

# Oxidation of cumene in the liquid phase in the presence of halogen compounds\*

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The amount of phenol forming in the oxidation of cumene in the liquid phase initiated by halides increases with reaction temperature, oxygen pressure, and hydrogen bromide concentration. An addition of pyridine in the reaction system causes a decrease in the amount of the forming phenol which is likely to be a result of the formation of adducts with active bromine atoms. The reaction is poorly selective, and cumyl alcohol and acetophenone are formed as further main products.

Изучалось образование фенола при жидкофазном окислении кумола инициированным галогенидами. Его образование возрастает с температурой реакции, давлением кислорода и концентрацией бромистого водорода и является низко селективным. Добавление пиридина в реакционную систему вызывает понижение образования фенола, вероятно, вследствие образования продуктов присоединения активных атомов брома. Окислением образуются в качестве других главных продуктов куминовый спирт и ацетофенон.

Owing to lability of the tertiary C—H bond, cumene is easily oxidized even under mild conditions by oxygen to give hydroperoxide which is the primary reaction product. Initiators of radicals and metal catalysts considerably accelerate the oxidation and simultaneously favour the formation of other products, especially cumyl alcohol, acetophenone, dicumyl peroxide, and phenol [1].

Phenol is formed as a product of acid-catalyzed decomposition of hydroperoxides using agents of acid character which accelerate the oxidation [2—5]. For instance, hydrogen bromide increases the rate of cumene oxidation [6], but it decomposes the forming hydroperoxide in the subsequent step favoured by acid catalysis and thus inhibits the reaction. In the patent literature [7] we can find procedures for the one-step selective oxidation of cumene to phenol performed in the liquid phase and in the presence of hydrogen bromide. The solvent and the used

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\*Part XII: Oxidation of polyalkyl aromates.  
For Part XI see Ref. [8].

metals play an important role in this reaction. In order to obtain a deeper insight into the role of halides in the oxidation reactions of hydrocarbons in the liquid phase, the influence of the type of halogenides and solvent on the oxidation of cumene from the view-point of the phenol formation has been investigated.

## Experimental

### *Materials*

Cumene, pyridine, and solvents were purified by usual procedures. Bromides and complexes were synthesized according to literature [8]. Bis(1,2-diphenylethylene-1,2-dithiolate)nickel  $\text{Ni}[\text{S}_2\text{C}_2(\text{C}_6\text{H}_5)_2]_2$  was prepared according to [9]. Hydrogen bromide was used in the form of 48% aqueous solution. Other chemicals were of anal. grade purity. They were used without purification.

### *Procedure*

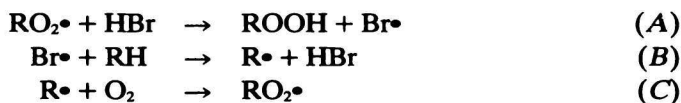
Oxidation was studied in a 50 ml stainless steel reactor which was intensively shaken in a thermostated oil bath. The reactor was connected with a pressure manostat which kept constant pressure in the system and enabled to record the volume of the consumed oxygen. The maximum rate was calculated from the dependence of the consumed oxygen vs. time.

### *Analysis*

After spontaneous stop of the oxidation, the reaction mixture was analyzed by gas chromatography using a Hewlett—Packard 5830 apparatus and 2,6-xyleneol as an internal standard.

## Results and discussion

Besides many other oxidation products, the oxidation of cumene in the presence of halides gives rise to phenol, the amount of which increases with reaction temperature (Fig. 1), oxygen pressure (Fig. 2), and bromide concentration (Fig. 3). These factors substantially enhance the conversion of cumene and reaction rates. The effect of bromides on the increase of the reaction rate is to be explained by the following scheme in which an atom of bromine replaces alkylperoxy radicals in the reaction sequence [10]



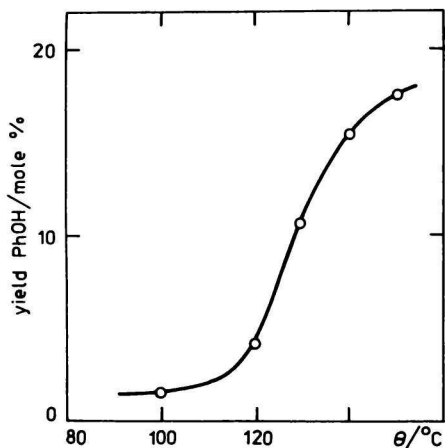


Fig. 1. Dependence of the phenol yield upon temperature.

Conditions: 0.7 MPa total pressure, 5 ml of cumene, 5 ml of AcOH, 0.85 mmol of HBr.

