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Rate Constants for Hydrogen Atom Attack on Some Chlorinated Benzenes at High Temperatures

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Hydrogen atoms from the decomposition of hexamethylethane were reacted with chlorobenzene, *o*-dichlorobenzene, *p*-dichlorobenzene, and 1,2,3-trichlorobenzene in the presence of toluene or 1,3,5-trimethylbenzene in single-pulse shock tube experiments. Using the rate expression for the displacement of the methyl group from the methylated aromatics as standards we find $k(\mathrm{H} + \mathrm{C_6H_5Cl} \rightarrow \mathrm{C_6H_6} + \mathrm{Cl}) = (2.2 \times 10^{10}) \exp(-4531/T)$ L/(mol·s), $k(\mathrm{H} + o\text{-}\mathrm{C_6H_4Cl_2} \rightarrow \mathrm{C_6H_5Cl} + \mathrm{Cl}) = (9.2 \times 10^{10}) \exp(-5196/T)$ L/(mol·s), $k(\mathrm{H} + p\text{-}\mathrm{C_6H_4Cl_2} \rightarrow \mathrm{C_6H_5Cl} + \mathrm{Cl}) = (4.6 \times 10^{10}) \exp(-4541/T)$ L/(mol·s), $k(\mathrm{H} + 1,2,3\text{-}\mathrm{C_6H_3Cl_3} \rightarrow o\text{-}\mathrm{C_6H_4Cl} + \mathrm{Cl}) = (1.9 \times 10^{10}) \exp(-2954/T)$ L/(mol·s), and $k(\mathrm{H} + 1,2,3\text{-}\mathrm{C_6H_3Cl_3} \rightarrow m\text{-}\mathrm{C_6H_4Cl} + \mathrm{Cl}) = (3.7 \times 10^{9}) \exp(-1856/T)$ L/(mol·s) at temperatures of 1050–1150 K and pressures between 2.5 and 3.2 atm. In this temperature range the relative rate constants on a per-chlorine basis for the five processes are 1:1.15:1.05:1.8:2.4. The absolute uncertainty in the rate expressions are of the order of 8 kJ in the activation energy and a factor of 2.5 in the *A* factor. The relative rate constants have an uncertainty of no more than a factor of 1.1. Rate expressions for the reverse chlorination processes have been calculated to be $k(\mathrm{Cl} + \mathrm{C_6H_6} \rightarrow \mathrm{C_6H_5Cl} + \mathrm{H}) = (4.7 \times 10^{10}) \exp(-13453/T)$ L/(mol·s), $k(\mathrm{Cl} + \mathrm{C_6H_5Cl} \rightarrow o\text{-}\mathrm{C_6H_4Cl_2} + \mathrm{H}) = (2.9 \times 10^{10}) \exp(-15075/T)$ L/(mol·s), and $k(\mathrm{Cl} + \mathrm{C_6H_5Cl} \rightarrow p\text{-}\mathrm{C_6H_4Cl_2} + \mathrm{H}) = (8.8 \times 10^{9}) \exp(-13614/T)$ L/mol·s.

Introduction

This paper is concerned with the reaction of hydrogen atoms with chlorobenzene (ClB), *o*-dichlorobenzene (*o*DClB), *p*-dichlorobenzene (*p*DClB), and 1,2,3-trichlorobenzene (123TClB) at temperatures near 1100 K. Of particular interest are the rate constants and expressions for the displacement of the chlorine atom and the importance of substituent effects in this process. There have been no previous studies of these reactions. We have recently studied the mechanisms and rate constants for hydrogen atom attack on *o*- and *p*-chlorotoluene[1] under conditions similar to those used the present work. The results together with other applicable data can be found in Table I. It is clear that displacement of the methyl group is favored over that of the chlorine atom and that the absolute value of the rate constant for the latter is very close to that for the displacement of OH from phenol. There appears to be a measurable difference in the rate constants for the ejection of a chlorine depending on the position of the methyl grouping. Overall, the variations in the rate constants for displacement for the systems that have been studied are not very large. At the high temperatures of these and earlier experiments, differences in rate constants arising from activation energy variations will have much smaller effects than at room temperature. Kerr[8] has summarized room-temperature rate constants for hydrogen atom attack on olefins. Variations in rate constants were less than an order of magnitude. There does not appear to be any large effect upon fluorine substitution. The room-temperature numbers are in general not site-specific. Thus interpretation is difficult. It is well-known that for simple olefins hydrogen atoms add preferentially to the site that is not methylated.

