Experimental and Transition-State Theory Studies of the Gas-Phase Reactions of AlCl with N_2O , CO_2 , and SO_2

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The high-temperature fast-flow reactor technique has been used to make kinetic measurements. A weighted fit to the AlCl + N₂O data gives $k(700-990 \text{ K}) = 5.6 \times 10^{-11} \exp(-7380 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A weighted fit to the AlCl + CO₂ measurements leads to the expression $k(900-1790 \text{ K}) = 4.4 \times 10^{-23} (T/\text{K})^{3.0} \exp(-3900 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. 2σ accuracy limits are about $\pm 25\%$. An upper limit $k(800-1100 \text{ K}) < 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ has been determined for the AlCl + SO₂ reaction. An alternate form of classical transition-state theory is developed to allow predictions on the preexponential part of rate coefficient expressions for metallic species. This model-based transition-state-theory (MTST) method uses a valence-force molecular model to estimate rotational constants and vibrational frequencies of the transition state and is applicable to reactions with early barriers, typical of many exothermic charge-transfer reactions. The geometrical parameters and force constants that describe the molecular model are derived from properties of the reactants. For the N₂O reaction good agreement between MTST and experiment is obtained, based on the assumption of an O atom abstraction reaction leading to OAlCl. No such agreement is found for the CO₂ reaction, which indicates adduct formation as the main AlCl consumption channel. For the previously measured AlCl + O₂ reaction MTST calculations suggest that abstraction can be of some significance above about 1500 K; however, adduct

formation appears to dominate over most of the 490-1750 K range.

Introduction

As part of an ongoing study of the temperature dependence of the rate coefficients of reactions of small Al- and B-containing species, we report here experiments on the reactions

 $AlCl + N_2O \rightarrow products$ (1)

$$AlCl + CO_2 \rightarrow products \tag{2}$$

$$AlCl + SO_2 \rightarrow products$$
 (3)

We previously studied the AlCl reactions with $O_{2,1} CO_{2,2} Cl_{2,3}$ and HCl,⁴ the results of which have been summarized.⁵ The measurements of reaction 2 are repeated here, as the hightemperature fast-flow reactor (HTFFR) technique used has been much improved^{5,6} since the previous² study, where the data showed wide scatter. The O₂ and CO₂ reactions were originally thought to lead directly to OAlCl. However, a recent ab initio study of the thermochemistry⁷ of OAlCl suggests these two channels to be too endothermic⁸ for reaction along this path with the observed rate coefficients.

To investigate the mechanism of all these AlCl reactions with oxygen-containing oxidants, we present here a semiempirical transition-state theory based method for predicting the temperature dependence of rate coefficients. In this model-based transition-state theory (MTST) the rotational constants and vibrational frequencies of the transition state are derived from molecular models based on the assumption of valence forces. This approach, the limitations of which are discussed, should be widely applicable to reactions with early activation barriers since the required input data, namely, geometrical parameters and force constants, of the transition state can be estimated from reactant properties in accord with Hammond's postulate.⁹ Reactions occurring by a crossing of neutral and ionic potential energy surfaces, typical of oxidation reactions of metal species, are included. MTST is thus useful for such reactions when the input data for the widely used semiempirical TST method developed by Benson,¹⁰ principally for H/C/O/N species reactions, are not available.

Experimental Section

Detailed descriptions of the HTFFR used in this work have been given elsewhere.^{5,6} The reactor consists of a vertical mullite reaction tube (2.2-cm i.d.) surrounded by SiC heating elements. This assembly is sealed inside an insulated water-cooled vacuum housing. Two methods were used to produce AlCl. In the first, previously used method, a trace amount of Cl₂ or HCl was added to the Ar bath gas flowing over the Al-wetted resistively-heated tungsten vaporization coil, located 7-17 cm upstream from the reaction zone.^{1,3} In the second method, similar to that used in the BCl studies,^{6,11} AlCl₃ was vaporized from a quartz crucible (4-mm i.d.) into a stream of Ar. This stream then flowed through a 2450-MHz, nominally 100-W, microwave discharge in a quartz tube (1.2-cm i.d.) and then into the reaction tube. Both methods were used in the AlCl + CO_2 study in the 1200-1690 K temperature range and found to yield identical results. The second method would in general be especially useful for HTFFR studies near room temperature; such temperatures are not accessible by the first method because the heat generated by the vaporization coil heats the reaction tube to temperatures greater than 450 K. Downstream from the source, a mixture of Ar and the oxidant gas $(N_2O, CO_2, or SO_2)$ was introduced into the reaction tube through a movable inlet. The molar flow rate of gas through the inlet was kept constant during a given rate coefficient determination, which consisted of five or six measurements at varying oxidant concentrations. A small amount of O2 was added to the inlet gas to rapidly⁵ remove any remaining Al atoms entering the reaction zone. Such atoms otherwise may continue to produce AlCl and hence interfere with the measurements.