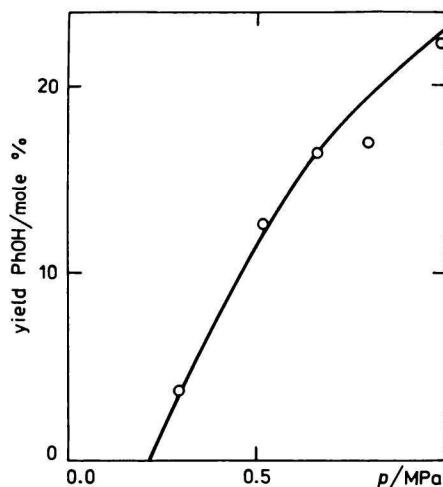


Fig. 2. Influence of pressure on the formation of phenol at 140°C.

Conditions as in Fig. 1.

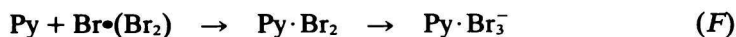
Furthermore higher concentrations of hydrogen bromide result in an acid-catalyzed decomposition of the forming cumene hydroperoxide into phenol. The competitive reaction



causes an inactivation of bromine atoms. It is, however, hindered by a higher concentration of oxygen in the solution favouring reaction (C). That indicates the high positive influence of oxygen pressure. On the contrary, if the concentration of bromine atoms or free hydrogen bromide is reduced by an addition of pyridine, the formation of phenol is suppressed (Fig. 4). Namely pyridine easily reacts with free hydrogen bromide according to the reaction



forming a poorly dissociated pyridinium bromide [11]. In this way, the concentration of hydrogen bromide in the system is reduced and the acid-catalyzed decomposition of hydroperoxide into phenol is prevented. Simultaneously, it affects also the propagation step by removing the reactive bromine atoms [12] which are bonded to pyridine in the form of adducts according to the following reaction



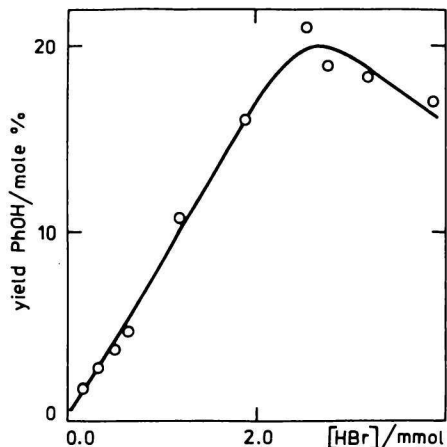


Fig. 3. Influence of hydrogen bromide concentration on the formation of phenol at 140°C and 0.7 MPa.

Cumene : AcOH = 1 : 1 (by volume).

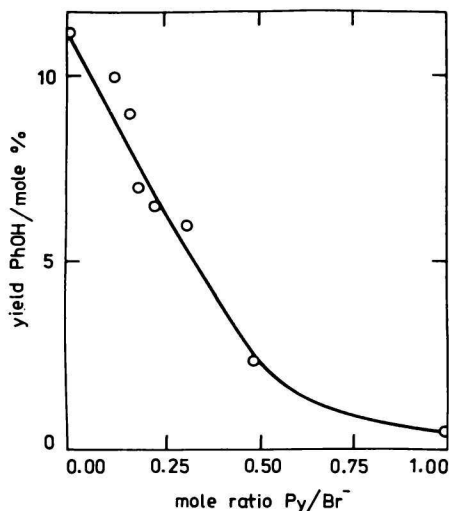


Fig. 4. Influence of pyridine on the formation of phenol at 140°C.

Conditions as in Fig. 1.

The influence of different bromide compounds on the rate of cumene oxidation and the formation of phenol in acetic acid solution is summarized in Table 1. The bromine complexes of metals are catalytically highly active [8]. But the results given in Table 1 show that phenol appears only in small concentrations among the

Table 1

Influence of bromide compounds on the maximum rate of cumene oxidation in acetic acid and the yield of phenol at 140°C and 0.7 MPa pressure

Cumene 5 ml, AcOH 5 ml, and 0.85 mmol Br<sup>-</sup> concentration

Compound	Reaction time <i>t</i> /min	$r_{\max}$	
		[PhOH]/mole %	
		mmol O <sub>2</sub> (mol RH min) <sup>-1</sup>	
HBr	65	33.2	6.1
CsBr	60	58.2	9.6
(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> NH·Br	95	38.8	12.7
(CH <sub>3</sub> ) <sub>4</sub> N·Br	25	49.9	13.2
( <i>n</i> -Bu) <sub>4</sub> ·P·Br	16	55.4	15.2
(Ph <sub>2</sub> Bu) <sub>3</sub> S·Br	90	23.1	8.4
(Ph <sub>3</sub> Bu)As·Br	95	6.1	9.1
Co[(HOCH <sub>2</sub> CH <sub>2</sub> ) <sub>3</sub> N] <sub>2</sub> Br <sub>2</sub>	18	79.8	0.7
CoPy <sub>2</sub> Br <sub>2</sub>	18	21.3	0.9
CoBr <sub>3</sub> ·(PPh <sub>3</sub> ) <sub>2</sub> ·N(CH <sub>3</sub> ) <sub>4</sub>	18	59.9	0.7

products. It is known [6] that the acid-catalyzed decomposition of hydroperoxides is suppressed in the presence of cobalt because free hydrogen bromide is bonded in complexes with cobalt according to the reaction



Besides, we cannot eliminate the subsequent oxidation of the phenol into other products with the cobalt complex.