Chloroaromatics are important constituents of hazardous waste mixtures.[9] There is much current interest in dioxin (2,3,7,8-tetrachloro-*p*-benzodioxin) formation during municipal solid waste (MSW) incineration.[10] A particularly interesting observation is the detection in the effluents of MSW combustion not only of dioxins but also of chlorophenols and chlorobenzenes and the surprising similarities in the number of chlorines on the basic aromatic framework. Any explanation of dioxin formation and destruction must be able to predict the chlorine distribution. Furthermore, the presence of the polychlorinated dioxins suggests that the 2,3,7,8-dioxin of greatest interest may well be an intermediate product that can be formed as well as destroyed from these compounds during incineration. This has important implications on the nature of the "window" for its formation and destruction. It has similar implications on the stability of possible precursors such as the chlorophenols. The displacement of chlorine by hydrogen atoms provides a very simple means for dechlorination. In any combustion system hydroxyl radicals and hydrogen atoms play an important role in attacking organics. We have previously demonstrated[11] that much of the observed organic effluent from incineration systems is probably due to unmixed pockets of organics. In this essentially pyrolytic situation hydrogen atom reactions play a particularly important role. Finally, given the rate constant for chlorine displacement by hydrogen, we can calculate the rate constant for the reverse, or chlorination of the aromatic ring, through the equilibrium constant. By comparing these rate constants with rates of other processes involving chlorine atoms, we can infer the importance of chlorination of aromatics as a mechanism for the formation of hazardous wastes during incineration.

Our experiments are carried out in a heated single-pulse shock tube. We have recently developed a new method for studying hydrogen atom reactions at the high temperatures that are readily generated in such a device. It has been successfully used in earlier experiments on hydrogen atom attack on toluene,[2] phenol,[3] aniline,[4] and *o*-chlorotoluene[1] and *p*-chlortoluene.[1] It has the particular capability of determining the rate constants for multiple channel

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TABLE I: Rate Constants for Hydrogen Atom Attack on Some Organic Compounds

compound [displaced group] (ref)	rate expressions, L/(mol·s)	rate constants (1085 K), L/(mol·s)
	A: Abstraction (Hydrogen on Side Chain from Substituted Aromatics)	
hexamethylethane (7)		64×10^8 (3.4×10^8, per H)
toluene (2)	$(1.2 \times 10^{11}) \exp(-4138/T)$	27×10^8 (8.5×10^8, per H)
o-chlorotoluene (1)		22×10^8 (7.5×10^8, per H)
p-chlorotoluene (1)	$(9.6 \times 10^{10}) \exp(-4265/T)$	19×10^8 (6×10^8, per H)
aniline (4)	$(1.8 \times 10^{11}) \exp(-5846/T)$	8.1×10^8 (3.9×10^8, per H)
methane (5)	$(2.4 \times 10^{11}) \exp(-7000/T)$	3.8×10^8 (9×10^7, per H)
phenol (3)	$(1.1 \times 10^{11}) \exp(-6240/T)$	3.5×10^8
ammonia (6)	$(1.8 \times 10^{11}) \exp(-8067/T)$	1.1×10^8 (3.3×10^7, per H)
water (5)	$(2.4 \times 10^{11}) \exp(-11310/T)$	0.07×10^8 (3.2×10^7, per H)
	B: Displacement	
1,2,3-trichlorobenzene		
[1 or 3-Cl]	$(1.9 \times 10^{10}) \exp(-2954/T)$	12.5×10^8
[2-Cl]	$(3.7 \times 10^9) \exp(-1856/T)$	6.7×10^8
total		19.2×10^8
o-chlorotoluene [CH_3] (1)		13×10^8
p-chlorotoluene [CH_3] (1)	$(3.5 \times 10^{10}) \exp(-3710/T)$	12×10^8
toluene [CH_3] (2)	$(1.2 \times 10^{10}) \exp(-2578/T)$	11×10^8
o-chlorotoluene [Cl] (1)		7.6×10^8
o-dichlorobenzene [Cl]	$(9.2 \times 10^{10}) \exp(-5196/T)$	7.7×10^8
p-dichlorobenzene [Cl]	$(4.6 \times 10^{10}) \exp(-4541/T)$	7.0×10^8
aniline [NH_2] (4)	$(2.2 \times 10^{10}) \exp(-3735/T)$	7.0×10^8
p-chlorotoluene [Cl] (1)	$(4.8 \times 10^{10}) \exp(-4795/T)$	5.8×10^8
phenol [OH] (3)	$(2.2 \times 10^{10}) \exp(-3990/T)$	5.6×10^8
chlorobenzene [Cl]	$(2.2 \times 10^{10}) \exp(-4531/T)$	3.4×10^8

