AN HT FFR KINETICS STUDY OF THE REACTION BETWEEN AICI AND CO₂ FROM 1175 TO 1775 K

Donald F. ROGOWSKI and Arthur FONTIJN

Department of Chemical Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180-3590, USA

Received 24 September 1986

Rate coefficients for the reaction AlCl + CO₂ \rightarrow OAlCl + CO have been measured in a high-temperature fast-flow reactor (HT FFR). These fit the expression $k(T) = 2.5 \times 10^{-12} \exp(-7550 \text{ K/T}) \text{ cm}^3$ molecule⁻¹ s⁻¹. The existence of a large energy barrier for this exothermic reaction is in agreement with that suggested for the OAlCl channel of the AlCl + O₂ reaction. The presence of such barriers is in sharp contrast to the AlO reactions with CO₂ and O₂.

1. Introduction

The use of the HT FFR technique is providing a data base for the kinetics of homogeneous gas-phase oxidation reactions of metallic species in the 300–1900 K range; results have been summarized in several reviews [1-3]. Following measurements of Al atom and AlO radical reactions, we recently initiated work on the AlCl radical with a study of its reaction with O_2 [4]. Here we report results for

$$AlCl + CO_2 \rightarrow OAlCl + CO \tag{1}$$

and compare its $\ln k(T)$ versus T^{-1} behavior to that established in the AlCl + O₂ study and for the AlO reactions with CO₂ [5] and O₂ [6].

2. Experimental

The basic HT FFR design and methodology has been described previously [2]. The modifications used for AlCl measurements have been discussed elsewhere [4]. Briefly, a vertical 2.2 cm inner diameter mullite reaction tube is heated by silicon carbide rod-type heating elements. The reaction tube and heating elements are housed inside an insulated vacuum can. An Al-wetted tungsten coil is heated in the upstream end of the reaction tube producing gaseous Al. Ar bath gas with a trace ($\approx 5 \times 10^{12}$ cm⁻³) of Cl₂ is passed over the coil. Al atoms are entrained and react at near gas

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kinetic rates [7] to produce AlCl. Further downstream CO₂ is introduced through a movable inlet; the distance between it and the observation plane varies from 20 to 10 cm. Relative AlCl concentrations are measured at the observation plane by laser-induced fluorescence (LIF), using the A-X(0, 0) transition at 261.4 nm. To ensure that AlCl production ceases at the CO₂ introduction point, some O₂ ($\approx 5 \times 10^{13}$ cm⁻³) is added through the CO₂ inlet to consume any remaining free Al by the fast Al + O₂ reaction ($k \approx 3 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ [6]). The gases used, are 99.5% Cl₂, 99.998% Ar (from liquid), 99.6% O₂, and 99.99% CO₂, all obtained from Linde.

3. Results

Plots of ln [AlCl]_{relative} versus [CO₂] yield straight lines with slopes k_1t , where t is reaction time. k_1 at each experimental condition is determined by using a weighted linear regression of the data. The random experimental errors are used to determine the weighting by a propagation of errors method [2]. From this treatment the σ_{k_1} associated with each k_1 , is calculated.

Below about 1175 K reaction (1) has been found to be too slow to allow meaningful HT FFR observation. Fifty-nine measurements of k_1 between 1175 and 1775 K have been made. Of these the fifty-four which have correlations r > 0.85 for ln [AlCl]_{relative}

Table 1 Summary of rate coefficient measurements of AlCl + $CO_2 \rightarrow OAlCl + CO^{a}$

