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THERMAL DESTRUCTION OF POLYCHLORINATED COMPOUNDS: FLOW TUBE KINETICS OF TEN DIBENZO-PARA-DIOXINS

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ABSTRACT

Thermal decomposition curves of ten chlorinated dibenzo-para-dioxins were measured by a flow tube reactor with integrated gas chromatographic analysis of the reaction products. Residence times between .4 to 1 seconds were chosen for a direct comparison with hazardous waste disposal incinerators. The dependence of the decomposition rates on the carrier gas was studied and the rates were found to increase with added oxygen in nitrogen-oxygen mixtures. All dioxins studied were found to decompose between 850 and 1100°C in nitrogen. The observed decomposition rate constants in nitrogen decreased with increasing chlorination of the dioxins. This finding is in agreement with expectations for pure pyrolysis and suggests that C-O bond rupture is the rate determining step.

INTRODUCTION

Inspite of a large body of literature on polychlorinated dioxins and their occurence in effluents of municipal incinerators (ref.1), almost no reliable kinetic information on the thermal behavior of these compounds has been published in the past. The present report deals with the high temperature pyrolysis and it should serve as an illustration of our ongoing effort to establish a firm data base on the kinetic behavior of these substances (ref.2).

METHODS AND RESULTS

A detailed discussion of the flow tube reactor will be published elsewhere (ref.2). The fully integrated and automatic instrument was built from a gas saturation vapor pressure instrument (Fig. 1). A resistance heated quartz flow tube reactor with a heated length of 13 cm and an inner diameter of .18cm was used. Substance decomposition at the walls is reduced to acceptable levels in such a configuration (ref.2-3). The kinetic data can easily be corrected for the temperature profile of the reactor by an iterative procedure (ref.2) and this replaces the use of capillary reactors to smoothen the temperature (ref.4).

At least 30 decomposition analysis obtained at ten representative reactor settings between 400 and 1000°C were measured for a single decomposition curve. The fraction of educt remaining after the heat treatment was plotted as a function of exposure temperature (Fig.2a). The decomposition curves were found to be independent of educt concentration within the partial pressure region studied (10^{-7} to 10^{-5}). Decomposition rate constants as a function of temperature were therefore obtained from the raw data in a first order kinetic evaluation. The enthalpy of activation and the frequency factor could be obtained by

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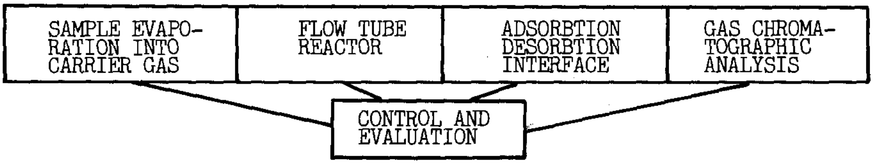

Fig. 1. Block diagram showing the dynamic gas phase reaction analysis instrument.

linear regression on the arrhenius plot (log K versus 1/T plot) of this kinetic data (Fig.2b). Each temperature dependent rate constant has been determined for a single reaction time. The arrhenius parameters are therefore only estimates and are at most valid over the fairly narrow temperature region (typically 100^{o} C) of intermediate decomposition rates (Table 1). Decomposition temperatures and exposure times for a residual educt concentration of one part per billion (1ppb) could then be predicted by extrapolation with the arrhenius parameters (Fig.2c). The area above the curve represents save combustion conditions and the combustion yields of an industrial incinerator can be estimated by superposing its temperature / residence time characteristics on to this representation.

DISCUSSION

The measured rate constants of Table 1 are in good agreement with predictions for the unimolecular decay by C-O bond rupture in the high pressure limit (ref.5). A rate constant of .16/sec is predicted for 800^{o}C using an estimated frequency factor of $10^{15.5}$ and an activation energy for C-O bond rupture of 335 kJ/mol.

The observed rate constants for the decomposition in nitrogen increase slightly with increasing chlorination. This is additional evidence that we are observing the destruction of the dioxins by unimolecular decomposition. A strong and

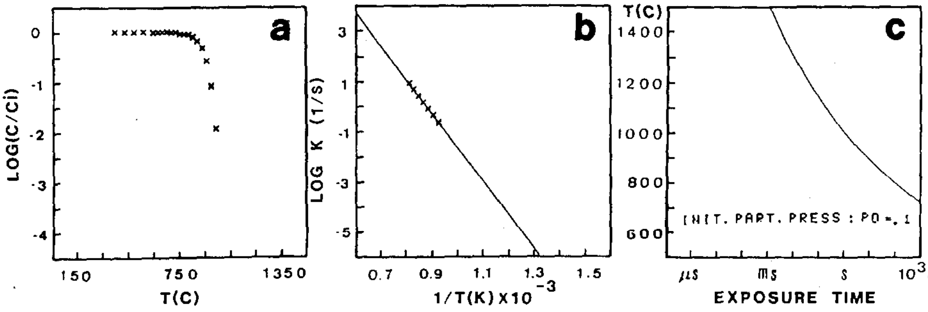

Fig.2. Thermal destruction of 1,2,3,4-tetrachlorodibenzo-p-dioxin in nitrogen (< 10 ppm oxygen) at atmospheric pressure.

TABLE 1

Kinetic data for the thermal destruction of chlorinated dibenzo-p-dioxines in nitrogen, nitrogen-oxygen mixtures and air. The experimental decomposition rate data is represented for the indicated temperature intervall by activation energies and frequency factors. The precision of the present data does not permit a kinetic interpretation of the indicated parameters (see text).

