

# The mechanism of phenol formation in the Dow Phenol Process

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## Abstract

The Dow Phenol Process utilises toluene as feedstock. In two separate steps, toluene is first oxidised to benzoic acid; thereafter benzoic acid is converted to phenol, using copper benzoate as the principal catalyst. The latter reaction, extensively described by Kaeding, is the so-called Dow Phenol reaction. Recent work at DSM Research showed remarkable differences in product distribution, kinetics, and influences of solvent and cocatalyst. The accepted mechanism of the Dow Phenol reaction described it as two separate single electron transfers by a pair of Cu(II) ions in a radical cage process with regiochemistry control via a flat six-membered ring. Based on all available data, however, the reaction could be better described as an electrophilic aromatic substitution on benzoic acid or benzoate as substrate, and the benzoyloxy cation as electrophile. The electrophile most likely originates from the thermal decomposition of the typical paddlewheel structure of a dinuclear Cu(II) carboxylate. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Phenol formation; Dow Phenol Process; Toluene

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## 1. Introduction

### 1.1. Thermal decomposition of Cu(II) benzoate

Dow Phenol chemistry has a very long history. In 1845, Ettling [1], Stenhouse [2], and List and Limpricht [3], independently investigated dry distillation of benzoic acid in the presence of CuO. They found some salicylic acid among the main reaction products which were called “neutrals” since they could not be dissolved in diluted caustic. It is remarkable that the name “neutrals” has survived more than

150 years of history, and still is a common description for certain side products in the Dow Phenol Process.

In the following decades, the pyrolysis of Cu(II) benzoate was further investigated. In 1880, Smith [4] synthesised salicylic acid from Cu(II) benzoate and water at 180°C under pressure. He also found that Cu(II) benzoate was converted in Cu(I)<sub>2</sub>O. At temperatures between 200 and 300°C, Schrader and Wolter [5] found Cu(I)<sub>2</sub>O and metallic Cu. The reaction products had the characteristic smell of phenol.

A hundred years after the first attempts, Kanevskaya and Shemyakin [6], and Bamdas and Shemyakin [7,8] made a more or less accurate analysis of the pyrolysis of Cu(II) benzoate at 180–200°C. He found 16% benzoic acid an-

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hydride, 28% benzoic acid, 8% phenyl benzoate, 1.4% phenol and a trace of Cu salicylate.

## 2. Transformation into the Dow Phenol Process

The scope of the research changed dramatically with the appearance of a series of patents on the production of phenol, soon to be followed by numerous publications [9–18] on specific aspects ranging from mechanistic chemistry to general process description.

Thermal decomposition of Cu(II) benzoate was still considered as a crucial part of the catalytic cycle, but was almost only studied in combination with all other reactions, like regeneration of Cu(II) benzoate, hydrolysis of ester intermediates, and formation of side products.

The reaction showed a broad scope. From results of experiments with *meta* and *para* methyl benzoic acids, it was concluded that the hydroxy group in the phenolic product was introduced *ortho* adjacent to the carboxyl group of the parent benzoic acid [9,10].

The formation of phenol was thus rationalised as a regiospecific coupling of two benzoic acid molecules via a flat six membered ring Transition State, leading to salicylic benzoate. The latter undergoes facile decarboxylation and hydrolysis, to yield phenol. Second order kinet-

ics were reported for the coupling [9,10]. Fig. 1 shows the geometric quintessence of the Transition State of the Thermal Decomposition, as described above.

Thermal decomposition of *basic copper benzoate*, Cu(II)(OH)(benzoate), yielded almost exclusively salicylic acid, and for some time Kaeding stated that this reaction was the main route to phenol in the process [12]. A serious amount of work [14,15] was focused on salicylic acid, and its conversion into phenol. However, later Kaeding turned back to the original proposal, starting from normal Cu(II) benzoate, without further explanation [16–18] for his change.

First serious proposals concerning the nature of the reaction, in addition to the proposed geometry of the Transition State, were made by Toland [11], and by Schoo [13].

Toland proposed a nucleophilic attack of a benzoate to the *ortho* position of the adjacent benzoate, followed by a two-electron transfer to one Cu(II) ion to yield a Cu(0) species, which in turn was oxidised by a second Cu(II) ion leading to two Cu(I) ions.

Schoo favoured a radical cage process with two separate single electron transfers to two Cu(II) ions.