reactions. The experimental procedure involves decomposing trace quantities of a highly unstable hydrocarbon, hexamethylethane, in the presence of overwhelming amounts of the aromatic compound in question. At sufficient excesses (>100 to 1) the main processes are the abstraction of a hydrogen from the side chain and the displacement of the side chain. The latter leads to a stable product. Since the decomposition of hexamethylethane leads to the formation of equal quantities of atomic hydrogen atoms and isobutene, then subtraction of the displacement product from the isobutene concentration leads to the contribution from side chain abstraction. This yields a ratio of the displacement to abstraction rate constants. Under our temperature conditions abstraction from the ring is not competitive. If we now add into such a mixture large quantities of methane, the yields of the displacement product will be reduced, since hydrogen atoms will be removed via the reaction $H + CH_4 \rightarrow CH_3 + H_2$. Comparing this with the situation where there is no methane leads to the determination of the relative rates of attack on methane and the compound in question. Since the rate expression for hydrogen attack on methane is well established, we can then place all our results on an absolute basis.

In the present case, the reaction temperatures are such that the most likely route for hydrogen atom reaction with the chlorinated benzenes is displacement. This leads to a stable product. We have accordingly carried out copyrolysis experiments with trace amounts of hexamethylethane in 1,3,5-trimethylbenzene or toluene and the appropriate mono-, di- and trichlorobenzene and determined the ratios of the displacement products formed from methyl and chlorine ejection. We then derive the rate expression for chlorine displacement from our previously determined values for the displacement of methyl. Finally, we note that the yields of isobutene not only establish the absolute number of hydrogen atoms released into the system but also serve as a mark of the extent of hexamethylethane decomposition. We use this as an internal standard for the determination of an average reaction temperature. This eliminates the necessity for determining the reaction temperature and removes the greatest source of errors from single-pulse shock tube experiments.

Experimental Section

Our experiments are carried out in a heated single-pulse shock tube that is maintained at 110 °C. All of the gas handling and storage systems are maintained at a similar or higher temperature. With such a configuration we are able to work with and extract from the shock tube low-vapor-pressure organic compounds (bp, 1,2,3-trichlorobenzene, 218 °C). Gas chromatography with a 30-m poly(dimethylsiloxane) column and flame ionization detection are used for analysis. All of the chlorobenzenes are from Aldrich and are used without further purifcation. The argon is of ultra pure grade and is from Matheson, and the hexamethylethane is from Wiley Organics.[12] Our experiments are carried out with mixtures having the compositions given in Table II. The standards used in deriving the rate constants and expressions are the displacement of methyl from toluene (TOL) and 1,3,5-trimethylbenzene (135TMB). The rate expressions[2,13] are as follows:

TABLE II: Mixtures Used in Single-Pulse Shock Tube Experiments

97 ppm hexamethylethane in 0.928% *p*-dichlorobenzene and 0.459% 1,3,5-trimethylbenzene
97 ppm hexamethylethane in 0.97% dichlorobenzene and 0.44% 1,3,5-trimethylbenzene
159 ppm hexamethylethane in 1.48% chlorobenzene and 0.49% 1,3,5-trimethylbenzene
57 ppm hexamethylethane in 1% 1,2,3-trichlorobenzene and 2% toluene

$$k_{\mathrm{disp}}(\mathrm{TOL}) = (1.2 \times 10^{10}) \exp(-2578/T)\ \mathrm{L/(mol \cdot s)}$$

$$k_{\mathrm{disp}}(\mathrm{135TMB}) = (5.3 \times 10^{10}) \exp(-3055/T)\ \mathrm{L/(mol \cdot s)}$$