COMPOUND	KINETIC EVAL BETWEEN (C)	ACTIVATION ENERGY (KJ/MOL)	FREQUENCY FACTOR (1/S)	RATE CONST AT 800 C (1/S)
A) in Nitrogen (<10ppm Oxygen)				
Dibenzo-p-Dioxin	925 - 1000	256.3	3.0E11	0.10
1-Chlorodibenzo-p-Dioxin	865 - 975	(353.3)	(5.0E15)	(0.03)
2-Chlorodibenzo-p-Dioxin	895 - 1000	270.9	1.4E12	0.09
23-Chlorodibenzo-p-Dioxin	785 - 975	247.4	1.4E11	0.13
27-Chlorodibenzo-p-Dioxin	810 - 975	255.0	3.1E11	0.12
28-Chlorodibenzo-p-Dioxin	790 - 975	198.3	1.5E9	0.33
137-Chlorodibenzo-p-Dioxin	735 - 990	238.1	8.2E10	0.21
124-Chlorodibenzo-p-Dioxin	895 - 975	226.5	3.5E10	0.34
1234-Chlorodibenzo-p-Dioxin	755 - 965	256.0	6.0E11	0.19
Octachlorodibenzo-p-Dioxin	840 - 950	200.4	2.6E9	0.46
B) in Air				
137-Chlorodibenzo-p-Dioxin	625 - 810	182.7	1.02E9	1.32
1234-Chlorodibenzo-p-Dioxin	730 - 810	194.5	4.2E9	1.43
C) 1234-Chlorodibenzo-p-Dioxin in Nitrogen-Oxygen Mixtures				
0.001 % Oxygen	755 - 965	256.0	6.0E11	0.19
2.1 % Oxygen	725 - 810	228.6	1.5E11	1.15
7.5 % Oxygen	725 - 810	244.8	1.2E12	1.43
15 % Oxygen	755 - 810	224.5	1.6E11	1.85
30 % Oxygen	725 - 810	196.7	8.8E9	2.36

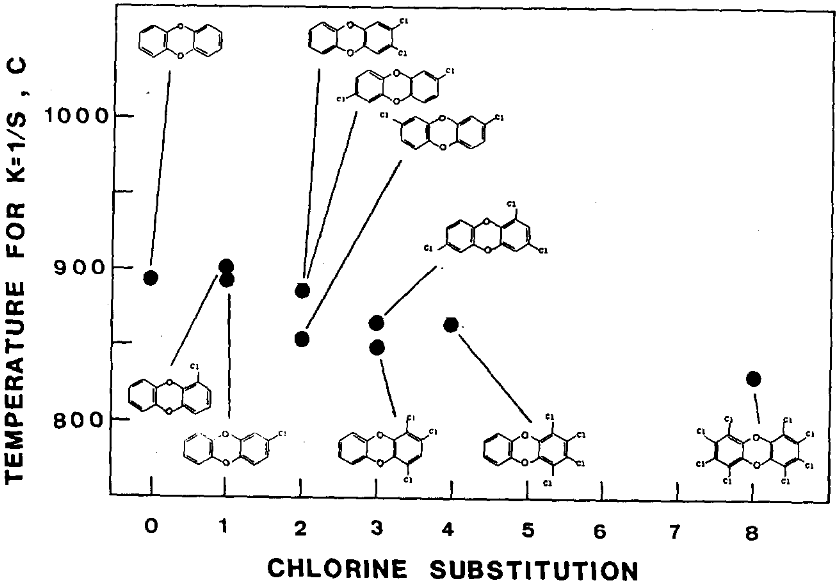

Fig. 3. Substitution effect on the pyrolysis of chlorinated dibenzo-p-dioxines. The dots indicate the temperatures for which the rates of destruction equal 1 per second.

inverse dependence would have been expected for oxidative combustion processes.

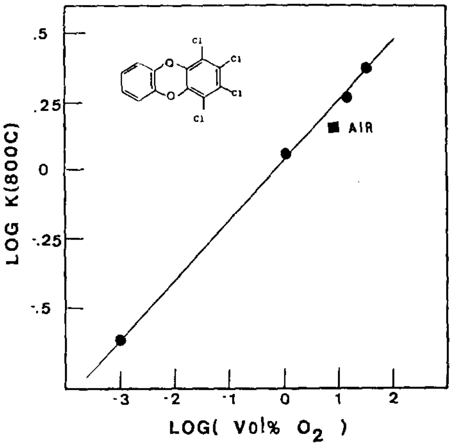

Fig.4. Rate of destruction (1/sec) of 1,2,3,4- chlorodibenzo-p-dioxin at 800°C as a function of the oxygen concentration in nitrogen-oxygen mixtures.

Additional reaction channels are opened in the presence of oxygen, leading to an increase in the observed rates (Fig.4). The rate constants are now composed of the unimolecular and various bimolecular parts due to oxygen attack and the arrhenius parametersno longer have a clear physical meaning. We expect decreasing slopes of the oxygen dependencies with increasing chlorination based on prior studies of the reactivities of chlorinated organic molecules with hydroxyl radicals (ref.6).

The arrhenius parameters can be estimated for 2,3,7,8,tetrachlorodibenzo-p-dioxin, which is highly toxic to small animals, by correlations of the activation energies and the frequency factors with the extent of chlorine substitution. With a frequency factor of $10^{9.8}$ to $10^{11.6}$ /sec and an activation energy of 215 to 250 kJ/mol we find an estimated rate of .2 to .3 /sec at 800°C for the pyrolisis of TCDD.

The present pyrolysis data give an ultimate safety limit for the industrial incineration of hazardous wastes such as dioxines. If a homogenous exposure in time and in temperature of all of the feedstock is guaranteed, an exposure for one second at 1100°C is sufficient to destroy all of the dioxins studied, even in the complete absence of oxygen.

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