Experimental and Theoretical Kinetics for the Reaction of Al with O_2 at Temperatures between 23 and 295 K

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The first study of the kinetics of Al atoms with O_2 at low and ultralow temperatures is reported. Rate constants have been measured from 295 to 23 K using the pulsed laser photolysis−laser-induced fluorescence (PLP-LIF) technique in a CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme) apparatus. Rate constants were found to increase monotonically with decreasing temperature: $k(T) = (1.75 \pm 0.10) \times 10^{-10}(T/298)^{-0.25\pm0.02} \exp[(7.3 \pm 3.0)/T]$ cm^3 s^{-1}. The rate constant for the reaction Al with O_2 has also been calculated as a function of temperature using a theoretical approach based on the adiabatic capture centrifugal sudden approximation (ACCSA) method. These calculations were found to be in good agreement with experimental results and were able to explain the observed temperature dependence by the open-shell nature of the reactants. Possible astrophysical implications are also discussed concerning the chemistry of aluminum atoms in the interstellar medium.

Introduction

Interest in reactions involving metals in the gas phase began in the 1930s with the work of Polanyi[1] and Bawn,[2] who studied atomic diffusion in flames. The first quantitative approaches to kinetic studies of elementary homogeneous reactions of metal atoms, however, were only published in 1972 by Husain et al.[3] and Fontijn et al.[4]

More recently,[5] the chemistry of several metals such as Na, K, Li, or Mg has been studied because of its importance in the mesopause region of the earth's atmosphere. In this region (about 90 km altitude), where the temperature can vary from 140 to 230 K,[6] a thin layer of neutral metal atoms, principally originating from meteoritic ablation, has been observed.[7] In the interstellar medium, several metal atoms have been detected essentially (but not exclusively) in their ionic form.[8−11] With regard to aluminum, the Al^+ 167 nm line has been observed using the Copernicus satellite,[12] in several stellar environments, and some attempts were also made to detect the neutral species by searching for the 394.40 and 396.15 nm lines.[13] Only a few metal-containing species, however, such as AlF, AlCl, NaCl, or KCl have been observed and, then, only in C-rich circumstellar envelopes.[14]

Reactions involving metal atoms are also of great importance in the field of combustion chemistry.[15] As aluminum is used in liquid propellant slurries and in explosives, an extensive investigation of the kinetics and dynamics of aluminum atoms with several molecules such as O_2, CO_2, NO_2, alkenes, arenes, etc., has been carried out using a large number of techniques including reaction cells,[16−18] high-temperature reactors,[19] and molecular beam methods.[20,21] The reaction mechanisms of aluminum atoms, or transient molecules of Al, therefore, have been studied quite extensively.[15,18,22]

The kinetics and dynamics of the reaction of Al with O_2 have been investigated both theoretically[23−26] and experimentally.[19,21,26−28] There is, however, no detailed theoretical model for this reaction although several authors have studied the main features of the fundamental potential energy surface. Marshall[23] has performed some ab initio calculations and has demonstrated that there is no barrier in the reactants valley. He has shown that, under most laboratory and combustion conditions, the total removal of Al atoms is essentially due to the $Al + O_2 \rightarrow AlO + O$ channel, the stabilization of AlO_2 via a termolecular process $Al + O_2 + M$ being completely negligible. Marshall derived from this study an equation for the temperature dependence of the rate coefficient: $k(T) = 6.5 \times 10^{-11}T^{1/6}$ cm^3 s^{-1}. Garland, in the early 1990s,[19] using a high-temperature reactor, studied the dependence of the rate coefficient, $k(T)$, for temperatures in the range $T = 298-1083$ K. Fitting of the rate constants to the Arrhenius expression $k_0 \exp(-E_a/kT)$, yielded $k_0 = (1.27 \pm 0.12) \times 10^{-10}$ cm^3 s^{-1} and $E_a = -0.17 \pm 0.09$ kcal mol^{-1}. These results were found to be consistent with the mechanism of complex formation suggested by Fontijn and coworkers in 1977.[27] The variation of the thermal rate constant has also been calculated by Naulin and Costes[28] via an excitation function (i.e., the translational energy dependence of the reaction cross section for each combination of reactant internal states), derived from cross-section measurements using supersonic molecular beams.[21] They found an analytical expression for the rate coefficient in excellent agreement with measurements of Garland:[19] $k(T) = 0.66 \times 10^{-10}T^{0.2}/(1 + T/2100)^{1.7}$ cm^3 s^{-1} with $T \geq 295$ K.