Relative AlCl concentrations were monitored by laser-induced fluorescence using a pulsed Lambda Physik EMG 101 excimer/ Fl 2002 dye laser combined with a KDP doubling crystal. The

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TABLE I: Summary of Rate Coefficient Measurements for AlCl + N_2O^4

eaction zone length (cm)	P (mbar)	[M] (10 ¹⁷ cm ⁻³)	$[N_2O]_{max}$ (10 ¹⁵ cm ⁻³)	F	0 (m s ⁻¹)	Т (К)	$k \pm \sigma_k (\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$
20	50.9	4.0	16.4	40 ^b	20	919	$2.01 \pm 0.13 (-14)^c$
10	50.9	4.0	16.5	73	20	919	$2.16 \pm 0.17(-14)$
20	50.9	4.0	13.7	36	21	921	$2.01 \pm 0.12 (-14)$
10	50.9	4.0	13.6	27	21	924	$2.18 \pm 0.19 (-14)$
10	101.0	7.7	14.1	34	14	948	$2.29 \pm 0.22 (-14)$
10	101.2	7.6	13.9	37	14	964	$2.08 \pm 0.22 (-14)$
20	29.6	2.2	14.3	50	39	984	$2.75 \pm 0.21 (-14)$
20	29.7	2.2	14.2	62	39	991	$2.82 \pm 0.25 (-14)$
20	54.1	5.3	23.9	23	16	735	$2.40 \pm 0.33 (-15)$
20	54.1	5.4	24.2	22	16	726	$2.19 \pm 0.32 (-15)$
20	78.6	8.1	52.3	30	7	704	$1.44 \pm 0.14 (-15)$
20	78.6	8.1	52.3	17	7	704	$1.80 \pm 0.13(-15)$
20	66.7	6.9	40.0	49	14	704	$1.31 \pm 0.22 (-15)$
20	66.7	6.8	39.7	48	14	709	$1.11 \pm 0.22 (-15)$
20	41.6	4.2	22.2	35	13	726	$2.23 \pm 0.22 (-15)$
20	41.6	4.1	22.1	33	13	731	2.45 ± 0.21 (-15)
20	55.2	5.4	28.9	34	10	740	$2.80 \pm 0.21(-15)$
20	55.2	5.3	28.6	41	10	748	$3.13 \pm 0.22 (-15)$
20	78.5	7.2	35.6	31	12	795	$4.17 \pm 0.35 (-15)$
20	62.9	5.5	32.7	50	17	830	$7.68 \pm 0.72 (-15)$
20	62.9	5.4	32.2	54	17	842	$9.51 \pm 0.64 (-15)$
10	62.9	5.5	32.3	59	17	836	$9.35 \pm 0.67 (-15)$
10	49.9	4.2	15.0	23	19	856	$1.04 \pm 0.08 (-14)$
20	49.9	4.2	15.1	26	19	853	$9.80 \pm 0.70 (-15)$
20	42.5	3.6	13.5	31	21	846	9.20 ± 0.79 (-15)
20	42.8	3.6	13.5	24	21	852	$1.08 \pm 0.08 (-14)$
20	44.3	3.6	17.3	42	32	879	$1.30 \pm 0.16 (-14)$
20	44.3	3.6	17.3	34	32	882	$1.48 \pm 0.10 (-14)$
20	35.2	2.9	13.9	17	40	873	$1.50 \pm 0.15(-14)$
20	50.7	4.2	20.0	9	27	871	$8.86 \pm 0.82 (-15)$
20	68.4	5.7	17.3	52	16	875	$1.07 \pm 0.07 (-14)$

^a The measurements are reported in the sequence in which they were obtained. ^b In arbitrary units. ^c Should be read as $(2.01 \pm 0.13) \times 10^{-14}$ cm³ molecule⁻¹ s⁻¹.

AlCl(A¹ Π -X¹ Σ ⁺) transition¹² was pumped on the (0,0) band at 261.4 nm, and the fluorescence intensity was observed through a 262-nm (26-nm fwhm) filter by an EMI 9813QA photomultiplier tube coupled to a Data Precision Analogic 6000/620 100-MHz transient digitizer. Rate coefficient measurements were made in the stationary inlet mode¹³ with observed reaction zone lengths of 10 or 20 cm. The oxidant concentrations were maintained in great excess over the AlCl concentrations. Rate coefficients and their uncertainties were obtained from the slopes of linear plots of ln [AlCl]_{relative} vs oxidant concentration by a weighted linear regression.¹⁴

The gases used were 99.998% Ar from the liquid, "Precision Aquarator" 99.99% CO_2 , Cl_2 (1% in Ar), and "Atomic Absorption" 99.0% N₂O from Linde, "Ultra High Purity" 99.99% N₂O and "Anhydrous" 99.98% SO₂ from Matheson, HCl (5% in He) from Spectra, and O₂ (5.0% in Ar) from Scott.