Kaeding et al. [18], reluctant about the nature of the reaction, eventually agreed with Schoo; however, uncertainties did remain.

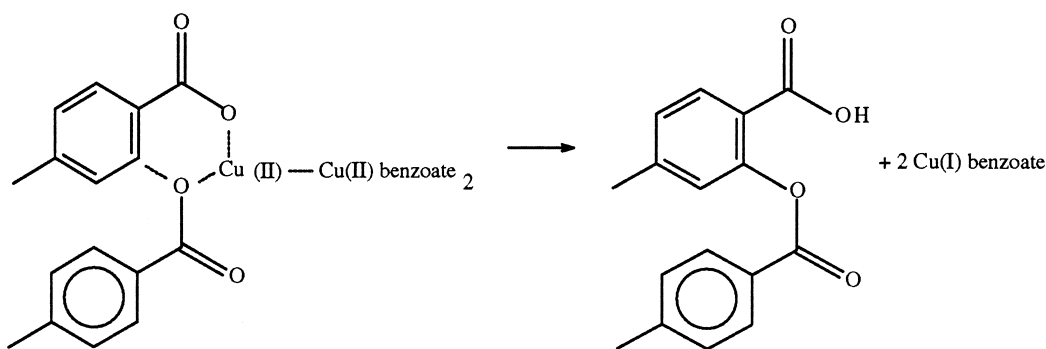


Fig. 1. Geometry transition state of thermal decomposition of Cu(II) benzoate [9,10].

The final scheme of Kaeding is shown above in Fig. 2. A striking difference of this representation compared to the first one, is the apparent ignorance of the dimeric nature of Cu(II) benzoate. Furthermore his reasoning in favour of a radical process, instead of a kind of heterolytic process, is quite confusing. It was stated [18] that thermal decomposition of Cu(II) benzoate and decomposition of dibenzoyl peroxyde in the presence of toluene, showed similarities in substitution pattern; however, no similarities are actually observed.

The latter is indeed a radical process, and shows the usual isomeric distribution with a preference for *ortho*-products. But thermal decomposition of Cu(II) benzoate in the presence of toluene shows a distinct preference for *meta*-products!

This can hardly be explained by the radical *cage* character of the reaction, because the reaction with toluene was stated to occur not in the cage.

With this final contribution of Kaeding, closely related with the early development of the Dow Phenol Process, virtually all mechanistic research came to a preliminary end.

Still the chemical performance in the real plants over the years showed a remaining serious negative discrepancy both with the current labresearch, and the research reported by Kaeding. This was contributed to the difficult experimental access to realistic process conditions, and rather huge scale effects, also including process recycles.

The rapid development of experimental and analytical equipment, and progress in mechanis-

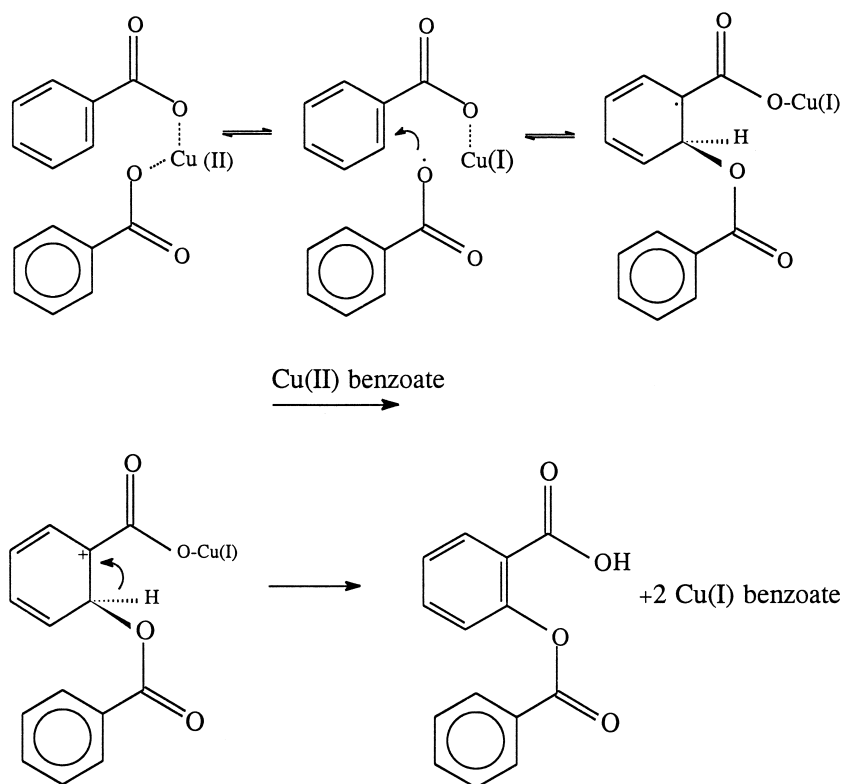


Fig. 2. Final reaction scheme of thermal decomposition of Cu(II) benzoate according to Kaeding et al. [18].

tic chemistry evoked, and enabled, new interest in the mechanism of the Dow Phenol reaction.

