Dioxin Formation And Destruction During Combustion: Thermodynamic Data From Molecular Modelling Computations

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Knowledge of the thermodynamics involved in dioxin formation would provide a powerful tool for the quantitative prediction of dioxin levels in particular combustion systems and for the optimisation conditions required to minimise the formation of the super-toxic dioxin 2,3,7,8-congeners. For "de novo" dioxin formation in fly ash, there is some evidence suggesting that the isomer distribution within an individual dioxin homologue is determined by thermodynamics.[1] To evaluate the relevance of thermodynamic equilibria in dioxin-forming reactions, values of the standard ideal gas phase Gibbs Energy of formation (ΔG_f^0) are required as a function of temperature for a range of dioxins and intermediates. Such ΔG_f^0 values can be calculated from a knowledge of enthalpy of formation (ΔH_f^0) and entropy change (ΔS^0) at 298 K, and heat capacity (C_p) for the appropriate temperatures. For just a few dioxin intermediates (i.e. several chlorobenzenes and some polychlorobiphenyls) such data have been measured experimentally. To extend this database to the entire range of dioxins and intermediates, which is in excess of 10,000 compounds (many of which are extremely toxic and available only in μg amounts) is an impossible task. Consequently, one must utilise methods for predicting thermodynamic properties.

ΔH_f^0, ΔS^0 and C_p values can often be estimated with reasonable accuracy by the group additivity approach,[2] though this procedure is less successful for aromatic compounds than it is for aliphatics. By using substituent terms to allow for Cl-Cl and Cl-OH interactions (derived mainly from chlorophenols), this method has been used to predict ΔH_f^0 (298 K) for many dioxins,[3,4] Another approach has been applied to several chlorinated phenols and dibenzo-*p*-dioxins: ΔS^0 and C_p were calculated for various temperatures by statistical mechanics after first estimating the fundamental vibrational spectroscopic frequencies by extrapolation from data for analogous compounds.[5] These procedures have several shortcomings. First, there is a lack of basic experimental data for analogous compounds from which Cl-O (or Cl-OH) interaction terms can be derived with confidence. Furthermore, it is assumed that the interaction with chlorine substituents caused by the heterocyclic oxygen(s) in the furan or dioxin ring (in which there is no H-bonding) is equivalent to that of a phenolic O-H group where H-bonding within Cl-substituents certainly does occur. The Cl-O terms for *meta* and *para*-interactions are quite large, $\sim$ -5 kcal/mole per Cl for ΔH_f^0 and profoundly affect the values obtained. Consequently, the range of ΔH_f^0 values calculated thus for isomers within a single dioxin homologue is unrealistically wide, e.g. -82.8 to -43.4 kcal/mole for the tetrachlorodibenzo-*p*-dioxins

(T4CDD). This is particularly so if the presence of all 22 T4CDD isomers in incinerator fly ash is considered.[2] Such data have hitherto been the best available and have been used, for example, to predict equilibrium gas compositions of combusted chlorinated hydrocarbons.[6]

An alternative approach to thermodynamic property estimation is to use computational molecular modelling. One such molecular orbital programme (MOPAC)[7] implements four different semi-empirical Hamiltonians (MNDO, AM1, MINDO/3 and PM3) to solve Schroedinger's equation; each of these are self-consistent field methods which take account of electrostatic repulsion and exchange stabilisation. Essentially, the optimised molecular geometry of a compound is computed by calculating ΔH_f^0 as the molecular geometry is changed, until ΔH_f^0 reaches a minimum. After computing the force constants between each atom, the individual fundamental vibrational frequencies can be calculated, and hence ΔS^0 and C_p, and ΔG_f^0 obtained as a function of temperature.

To test the accuracy of MOPAC predictions, ΔH_f^0, ΔS^0 and C_p values were calculated at 298 K by the four different Hamiltonians for 12 chlorobenzenes and compared with experimental values. Satisfactory agreement between measured and calculated values was achieved for ΔS^0 and C_p - the best results from using the PM3 and MNDO methods respectively (mean difference between predicted and measured values is <0.2 cal/mole). Prediction of ΔH_f^0 was less good - all methods generated values biased high with the best agreement coming from the AM1 and MNDO methods (with mean differences between predicted and observed ΔH_f^0 (298 K) in the range 2-3 kcal/mole, which is of a comparable magnitude to the errors quoted for ΔH_f^0 (298 K) estimated by group additivity or for many direct measurements.[4] The MINDO/3 Hamiltonian produced the worst fit for all three parameters.