Results

The AICl + N₂O Reaction. Reaction 1 was studied from 700 to 990 K. No measurements at higher temperatures are included as thermal dissociation of N₂O is sufficiently large to interfere with rate coefficient measurements.¹¹ Below 700 K the reaction was too slow to measure. Table I summarizes the rate coefficients and the temperatures at which they were obtained along with the experimental parameters: reaction zone length, total pressure P, total concentration [M], maximum oxidant concentration $[N_2O]_{max}$, fluorescence intensity F (a measure of [AlCl] at the start of the reaction zone), and average velocity \bar{v} . The independence of the individual rate coefficients k_i of these parameters was checked by examining plots of $[k(T) - k_i]/k(T)$, where k(T) is obtained from the fitted rate coefficient expression given below, vs the above experimental parameters. It can be seen from Figure 1 that over the limited temperature range studied



Figure 1. Arrhenius plots of experimental rate coefficients for the AlCl $+ N_2O$ (open circles) and AlCl $+ CO_2$ (open squares) reactions. The experimental rate coefficient expressions are shown as full lines.

the k_i measurements show no deviation from Arrhenius behavior. A weighted nonlinear fit¹⁵ of the data to the expression $k(T) = A \exp(-E/RT)$ gives

$$k_1(700-990 \text{ K}) = 5.6 \times 10^{-11} \times \exp(-7380 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (4)

with covariance matrix elements¹⁶

$$(\sigma_A/A)^2 = 0.113, \ \sigma_E^2 = 79\ 900\ \text{K}^2, \ \sigma_{AE}/A = 94.6\ \text{K}$$
(5)

Combining these matrix elements by the propagation of errors technique^{4,10} yields $\pm 2\sigma_k$ precision limits of 15% at 700 K, 6% at 850 K, and 12% at 990 K. Allowing 10% uncertainty associated with the flow profile factor and 20% for further systematic errors yields $\pm 2\sigma_k$ accuracy limits of 27% at 700 K, 23% at 850, and 25% at 990 K.

The AlCl + CO₂ Reaction. Reaction 2 was studied over the 900-1790 K temperature range. The rate coefficient data summarized in Table II are again independent of reaction zone length, P, [M], $[CO_2]_{max}$, F, and \bar{v} . The Arrhenius plot of the rate coefficients shown in Figure 1 exhibits slight upward curvature. The rate coefficient data were fitted to the three-parameter expression $k(T) = AT^n \exp(-E/RT)$. The goodness of the fit χ^2 is found to be relatively insensitive to the value of the parameter *n* over the approximate range 2.0-4.0. We therefore fix *n* at 3.0. A two-parameter nonlinear regression analysis of the data gives

$$k_2(900-1790 \text{ K}) = 4.4 \times 10^{-23} (T/\text{K})^{3.0} \times \exp(-3900 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (6)

with covariance matrix elements

$$(\sigma_A/A)^2 = 0.0182, \ \sigma_E^2 = 38\ 000\ \text{K}^2, \ \sigma_{AE}/A = 26.0\ \text{K}$$
(7)

Combining the covariance matrix elements by the propagation of errors technique yields $\pm 2\sigma_k$ precision limits of 17% at 900 K, 5% at 1350 K, and 6% at 1790 K. Allowing 10% uncertainty associated with the flow profile factor and a conservative 20% for further systematic errors yields $\pm 2\sigma_k$ confidence limits of 28% at 900 K, 23% at 1350, and 23% at 1790 K. The present rate