Oxidant inlet	\overline{P}	[M]	[CO ₂] range	ΰ	F ^{c)}	\overline{T}	<i>k</i> ^d)	±σ ^d)
position	(Torr) ^{b)}	$(10^{17} \text{ cm}^{-3})$	(cm ⁻³)	(m s ⁻¹)		(K)		
20	10.7	1.34	1 02(15) 9 95(15)	40	40	1529	2.02(14)	A 1A(15)
20	19.7	1.24	1.03(13) - 0.03(13) 1.07(15) - 0.07(15)	40	49	1530	3.93(-14) 3.84(-14)	321(-15)
20	24.6	1.24	$1.07(15) \sim 9.07(15)$ $1.02(15) \approx 9.07(15)$	40	28	1535	1.04(-14)	1.42(-15)
20	24.0	1.50	1.03(15) - 0.30(15) 1.04(15) - 0.26(15)	42	20	1525	1.04(-14) 1.20(-14)	1.42(-15) 1.48(-15)
20	24.0	1.50	1.04(13) - 0.20(13) 1.27(15) - 1.10(16)	444	24	1526	1.30(-14) 1.20(-14)	8 35(16)
20	32.0	2.07	1.57(15) - 1.10(10) 1.67(15) - 1.20(16)	26	25	1527	1.33(-14) 1.04(-14)	1.01(-15)
20	24.2	2.47	1.02(15) - 1.50(10) 1.72(15) - 1.27(16)	20	25	1517	1.04(-14)	1.01(-15) 2.23(-15)
10	34.2	2.10	1.72(15) - 1.57(10) 1.97(15) - 1.26(16)	25	20	1517	1.17(-14) 1.25(-14)	2.23(-15)
10	34.2	2.10	1.07(15) - 1.50(10) 1.17(15) - 0.76(15)	25	34	1422	1.23(-14) 1.27(-14)	2.31(-13)
20	23.0	1.55	1.17(15) - 7.70(15) 1.25(15) - 1.00(15)	25	24	1433	1.27(-14)	1.40(-15)
20	23.0	1.50	1.23(15) - 1.00(10) 1 18(15) 8 59(15)	30	22	1416	1.17(-14)	1.49(-15)
20	23.7	1.02	1.10(15) - 0.57(15) 1.06(15) - 8.67(15)	20	22	1410	9.25(-15)	1.49(-15) 1.08(-15)
10	25.7	1.02	1.00(15) - 0.02(15) 1.24(15) - 0.68(15)	35	25	1417	9.23(-15) 8.37(-15)	1.00(-15) 1.17(-15)
10	26.5	1.00	1.24(15) - 9.60(15) 1.24(15) - 9.63(15)	35	25	1418	9.37(-15)	9.92(-16)
10	20.0	1.35	1.24(15) - 9.63(15) 1.28(15) - 9.67(15)	35	23 41	1474	9.70(-15)	1.55(-15)
10	20.0	1.35	1.26(15) - 1.00(16)	35	40	1425	1.24(-14)	2.22(-15)
20	25.7	1.50	1.20(15) - 1.00(16) 1.62(15) - 1.21(16)	29	36	1325	3.49(-15)	6.95(-16)
20	25.7	1.89	1.52(15) - 1.21(16)	29	36	1320	4 75(15)	9.77(-16)
20	37.0	2.73	2.27(15) - 1.20(10)	20	14	1307	2.82(-15)	2.89(-16)
20	36.9	2.75	2.27(15) - 1.70(10) 2.26(15) - 1.74(16)	20	11	1304	2.02(-15) 2.77(-15)	4.63(-16)
20	19.9	1 47	2.20(15) - 1.7 + (10) 1 07(15) - 7 92(15)	43	54	1310	1.00(-14)	1.75(-15)
20	20.0	1.47	1.07(15) - 7.02(15) 1.12(15) - 8.02(15)	43	44	1311	1.00(-14) 1.04(-14)	1.32(-15)
