Metal ion-molecule kinetics at combustion temperatures. The reaction of Ca^+ with O_2 .

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Abstract

The high-temperature photochemistry (HTP) technique, previously used for reactions of neutral species, has been adapted to the study of atomic metal ion-molecule reactions. Ca^+ ions were generated by 193 nm multi-photon photolysis of calcium acetyl acetonate and its pyrolysis fragments. The relative ion concentrations were monitored by laser-induced fluorescence at 393.4 nm. Ar was used as the bath gas. The data for the $\text{Ca}^+ + \text{O}_2 + \text{M} \rightarrow \text{CaO}_2^+ + \text{M}$ association reaction (1) are fitted by $k_1(907 - 1425 \text{ K}) = 3.5 \times 10^{-32} \exp(+3161 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. Combining with an approximate $k_1(296 \text{ K})$ value in the literature leads to $k_1(296 - 1425 \text{ K}) = 5.8 \times 10^{-22} (\text{T/K})^{-2.9} \exp(-601 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. Over much of the observed temperature range reaction (1) has much smaller rate coefficients than the corresponding neutral Ca association reaction. Reaction (1) is shown to behave very similarly to the O_2 association reaction with neutral K atoms, with which Ca^+ is iso-electronic. This suggests that the initial step is ion-pair complex formation of the superoxide $\text{Ca}^{2+}(\text{O}_2)^-$, which is also consistent with results from density functional calculations. The k_1 values are rationalized via Troe's unimolecular formalism, which leads to good accord with the experiments.

Keywords

Metal ions, Elementary reactions, Temperature dependence, High-temperature reactors

1. Introduction

In an extensive series of papers, starting with the 14th Combustion Symposium [1], we have reported kinetic data on combustion reactions of metal-atoms, -monohalides, and -monoxides, at temperatures T in the 300 to 1800 K range, e.g., Refs. 2-8. Little information on such kinetics and its T -dependence was available at the time. To fill this gap in knowledge we developed the high-temperature fast-flow reactor, HTFFR, technique, with which most of our data were obtained. In this thermostatted reactor small quantities of the reactants are introduced in an excess of bath gas. The reaction temperatures and pressures are essentially those of the bath gas. As no other reactive species are present, the observations can be made free of interference of such species. These present a problem in most other high-temperature environments, such as flames. The metal species are introduced upstream from the oxidant inlet and reaction time is proportional to flow time. This work has been complemented by the development of a semi-empirical, quantum-mechanics based, theory for the determination of activation barriers for series of homologous reactions, e.g., Refs. 9-11.

A second thermostatted reactor type the high-temperature photochemistry reactor, HTP, was later developed. Briefly, this is a slow flow apparatus where the metallic species are produced from precursor molecules and their reactions are observed in the same volume element as in which they are formed. Because diffusion times to the walls are long compared to reaction times, wall reactions do not present a potential interference source. Several reactions have been studied with this technique and comparisons to HTFFR measurements have shown good agreement, e. g., Refs. 12-15.

Today our knowledge of metal ion kinetics at combustion temperatures is as scarce as that of the neutral species was in 1972. We have now begun to measure the kinetics of atomic ion reactions, for which we find the HTP apparatus, in a slightly modified form, highly suitable. The importance of obtaining such data lies in the fact that nearly all practical combustion systems (i) contain metals as impurities, additives, or inherent parts of the fuels [16-19], and (ii) are, at least weakly, ionized. As metal atoms have low ionization potentials they become readily ionized at high temperatures; moreover, the chemi-ions formed in fossil fuel and other organic compound flames have largely higher ionization potentials and rapidly transfer their positive charges to metal atoms [20]. As a result these can become the major charge carriers, even when the metals are present in low concentrations. The ionization processes and the large number of practical and proposed combustion applications involving ions have been extensively discussed, see especially Weinberg [21-23].

