in the coordination sphere of Cu(I). As a consequence the reaction is very unselective, in the way of not showing any preference for a specific carbon halogen bond or a specific substrate. All substrates, including partly reduced intermediates, are reduced with the same rate.

Side reactions are limited to some nucleophilic substitutions, leading to 1,2-dichloro benzene in the case of 1-bromo, 2-chloro benzene and to 4-benzoato diphenylether in the case of 4-bromo diphenylether. These substitutions are also known to be Cu(I) assisted [9].

Though the structural properties of Cu(I) carboxylates are well established, its catalytic properties are not. Cu(I) benzoate in benzoic acid is known to be dimeric [10]. It is also known that Cu(I) has a great tendency to interact with p- or π-electrons.

Now the reaction starts with either the coordination of the aromatic nucleus or the halogen to the dimeric Cu(I) benzoate. Thereafter a first Cu(I) donates an electron into the carbon halogen bond, leading formally to a radical-anion.

Thusfar the mechanism fully parallels the description of the mechanism of the Cu(I) assisted nucleophilic substitution of the aryl halogen [9], which, as was noted before, is a minor side reaction in some cases.

However, the reaction now takes a different course by the donation of a second electron from the second Cu(I) available in the dimeric complex, which lead formally to the breaking of the carbon-halogen bond into a coordinated carbanion and a coordinated halide. At this stage, not necessarily, neither a transition state nor an intermediate is shown (Fig. 4).

After protonation of the formal carbanion by benzoic acid, leading to the release of the reduced hydrocarbon by ligand exchange with the benzoate, a 'normal' paddlewheel dimeric Cu(II) carboxylate is left, with still the halide as a bidentate ligand.

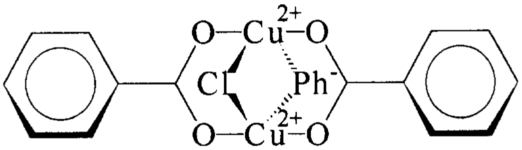

Fig. 4. A geometric proposal for the reduction of a carbon–halogen bond by Cu(I) benzoate, showing a bidentate coordinated carbanion and halide to 2 Cu(II) ions.

Essential in this proposal is thus the presence of dimeric Cu(I) and Cu(II) benzoates, controlling both geometry and electronics of the reaction. This is often observed in transition metal ion catalysis.

The proposed mechanism also explains why this reduction is not dominant under the basic conditions of the Cu(I) assisted nucleophilic substitutions.

Of course the status of the mechanism is still hypothetical and further research is needed to elucidate the actual mechanism. The scope most likely can be broadened to iodine, and perhaps even fluorine, with respect to the halogens and to aliphatic substrates, with respect to the organic skeleton.

The unexpected coupling of the 2 stoichiometric reactions, the reduction of an aromatic carbon-halogen bond and the thermal decomposition of Cu(II)benzoate in benzoic acid, leads to an overall catalytic process which easily can be described as a kind of Dow-Phenol cycle. The *R–X* bond has taken the role of the oxygen. This also leads to the use of additional H_2O to hydrolyse the phenyl benzoate. Thus from a reaction point of view, one mole of benzoic acid and H_2O, will be converted to one mole of phenol and CO_2 per mole of carbon–halogen bond reduced.

$$\begin{aligned}&2\mathrm{Cu(II)} + 2\mathrm{ArCOOH}\\ &\quad \rightarrow 2\mathrm{Cu(I)} + 2\mathrm{H}^+ + \mathrm{ArCO_2Ar} + \mathrm{CO_2} \qquad (1\mathrm{a})\end{aligned}$$

$$\begin{aligned}&2\mathrm{Cu(I)} + \mathrm{Ar}\text{–}X + 2\mathrm{H}^+ \rightarrow 2\mathrm{Cu(II)}\\ &\quad + \mathrm{Ar}\text{–}\mathrm{H} + \mathrm{H}\text{–}X^a \qquad (2\mathrm{a})\end{aligned}$$

$$ArCO_2Ar + H_2O \rightarrow ArOH + ArCOOH \quad (3a)$$

$$ArCOOH + Ar\text{–}X + H_2O \rightarrow ArOH + Ar\text{–}H + H\text{–}X + CO_2 \quad (4a)$$

[a] Formal reaction product; halide will coordinate to Cu(I) and Cu(II)!

3.5. Development to an environmental technology

As was noted before, during the exploration of the reaction, its potential as an environmental technology was recognised. Therefore a model process was developed [11].

The overall reaction rate is determined both by temperature and available concentration of Cu(I). As described earlier, 235°C seems to be the optimum temperature. The solubility of especially Cu(I) benzoate is very high in benzoic acid (> 1 kmol/m^3). The thermal decomposition of Cu(II) benzoate is not inhibited by the presence of other metal-ions, salts or organics, with only very few exceptions, which means that the use of benzoic acid can be minimised. These properties perfectly suit the Dow-Phenol system for the reduction of halogenated waste.

The final decrease in reaction rate, caused by the precipitation of Cu(I) halide, leads to the loss of active catalyst. At a first glance this looked like a very serious disadvantage, but later it was realized that this precipitation in fact is a great advantage because separation of free halide from the reaction mixture is not easy to accomplish.

