between this mode and combinations/overtones closely located in frequency to this mode. If there is any strong coupling between the mode under study and a mode closely located in frequency to the former, the dephasing is greatly accelerated. An example of such a case has been found for the two C=N stretchings in dinitriles.

It has been confirmed that the hydrogen bonding with extrinsic molecules (solvent) is an intermolecular factor causing the dephasing of the C=N stretching. However, it is not possible to estimate, from the available data, intermolecular contributions other than that due to the hydrogen bonding of *extrinsic* origin. Nevertheless, intrinsic intermolecular interactions, which are thought to be strong in polar liquids like neat nitriles, seem to play a basic role in determining the dephasing time constant. A careful study of concentration dependence of the dephasing time constant in nonpolar solvents would be necessary to quantify the effect of intrinsic intermolecular interactions.

Finally, we give brief consideration to the S/N (signal-to-noise) ratio of the present experiment. As mentioned in the Introduction, the S/N ratio of the correlation function obtained from the time-domain experiment is expected to be better than that obtained from the frequency-domain experiment, particularly in the lowintensity or long-delay time (i.e., $t > T_2$) region. In the present experiment, the dynamic range of the observed CARS signal intensity is approximately 10^{3} - 10^{4} , which is comparable to that of the correlation function obtained by Fourier-transforming the frequency-domain data. In this sense, the S/N advantage of the time-domain measurement has not been fully realized in the present study. However, the dynamic range of the time-resolved CARS method can reach as wide as 10⁷-10⁸, according to a recent report on subpicosecond time-resolved CARS by Fickenscher et al.³⁸ This suggests that the S/N advantage of the time-domain measurement will be achieved with developments of the light source (higher peak power and higher stability) and/or improvements in the detection sensitivity.

Registry No. CH₃CN, 75-05-8; C₂H₅CN, 107-12-0; C₃H₇CN, 109-74-0; C4H9CN, 110-59-8; C5H11CN, 628-73-9; CH3CH(CH3)CN, 78-82-0; C₂H₄CH(CH₄)CN, 18936-17-9; CH₃CH(CH₄)C₂H₄CN, 542-54-1; (CH₃)₃CCN, 630-18-2; NCCH₂CN, 109-77-3; NCC₂H₄CN, 110-61-2; NCC₃H₆CN, 544-13-8; NCC₄H₈CN, 111-69-3; NCC₅H₁₀CN, 646-20-8; NCC₆H₁₂CN, 629-40-3.

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Pressure and Temperature Dependence of the Kinetics of the Reaction AI + CO₂

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We measured the pressure and temperature dependence of the rate constants of the reaction of $Al + CO_2$ between 10 and 600 Torr total pressure and 298 and 1215 K in our high-temperature reactor. The Al atoms were generated by the 248-nm photolysis of AI(CH₃)₃ and probed by laser-induced fluorescence. Below 700 K, the rate constants show a strong pressure dependence suggesting that the reaction is proceeding through a complex formation mechanism with some decomposition of the complex to the products AlO and CO. Above 700 K, the observed rate constants are pressure independent, indicating that a direct abstraction channel becomes dominant. An Arrhenius fit to the rate constants measured in this high-temperature regime results in a preexponential factor of $(2.9 \pm 0.7) \times 10^{-10}$ cm³ s⁻¹ and an activation energy of 6.4 ± 0.4 kcal mol⁻¹.

Introduction

Aluminum is a standard component in many solid propellants and explosives. It is an attractive solid fuel because of its high heat of combustion and because alternatives such as boron are difficult to burn efficiently and fuels such as beryllium are highly toxic.¹ A typical solid propellant contains 4-20% aluminum powder and 70-80% ammonium perchlorate oxidizer, and the remainder is a binder.¹ Modeling of the combustion of such mixtures is difficult because there is a limited amount of kinetic

⁽¹⁾ Oxtoby, D. W. Adv. Chem. Phys. 1979, 40, 1.

