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Rate constants for the homogeneous gas-phase Al/HCl combustion chemistry

Mark T. Swihart[a,]*, Laurent Catoire[b], Benjamin Legrand[c], Iskender Gökalp[c], Claude Paillard[b]

[a]*Department of Chemical Engineering, University at Buffalo (SUNY), Buffalo, NY 14260-4200, USA*
[b]*Laboratoire de Combustion et Systèmes Réactifs (LCSR), CNRS, and University of Orleans, 1C, av. de la recherche scientifique, 45071 Orleans cedex 2, France*
[c]*Laboratoire de Combustion et Systèmes Réactifs (LCSR), CNRS, 1C, av. de la recherche scientifique, 45071 Orleans cedex 2, France*

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Abstract

Experimental reaction rate data for the Al/HCl system are very scarce. Such data are needed for the comprehension and for the numerical simulation of the combustion of aluminum particles as encountered in solid segmented motors. Toward this end, we have examined the homogeneous chemistry of this system, computed rate parameters for important reactions using conventional Transition State Theory (TST) and RRKM/master equation simulations, and estimated rate parameters for reactions where rigorous computations are not presently feasible. The reaction mechanism presented in this study consists of 15 species participating in 39 reversible elementary reactions for which rate parameters have been estimated or computed. © 2003 The Combustion Institute. All rights reserved.

Keywords: Aluminum; Combustion chemistry; Solid propellants; Reaction Mechanism

1. Introduction

The addition of aluminum particles to solid propellant is principally used to increase motor specific impulse. The combustion process involved is complicated and not easily modeled. Some of the reactions of interest during this process involve gaseous Al atoms and the gaseous products of combustion of the solid propellants, including HCl, CO_2, N_2, and H_2O. Quantitatively, one of the most important species is HCl. From a kinetic point of view, the Al/HCl reaction system has been only partially studied experimentally. Moreover, these reactions have been studied in a rather small temperature range and/or at temperatures much lower than the temperatures encountered during combustion in practical systems (above 2000 K). The extrapolation to higher temperatures is not always reliable, since modified Arrhenius behavior is frequently observed in the 1000–4000 K temperature range. The pressure effect on the kinetics is also an important factor to be considered as the aluminum particles burn in an oxidizing gas mixture at about 50 atm while most chemical kinetics experiments have been conducted at much lower pressures. The aims of this work are to (1) identify the most likely products of potentially important elementary reactions in this system; (2) to develop rate expressions suitable for use in combustion modeling

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* Corresponding author. Tel.: +1-716-645-2911; fax: +1-716-645-3822.

E-mail address: swihart@eng.buffalo.edu (M.T. Swihart).

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up to 4000 K and up to 50 atm for the Al/HCl system; and (3) to compare them with experimental data when available.

2. Computational methods

For bimolecular reactions, the rate constant for each elementary reaction was obtained using conventional transition state theory (TST), if relevant. Tunneling was accounted for using the Wigner correction. This correction is approximate, but for the high temperatures (1500–4000 K) of interest in this study the tunneling correction factor is close to 1. Tunneling has been taken into consideration primarily to allow for comparison of these calculations with experiments from the literature performed at temperatures below 1000 K. For unimolecular reactions and chemically activated reactions, the RRKM theory has been used in master equation calculations to compute the pressure and temperature dependent rate constants. For different reactions, this was implemented using the UNIMOL program [1], the ChemRate program [2], and the Variflex program [3]. The rate constants for unimolecular decomposition reactions were parameterized in terms of k_∞, k_0, and F_c. All the data needed, both for the TST and RRKM theories, have been determined from ab initio molecular orbital calculations performed using the GAUSSIAN94 suite of programs [4]. For the reactions with tight transition states, the transition state geometry and vibrational frequencies were calculated using density functional theory at the B3LYP/6-31G* level. Frequency calculations confirmed that each of these transition states had a single imaginary frequency, and was therefore, a first-order saddle point. The energy difference between the reactant and transition state was calculated using the CBS-Q complete basis set method [5], using the G-2 method [6], and using the CBS-RAD complete basis set method [7]. For unimolecular decompositions that are simple bond fission reactions, the geometry was optimized at the B3LYP/6-31G* level at a series of fixed lengths of the breaking bond, and moments of inertia for overall rotations and free internal rotations were calculated at each bond length. The profile of energy versus bond length was fit to a Morse form to match the outer part of the potential. The bond dissociation energy was calculated at the G-2 level. In the RRKM calculations, the transition state position was varied to minimize the high-pressure rate coefficient for the simple bond-breaking reaction channel. That is, the conventional Variational Transition State Theory (VTST) approach was used. Detailed results of the molecular orbital calculations have been presented elsewhere [8]. For enthalpies of formation of small molecules, the G-2 method and the complete basis set methods used here are generally accurate to within 2 kcal/mol. For barrier heights, the uncertainty in these calculations is less clear and depends on the nature of the transition state, but is likely to be slightly larger. Therefore, barrier heights quoted here should probably be considered to be best estimates with uncertainties of 1 to 4 kcal/mol. Future research, both computational and experimental, will be required to refine the calculated barrier heights.

The standard enthalpies of formation at 298 K, the standard entropies at 298 K, and the heat capacities for the species $AlH_xCl_y(x = 0–3, y = 0–3)$ have been determined from ab initio molecular orbital calculations [9].

3. Results and discussion

3.1. Bimolecular reactions

3.1.1. Rate constants derived from conventional TST

The conventional TST has been applied to potential energy surfaces for bimolecular reactions where a single potential maximum at the transition structure separates reactant and product species [see [8] for the potential energy surfaces (PES)]. The TST is recognized to do a good job describing a wide variety of chemical reactions, despite some limitations [10]. Unfortunately, the majority of possible bimolecular reactions in this system cannot be treated by conventional TST. These reactions occur either (1) via barrierless, direct reaction paths, in which case variational transition state theory, rather than conventional transition state theory, would have to be applied or (2) via chemically activated reaction paths, proceeding through a bound intermediate, in which case more complex unimolecular reaction rate theories that explicitly treat energy transfer between the reactive species and the bath gas must be considered. Those reactions that can be treated using conventional transition state theory are discussed here and their rate constants are reported in Table 1.