At flame temperatures atomic ions can have a relatively long lifetime, as they would principally become neutralized by relatively slow three-body reactions with electrons, e.g. $\text{Ca}^+ + \text{e}^- + \text{M}$. However, if such ions react to become molecular ions such as CaO^+ , then the much faster dissociative recombination route $\text{CaO}^+ + \text{e}^- \rightarrow \text{Ca} + \text{O}$ will determine the lifetime and concentrations of the charge carriers. Thus, kinetic data on atomic metal ion oxidation reactions are needed to model combustion systems. For the first HTP measurements of this kind we have selected Ca^+ reactions. This ion is readily monitored by our diagnostic technique, laser-induced fluorescence, LIF, and calcium is a common impurity. Moreover, this ion is iso-electronic with the neutral K atom, oxidation reactions of which have been studied and thus allow for ready comparison.

In one HTP study, made essentially simultaneously with the present work, $\text{Ca}^+ + \text{N}_2\text{O}$ was investigated from 480 to 1210 K. The results are reported [24] together with those from J. M. C. Plane's group, who made measurements in the 190 to 370 K temperature domain, of atmospheric interest. This bimolecular reaction leading to $\text{CaO}^+ + \text{N}_2$ is exothermic and has a small, but complex, T-dependence. This thus deviates from the T-independence predicted by Langevin-Giomousis-Stevenson ion-induced dipole theory [25]. The $\text{K} + \text{N}_2\text{O}$ reaction behaves quite differently. By contrast, the reaction

has a negative T-dependence, as is to be expected for a termolecular association process. It will be shown here to closely resemble the reaction [26,27]

2. Technique

Reaction (1) was investigated in an HTP reactor by laser photolysis/laser - induced fluorescence. Briefly, the reactor, Fig. 1, consists of an alumina reaction tube surrounded by SiC resistance heating rods and enclosed in an insulated water-cooled stainless steel vacuum housing. The reactor has three optical ports, at 90° angles, equipped with Suprasil quartz windows, which define the observation/reaction zone. For

the Ca^+ studies a separately heatable L-shaped quartz tube has been added to the apparatus. It contains a quartz boat on which the Ca^+ precursor photolyte $\text{Ca}(\text{C}_5\text{H}_7\text{O}_2)_2$, calcium acetyl acetonate, is placed. In the experiments the $\text{Ca}(\text{C}_5\text{H}_7\text{O}_2)_2$ was heated to temperatures of 450 to 480 K and the resulting vapor was entrained in a small Ar flow. The exit of this tube is located 5 cm from the bottom plate of the reactor, 20 cm upstream from the observation/reaction zone. Mixtures of Ar with varying amounts of O_2 flowed into the reactor through a second inlet, level with this plate. These distances are sufficient for the mixing of the reactants to be at least 99% complete [28] at the linear gas velocities used.

The Ca^+ ions were generated by multi-photon photolysis of the $\text{Ca}(\text{C}_5\text{H}_7\text{O}_2)_2$ vapor and its pyrolysis fragments. The focused output of an ArF excimer laser at 193 nm was used. The focusing lens was placed at about one focal length (25 cm) distance from the observation/reaction zone. The decrease in the relative concentrations of the Ca^+ ions was monitored via LIF at 393.4 nm ($4^2\text{P}_{3/2} - 4^2\text{S}_{1/2}$) using an excimer pumped dye laser. Variable time delay between the photolysis and diagnostic lasers was achieved using a Stanford Research Systems SR 250 boxcar. The LIF signal was detected through an interference filter (396 nm, 10 nm fwhm) by an EMI 9831 QA PMT, equipped with an SR 445A preamplifier. The photolysis laser pulse rates were 1 Hz, sufficient to provide a fresh reaction mixture for each laser pulse.

The temperature of the reaction zone was measured before and after each experiment with a Pt-Pt/13% Rh thermocouple, which was shielded to minimize radiation effects. Pressure was measured with a pressure transducer and the gas flow rates were regulated by calibrated mass flow controllers. The gases used were Ar (99.998%) from

the liquid and O₂ (99.99%), both from Praxair. Ca(C₅H₇O₂)₂ (99%) from Alfa Aesar was dried overnight in the reactor, under vacuum, at 380 to 400 K.

