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# On the possible role of acetylene in gas-phase dioxin formation

Mariusz K. Cieplik, Maria Cairols Oviedo, Robert Louw\*

Center for Chemistry and the Environment, Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands

## Abstract

The slow combustion of benzene/phenol gives rise to dibenzofuran (DBF) as major product of incomplete combustion, with negligible proportions of dibenzo-*p*-dioxin (DBD), or benzofuran (BF). Contrary to a recent proposal that acetylene growth reactions, e.g.  $BF \rightarrow DBF$ , are important in dioxin formation, co-combustion of benzene/phenol with acetylene – around 550°C – did not alter this product pattern. Also, BF was identified as a product from degradation of DBF. © 1999 Elsevier Science Ltd. All rights reserved.

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## 1. Introduction

Acetylene growth is an important pathway in gasphase PAH formation and sooting. Model reactions proposed by Frenklach et al. (1985) were adopted and paraphrased by Huang and Buekens (1998) for an oxidative environment where dibenzo-*p*-dioxins and dibenzofurans, commonly named dioxins, are formed. In their proposed model set of reactions, the pertinent steps can be represented as shown in Schemes 1 and 2.

Computer modeling by said authors with a selfwritten PASCAL-operated program gave results matching experimental outputs reported by Kanters for the slow combustion of phenol, with excess of oxygen (Kanters, 1996), with respect to the formation of DBF. However, in their model, the rate constant for addition of phenoxy radical to acetylene, the first step to DBF (Scheme 1), was taken equal to that for the analogous, rapid reaction of phenyl radical. This is probably a gross overestimation, as explained below. In addition, the possible reversal of the addition of phenoxy radical to acetylene was not taken into account. Anyway, acety-

\*Corresponding author. Tel.: +31-71-527-44-98; fax: +31-71-527-44-92. lene growth was advanced to be a rather important pathway in gas-phase dioxin/furan formation (Huang and Buekens, 1998). Indeed, Kanters' reaction did yield some acetylene also, but DBD could not be found.

In their model Huang and Buekens ignored the fast reaction of phenyl radical with oxygen to yield phenoxy radical (Frank et al., 1994), which can give rise to dibenzofuran upon recombination with another phenoxy radical (Grotheer and Louw, 1998).

We decided to investigate the possible role of acetylene in the slow combustion of benzene and phenol, to check the Huang–Buekens hypothesis. The combined slow combustion of benzene/phenol in the presence of acetylene can also serve to see if the latter hydrocarbon, by analogy, produces intermediate  $C_2$ -oxy radicals capable of (cross)combining with phenoxy radicals to give, e.g. BF, the key intermediate to DBF in the Huang–Buekens mechanism.

# 2. Experimental

# 2.1. Chemicals

The following chemicals have been used as such: phenol (Merck p.a.; 99%); dibenzofuran (99% purity by

E-mail address: r.louw@chem.leidenuniv.nl (R. Louw)



Scheme 1. Postulated formation of dibenzofuran (DBF) (Huang and Buekens, 1998).

GC, synthesised); benzene (Merck p.a.; 99% (distilled)); acetone (Acros p.a. (>99.5%)); monobromobenzene (Baker; >99%); acetylene (Air Products; 98% (ca. 1% acetone)); methane (Air Products; 99.5%), nitrogen (Air Products; 99.999%), oxygen (Air Products; 99.6%).

#### 2.2. Apparatus

The experimental setup is depicted in Fig. 1.

The operating procedure was the same in all experiments and consisted of the following main stages:

- First, the setup was heated to the required temperature under a slow stream of nitrogen. Then, flows of the bulk gases, nitrogen and oxygen, were increased to the desired values.
- After stabilizing these flows a 'zero' gas sample was analyzed to check if the levels of CO and CO<sub>2</sub> were near baseline, proving that there were no leaks, and no burn-out of left organics or deposits. These backgrounds, where found, were subtracted from the concentrations measured during the experiment.
- Next, the substrates were led into the reactor; the collecting time was measured from the moment the liquid substrates entered the evaporator (number 9 in Fig. 1).
- The experiment was finished by ending the inflow of substrates, while continuing the flow of carrier gases for another 5 min to allow the residual substrates and products to properly elude to the cold trap.
- The cold trap was then detached from the setup and the liquid samples were treated as described below.

# 2.3. Analysis

The liquid product of each experiment, collected in the cold trap, was analyzed by gas chromatography using monobromobenzene as an internal standard (ca. 0.1 g per sample). GC–MS (on a Hewlett Packard 5890 GC equipped with a HP 5872 MSD, scan mode (MM range 30–350), with a standard NIST NBS75 spectra library) both in split/splitless modes for maximum resolution, provided product identification. Quantitative analyses were done by gas chromatography on a Hewlett Packard 5890 GC, equipped with a capillary column (Chrompack, CP-SIL 5 CB, 50 m  $\times$  0.32 mm  $\times$  0.4 µm) and an FID detector. The standard injection volume was 0.2 µl.