Note that in terms of the rate constants on a per methyl basis at the reaction temperatures the values differ by less than 10%. Thus we strongly suspect that the 4-kJ/mol difference in activation energy is probably too large.

Results

Our experimental results are summarized in Figures 1 and 2. The rate constant ratios are derived from the relation

$$k_{\mathrm{disp}}(\mathrm{Cl})[\text{chlorinated benzene}]/k_{\mathrm{disp}}(\text{methyl})[\text{methylated benzene}] = [\text{dechlorinated benzene}]/[\text{demethylated benzene}]$$

where the square bracket denotes concentration and we are considering the removal of one chlorine or methyl group. The

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(12) Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment is necessarily the best available for the purpose.

(13) Cui, J. P.; He, Y. Z.; Tsang, W. "H-atom Attack on Methylated Benzenes", to be submitted for publication.

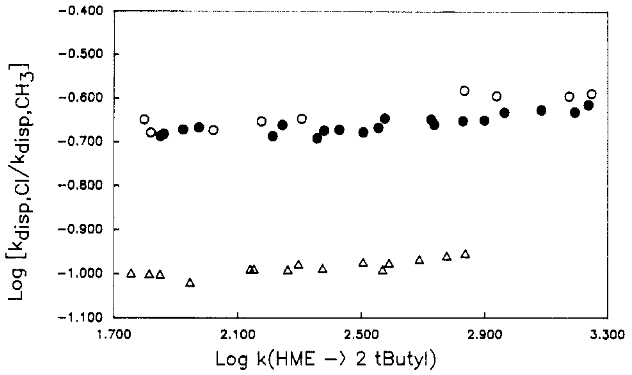

Figure 1. Ratio of rate constants for the displacement of chlorine from *o*-dichlorobenzene (○), *p*-dichlorobenzene (●), and chlorobenzene (△) and that of methyl from 1,3,5-trimethylbenzene as a function of the rate constant of hexamethylethane composition. Conditions: 97 ppm hexamethylethane in 0.928% *p*-dichlorobenzene and 0.459% 1,3,5-trimethylbenzene; 97 ppm hexamethylethane in 0.97% dichlorobenzene and 0.44% 1,3,5-trimethylbenzene; 159 ppm hexamethylethane in 1.48% chlorobenzene and 0.49% 1,3,5-trimethylbenzene; temperature, 1050–1150 K; pressure, 2.5–3.0 atm of argon.

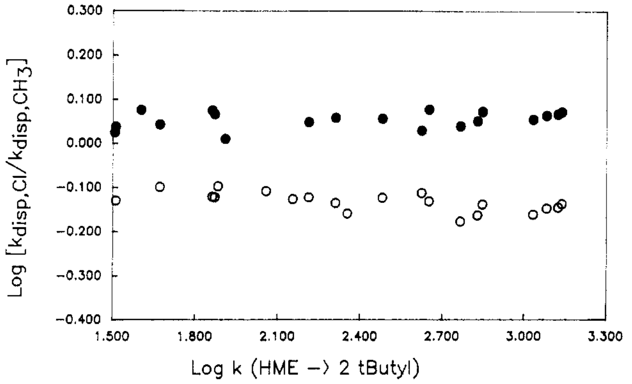

Figure 2. Ratio of rate constants for the displacemement of chlorine from 1,2,3-trichlorobenzene: (●) 1 and 3 position; (○) 2 position and the displacement of a methyl group from toluene. Conditions: 57 ppm hexamethylethane in 1% 1,2,3-trichlorobenzene and 2% toluene; temperature, 1050–1150 K; pressure, 2.5–3.0 atm of argon.