$AlHCl_2 + H \rightarrow products$

Two reactions have to be considered with $AlHCl_2$ and H as reactants:

$$AlHCl_2 + H \rightarrow AlHCl + HCl$$

$$\Delta H^o_{rxn}\,(298\text{ K}) = 16.1\text{ kcal mol}^{-1}$$

$$AlHCl_2 + H \rightarrow AlCl_2 + H_2$$

$$\Delta H^o_{rxn}\,(298\text{ K}) = 18.3\text{ kcal mol}^{-1}$$

The two abstraction reactions both have energetic barriers and can be treated using conventional TST.

Table 1
Rate constants computed by conventional TST theory. $\Theta = E/R$ is the activation temperature in K

Reaction	k (cm^3 mol^{-1} s^{-1}) $= A \times T^n \exp(-\Theta/T)$
$AlHCl_2 + H \rightarrow AlHCl + HCl$	$3.45 \times 10^8\ T^{1.64} \exp(-10610/T)$
$AlHCl_2 + H \rightarrow AlCl_2 + H_2$	$1.25 \times 10^8\ T^{1.78} \exp(-318/T)$
$AlCl_3 + H \rightarrow AlCl_2 + HCl$	$7.76 \times 10^8\ T^{1.63} \exp(-10321/T)$

No data have been found in the literature for these reactions. The calculated points can be fit well by k (cm^3 mol^{-1} s^{-1}) $= 3.45 \times 10^8\ T^{1.64}$ exp $(-10610/T)$ at the CBS-RAD level for $AlHCl_2 + H \rightarrow AlHCl + HCl$ and by k (cm^3 mol^{-1} s^{-1}) $= 1.25 \times 10^8\ T^{1.78}$ exp $(-318/T)$ at the CBS-RAD level for $AlHCl_2 + H \rightarrow AlCl_2 + H_2$. The temperature exponent is as expected (around 1.4 without tunneling effect correction factor for both reactions following Zellner [11]) for abstraction of an atom from a stable species by an atom.

$$AlCl_3 + H \rightarrow AlCl_2 + HCl$$

$$\Delta H^o_{rxn}\,(298\ \text{K}) = +13.8\ \text{kcal mol}^{-1}$$

No data have been found in the literature for this reaction. The calculated points can be fit well by k (cm^3 mol^{-1} s^{-1}) $= 7.76 \times 10^8\ T^{1.63}$ exp $(-10321/T)$ at the CBS-RAD level. The temperature exponent is, from the considerations cited above, as expected.

3.1.2. Estimated bimolecular rate constants for barrierless reactions

Potential energy surface scans at the HF/6-31G* or B3LYP/6-31G* levels [8] show that, considering only reactions involving a single aluminum atom and only reactions involving five or fewer total atoms, more than 30 possible reactions have no electronic potential energy barrier on the reaction path. These reactions are not amenable to treatment by conventional TST because the choice of transition state is not clear. One possibility is to use the canonical Variational Transition State Theory (VTST), according to which the transition state must be defined so as to minimize the calculated reaction rate. However, the practical difficulties and computational expense of applying the VTST procedure to these reactions at sufficiently high levels of theory has thus far prevented us from considering them in detail. This will remain to be considered in future studies. Unfortunately, among these numerous reactions, only two have been experimentally studied, namely $Al + Cl_2 \rightarrow AlCl + Cl$ [12] and $AlCl + Cl_2 \rightarrow AlCl_2 + Cl$ [12]. Therefore, some semi-empirical procedures have been used to estimate the rate constants for these reactions. All these reactions are expected to be very fast (close to the gas kinetic collision rate) and to have zero or slightly negative enthalpy of activation (enthalpy difference between the transition state and reactants in the thermodynamic formulation of transition state theory), but the temperature dependence of the pre-exponential factor can vary from one class of reactions to another. Because the equations used by the conventional VTST are the same as the conventional TST, the temperature dependence of the pre-exponential factor can provisionally be taken to be the same in the two cases for a given class of reactions. Therefore, for these reactions we have used a power-law temperature dependence based on the expected maximum temperature dependence of the pre-exponential factor for similar reactions [11,13], with no Arrhenius term in the temperature dependence. Because the power laws have positive exponents (T^n with $n > 0$) these all result in rate constants that increase with temperature and have, locally, a positive activation energy when it is formally defined as $E_a = -d(\ln k)/d(1/(RT))$. Thus, for all these, we end up with rate parameters slightly below the gas-kinetic collision rate, which is a reasonable range for them, but should be considered an educated guess, open to correction. Further refinement of the rate parameters for these reactions will be necessary in subsequent experimental or computational studies. This may need to include consideration of competing chemically activated paths for these reactions proceeding through bound complexes. At present, for all reaction channels in which a barrierless direct abstraction path is possible, we have neglected chemically activated paths, even if those paths are also barrierless. Very loosely speaking (pun intended) the (variational) transition state for the barrierless abstraction reactions is expected to be looser (have higher entropy and greater density of states) than those leading to and from the bound complex. So, if there is no barrier on the direct reaction path, it is expected to dominate these parallel processes. However, there is clearly no guarantee that this will always be the case, and more detailed consideration of additional chemically activated paths is warranted in future studies.

