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Kinetics of Ground-State Cd Reactions with Cl_2, O_2, and HCl over Wide Temperature Ranges

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Reactions of ground-state Cd(^{1}S) have been investigated in the 10−80 mbar pressure range using the high-temperature fast-flow reactor (HTFFR) technique. The Cd + $Cl_2 \rightarrow$ CdCl + Cl reaction yielded $k(466-875\ \mathrm{K}) = 9.0 \times 10^{-10} \exp(-5959K/T)$ cm^3 molecule^{-1} s^{-1}, with a 2σ precision of about ±15% and corresponding accuracy of ±27%. For Cd + O_2 and Cd + HCl reactions the upper limits are $k(300\ \mathrm{K}) < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}, or $< 5 \times 10^{-34}$ cm^6 molecule^{-2} s^{-1}. Orbital symmetry rules are used to deduce the reaction products and, along with electron configuration arguments, help explain the slowness of the latter two reactions. The importance of these results for the speciation of Cd, Hg, and Zn in waste incineration is discussed, and the consequences of the present findings for transition metal reactions are mentioned.

1. Introduction

Reactions of excited Cd(^{3}P) and Cd(^{1}P) atoms have been extensively studied,[1] but there is only one reported investigation of Cd(^{1}S) reactions, i.e., with O_2, NO_2, and N_2O.[2] Information on Cd(^{1}S) reactions is of inherent interest and is needed for modeling of waste incineration because of the presence of this highly toxic metal in many combustible wastes in environmentally significant concentrations.[3,4] Metals in incineration partition among residual ash, gases, and airborne submicron particles, such as fly ash and aerosols. These metal-enriched combustion emissions are particularly difficult to clean up and are considered to be among the most hazardous forms of airborne pollution.[3,4]

Recent thermodynamic equilibrium calculations for simulated incineration conditions have shown that Cd can start volatilizing at ∼600 K in the form of $CdCl_2$, but above 1300 K it is mostly present as atomic Cd; the formation of CdO is not favored, even under oxidizing conditions.[5] However, equilibrium calculations can be misleading, since on a given time scale the actual concentrations of metallic species will be kinetically controlled.[4,6] Therefore, kinetic data on reactions leading to cadmium chlorides and oxides are needed. Furthermore, the Cd + Cl_2 reaction is of interest, since because of its endothermicity (34 kJ mol^{-1}),[7,8] it could show evidence for competition between abstraction and addition channels. Such behavior has been observed for the Cr + O_2 and AlO + O_2 reactions.[9,10] This endothermicity is in contrast to most metal atom reactions with Cl_2, which tend to be strongly exothermic.

In the present work the kinetics of the

$$\mathrm{Cd}(^1\mathrm{S}) + \mathrm{Cl}_2 \rightarrow \text{products} \tag{1}$$

$$\mathrm{Cd}(^1\mathrm{S}) + \mathrm{O}_2 \rightarrow \text{products} \tag{2}$$

and

$$\mathrm{Cd}(^1\mathrm{S}) + \mathrm{HCl} \rightarrow \text{products} \tag{3}$$

reactions are investigated using the high-temperature fast-flow reactor (HTFFR) technique.

2. Experimental Section

The HTFFR technique and the present data analysis procedures have been discussed in detail in earlier publications.[11,12] The reactor used consists of an industrial grade quartz reaction tube surrounded by SiC resistance heating elements, insulation, and a water-cooled steel vacuum housing. Gaseous Cd atoms were produced from Cd powder or granules, placed in a resistively heated alumina crucible. The vapor was entrained in a stream of Ar bath gas. Mixtures of oxidant, Cl_2, O_2, or HCl, in Ar were introduced downstream from the evaporation source through a movable quartz inlet. For a given rate coefficient measurement, the total flow rate of these mixtures was kept constant while the oxidant flow was varied. A retractable Pt−Pt/13% Rh thermocouple was used to measure temperature in the reaction zone. Pressure was measured downstream from the reaction zone using an MKS Baratron pressure transducer. Gas flow rates were determined by calibrated Hastings−Teledyne mass-flow controllers. Relative Cd concentrations were monitored by atomic resonance absorption spectrometry (ARAS) using the Cd 5s^2(^{1}S$_0$) to 6s(^{1}P$_0$) resonance transition at 228.8 nm. The resonance radiation was supplied by a Buck Scientific hollow cathode lamp, and the signals were detected by a Thorn RFI/B-213F photomultiplier tube equipped with a 228.5 nm (9.1 nm fwhm) filter and transferred to a Keithley 614 electrometer.