### 3. Experimental

#### 3.1. Equipment

All experiments were carried out in a reaction vessel (250 ml) equipped with a mechanical stirrer (1200 rpm), a N<sub>2</sub>/steam inlet (1.5 Nl/h) under the liquid surface with a flow control, a gas outlet leading to a condenser (oil heated;  $T = -5^{\circ}\text{C}$  above the melting point of (substituted) benzoic acid, and a sample point, also used for temperature metering. The reaction vessel was heated with an oil bath.

#### 3.2. Experimental procedure

The reaction vessel was filled with 100 g of (substituted) benzoic acid under a nitrogen flow. After adjusting the above mentioned control systems, the experiment was continued. Stirring was started only on complete melting of the (substituted) benzoic acid to avoid severe damage. Next, the desired amount of Mg(II) benzoate could be added to the melt, because it is inert and dissolves rapidly above the melting point of the benzoic acid. Then the appropriate amount 3–5% of Cu (by weight) could be added. In case of Cu(II) benzoate, it was carefully added to the melt at reaction temperature. In case of Cu(II)O, the addition was done below 200°C, followed by raise of temperature to the reaction temperature (220–230°C).

*Warning:* this procedure is safer as doing it the other way around because Cu(II)O dissolves vigorously from approximately 210°C. The experimental error is acceptable because normally it takes a few minutes only after dissolving Cu(II)O to reach reaction temperature.

During reaction at regular time intervals, samples were taken and analysed by HPLC. Alternatively, CO<sub>2</sub> was absorbed in a wash column and quantitatively determined by titration using standard techniques and equipment.

This procedure was also used in kinetic runs. Specific attention was given to residence time distribution of the offgas system because this can be a serious source of errors in the kinetics. Plug flow of the offgas stream could be established.

#### 3.3. Reversed phase HPLC

One hundred fifty milligrams of solidified reaction mass sample was first dissolved in 15 ml DMF, and thereafter diluted to 100 ml with a 20/80 v/v mixture of acetonitrile/0.05 M phosphate buffer pH = 3.

The samples were analysed on a HP 1090 A system with an ET 280/8/4 Nucleosil 120-5-C18 column at 40°C, using a gradient system moving from 20/80 v/v acetonitrile/0.05 M phosphate buffer pH = 3, to 80/20 v/v acetonitrile/0.05 M phosphate buffer pH = 3, and finally backwards. A DAD was used for detection. The method can be optimised for the different substrates.

#### 3.4. Materials

All (substituted) benzoic acids, and Cu(II)O, were obtained from regular companies and used without further purification. Cu(II)- and Mg(II) benzoates were prepared using standard methods. *Ortho*-, *meta*-, and *para*-coupling products were independently prepared in situ from the corresponding acids (excess!), hydroxy acids, and phenols by removing water with a N<sub>2</sub>-stream at reaction temperature. Analytical data of both samples proved to be identical.

## 4. Results

#### 4.1. The influence of solvent composition on the regioselectivity of thermal decomposition of Cu(II) benzoate

Thus far, it was generally accepted that the initial selectivity of the Dow Phenol reaction to

*ortho*-coupling in a benzoic acid environment was close to 100% [18,19]. Reinvestigation of that work showed a different picture. In a first series of experiments, it was shown that the *ortho*-selectivity was very susceptible to the exact solvent composition. Table 1 lists the results.

In a virtually water-free benzoic acid solution, the *ortho*-selectivity is only about 50%. Surprisingly, the remaining 50% consists of 45% *meta*-benzoyloxy benzoic acid and 5% *para*-benzoyloxy benzoic acid. The presence of Mg(II) benzoate leads to an increase of *ortho*-product to 71%, a decrease of *meta* to 26%, and a decrease of *para* to 3%, irrespective of Mg(II) concentration. The co-presence of neither 1% benzoic acid anhydride (not shown) nor 5% xylene, with Mg(II) benzoate did not have any effect on the observed selectivities.

