Formation of Dibenzodioxins and Other Condensation Products from Chlorinated Phenols and Derivatives

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Introduction

Chlorodioxins can be formed in a two-step condensation reaction from *ortho*-substituted chlorophenoxy radicals or anions (*1–3*). The first route is of significance only where strongly oxidizing conditions exist such as a reaction of chlorine with pentachlorophenol at elevated temperature. For the second route we have investigated the condensation of alkali metal salts of chlorinated phenols which occurs spontaneously when these metal salts are heated to temperatures above 300°C. Since this reaction is strongly exothermic, it proceeds to completion in a very narrow temperature range once initiated.

For bimolecular reactions involving *ortho* chlorines of both phenate molecules, dioxins would be formed according to the scheme shown in eq. (1) as one of the possible reaction pathways. If these phenates contain halogen substituents in *meta* or *para* positions, these also are involved in the condensation reactions and the product distribution depends on a variety of factors such as (1) the total number of halogen substituents which determines the ease of removal of halogen; (2) the arrangement of the molecules within a crystal if this reaction takes place in the solid state, which in turn is influenced by the metal cation involved; (3) steric effects which may facilitate the attack by the second molecule at a particular carbon or may prevent a nucleophilic attack at a particular site; (4) electronic effects which in this case allows halogen atoms in *meta* positions to be removed more readily than those in the other ring positions (*4*).

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Experimental

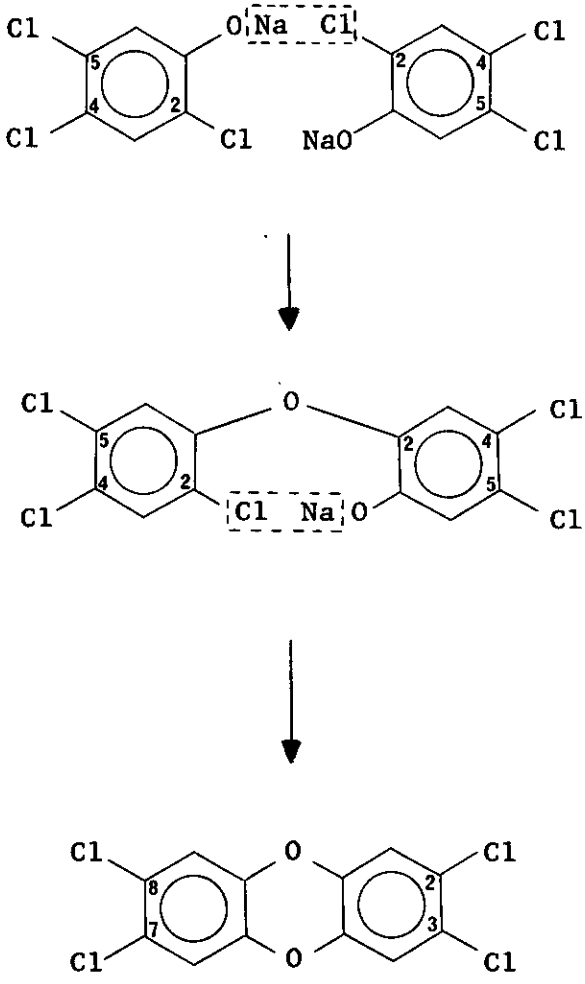
Thermal reactions were carried out in bulk as described below or in a differential thermal analysis cell using a DuPont 900 Differential Thermal Analyzer.

Residues and sublimates were analyzed by mass spectrometry on an A.E.I. MS-12 instrument coupled to a D.E.C-PDP-12 computer using a program called MASH (*5*).

Results

The results of our extensive studies are summarized in Table 1, which contains all the pertinent information on this complicated reaction system and with this the answers to many questions regarding dioxin formation.