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data on aluminum species such as Al^{2-7} AlCl,⁸ AlH,⁹ and AlO.¹⁰⁻¹² As a part of our program to study the oxidation chemistry of Al and Al oxides, we have examined the kinetics of the reaction of Al with CO₂:

$$Al + CO_2 \rightarrow AlO + CO \qquad \Delta H_r = 4.8 \text{ kcal mol}^{-1}$$
 (1)

Two previous experimental studies of the kinetics of reaction 1 have been reported. In the first study, Fontijn and Felder² generated Al atoms by evaporation from an Al-wetted tungsten wire in a fast flow reactor; the atoms were detected by resonance absorption or fluorescence. The rate constant was reported to be pressure-independent between 3 and 20 Torr total pressure and to display distinct non-Arrhenius behavior between 300 and 1900 K. In a more recent study, Parnis, Mitchell, and Hackett⁵ examined the pressure dependence of the rate constant of reaction 1 at room temperature under static conditions. Al atoms were generated by 440-nm multiphoton dissociation of trimethylaluminum (TMA) and were detected by laser-induced fluorescence (LIF). In contrast to the earlier study of Fontijn and Felder, Parnis et al. found that the rate constant increases with increasing total pressure, and they proposed the following mechanism:

$$Al + CO_2 \stackrel{k_t}{\underset{k_r}{\leftarrow}} AlCO_2^* \stackrel{k_t[M]}{\longrightarrow} AlCO_2$$
$$\stackrel{k_p}{\longrightarrow} AlO + CO$$

Al and CO₂ react to form an energized complex AlCO₂^{*} with rate constant $k_{\rm f}$. This complex can be stabilized by collisions $(k_{\rm s}[M])$, or else it can decompose either back to reactants $(k_{\rm r})$ or on to products $(k_{\rm p})$. The observed rate constant is then equal to the product of the rate of complex formation and the fraction of complexes which do not decompose back to reactants:

$$k_{\rm obs} = k_{\rm f} \frac{k_{\rm p} + k_{\rm s}[{\rm M}]}{k_{\rm r} + k_{\rm p} + k_{\rm s}[{\rm M}]} \tag{2}$$

As support for this mechanism, Parnis et al.⁵ found that the yield of the product AlO, also monitored by LIF, decreased as the total pressure increased.

Additional information about the reaction of $Al + CO_2$ is provided by the molecular beam studies of Costes, Naulin, Dorthe, Vaucamps, and Nouchi,¹³ the matrix isolation studies of Le Quéré, Xu, and Manceron,¹⁴ and the chemiluminescence studies of Gole and co-workers.^{15,16} Costes et al. crossed pulsed supersonic beams of Al atoms and CO₂ and probed the AlO products by laser-induced fluorescence. The aluminum atoms were generated by laser vaporization of the solid metal. The reactive cross section was found to increase with increasing collision energy, consistent with an endothermic reaction. The excitation function shows evidence of a second threshold at ~ 0.5 eV; two possible explanations for this second threshold were proposed. First, the difference in energy between the first and second threshold corresponds approximately to the energy of a vibrational quantum of the CO product so that the increase in the reactive cross section may correspond to the opening up of a new product channel. Alternatively, the reaction may exhibit a change in mechanism (end-on approach of the Al to the CO_2 vs a perpendicular approach) at energies above 0.5 eV. A statistical distribution of vibrational and rotational energy in the AlO product was found near the energetic threshold for AlO production, suggesting formation of an intermediate complex. The reaction endoergicity, derived from excitation scans near threshold, of 0.19 \pm 0.03 eV (4.4 kcal mol⁻¹) is in excellent agreement with the endothermicity of the reaction of 4.8 kcal mol⁻¹ calculated using heats of formation from the JANAF tables.¹⁷

Le Quéré et al.¹⁴ measured infrared spectra of argon matrices in which Al and CO₂ were codeposited. The spectra showed evidence of two geometric isomers of an AlCO₂ complex. One isomer, probably a planar ring, has C_{2v} symmetry; the other isomer has inequivalent AlO bonds and either C_s or C_1 symmetry. Oblath and Gole¹⁵ did not observe any electronically excited AlO product when they reacted Al + CO₂. McQuaid, Woodward, and Gole¹⁶ studied the oxidation reactions of Al(CO)_x and AlCO₂ by monitoring AlO chemiluminescence; indirect spectroscopic evidence of an AlCO₂ association complex was found.