The experiments were carried out under pseudo-first order conditions, where [Ca⁺] << [O₂] << [Ar]. The rates of reaction (1) were found to be proportional to pressure, indicating a third-order process. Typical Ca⁺ fluorescence intensity vs. time plots, Fig. 2a, show, due to ongoing Ca⁺ production, an early maximum, followed by a region of non-exponential decay. After a time t_i, the plots are exponential and then, at a given T, P, [O₂], and [Ar], can be represented by

$$I = I_0 \exp(-k_{ps1}t) + B \quad (3)$$

Here, k_{ps1} is a pseudo-first-order rate coefficient, I₀ is the fluorescence intensity at t = t_i, I is the intensity at t > t_i, and B is background. Values of k_{ps1} ± σ_{kps1} are obtained by a weighted fit of the observed I vs. t profiles to Eq. (3) [29]. Residual analysis, Fig. 2b, and goodness of fit tests are used to determine the exponentiality of the decays [14, 30].

Typically five k_{ps1} measurements at varying [O₂], with the minimum [O₂] a factor of about 5-10 lower than the maximum values listed in Table 1, are used to obtain the pseudo-second order coefficients k_{ps2} ± σ_{kps2} at the temperatures and pressures of the experiments by

$$k_{ps1} = k_{ps2}[O_2] + k_d \quad (4)$$

where k_d represents Ca^+ loss other than by reaction (1), such as by diffusion and reaction with the precursor. A weighted least-squares fitting routine, with propagation of errors is used [31]. The same routine is then used to obtain the third-order rate coefficients $k_1 \pm \sigma_{k1}$ from the slope of plots of k_{ps2} vs. $[\text{M}]$.

3. Results

Measurements have been made at about 907, 1150, and 1425 K. The conditions used at each of these temperatures, as well as the $k_{ps2} \pm \sigma_{kps2}$ values obtained, are summarized in Table 1. The following experimental parameters were varied over wide ranges: total pressure P , and the corresponding total gas concentration $[\text{M}]$, the $[\text{O}_2]$, and the average gas velocity $\bar{v}$. At each T , P , $[\text{M}]$, $[\text{O}_2]$, and $\bar{v}$ at least two different photolysis laser energies, L.E., were used. No influence of laser energy was observed, indicating the absence of significant transient heating or secondary chemistry effects. The data at various L.E. are combined on the k_{ps1} vs. $[\text{O}_2]$ plots. These yield k_{ps2} , e.g., Fig. 3. At each temperature the k_{ps2} vs. $[\text{M}]$ plots, yielding k_1 , are best fitted by a straight line. However, while the lower temperature plots appear to pass through the origins, Fig. 4, the 1425 K plot, Fig. 5, has a definite intercept. The k and $k_{\text{int(ercept)}}$ values thus obtained are summarized in Table 2. The k_1 data are fitted by the Marquardt algorithm [32] to the form $A \exp(-E/T)$. σ_{k1} and a possible $\sigma_T/T = \pm 2\%$ contribute to the weighting of each point. The resulting expression is

$$k_1(907 - 1425 \text{ K}) = 3.5 \times 10^{-32} \exp(+3161 \text{ K}/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (5)$$

The variances and covariances are $\sigma_A^2 / A^2 = 6.82 \times 10^{-2}$, $\sigma_E^2 = 7.80 \times 10^4$, $\sigma_{AE} / A = 7.16 \times 10^1$. These are combined using the method of Wentworth [33] to calculate precision at the 2σ level to vary from $\pm 58\%$ to $\pm 47\%$. Allowing for a possible systematic error of $\pm 20\%$ we calculate the accuracy for the k_1 measurements to vary from $\pm 61\%$ to $\pm 52\%$ at the 2σ statistical confidence limit. Eq. (5) is the form most often used for neutral combustion reactions compilations and comparisons. It transforms to

$$k_1(907-1425 \text{ K}) = (2.9 \pm 1.1) \times 10^{-22} (\text{T/K})^{-2.85 \pm 0.15} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (6)$$

which is the format preferred in most of the ion-molecule kinetics literature.