zone zone	P	[M]	$[CO_2]_{max}$		D (m	τ	$k \pm \sigma_{\rm b} ({\rm cm}^3$
(cm)	(mbar)	cm ⁻³)	cm-3)	F	s ⁻¹)	(K)	molecule ⁻¹ s ⁻¹)
20	43.3	2.5	18	185	25	1273	$4.20 \pm 0.55 \ (-15)^{c,d}$
20	78.4	4.5	33	71	13	1254	$3.73 \pm 0.50 \ (-15)^d$
20	78.6	4.5	32	64	14	1273	$3.21 \pm 0.22 (-15)^d$
10	78.6	4.4	32	62	14	1281	$3.86 \pm 0.53 (-15)^{a}$
10	78.6	4.4	32	108	14	1284	$4.15 \pm 0.28 (-15)^{a}$
10	03.3	3.2	1/	33	14	1429	$8.71 \pm 0.98 (-15)^{4}$
10	03./	3.2	21	4/	14	1440	$9.99 \pm 0.91 (-15)^{\circ}$
20	62.8	3.1	12	50	14	14/5	$9.09 \pm 0.98 (-13)^{-1}$
20	42.5	3.0	12	12	10	1132	$1.20 \pm 0.13 (-14)^{2}$
20	43.5	2.0	15	18	10	1132	$2.34 \pm 0.30 (-15)^{4}$
20	58 1	43	23	10	13	990	$7.83 \pm 2.20 (-16)^d$
20	57 7	4.3	23	23	13	1010	$1.06 \pm 0.18 (-15)^d$
20	88.1	6.2	27	27	11	1031	$1.15 \pm 0.17 (-15)^d$
20	46.4	3.1	20	59	22	1091	$1.27 \pm 0.34 (-15)^d$
20	46.1	3.1	20	48	22	1094	$1.34 \pm 0.45 (-15)^d$
20	53.5	2.4	14	21	31	1584	$1.33 \pm 0.19 \ (-14)^d$
10	53.3	2.4	14	24	31	1602	$1.74 \pm 0.21 \ (-14)^d$
10	53.2	2.4	14	21	31	1 609	$2.04 \pm 0.18 (-14)^d$
10	92.0	4.0	20	21	15	1679	$1.62 \pm 0.24 \ (-14)^d$
10	92.0	4.0	20	17	15	1686	$2.05 \pm 0.21 \ (-14)^d$
20	53.7	4.2	21	55	11	930	$7.20 \pm 3.38 \ (-16)^d$
20	53.7	4.1	21	43	11	942	$9.32 \pm 3.11 \ (-16)^d$
20	65.3	5.1	27	74	16	920	$5.70 \pm 2.62 \ (-16)^d$
20	65.7	5.1	27	54	16	925	$6.69 \pm 1.47 \ (-16)^d$
20	78.6	6.3	36	39	16	900	$5.97 \pm 1.34 (-16)^{a}$
20	43.1	2.3	17	19	34	1368	$5.49 \pm 1.38 (-15)^{4}$
20	43.1	2.3	17	40	35	13/3	$5.24 \pm 0.71 (-15)^{a}$
10	43.1	2.3	17	00	25	1374	$0.10 \pm 2.70 (-15)^{-1}$
10	45.1	2.5	17	40	19	1207	$6.77 \pm 0.65 (-15)^{-1}$
10	854	4.5	33	10	18	1300	$6.00 \pm 0.08 (-15)^{4}$
20	83.6	43	17	30	18	1401	$5.74 \pm 1.00 (-15)^d$
20	99.6	6.0	30	113	18	1210	$3.69 \pm 0.41 (-15)^{\circ}$
20	113.3	6.8	30	87	18	1204	$2.72 \pm 0.28 (-15)^{\circ}$
20	73.3	4.2	25	59	17	1250	$3.75 \pm 0.32 (-15)^{\circ}$
20	60.4	2.8	12	36	45	1540	$1.81 \pm 0.15 (-14)^{e}$
20	60.4	2.8	12	39	46	1556	$1.80 \pm 0.23 (-14)^{e}$
20	91.4	4.2	16	39	25	1 590	$1.83 \pm 0.10 \ (-14)^{e}$
20	91.6	4.2	16	78	25	1590	1.90 ± 0.11 (-14) ^e
10	92.8	4.2	21	53	25	1599	1.71 ± 0.12 (−14) ^e
10	93.0	4.2	21	54	25	1599	1.74 ± 0.12 (-14) ^e
10	61.9	2.7	18	62	22	1632	$2.14 \pm 0.15 (-14)^{e}$
20	60.5	2.7	12	65	22	1638	$2.32 \pm 0.14 \ (-14)^{e}$
20	52.9	2.6	17	87	33	1448	$6.59 \pm 0.54 (-15)^{\circ}$
20	52.8	2.6	16	59	33	1449	$6.98 \pm 0.64 (-15)^{\circ}$
10	52.8	2.6	16	60	33	1454	$9.33 \pm 1.11 (-15)^{e}$
10	52.8	2.0	10	50	33	1454	$9.08 \pm 1.06 (-15)^{\circ}$
10	75.0	3.1	12	10	31	1765	$2.75 \pm 0.28 (-14)^{\circ}$
20	719	3.1	14	07 27	30 27	1/03	$2.01 \pm 0.20 (-14)^{\circ}$
20	74.0	3.0	12	0/ 82	37	1777	$2.20 \pm 0.14 (-14)^{6}$ 2.57 $\pm 0.24 (-14)^{6}$
20	41 0	17	8	91	68	1787	$2.57 \pm 0.24 (-14)^{\circ}$ 2.61 ± 0.21 (-14) ^e
20	42.1	1.7	8	125	67	1787	$2.51 \pm 0.21 (-14)^{\circ}$
20	42.1	1.7	8	39	67	1791	$2.98 \pm 0.26 (-14)^{e}$