3.1.2a. Atom-molecule barrierless abstraction reactions. The $Al + Cl_2$ reaction was studied experimentally by Rogowski et al. [12]. They measured a rate constant of $4.75 \times 10^{+14} \exp(-780/T)$ cm^3 mol^{-1} s^{-1} for $Al + Cl_2 \rightarrow AlCl + Cl$. Our computational results at first appear to be inconsistent with Ro-

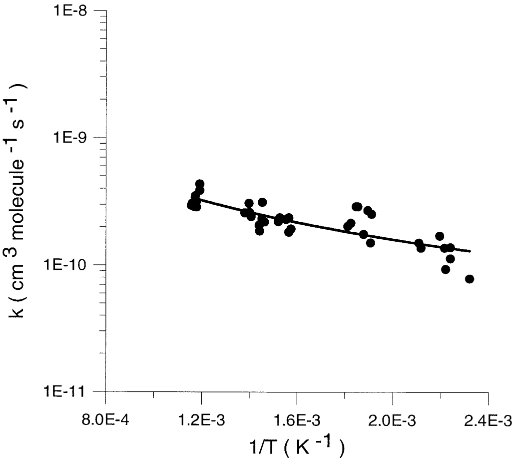

Fig. 1. Fit obtained when the temperature exponent is fixed at 1.5 for the reaction Al + Cl_2 → AlCl + Cl. Experimental points from Rogowski et al. [12].

gowski et al.'s observation of a positive activation energy for this reaction when fit to the Arrhenius form. However, as discussed by Dean and Bozzelli [13], following Zellner [11], a maximum temperature exponent of around 1.5 is expected for an atom abstraction from a stable species by an atom. If this temperature exponent is held fixed, the experimental data can be fit well by 7.43 × 10^9 $T^{1.5}$ exp(+74/T) cm^3 mol^{-1} s^{-1} with goodness of fit similar to the Arrhenius fit presented by Rogowski et al. (see Fig. 1). Our prediction of a zero or slightly negative enthalpy of activation for this reaction is thus consistent with the experimental data when the expected temperature dependence of the pre-exponential factor is taken into account. Pre-exponential factors for this class of reactions can then be derived as follows. Assuming a temperature exponent of 1.5 for the atom-molecule abstraction reactions and dividing the experimental or computed TST pre-exponential factor by the number of abstractable atoms for a given reaction leads to an average log A value of 8.9 ± 0.2 for a H-atom or Cl-atom abstraction from a stable species by a H-atom and to an average value of log A of 9.5 for a Cl-atom abstraction from a stable species by an Al-atom. In fact, a unique value of log A equal to 9.2 ± 0.3 per abstractable atom can be given for these reaction types. In all cases this value is per abstractable atom. For these reactions the following rate constant can thus, be proposed: k (cm^3 mol^{-1} s^{-1}) = $m \times 10^{9.2}\ T^{1.5}\ e^0$ where m represents the number of abstractable atoms for the reaction considered. All the rate constants estimated for this reaction class are given in Table 2.

Table 2
Estimated rate constants for molecule-atom barrierless atom abstraction and molecule-polyatomic radical barrierless atom abstraction reaction

Reaction	k (cm^3 mol^{-1} s^{-1}) = $A\ T^n$
AlH_3 + Cl → AlH_2 + HCl	$3 \times 10^{9.2}\ T^{1.5}$
AlH_3 + H → AlH_2 + H_2	$3 \times 10^{9.2}\ T^{1.5}$
AlH_2Cl + H → AlHCl + H_2	$2 \times 10^{9.2}\ T^{1.5}$
AlH_2Cl + Cl → AlHCl + HCl	$2 \times 10^{9.2}\ T^{1.5}$
$AlHCl_2$ + Cl → $AlCl_2$ + HCl	$10^{9.2}\ T^{1.5}$
AlHCl + Cl_2 → $AlHCl_2$ + Cl	$2 \times 5 \times 10^2\ T^3$
$AlCl_2$ + Cl_2 → $AlCl_3$ + Cl	$2 \times 5 \times 10^2\ T^3$
AlH_2 + HCl → AlH_2Cl + H	$5 \times 10^2\ T^3$

3.1.2b. Diatomic radical-molecule barrierless abstraction reactions. The AlCl + Cl_2 → $AlCl_2$ + Cl reaction was also studied by Rogowski et al. [12]. Their measured rate constant for this reaction for temperatures from 400 to 1025 K was 5.77 × 10^{13} exp (−610 K/T) cm^3 mol^{-1} s^{-1}. As was the case for the Al + Cl_2 reaction, our results at first appear to be inconsistent with the positive activation energy measured by Rogowski et al. [12]. However, according to Dean and Bozzelli [13], a temperature exponent near 2 is expected for an atom abstraction from a stable species by a diatomic radical. The experimental data can be well fit by 1.97 × 10^{+7} T^2 exp (+574/T) cm^3 mol^{-1} s^{-1} with an accuracy similar to that obtained with the Arrhenius fit given by Rogowski et al. (see Fig. 2). Our prediction of a negative enthalpy of activation for this reaction is therefore consistent with the experimental data. This result suggests a log A of 7 per abstractable atom. Therefore, an estimated

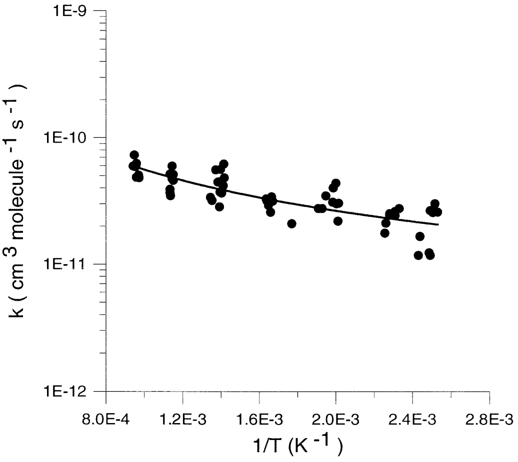

Fig. 2. Fit obtained when the temperature exponent is held fixed at 2.0 for the reaction AlCl + Cl_2 → $AlCl_2$ + Cl. Experimental points from Rogowski et al. [12].

rate constant can be proposed for this class of reactions as k (cm^3 mol^{-1} s^{-1}) $= m \times 10^{+7}\ T^2\ e^0$ where m represents the number of abstractable atoms for the reaction considered. Among the reactions considered here, the $AlCl + Cl_2$ reaction is the only exothermic diatomic radical-molecule reaction, so no reactions of this type are included in Table 2. Endothermic reactions of this type are included via microscopic reversibility.

