

Kinetic Studies of the Reaction of Atomic Chlorine with Chlorobenzene

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Abstract

The rate constant k_I for $\text{Cl} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{products}$ has been studied via the pulsed laser photolysis – time-resolved resonance fluorescence technique over 710 – 1030 K. The results may be summarized as $k_I = (1.36 \pm 0.47) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \exp\{-(42.5 \pm 2.5) \text{ kJ mol}^{-1}/RT\}$. The quoted uncertainties are $\pm 1\sigma$, and the 95% confidence limit for k_I is $\pm 21\%$. The major pathway is proposed to be formation of HCl and chlorophenyl radicals. Density functional calculations suggest the most favorable product is 3-chlorophenyl arising from attack *meta* to the C-Cl bond.

1. Introduction

Chlorobenzene is a model compound for analysis of destruction of chlorinated aromatic molecules by combustion, where avoidance of formation of toxic chlorinated dibenzodioxins is a significant issue [1-5]. Burfeindt and Homann showed that C₆H₅Cl is a major initial product in benzene flames doped with chlorine compounds, and that in turn C₆H₅Cl is transformed to further products [6]. We have proposed the reaction



may lead to chlorophenyl radicals which could react with chlorobenzene in part via H-atom displacement [7]. These steps can form part of a combustion chain reaction where H atoms then consume chlorobenzene by abstraction of Cl. The present study is part of an overall effort to quantify the high-temperature chemistry of chlorobenzene.

Reaction 1 has been studied previously in the context of atmospheric chemistry, via relative rate methods. Sokolov et al. determined an upper limit of $2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for HCl formation at room temperature [8]. This is below a prior measured total rate constant of $9.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Shi and Bernhard [9]. A potential reaction path under these conditions is formation of dichlorocyclohexadienyl radicals by addition. There have been no measurements at elevated temperatures. Here we use the laser flash photolysis – resonance fluorescence technique to obtain the first kinetic data at 710 - 1030 K for the total rate constant k_1 , and apply density functional theory to assess likely product channels.

2. Methodology

Chlorobenzene (Mallinckrodt, 99.9% purity AR grade) was degassed via two freeze-pump-thaw cycles at 77 K and then distilled twice from room temperature. In these distillations the middle 80% was trapped at 77 K. Details of the apparatus have been given elsewhere [7,10]. Briefly, atomic Cl is formed by pulsed laser photolysis of a small fraction of chlorobenzene at 193 nm. We have determined an absorption cross section of $(9.62 \pm 0.14) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ which is temperature-independent over 300-500 K, and the quantum yield for dissociation to $\text{C}_6\text{H}_5 + \text{Cl}$ is unity [11,12]. For the purpose of estimating the initial concentrations of Cl and C_6H_5 we assume these properties of $\text{C}_6\text{H}_5\text{Cl}$ do not vary with temperature over 700 – 1000 K. Deviations will not be critical because we use pseudo-first-order conditions and knowledge of absolute radical concentrations is not required. The concentration of Cl is probed by time-resolved resonance fluorescence at 130 - 140 nm, excited by a microwave discharge lamp and monitored with a solar-blind photomultiplier tube operated in a photon-counting mode with signal averaging in a multi-channel scaler. Calcium fluoride optics block any H-atom radiation. Experiments were conducted in a large excess of Ar bath gas (Air Liquide, 99.9997%), which thermalized the reactants and slowed diffusion of radicals out of the observation zone defined by the intersection of the beams of photolysis and probe radiation.

Under the condition $[\text{C}_6\text{H}_5\text{Cl}] \gg [\text{Cl}]$, we may write

$$d[\text{Cl}]/dt = -k_1[\text{C}_6\text{H}_5\text{Cl}][\text{Cl}] - k_{diff}[\text{Cl}] = -k_{ps1}[\text{Cl}] \quad (2)$$

where k_{diff} accounts for loss of Cl by diffusion and by any reaction with photolysis fragments of $\text{C}_6\text{H}_5\text{Cl}$. These processes were found to be sensibly first-order. k_{ps1} is the

effective pseudo-first-order decay coefficient, and is derived via non-linear fitting to the exponential decay profiles such as that shown in the inset of Fig. 1. Plots of k_{psl} vs. $[C_6H_5Cl]$ like those shown in Fig. 1 yield k_I and its uncertainty from the slope, and the intercept corresponds to k_{diff} . As expected for a process dominated by diffusion, k_{diff} increased with increasing T and decreased with increasing total pressure P, as can be seen in Fig. 1.