If, instead of starting from Cu(II) benzoate, Cu(II)O was used as a copper source, an increase of *ortho*-selectivity to 90%, a decrease of *meta*-selectivity to 6%, and an increase of *para*-selectivity to 4% was observed. Further experiments showed that in this case the initial selectivity to salicylic acid was > 94%, eventually dropping to 87%. Starting from Cu(II)O, in the presence of Mg(II) benzoate, *ortho*-selectivity raised to almost 100%, phenyl benzoate and phenol being major products. Only in experiments using Cu(II)O, *ortho*-selectivity was related to salicylic acid.

When a steam flow was lead through the solution, the *ortho*-selectivity was increased to 84%; however, phenyl benzoate was the major product. The addition of Mg(II) benzoate to this system lead to a further increase of the *ortho*-selectivity to > 99%, independent of conversion.

Summarising, it can be said that very small amounts of water, the source of Cu, and Mg(II) benzoate have a great influence on the observed initial selectivities.

#### 4.2. Kinetics of thermal decomposition of Cu(II)benzoate

A series of kinetic experiments were performed on the system consisting of Cu(II) benzoate, and Mg(II) benzoate. A steam flow was used to maintain a constant [H<sub>2</sub>O] in solution. A full kinetic analysis however would require an additional paper. Therefore only main results will be presented. Fig. 3 shows a typical example of a thermal decomposition run.

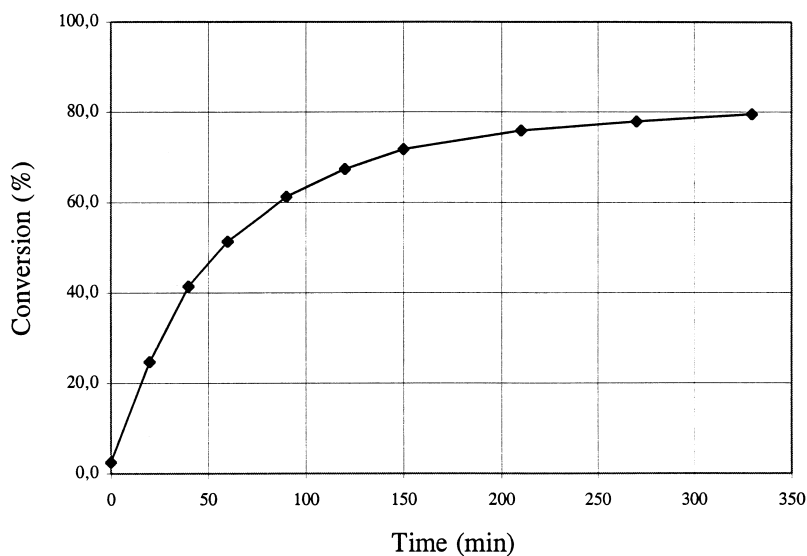
The conversion was based on the cumulative CO<sub>2</sub>-production in time, corrected for differences in *ortho*-selectivity etc. by HPLC. The range of [Cu(II)] was from 0.5–5.0 (w) %, and for [Mg(II)] from 0.1–5.0 (w) %. The temperature was varied between 210 and 230°C.

No simple first- or second-order kinetics was observed. Instead of that, the reaction could be described only by a assuming a rapid monomer/

Table 1

Influence of solvent composition on the regioselectivity of thermal decomposition of Cu(II) benzoate:  $T = 220^{\circ}\text{C}$   $P = 1$  bar

Solvent system	Product composition: (trivial) names		
	% (mol/mol);	Orientation to initial COOH group	
Benzoic acid with:	<i>ortho</i>	<i>meta</i>	<i>para</i>
1% Benzoic acid anhydride	49.4	46.1	4.5
2.5% Mg(II) benzoate	70.6	26.4	3.0
4.5% Mg(II) benzoate; 5.3% xylene	71.2	25.7	3.1
Start Cu(II)O	90.5	5.7	3.8
Start Cu(II)O; 3.5% Mg(II) benzoate	99.2	0.8	0.0
Steam flow	83.8	9.6	6.6
Steam flow; 3.5% Mg(II) benzoate	99.4	0.6	0.0



*Ortho*-selectivity: 86%

Fig. 3. Thermal decomposition of Cu(II) benzoate 230 C, steamflow, 0% Mg(II) benzoate.

dimer pre-equilibrium, followed by a relatively slow first-order decay. Using this simple model, measured and fitted curves were almost indistinguishable. The overall activation energy of the

reaction was 44 kcal/mol, roughly equally divided between the two steps. No relation could be established between [Mg(II)] and the pre-equilibrium constant for dimerisation.