^a The measurements are reported in the sequence in which they were obtained. ^b In arbitrary units. ^c Should be read as $(4.20 \pm 0.55) \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹. ^d AlCl produced by the microwave-discharge method. ^e AlCl produced by the reacting Cl₂ or HCl with an Al-wetted vaporization coil.

coefficient recommendation is in good agreement with that determined in the previous investigation;² however, the scatter in the measurements is now greatly reduced.

The AlCl + SO₂ Reaction. The rate coefficients of reaction 3 could not be accurately determined because of absorption and emission of laser radiation by SO_2 ,¹² which greatly lowered the sensitivity of AlCl detection. Corrections were made to the integrated fluorescence signal to remove the SO₂ contribution. Over the 800–1100 K temperature range no significant change in the AlCl signal could be observed as the SO₂ concentration was varied, which indicates an upper limit to the rate coefficient

$$k_3(800-1100 \text{ K}) < 5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (8)

We were unable to investigate reaction 3 at higher temperatures because the emitted radiation from species other than AlCl was too intense. Thermochemical⁸ equilibrium calculations indicate that above 1100 K SO, which also absorbs and emits radiation near the AlCl transition,¹² can be present in significant quantities.

Model-Based Transition-State Theory (MTST)

According to conventional transition-state theory the rate coefficient for a reaction occurring on a single potential energy surface is given by¹⁷

$$k(T) = \frac{k_{\rm B}T}{h} \frac{q_{\rm t}}{q_{\rm A}q_{\rm B}} \exp(-\Delta E^{\rm t}/RT)$$
(9)

in which q_{t} is the partition function for the transition state, q_{A} and $q_{\rm B}$ are partition functions for the reactants, and ΔE^{\ddagger} is the difference in zero-point levels of the transition state and the reactants. q_A and q_B are readily evaluated from experimental values of the rotational constants and vibrational frequencies of the reactants. The data needed to evaluate q_t are seldom available and must therefore be estimated. The MTST approach for this evaluation is suitable for transition states which arise from an early crossing of neutral and ionic potential surfaces, such as is the case for many metal species reactions. For such a transition state reasonably good estimates of the geometrical parameters and vibrational frequencies can be made using Hammond's postulate.9 It can then be assumed that the internuclear distances, valence angles, and force constants of the transition states are closely related to the properties of the reactants for an exothermic reaction and properties of the products for an endothermic reaction.

Vibrational frequencies for transition states are obtained from molecular models. The molecular model used here assumes that harmonic restoring forces oppose changes in bond lengths, angles between valence bonds, and dihedral angles. The potential energy V in the region near the transition state is thus given by¹⁸

$$2V = \sum_{i} F_{ri} \Delta r_i^2 + \sum_{j} F_{\theta j} \Delta \theta_j^2 + \sum_{k} F_{\tau k} \Delta \tau_k^2 \qquad (10)$$

where F_r , F_{θ} , and F_r are force constants for changes in internuclear distances r, valence angles θ , and dihedral angles σ from their respective equilibrium values. A normal-coordinate analysis of the model, which procedure has been described in detail by Pauling and Wilson,¹⁹ is carried out. The secular equation thus obtained is solved numerically by reducing the determinant to the tridiagonal form using Householder's algorithm.¹⁵ The characteristic polynomial of the resulting matrix is then evaluated by the *QL* algorithm with implicit shifts.¹⁵ Vibrational frequencies v_i are obtained from the relation¹⁹

$$\nu_i = \lambda_i^{0.5} / 2\pi c \tag{11}$$

in which λ_i are the eigenvalues of the secular equation. Rotational constants B_i for the transition state are obtained from the eigenvalues of the inertia tensor,²⁰ that is, from the principal moments of inertia I_i by the relation²¹

$$B_i = h/(8\pi^2 c I_i) \tag{12}$$

Several examples of accordingly estimating transition-state parameters for AlCl reactions are given in the Discussion.