The CRESU apparatus (Cinétique de Réaction en Ecoulement Supersonique Uniforme), at the Université de Rennes I, allows us to study reaction kinetics at temperatures as low as 13 K. In particular, since 1992, the apparatus has been used in conjunction with the PLP-LIF (pulsed laser photolysis−laser-induced fluorescence) technique for the production and detection of gas-phase radical species, and several different systems have been

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investigated, including reactions involving CN,[29,30] OH,[31,32] and CH[33−37] radicals. Up until now, 26 reactions have been studied, most of them showing an increase in the rate coefficient as the temperature decreases. This behavior was not generally predicted by existing theories at the time when these studies were performed at our laboratory and therefore stimulated further theoretical investigations of the kinetics of neutral−neutral reactions at very low temperatures. This interest was initiated by the work of Clary on radical reactions involving ionic[38] or neutral[39] species. More recently, the dependence of the reactivity of atom−diatom collisions on initial fine structure populations has been investigated theoretically for the $O(^3P) + OH(X^2P)$[40] and $C(^3P) + NO(X^2P)$[41] reactions. These studies demonstrated that the influence of the open-shell nature of the reactants on the kinetics of these reactions could be very important at low temperature.

As shown above, a slight increase in the rate coefficient for $Al + O_2 \rightarrow AlO + O$ with decreasing temperature has been found in previous studies.[19,21] This may suggest that high rate coefficients could be obtained at very low temperatures (i.e., much lower than room temperature). This reaction was chosen, therefore, as a suitable candidate for the first experimental study of the kinetics of a reaction between an atom and a stable radical at very low temperatures. The CRESU apparatus will be described briefly in the following section. Experimental results, obtained in the temperature range 23−295 K, will then be presented and compared to previous studies. Using an extension of our previous theoretical approach concerning the $C(^3P) + NO(X^2P)$ reaction,[41] based on the ACCSA[42−44] (adiabatic centrifugal capture sudden approximation) method, the rate coefficient for the reaction between Al and O_2 has been calculated as a function of temperature and compared to our experimental data. Finally, we will discuss the possible implications of our data to the modeling of the chemistry of metallic species in interstellar clouds where the temperature can be as low as 10 K.

Experimental Section

The CRESU technique and its adaptation to the study of neutral−neutral reactions via the PLP-LIF technique has been described in detail elsewhere.[30] Only a short description will be given here, drawing attention to those aspects of the experiments that relate to measurements of the reaction involving Al atoms. A diagram of the experimental apparatus is given in ref 30.

In the CRESU technique, low temperatures are achieved via the isentropic expansion of a buffer gas through a Laval nozzle. Each nozzle employed provides an axially and radially uniform supersonic flow at a particular temperature, density, and velocity for a given buffer gas. The relatively high density of the supersonic flow (10^{16}−10^{17} cm^{-3}) ensures frequent collisions, thus maintaining thermal equilibrium. All these properties are conserved in the core of the supersonic flow over a typical distance of a few tens of centimeters along the flow. The Laval nozzle is mounted on a reservoir into which both the buffer gas and the reagent gases were injected.

Different techniques such as laser vaporization of an aluminum rod,[21,26] photolysis of trimethylaluminum (TMA),[16,19] or photolysis of triethylaluminum (TEAL)[15] have been used previously to produce Al atoms. In this work, TMA ($Al(CH_3)_3$) was chosen as the aluminum atom precursor. A 100 g aliquot of liquid TMA (Aldrich, 97%), having a vapor pressure of 12 Torr at 25 °C, was mixed with helium gas in a 30 L stainless steel cylinder at a pressure of 2 bar. Before filling, the container was carefully pumped to about 10^{-6} Torr because of the high flammability of TMA and its tendency to explode on contact with water. The He−TMA vapor mixture was injected into the reservoir by means of a rigid stainless steel pipe and a flexible PTFE tube. The flow was regulated using a micrometric stainless steel valve. The time necessary to carry out a measurement was short enough to ensure that a constant He−TMA pressure was maintained in the cylinder. The concentration of TMA was therefore kept constant.