3.1.2c. Polyatomic radical-molecule barrierless abstraction reactions. No experimental data have been published concerning such reactions with aluminum based species. According to Dean and Bozzelli [13], following Zellner [11], a maximum temperature coefficient of 3 is to be expected for an atom abstraction from a molecule by a polyatomic radical. The reverse of the reactions given above in the section entitled "rate constants derived from conventional TST" are polyatomic radical-molecule abstraction reactions. The rate constants for these reverse reactions have been calculated by using the principle of microscopic reversibility (which gives the same result as calculating the rate constant directly using conventional TST). The calculated points can be fit well, in the 500 to 4000 K temperature range, without constraint, by:

$$k\ (\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 1.52 \times 10^2\ T^{3.10}\ \exp(-3031/T)\ \text{for}\ AlCl_2 + HCl \rightarrow AlCl_3 + H,$$

$$k\ (\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 2.60 \times 10^2\ T^{3.02}\ \exp(-2117/T)\ \text{for}\ AlHCl + HCl \rightarrow AlHCl_2 + H,$$

$$k\ (\mathrm{cm^3\ mol^{-1}\ s^{-1}}) = 5 \times 10^3\ T^{2.93}\ \exp(-9058/T)\ \text{for}\ AlCl_2 + H_2 \rightarrow AlHCl_2 + H$$

The temperature exponent is, from the considerations cited above, as expected. By assuming a temperature exponent of 3, this leads to an average log A value of 2.7 ± 0.4 per abstractable atom. This leads us to propose a rate constant of k (cm^3 mol^{-1} s^{-1}) $= m \times 5 \times 10^{+2}\ T^3\ e^0$ where m is the number of abstractable atoms for the reaction considered. This value seems reasonable, because a value of log A equal to 2.5 per abstractable H-atom is derived from experiments for the reaction $CH_3 + H_2 \rightarrow CH_4 + H$ [14]. All the rate constants estimated for this reaction class are given in Table 2.

3.1.2d. Radical-radical and atom-radical barrierless abstraction reactions. According to Phillips [15], radical-radical or atom-radical barrierless abstraction reactions have almost no temperature dependence. However, this does not mean that all the radical-radical and atom-radical abstraction reactions are barrierless (see for instance the atom-radical abstraction reaction $AlHCl + H \rightarrow AlH + HCl$ for which a 3 kcal mol^{-1} barrier has been computed [8]). By considering different atom-radical and radical-radical abstraction reactions with no electronic potential barrier to reaction, it appears that k can be taken equal to k (cm^3 mol^{-1} s^{-1}) $= m \times 10^{+13}\ T^0\ e^0$ where m is the number of abstractable atoms for the reaction considered. All the rate constants estimated for this reaction class are given in Table 3.

Table 3
Estimated rate constants for radical-atom barrierless atom abstractions

Reaction	k (cm^3 mol^{-1} s^{-1})
$AlH + H \rightarrow Al + H_2$	10^{13}
$AlH + Cl \rightarrow AlCl + H$	10^{13}
$AlH + Cl \rightarrow Al + HCl$	10^{13}
$AlH_2 + H \rightarrow AlH + H_2$	2×10^{13}
$AlH_2 + Cl \rightarrow AlH + HCl$	2×10^{13}
$AlHCl + H \rightarrow AlCl + H_2$	10^{13}
$AlHCl + Cl \rightarrow AlCl + HCl$	10^{13}

3.1.3. Complex (chemically activated) bimolecular reactions

The rate constants discussed here are reported in Table 4.

3.1.3a. Al + HCl → products. Three possible reactions have to be considered with the reactants Al and HCl:

$$Al + HCl \rightarrow AlCl + H$$

Table 4
Rate constants for complex bimolecular reactions (see text)

Reaction	k (cm^3 mol^{-1} s^{-1})
$Al + HCl \rightarrow AlHCl^* \rightarrow AlCl + H$	$9.27 \times 10^8\ T^{1.5}\ \exp(+326/T)$[a,b]
$AlCl + HCl \rightarrow AlHCl_2^* \rightarrow AlCl_2 + H$	$4.75 \times 10^{-2}\ T^{3.98}\ \exp(-7734/T)$[b,c]
$AlCl + HCl \rightarrow AlCl_2 + H$	$9.55 \times 10^4\ T^{2.55}\ \exp(-15970/T)$[d]

[a] Experimental points from [12].

[b] Chemically activated reaction.

[c] Experimental points from [17].

[d] Direct abstraction reaction derived from TST theory.

ΔH^{o}_{rxn} (298 K) $= -17.5$ kcal mol^{-1}

$Al + HCl \rightarrow AlHCl \qquad \Delta H^{o}_{rxn}$ (298 K)

$= -52.0$ kcal mol^{-1}

$Al + HCl \rightarrow AlH + Cl \qquad \Delta H^{o}_{rxn}$ (298 K)

$= +30.0$ kcal mol^{-1}

Rogowski et al. [12] studied the reaction Al + HCl → AlCl + H in the temperature range 400 to 1275 K. From their experiments, they obtained a rate constant k (cm^3 mol^{-1} s^{-1}) $= 9.03 \times 10^{13} \exp(-800/T)$. At conditions of interest for aluminum combustion, the channels leading to AlCl + H are expected to dominate. The third channel can be ruled out on energetic grounds and calculations, described further below, show that the second channel is negligible as well for temperatures above 500 K and pressures up to 50 atm. Ab initio calculations [8] show that the first reaction can occur either via a direct reaction path, which has a small barrier of about 4 kcal/mol, or via a barrierless path proceeding through chemically activated AlHCl. Interestingly, simply applying conventional transition state theory to the direct reaction path gives predictions that are in quite good agreement with the experimental results of Rogowski et al. However, because the chemically activated path has no energetic barrier, we expect it to dominate, and therefore expect the rate to be greater than that predicted for the direct path.