Some limitations of MTST are that force constants arising from the reaction, which includes one stretching force constant and one or more bending or torsional force constants, must be estimated from the available ab initio calculations on similar reactions. The most important of these are the torsional force constants, since the torsions can be of low frequency and hence influence the TST rate expression. Also, MTST is not suitable

TABLE III: Transition-State Parameters for ClAIONN[‡]

geometrical	parameter ^{a,b}	force constant ^c		
r(ClAl)	2.13	Fr(CIAI)	2.1	
r(AlO)	2.25	$F_r(AlO)$	-2.0	
r(ON)	1.18	$F_{r}(ON)$	5.85	
r(NN)	1.13	$F_r(NN)$	18.7	
θ (CIAIO)	120	$F_{\theta}(ClAlO)$	0.2	
θ (AlON)	90	F ₀ (AlON)	0.6	
θ(ONN)	160	$F_{\theta}(ONN)$	0.67	
τ (ClAlÓN)	0	F_{τ} (CIAION)	0.02	
τ(AlONN)	0	$F_{\tau}(A ONN)$	0.02	

rotational constants $(B_1B_2B_3)$: 9.51 × 10⁻⁴ cm⁻³

vibrational frequencies v_i : 39, 89, 150, 291, 478, 605, 991, 2221 cm⁻¹

^a We assume trans arrangements for the atoms in the ClAION and AlONN groups. ^b Units of r are 10⁻¹⁰ m; units of θ and τ are deg. ^c Units of F_r are 10² N m⁻¹; units of F_{θ} and F_{τ} are 10⁻¹⁸ N m rad⁻².

for reactions with a centrally located transition state, e.g., $H + HCl \rightarrow H_2 + Cl$, because the potential energy function (cf. eq 10) would have to be modified to include a cross-term for the interaction between the H-H and H-Cl bonds.²² Furthermore, the transition state would resemble both the reactants and the products in part; hence, there would be considerable uncertainty in estimating geometrical parameters and force constants.

Discussion

The AlCl + N_2O Reaction. The lowest channel of the abstraction reaction

$$AlCl + N_2O \rightarrow OAlCl + N_2$$
 (1a)

is spin-allowed and 267 kJ mol⁻¹ exothermic.²³ The parameters of the transition state ClAlONN[‡] are derived from properties of the reactants and are summarized in Table III. The distances r(ClAl), r(ON), and r(NN) are from values for the AlCl and N₂O molecules. The internuclear distance along the reaction coordinate r(AlO) is estimated by

$$r(A|O) = [r(A|^{+}) + r(O^{-})]0.50^{1/(\delta-1)}$$
(13)

Equation 13 is based on a relation given by Pauling²⁴ between univalent radii and the bond distances of diatomic alkali-metal halide molecules. We assume that the relation applies to chargetransfer complexes and hence to transition states, which are located fairly close to the complexes. Values for the univalent radii $r(Al^+)$ and $r(O^{-})$ and the average Born exponent δ are obtained as described in ref 25. The constant 0.50 is obtained such that eq 13 gives good agreement with ab initio computations^{26–28} of B-O, Al-O, and H-O distances for transition states of the respective BCI + O_2 , Al + CO₂, and H + N₂O reactions. Lacking information on the valence and dihedral angles of the transition state, we assume the values given in Table III based on optimized geometries from ab initio computations.^{26–28} The force constant $F_r(ClAl)$ is taken as that in AlCl,²⁹ while $F_r(NN)$ and $F_{\theta}(ONN)$ are obtained from data for N_2O .³⁰ The remaining force constants in Table III are estimated by a scheme that gives good agreement with ab initio computations²⁶⁻²⁸ of vibrational frequencies. For example, $F_r(ON)$ is taken as one-half the N–O stretching force constant in N₂O. In addition, all torsional force constants are taken as 0.02×10^{-18} N m rad⁻² and the stretching force constants corresponding to reaction coordinates are taken as -2.0×10^2 N m⁻¹. These data are used to calculate the transition-state rotational constants and vibrational frequencies, which are summarized in Table III.

To allow comparison between theory and experiment, the preexponential factor of eq 9 is calculated for the 500-2000 K temperature range and fitted to the expression AT^n . To calculate the barrier height, the experimental rate coefficient expression is set equal to the TST equation (9) at 820 K, the temperature



Figure 2. Arrhenius plots of experimental rate coefficients for the AlCl $+ N_2O$ (open circles) and AlCl $+ CO_2$ (open squares) reactions. Rate coefficient expressions for the O atom abstraction channels for these reactions derived using the MTST method are shown as solid lines.