Rate coefficient measurements were performed in the stationary inlet mode[13] with reaction zone lengths of 10 or 20 cm. The gas concentrations were chosen such that [Cd] $\ll$ [oxidant] $\ll$ [Ar], providing for pseudo-first-order conditions in the reactor. Individual rate coefficients, k_i, were obtained from the slope of linear plots of $\ln[\mathrm{Cd}]_{\mathrm{relative}}$ vs [oxidant]. A weighted linear regression was used to determine k_i and σ_{k_i}.[14] Typically, five oxidant concentrations, providing variation by a factor of 5, were used.

The gases used were Ar from the liquid (99.998%) from Praxair, Cl_2 (99.9%), O_2 (99.99%), and HCl (99.99%) all from Matheson, 3.00% Cl_2 (99.9%) in Ar (99.995%) from Linde, HCl (99.995%) from Spectra. Cd powder (99.5%, 325 mesh) and granules (99%, 5−20 mesh) were obtained from Aldrich. All gases, except for Ar, flowed through Drierite ($CaSO_4$) drying towers.

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TABLE 1: Summary of Rate Coefficient Measurements of Cd + Cl_2[a]

P (mbar)	[M] (10^{17} cm^{-3})	$[Cl_2]_{max}$ (10^{14} cm^{-3})	initial Cd absorption (%)	$\bar{v}$ (m s^{-1})	reaction zone length (cm)	T (K)	$k_i \pm \sigma_{k_i}$ (cm^3 molecule^{-1} s^{-1})
12.4	1.41	38.0	18	49	20	637	$(1.03 \pm 0.14) \times 10^{-13}$
13.4	1.41	78.0	9	50	10	687	$(2.50 \pm 0.32) \times 10^{-13}$
12.6	1.43	96.7	35	49	20	634	$(6.93 \pm 0.85) \times 10^{-14}$
41.2	4.85	35.7	19	14	20	615	$(6.22 \pm 0.52) \times 10^{-14}$
41.2	4.89	53.1	24	14	10	610	$(6.06 \pm 0.49) \times 10^{-14}$
32.4	3.76	68.6	14	15	20	625	$(5.88 \pm 0.69) \times 10^{-14}$
32.4	3.70	99.9	35	15	10	635	$(6.55 \pm 0.56) \times 10^{-14}$
27.4	3.76	82.1	18	18	20	527	$(1.07 \pm 0.09) \times 10^{-14}$
28.0	3.93	167	17	17	10	516	$(8.57 \pm 0.80) \times 10^{-15}$
40.1	5.98	170	20	17	20	486	$(4.53 \pm 0.34) \times 10^{-15}$
14.8	2.03	169	40	17	20	530	$(7.76 \pm 0.87) \times 10^{-15}$
8.1	1.09	76.0	41	32	20	534	$(9.28 \pm 1.64) \times 10^{-15}$
79.6	11.8	282	19	9	20	488	$(4.23 \pm 0.29) \times 10^{-15}$
79.4	11.9	284	21	9	20	484	$(4.91 \pm 0.39) \times 10^{-15}$
73.3	11.1	396	13	6	20	479	$(2.87 \pm 0.18) \times 10^{-15}$
73.1	11.4	406	13	6	10	466	$(2.43 \pm 0.25) \times 10^{-15}$
16.2	1.92	130[b]	44	37	20	610	$(5.04 \pm 0.58) \times 10^{-14}$
10.1	1.28	86.4[b]	33	55	20	571	$(3.01 \pm 0.43) \times 10^{-14}$
10.1	1.29	111[b]	42	55	10	568	$(2.29 \pm 0.33) \times 10^{-14}$
56.6	7.43	132[b]	18	9	10	552	$(2.69 \pm 0.18) \times 10^{-14}$
11.2	0.927	20.2	48	73	20	875	$(1.12 \pm 0.15) \times 10^{-12}$
12.0	0.993	54.3	49	70	10	875	$(7.51 \pm 1.06) \times 10^{-13}$
18.5	1.67	16.4	38	61	20	804	$(5.63 \pm 0.59) \times 10^{-13}$
18.5	1.65	38.9	30	62	10	810	$(5.08 \pm 0.49) \times 10^{-13}$
15.0	1.34	31.9	25	76	20	806	$(7.11 \pm 0.78) \times 10^{-13}$
34.0	2.90	5.02[b]	49	24	20	849	$(7.30 \pm 0.57) \times 10^{-13}$
59.3	6.18	14.6[b]	48	11	20	695	$(1.09 \pm 0.09) \times 10^{-13}$
49.9	5.51	5.50[b]	34	22	20	656	$(1.71 \pm 0.11) \times 10^{-13}$
57.2	6.05	11.0[b]	29	17	20	685	$(1.41 \pm 0.09) \times 10^{-13}$
57.1	5.97	10.9[b]	49	17	10	692	$(1.43 \pm 0.10) \times 10^{-13}$
24.9	2.54	60.5	50	40	20	712	$(1.67 \pm 0.17) \times 10^{-13}$
25.2	2.50	159	48	41	10	729	$(1.41 \pm 0.16) \times 10^{-13}$

[a] The measurements are reported in the sequence in which they were obtained. [b] Used 3.00% Cl_2 from Linde; otherwise, used pure Cl_2 from Matheson.