There are two other published determinations of k_1 . These were made at about 296 K in flowing afterglows, which yielded 6.6×10^{-30} and $2 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ for $M = \text{Ar}$ and He , respectively [34, 35]. These results are according to these authors approximate, but they can be used to estimate a $k_1(T)$ unweighted non-linear least-squares fit expression [32] over a wider range. Using the value for Ar we obtain

$$k_1(296-1425 \text{ K}) = 5.8 \times 10^{-22} (\text{T/K})^{-2.9} \exp(-601 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (7)$$

4. Discussion

The proportionality of the k_1 data with $[M]$ shows that, under the investigated conditions, the termolecular reaction (1) is in its third order regime. In Fig. 6, the measured $k_1(T)$ are compared to $k(T)$ of the neutral Ca [36, 37] and K [26, 27] reactions with O_2

Reaction (8) is a relatively rare example of an association reaction with a positive T-dependence, contrary to the negative T-dependence of reaction (1). Reaction (8) is at the higher temperatures much faster than reaction (1) and proceeds [36] via an insertion reaction leading to the dioxide O-Ca-O. The $k_2(T)$ behavior can be seen to be similar to $k_1(T)$. This may suggest a similar chemistry for the single s^1 valence electron species K and Ca^+ , for which the insertion path involving two s electrons is not available. Reaction (2) proceeds via ion-pair complex formation to the superoxide $K^+(O_2)^-$ [26]. The analogous complex for reaction (1) is $Ca^{2+}(O_2)^-$ and the reaction may be analyzed in terms similar to those applicable to reaction (2) and other neutral-neutral association processes.

Density functional theory, B3LYP/6-311+G(3df), yields the $\text{Ca}^+ + \text{O}_2$ adduct structure shown in Fig. 7. The Mulliken charge on Ca is computed as 1.4, but inspection of the geometry and frequencies suggests more complete charge transfer to oxygen. For comparison, the O-O separation and vibrational frequency are computed as 1.203 Å and 1645 cm^{-1} for neutral oxygen, and 1.341 Å and 1182 cm^{-1} for the O_2^- anion. As seen from Fig. 7 the O-O separation in the adduct is much closer to O_2^- than to O_2 and the same holds for the O-O stretching frequency. This is consistent with the $\text{Ca}^{2+}(\text{O}_2)^-$ structure.

The recombination kinetics are rationalized in terms of Troe’s unimolecular formalism [38], as applied previously to reaction (2) [27]. We may write

$$k_1 = \beta_c Z_{\text{LJ}} F_E F_{\text{anh}} F_{\text{rot}} \frac{\rho_{\text{vib}}(E_0) RT}{Q_{\text{vib}}(\text{CaO}_2^+)} \frac{Q(\text{CaO}_2^+)}{Q(\text{Ca}^+)Q(\text{O}_2)} \quad (9)$$

where the symbols follow standard notation [38]. Several of these terms are not known well. We employ Lennard-Jones parameters for adduct-bath gas collisions similar to those used earlier [27], namely $\sigma = 5$ Å and $\epsilon/k_B = 500$ K, to obtain the Lennard-Jones collision rate $Z_{\text{LJ}} \approx 1.1 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 1150 K, which is about twice the Langevin collision rate for Ar. The present density functional theory results yield a bond strength E_0 of 230 kJ mol^{-1} . However, because the thermochemistry of calcium containing molecules is particularly hard to compute accurately [39], E_0 is treated here as an adjustable parameter in the unimolecular analysis. Good results were obtained with $E_0 = 250 \text{ kJ mol}^{-1}$, which is in line with the theoretical value.