The important role of free hydrogen bromide in the formation of phenol is evident from Figs. 3 and 4. It results from these figures that the content of phenol in products increases with concentration of bromides in the system up to certain values. The decrease appearing at higher concentrations may be due to consecutive bromination of phenol. This assumption has been confirmed by detection of these substances in products. In the presence of poorly dissociated ammonium bromides, the maximum content of phenol is reached at concentrations of the bromide ions which are several times lower in comparison with aqueous solution of hydrogen bromide (Figs. 3 and 5). This amount still decreases with increasing temperature which favours the dissociation of ammonium bromides. In these cases, an "equilibrium" concentration of free hydrogen bromide is kept in the system, *e.g.*



The bromine atoms consumed in reaction (D) are replaced by dissociation according to reaction (H).

The presence of substances of acid type does not significantly affect the formation of phenol. But it reduces the rate of oxidation and conversion of cumene (Table 2). All the above-mentioned oxidations of cumene were carried out in acetic acid solvent. The oxidation of cumene initiated by hydrogen bromide gives rise to phenol in other solvents as well. The amount of phenol thus formed depends

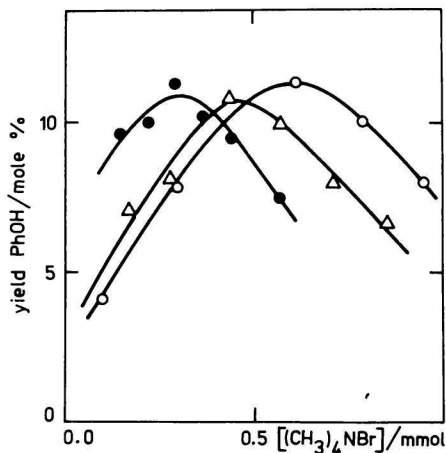


Fig. 5. Influence of tetramethylammonium bromide concentration on the formation of phenol at 125°C (O), 133°C (Δ), and 140°C (●).

Conditions as in Fig. 1.

Table 2

Influence of some compounds of the acid type on the oxidation of cumene initiated by hydrogen bromide in acetic acid

Temperature 140°C, 0.7 MPa pressure, cumene 5 ml, AcOH 5 ml, and 0.55 mmol HBr in the form of 48% aqueous solution

Compound mmol	Reaction time t/min	$r_{max}$	
		mmol O <sub>2</sub> (mol RH min) <sup>-1</sup>	[PhOH]/mole %
None <sup>a</sup>	115	13.29	5.9
HCl (0.49)	100	8.39	8.5
HCl (1.7)	30	4.84	7.7
FeCl <sub>3</sub> <sup>b</sup> (0.45)	8	4.66	0.8
<i>p</i> -Toluenesulfonic acid (0.4)	136	3.66	6.2
[Et <sub>2</sub> CS <sub>2</sub> ] <sub>2</sub> Fe (0.45)	85	9.98	6.7
Ni[S <sub>2</sub> C <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> ] <sub>2</sub> (0.4)	18	13.31	2.3

a) Initiator HBr; b) without HBr.

on the type of the solvent (Table 3). In all investigated cases, the oxidation spontaneously stops at a certain conversion of cumene depending on reaction conditions, which may be due to an inhibiting effect of the forming phenol or its further products. If the oxidation of phenol is hindered, *e.g.* by blocking the phenolic group by acetic anhydride, the amount of phenol in products increases up to technologically interesting concentrations [2—4].

Table 3

Influence of solvent of the oxidation of cumene initiated by hydrogen bromide  
Temperature 140°C, 0.7 MPa pressure, 1.62 mmol HBr, cumene 5 ml, solvent 5 ml

Solvent	Reaction time t/min	[PhOH]/mole %
AcOH	60	11.1
AcOH + 10% H <sub>2</sub> O	110	8.9
Ac <sub>2</sub> O	110	16.7
CCl <sub>3</sub> COOH	70	8.4
Propionic acid	40	8.6
Butyric acid	150	7.9
Isobutyric acid	85	5.9
Benzoic acid	90	3.7
Dimethyl sulfoxide	18	15.1
Dioxan	25	2.0
Ethyl acetate	35	5.1
CH <sub>2</sub> Cl <sub>2</sub>	12	7.8

In other cases, a direct oxidation of cumene into phenol in the presence of bromine compounds is little selective. Cumyl alcohol and acetophenone always represent the main products.

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