From electronic considerations Cl atoms marked with an asterisk (*) and located in *meta* positions are more likely to be removed than any of the others (*4*). The first two reactions occur in the solid state where the molecules—anions as well as alkali metal cations—are locked into positions which may have an important effect on the reaction



TCDD

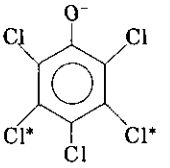
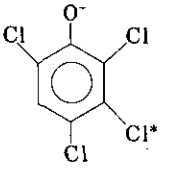
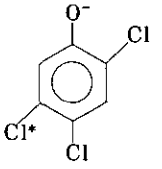
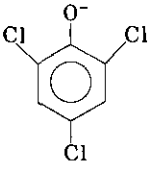
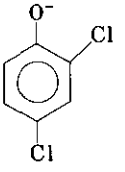
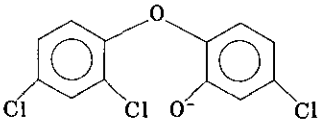
(1)

pathway. For sodium pentachlorophenate we notice a surprisingly high dioxin yield which must be attributed to such lattice effects or a steric effect which provides an opening for attack only in the vicinity of the oxygen atom and thus leads to the formation of dioxins. For the tetrachlorophenate, some of the steric hindrance is removed and we observed two isomers of hexachlorodioxins with a considerably lower overall yield. The condensation of sodium 2,4,5-trichlorophenate occurs immediately following the melting process. Molecular motion is no longer restrained and one would expect the most labile *meta* chlorine to be released preferentially. Indeed, only trace amounts of the tetrachlorodioxin could be observed (*6*). On the other hand, for the 2,4,6-isomer no *meta* chlorine is available; instead two ortho chlorines are in a favorable position for dioxin formation. Thus, the higher yields of the tetrachlorodioxin should not come as a surprise. For sodium 2,4-dichlorophenate, with only one *ortho* chlorine available, the dioxin yield drops to less than 3%. The final example shows only the second step of the condensation with a chlorinated phenoxy phenate. From the overall low yield of dioxins and the high percentage of higher molecular weight condensation product it is obvious that in the molten state with free mobility of the molecule and within the molecule the easily released *meta* chlorine plays an important part in the reaction.

Having established reaction conditions most likely to produce dioxins from chlorophenates we investigated conditions which might produce these dioxins from chlorophenoxy derivatives, primarily 2,4,-D, 2,4,5-T, and Silvex and their salts and esters. No dioxins were detected by heating the following compounds under various conditions: (1) 2,4-D to 335°C (sublimation); (2) 2,4-D, Na salt to 340°C (decomposition); (3) 2,4-D reflux in trichlorobenzene (24 hr at 213°C); (4) 2,4,5-T to 345°C (decomposition); (5) 2,4,5-T Na salt to 300°C (decomposition); (6) 2,4,5-T reflux in trichlorobenzene (24 hr at 213°C); (7) 2,4,5-T reflux in 20 equivalents aqueous NaOH (≈100°C; 18 days); (8) 2,4,5-T dispersed in dry K_2CO_3 or $CaCO_3$ 300°C, 120 hr; (9) 2,4,5-T in *n*-butyl ester to 360°C (boiling); (10) 2,4,5-T reflux in tetraglyme (275°C, 1 week); (11) Silvex to 350°C; (12) Silvex, Na salt to 350°C.

Let us remember that we will have to postulate the formation of the respective phenoxy anions before we can expect condensation to the dioxins. We should also remember that the reactions are exothermic and occur above 300°C and that for bimolecular reactions any dilution will necessarily result in lower yields. The negative results listed above demonstrate that either the phenoxide anions were not formed or that the temperatures obtainable in solutions were too low to affect condensation.

Table 1. Pyrolysis products from Na chlorophenates by mass spectrometry.