10	20.0	1.46	1.12(15) - 0.02(15) 1.06(15) - 8.15(15)	43	43	1320	1.04(-14) 1.75(-14)	1.52(-15) 1.58(-15)
10	20.0	1.46	1.00(15) - 8.14(15)	43	39	1320	1.95(-14)	3.32(-15)
20	31.5	1.00	1.09(15) = 0.11(15) 1.38(15) = 1.09(16)	31	17	1591	1.36(-14)	1.97(-15)
20	31.6	1.92	1.33(15) - 1.13(16)	31	17	1587	1.29(-14)	1.17(-15)
10	31.6	1.91	1.36(15) - 1.08(16)	31	12	1596	1.70(-14)	1.76(-15)
10	31.6	1.92	1.33(15) - 1.13(16)	31	10	1592	1.18(-14)	2.60(-15)
20	31.5	1.91	1.63(15) - 1.40(16)	25	40	1588	1.66(-14)	1.26(-15)
20	31.6	1.92	1.80(15) - 1.40(16)	24	32	1586	1.60(-14)	1.42(-15)
10	31.5	1.91	1.82(15) - 1.39(16)	25	41	1594	1.77(-14)	1.68(-15)
10	31.8	1.92	1.74(15) - 1.40(16)	24	35	1593	1.91(-14)	1.40(-15)
20	22.1	1.25	1.12(15)-9.17(15)	37	40	1705	2.43(-14)	3.15(-15)
20	22.1	1.25	1.20(15)-9.09(15)	38	56	1703	1.84(-14)	1.26(-15)
10	22.1	1.25	1.19(15)-9.25(15)	38	55	1708	1.94(-14)	2.94(-15)
10	19.9	1.14	9.94(14)-8.47(15)	41	45	1689	3.79(-14)	5.91(-15)
20	20.4	1.17	7.80(14)-6.32(15)	55	24	1680	2.01(-14)	3.33(-15)
20	20.4	1.17	8.23(14)-6.41(15)	55	21	1679	1.53(-14)	3.10(-15)
20	16.9	0.924	7.24(14)-5.74(15)	60	55	1764	1.34(-13)	2.28(-14)
20	16.9	0.925	7.01(14)-5.68(15)	60	53	1762	1.01(-13)	6.75(-15)
10	27.1	1.50	1.38(15)-1.06(16)	32	58	1740	4.17(-14)	2.74(-15)
10	27.1	1.50	1.41(15)-1.07(16)	32	59	1745	2.88(-14)	3.14(-15)
20	19.1	1.05	8.28(14)-6.55(15)	53	121	1759	4.72(-14)	9.22(-15)
20	19.1	1.05	7.97(14)-6.64(15)	53	112	1756	4.88(-14)	4.93(-15)
10	19.1	1.06	8.34(14)-6.58(15)	52	82	1747	4.92(-14)	5.67(-15)
10	19.1	1.06	8.71(14)-6.60(15)	52	71	1739	4.74(-14)	5.74(-15)
10	32.9	1.84	1.35(15)-1.05(16)	33	39	1727	2.77(-14)	2.88(-15)
10	32.9	1.84	1.33(15)-1.02(16)	33	33	1726	3.04(-14)	3.31(-15)
20	31.4	2.55	1.87(15)-1.42(16)	24	35	1190	2.66(-15)	3.42(-16)
20	19.8	1.61	1.25(15)-9.14(15)	38	30	1190	1.32(-14)	1.55(-15)
20	19.8	1.61	1.18(15)-9.28(15)	38	49	1186	1.53(-14)	1.28(-15)
20	29.0	2.39	1.88(15)-1.36(16)	25	24	1175	7.09(-15)	7.52(-16)
20	22.6	1.67	1.28(15)-1.04(16)	34	23	1307	9.33(-15)	1.67(-15)
20	29.7	2.22	1.32(15)-1.01(16)	34	10	1291	1.01(-14)	1.85(-15)