The Al−C bond dissociation energy in $Al-CH_3$ has been evaluated at ca. 271 kJ mol^{-1} (441 nm) by Mitchell and coworkers.[17] A frequency-quadrupled, Nd:YAG laser (GCR 190, Spectra Physics) with a typical pulse energy of 75 mJ at 266 nm was used to generate Al atoms in the $^2P_{1/2}$ and $^2P_{3/2}$ doublet ground state by UV multiphoton photolysis. Al atoms were then excited and detected by resonance LIF, using the 394.40 nm ($^2S_{1/2}-^2P_{1/2}$) and 396.15 nm ($^2S_{1/2}-^2P_{3/2}$) lines. Probe laser radiation was provided by a MOPO 730 laser (Spectra Physics) pumped by frequency-tripled radiation from a Nd:YAG laser (Spectra Physics, GCR 230) and then frequency-doubled by means of the MOPO internal FDO (frequency-doubling option) device. To reduce scattered light in the CRESU chamber, the pulse energy was reduced to a few tens of microjoules, using a neutral density filter.

The photolysis and probe laser beams were slightly focused by means of quartz lenses (4 and 2 m focal length, respectively) and combined on a dichroic mirror. The beams were directed along the axis of the supersonic flow, entering the CRESU apparatus through a Brewster window, passing through another such window mounted on the back of the reservoir, and copropagating out through the throat of the Laval nozzle and along the axis of the flow, before leaving the vacuum chamber via a third Brewster window. Laser-induced fluorescent light was collected at a known distance downstream of the Laval nozzle (usually 10−30 cm) using a UV-enhanced, optically fast telescope−mirror combination mounted inside the main vacuum chamber, focused through a slit, and directed onto the photocathode of a UV-sensitive photomultiplier tube (Thorn EMI 9235 QB) after passing through a narrow band filter centered at 400 nm (BW 40 nm, Optosigma) to reduce the scattered light from the photolysis laser. The signals were accumulated, processed, and analyzed as described previously elsewhere.[30] Figure 1 shows typical Al LIF excitation spectra at different temperatures. The two lines of the ground state of Al are shown, and the $^2S_{1/2}-^2P_{1/2}$ line used for kinetics experiments is indicated by an arrow. For certain lower density nozzles, a significant rise time was observed for the Al LIF signal (see Figure 2). This was due to the collisional spin−orbit relaxation of $Al(^2P_{3/2})$ to the $Al(^2P_{1/2})$ state. This process has also been studied and will be the subject of a future publication. To avoid contamination of the data, the nonlinear least-squares fits of the exponential decays of the Al LIF signal were started after the rise was complete (see Figure 2). This point in time was determined by taking a scan of the Al LIF signal vs time with no O_2 present. As usual, the LIF scans were then taken at different O_2 concentrations in order to construct a kinetic plot (see Figure 3), from which the second-order rate coefficient at a particular temperature could be deduced. A chemiluminescence phenomenon was observed for high concentrations of O_2. This chemiluminescence is known[45] to come from the production of electronically excited AlO molecules and therefore constrained the usable reactant flow densities to low values (see Table 1).

The flows of O_2 (from Air Liquide, 99.998%) and carrier gas (Ar, He; Air Liquide, 99,995%) were taken directly from cylinders and regulated by means of Tylan mass flow controllers. Knowledge of the total gas density along the flow, obtained from impact pressure measurements using a Pitot tube,[30] and of the individual gas flow rates allowed the O_2 concentration