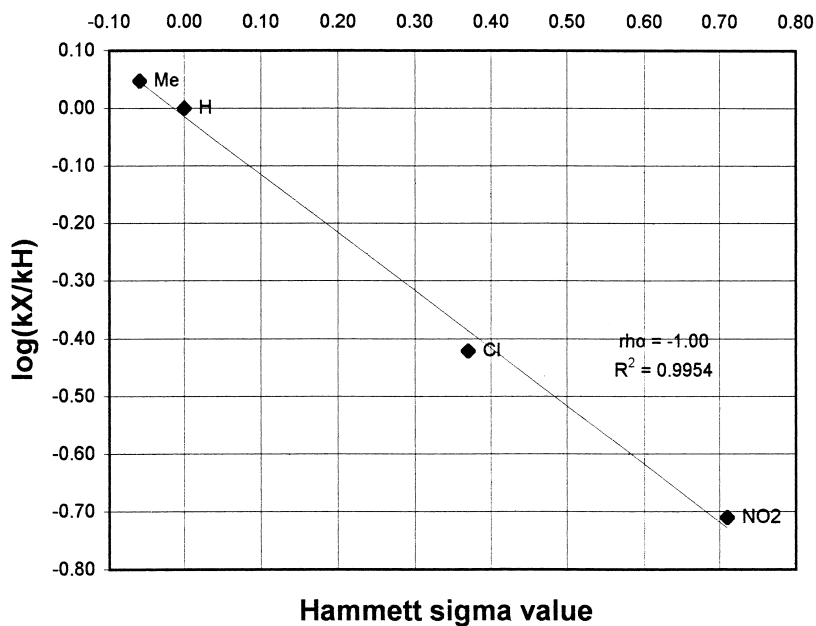


Fig. 4. Hammett plot thermal decomposition of Cu(II) *meta*-X-benzoates 230 C steam flow.

Table 2

Influence of *meta*-substituents on the regioselectivity of thermal decomposition of Cu(II) *meta*-X-benzoates steam flow:  $T = 230\text{ C}$ ,  $P = 1\text{ bar}$

<i>meta</i> -X-benzoate X =	Product composition: (trivial) names				
	% (mol/mol);		Orientation to initial COOH group		
	<i>ortho</i> (2)	<i>ortho</i> (6)	<i>ortho</i> (2 + 6)	<i>meta</i>	<i>para</i>
H	43	43	86	10	4
CH <sub>3</sub>	35	47	82	11	7
Cl <sup>a</sup>	67	32	99	1	0
NO <sub>2</sub> <sup>b</sup>	1	99	100	0	0

<sup>a</sup>Response factor not very accurate; probably more *ortho*(2) product.

<sup>b</sup>Based on CO<sub>2</sub>/*ortho* products molar balance.

### 4.3. The electronic character and the influence of *meta*-substituents on the regioselectivity of the Dow Phenol reaction

A third series of experiments was carried out to obtain a deeper insight in the electronic nature of the actual coupling process. A classical Hammett approach was tried to use despite obvious complications. Firstly the benzoic acid analogues are coupled to each other during reaction, thus acting as donor and acceptor. Secondly the compounds also act as solvent. Finally no comparable  $\rho$ -data exist at this temperature level. On the other hand, it should be realised that in a thermal decomposition the formation of the attacking species is the rate-limiting process.

Fig. 4 shows the Hammett plot obtained, using benzoic acid, *meta*-methyl, *meta*-chloro, and *meta*-nitro benzoic acid as substrates.

At 230°C, the  $\rho$ -value is  $-1.0$ . The correlation seems quite good. Using  $\sigma^+$ -values, an almost identical correlation is obtained with a slightly lower  $\rho$ -value. Correlations are based on initial rates of reaction because *meta*-chloro, and *meta*-nitro benzoic acid undergo reduction by Cu(I), leading to extra Cu(II) thus spoiling kinetics. A  $\rho$ -value of  $-1.0$  is indicative for an electrophilic reaction. Among these reactions are electrophilic aromatic substitutions, like arylations in acetonitrile at 40°C [20]. In combination with the Hammett equation, the observed

regiochemistry with these substrates is another important factor. Results are shown in Table 2.