3. Results

Table 1 summarizes 21 measurements of k_I over 710 - 1030 K. For each measurement data were typically obtained at 6 values of $[C_6H_5Cl]$ up to $[C_6H_5Cl]_{max}$. The listed uncertainties are the statistical standard deviations of the slopes of plots like Fig. 1. An important check is that there is no consistent variation with the initial Cl concentration, as determined from the laser photolysis energy F and the concentration and UV cross-section of chlorobenzene. This confirms that pseudo-first-order conditions were attained and that reaction 1 was successfully isolated from secondary chemistry. Very low laser photolysis energies, below 50 μJ , were used to provide low initial radical concentrations, in the range $(1-13) \times 10^{10}$ molecule cm^{-3} . Consistent with the lack of influence of photolytic or reaction products, if Cl is removed by reaction with C_6H_5 or chlorophenyl with a rate constant of 10^{-10} cm^3 molecule $^{-1}$ s $^{-1}$, then the contribution of ≤ 13 s $^{-1}$ to k_{psl} is negligible. The independence of k_I from the pressure P and the average residence time of the reaction mixture in the heated cell, τ_{res} , observed previously [7], indicate that thermal decomposition of C_6H_5Cl is not significant in our apparatus. This is in accord with the

work of Ritter et al. who determined a C₆H₅Cl dissociation rate of less than 10⁻⁴ s⁻¹ at 1070 K [4].

The data for reaction 1 are plotted in Arrhenius form on Fig. 2. A linear fit, weighted according to the statistical uncertainties listed in Table 1 and $\sigma_T/T = 2\%$, may be expressed as

$$k_I = (1.36 \pm 0.47) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \exp\{-(42.5 \pm 2.5) \text{ kJ mol}^{-1}/RT\}$$

(3)

over 710 – 1030 K. The quoted uncertainties are $\pm 1\sigma$ for the pre-exponential factor and the activation energy E_a . Consideration of the covariance of -102.8 K^{-1} yields statistical 2σ error limits of up to 20% in k_I . Combination in quadrature with propagated instrumental uncertainties of $\sim 5\%$ yields a 95% confidence limit of $\pm 21\%$ for k_I .

4. Discussion

Extrapolation of eq. 3 to 298 K yields $5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with a 2σ uncertainty of a factor of 3. This indicates that the determination of Shi et al. [9], which is 200 times larger, is likely too high. This is in accord with arguments of Sokolov et al. [8] concerning the reaction



who noted that impurities or secondary chemistry might have been important in earlier work. Sokolov et al. observed no formation of HCl and set an upper limit of $k_I < 2.5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which agrees with extrapolation of our data. We may also compare k_I with our previous measurements of the analogous reaction 4 [10]. The latter is faster by about a factor of 3 at 700 K and a factor of 2 at 1000 K.

Next we consider possible product channels. Cui et al. [3] showed that, at 1050 K, H atoms can be displaced by atomic Cl with a rate constant below $10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is too slow to contribute significantly to the Cl consumption we observed. Density functional theory calculations outlined below indicated no barrier to Cl-atom addition, which suggests that when thermodynamically favored (at low temperatures) addition may be a fast process. By analogy with Cl addition to benzene [8], adduct formation between Cl and $\text{C}_6\text{H}_5\text{Cl}$ will be thermodynamically unfavorable at elevated temperatures. The estimated thermochemistry for adduct formation between Cl and benzene [8] implies that, if similar interactions occur between Cl and chlorobenzene, then under our conditions less than 1 part in 10^6 of atomic Cl would be bound at equilibrium, and thus formation of dichlorocyclohexadienyl may be neglected here. The corresponding lifetime for this adduct at 700 K is less than 20 ns. A third possible pathway is Cl abstraction to form phenyl + Cl_2 . The computed reaction enthalpy is $+163 \text{ kJ mol}^{-1}$ at 0 K, so Cl_2 formation may be ruled out.