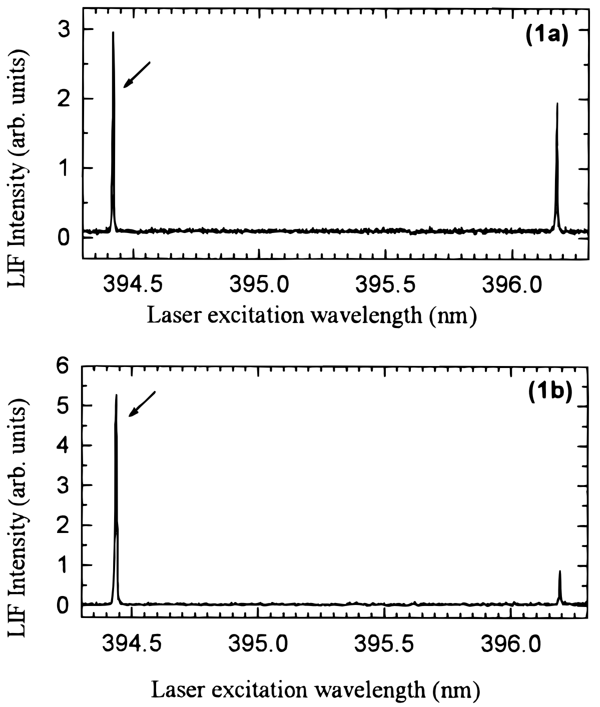

Figure 1. LIF spectra of the $^2S_{1/2}-^2P_{1/2}$ and $^2S_{1/2}-^2P_{3/2}$ transitions of aluminum recorded in the CRESU apparatus at two different temperatures: (1a) 141 and (1b) 52 K. In both cases, the delay times between the photolysis and probe laser pulses were made sufficiently long (50 μs) to allow total spin–orbit relaxation.

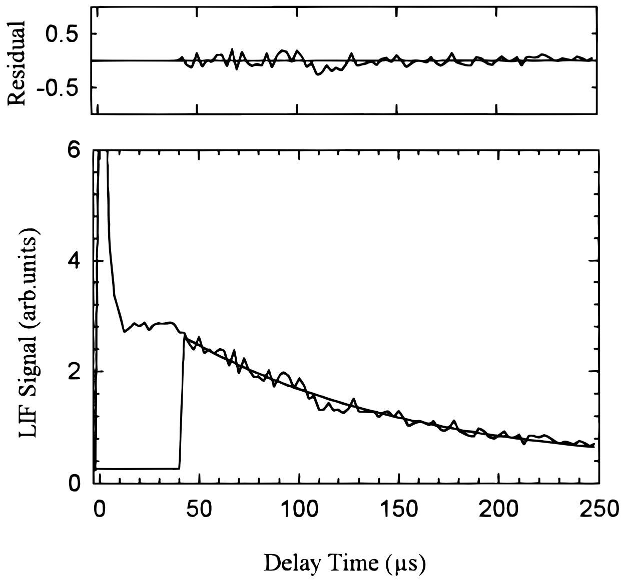

Figure 2. First-order decay of the LIF signal from Al($^2P_{1/2}$) in the presence of 1.5×10^{13} molecules cm^{-3} O_2 at 52 K in Ar, fitted to a single-exponential decay, with residual shown above. The abscissa corresponds to the delay time between the photolysis and probe laser pulses.

in the supersonic flow (necessary for the kinetic measurements) to be calculated.

Results and Discussion

Rate coefficients for the reaction of Al with O_2 measured in the CRESU apparatus over the range $T = 23-295$ K are shown in Table 1. Only statistical errors are quoted. Contributions from potential sources of systematic errors, such as the calibration of flow controllers and inaccuracies in the determination of the total gas density and temperature, are not included. Every effort was made to minimize these, and we estimated that the additional error does not exceed 10% and is likely to be much less.

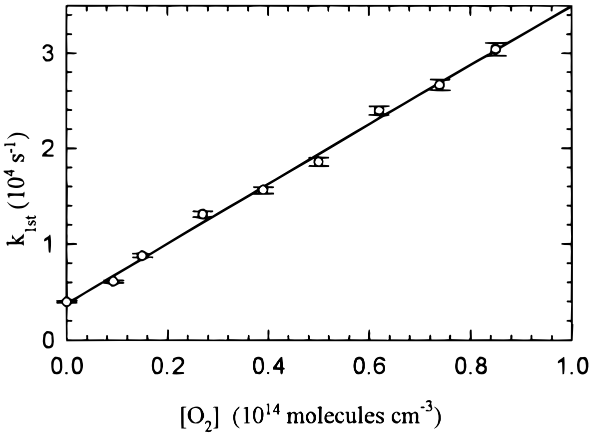

Figure 3. First-order decay constants for Al($^2P_{1/2}$) at 52 K in Ar plotted against the concentration of O_2.