Two calculations of the reaction path energetics of reaction 1 have been reported recently. Sakai¹⁸ calculated geometries at the Hartree-Fock level using UHF wave functions and energetics using MP2, MP3, and MP4 perturbation theory. He finds that the initial interaction involves the formation of a trans-AlOCO complex with a barrier of 2.3 kcal mol⁻¹ which rapidly isomerizes to a symmetrical, C_{2v} structure. He calculates that dissociation of this complex to AlO + CO products proceeds over a large barrier (17.8 kcal mol⁻¹ barrier for the reverse reaction) and thus does not occur at low temperatures. This is in contrast to the experimental observation of AlO at room temperature by Parnis et al.⁵ A similar calculation has been performed by Marshall, O'Conner, Chan, Kristof, and Goddard.¹⁹ The geometries and vibrational frequencies of intermediate and product species were calculated at the unrestricted Hartree-Fock and many-body perturbation level of theory, and these results were combined with the quantum RRK model to predict rate constants. The authors predict that the Al approaches an oxygen atom of the CO_2 from the side and forms a trans-AlCO₂ complex with a 5.5 kJ mol⁻¹ (1.3 kcal mol⁻¹) barrier. They calculate a large barrier to dissociation of $C_{2\nu}$ AlCO₂ to AlO + CO (432 kJ mol⁻¹) and a lower barrier to dissociation of trans-AlCO₂ which they further reduce from 89 to 57 kJ mol⁻¹ to more closely match experiment.

In a very recent study, Selmani and Ouhlal²⁰ report a local spin density functional method calculation of the energetics and vibrational spectra of several bound AlCO₂ complexes. They find that the lowest energy complex (bound by 19.5 kcal mol⁻¹) involves the Al bonded to the carbon of CO₂ with one of the oxygens forming a bridge between them. The next lowest structure (~1.5 kcal mol⁻¹ higher) is the symmetrical, C_{2v} structure.

We report here a study of the pressure and temperature dependence of the rate constant of reaction 1 undertaken in order to resolve the discrepancies in the literature and attempt to clarify the mechanism of this reaction. In most experiments, we measured the rate of the reaction by monitoring the disappearance of the Al atoms; however, in some cases we measured the production and subsequent decay of the product AlO.

Experimental Section

The kinetics experiments are conducted using laser pumpand-probe techniques. Most experiments were carried out in a high-temperature reactor which has been described in detail previously.²¹ Briefly, the high-temperature reactor is a stainless steel vacuum chamber; inside the vacuum chamber lies a mullite reaction tube surrounded by silicon carbide rods which are resistively heated. The photolytic precursor TMA, the CO₂ reactant, and the buffer gas slowly flow through the reactor. A small flow of buffer gas is directed over the windows to prevent deposition of photolysis products.

Since the power supplied to the heating rods is constant, the gas temperature in the reactor depends on the total gas flow rate, the total pressure in the system, and molecular properties such as the heat capacity of the buffer gas. It is difficult to maintain the same temperature in the reactor to better than ± 20 K as the total pressure varies from 10 to 600 Torr. For one set of experiments in which the pressure dependence of the rate constant is determined at 483 K, a stainless steel cell contained in a Blue-M convection oven is used.²² Temperatures are constant to ± 1 K in this arrangement.

Species Generation and Detection. The TMA is photolyzed with the unfocused output of an excimer laser (Lambda Physik 201MSC) operating at 248 nm. The Al atoms are monitored by resonance laser-induced fluorescence (LIF) via the ${}^{2}S_{1/2}-{}^{2}P_{1/2}$ transition near 394.4 nm using the output of an excimer-pumped dye laser (Lambda Physik EMG102/FL2002). The photolysis and probe laser beams collinearly counterpropagate through the reactor. Fluorescence is collected perpendicular to the path of the laser beams and focused onto a filtered photomultiplier tube (PMT). A narrow-band filter (Corion SS-4000-2) and an acetone filter are used in the Al experiments while a Corion P10-490-S



Figure 1. Plot of the observed Al ${}^{2}S_{1/2} {}^{-2}P_{1/2}$ LIF intensity as a function of time in the presence of 315 mTorr of CO₂ at 1215 K. The points are the measured intensities, and the solid line is the result of a linear least-squares fit to the log of the data.

filter is used for AlO. The output from the PMT is directed to a gated integrator and computer for data analysis and storage.

Kinetic Measurements. Al atom disappearance rates are obtained by monitoring the Al LIF signal at increasing probe laser delays following photolysis of TMA. A minimum delay of $2-5 \mu s$ is used to allow any electronically excited photoproducts to decay and to allow for thermalization of the Al atoms. All experiments are carried out under pseudo-first-order conditions. With no CO₂ present, the Al signal decays due to reaction with the precursor and/or photoproducts and to diffusion out of the viewing region. In several experiments, we obtained rate constants by monitoring the temporal profile of the AlO LIF signal.