Compound	*m/e*	Relative intensity, %	Species		Approx. yield, %	
Sodium pentachlorophenate (solid)	456	100	Dioxin	(8 Cl)	80	
	684	2	Trimer	(12 Cl)		
	912	0.3	Tetramer	(16 Cl)		
Sodium 2,3,4,6-tetrachlorophenate (solid)	388	100	Dioxin	(6 Cl)	30	
	582	3	Trimer	(9 Cl)		
Sodium 2,4,5-trichlorophenate (at mp)	320	100	Dioxin	(4 Cl)	<1	
	35–356	30	Dimers	(5 Cl)		
	480	4	Trimers	(6 Cl)		
Sodium 2,4,6-trichlorophenate (at mp)	320	100	Dioxin	(4 Cl)	up to 15	
	480	33	Trimer	(6 Cl)		
	640	50	Tetramer	(8 Cl)		
	800	30	Pentamer	(10 Cl)		
Sodium 2,4-dichlorophenate (at mp)	252	100	Dioxin	(2 Cl)	<3	
	378	10	Trimer	(3 Cl)		
	504	1	Tetramer	(4 Cl)		
Sodium Irgasan (molten)	252	100	Dioxin	(2 Cl)	7	
	378	10	Trimer	(3 Cl)		
	414	20	Trimer	(4 Cl)		
	504	16	Tetramer	(4 Cl)		
	540	12	Tetramer	(5 Cl)		

On the other hand, we were able to detect traces of tetrachlorodioxin when drastic conditions were used to cleave the molecule, producing measurable amounts of alkali salts of 2,4,5-trichlorophenol and subsequently subjecting it to pyrolysis above 300°C. As an example, a mixture of 0.25 g 2,4,5-trichlorophenoxyacetic acid, 2 g H_2O, and 10 g K_2CO_3 was refluxed at 100°C for 3 hr, then heated at 200°C for 15 hr, then at 400°C for 43 hr. A total of 0.13% of tetrachlorodioxin (TCDD) could be detected, after this rigorous treatment by quantitative analysis on an LKB–9000 GC–MS instrument with the use of Dow method ML–AM71–48.

Turning now to the ultimate question, should we or can we expect to produce dioxins in the field by the use of 2,4-D, 2,4,5-T, Silvex, or their derivatives?

The answer must be that it is extremely unlikely. Yet, Buu-Hoi reported (*6*) a yield of 60% TCDD from 2,4,5-trichorophenol in the presence of dry K_2CO_3 and Cu at 240–250°C, up to 5% TCDD from 2,4,5-T at 500–600°C, and up to 15% TCDD by pyrolysis of sodium 2,4,5-trichlorophenoxy acetate. He concluded that quantities of this dioxin are formed by burning herbicide-treated plant material.

In fact, his data do not support this conclusion. His reaction product gave the mass spectrum (*6*), reproduced here in Figure 1*a*. This is not the mass spectrum of tetrachlorodioxin. Authentic 2,3,7,8-tetrachlorodioxin, verified by single crystal x-ray analysis (*7*) shows the mass spectrum given in Figure 1*b*. The spectrum obtained by Buu Hoi may be explained by formation of polymeric materials according to eq. (2) which we have observed in our own studies.