H-abstraction to form HCl and chlorophenyl radicals is a plausible pathway at higher temperatures because for the analogous Cl + benzene reaction the endothermicity is $40.5 \pm 2.5 \text{ kJ mol}^{-1}$ at 298 K [10]. We investigate this possibility further using density functional theory, with the MPWB1K functional and the MG3 basis set [13]. These calculations were carried out with the Gaussian 03 program suite [14]. There are three sites for Cl attack leading to HCl: *ortho*, *meta* and *para* to the C-Cl bond. Qualitatively similar reaction paths were obtained in each case. A planar abstraction transition state (TS) lies below the energy of chlorophenyl radical plus HCl. Between the TS and final products there is a local minimum on the classical potential energy surface (i.e., the PES

without zero-point vibrational energy, ZPE), where the HCl is approximately perpendicular to the aromatic ring and the H atom points towards the ring. A second planar conformation has the radical center on the phenyl ring pointing towards the H end of the HCl molecule. As an example, Figure 3 shows the structures for attack at the *meta* position. With the inclusion of ZPE the 0 K enthalpies of the possible adducts lie within ± 2 kJ mol⁻¹ of the TSs, which indicates a fairly flat PES in this region and that the bond strengths of the apparent adducts are very small, if they are bound at all. The density functional results are summarized in Table 2 and full details are given in the Supplementary Material.

Quantitative kinetic analysis of this kind of PES requires RRKM or modified transition state theory approaches [15,16], but three qualitative conclusions may be drawn here. The first is that the most favorable path, both kinetically and thermochemically, is *meta* attack, which has a reaction path degeneracy of two. The next most favorable path is *para* attack, which has a slightly higher barrier and whose contribution will be further reduced by its reaction path degeneracy of one. *Ortho* attack is the least favorable pathway.

The second conclusion is that, because the energy of the TS lies below that of the products, a negative activation energy is likely for the reverse reaction of chlorophenyl radicals with HCl. This prediction is consistent with the negative temperature dependence we observed for the reaction of C₆H₅ with HCl [10]. If k_{-1} exhibits $E_a < 0$, then E_a for k_1 will be somewhat less than the endothermicity [17].

Third, the computed 0 K reaction enthalpy for *meta* attack is close to the value of 38.2 kJ mol⁻¹ computed for $\text{Cl} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_5 + \text{HCl}$. If the C-H bond reactivity is

similar at the 6 positions in benzene and the 2 *meta* positions of chlorobenzene, then a ratio of reactivity of 3:1 would be likely. With smaller reactivity contributions from the *para* and *ortho* positions, the expected ratio of somewhat less than 3 to 1 is in line with that observed.

5. Conclusions

Rate constants for the reaction of Cl atoms with chlorobenzene have been obtained over about 710 – 1030 K, and this reaction is found to be a factor of 2-3 slower than the analogous reaction of benzene. The most likely pathways involve H abstraction, via transition states lower in energy than the final products, to yield HCl and chlorophenyl radicals. Density functional calculations suggest the most favorable of these is the 3-chlorophenyl radical, produced by attack at the C-H bond *meta* to the C-Cl bond.

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References

- [1] J. A. Manion, P. Mulder and R. Louw, *Environ. Sci. Technol.* 19 (1985) 280.
- [2] J. A. Manion and R. Louw, *J. Phys. Chem.* 94 (1990) 4127.
- [3] J. P. Cui, Y. Z. He and W. Tsang, *J. Phys. Chem.* 93 (1989) 724.
- [4] E. R. Ritter, J. W. Bozzelli and A. M. Dean, *J. Phys. Chem.* 94 (1990) 2493.
- [5] B. R. Stanmore, *Combust. Flame* 136 (2004) 398.
- [6] J. Burfeindt and K.-H. Homann, *Chemosphere* 42 (2001) 439.
- [7] Y. Gao and P. Marshall, *Proc. Combust. Inst.* 32 (2009) 351.
- [8] O. Sokolov, M. D. Hurley, T. J. Wallington, E. W. Kaiser, J. Platz, O. J. Nielsen, F. Berho, M.-T. Rayez and R. Lesclaux, *J. Phys. Chem. A* 102 (1998) 10671.
- [9] J. Shi and M. Bernhard, *Int. J. Chem. Kinet.* 29 (1997) 349.
- [10] I. M. Alecu, Y. Gao, P.-C. Hsieh, J. P. Sand, A. Ors, A. McLeod and P. Marshall, *J. Phys. Chem. A* 111 (2007) 3970.
- [11] T. Ichimura and Y. Mori, *J. Chem. Phys.* 58 (1973) 288.
- [12] T. Ichimura, Y. Mori, H. Shinohara and N. Nishi, *Chem. Phys. Lett.* 189 (1994) 117.
- [13] Y. Zhao and D. G. Truhlar, *J. Phys. Chem. A* 108 (2004) 6908.
- [14] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. J. A. Montgomery, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo,

R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03. Gaussian, Pittsburgh, 2003.