x axis is the rate constant for the breaking of the most highly substituted C–C bond in hexamethylethane (HME). We have previously established the rate expression to be

$$k(C_8H_{18} \rightarrow 2t\text{-}C_4H_9) = k(\text{HME}) = (3 \times 10^{16}) \exp(-34500/T)/\text{s} = (\ln (1 - 2(i\text{-}C_4H_8)_f/(C_8H_{18})_i))/t$$

or

$$\log (k(\text{HME})) = 16.5 - 14980/T$$

where *t* is the residence time of the order of 500 μs and the subscripts i and f refer to the initial and final concentrations. From the above, it can be seen that the *x* axis is proportional to $-1/T$. We have chosen to represent the data in this form because it explicitly displays the fact that a measured temperature, the principal source of error in single-pulse, and in fact most, shock tube experiments, is no longer a factor in these studies. Actually, since the temperature dependence of the ratios that we are measuring is small, virtually no errors are introduced by uncertainties in the standard rate expression. Thus by concentrating on the measurement of ratios of concentrations, we reduce the scatter to that of the chromatographic determinations. The errors in the ratio of rate constants are due to uncertainties in calibration and the concentration of the test mixtures. They should not exceed a factor of 1.1.

Least-squares treatment of the data leads to the following results:

$$\log (k_{\text{disp}}(\text{ClB})/k_{\text{disp}}(\text{135TMB})) = (0.0428 \pm 0.007) \log (\text{HME}) - (1.084 \pm 0.015)$$

$$\log (k_{\text{disp}}(o\text{DClB})/k_{\text{disp}}(\text{135TMB})) = (0.0621 \pm 0.01) \log (\text{HME}) - (0.783 \pm 0.024)$$

$$\log (k_{\text{disp}}(p\text{DClB})/k_{\text{disp}}(\text{135TMB})) = (0.0431 \pm 0.066) \log (\text{HME}) - (0.769 \pm 0.016)$$

$$\log (k_{\text{disp}}(\text{123TClB}, o\text{DClB})/k_{\text{disp}}(\text{TOL})) = (0.0109 \pm 0.0075) \log (\text{HME}) + (0.028 \pm 0.018)$$

$$\log (k_{\text{disp}}(\text{123TClB}, m\text{DClB})/k_{\text{disp}}(\text{TOL})) = (-0.0271 \pm 0.0076) \log (\text{HME}) + (-0.067 \pm 0.018)$$

where the compounds after the 123TClB are the products formed as a result of the displacement, and where *o*DClB and *m*DClB refer to *o*-dichlorobenzene and *m*-dichlorobenzene, respectively. Substituting into these relations the rate expression for hexamethylethane decomposition and that for hydrogen atom displacement of a methyl group leads to the following rate expression for the displacement of a chlorine from the four compounds that we have studied:

$$k_{\text{disp}}(\text{ClB}) = (2.2 \times 10^{10}) \exp(-4531/T)\ \text{L/(mol·s)}$$

$$k_{\text{disp}}(o\text{DClB}) = (9.2 \times 10^{10}) \exp(-5196/T)\ \text{L/(mol·s)}$$

$$k_{\text{disp}}(p\text{DClB}) = (4.6 \times 10^{10}) \exp(-4541/T)\ \text{L/(mol·s)}$$

$$k_{\text{disp}}(\text{123TClB} \rightarrow o\text{DClB} + \text{Cl}) = (1.9 \times 10^{10}) \exp(-2954/T)\ \text{L/(mol·s)}$$

and

$$k_{\text{disp}}(\text{123TClB} \rightarrow m\text{DClB} + \text{Cl}) = (3.7 \times 10^{9}) \exp(-1856/T)\ \text{L/(mol·s)}$$

It should be noted that while the first three rate expressions are based on the displacement of methyl from toluene, the last two expressions are based on methyl displacement from 1,3,5-trimethylbenzene. This was necessary in order to avoid interferences from the gas chromatographic analysis. As noted earlier, we doubt the accuracy of the measured 4-kJ difference in activation energy for the two processes, and for comparison, the differences in activation energies should be decreased by 4 kJ/mol. We estimate that the absolute uncertainties in the rate expressions are 8 kJ in the activation energy and a factor of 2.5 in the *A* factor. The measured rate constants are undoubtedly more reliable. The values at an intermediate temperature are summarized in Table I. For purposes of comparison we have also included the rate constants for displacement for a variety of other compounds.

