THERMODYNAMIC INSIGHTS ON PATHWAYS TO FORMATION OF CHLORINATED DIOXINS AND DIBENZOFURANS

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ABSTRACT

A method is developed for estimation of thermodynamic properties of multiply substituted aromatics inclusive of chlorinated dioxins and dibenzofurans based on principles of group additivity and non-next-nearest neighbor interactions on the aromatic ring. This includes estimates of bond energies, entropies and heat capacities of radical intermediates in pathways to chlorodioxin formation. We use these thermo calculations to show the feasibility of several elementary reaction pathways leading to dioxin formation, where the presence of chlorine acts to enhance or lower the Gibbs free energy of the reactions.

INTRODUCTION

Chlorinated dibenzodioxins and dibenzofurans are often observed in effluent from oxidation or incineration of chlorinated hydrocarbons or aromatics such as chlorinated benzenes, biphenyls, and phenols(1). These species are thought to be highly toxic, and as a consequence are highly undesirable products of incomplete combustion (PIC's). It would be of significant value to have an accurate and fundamental understanding of the mechanism for their formation, in addition to knowledge of their thermodynamic properties in order assist in design of strategies to effectively control or eliminate emissions of these compounds.

Very little has been published on the thermodynamic properties and elementary reactions which lead to formation of dioxins and chlorinated dioxins. Benson's group method(2-4), when used for the estimation of thermodynamic properties of molecules, does not account for all interactions between functional groups or atoms on aromatics, such as chlorines, hydroxyl or ether linkages. To obtain correction values for these interacting groups one may use the differences between literature thermodynamic values and those obtained using group additivity. Due to the limited literature data, however, one must often proceed by obtaining the corrections based on known properties for only a few molecules and then apply these to more complex species. This has been previously demonstrated by Shaub (5,6) for chloro and oxy substituted aromatics.

THERMODYNAMIC PROPERTY ESTIMATION

As an initial step towards understanding chlorinated dioxin formation, we have developed a data set for groups representing non-next-nearest neighbor contributions from substituents on aromatic rings, such as Br, Cl, F, OH, CH_3O, CH_3, and CO_2H. These non-next-nearest neighbor corrections are tabulated in Table I for the Cl and OH groups and include enthalpy and entropies of formation (298 K) and heat capacities to $C_{p\infty}$ where data was available. We utilize these group values in conjunction with existing Benson Groups to calculate thermodynamic properties for a number of chlorinated dibenzodioxins, dibenzofurans, and likely radical precursors to their formation in incinerator type reactive atmospheres. The data in Table I are optimized for disubstituted single ring aromatics and we therefore developed a formalism empirically for counting the number of interactions required to yield accurate thermo estimations of multi substituted aromatics. This formalism counts all the ortho interactions, and only one half the number of meta and para interactions using integer values only. Thus 1,3 di- and 1,3,5 tri- chlorobenzene would have and have counted 1 and 3 meta Cl/Cl interactions respectively. 1,2,3,5 Tetrachlorobenzene would have 2 ortho, 3 meta and 1 para but only have 2 ortho and 1 meta Cl/Cl interactions counted. This empirical formalism results because effects of the interactions in multi-substituted aromatics are not linearly additive. We define multi-interactions as occurring on aromatic rings that have more than one type - ortho, meta or para interaction.

Table II compares calculations of H_f^{298} from literature data with those using Benson Groups with interaction terms derived here, and using Benson groups alone. There is a definite improvement, as one might expect, using the added interaction terms.

REACTION PATHWAYS TO DIOXIN

Figure 1 shows an energy level diagram for the isomerization of a polychlorinated phenylether phenoxy radical, where the oxy radical attacks the aromatic ring at a position of H atom substitution. The figure shows the H atom being displaced in a reaction which is 19 Kcal endothermic, but at temperatures above 500 K it has a negative ΔG_{rxn} (entropy driven) to form the 2,3,7,8 tetrachloro dibenzodioxin. Pathways forming the aromatic ethers include phenoxy radical additions to aromatics and chloroaromatics and oxyxgen atom addition to fused ring groups of biphenyls. The oxy radicals can be formed by oxygen atom or hydroxyl radical addition to the ring with exothermic displacement of H or Cl atom, or by HO_2 or O_2 reaction with phenyl radical. Note that the Cl atom meta to the other linkage being formed enhances the newly formed ether bond by 6.26 Kcal/mole (Cl/O-R Meta)

Figure 2 shows a similar reaction producing the tetrachlorinated dioxin, but in this reaction O atom is displacing a chlorine atom and the process is thermodynamically favored both by entropy and enthalpy.

CONCLUSION

The reaction paths presented here demonstrate that dioxin and dibenzofuran formation from chlorinated ring systems are more favorable than formation form the analogous non-chlorinated systems.

There are several regimes in an incinerator or pyrolysis reactor where dibenzodioxins may be formed. One of these regimes is the fuel rich zone where hydrocarbons or fuel are inlet to the reactor and where mixing is not complete. Temperatures in this region are high enough for pyrolysis reactions to occur and molecular weight growth forms aromatic, poly-aromatic and poly-phenyl systems. In addition, there is a significant amount, but not excess, of oxygen and oxy radicals present to react with some of these aromatic compounds. A second regime is where there are benzene, biphenyl, terphenyl etc. present with oxygen and oxy radicals at lower temperatures where oxidation reactions are slow but addition reactions are favored. This could occur at the outlet where these species formed in the combustor have not been converted to CO_2 and H_2O. The addition and displacement reactions, as illustrated in figures 1 and 2 would readily occur in cooldown sections of reactor exhaust zones for example.

