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Kinetics of High Excited State Cr(a^5G_J) Depletion by O_2, NO, N_2O, and N_2

K. Honma*

Department of Material Science, Himeji Institute of Technology,
1475-2 Kanaji, Kamigori, Hyogo 678-1297, Japan

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The depletion kinetics of highly excited state Cr(a^5G_J) upon interaction with O_2, NO, N_2O, and N_2 are studied in a discharged flow reactor at a He pressure of 0.7 Torr. The state lying more than 20000 cm^{-1} above the ground state shows very efficient depletion by three oxygen-containing molecules, and the depletion rate constants are $(119 \pm 12) \times 10^{-12}$, $(124 \pm 12) \times 10^{-12}$, and $(78 \pm 8) \times 10^{-12}$ $cm^3\ s^{-1}$, for O_2, NO, and N_2O, respectively. Five spin−orbit levels show identical rate constants. This result and the previous ones for Cr(a^5S, a^5D) suggest that an electron-transfer mechanism is important for the interaction of Cr with O_2. Attractive interaction to form an intermediate is also suggested for the interaction with NO and N_2O. However, it is suggested that electronic energy-transfer processes are more important than chemical reactions. On the interaction with N_2, the depletion rate constant is $(15 \pm 2) \times 10^{-12}$ $cm^3\ s^{-1}$. This value is similar to the formation rate constants for Cr(a^5S, a^5D) upon the interaction with N_2, and the electronic energy transfer from Cr(a^5G_J) to Cr(a^5S_2, a^5D_J) is suggested.

Introduction

Since the flow tube LIF (laser induced fluorescence) technique was introduced to investigate the reactions of transition metal atoms,[1] a considerable amount of research has been devoted to this area.[2−5] One advantage of the flow tube technique is the ability to form electronically excited states with measurable concentrations. Combined with the narrow line width of a tunable laser, reactions of metal atoms in their excited states have been measured upon interaction with various molecules.[6−10] The results obtained for the excited states have provided useful information to better understand depletion reaction mechanisms of the gas-phase transition metals. In the previous paper, we extended these measurements to two excited states of Cr, Cr(a^5S_2, a^5D_J).[11] One advantage of these systems is that the Cr(a^5D_J) and Cr(a^5S_2) have different electronic configurations, $3d^44s^2$ and $3d^54s^1$, respectively, but similar electronic energies. Thus, the study was expected to provide a unique opportunity to clarify which is the more important factor between electronic configuration or electronic energy. On the interaction with O_2 and NO, these two states showed similar depletion rate constants. The similarity of the two has implied that the electronic energy is more important and the reactions proceed via an electron-transfer mechanism.

One interesting result in the previous study was observed for the interaction of Cr(a^5S_2, a^5D_J) with N_2. Two excited states showed an increase of their concentration instead of depletion by adding N_2. On the interaction with N_2O, these two states were depleted but nonexponential depletion curves were observed. These results have indicated the presence of higher excited electronic states in our flow tube which can be quenched to Cr(a^5S_2, a^5D_J) by the collisions with N_2 or N_2O. Since the processes in the flow tube become complicated by the quenching, the presence of the higher excited states is a disadvantage of the flow tube technique for the measurement of Cr(a^5S_2, a^5D_J). However, this could also provide a unique opportunity to study the interaction of the higher excited states. In this study, we take advantage of this to extend kinetic study of excited states of Cr up to Cr(a^5G_J). The atomic configurations and energies of chromium are summarized in Table 1.[12] Cr(a^5G_J) has more than 20000 cm^{-1} of electronic energy. The highest excited state measured by the flow tube technique is V(a^4D), 8596.41 cm^{-1}, which has been achieved by a stimulated emission pumping technique.[13] In the laser photolysis/LIF technique, the measurement has been achieved for Mo(a^5G_J), 16747 cm^{-1}.[14] Thus, this study presents the kinetic measurement for the transition metal atom with the highest energy ever measured.

TABLE 1: Configurations and Energies of the Low-Lying States of Chromium[a]

term	configuration	*J*	energy, cm^{-1}
a^7S	$3d^54s$	3	0.00
a^5S	$3d^54s$	2	7593.16
a^5D	$3d^44s^2$	0	7750.78
		1	7810.82
		2	7927.47
		3	8095.21
		4	8307.57
a^5G	$3d^54s$	2	20517.40
		6	20519.60
		3	20520.92
		4	20523.69
		5	20523.94

[a] Data taken from ref 12.