Acknowledgement

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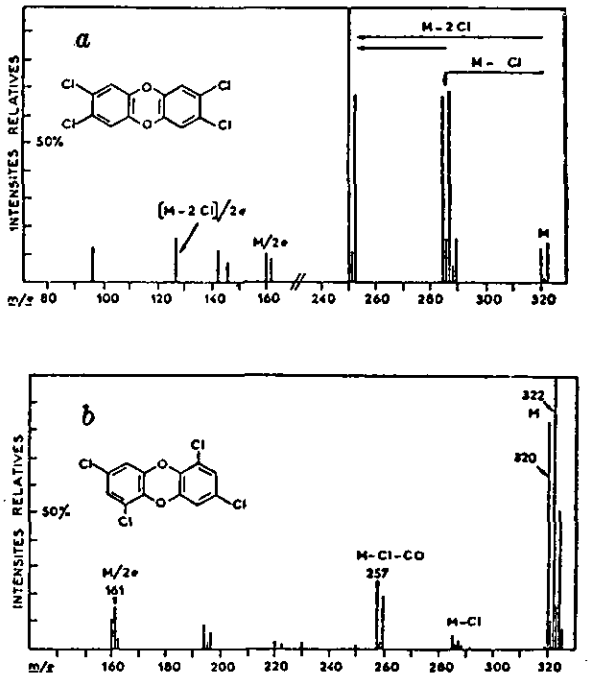
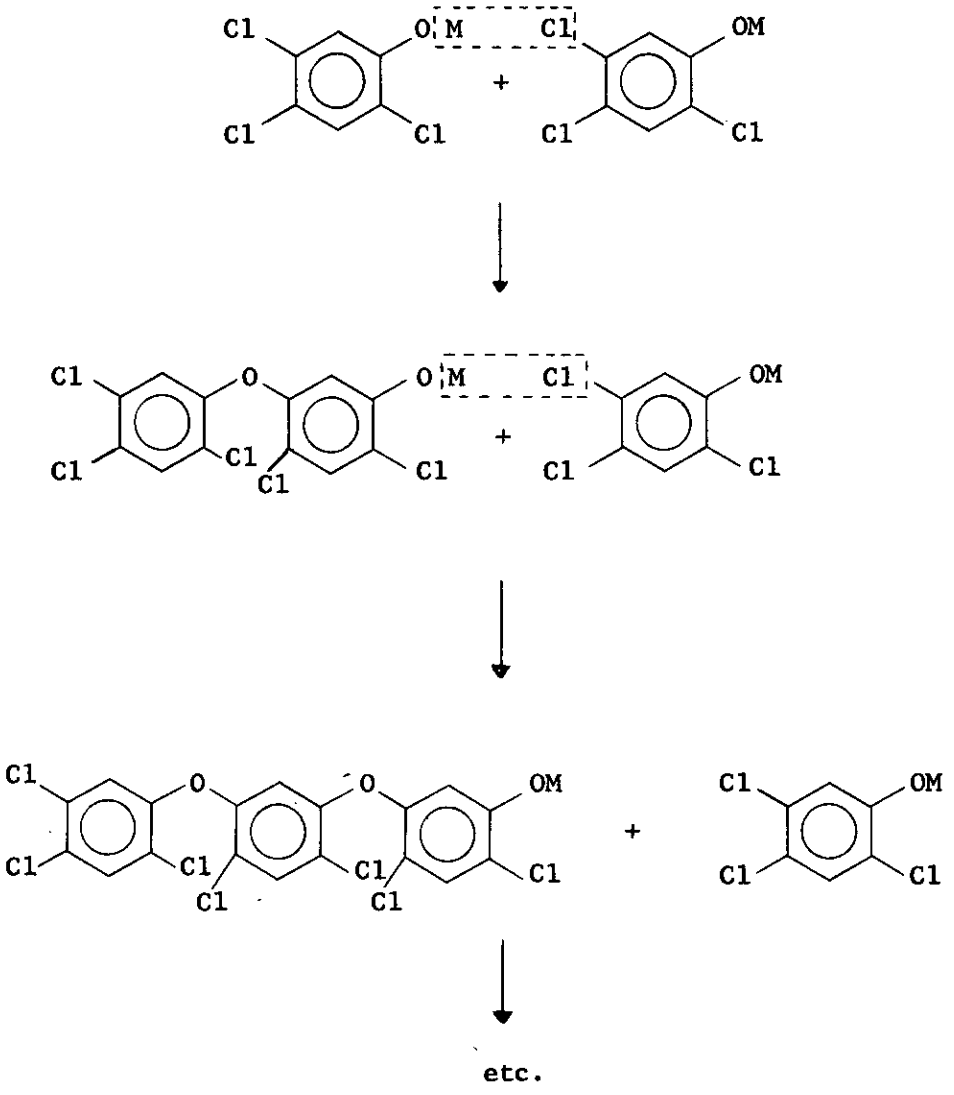


FIGURE 1. Mass spectra reported by Buu Hoi (*6*).



(2)

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