Furthermore Cu(I) halides can be converted easily into solid Cu(I)$_2$O and an almost saturated solution of sodium halide, by reaction with NaOH in H_2O.

The scale of the model process was (quite arbitrarily) chosen to be 500 t/year, based on data of the Dutch government [12] on the amount officially delivered to detoxify.However annual production of halogenated aromatics exceeds this number with more than 1000%. It should be noted that such a scale is not an economic optimum for a continuous process. Therefore a semi-continuous process was chosen.

Chlorobenzene was chosen as a model substrate because it can be considered as a worst case scenario because of its low halogen content and the formation of the carcinogenic product benzene, which needs specific attention before it can be burned. PCB's are converted into biphenyls, which can be burned easily.

It should be noted that all halogenated benzenes eventually lead to the formation of benzene in this process.

Specific care was also taken to avoid leakage of any trace of halogenated compounds, salts and copper compounds to the environment.

To avoid expensive unit operations with solid Cu(I) chloride and Cu(I)$_2$O, a reactor with an internal filter was chosen, to keep essentially all Cu in the reactor. In principle only losses due to the very limited solubility of Cu(I) chloride must be compensated. The reactor is optimised with respect to scale and geometry. The geometry of the reactor is dominated by the requirements for effective filtering of solid materials.

The description of the process starts with the (first) introduction of Cu(I)$_2$O in the reactor. Liquid benzoic acid is fed to the reactor and the Cu(I)$_2$O dissolves. Thereafter chlorobenzene is fed continuously and the catalytic cycle begins. In addition a small amount of steam is fed to compensate the loss of H_2O via the offgas.

The reaction rate is controlled by the amount of CO_2 in the dried offgas which can easily be monitored. Specific cooling will avoid both plugging of the offgas system with benzoic acid and emission of chloro benzene and benzene to the environment.

The reaction rate (CO_2 production!) will go down as Cu(I) chloride precipitates. At a preset value, the feed of chlorobenzene is stopped to drive the reaction to completion with respect to chloro benzene. The (verified) idea is that thermal decomposition of Cu(II) benzoate goes to completion, creating a relatively large excess of Cu(I) benzoate for the amount of chloro benzene left in the reactor, after stopping its feed.

After removal of the liquid reaction mass from the reactor, a NaOH solution is introduced to convert the Cu(I)Cl into $Cu(I)_2O$ and an almost saturated NaCl solution. The amount of soluble Cu in the NaCl solution is controlled with the pH. At pH = 13, $\Sigma[Cu]_{liq} < 1$ μmol/l. After removal of the NaCl solution, the process is ready for a new cycle.

The liquid reaction mass from the reaction is cooled to about 140°C and mixed with toluene, prior to an extraction with H_2O. The remaining Cu(I) in the reaction mass is extracted to the aqueous phase and subsequently converted to insoluble $Cu(I)_2O$. After separation of the phase, the aqueous phase is also brought to pH = 13 to ensure no soluble Cu is left. This $Cu(I)_2O$ can be recycled to the reactor.

In principle the toluene phase can be worked up by distillation to yield a variety of products: benzene, toluene, phenol and benzoic acid. However, apart from the recovery of toluene and benzoic acid, this is not an economically attractive option, so benzene and phenol will be burned.

Most unit operations described consist of proven technology, using existing knowledge on Dow-Phenol technology.

A PFD of the whole process is available on serious request, including overall mass balances, energy requirements and a complete equipment list, including a specification for the materials of construction. Of course the process can be adapted to need the constraints of specific waste streams.

3.6. Generic economics

An economic estimate (greenfield situation) of the integral cost/t to detoxify chloro benzene, was made, including fixed and variable cost, depreciation and ROI = 20%. The overall economics are based on a estimate of the full investment cost and current practice on labour, maintenance, etc. of Dow-Phenol Technology.

The o.o.p cost are about US$ 2000/t, which leads to an integral cost price, including ROI = 20%, of about US$ 5700. By increasing the capacity from 500 t/year to 5000 t/year, the o.o.p cost reduce to about US$ 1400/t and integral cost of US$ 2700.

In the Netherlands the current price for the conversion of chlorinated waste (maximum chlorine content: 5.0 m/m %, process scale > 50 000 year t!) is about US$ 3900/ton. Thus even at the present small scale of 500 t/year, the new technology is fully competitive. Brominated waste can not be converted until now, however, this new technology can do it, even in the presence of chlorinated compounds, without changes in the process.

Since the variable cost (mainly the conversion of benzoic acid to phenol) of the proposed new process are directly proportional to the halogen content, the o.o.p cost will not decrease on increasing chlorine content, however, they will decrease for brominated compounds directly related to the difference in molecular weight between chlorine and bromine.

4. Main conclusion

Copper catalysed reduction of halogenated aromatic hydrocarbons under Dow-Phenol conditions, is a very promising environmental technology, from the point of view of the chemistry, the technology and the process economics.

Acknowledgements

The author likes to express his special thanks to Mrs. M. van Asten-Broeders for her contribution to the chemical experiments and to Mr. R. Schraa for his contribution to the process development.

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