In this study, the depletion kinetics of Cr(a^5G_J) is presented for the interaction with three oxygen-containing molecules, O_2, NO, N_2O, and N_2. Among the group 6 transition metal atoms Cr, Mo, and W, the ground state and low lying excited states have been studied on the interactions with O_2, NO, N_2O, and N_2.[11,14−19] For higher electronic states, Mo(a^5G_J) has been studied upon the interaction with O_2.[14] Therefore, we believe that the present study extends the series of data of Cr and enables one to obtain a more detailed understanding of the interaction between the group 6 metal atoms and the oxygen-containing molecules.

Experimental Section

General. The flow tube/LIF instrument used in this study has been discussed in detail previously.[6] Briefly, metal atoms

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TABLE 2: LIF Transitions Used to Probe $Cr(a^5G_J)^a$

transition	energy (cm^{-1})	wavelength (nm)
$z^5G_3-a^5G_2$	22021.41	454.10
$z^5G_6-a^5G_6$	22086.21	452.77
$z^5G_3-a^5G_3$	22017.89	454.18
$z^5G_3-a^5G_4$	22015.12	454.23
$z^5G_6-a^5G_5$	22081.87	452.86

[a] Energies and wavelengths are derived from data in ref 12.

were created in a DC-discharge source where a chromium rod was used as a cathode. The atoms are carried downstream in the He buffer gas (300 K). Less than 5% Ar was added to the flow to stabilize the discharge. The densities of unreacted metal atoms were measured by laser-induced fluorescence (LIF) at known atomic transitions for $Cr(a^5G_J)$ summarized in Table 2. He (99.9999%), Ar (99.999%), O_2 (99.999%), NO (99.9%), N_2O (99.9%), and N_2 (99.9999%) gases were obtained from NIHON SANSO and used without further purification. A capacitance manometer (MKS Baratron, type 122A) was used to measure the total pressure inside the flow tube. Thermal mass flow meters (KOFLAC model 3710) were used to measure the flow rates of the reactant gas and He.

A tunable dye laser (Lambda Physik SCANMATE 2) pumped by a XeCl excimer laser (Lambda Physik Compex 102) were used to measure the density of the chromium atoms. Courmarin 460 was used for a dye. Spectrally unresolved fluorescence was collected by a lens system and detected by a photomultiplier tube (PMT) (HAMAMATSU Photonics R-928). The PMT current was amplified by a wide band preamplifier (NF Electronics, model BX-31) and the amplified voltage pulse was integrated by a boxcar integrator (SRS, model SR-250).

Rate Constant Determination. The following three processes are possible for the interaction of excited-state Cr atoms, $Cr(a^5G_J)$, with reactant molecule, X:

$$Cr(a^5G_J) + X \rightarrow \text{products} \tag{1}$$

$$Cr(a^5G_J) + X \rightarrow Cr(a^7S_3, a^5S_2, a^5D_J) + X' \tag{2}$$

$$Cr(a^5G_J) + X + He \rightarrow CrX + He \tag{3}$$

The termolecular association reaction, eq 3, is less likely for $Cr(a^5G_J)$, because associated adducts with high internal energy are expected to dissociate with a very short lifetime. Hence, this process is neglected for the following discussion. The time-integrated rate expressions for the simple bimolecular processes, eqs 1 and 2, are given by eq 4.

$$\ln[Cr(n_X)/Cr_0] = -(k_{rxn} + k_q)t_{rxn}n_X \tag{4}$$

$Cr(n_X)$ is the time-integrated $Cr(a^5G_J)$ atom concentration, Cr_0 is the $Cr(a^5G_J)$ atom concentration when no reactant gas is present, t_{rxn} is the mean reaction time, n_X is the reactant number density, and k_{rxn} and k_q are the rate constants of the bimolecular reaction and quenching, respectively.

Laser-induced fluorescence intensities with reactant concentration n_X and without reactant gas, $I(n_X)$ and I_0, are proportional to $Cr(n_X)$ and Cr_0, respectively. Therefore, the rate constants, $(k_{rxn} + k_q)$, were derived by fitting semilogarithmic plots of $I(n_X)/I_0$ vs n_X using a least-squares routine. Because the depletion signal that we measure could be affected by the processes 1 and 2, we refer to these values as *effective* rate constants rather than absolute values. The reaction time, t_{rxn}, was determined by laser vaporization−chemiluminescence measurement.[6] In this study, we used 0.7 Torr of He pressure and an inlet port 30 cm downstream of the discharge. The reaction time for this inlet port was 1.00 ms.

