

## Kinetics and Mechanism of Dioxin Cycle Formation in the Reaction of Hexachlorobenzene with Potassium Salt of Catechol in DMSO

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### Abstract

The kinetics of formation of 1,2,3,4-tetrachlorodibenzo-p-dioxin (I) in the reaction of hexachlorobenzene (HCB) with potassium salt of catechol in DMSO has been studied. It has been found that the slow stage of formation of (I) is the intermolecular substitution of chlorine in HCB by the catechol residue rather than the intermolecular substitution of halogen in the intermediate potassium 2-(pentachlorophenoxy)phenoxide (II). It has been shown that formation of dioxin (I) from (II) occurs at appreciable rate even at room temperature. This illustrates the potential hazard of this type of the halo-derivatives of diphenyl ether as possible precursors of toxic dioxins.

### Introduction

The  $S_NAr$  processes play an important role in dioxin chemistry and in dealing with various problems related to these xenobiotics. To remind, these were the reactions that made "Seveso", "Agent orange", etc. notorious <sup>1</sup>. At present, these reactions are widely used in the synthesis of various dioxin derivatives to provide standards for physico-chemical and immuno-chemical analyses and to develop methods of degassing of halogen-containing xenobiotics by dehalogenation <sup>2</sup>. Since the aromatic compounds or their fragments appear in many currently used or prospective pesticides, the environment faces the risk of being contaminated by dioxins formed from these compounds on their metabolites, activated to  $S_NAr$  processes by acceptor substituents by  $\sigma$ - or  $\pi$ -coordination with transition metals or by different types of radiation.

### Experimental Methods

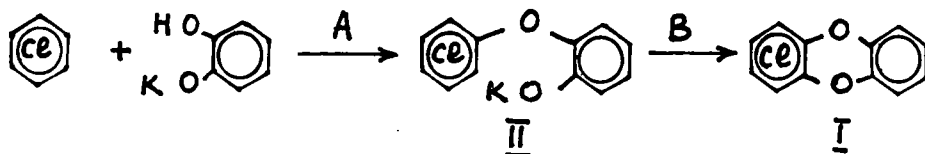
The kinetic measurements were carried out by the sampling procedure under argon. The reaction mixtures were analyzed by the chloride ion determination procedure, and by GLC for the HCB, ether (II) and dioxin (I) content. The starting reagents and DMSO were purified by conventional techniques.

### Results and Discussion

In our previous paper <sup>3</sup> we have studied conditions of dioxin formation from aryl halides activated by  $\pi$ -coordination with metal complex fragments. The aim of this work is to study the tendencies of formation of the dioxin ring in aromatic compounds activated by the presence of many chlorine atoms.

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For that purpose we have studied the kinetics of dioxin (I) formation from HCB and the direct precursor of dioxin, ether (II), in the presence of an excess of the potassium salt of catechol and free catechol in DMSO at different temperatures.



We have found that in the reactions (A) and (B), at different extents of HCB and ether (II) conversion, there is a correlation between substrate consumption and accumulation of reaction products dioxin (I) and potassium chloride formed in nearly 100% yields. In (A), the intermediate (II) was not detected even at the lowest extents of HCB conversion at different temperatures.

The rate constants were independent of reaction times of (A) and (B) only when using second-order reaction equations. The calculated or graphically determined (E, H) activation parameters of both reactions are given below.