- [15] D. M. Golden, *J. Phys. Chem.* 83 (1979) 108.
- [16] L. N. Krasnoperov, J. Peng and P. Marshall, *J. Phys. Chem. A* 110 (2006) 3110.
- [17] Y. Gao, I. M. Alecu, P.-C. Hsieh, B. P. Morgan, P. Marshall and L. N. Krasnoperov, *J. Phys. Chem. A* 110 (2006) 6844.

Table 1. Summary of rate constant measurements for $\text{Cl} + \text{C}_6\text{H}_5\text{Cl} \rightarrow \text{C}_6\text{H}_5 + \text{HCl}$

T, K	$\tau_{\text{res}},$ s	F, mJ	P, mbar	$[\text{C}_6\text{H}_5\text{Cl}]_{\text{max}},$ 10^{14} molecule cm^{-3}			$[\text{Cl}]_{0,\text{max}},$ 10^{10} molecule cm^{-3}	$k_I \pm \sigma_{k_I},^a$ $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$		
713	2.0	0.046	159	1.88	±	0.08	2.5	1.43	±	0.07
713	2.0	0.017	159	1.88	±	0.08	2.5	0.87	±	0.07
713	2.0	0.043	159	1.88	±	0.08	6.3	1.32	±	0.06
812	0.3	0.017	71	2.35	±	0.09	2.5	2.17	±	0.19
813	0.5	0.010	73	3.19	±	0.13	1.5	2.35	±	0.15
813	0.2	0.012	29	1.53	±	0.06	1.8	2.18	±	0.19
813	0.2	0.007	29	1.53	±	0.06	1.0	2.52	±	0.16
814	0.3	0.010	76	1.70	±	0.07	1.5	2.31	±	0.17
914	0.2	0.007	69	1.69	±	0.07	1.0	3.33	±	0.21
915	0.2	0.090	72	1.39	±	0.06	13.3	5.41	±	0.25
915	0.2	0.040	72	1.39	±	0.06	5.9	4.98	±	0.23
915	0.2	0.026	36	1.34	±	0.05	3.8	6.11	±	0.35
915	0.2	0.013	36	1.34	±	0.05	1.9	4.55	±	0.39
1025	0.4	0.020	72	1.90	±	0.08	3.0	7.14	±	0.51
1025	0.4	0.009	72	1.90	±	0.08	1.3	8.79	±	0.49
1025	0.2	0.019	75	1.37	±	0.05	2.7	9.95	±	0.62
1025	0.2	0.017	71	1.25	±	0.05	2.5	10.60	±	0.85
1026	0.2	0.017	44	1.55	±	0.06	2.5	12.40	±	0.65
1026	0.2	0.036	44	1.55	±	0.06	5.3	11.50	±	0.71
1027	0.2	0.028	28	1.33	±	0.05	4.1	9.91	±	0.65
1027	0.2	0.010	28	1.59	±	0.06	1.5	7.56	±	0.61

^a Statistical uncertainty in plot of k_{ps1} vs $[\text{C}_6\text{H}_5\text{Cl}]$.

Table 2. Relative enthalpies at 0 K in kJ mol^{-1} for stationary points in the $\text{C}_6\text{H}_5\text{Cl} + \text{Cl} \rightarrow \text{C}_6\text{H}_4\text{Cl} + \text{HCl}$ system, based on MPWB1K/MG3 calculations and including zero-point vibrational energy scaled by a standard factor of 0.9567 and a 3.5 kJ mol^{-1} spin-orbit correction to the energy of atomic Cl .

pathway	TS	adduct (perpendicular)	adduct (planar)	chlorophenyl + HCl
<i>ortho</i> attack	41.7	40.1	41.7	45.7
<i>meta</i> attack	32.9	33.5	34.6	39.1
<i>para</i> attack	34.6	36.0	36.6	41.9

Figure captions

Fig. 1

Example plots of pseudo-first-order decay coefficient vs. chlorobenzene concentration at 713 K and 159 mbar Ar bath gas (circles) and 1026 K and 44 mbar Ar bath gas (squares). The error bars represent $\pm 1\sigma$. The inset shows the decay of fluorescence photon counts corresponding to the filled circle.

Fig. 2

Arrhenius plot of rate constants for $\text{Cl} + \text{C}_6\text{H}_5\text{Cl}$. Error bars represent $\pm 1\sigma$ statistical uncertainties.

Fig. 3

Density functional theory geometries for structures along the reaction path for abstraction of H from the *meta* position in chlorobenzene. From top to bottom: transition state, perpendicular adduct between chlorophenyl and HCl, planar conformation of the adduct.