Due to the presence of a *meta*-substituent, the *ortho*-positions are no longer identical, and can be quite easily distinguished. With the *deactivating* Cl- and NO<sub>2</sub>-group very high overall *ortho* selectivities were obtained, close to 100%. The *mildly activating* methyl-group shows a slightly lower *ortho*-selectivity. Closer inspection showed however striking differences between the Cl- and the NO<sub>2</sub>-group. *Meta*-chloro benzoic acid leads to 67% *ortho*-substitution between the original COOH and the Cl-group, and 32% “*ortho*”, which is “*para*” to the Cl.

On the other hand, *meta*-nitro benzoic acid leads almost exclusively (> 99%) to the *ortho*-product which is *para* to the NO<sub>2</sub>-group.

## 5. Discussion

### 5.1. Differences with the work of Kaeding

The striking difference in selectivity of the Dow Phenol reaction between the work of Kaeding and the work reported here, might be explained partially, but most will remain in the mist of time. One plea could be the earlier mentioned focus of the research towards a phenol *process*, thus concentrating on circumstances yielding almost 100% initial *ortho*-selectivity.

Indeed it is true that under usual (lab) conditions, using air/steam mixtures and the cocatalyst Mg(II), an almost 100% initial *ortho*-selectivity is obtained. However, already small deviations cause serious changes in the reaction pathway.

Another important issue with respect to this discussion is the difference between the Salicylic Acid reaction, the Dow Phenol reaction, and the Ester reaction. Though Kaeding actually made this discrimination, and was fully aware of the differences [9,11,18], it did not have any consequence for his description of these reactions. They were all treated in merely the same way [18]. In case of the Dow Phenol reaction and the Salicylic Acid reaction, exclusive *ortho*-selectivity was rationalised by the flat six-membered ring Transition State with strong radical-cage character. In case of the Ester reaction, a certain preference for *meta*-selectivity was explained by a kind of free radical process with sterical hindrance of the substituent. As stated in the introduction, this is quite confusing, and not consistent.

The reported finding here of substantial *meta*-selectivity in the thermal decomposition of Cu(II) benzoate in a benzoic acid environment, almost definitely rules out Kaeding's explanation of *ortho*-selectivity via a flat six-membered ring Transition State.

The results obtained in the thermal decomposition reactions, starting from Cu(II)O could be nicely explained by the Salicylic Acid reaction. However, kinetic and mechanistic studies are still difficult to perform and interpret due to the rapid loss of water, and conversion to normal Cu(II) benzoate. At 230°C, using nitrogen/steam = 50/50, the equilibrium concentration of H<sub>2</sub>O is about 2 mmol/l only. On ranging the [Cu(II)] from 150–900 mmol/l, no effect was observed neither on kinetics nor selectivity. For that reason, it was concluded that the Salicylic Acid reaction has no practical meaning for the Dow Phenol Process. This might be the explanation for Kaeding's return to the normal Dow Phenol reaction, the coupling of two benzoic

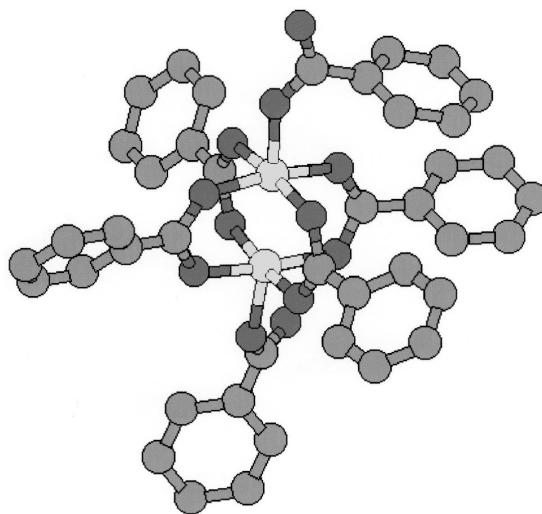


Fig. 5. Typical paddlewheel structure of Cu(II)<sub>2</sub>benzoate<sub>4</sub>.

acid molecules. Still the effect of a small amount of water is dramatically. It will be discussed in more depth in the next part.