3. Results

3.1. Cd(^{1}S) + Cl_2. Table 1 summarizes the individual rate coefficients measured and the conditions under which they were obtained. Below 466 K rate coefficients for reaction 1 were too low to be measured in our apparatus, and above 875 K excessive evaporation of Cd occurred, even with the use of granulated Cd and when the crucible was covered except for a ca. 1 mm diameter hole. This excessive evaporation led to initial Cd absorption higher than the recommended 50%[13] and resulted in nonlinear $\ln[Cd]_{relative}$ vs $[Cl_2]$ plots, which were discarded. The reaction conditions varied include pressure P from 8 to 80 mbar corresponding to total gas concentrations [M] from 9.3×10^{16} to 1.2×10^{18} molecule cm^{-3}, maximum oxidant concentration $[Cl_2]_{max}$ from 5×10^{14} to 4×10^{16} molecule cm^{-3}, initial Cd absorption, which is a measure of initial [Cd] from 9 to 50%, average flow velocity $\bar{v}$ from 6 to 76 m s^{-1}, and the observed reaction zone length, which was either 10 or 20 cm. To ascertain that individual rate coefficient measurements, k_i, were independent of the conditions used, plots of $[k(T) - k_i]/k(T)$ vs P, [M], $[Cl_2]_{max}$, initial Cd absorption, $\bar{v}$, and reaction zone length were examined. Here $k(T)$ represents the rate coefficient at each individual temperature calculated from eq 4 below. The data are well fitted by a linear regression fit[15] based on k_i and σ_{k_i} to the form $k(T) = A \exp(-E/T)$:

$$k_1(466-875\ \mathrm{K}) = 9.08 \times 10^{-10} \exp(-5959\ K/T)\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}} \quad (4)$$

with associated variances and covariances[16] $\sigma_A{}^2 = 4.64 \times 10^{-2}A^2$, $\sigma_{AE}{}^2 = 2.83 \times 10^1 A$, and $\sigma_E{}^2 = 1.79 \times 10^4$. The resulting $2\sigma_k$ precision limits are ±18% at 466 K, ±9% at 670 K, and ±13% at 835 K. Allowing ±10% for the uncertainty associated with the flow profile factor[13] and ±20% for possible systematic errors, we obtain 2σ accuracy limits varying from ±28% at 466 K to ±26% at 835 K.

3.2. Cd(^{1}S) + O_2. For reaction system 2 no measurable reaction was observed over the temperature range 300−1000 K and an $[O_2]_{max}$ range of 9×10^{15} to 1×10^{17} molecule cm^{-3} at similar conditions as employed for reaction 1, from which we conclude $k_2 < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} or $k_2 < 5 \times 10^{-34}$ cm^6 molecule^{-2} s^{-1}. The only previous study of this reaction was made in a diffusion flame apparatus,[2] which suggested that a second-order reaction occurred with $k(800-960\ \mathrm{K}) = 8.5 \times 10^{-10} \exp(-8250K/T)$ cm^3 molecule^{-1} s^{-1}, corresponding to an activation energy of 69 kJ mol^{-1}. This result is in conflict with the data presented here and is inconsistent with the endothermicity for abstraction of 258 ± 84 kJ mol^{-1}.[7,17] The use of diffusion flames for rate coefficient measurements has previously been shown to be often inaccurate.[18]

3.3. Cd(^{1}S) + HCl. For this system no measurable reaction was observed over the temperature range 300−1000 K and an $[HCl]_{max}$ range 6×10^{15} to 9×10^{16} molecule cm^{-3} at operating conditions similar to those for the other two reactions. Based on this, the upper limit for reaction 3 is $k_3 < 1 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1} or $k_3 < 5 \times 10^{-34}$ cm^6 molecule^{-2} s^{-1}.