Temperature Measurement. For the kinetics experiments in the high-temperature reactor, we use rotational temperatures obtained from LIF spectra of the AlO radical. We excite transitions in the R₁ branch of the $B^2\Sigma^+-X^2\Sigma^+$ (1,0) band near 466 nm and detect fluorescence in the (1,1) band. The rotational assignments are derived using constants of Coxon and Naxakis,²³ the line strengths are calculated using formulas for ${}^2\Sigma^-{}^2\Sigma$ transitions.²⁴ We record excitation spectra at various probe delays (10-100 μ s) and probe laser energies (2-45 μ J/pulse). These spectra yield the same rotational temperatures within experimental error, ensuring that we are probing thermalized AlO radicals and that we are not optically saturating the transitions.

For experiments carried out in the convection oven, we monitor temperature by two separate techniques. We use a copperconstantan thermocouple maintained in thermal contact with the cell wall for direct temperature measurement. For comparison with our higher temperature experiments, we also measure the rotational temperature using AlO excitation spectra. The temperatures derived from these two techniques agree within experimental error.

Gases. The gases flow through calibrated mass flow meters or controllers, are mixed, and then flow through copper tubing to the reactor. It is necessary to flow TMA through the system for about 30 min to passivate the walls of the flow system and the reactor. For the experiments in the convection oven, the pressure gauge is external to the oven and connected to the cell via 1/2-in. tubing. Care was taken to ensure that no pressure drop was introduced by placing the gauge outside of the oven.

Typical flow rates are 30 sccm of 0.1% TMA in argon buffer gas mixture, 15-25 sccm of buffer gas flowed over the windows, 100-10000 sccm of main buffer gas (Ar or N₂), and 0-500 sccm of CO₂. Ar (Air Products 99.995%), CO₂ (Matheson, 99.99%), and N₂ (Air Products, 99.998%) are used as received. Trimethylaluminum (Texas Alkyls) is subjected to several freezepump-thaw cycles before precursor/buffer gas mixtures are prepared.



Figure 2. Plot of the pseudo-first-order disappearance rate constants for Al as a function of CO_2 pressure at 1106 K and 20 Torr total pressure. The symbols are measured decays, and the solid line is the result of a linear least-squares fit to the measurements.

Results and Discussion

Kinetics Measurements. The bimolecular rate constants are obtained from pseudo-first-order plots of the Al disappearance rate vs reactant CO_2 pressure. A typical Al decay recorded in the presence of 0.315 Torr of CO_2 and at 1215 K is illustrated in Figure 1. As can be seen, the observed temporal profile is well represented by a single-exponential decay over several reaction lifetimes. Some preliminary experiments were carried out using 193-nm photolysis of TMA, but the Al decays were not single exponential. With 248-nm photolysis light and no focusing lens, the Al decays were single exponential except near 600 K at pressures above 100 Torr. These non-single-exponential decays could be the result of an equilibrium between reactant Al and intermediate complex AlCO₂ similar to behavior observed in the association reactions of Al with alkenes, arenes, and ethers.^{11,12} This anomalous behavior was not further explored.

An example of the first-order plot at 20 Torr total pressure and at 1106 K is found in Figure 2. Photolysis of TMA generates aluminum in the ${}^{2}P_{1/2}$ and ${}^{2}P_{3/2}$ states. Excitation spectra of the Al atoms taken at $1-\mu$ s delay and 20 Torr show that the populations of these spin-orbit states are equilibrated as the rate of spin-orbit-changing collisions is rapid.⁵ Separate kinetics experiments probing each fine-structure state were carried out at 100 Torr total pressure and at 483 K; the rate constants are the same within experimental error. At 483 K and at a total pressure of 42 Torr, we measured the rate constant of the reaction at two different total flow rates (300 and 900 sccm). The rate constants were the same within experimental error, showing no dependence of the rate constant on the total flow rate.

Measurements near Room Temperature. Near room temperature, the observed rate constant for reaction 1 is pressure dependent. We measured the pressure dependence of the rate constant at 298, 365, 398, and 483 K, and the results are listed in Table I. The kinetics measurements at 483 K were carried out in the convection oven. At room temperature and at a total pressure of 100 Torr, we measured the rate constant for reaction 1 by monitoring the disappearance of Al and, in a separate experiment, the appearance of AlO. The rate constants agree within experimental error, showing that AlO is a product of this reaction. The data at 298 and 365 K are plotted in Figure 3. At each temperature, we fit the data to the expression given by eq 2 after correcting the observed rate constants for the small contribution of the direct abstraction channel discussed in the next section. (The largest correction is to the lowest pressure measurement at the highest temperature and corresponds to 16% of the measured value.) The only rate constant we can determine absolutely is that of complex formation; we can obtain only relative values of the other rate constants. The fitted complex formation rate constants are listed in Table II and shown as an Arrhenius plot in Figure 4; we determine a preexponential factor of (5.6 ± 1.3) $\times 10^{-12}$ cm³ s⁻¹ and an activation energy of 0.48 ± 0.16 kcal mol⁻¹. Thus, there is a slight barrier to complex formation.