We have used the VariFlex [3] program to conduct master equation simulations of the chemically activated reaction Al + HCl ↔ AlHCl* → AlCl + H. In these calculations, energy and angular momentum resolved microcanonical rate constants for the barrierless Al + HCl → AlHCl and AlCl + H → AlHCl processes were computed, and the fragment separations in the transition states were selected variationally to minimize the rate constant for each energy and angular momentum pair for each channel. A one-dimensional master equation, in energy, was solved after averaging over the angular momentum distribution as described in [16]. These calculations showed conclusively that for pressures up to 50 atm and temperatures from 500 to 4000 K, collisional stabilization of chemically activated AlHCl* to give AlHCl is negligible. That is, in these calculations, essentially all of the chemically activated AlHCl* formed from Al + HCl decomposes to AlCl + H or back to Al + HCl.

However, these calculations significantly overestimate (by a factor of 10 to 20) the overall reaction rate compared to the experimental results of Rogowski et al. [12]. This overestimation of the reaction rate can be understood based on angular momentum restrictions for the overall reaction Al + HCl → AlCl + H. Rogowski et al. [12] discussed this to rationalize their experimentally observed pre-exponential factor, which is smaller than one would ordinarily expect. Because of its small mass, the H atom product simply cannot carry away much angular momentum from the reactive collision. This leads to additional angular momentum restrictions on the reaction that are not accounted for in the 1-dimensional master equation simulations, even when angular momentum resolved microcanonical rate parameters are used. These calculations still average over a distribution of angular momenta for the Al + HCl → AlHCl transition state and the AlHCl → AlCl + H transition state. In the limit of low pressures, where angular momentum is conserved in going from Al + HCl to AlCl + H, the angular momentum restrictions could be fully taken into account via classical trajectory simulations. At finite pressures, where collisions can alter the angular momentum of the AlHCl* complex, one could potentially perform two-dimensional master equation calculations in which the Al + HCl reaction produces activated AlHCl that has both a non-equilibrium energy distribution and a non-equilibrium angular momentum distribution, and in which both energy transfer and angular momentum transfer between AlHCl complex and the bath gas are treated explicitly. However, it is not presently feasible for us to do these calculations.

Our best recommendation for this reaction, therefore, is to use the extrapolated rate constants of Rogowski et al. [12]. However, the extrapolation of this rate constant using the Arrhenius form over such a large temperature range may be unreliable. As a barrierless reaction, the chemically activated Al + HCl → AlCl + H is expected to exhibit a negative enthalpy of activation, and this appears at a first glance to be inconsistent with Rogowski et al.'s observation of a positive activation energy for this reaction when they fit their data to the Arrhenius form. As an atom-molecule abstraction reaction, a temperature exponent of 1.5 for the pre-exponential factor is likely. Including this in a modified Arrhenius fit to the data gives

$$k\ (\text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 9.27 \times 10^{8}\ T^{1.5} \exp(+326/T)$$

Note that this rate constant should, in principle, only be valid in the experimental 12.1 to 40.7 torr pressure range. The one-dimensional RRKM/master equation calculations described above showed little pressure dependence up to 50 atm. However, a 2-dimensional master equation treatment in which re-distribution of angular momentum by collisions is explicitly taken into account, might be expected to show greater pressure dependence. The pressure dependence of this rate constant therefore remains to be fully evaluated.

3.1.3b. AlCl + HCl → products. Three reactions have to be considered with the reactants AlCl + HCl:

$$AlCl + HCl \rightarrow AlCl_2 + H \qquad \Delta H^o_{rxn}\,(298\,\mathrm{K}) = +35.3\ \mathrm{kcal\,mol^{-1}}$$

$$AlCl + HCl \rightarrow AlHCl_2 \qquad \Delta H^o_{rxn}\,(298\,\mathrm{K}) = -50.6\ \mathrm{kcal\,mol^{-1}}$$

$$AlCl + HCl \rightarrow AlHCl + Cl \qquad \Delta H^o_{rxn}\,(298\,\mathrm{K}) = +68.7\ \mathrm{kcal\,mol^{-1}}$$

This reaction has been studied experimentally in the 1330 to 1610 K temperature range by Slavejkov and Fontijn [17]. They found a rate constant k ($\mathrm{cm^3\,mol^{-1}\,s^{-1}}$) = 6.62×10^{12} exp ($-13100/T$). They assumed that the reaction products were $AlCl_2$ + H but the product $AlHCl_2$ has to be considered as well. The remaining reaction, AlCl + HCl → AlHCl + Cl, is too endothermic to be of importance. As was the case for the Al + HCl reaction, the reaction AlCl + HCl → $AlCl_2$ + H can occur either via a direct path with a barrier, or via a path proceeding through chemically activated $AlHCl_2$. However, unlike the Al + HCl reaction, the overall reaction AlCl + HCl → $AlCl_2$ + H is endothermic, and there is a barrier for the formation of $AlHCl_2$ from AlCl + HCl. The transition state for AlCl + HCl → $AlHCl_2$ is about 19 kcal/mol above the reactants, and therefore the chemically activated $AlHCl_2$ is formed with a total of 70 kcal/mol of excess energy. However, this is still about 13 kcal/mol below the energy of $AlCl_2$ + H. Therefore, at high temperatures and moderate pressures where stabilization of $AlHCl_2$ by collisional energy transfer is slow, the majority of the chemically activated $AlHCl_2$ formed will simply decompose back to AlCl + HCl. Some small fraction of it may be stabilized, and some may decompose to $AlCl_2$ + H. Both of these processes would be included in the experimental measurements of Slavejkov and Fontijn [17], since they measured disappearance of AlCl and not appearance of any products.