Discussion

Although we have cast our results in the form of a displacement process, it is also possible that the rate constants contain a component from the direct abstraction of the chlorine atom from the aromatic ring. Note that direct abstraction will lead to a phenyl radical, which under our conditions will abstract a benzyl hydrogen. The product formed will therefore be the same as that resulting from displacement. Strictly speaking, our measured rate constant is the sum of the rate constants for these two processes. However, we believe that abstraction cannot be more than a minor channel. Nevertheless, the evidence is all indirect. In the case of H-atom attack on dimethyl ether,[14] no methanol was detected and displacement could not have occurred. Westenberg and deHaas[15] determined the rate constant for hydrogen atom attack on methyl fluoride, chloride, and bromide. They claimed that in all cases the halogen is abstracted. This is based on their belief that the C–H bonds in these compounds have bond strengths similar to that in methane and therefore under their conditions cannot be abstracted. This is grossly in error. The actual values of the C–H bond strengths are 20 kJ/mol lower.[16] The truly

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significant observation is that the rate constants for the fluoride and chloride are the same, while that for the bromide is much larger. We believe that this indicates a hydrogen abstraction process for the fluoride and chloride. On that basis, and in view of the fact that abstraction of the halide from the benzene ring is a further 50 kJ/mol less exothermic than abstraction from methyl chloride, a significant contribution from abstraction is unlikely and displacement must be the main reaction.

Our results demonstrate that the range of rate constants for displacement of chlorine by hydrogen is not particularly large. On a per-chlorine basis it is a factor of 2.4. Nevertheless, the small changes are worthy of comment. The rate constant for displacement per chlorine atom is virtually constant for the three systems, chlorobenzene, *o*-dichlorobenzene, and *p*-dichlorobenzene. However, for 1,2,3-trichlorobenzene the values are increased by a factor of 1.8 for the outer two chlorines and by a factor of 2.4 for the inner chlorine. In the case of methyl substitution displacement is enhanced, and the rate constants on a per-chlorine-atom basis are close to that for the trichloro system. It is also interesting that, unlike the situation for the *o*-dichlorobenzene, methyl substitution in the ortho position increases the rate constant for chlorine displacement. For the system toluene, aniline, phenol, and chlorobenzene, there is steady decrease in rate constants. From the data in Table I, the relative rates are 1:0.6:0.5:0.3.

The elementary process that should be associated with the reported rate constant for displacement is addition of hydrogen to the chlorine site or the formation of the chlorinated cyclohexadienyl radical. This is because the thermodynamics strongly disfavors the reverse hydrogen atom removal reaction. Addition will always be followed by chlorine ejection. The differences in the rate constants for the chlorinated benzenes are worthy of comment. At first glance it is surprising that there should be a difference between the rate constant for the displacement of a chlorine in *o*-dichlorobenzene and the 1 and 3 chlorine in 1,2,3-trichlorobenzene. However, the chlorines in a compound such as hexachlorobenzene are bent 12° out of the ring plane.[17] It may be that in the 1,2,3-trichlorobenzene there is already some manifestation of this effect. The increased rate constant may well be due to the energy gained in returning to the planar configuration upon hydrogen addition. Together with our earlier observations on the effect of methyl substitution, it would appear that steric effects are of prime importance. The differences we have observed are in the 1000–1150 K regime. If these are all due to the activation energy barrier, the effects will be much larger at room temperature. For example, in the case of the chlorotoluenes one would expect that at the lower temperature, the rate constant for hydrogen atom addition at the Cl site will be close to an order of magnitude smaller than that for addition at the methyl group site.

The rate expressions that we have obtained are not as accurate as the rate constants. It does appear however that in all cases except for 1,2,3-trichlorobenzene the activation energies for chlorine displacement are substantially higher than that for methyl displacement, and this is responsible for the lower rate constant. In the case of the trichloro compound the increased rate appears to be due to a lowering of the activation energy. This is most strongly manifested in the case of the middle chlorine. It is, however, partly compensated for by a stiffened transition state, leading to a somewhat lowered *A* factor. This is surprising, since the relief of strain upon hydrogen addition should lead to a looser transition state and hence a higher *A* factor.[18] It would certainly be interesting to study other highly substituted aromatics.