		$k_{obs} \pm 1\sigma$
$T \pm 1\sigma$ (K)	P (Torr)	$(10^{-12} \text{ cm}^3 \text{ s}^{-1})$
298 ± 5	10	0.46 ± 0.04
	20	0.60 ± 0.05
	31	0.64 ± 0.05
	50	0.78 ± 0.07
	101	0.99 ± 0.09
	108	1.15 ± 0.12^{a}
	158	1.08 ± 0.09
	225	1.40 ± 0.12
	299	1.53 ± 0.12
	416	1.68 ± 0.13
	502	1.76 ± 0.15
	604	1.90 ± 0.20
362 ± 11	20	0.74 ± 0.07
	31	0.78 ± 0.07
	50	0.96 ± 0.09
	99	1.27 ± 0.12
	146	1.47 ± 0.14
	199	1.64 ± 0.20
	315	1.91 ± 0.17
	398	2.08 ± 0.19
398 ± 16	21	0.83 ± 0.07
	51	1.17 ± 0.11
	98	1.37 ± 0.13
	308	2.09 ± 0.19
483 ± 1^{b}	10	1.26 ± 0.10
	20	1.32 ± 0.10
	41	1.39 ± 0.12
	43	1.44 ± 0.13
	43	1.54 ± 0.15
	73	1.76 ± 0.14
	100	1.96 ± 0.16
	200	2.30 ± 0.18
	298	2.54 ± 0.20
	399	2.76 ± 0.31

^aRate constant obtained by probing AlO product. ^bRate constants obtained in convection oven.



Figure 3. Plot of the measured bimolecular rate constants for the reaction of Al with CO_2 as a function of pressure at two temperatures near room temperature. The symbols are the measured rate constants, and the lines are the results of least-squares fits to the data using eq 2 as discussed in the text.

Also listed in Table II are the fixed values of k_s used in the fit and the resulting values for k_r and k_p . From these values for k_r it appears that the calculated lifetime for dissociation of the energized complex back to reactants $(1/k_r)$ increases as the temperature (and the average energy in the energized complex) increases. This parameter is poorly determined from these data (notice the large uncertainties), and the trend over this small temperature range is probably not significant.

Our experimental results at room temperature are in excellent agreement with the room temperature values of Parnis et al.⁵ Our high-pressure-limiting and extrapolated zero-pressure rate con-



Figure 4. Arrhenius plot of the calculated complex formation rate for the reaction of Al with CO₂ for temperatures below 700 K. The symbols are derived from eq 2 as discussed in the text. The error bars represent 1σ errors in the fitted rate constants. The solid line is the result of a weighted, linear least-squares fit to the data.



Figure 5. Arrhenius plot of the measured abstraction rate constants for the reaction Al + CO₂. The vertical and horizontal error bars represent 1σ error bars in the rate constants and temperatures, respectively. The solid line is the result of a weighted, linear least-squares fit to the data.

TABLE II: Fitted Values of the Rate Constants in Eq 2

			-	
$T \stackrel{\bullet}{=} 1\sigma$ (K)	k_s^{a} (10 ⁻¹⁰ cm ³ s ⁻¹)	$k_{\rm r} \pm 1\sigma$ (10 ⁸ s ⁻¹)	$k_{\rm p} \stackrel{\bullet}{=} 1\sigma$ (10 ⁸ s ⁻¹)	$k_{\rm f} \pm 1\sigma$ (10 ⁻¹² cm ³ s ⁻¹)
$298 \pm 5362 \pm 11398 \pm 16483 \pm 1$	1.85 2.04 2.14 2.36	$12.9 \pm 2.8 \\ 10.6 \pm 1.1 \\ 8.93 \pm 5.12 \\ 8.54 \pm 2.23$	$2.65 \pm 0.70 \\ 2.12 \pm 0.27 \\ 1.99 \pm 1.30 \\ 2.39 \pm 0.60$	$2.48 \pm 0.17 2.93 \pm 0.11 2.99 \pm 0.56 3.33 \pm 0.28$

"The value of $k_{\rm s}$ was fixed at $^2/_3k_{\rm coll}$.

stants of $(2.5 \pm 0.2) \times 10^{-12}$ and 4.2×10^{-13} cm³ s⁻¹ are in excellent agreement with their values of $(2.4 \pm 0.6) \times 10^{-12}$ and $(3.7 \pm 0.6) \times 10^{-13}$ cm³ s⁻¹, respectively. The extrapolated zero-pressure rate constants are larger than the value of $(1.5 \pm 0.6) \times 10^{-13}$ cm³ s⁻¹ reported by Fontijn and Felder for this reaction at room temperature; the source of the discrepancy is not known.