TABLE IV: Transition-State Parameters for ClAlOCO[‡]

geometrica	l parameter ^{a,b}	force constant ^c		
r(ClAl)	2.08	F _r (ClAl)	3.2	
r(AlO)	1.63	Fr(AlO)	4.2	
r(OC)	1.81	$F_r(OC)$	-2.0	
r(CO)	1.13	$F_r(CO)$	19.0	
θ (ClÁlO)	160	$F_{\theta}(ClAlO)$	0.3	
$\theta(AlOC)$	90	$F_{\theta}(AlOC)$	0.6	
$\theta(OCO)$	120	F ₀ (OCO)	0.2	
τ (ClAlOC)	0	$F_{r}(C A OC)$	0.02	
τ (AlOCO)	0	F _r (AlOCO)	0.02	

rotational constants ($B_1B_2B_3$): 9.46 × 10⁻⁴ cm⁻³

vibrational frequencies v_i : 75, 91, 141, 216, 231, 523, 908, 2164 cm⁻¹

^a We assume trans arrangements for the atoms in the ClAlOC and AlOCO groups. The parameters of the transition state are based on the products of the endothermic reaction AlCl + $CO_2 \rightarrow CO$ + OAlCl. ^b Units of r are 10⁻¹⁰ m; units of θ and τ are deg. ^c Units of F_r are 10² N m⁻¹; units of F_{θ} and F_{τ} are 10⁻¹⁸ N m rad⁻².

corresponding to the middle of the T^{-1} range of the experiments. The value $\Delta E^{\ddagger} = 45.9$ kJ mol⁻¹ is thus obtained, which yields

$$k_{\text{MTST}} = 5.74 \times 10^{-18} (T/K)^{2.06} \times \exp(-5520 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (14)

A comparison between eq 14, the MTST rate coefficient for reaction 1a, and experiment is shown in Figure 2. Over the temperature range of the experimental data the agreement can be seen to be excellent, which suggests that the dominant channel for reaction 1 is abstraction, i.e., channel 1a.

The AlCl + CO_2 Reaction. The abstraction reaction

$$AlCl + CO_2 \rightarrow OAlCl + CO$$
 (2a)

is 98 kJ mol⁻¹ endothermic.²³ The parameters of the transition state ClAlOCO[‡], which are summarized in Table IV, have been derived based on properties of the products OAlCl + CO. The estimation scheme is very similar to that for the AlCl + N₂O transition state so only the differences will be discussed here. The r(CO), r(ClAl), and r(AlO) distances are taken as those in CO and OAlCl. The internuclear distance along the reaction coordinate is estimated by $r(OC) = [r(O⁻) + r(C⁺)]0.50^{1/(\delta-1)}$. The force constant $F_r(CO)$ is taken as that in the CO molecule, while $F_r(C|A|)$ and $F_{\theta}(C|A|O)$ are taken as equal to force constants derived from ab initio calculations⁷ of the vibrational frequencies of OA|C|. Table IV summarizes the resulting rotational constants and vibrational frequencies.

We calculate the preexponential factor of eq 9 in the 500– 2000 K temperature range and fit the results to the expression AT^n expression. A barrier height of 118 kJ mol⁻¹ for the forward reaction is estimated based on the endothermicity of reaction 2a plus a barrier height for the reverse reaction of 20 kJ mol⁻¹, which is probably too small in view of the fact that CO + OAICI is isoelectronic with AlCl + N₂O, for which we obtained a barrier height of 45.9 kJ mol⁻¹. Combining the calculated A, n, and ΔE^{\ddagger} values leads to the expression

$$k_{\text{MTST}} = 1.27 \times 10^{-18} (T/\text{K})^{2.44} \times \exp(-14190 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$
 (15)

Equation 15 is plotted in Figure 2 to allow for comparison with experiment. It may be seen that the rate coefficients thus calculated are too low to account for the experimental data below about 1400 K. If a higher barrier for the reverse reaction were to be included, the calculated rate coefficients would decrease further, reinforcing this conclusion. We thus speculate that at least below 1400 K the main products of reaction 2 are adducts correlating with the singlet and triplet potential energy surfaces of AlCl⁺ with CO_2^{-} .

The AlCl + SO_2 Reaction. The abstraction reaction

$$AlCl + SO_2 \rightarrow OAlCl + SO$$
 (3a)

has an endothermicity²³ of 119 kJ mol⁻¹ and is spin-forbidden. For temperatures between 800 and 1100 K the rate coefficient for abstraction is much lower than the upper limit determination (cf. eq 8) because of the large endothermicity. There may be channels leading to the formation of adducts. However, since no reaction could be detected, the adducts must have low binding energies and the addition channels may have significant activation barriers.

The AlCl + O_2 Reaction. In the study¹ of the rate coefficients of the AlCl + O_2 reaction from 490 to 1750 K, it was speculated that the dominant low temperature channel could be

$$AlCl + O_2 \rightarrow AlO_2 + Cl$$
 (16a)

while at higher temperatures the channel

$$AlCl + O_2 \rightarrow OAlCl + O \tag{16b}$$

was considered a possibility. Thermochemical data available at that time indicated that the thermochemistry of channel 16a was uncertain, while channel 16b was thought to be exothermic.¹ Recent high-level ab initio computations⁷ on AlO₂ now indicate that channel 16a is 87 kJ mol⁻¹ endothermic, confirming the $\Delta H_f(AlO_2)$ assumed in the JANAF tables.⁸ That theoretical work²³ also suggests that channel 16b is 66 kJ mol⁻¹ endothermic. These data and the use of MTST allow a reevaluation of the measurements of the AlCl + O₂ reaction.