## 5.2. Alternative explanation

Thus far, no attention was paid to the structure of Cu(II)benzoate. Generally the (crystal) structure of Cu(II) carboxylates is built up from so called dinuclear paddlewheels<sup>1</sup> [21]. Paddlewheel structures of metal carboxylates are very common, and not restricted to Cu(II)carboxylates [22].

Fig. 5 shows the typical paddlewheel structure of Cu(II)<sub>2</sub>benzoate<sub>4</sub>. The structure shown, was obtained by molecular modelling,<sup>2</sup> starting from the crystal structure, and investigating the effect of rotating the phenyl groups of all benzoates.

Four benzoates act as didentate ligands, equatorially coordinated to the two Cu(II) ions.

Cu–O<sub>eq</sub> distances are 1.946 Å. Cu–O<sub>ap</sub> distances are 2.191 Å. The Cu–Cu distance is 2.609 Å. Most relevant angles around Cu are

<sup>1</sup> Established by a search in the Cambridge Structural Database (1994).

<sup>2</sup> The results of a modelling study on this subject will be reported separately.



close to 90 degrees. The *trans*  $O_{eq}-Cu-O_{eq}$  angle, however, is 168.9°.

In such paddlewheel structures, the second lone pair of coordinated oxygens can coordinate to a Cu of another paddlewheel in the apical positions. In that case stepped polymeric structures can be obtained. See Ref. [23] for an example. It is generally accepted that all anhydrous Cu(II) carboxylates can adopt such structures.

In a close collaboration of DSM Research with Prof. J. Reedijk, Agterberg [24] showed, using rapid freeze-EPR, that a solution of Cu(II) benzoate in benzoic acid at 220°C contained mono nuclear, paddlewheel, and polymeric Cu(II) species. However in the presence of Mg(II), mono nuclear Cu(II) species seemed to be the only detectable species, irrespective of [Mg(II)].

The presence of (low amounts) of dinuclear Cu(II) benzoate paddlewheels in benzoic acid solution at 220°C, combined with the observed kinetics, the Hammett  $\rho$ -value of  $-1.0$ , and the observed trends in regiochemistry of the thermal decomposition of *meta*-substituted Cu(II) benzoates, lead to the idea to describe the Dow Phenol reaction as an electrophilic aromatic substitution.

The rapid pre-equilibrium in the kinetics could be interpreted as the formation of a dinuclear Cu(II) benzoate paddlewheel, required to perform the rather slow (first order) two-electron oxidation to the benzoyloxy cation. The benzoyloxy cation then reacts with a benzoic acid moiety.

The huge effect of a very small amount of water both on kinetics and selectivity might be explained by the relative ease of proton release of the resulting  $\sigma$ -complex. The almost exclusive formation of phenylbenzoate instead of salicylic benzoate could be explained in the same way: proton transfer to  $\alpha$ -C of the salicylic benzoate is greatly eased by the presence of  $H_2O$ .

Furthermore, the different selectivities obtained in the first series of experiments could

now be explained in terms of benzoic acid versus benzoate. Theoretical calculations (6–31  $G^*$ ) showed that the HOMO of benzoic acid has an almost equal density on the *ortho* and *meta* position, while the HOMO of benzoate indeed is more directed to the *ortho* position. <sup>2</sup>

The differences found in the *ortho*-selectivity of the thermal decomposition of *meta*-substituted benzoates, could be explained with the so-called Reactivity–Selectivity Principle: the less reactive *meta*-substituted benzoic acids should show a higher *ortho*-selectivity [20].

So, using the concept of electrophilic aromatic substitution enabled by a dinuclear Cu(II) carboxylate paddlewheel structure, no flat six-membered ring Transition State is needed to explain the observed selectivities.

The results obtained by Kaeding in the *Ester-reaction* with substrates like toluene, and diphenyl ether with their preference for *meta*- and *para* adducts, as well as the results obtained with *meta*-nitro benzoic acid with its preference for *ortho*(6)-product should still be considered as an indication for a sterical factor, apart from the electronics, discussed so far.

An obvious possibility for such a sterical factor, is the apical position in the Cu(II) benzoate paddlewheel structure: the distance of an attacking  $O_{eq}$  to the *ortho*-C of the apical benzoic acid is 3.4 Å only, and to the *meta*-C it is about 3.8 Å (Fig. 5). By doing this, the Dow Phenol reaction and the Ester reaction could be unified as one reaction, in a consistent way.

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