Marshall et al. predict that Al attacks the oxygen atom of CO_2 from a side-on approach with a slight barrier (5.5 kJ mol⁻¹). A *trans*-AlCO₂ complex is formed which then decomposes or is stabilized as described earlier. Their predicted pressure dependence of the rate constant is in excellent agreement with our room temperature results.

Measurements above 700 K. Above 700 K, the observed rate constants are independent of total pressure; the results are listed in Table III and shown as an Arrhenius plot in Figure 5. At 820 K, we determined the rate constant for reaction 1 by monitoring the disappearance of Al and in a separate experiment, the ap-

TABLE III: Temperature Dependence of Rate Constants of the Reaction Al + CO₂ above 700 K

		$k_{obs} \pm 1\sigma$
$T \pm 1\sigma$ (K)	P (Torr)	$(10^{-12} \text{ cm}^3 \text{ s}^{-1})$
746 ± 23	300	4.19 ± 0.37
766 ± 19	101	4.97 ± 0.45
814 ± 13	22	5.93 ± 0.54
820 ± 15	50	5.53 🏚 0.50
826 ± 15	21	5.42 ± 0.49^{a}
856 ± 23	300	6.98 ± 0.62
866 ± 47	100	7.65 ± 0.70
922 ± 35	101	9.76 ± 0.88
931 ± 24	20	9.32 ± 0.84
954 ± 25	50	8.79 ± 0.78
958 ± 40	301	9.20 ± 0.82
965 ± 29	49	10.7 ± 1.0
986 ± 37	20	11.5 ± 1.0
1087 ± 30	50	14.9 ± 1.3
1106 ± 36	20	18.9 ± 1.7
1215 ± 104	50	15.8 ± 1.6

^aRate constant obtained by probing AlO product.

pearance of AlO. The reaction of AlO + CO_2 , the primary loss process for the product AlO in our experiment, is also pressure and temperature dependent¹¹ with a rate constant near that for $Al + CO_2$; the rate constant for reaction 1 is derived from the fall of the AlO signal at room temperature and the rise at 820 K. A weighted, linear least-squares fit to the data (weighted using the uncertainties in temperature and rate constant listed in Table III) yields a preexponential factor of $(2.9 \pm 0.7) \times 10^{-10}$ cm³ s⁻¹ and an activation energy of 6.4 ± 0.4 kcal mol⁻¹.

It appears that at temperatures above 700 K an additional product channel with an activation energy of ~ 6.4 kcal mol⁻¹ becomes important. One explanation is that this channel is a direct O-atom abstraction. The observed activation energy is 1.5-2 kcal mol⁻¹ larger than the reaction endothermicity, and the Arrhenius A factor is in line with that expected for an abstraction reaction. Marshall et al.¹⁹ predict that the lack of pressure dependence above \sim 600 K is due to the decreasing efficiency of adduct stabilization as temperature increases. Our measured rate constants above 700 K are, however, substantially larger than the extrapolated complex formation rate constants shown in Figure 4. This argues, we believe, for a separate channel.

Additional experiments on the pressure dependence of the AlO yield at intermediate temperatures are needed to clarify the mechanism. The two competing mechanisms predict different behavior for the yield of AlO as a function of pressure at temperatures between 300 and 500 K. If there is a competing, direct abstraction channel, the yield of AlO approaches a limiting value as the pressure is increased. If the reaction proceeds entirely through an intermediate complex, then at high pressures and low temperatures the yield of AlO should go to zero. Experiments

are currently underway in our laboratory to distinguish between these two cases.

Summary

The rate constants of the reaction of $Al + CO_2$ were measured between 20 and 600 Torr total pressure and over the temperature range 300-1200 K. At temperatures near room temperature the reaction proceeds by formation of an AlCO₂* followed by either stabilization or decomposition back to reactants or to AIO + COproducts. At temperatures above 700 K, the reaction proceeds by direct O-atom abstraction to produce AlO + CO.

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Registry No. Al, 7429-90-5; CO₂, 124-38-9.

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