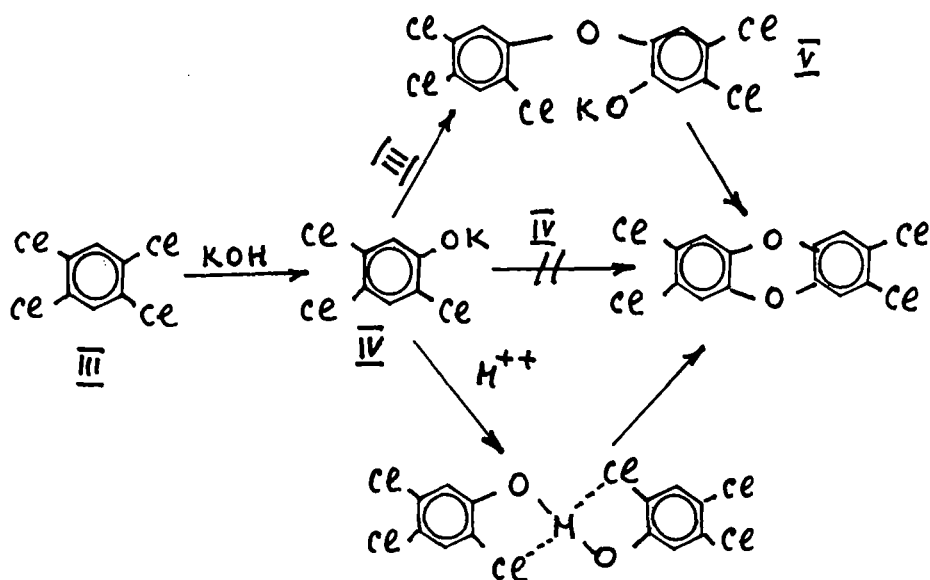
	E	lg A	$\Delta H_{st}$	$\Delta S_{st}$	$\Delta G_{st}$
	kJ/mol		kJ/mol	J/mol K	KS/mol
React. A: t°C	90 100 110 120 130				
k 10 <sup>4</sup> L/(mol s)	0.21 0.48 1.1 2.5 5.5	9.5	94	-24	123
		$k^{25°C}_{B/A} = 10^6$			
React. B: t°C	11 21 31 41				
k 10 <sup>4</sup> L/(mol s)	2.7 11 43 170	16	108	15	89

To take into account the statistical factor, the reaction rate constants of (A) and (B) were decreased by a factor of 6 and 2, respectively. Since the Arrhenius plots are linear for both reactions, the measured k values are not complex, and the limiting stages of the reactions remain unchanged in the given temperature range. We suggest a two-step mechanism of chlorine substitution, the slow step of which is known to be the formation of the intermediate anion of the type of Meisenheimer-complexes. The enthalpy and entropy values of (A) are the typical values of S<sub>N</sub>Ar processes of aryl halides activated by acceptor substituents proceeding under the influence of charged nucleophiles. The slow step is the reaction of intermolecular nucleophilic substitution in HCB by the catechol residue rather than the intramolecular cyclization in ether (II). Indeed, the k<sub>25°C</sub> ratio is six orders in favor of reaction (B). With about equal enthalpy factors there is a great difference in pre-exponential terms. Positive or small negative S values are known to be generally characteristic of basic first-order reactions if they occur via cyclic activated complex. The structure of ether (II) seems to include favorable steric orientation of reaction centers to form an activated complex. Moreover, the intermediate-like transition state, where the negative charge is more delocalized than in the starting molecule, should be less solvated. Both factors are known to shift the  $\Delta S$  values towards more positive values.

Thus, the higher reactivity of ether (II) compared to HCB is due to entropy factors. The ease of dioxin (I) formation in reaction (B) illustrates the hazard of diphenyl ether derivatives containing

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hydroxyl and halogen in the 2- and 2'-positions. Such compounds (V), possibly, play an active part in the dioxin-forming reaction of 1,2,4,5-tetrachlorobenzene with alkalis. Formation of dioxin from two



trichlorophenoxide molecules (IV) seems unlikely, as the  $S_NAr$  process in this case is extremely hindered by the strong deactivating effect of the most powerful donor substituent (-O<sup>-</sup>). This route may take place only in the presence of some transition metals which may be contained, e.g. in autoclave walls, capable of producing a strong catalytic effect in such molecules.

## Literature cited

- (1) Reggiani G.H. in *Agent Orange and its associated dioxins assessment of a controversy* (Eds. A.L. Young, G.M. Reggiani), Elsevier, Amsterdam, 1988. P.31; 225.
- (2) Kunzevich A. D., Golovkov V. F. Rembovsky V. R. *Uspekhi khim.*, 1996, 65 (1), p. 29.
- (3) Litvak V. V., Gorynov L. I., Shteingarts V. D. *Zh. Org. Chem.* 1986, 22, p. 127; 1988, 24, p.401.