Values of ΔH_f^0 (298 K) predicted by three MOPAC methods and by group additivity[3-5] have been compared for a number of dioxins, Figure 1. Our MNDO values of ΔH_f^0 (298 K) for PCDDs and PCDFs are almost the same ($\approx$ 0.4 kcal/mole higher) as those published without comment elsewhere,[8] but they are markedly different from those calculated by group additivity. For most dioxins, group additivity predicts much lower (more negative) ΔH_f^0 (298 K) values than does MOPAC, e.g. O8CDD and 2,3,7,8-T4CDD. However, there are also significant differences in values obtained from the MOPAC methods. For most dioxin molecules, ΔH_f^0 (298 K) values increase in the order MNDO < PM3 < AM1. The MNDO method gives the best agreement with related oxygen heterocyclic compounds, such as unsubstituted dibenzofuran,[9] for which experimental values of ΔH_f^0(298 K) are available.

Such thermodynamic parameters can usefully be applied for isomers of the same homologue regardless of their absolute value. Figure 2 compares MNDO values of both ΔG_f^0 and equilibrium composition for the T4CDD isomers at two temperatures, 298 and 1500 K. ΔG_f^0 is expressed as differences from ΔG_f^0 for the most thermodynamically stable isomer (1,3,7,8-T4CDD). At 298 K, the super-toxic 2,3,7,8-T4CDD is the forth most thermodynamically stable of the 22 isomers. However, at higher temperatures, it becomes less favoured, such that at 1500 K 2,3,7,8-T4CDD is the sixth least stable isomer. This change is caused primarily by the influence of rotational symmetry number (R_s) on the calculation of entropy. Thus in Figure 2, all the isomers with $R_s > 1$ become less thermodynamically stable with respect to 1,3,7,8-T4CDD as temperature increases.

Such MNDO-derived data have been compared with isomer concentrations reported for "de novo' dioxin forming model systems[1] and for incinerator fly ash.[10,11] The three most abundant T4CDD isomers in incinerator fly ash are 1,3,7,8-, 1,3,6,8-, and 1,3,7,9- (present at levels of ~ 10-20%w).[1,10,11] These are also the three most thermodynamically stable at temperatures below 1000 K with equilibrium concentrations of 12-25%w predicted for 600 K. 2,3,7,8-T4CDD is the fourth most abundant (~ 5%w)[10], whereas at 600 K it is the sixth most thermodynamically stable isomer with a predicted equilibrium concentration of 5.0%w. These four T4CDD-isomers have been identified as the ones showing most variance with reaction time at 573 K or temperature change (473-673 K).[10] This is consistent with the sensitivity of equilibrium concentration to temperature shown in Figure 2, particularly for 1,3,7,8-, 1,3,6,8-, and 1,3,7,9-T4CDD.

The above provides evidence to support both the validity of the thermodynamic data obtained by molecular modelling and the suggestion that the isomer distribution of individual dioxin homologues may be thermodynamically controlled.