4. Discussion

These studies have revealed that several of the potential reactions occur, if at all, at immeasurably slow rates. To explain these observations, we invoke thermochemical, molecular orbital, and symmetry arguments. This discussion addresses

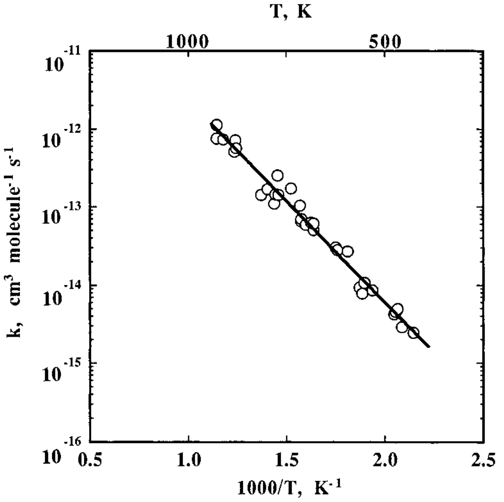

Figure 1. Summary of the Cd(^{1}S) + $Cl_2 \rightarrow CdCl + Cl$ rate coefficent measurements: (○) individual rate coefficient measurements; (−) fit of the measurements (eq 4).

reaction systems 1, 2, and 3 separately. Additionally, predictions are made for some Cd(^{3}P) reactions based on symmetry arguments.

4.1. Cd(^{1}S) + Cl$_2$. The preexponential of reaction 1 is comparable to those of other metal atom Cl$_2$ reactions.[19−25] The following three paths can be envisaged:

$$Cd + Cl_2 \rightarrow CdCl + Cl \qquad (5)$$

$$Cd + Cl_2 \rightarrow CdClCl \qquad (6)$$

$$Cd + Cl_2 \rightarrow ClCdCl \qquad (7)$$

The reaction was found to be pressure independent. Thus, there is no experimental evidence for association or insertion reactions 6 and 7. The unlikelihood of any such form of an addition process is in accord with the following theoretical considerations.

Cl$_2$, as the more electronegative reactant, would attract an electron pair from Cd(^{1}S) into its unoccupied σ^* orbital. This orbital is strongly antibonding, and its interaction with the Cd atom would invariably result in bond breaking,[26] i.e., in abstraction (reaction 5) or insertion (reaction 7) but not in association.

In order for Cd(^{1}S) to insert into Cl$_2$, collision has to happen in a direction nearly perpendicular to the Cl−Cl bond. In the limiting case the collision will occur under C_{2v} symmetry, as shown in Figure 2a. For Cd and Cl$_2$, the interacting orbitals are the doubly occupied 5s and the unoccupied σ^* orbital. Those transform under C_{2v} symmetry as a_1 and b_2, respectively. Symmetry rules predict large activation barriers for the interaction of species that have different symmetries, i.e., they are forbidden.[26] In the language of molecular orbital theory, the net overlap between the Cd 5s orbital and the σ^* orbital of Cl$_2$ would be zero, as shown in Figure 2b, where the "+" and "−" signs refer to the parity of the wave function. The orbital overlap yields two identical lobes of opposite sign that cancel each other out. Hence insertion also should not occur.

The end-on collision of Cd with Cl$_2$, resulting in abstraction, would produce nonzero overlap (Figure 2c), and it is therefore allowed. Thus, reaction 5 should be the operative reaction.

4.2. Cd(^{1}S) + O$_2$. The possible channels here are

$$Cd + O_2 \rightarrow CdO + O \qquad (8)$$

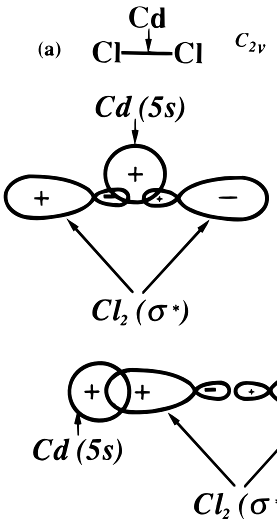

Figure 2. Analysis of the Cd(^{1}S) + Cl$_2$ reaction system: (a) collision complex with C_{2v} symmetry; (b) molecular orbital representation of the insertion of Cd(^{1}S) into the Cl$_2$ bond; (c) molecular orbital representation of the abstraction reaction.

$$Cd + O_2 \rightarrow OCdO \qquad (9)$$

$$Cd + O_2 \rightarrow CdOO \qquad (10)$$

Abstraction (reaction 8) would be 258 kJ mol^{-1} endothermic, which makes it too slow for measurement at the temperatures of interest. The absence of insertion (reaction 9) follows again from symmetry considerations. In O$_2$ the interacting orbitals are partially occupied degenerate π_g orbitals. These transform under C_{2v} symmetry as $a_2 + b_2$. Hence, their interaction with the a_1 ground-state Cd 5s orbital under C_{2v} symmetry would again be forbidden.