The rotational correction F_{rot} is sensitive to the long range potential, which is unknown. Here we modified Troe's equations based on a $-C^*/r^6$ pseudo-diatomic van der Waals force model [38] to take account of a $-C^*/r^4$ ion-induced dipole interaction between Ca^+ and O_2 . This yields a centrifugal barrier pattern again of the form $C_v J(J+1)^v$, but now with $C_v = (B_{\text{eff}} q_e^2)^2/4C^*$ and $v = 2$. At 1150 K we derive $F_{\text{rot}} = 7.4$. More sophisticated approaches might include changes in zero point energies and the influence of valence forces as Ca^+ and O_2 approach, and there is probably a factor 3 or more uncertainty in F_{rot} and the resulting $k_1(T)$.

The average energy lost by the adduct per stabilizing collision with the bath gas was adjusted to a best fit value of 7.4 kJ mol^{-1} (assumed independent of temperature), which implies collisional efficiencies β_c varying from 0.62 at room temperature to 0.28 at 1425 K. These are higher than typical for stabilization of neutral species [38], and might indicate a special role for ion-induced forces. The data base for stabilization of ionic species is sparse, although recent experiments yielded a range of 1.6 to 5.2 kJ mol^{-1} for stabilization of $\text{C}_8\text{H}_{10}^+$ by N_2 [40]. It should be noted that here β_c compensates for any errors in the other parameters of Eq. (9), and is not therefore tightly determined. The calculated rate coefficients may be summarized as

$$k_1(296\text{-}2000 \text{ K}) = 2.4 \times 10^{-25} (\text{T/K})^{-1.8} \exp(-220 \text{ K/T}) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (10)$$

In Fig. 8 the line corresponding to this expression is compared to that of the experimental result, Eq. (7), showing good accord, especially in view of the approximate nature of the 296 K point.

A few words need to be said about the intercept of the 1425 K data, Fig.5. Very small intercepts may be present at the lower temperatures as well; these are statistically insignificant, but increase with temperature. It is tempting to attribute this to an abstraction channel competing effectively with reaction (1) with increasing temperature, as has been observed for several neutral metal - atom oxidation reactions [4]. However, this process

would be between 150 and 172 kJ mol⁻¹ endothermic, according to various determinations of the CaO⁺ bond energy [41,42]. This would make reaction (11) immeasurably slow at 1425 K. As it is unlikely that this bond energy is radically in error, another process must be involved. Various possibilities have been considered, but found wanting.

5. Conclusion

Kinetic data and their temperature dependence for metal ion - molecule reactions at temperatures and pressures of combustion significance are of inherent interest, as well as are needed for modelling. The few available data are either (i) from flame studies, where particularly for the temperature dependence only approximate values have been obtained [43], or (ii) largely from near or below room temperature measurements in isolated reaction environments at low pressures (typically < 10 mbar). The HTP

development, here described, has now made it possible to extend those reaction studies to temperatures above 900 K and to pressures approaching atmospheric. Two essentially simultaneous studies with this technique have now been made. The rate coefficients of the exothermic bimolecular $\text{Ca}^+ + \text{N}_2\text{O}$ reaction showed a small positive T-dependence from 600 to 1200 K [24]. The rate coefficients of the present $\text{Ca}^+ + \text{O}_2 + \text{Ar}$ reaction have a negative T-dependence similar to that of the equivalent reaction of neutral atoms of K, the element preceding Ca in the periodic table. Both these O_2 reactions are thought to proceed through ion-pair complex formation. The HTP technique is suitable to be applied to other categories of metal-ion reactions.

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Table 1. Summary of the Pseudo-Second-Order Rate Coefficient Measurements on the $\text{Ca}^+/\text{O}_2/\text{Ar}$ Reaction System