References

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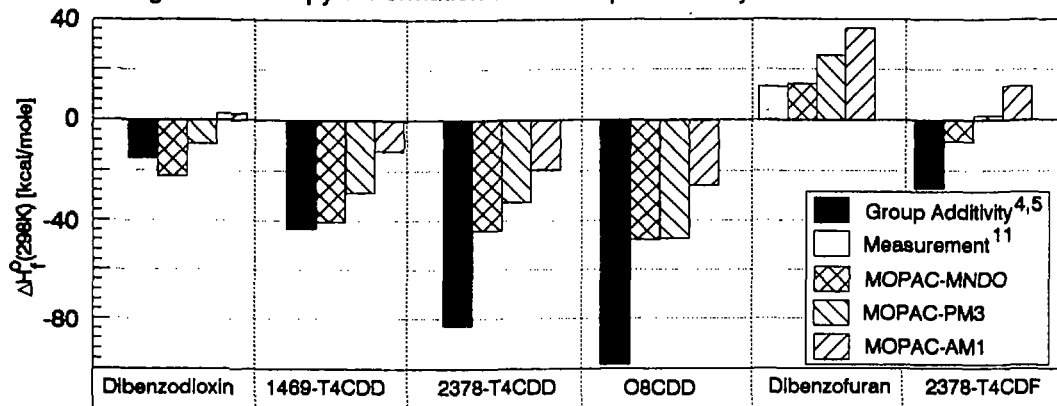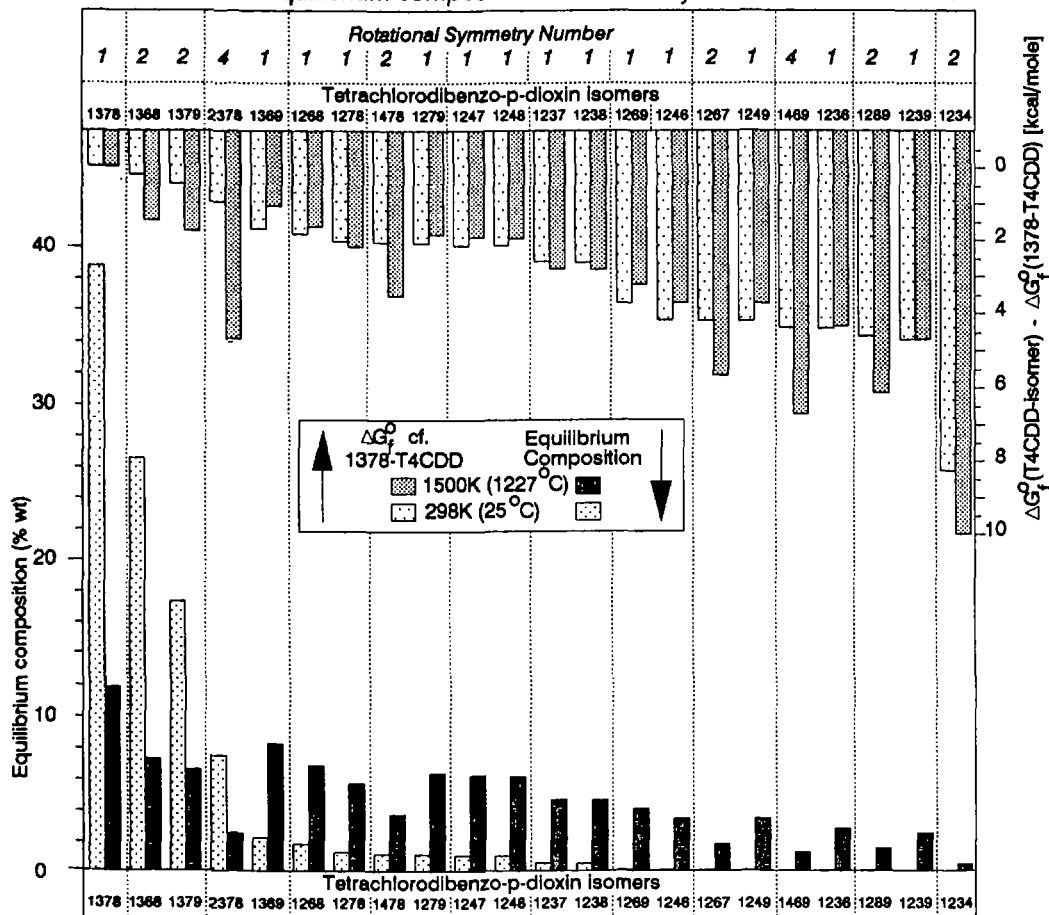Figure 1. Enthalpy of Formation of Dioxins predicted by various methods

Figure 2. Temperature dependence of relative Gibbs Free Energy of Formation [a]
and equilibrium composition calculated by MNDO for T4CDD-isomers

a. Relative to ΔG_f^o (1378-T4CDD) i.e. -11.9 kcal/mole @ 298K & +122.1 kcal/mole @ 1500K