To express the amounts of the compounds in timedependent units [mmol/h], the results were divided by the collecting time of the liquid sample.

Gas samples were analyzed for  $C_1/C_2$  compounds online by means of a Packard model 438 A GC, equipped with a packed column (Alltech, Carbosphere, 86-100 MESH), an FID detector and a methanizer. In this case methane was utilized as an internal standard at the flow of ca. 2 mmol/h.

Analyses were carried out using the following parameters: initial temperature 150°C, initial time 2 min, rate 20 °/min, final temperature 280°C, final time 20 min, injection port temperature 280°C, injection volume 0.5 ml. The column head pressure was kept constant throughout at 100 kPa.

## 3. Results

The experimental conditions and outputs of products are summarized in Table 1.

Experiments with acetylene have been performed at three different temperatures. For comparison, runs involving benzene/phenol only have also been conducted. The reactivity of benzene has been evaluated on the basis of data from slow combustion of benzene only (Wiater et al., 1999) and was concluded to be of little influence on our target chemistry.

Substrates (phenol or dibenzofuran), were introduced as benzene solution with molar ratio 10:1 by means of the motorized syringe (number 1 in Fig. 1).

Based on introductory runs not specified here, the experimental parameters (residence time,  $O_2$ /aromatics ratio, flows, etc.) were optimized. Here we show the average results for every temperature studied. Standard deviation in the products' outputs in different runs at the same temperature, did not exceed 5% of the values.

The oxygen and nitrogen flows were kept constant throughout at 30 and 150 mmol/h, respectively. Residence times in the reactor, based on the volume flow of the gases and corrected for the temperature used were 10-12 s.



Scheme 2. Postulated formation of dibenzo-p-dioxin (DBD) (Huang and Buekens, 1998).



Fig. 1. Schematic representation of the experimental setup.

At ca. 500°C (experiment (I)) little reaction occurs; acetylene is still almost as inert, as is benzene. The incomplete recovery of benzene is due to some of it having passed the cold trap – a phenomenon observed also in our previous studies. DBF is clearly formed, substantiating some conversion of phenol, estimated to be ca. 10% (mol). In experiment (II) at ca. 540°C, the reaction of acetylene is measurable and that of phenol

substantial. DBF is found in amounts of ca. 3% (mol) on converted phenol.

At 590°C (experiment (III)) some 75% of acetylene has reacted (burnt). Benzene recovery is less than 50% and the output of phenol is about one-half of the original level. Although phenol is more reactive than benzene, it is now being produced from the latter at a perceptible level. Altogether this experiment combines

Table 1	
Summary of experimental conditions and result	ts

	Experiment no.						
	Ι	II	III	IV	V		
<i>T</i> (°C)	502	538	590	550	580		
Substrates' inputs (mmol/h)							
Acetylene	2.52	3.92	2.52	-	_		
Benzene	3.32	4.14	3.33	4.16	3.95		
Phenol	0.34	0.42	0.33	0.39	_		
DBF	_	_	_	_	0.355		
Products' outputs (mmol/h)							
Benzene	2.56	2.75	1.00	2.84	2.84		
Phenol	0.29	0.26	0.17	0.20	0.010		
DBF	0.00029	0.0023	0.0021	0.0039	0.224		
BF	nd	nd	nd	nd	0.0027		
СО	0.30	0.34	8.14	0.48	0.47		
CO <sub>2</sub>	0.25	0.20	2028	0.33	0.29		
$C_2H_2$	2.43	3.45	0.61	0.01	0.01		
$C_2H_4$	0.007	0.017	0.145	0.010	0.013		
$C_2H_6$	0.0018	0.0062	0.0026	0.019	0.0052		
Substrates' recoveries (% mol)							
Benzene	77	66	30	68	72		
Phenol	85	62	51	51	_		
Acetylene	97	88	24	_	_		
DBF	_	_	_	_	63		
DBF/BF outputs on converted phenol/DBF (% mol)							
DBF/phenol	1.2	2.8	2.6	4.0	_		
BF/DBF	_	_	_	_	_		

quite substantial degrees of conversion with still wellcontrolled levels of the target reactant species. The output of DBF comprises ca. 2.5% (mol) on the apparent converted phenol.

To compare with product levels in absence of acetylene, a temperature in between those of experiments (II) and (III) was chosen. In experiment (IV) only traces of acetylene were formed as a result of the decomposition of aromatics. Phenol shows an expected degree of conversion. The DBF output is in an absolute sense *higher* than in both experiments with acetylene, (II) and (III), and it comprises ca. 4% (mol) on converted phenol. On the whole, in experiments (I)–(IV) both BF and DBD were below the detection limit, which is equivalent to ca.  $10^{-5}$  mmol/h.