a) The measurements are reported in the sequence in which they were obtained. b) 1 Torr = 133.3 Pa. c) In arbitrary units. d) In cm³ molecule⁻¹ s⁻¹.

versus $[CO_2]$ are presented in table 1. Inspection of the data in table 1 shows k_1 to be independent of \overline{P} , $[\overline{M}]$ and the experimental parameters: inlet position, \overline{v} (the average gas velocity) and F (the initial fluorescence intensity, which is approximately proportional to the initial [AlCl]). It may also be seen that k_1 is independent of the position, which shows that the AlCl consumption measurements are not measurably influenced by quenching of AlCl(A) by CO₂. Temperatures given are averages of the temperatures at 5 cm intervals from the CO₂ inlet position to the observation plane. The standard deviation about the mean gas temperature varied from ± 3 to ± 17 K depending on the reaction conditions. In view of systematic uncertainties in T [2], σ_T is taken as 25 K.

While at least some curvature may be expected in an Arrhenius plot covering a wide temperature range, within the scatter of the present results a normal Arrhenius expression $k = A \exp(-B/T)$ provides the best weighted least-squares fit [8] taking into account σ_{k_1} and σ_T . The resulting rate expression is

$$k_1(T) = 2.53 \times 10^{-12} \exp(-7550 \text{ K/T})$$

 $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$ (2)

The standard deviation for $k_1(T)$ determined by a standard propagation of errors technique [8,9] is

$$\sigma_{k_1}(T) = k_1(T) [(\sigma_A/A)^2 + (\sigma_B/T)^2 - \sigma_{AB}/AT + (0.1)^2]^{1/2},$$

with variances and covariance

$$\sigma_A^2 = 4.08 \times 10^{-1} A^2,$$

 $\sigma_B^2 = 9.58 \times 10^5,$
 $\sigma_{AB} = 6.21 \times 10^2 A.$

In the determination of σ_{k_1} the 0.1 is σ_n/n , the systematic uncertainty in the flow profile factor [2]. The covariance term $-\sigma_{AB}/AT$ must be taken into account in the determination of σ_{k_1} , since A and B are dependent parameters [9]. The resulting $2\sigma_{k_1}$ confidence levels are $\pm 23\%$ at 1175 K, $\pm 16\%$ at 1300 K, $\pm 12\%$ at 1550 K and $\pm 15\%$ at 1775 K. It should be noted that $\sigma_{k_1}(T)$ represents the uncertainty of the fitted expression, not the deviation of the measurements of k_1 .

4. Discussion

 ΔH_R^0 (298 K) for reaction (1), as written, is -14 \pm 22 kJ mol⁻¹ [10]. Other product channels would be at least some 750 kJ mol⁻¹ endothermic and do not need to be considered in the temperature range investigated. The 490 to 1750 K HT FFR study of the reaction

$$AlCl + O_2 \xrightarrow{\rightarrow} OAlCl + O \tag{3a}$$
$$\xrightarrow{\rightarrow} AlO_2 + Cl \tag{3b}$$

showed a strongly concave upward Arrhenius-type plot and yielded a rate coefficient expression [4]

$$k_2(T) = 1.3 \times 10^{-12} \exp(-3400 \text{ K/T})$$

+ 3.4 × 10⁻⁹ exp(-16100 K/T)
cm³ molecule⁻¹ s⁻¹.

Since neither OAlCl nor AlO_2 have identified electronic transition spectra, LIF could not be used for positive channel identification. However, arguments were advanced in that work, which suggest that the first term in the $k_2(T)$ expression essentially describes the behavior of channel (3b) and the second term that of reaction (3a). The second term becomes dominant only above 1650 K. Since it is thus determined over a narrow temperature interval it has a large associated uncertainty. However, this term clearly involves an activation energy well in excess of the 28.3 kJ mol⁻¹ of the first term. Such a large activation energy for a simple exothermic abstraction reaction (ΔH_R^0 (298 K) = -47 kJ mol⁻¹ [10]) is somewhat unexpected. The $k_1(T)$ expression derived in the present work shows that there is a considerable barrier for OAlCl formation from AlCl and thus tends to strengthen the interpretation of the study of reaction (3). An HT FFR mass spectrometer apparatus is currently being constructed and should allow direct product identification.

HT FFR studies of

$$AlO + CO_2 \rightarrow AlO_2 + CO, \tag{4}$$

$$AIO + O_2 \rightarrow AIO_2 + O \tag{5}$$

showed slightly negative T dependences of their rate coefficients from 500 to 1300 K [5] and 300 to 1400

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K [6], respectively. Replacing the O atom in AlO with a Cl atom thus appears responsible for the appearance of major barriers in the reaction potential energy surfaces.

Acknowledgement

This work was supported under grant AFOSR-86-0019.

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