The parameters for the molecular model as well as the rotational constants and vibrational frequencies of the transition state for channel 16a are summarized in Table V. The geometry and force constants have been obtained based on the assumption that the transition state resembles the products OAIO + Cl, with the halogen atom attacking the Al atom by a side-on approach. We assume the AlO distance and force constants F_r (AlO) and F_{θ^-} (OAIO) for the transition state are equal to those of AlO₂.⁸ The remaining parameters have been obtained similarly to those for the AlCl + N₂O, CO₂ reactions. If the barrier height for the

TABLE V: Transition-State Parameters for AlO₂Cl[‡]

geometrical	parameter ^{a,b}	force constant ^c		
r(AlCl)	2.34	Fr(AlCl)	-2.0	
r(AlO)	1.69	F,(AlO)	4.2	
$\theta(OAIO)$	160	F _e (OAlO)	0.24	
θ(OAICÍ)	100	F _e (OAlCI)	0.2	
τ (AlO ₂ Cl)	0	$F_{\tau}(AlO_2Cl)$	0.02	

rotational constants $(B_1B_2B_3)$: 1.72×10^{-3} cm⁻³

vibrational frequencies v_i: 119, 176, 200, 678, 981 cm⁻¹

^a We assume a C_{2p} arrangement for the atoms. The parameters of the transition state are based on the products of the endothermic reaction AlCl + $O_2 \rightarrow OAlO$ + Cl. ^b Units of r are 10^{-10} m; units of θ and τ are deg. ^c Units of F_r are 10^2 N m⁻¹; units of F_θ and F_τ are 10^{-18} N m rad⁻².

TABLE VI:	Transition-State	Parameters	for ClAlOO [‡]

geometrical parameter ^{a,b}		force constant ^c		
r(ClAl)	2.08	$F_r(ClAl)$	3.2	
r(AlO)	1.63	$F_r(AlO)$	4.2	
r(00)	1.72	$F_r(OO)$	-2.0	
$\theta(ClAlO)$	160	F ₀ (ClAlO)	0.3	
$\theta(A OO)$	90	F _e (AlOO)	0.6	
τ (ClAlOO)	0	F_{τ} (ClAlOO)	0.02	

rotational constants $(B_1B_2B_3)$: 3.27 × 10⁻³ cm⁻³

vibrational frequencies vi: 125, 131, 245, 522, 907 cm⁻¹

^a We assume a trans arrangement for the atoms. The parameters of the transition state are based on the products of the endothermic reaction AlCl + $O_2 \rightarrow O$ + OAlCl. ^b Units of r are 10^{-10} m; units of θ and τ are deg. ^c Units of F_r are 10^2 N m⁻¹; units of F_θ and F_r are 10^{-18} N m rad⁻².



Figure 3. Arrhenius plot of experimental rate coefficients for the previously¹ studied AlCl + O_2 (open circles) reaction. Rate coefficient expressions for the AlCl + $O_2 \rightarrow OAlCl + O$ (full line) and AlCl + $O_2 \rightarrow AlO_2 + Cl$ (dashed line) channels derived using the MTST method are shown for comparison with experiments.

reverse reaction is neglected, MTST calculations give

$$k_{\text{MTST}} = 2.75 \times 10^{-17} (T/\text{K})^{1.76} \times \exp(-10460 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (17)$$

As can be seen in Figure 3 the MTST calculations given by the dashed line indicate that channel 16a is insignificant at all temperatures.

The MTST parameters for channel 16b are summarized in Table VI and have been obtained similarly to those for the AlCl $+ CO_2$ reaction. If we assume a negligible barrier height for the reverse reaction, the MTST expression obtained is

$$k_{\text{MTST}} = 1.18 \times 10^{-17} (T/\text{K})^{1.87} \times \exp(-7938 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (18)$$

In Figure 3 the experimental rate coefficient measurements are shown along with those from eq 18. This comparison suggests that channel 16b can be of significance above about 1500 K in agreement with the earlier speculation.¹

Recent ab initio calculations²⁶ have indicated the existence of a stable adduct AlClO₂, which correlates with the reactants AlCl $+ O_2$. Hence, the dominant reaction pathway at temperatures below 1750 K is likely to be addition with the abstraction reaction 16b becoming of greater importance with increasing temperature.

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