For the direct reaction AlCl + HCl → $AlCl_2$ + H, the calculated points at the CBS-RAD level can fit well by k ($\mathrm{cm^3\,mol^{-1}\,s^{-1}}$) = $9.55 \times 10^4\,T^{2.55}$ exp ($-15970/T$). In the 1330 to 1610 K temperature range, the TST values are much lower, by about a factor 3 to 7, than the experimental ones. Therefore, in the 1330 to 1610 K temperature range, the reaction should proceed through the chemically activated path.

We have used ChemRate [2] to simulate the chemically activated reaction AlCl + HCl. These RRKM/master equation calculations show that in the temperature range from 500 to 4000 K and at pressures from 1 to 50 atm, stabilization of $AlHCl_2$ is negligible. That is, all of the chemically activated $AlHCl_2$ formed from AlCl + HCl either decomposes to $AlCl_2$ + H or decomposes back to the reactants. In this range of conditions, the branching ratio for formation of $AlCl_2$ + H from the chemically activated $AlHCl_2$ was typically in the range of 1 to 10 percent (0.01 to 0.1), increasing with temperature. The apparent rate constant for the AlCl + HCl → $AlCl_2$ + H reaction is the product of this branching ratio with the rate constant for AlCl + HCl → $AlHCl_2^*$ (the rate constant for formation of chemically activated $AlHCl_2$). Since the branching ratio increases with temperature, the apparent activation energy for the overall AlCl + HCl → $AlCl_2$ + H reaction is higher than the barrier for AlCl + HCl → $AlHCl_2^*$. However, it is still significantly lower than the endothermicity of the overall reaction (as observed experimentally by Slavejkov and Fontijn). The branching ratio was somewhat sensitive to the vibrational frequencies of the loose transition state for $AlHCl_2^*$ → $AlCl_2$ + H, and therefore the lowest frequencies of this transition state were adjusted to obtain good agreement with the experimental results of Slavejkov and Fontijn. This is the only reaction for which we have made any adjustments in transition state properties to improve agreement with experimental data (except that these same adjusted frequencies were used in the corresponding decomposition of $AlHCl_2$ through this same transition state). The reaction was found to be almost pressure independent from their experimental conditions (near 40 Torr) up to 50 atmospheres, with the rate constant increasing by less than 10% between 1 atmosphere and 40 atmospheres. Therefore, we have fit a pressure-independent rate expression for this reaction:

$$k\ (\mathrm{cm^3\,mol^{-1}\,s^{-1}}) = 4.75 \times 10^{-2}\,T^{3.98}\ \exp(-7734/T)$$

The temperature coefficient of about 4 cannot be rationalized in term of the TST theory because the reaction is both chemically activated and endothermic. It should also be noted that the same angular momentum restrictions that were discussed for the Al + HCl reaction arise for this reaction as well. However, the rate of this reaction is much more strongly influenced by the reaction energetics, since the overall reaction is endothermic and since there is a distinct barrier for formation of the activated complex. Therefore, the angular momentum effects are expected to be less important in this case.

The rate of reaction via the direct reaction path is found to be competitive with the chemically activated

Table 5
Rate constants obtained by applying the RRKM theory with master equation simulations. M is HCl. Units are K for the activation temperature

Reaction	k_∞ (s^{-1}) k_0 ($cm^3\ mol^{-1}\ s^{-1}$) Fc
$AlH_2 + M \rightarrow AlH + H + M$	$k_\infty = 1.46 \times 10^{15} \exp(-23376/T)$ $k_0 = 9.68 \times 10^{14} \exp(-19962/T)$ $Fc = -4.1 \exp(-T/21.6) + 5.1 \exp(-T/493) + \exp(-942/T)$
$AlHCl + M \rightarrow AlCl + H + M$	$k_\infty = 4.94 \times 10^{15} \exp(-17284/T)$ $k_0 = 3.36 \times 10^{14} \exp(-14180/T)$ $Fc = 1.6 \exp(-T/642) - 0.6 \exp(-T/4609) + \exp(-250/T)$
$AlCl_2 + M \rightarrow AlCl + Cl + M$	$k_\infty = 1.92 \times 10^{14} \exp(-32291/T)$ $k_0 = 1.63 \times 10^{15} \exp(-26915/T)$ $Fc = 1.17 \exp(-T/1307) - 0.17 \exp(-T/376) + \exp(-2209/T)$
$AlH_3 + M \rightarrow AlH + H_2 + M$	$k_\infty = 1.48 \times 10^{13} \exp(-30756/T)$ $k_0 = 1.01 \times 10^{15} \exp(-27089/T)$ $Fc = 0.94 \exp(-T/885) + 0.06 \exp(-T/552) + \exp(-3807/T)$
$AlH_2Cl + M \rightarrow AlH + HCl + M$	$k_\infty = 3.60 \times 10^{14} \exp(-37351/T)$ $k_0 = 1.96 \times 10^{15} \exp(-31774/T)$ $Fc = 0.35 \exp(-T/3323) + 0.65 \exp(-T/299) + \exp(-13590/T)$
$AlH_2Cl + M \rightarrow AlCl + H_2 + M$	$k_\infty = 4.47 \times 10^{13} \exp(-37840/T)$ $k_0 = 1.95 \times 10^{15} \exp(-31774/T)$ $Fc = 0.01 \exp(T/951) + 0.99 \exp(-T/1613) + \exp(-187/T)$
$AlH_2Cl + M \rightarrow AlHCl + H + M$	$k_\infty = 2.08 \times 10^{15} \exp(-42523/T)$ $k_0 = 7.67 \times 10^{12} \exp(-40050/T)$ $Fc = 1.7$
$AlHCl_2 + M \rightarrow AlCl + HCl + M$	$k_\infty = 1.63 \times 10^{12} \exp(-33016/T)$ $k_0 = 4.07 \times 10^{15} \exp(-29140/T)$ $Fc = 0.39 \exp(-T/1363) + 0.61 \exp(-T/189)$
$AlCl_3 + M \rightarrow AlCl_2 + Cl + M$	$k_\infty = 1.7 \times 10^{15} \exp(-54788/T)$ $k_0 = 3.9 \times 10^{16} \exp(-43602/T)$ $Fc = 0.62 \exp(-T/309) + 0.38 \exp(-T/5695) + \exp(-7478/T)$
$Al + H + M \rightarrow AlH + M$	k_0 ($cm^6\ mol^{-2}\ s^{-1}$) $= 1.6 \times 10^{17}\ T^{0.34}$
$Al + Cl + M \rightarrow AlCl + M$	k_0 ($cm^6\ mol^{-2}\ s^{-1}$) $= 1.2 \times 10^{17}\ T^{0.20}$