Our rate expressions can be used with the equilibrium constant to obtain rate expressions for hydrogen displacement by chlorine. This is particularly important in the context of the formation of chlorinated aromatics from organics and chlorine. The accuracy of such calculations should be very good since the thermodynamic properties of these compounds are fairly well established.[19] The results are given below:

$$k(\mathrm{Cl} + \mathrm{C_6H_6} \rightarrow \mathrm{C_6H_5Cl} + \mathrm{H}) = (4.7 \times 10^{10}) \exp(-13453/T)\ \mathrm{L/(mol{\cdot}s)}$$

$$k(\mathrm{Cl} + \mathrm{C_6H_5Cl} \rightarrow o\text{-}\mathrm{C_6H_4Cl_2} + \mathrm{H}) = (2.9 \times 10^{10}) \exp(-15075/T)\ \mathrm{L/(mol{\cdot}s)}$$

$$k(\mathrm{Cl} + \mathrm{C_6H_5Cl} \rightarrow p\text{-}\mathrm{C_6H_4Cl_2} + \mathrm{H}) = (8.8 \times 10^{9}) \exp(-13614/T)\ \mathrm{L/(mol{\cdot}s)}$$

Unlike the situation for the reverse reaction, the rate expressions given here are composite values, since addition of the chlorine atom will be usually reversed. In only a small percentage of the cases will hydrogen be displaced. These are reflected in our rate expressions. Chlorine atoms are extremely reactive in high-temperature systems. Thus the rate expression of Whytock et al.[20] gives

$$k(\mathrm{Cl} + \mathrm{CH_4} \rightarrow \mathrm{HCl} + \mathrm{CH_3}) = (3 \times 10^{2}) T^{2.5} \exp(-264/T)\ \mathrm{L/(mol{\cdot}s)}$$

This leads to a value of 9.1×10^9 L/(mol·s) at 1085 K. This is over 10 000 times larger than the comparable value for hydrogen displacement by chlorine in benzene. Thus, unless the aromatic or chlorine content is extremely high in comparison to that of other hydrocarbons, ring addition cannot occur during incineration. Note that after the first displacement the rate constant of a second chlorine is even slower. The general conclusion is that displacement by chlorine is slow both in an absolute as well as relative sense. This provides very satisfactory support for the unlikelihood of forming highly chlorinated aromatics in the combustion zone of a municipal solid waste incinerator without the aid of appropriately chlorinated precursors or catalytic effects.

With respect to incineration problems, our results provide two distinct pieces of information. First, we now have a basis for estimating the minimum quantity of hydrogen atoms that must be present in order to break down a given chlorinated aromatic compound to a certain level. This is a conservative number since the primary mechanism for the destruction of organic molecules in combustion is undoubtedly through OH attack. Here we are considering the pockets of unburned gas. Secondly, since we have measured the rate constant for H-atom attack on a number of chlorinated aromatics, we are able to draw conclusions on how initial distribution of chlorinated aromatics will be affected by these processes. For this purpose we recall the most important conclusion: that is, on a per-chlorine-atom basis the rate constants for displacement will increase with increasing degree of chlorination. The consequence is that hexachlorobenzene is the least stable of the chlorinated benzenes with a rate constant for chlorine displacement that is perhaps as much as a factor of 15 larger than that for chlorobenzene. With this as a guide, if one beings with the most highly chlorinated aromatic, then under pyrolysis conditions, and given a certain concentration of hydrogen atoms and sufficient reaction time, one should be able to obtain the observed chlorine distribution. The reverse cannot be true. A distribution that is peaked toward low chlorine cannot through dechlorination lead to one that favors the highly chlorinated aromatic compounds. These results strongly suggest that in a municipal solid waste incinerator where dioxin type compounds can be detected, heavily chlorinated aromatics are in fact being fed into the combustion zone.

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