

REACTIONS OF ARYLHALIDES ON COPPER SURFACES (ULLMANN REACTION) INVESTIGATED
BY SURFACE FTIR SPECTROSCOPY

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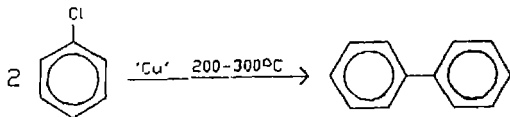
ABSTRACT

The coupling of bromobenzene to biphenyl on specially prepared copper was monitored by surface FTIR spectroscopy. The inhibition of this reaction was observed by addition of ethanolamine.

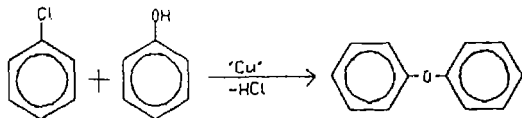
INTRODUCTION

The formation of halogenated dibenzodioxines and -furanes during technical incineration processes, like municipal waste incineration (MWI), are controlled by catalytic processes on the surface of fly-ash particles in the post-combustion zone (1). As catalytically active components of the fly-ash, produced during MWI, copper species have been proposed (1), which are known to promote aryl-aryl coupling (2) and bisarylether formation (3).

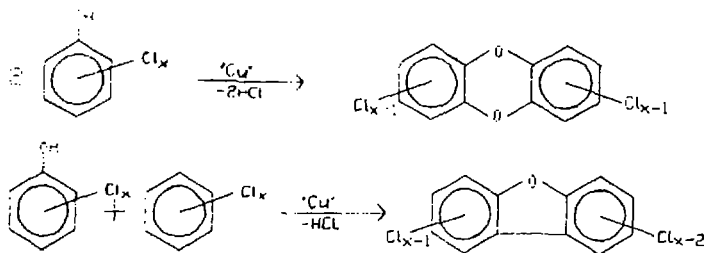
Aryl-coupling (Ullmann I reaction):



Bis-aryl-ether formation (Ullmann II reaction):



Both heterogeneous reactions could be responsible for the formation of PCDD/F from PCB (polychlorinated benzenes) and PCP (polychlorinated phenols) present in the stack gases (4), as may be seen from the following equation:



Recently methods have been developed to block the catalytic activity of fly-ash particles by using the technique of inhibition (5).

EXPERIMENTAL

To increase our understanding of these surface reactions, we have used diffuse reflectance FTIR spectroscopy (DRIFT) to investigate the reactions of arylhalides on well defined, highly disperse copper samples supported on alumina. The catalysts were prepared from aluminium hydroxide and copper nitrate (10%), according to the procedure described in the Ref. (6). The apparatus is shown Fig. 1.

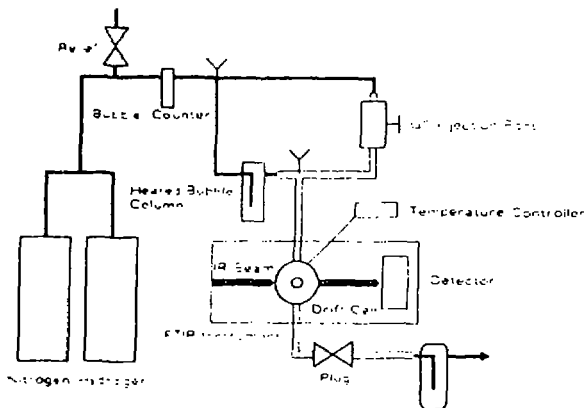
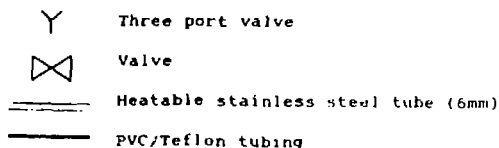


Fig. 1 Apparatus for detection of surface reactions on supported copper



Bromobenzene was added continuously by evaporation from a small vessel, filled with the neat liquid. Nitrogen was bubbled through the solution at a constant rate (35 cm³/min.). Gaseous bromobenzene was partly trapped on the copper surface, preheated to 200°C (+/- 2°C). The reaction was followed by FTIR spectroscopy. The reactant dosing system and the observation chamber are a modified version of the system described by Jobson et al. (7).

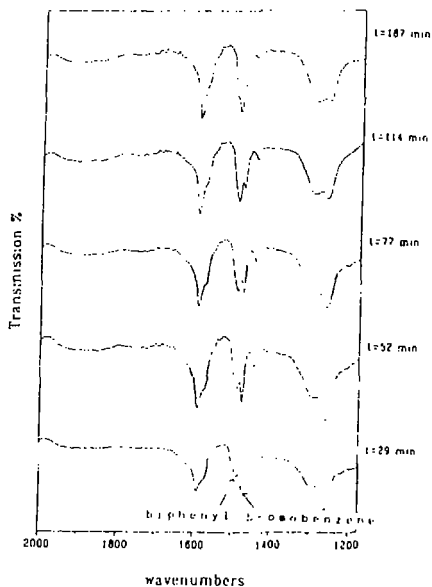


Fig.2 Time dependent IR spectra observed during the continuous addition of bromobenzene, see text

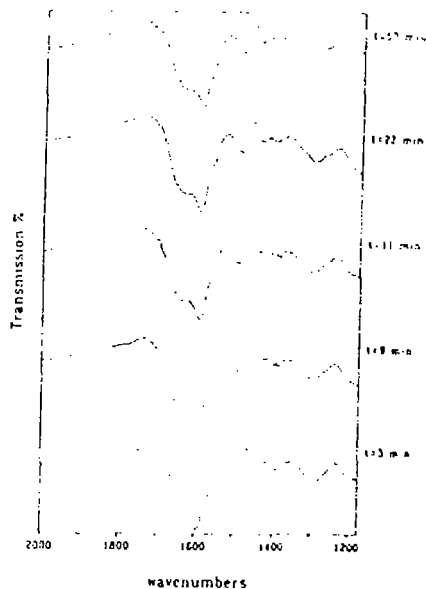


Fig.3 Continuous addition of bromobenzene, followed by pulsewise addition of 5 μ l of ethanolamine at t=0.

Effect of Ethanolamine as a Model for Inhibition:

We have investigated the effect of ethanolamine added to the surface during the reaction. This compound was delivered to the surface by injection small volumes of the liquid (5 μ l) into the carrier gas stream. The effect of this addition is observed by the time dependent FTIR spectra, cf. Fig.3. The amount of the reaction product, biphenyl, is decreased, as monitored by the typical band at 1481 cm⁻¹. Furthermore, some additional bands in the region of 1620-1680 cm⁻¹ due to special surface inhibitor reaction products can be observed. Species like protonated amines, aldehydes or imines bound to the surface of the copper or alumina are likely to be responsible for this bands.

SUMMARY

The experiments demonstrate that the Ullmann I reaction (bis-aryl formation) can be observed by DRIFT spectroscopy in the reaction of bromobenzene on carefully prepared copper catalyst surfaces. The addition of ethanolamine results in an inhibition of this reaction.

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