Figure 4 shows our results, together with Garland's measurements,[19] determined using a high-temperature reactor ($T = 298-1083$ K) and the analytical expression calculated from cross-section measurements for high temperatures ($k = 0.66 \times 10^{-10}\ T^{0.2}/(1 + T/2100)^{1.7}$) by Naulin and Costes.[28]

Garland's results are in very good agreement with the rate coefficient obtained using the CRESU apparatus at room temperature. Measurements at 295 K can be made with any nozzle by increasing the pressure in the main chamber, causing a shock front to form, thus ensuring the recovery of the original reservoir temperature (295 K) within the subsequent flow. In the experiment of Garland, the room-temperature rate coefficient was measured for pressures ranging from 10 to 100 Torr, and these results show no pressure dependence. This was also verified by us at 52 K for two nozzles working at 0.29 and 0.58 Torr, respectively. Our results, furthermore, indicated no buffer gas (He or Ar) dependence at ca. 50 K, as shown in Table 1. The rate coefficient, $k(T)$, is found to increase monotonically as the temperature is lowered from 295 to 23 K.

Our results can be well fitted by an expression of the form

$$k(T) = A(T/298)^n \exp(-\theta/T) \quad \mathrm{cm^3\,s^{-1}} \tag{1}$$

with $A = (1.75 \pm 0.10) \times 10^{-10}$ cm^3 s^{-1}, $n = -0.25 \pm 0.02$, and $\theta = -7.3 \pm 3.0$ K.

It should be pointed out that they can also be fitted using a simple power law of the form

$$k(T) = A(T/298)^n \quad \mathrm{cm^3\,s^{-1}} \tag{2}$$

with $A = (1.72 \pm 0.13) \times 10^{-10}$ cm^3 s^{-1} and $n = -0.36 \pm 0.05$.

Such an expression, however, does not fit to Garland's results correctly, whereas eq 1 leads to an accurate fit to both experiments from 23 to ca.1100 K as shown in Figure 4. The analytical expression calculated from cross sections by Naulin and Costes[28] for high temperatures, on the other hand, does not fit to our results under room temperature although it matches Garland's results very closely (see Figure 4). This clearly shows the danger of extrapolating such equations beyond experimental domains, and therefore we advise the use of eq 1 only in the temperature range 23–1100 K.

The kinetics of the reaction was also theoretically studied using adiabatic capture theory.[46] In previous theoretical studies of O + OH[40] and C + NO[41] reactions, this method was demonstrated to give good agreement between theory and experiment when the open-shell nature of the reactants is taken

TABLE 1: Rate Coefficients Obtained in the CRESU Apparatus for the Reaction of Al Atoms with O_2 at Temperatures between 23 and 295 K

T (K)	carrier gas	no. of expts	total gas density (10^{16} molecules cm^{-3})	[O_2] range (10^{14} molecules cm^{-3})	k^a (10^{-10} cm^3 molecule^{-1} s^{-1})
23	He	6	4.73	0.05−0.26	4.63 ± 0.39
44.5	Ar	11	2.92	0.07−0.58	3.33 ± 0.22
49.1	He	8	10.4	0.17−0.91	3.24 ± 0.20
52.3	Ar	9	10.3	0.09−0.85	3.11 ± 0.14
97.4	Ar	11	15.5	0.28−2.45	2.56 ± 0.07
141	Ar	11	6.95	0.38−3.35	2.22 ± 0.32
295	Ar	7	29.7	0.88−4.27	1.79 ± 0.16

[a] Errors quoted are $\pm t\sigma$ statistical error where t is the appropriate value of the Student's t-distribution for the 95% point.