one above 2000 K and both channels have to be included in a kinetic model.

3.2. Unimolecular reactions: rate constants computed using RRKM theory and master equation simulation

3.2.1. Decomposition of $AlCl_3$

This reaction is important because $AlCl_3$ is the dominant aluminum-containing species at equilibrium. As it is a simple bond-breaking reaction, there is no energetic barrier beyond the heat of reaction for $AlCl_3 \rightarrow AlCl_2 + Cl$. The reverse of reaction $AlCl_3 \rightarrow AlCl + Cl_2$ (ΔH^o_{rxn} (298 K) = 126.9 kcal mol^{-1}) is also predicted to be barrierless [8], but it is predicted to be about 10 kcal mol^{-1} more endothermic than $AlCl_3 \rightarrow AlCl_2 + Cl$ (ΔH^o_{rxn} (298 K) = 117 kcal mol^{-1}). Because of this, the channel going to $AlCl_2 + Cl$ is expected to dominate. Because it is a simple bond fission that proceeds through a "loose" transition state, whereas $AlCl_3 \rightarrow AlCl + Cl_2$ will proceed through somewhat "tighter" transition state, it is expected to have a larger pre-exponential factor as well as a lower activation energy than the other channel. Rate parameters for the reaction $AlCl_3 \rightarrow AlCl_2 + Cl$ obtained using the canonical VTST approach are given in Table 5.

3.2.2. Decomposition of $AlHCl_2$

The decomposition of $AlHCl_2$ can proceed by two simple bond-breaking channels:

$AlHCl_2 \rightarrow AlCl_2 + H \qquad \Delta H^o_{rxn}$ (298 K)

$+85.9$ kcal mol^{-1}

$AlHCl_2 \rightarrow AlHCl + Cl \qquad \Delta H^o_{rxn}$ (298 K)

$= +119.3$ kcal mol^{-1}

and by two molecular elimination channels:

$AlHCl_2 \rightarrow AlH + Cl_2 \quad \Delta H^o_{rxn}$ (298 K)

$= +143.3$ kcal mol^{-1}

$AlHCl_2 \rightarrow AlCl + HCl \quad \Delta H^o_{rxn}$ (298 K)

$= +50.6$ kcal mol^{-1}

The energetic barrier for $AlHCl_2 \rightarrow AlCl + HCl$ is about 70 kcal/mol, and it proceeds through a relatively tight transition state, while the decomposition to $AlCl_2$ + H is a simple bond fission that will proceed through a loose transition state and will have an activation energy close to its enthalpy of reaction. The other two channels are too endothermic to require consideration. Two channel RRKM/master equation simulations performed using ChemRate confirmed that the energetically favored channel $AlHCl_2 \rightarrow AlCl + HCl$ dominates at temperatures from 500 to 4000 K and pressures from 1 to 50 atm, and that in this regime the decomposition to $AlCl_2$ + H is negligible. Rate parameters for the dominant channel have been fit to the Troe form and are included in Table 5.

3.2.3. Decomposition of AlH_2Cl

The decomposition of AlH_2Cl can proceed through the following channels:

$AlH_2Cl \rightarrow AlHCl + H \quad \Delta H^o_{rxn}$ (298 K)

$= +85.6$ kcal mol^{-1}

$AlH_2Cl \rightarrow AlH_2 + Cl \quad \Delta H^o_{rxn}$ (298 K)

$= +120.9$ kcal mol^{-1}

$AlH_2Cl \rightarrow AlH + HCL \quad \Delta H^o_{rxn}$ (298 K)

$= +64.4$ kcal mol^{-1}

$AlH_2Cl \rightarrow AlCl + H_2 \quad \Delta H^o_{rxn}$ (298 K)

$= +15.9$ kcal mol^{-1}

The activation barriers for $AlH_2Cl \rightarrow AlH + HCl$ and $AlH_2Cl \rightarrow AlCl + H_2$ are about 72 and 74 kcal/mol, respectively. Therefore, three reaction paths can potentially be competitive, $AlH_2Cl \rightarrow AlH_2 + Cl$ being too endothermic to be significant. Three-channel RRKM/master equation simulations for this reaction were carried out using ChemRate [2]. These showed that at temperatures up to 3000 K, the third channel ($AlH_2Cl \rightarrow AlH + HCl$) is dominant, with 95 to 99% of reaction occurring via this channel. The fraction of reaction going via the fourth channel ($AlH_2Cl \rightarrow AlCl + H_2$) is small and only weakly dependent on temperature and pressure. It is in the range 1 to 2% at 1 atm total pressure, increasing slightly with temperature, and in the range 3 to 7% at 50 atm. Above 3000 K, the first channel ($AlH_2Cl \rightarrow AlHCl + H$) becomes important. Although it has a higher energetic barrier than the others, it proceeds via a loose transition state, and therefore, has a larger high-pressure pre-exponential factor. At sufficiently high temperatures, this effect is larger than the energetic effect. Our calculations predict that its contribution to the total reaction rate increases from about 0.2% at 3000 K to 40% at 4000 K, at 1 atm total pressure, and from 4% to 37% of the total in this same temperature range at 50 atm total pressure. Rate parameters for all 3 channels have been fit to the Troe form and are included in Table 5.