T, K	P, mbar	[M], 10^{18} cm^{-3}	$[\text{O}_2]_{\text{max}},$ 10^{15} cm^{-3}	$\bar{v},$ cm s^{-1}	L.E. range, mJ	$k_{\text{ps2}} \pm \sigma_{k_{\text{ps2}}},$ $10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
910	54	0.43	46.1	33.1	55-80	5.08 ± 0.21
907	160	1.28	1.29	25.2	185-275	14.9 ± 0.8
907	257	2.05	29.5	24.2	100-170	25.5 ± 0.9
908	277	2.20	8.32	21.4	90-150	30.3 ± 1.0
910	408	3.25	9.11	16.8	120-185	38.7 ± 3.0
908	521	4.16	12.5	14.1	90-150	46.2 ± 1.8
905	651	5.20	14.6	10.5	120-190	58.7 ± 0.6
904	768	6.15	24.5	9.0	115-180	65.1 ± 4.6
1150	64	0.40	43.3	42.2	100-170	3.17 ± 0.11
1153	137	0.86	28.5	40.8	190-280	4.37 ± 0.12
1147	184	1.10	68.3	26.5	150-220	7.56 ± 0.62
1146	349	2.20	133.0	13.7	100-175	12.3 ± 2.0
1146	420	2.65	43.2	19.1	150-220	13.9 ± 0.6
1157	568	3.40	75.4	17.6	175-250	21.8 ± 0.8
1155	731	4.15	101.0	12.2	175-250	23.5 ± 1.9
1146	794	5.01	121.0	10.1	200-280	30.7 ± 1.5
1427	57	0.28	32.5	42.9	135-210	3.38 ± 0.47
1424	90	0.44	29.9	51.9	140-220	4.09 ± 0.50
1425	130	0.64	37.9	38.1	110-180	4.86 ± 0.39
1424	234	1.17	38.9	26.3	130-220	6.55 ± 0.39
1426	272	1.36	56.5	32.5	150-230	8.07 ± 0.62
1426	400	2.01	33.0	18.5	115-190	8.11 ± 0.67
1424	443	2.23	60.6	20.4	150-230	9.62 ± 0.83
1424	615	3.11	25.6	12.0	170-255	13.0 ± 0.73

Table 2. The Rate Coefficients for the $\text{Ca}^+/\text{O}_2/\text{Ar}$ Reaction System at Each Temperature

T, K	$k_1 \pm \sigma_{k1},$ $10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$k_{\text{int}} (\pm \sigma_{\text{int}}),$ $10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
907	11.4 $\pm$ 0.3	3.99 $\pm$ 5.38
1150	5.27 $\pm$ 0.57	5.59 $\pm$ 4.99
1425	3.21 $\pm$ 0.23	27.3 $\pm$ 3.0

List of Figure Captions

Fig. 1. Schematic of the HTP reactor.

Fig. 2. Example of a fluorescence decay of Ca^+ . $T = 1150 \text{ K}$, $P = 63.7 \text{ mbar}$, $[\text{M}] = 4.0 \times 10^{17} \text{ molecule cm}^{-3}$, $[\text{O}_2] = 2.1 \times 10^{16} \text{ molecule cm}^{-3}$.

a) The decay plot; solid line indicates its exponential part. b) The residuals of this part.

Fig. 3. Example of a k_{ps1} versus $[\text{O}_2]$ plot. $T = 1150 \text{ K}$, $P = 63.7 \text{ mbar}$, $[\text{M}] = 4.0 \times 10^{17} \text{ molecule cm}^{-3}$. Circles: laser energy 100 mJ, squares: laser energy 170 mJ.

Fig. 4. The k_{ps2} versus $[\text{M}]$ plots at two temperatures. Circles: 907 K, squares: 1150 K.

Fig. 5. The k_{ps2} versus $[\text{M}]$ plot for 1425 K.

Fig. 6. Comparison of the rate coefficients of the $\text{Ca}^+ + \text{O}_2 + \text{Ar}$ reaction to those of the neutral Ca and K atom reactions with O_2 . The bracketed numbers refer to the particular references.

Fig. 7. B3LYP/6-311+G(3df) structure of $\text{Ca}^+ + \text{O}_2$ adduct, $^2\text{A}_2$ state, with distances in Å. The computed vibrational frequencies are 432 cm^{-1} for B_2 asymmetric Ca-O stretch, 528 cm^{-1} for A_1 symmetric Ca-O stretch, and 1189 cm^{-1} for A_1 O-O stretch.

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