To learn more about the fate of DBF – expectedly of about the same reactivity as benzene – experiment (V) was conducted, using benzene/DBF as the substrate. Both benzene and DBF reacted to a limited degree. The origin of the small amount of phenol can be either from DBF or benzene. Interestingly BF is now positively identified at levels of ca. 2% (mol) on the converted DBF.

#### 4. Discussion

The key steps of the Huang–Buekens model imply altogether three acetylene molecules to add to aromatic species in order to form final products. Logically this pathway should dramatically gain in importance with increasing acetylene concentration. In our case, the flow of acetylene was ca. 1% (mol) of the total gaseous flow and also about equal to that of benzene. This is a value by far exceeding real concentrations in exhaust gases (ppm level, Lemieux and Ryan, 1999). Consequently, if formation of dioxins by reactions as depicted in Schemes 1 and 2 would play even a limited role in real combustion, it should have been clearly observable under our conditions. However, our data show that acetylene has no promotive effect at all on the formation of DBF as compared to the runs without acetylene.

Moreover dibenzo-*p*-dioxin has not been observed in any case, underscoring the unimportance of such multiple acetylene additions. Furthermore *o*-benzoquinone (BQ), the proposed intermediate (Scheme 2) has been shown to be thermally unstable with respect to loss of CO (Schraa et al., 1994).

It is known that phenyl radicals react with  $O_2$  irreversibly, with a rate constant close to the collision frequency (Frank et al., 1994; Sommeling et al., 1993). Also, phenyl radicals react with acetylene, to give phenylacetylene (Frenklach et al., 1985; Fahr and Stein, 1988). Both reactions are depicted in Scheme 3.

Overall rate parameters for both reactions at  $T = 530^{\circ}$ C, are: log ( $k_{\circ}$ , M<sup>-1</sup> s<sup>-1</sup>) = 8.8 (Frank et al.,



Scheme 3. Reaction of phenyl radicals with oxygen and acetylene.

1994);  $\log(k_a, M^{-1} s^{-1}) = 7.9$  (Fahr and Stein, 1988). Note that even if the rate constants of the two reactions were equal, 10% (10<sup>5</sup> ppm), of oxygen in a combustor would make reaction with acetylene even at 100 ppm practically impossible. Hence it is not surprising that phenylacetylene could not be detected in the liquid samples.

A likely conclusion will hold for analogous aryl-type radicals, such as that postulated in Scheme 1 (BF minus hydrogen atom).

In our experiments (I)–(IV) BF, if present at all, was just at the detection limit. If it were an intermediate for DBF, this would imply that its reactivity is very high, much higher than that of phenol, which is unrealistic. Rather, the reverse is true: BF is a degradation product of DBF. This is substantiated by the results of experiment (V).

In summary, we conclude that even in the presence of acetylene, DBF arises via recombination of two phenoxy radicals, as shown in the simplified Scheme 4. The overall rate constant is ca.  $10^{8.3}$  M<sup>-1</sup> s<sup>-1</sup> at 530°C (Grotheer and Louw, 1998). In this respect, the Huang–Buekens model is too simple, and it underestimates the pseudo-equilibrium concentration of phenoxy radicals. In slow combustion, species like hydroperoxy radicals (HOO) are always important (Scheme 5) Dryer and Sawyer (1997) and their participation will lead to the increase of the concentration of phenoxy radicals. Because of the bimolecular nature of the reaction as depicted in Scheme 4, a 30-fold increase in the phenoxy radical concentration would enhance the rate of DBF formation by three powers of ten.

While the Huang–Buekens mechanism cannot be valid under the conditions of slow, homogenous combustion with excess of oxygen, one may argue that reactions as depicted in Scheme 1 can be significant in real combustion, e.g. in oxygen-depleted flamefronts or



Scheme 4. Recombination of phenoxy radicals.



Scheme 5. Reactions of phenol with oxygen-centered radicals.

pockets. Focusing on DBF, phenoxy radicals should then be able at least to add to acetylene with sufficient ease.

We have shown that addition to benzenes requires over 20 kcal/mol (Grotheer and Louw, 1998; Wiater and Louw, 1999); this very slow reaction was made observable by displacement of a Cl or Br substituent. Except metathetical reactions of the type ArO  $\bullet$  +Ar'OH  $\rightarrow$  $ArOH + Ar'O \bullet$  (where Ar stands for an aromatic group), we are not aware of other examples of phenoxy radicals reacting with non-radical organic species. Phenoxy-type radicals are also very unreactive to  $O_2$ , and both characteristics explain why phenols are effective antioxidants in vivo and in vitro. Definitive answers on the possible role of acetylene in the formation of especially DBF, can only be given after further investigations with (labeled) phenoxy radicals and acetylene under conditions representative for pyrolysis with formation of PAH and soot.

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