End-on collision would be free of any symmetry restrictions and could result in diradical O$_2$ combining with Cd(^{1}S) to form an association complex (reaction 10). As discussed by Brown et al.,[27] metals with the ns^1 electronic configuration react rapidly with O$_2$ via an association mechanism, and those with the ns^2 configuration react slowly. They pointed out that association of transition metal atoms with O$_2$ proceeds by the end-on interaction of the metal s orbital with one of the half-filled O$_2$ π_g orbitals to form two new orbitals, one bonding and one antibonding. For reactions of metals with the ns^1 electronic configuration, one electron from the O$_2$ π_g orbital and a single s electron from the metal fill the bonding orbital, resulting in a stable configuration. For reactions involving metals with the ns^2 configuration, such as Cd, there is, in addition to the electrons in the bonding orbital, one electron in the antibonding orbital, which destabilizes the interaction. Hence, association also should not be expected to proceed at measurable rates, in agreement with the experimental results that show an absence of any reaction in the Cd(^{1}S)−O$_2$ reaction system.

4.3. Cd(^{1}S) + HCl. The paths here could be

$$Cd + HCl \rightarrow CdCl + H \qquad (11)$$

$$Cd + HCl \rightarrow CdClH \qquad (12)$$

$$Cd + HCl \rightarrow HCdCl \qquad (13)$$

Abstraction (reaction 11) is endothermic by 224 kJ mol^{-1} [7,8] and therefore does not need to be taken into consideration in this work. Association (reaction 12) can be ruled out on the basis of similar reasoning as in the Cl$_2$ case, i.e., HCl would react with its strongly antibonding σ^* orbital, and this would invariably lead to bond breaking. However, Cd insertion into the H−Cl bond (reaction 13) should be free of restrictions, since the collision complex formed would not possess any symmetry elements.[28] Such a process has been observed in the reaction of ground-state Cu with HCl, where in addition to CuCl, an HCuCl insertion product was identified.[29] However, Cu is an open shell atom. The closed shell structure of Cd apparently creates a sufficiently large barrier to make reaction 13 too slow to be observable under the conditions investigated.

4.4. Cd(^{3}P) Reactions. Although insertion can thus be ruled out for Cd(^{1}S) + Cl_2 and Cd(^{1}S) + O_2, it has been observed for Cd(^{3}P) + H_2.[30] This reaction is allowed, since Cd(^{3}P) has a 5p_y orbital of b_2 symmetry available for bonding with the H_2 σ^* orbital of b_2 symmetry. Similar considerations would suggest that further Cd(^{3}P) insertion reactions can occur. Hence, for example, the symmetry of Cd(^{3}P) + Cl_2 insertion is the same as that of H_2 insertion. The interacting orbitals of these reactants have a finite net orbital overlap. Similarly, Cd(^{3}P) could insert into the O_2 bond, since interaction with the π_{yz} orbital is allowed. Note, however, that interaction with the π_{xy} orbital is forbidden. The use of symmetry rules can also explain other observations in the literature. Thus, it has been reported that ground-state Cu(^{2}S) does not insert into O_2, but Cu(^{2}P) does.[31] This situation is analogous to the Cd case, since the interacting orbitals of Cu(^{2}S) and Cu(^{2}P) are again of, respectively, s and p character.

5. Conclusions

Among the reactions investigated here, only Cd + Cl_2 → CdCl + Cl proceeds at experimentally observable rates. Similar considerations, as advanced above, can be used to predict the behavior of the reactions of the ground states of the other two group 12 metals with the same reactants. Thus, Zn + Cl_2 → ZnCl + Cl should likewise occur. Hg + Cl_2 → HgCl + Cl would be highly endothermic[32] and would under normal combustion conditions not proceed at measurable rates. Neither do we expect a reaction of Zn and Hg with O_2 and HCl. These considerations are important, since both metals are significant toxics present in wastes. Therefore, we suggest that in incinerators Cd and Zn could form chlorides homogeneously but that for Hg only heterogeneous routes are open for the present reactants.

The symmetry arguments, advanced above, can also be applied to transition metal reactions. These are known to proceed by the interaction of the metal s orbitals, which have a larger spatial extent than the partially filled d orbitals.[33]

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(32) The heats of these processes are in kJ mol^{-1}, listed after each reaction:[6] Zn + Cl_2 → ZnCl + Cl, 14; Zn + O_2 → ZnO + O, 227; Zn + HCl → ZnCl + H, 203; Hg + Cl_2 → HgCl + Cl, 139; Hg + O_2 → HgO + O, 230; Hg + HCl → HgCl + H, 328.

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