TABLE I GROUP CORRECTION TERMS FOR CHLORINATED AND HYDROXY SUBSTITUTED AROMATICS

GROUP	H_f 298	S_F 298	C_p 300	C_p 500	C_p 800	C_p 1000	C_p 1500 K
CB/H	3.3	11.5	3.28	5.46	7.51	8.36	9.68
CB/Cl	-4.11	18.55	7.17	9.16	10.34	10.68	9.66
CB/O	-1.63	-10.04	4.2	6.54	7.07	7.09	6.96
Cl/Cl ORTHO	2.18	-0.31	-0.20	-0.47	-0.44	-0.38	1.01
Cl/Cl META	1.34	0.17	-0.12	-0.42	-0.43	-0.38	1.01
Cl/Cl PARA	0.52	-0.08	-0.10	-0.36	-0.37	-0.38	1.01
Cl/OH ORTHO	4.53	ND	ND	ND	ND	ND	ND
Cl/OH META	-6.26	ND	ND	ND	ND	ND	ND
Cl/OH PARA	-4.48	ND	ND	ND	ND	ND	ND
Cl/OH/Cl	13.85	ND	ND	ND	ND	ND	ND

Cl/O-Phenyl Ortho Meta and Para --- Same as corresponding Cl/OH

H_f values in Kcal/mole and S and C_p in Cal/mole-K, ND Not Determined

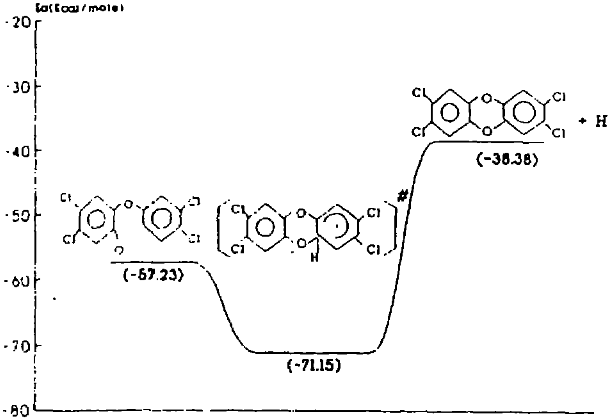
TABLE II COMPARISON OF H_f DATA WITH LITERATURE

SPECIES	▾ $H_{f(lit)}$	▾ $H_{f(calc)}$	▴	▾ $H_{f(Bsn)}$	▴
Hexachlorobenzene	-8.1	-7.04	-1.06	-9.6	1.5
Pentachlorophenol	-53.9	-52.63	-1.27	-49.	-4.9
Ortho Cresol	-30.7	-30.74	0.04	-29.72	-0.98
Meta Cresol	-31.59	-31.63	0.04	-30.29	-1.3
2,6 Dimethylphenol	-38.64	-38.43	0.21	-37.14	-1.5
Hexafluorobenzene	-228.49	-228.85	0.36	-226.8	-1.69

- ♦ All data in Kcal/mole, ▾ $H_{f(Bsn)}$ Value calculated using Benson groups only.
- ♦ ▴ are differences from Literature. Literature data from references 7 and 8.
- ♦ We have omitted species that we used in determining the group interaction values.

REFERENCES

1. O. Hutzinger, M. J. Blumich, M.v.d. Berg and K. Olie, Chemosphere, 14, pp 581-600, 1985.
2. S. W. Benson and J. H. Buss, J. Chem. Phys., 29, 546 (1958).
3. S. W. Benson and O'Neal Chem Rev., 69, 279 (1969).
4. S. W. Benson, Thermochemical Kinetics, John Wiley 1976.
5. W. M. Shaub, Thermochimica Acta, 55 (1982), 59-73.
6. W. M. Shaub, Thermochimica Acta, 62 (1983) 315-323.
7. D. R. Stull, E. F. Westrum Jr. , G. C. Sinke, The Chemical Thermodynamics of Organic Compounds, Robert E. Krieger Publishing, Malabar Florida, (1987).
8. *J. B. Pedley, R. D. Naylor and S. P. Kirby, Thermochemical Data of Organic Compounds*, 2^{nd} Ed., Chapman & Hall, London (1986).


Ea(Kcal/mole)
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-40
-50
-60
-70
-80
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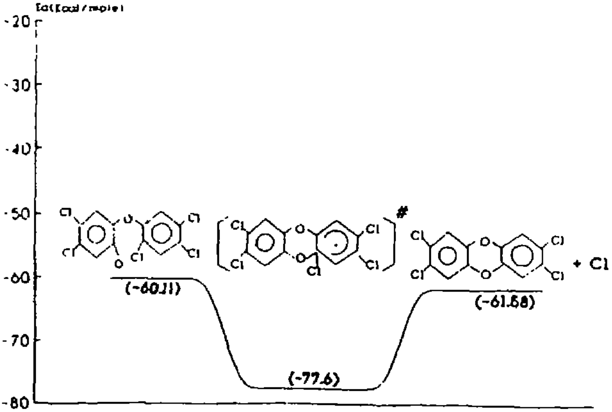
Ea(Kcal/mole)
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-50
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