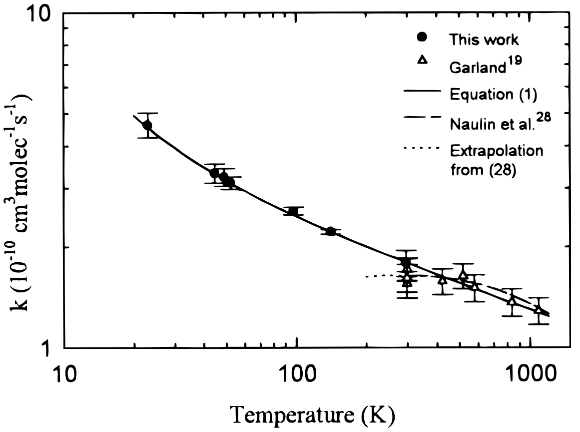

Figure 4. Rate coefficient for the reaction of aluminum atoms with O_2 as a function of temperature, displayed on a log−log scale. The filled circles represent the results obtained in the CRESU experiment. Results from Garland[19] and Naulin and Costes[28] are also shown as well as an extrapolation to temperatures lower than 295 K of the latter results (dotted line). CRESU results are fitted using the following formula: $k(T) = 1.75 \times 10^{-10}(T/298)^{-0.25} \exp(7.3/T)$ cm^3 molecule^{-1} s^{-1} (solid line).

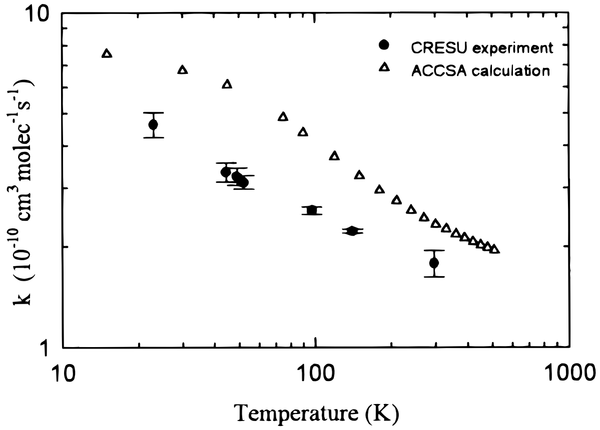

Figure 5. Rate coefficient for the reaction of aluminum atoms with O_2 as a function of temperature, displayed on a log−log scale. The filled circles show the results obtained with the CRESU apparatus whereas the open triangles represent our ACCSA calculation.

into account. The large rate coefficient values obtained in the present study suggest, moreover, that there is no barrier along the reaction path. The kinetics of this reaction is then expected to be determined by the long-range part of the interaction potential. We have used the adiabatic capture centrifugal sudden approximation (ACCSA[42−44]) method and a long-range potential made up of the sum of the quadrupole−quadrupole, dispersion, and spin−orbit (for the Al atom) contributions:

$$V = \frac{\Theta}{24R^5}\Big[36(3\cos^2(\gamma) - 1)\hat{Q}_2^0 - 24\sin(\gamma)\cos(\gamma)(\hat{Q}_2^1 + \hat{Q}_2^{-1}) + \frac{3}{2}\sin^2(\gamma)(\hat{Q}_2^2 + \hat{Q}_2^{-2})\Big] - \frac{3E^*(\mathrm{Al})\,E^*(\mathrm{O_2})}{2[E^*(\mathrm{Al}) + E^*(\mathrm{O_2})]R^6}\,\hat{\alpha}(\mathrm{Al})\Big[\alpha(\mathrm{O_2}) + \frac{1}{3}[\alpha_{\parallel}(\mathrm{O_2}) - \alpha_{\perp}(\mathrm{O_2})]\frac{3\cos^2(\gamma) - 1}{2}\Big] + A\vec{L}\cdot\vec{S}$$

where Θ, $\alpha(O_2)$, and $E^*(O_2)$ are respectively the quadrupole moment, the polarizability, and the ionization potential of the O_2 molecule. The matrix elements of this potential were calculated in the spin−orbit basis set of the Al atom, and the corresponding matrix was diagonalized. The lowest root was used to calculate the coupling between the rotational states of the diatomic molecule and then to obtain the rotationally adiabatic potential curves. The thermal fine structure distribution is taken into account by multiplying the calculated ACCSA rate constant $k_0^{\mathrm{ACCSA}}(T)$ by the probability of initiating the reaction on this single surface: $k^{\mathrm{ACCSA}}(T) = \rho(T)k_0^{\mathrm{ACCSA}}(T)$, with