3.2.4. Decomposition of AlH_3

The decomposition of AlH_3 can proceed through the following channels:

$AlH_3 \rightarrow AlH_2 + H \quad \Delta H^o_{rxn}$ (298 K)

$= +86.1$ kcal mol^{-1}

$AlH_3 \rightarrow AlH + H_2 \quad \Delta H^o_{rxn}$ (298 K)

$= +28.6$ kcal mol^{-1}

Calculations using ChemRate [2] with the two above channels show that the energetically favored decomposition to AlH + H_2 dominates, and the decomposition to AlH_2 + H can be neglected. The computed rate parameters are given in Table 5.

3.2.5. Decomposition of AlHCl

The decomposition of AlHCl can proceed through the following channels:

$AlHCl \rightarrow AlH + Cl \quad \Delta H^o_{rxn}$ (298 K)

$= +82.0$ kcal mol^{-1}

$AlHCl \rightarrow AlCl + H \quad \Delta H^o_{rxn}$ (298 K)

$= +34.5$ kcal mol^{-1}

$AlHCl \rightarrow Al + HCl \quad \Delta H^o_{rxn}$ (298 K)

$= +52.0$ kcal mol^{-1}

As the reaction channel $AlHCl \rightarrow AlCl + H$ proceeds through a loose transition state and has the lowest enthalpy of reaction, this channel is expected to dominate. The parameters from a fit to temperature and pressure dependent rate constants computed using UNIMOL [1] are given in Table 5.

3.2.6. Decomposition of $AlCl_2$

The decomposition reaction of $AlCl_2$ can proceed through the following channels:

Table 6
Rate constants for reactions that have been studied experimentally. k units are $cm^3\ mol^{-1}\ s^{-1}$

Reaction	$k = A\ T^n \exp(-E/RT)$ (reference)
$H_2 + M \rightarrow H + H + M$	$k_0 = 2.23 \times 10^{14} \exp(-48350/T)$ [14]
$Cl_2 + M \rightarrow Cl + Cl + M$	$k_0 = 2.3 \times 10^{13} \exp(-23630/T)$ [18]
$HCl + M \rightarrow H + Cl + M$ M = 10 for HCl [22]	$k_0 = 9 \times 10^{13} \exp(-44000/T)$ [19]
$Cl_2 + H \rightarrow HCl + Cl$	$k = 3.31 \times 10^{14} \exp(-1460/T)$ [20]
$H_2 + Cl \rightarrow HCl + H$	$k = 2.88 \times 10^8\ T^{1.58} \exp(-1610/T)$ [21]
$Al + Cl_2 \rightarrow AlCl + Cl$	$k = 7.43 \times 10^9\ T^{1.5} \exp(+74/T)$ [experimental points from 12]
$AlCl + Cl_2 \rightarrow AlCl_2 + Cl$	$k = 1.97 \times 10^7\ T^2 \exp(+574/T)$ [experimental points from 12]

$$AlCl_2 \rightarrow AlCl + Cl \qquad \Delta H^o_{rxn}\ (298\ K)$$

$$= +67.9\ kcal\ mol^{-1}$$

$$AlCl_2 \rightarrow Al + Cl_2 \qquad \Delta H^o_{rxn}\ (298\ K)$$

$$= +130.6\ kcal\ mol^{-1}$$

For the same reasons cited above, the reaction channel $AlCl_2 \rightarrow AlCl + Cl$ is expected to dominate. The $k_\infty k_O$, and Fc computed using UNIMOL [1] are given in Table 5.

3.2.7. Decomposition of AlCl and AlH

These decompositions are bimolecular at all pressures. The termolecular recombination reactions $Al + Cl + M \rightarrow AlCl + M$ and $Al + H + M \rightarrow AlH + M$ have been computed using Variflex [3] and are included in Table 5.

4. Reaction mechanism

The mechanism proposed consists of 39 reversible reactions among 15 species. This mechanism is composed of the reactions described above (Tables 1–5) as well as some additional reactions for completeness such as $H_2 + Cl \rightarrow H + HCl$ and others given in Table 6. The Al_2, Al_2Cl_6, and Al_2H_6 chemistry has not been introduced in the kinetic model as the equilibrium calculations predicts that these species are present at very low levels at equilibrium and there is no obvious reason to expect them (or other $Al_2H_xCl_y$ species) to be important reaction intermediates.

5. Summary and conclusions

A gas-phase Al/HCl kinetic mechanism has been assembled using transition state theory and unimolecular rate theories applied to results of ab initio quantum chemical calculations of reaction energetics and transition state properties in this system. Appropriate and validated estimation procedures have been used to provide approximate rate parameters for the many barrierless reactions in this system that cannot be treated by conventional transition state theory.

The present results represent a first pass at assembling a detailed reaction mechanism and determining rate parameters for this system. As such, they are open to revision in future studies, and they suggest several directions for future work on combustion of aluminum particles with the by-products of solid propellant combustion: (1) further investigation of the present reactions using higher levels of theory, particularly for some of the chemically activated reactions, (2) further experimental studies of individual chemical reactions, (3) simplified combustion or shock-tube kinetics experiments against which the overall mechanism can be tested (some such experiments have been done, and others are planned at LCSR-CNRS), (4) extension of the present kinetic mechanism to include reactions with CO_2 and (5) addition of simplified surface chemistry for reactions on solid or liquid aluminum particles.

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