$$\rho(T) = \frac{2}{2 + 4\exp(-161.2/T)}$$

where the numerator is the degeneracy of the reaction surface which is equal to the degeneracy of the AlO_2 complex[47] and the denominator is the partition function of Al. As can be seen in Figure 5, the rate constants, calculated with this approach, agree quite well with experiment insofar as the temperature dependence is concerned. The calculated values of the rate coefficient, however, are larger than the corresponding experimental measurements since adiabatic capture calculations give an upper limit to the reaction rate constant. The London formula, furthermore, used to model the dispersion potential, is too attractive for intermediate-range intermolecular distances and leads to an overestimate of the calculated value for the rate constant. Finally, since the main contribution to the interaction potential is a quadrupole−quadrupole potential, a simple approach neglecting the open-shell nature of the reactant would give a flat rate coefficient as a function of temperature. The agreement between the present theoretical approach and experiment demonstrates that the temperature dependence of this reaction is indeed due to the open-shell nature of the reactants.

In interstellar cloud models, metals were traditionally included because they are expected to be the main carriers of the positive charge of the cloud due to their low ionization potential.[48] The electron abundance which is of central importance in ion−molecule models is then largely dependent on the metal abundance. Although cosmic abundances of metals are generally high,[49] UV observations of diffuse clouds show that the gas-phase abundance of metals is far below cosmic abundance.[50,51] The depletion is typically 2 orders of magnitude, and it is likely that these depletions are even larger in cold dense clouds ($T \sim 10$ K, $n \sim 10^4$ cm^{-3}).[50,52] Cloud modelers, therefore, generally emphasize only the most abundant metals. In typical dense cloud models,[53,54] only Fe, Mg, and Na are included as metal species. Their chemistry, furthermore, is essentially limited to charge-transfer reactions.

For aluminum, UV diffuse cloud observations show that it is more depleted than Fe, Na, and Mg. The standard explanation for this larger depletion is that aluminum condenses onto grains in circumstellar envelopes ($T > 1000$ K) and therefore is almost completely removed from the gas. Al_2O_3, for example, would act as the condensation nuclei around which silicates could form as the gas cools, and unless there is some mechanism to destroy the grains completely, it is impossible to return any Al to the gas. Furthermore, in colder environments (cold diffuse clouds and cold dense clouds), photodesorption is less efficient than accretion onto grains,[50] and a mantle of refractory ices or organic material is expected to cover their cores. In these mantles, some Al is also supposed to be trapped mainly in the form of $Al(OH)_3$.[50] In the so-called "hot core regions" ($T = 100-200$ K, $n \sim 10^7$ cm^{-3}), however, these mantles desorb efficiently, and the released $Al(OH)_3$ is quickly dissociated into primary components Al, Al^+, and possibly AlO^+ via ion−molecule reactions.[50] Although no aluminum-bearing molecules have been detected in such regions, some upper limits for the abundance of AlO have been determined.[50,55] Turner has proposed a path for the production of AlO in hot cores. This involved radiative association of Al^+ with H_2 followed by dissociative recombination of AlH_2^+ and the reaction $AlH + O \rightarrow AlO + H$. Our experiment clearly provides a straight path for AlO formation, and therefore our results could then be included in hot core chemical models as a source of AlO.

As previously stressed, the chemistry of metal species is not well developed in interstellar cloud models. More particularly, neutral−neutral reactions are generally not taken into account. Although aluminum does not seem to be an important element in astrochemistry, our results suggest that reactions between metal atoms and neutrals could be very fast. In interstellar cloud models, metal atoms are supposed to be ionized by charge-transfer processes, but this work, shows, however, that small metal-bearing radicals can also be produced very efficiently, suggesting that a more complex chemistry could then be initiated by such diatomic radicals. Metal chemistry at very low temperature has presently been poorly studied. This field, and particularly neutral reactions, requires much more work, especially on reactions involving Fe, Mg, or Na which are the only metal species included in cold dense interstellar cloud models.

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