One possible error of the depletion rate constants may come from fluorescence quenching. Collisions of reactants during lifetimes of the excited states of the LIF transition quench the fluorescence and cause phenomenological depletion of metal atoms. It is possible to estimate collision frequencies during the lifetimes. Maximum partial pressures of reactants are typically 0.01 Torr. By using hard-sphere rate constants, k_{HS},[20] the estimated collision rate is around 1×10^5 s^{-1}. Fluorescence rates of the excited states are $(1-2) \times 10^7$ s^{-1}.[21] Since they are 2 orders of magnitude larger than the collision frequencies, we conclude that the fluorescence quenching is negligible for our experimental condition.

We report uncertainties by the larger of ±10% or ±2 standard deviations of the mean of multiple measurements. The absolute accuracies of the rate constants are estimated to be ±30% and are limited mainly by the atom production source. Other smaller contributions to our absolute uncertainty are from the measurement of t_{rxn}, incomplete mixing of the reagent gases, and the accuracy of the flow rate and pressure measurements. We estimate the absolute sensitivity of our instrument to be $\sim 5 \times 10^{-14}$ cm^3 s^{-1} based on our ability to easily observe a 5% decrease in our signal at a reagent gas flow rate of 100 sccm, which corresponds to about 5×10^{14} cm^{-3} of reactant number density.

According to eq 4, the normalized LIF intensity, $I(n_X)/I_0$, should be a single-exponential function of the reactant density, n_X. However, in some measurements of depletion of $Cr(a^5S, a^5D)$,[11] $I(n_X)/I_0$ showed not a single exponential but biexponential or multiexponential features. They were ascribed to the collisional quenching of higher lying excited states down to $Cr(a^5D_J, a^5S_2)$. In the present study, the depletion curves of $Cr(a^5G_J)$ showed nice single-exponential functions in all measurements. These results indicate that the concentrations of the excited states higher than $Cr(a^5G_J)$ are very small and/or most of them are lost by chemical reactions.

Results and Discussion

General. The depletion of $Cr(a^5G_6)$ upon the interaction with O_2, NO, N_2O, and N_2 is shown in Figure 1. All depletion curves show single-exponential functions which are consistent with the first-order decay given by eq 4. Effective rate constants obtained from these curves are summarized in Table 3. The rate constants are identical for five spin−orbit levels of $Cr(a^5G_6)$. The identical rate constants indicate that either the rate constants for individual *J* levels are the same or the reaction rate is much slower than interconversion of *J* levels from collisions with He. Because energy spacing among five *J* levels in $Cr(a^5G_J)$ is much smaller than the thermal energy, the latter is more likely for $Cr(a^5G_J)$. Recently, Wen, Yethiraj, and Weisshaar measured the rate of interconversion of *J* levels for $V(a^4D_J)$.[13] They observed almost constant populations of the *J* levels 80 μs after formation at 1.2 Torr of He flow. Because the energy level spacings of $Cr(a^5G_J)$ are much smaller than those of $V(a^4D_J)$,[22] it is reasonable to conclude that the interconversion rate is much faster than the reaction rate under our experimental condition (0.7 Torr of He). In Table 3, the rate constants averaged over all *J* levels are shown.

The rate constants of $Cr(a^5G_J)$ are very large for the interaction with O_2 and NO. Compared with the hard-sphere rate constants listed in the same table,[20] one-half of the collisions with reactants lead to the depletion of this state. The interaction with N_2O also shows very efficient depletion which needs only a few collisions. These large rate constants indicate that the

TABLE 3: Effective Bimolecular Rate Constants for the Reactions of Cr(a^5G_J) with O_2, No, N_2O, and N_2 at 300 K

reaction	$\Delta_rH^0_{298}$ (kJ/mol)	k_{obs} (10^{-12} cm^3 s^{-1})	k_{HS} (10^{-12} cm^3 s^{-1})	k_{HS}/k_{obs}
Cr(a^5G_J) + O_2	-209.1 ± 8.7[a]	119 ± 12	226	1.9
Cr(a^5G_J) + NO	-75.9 ± 8.7[a]	124 ± 12	233	1.9
Cr(a^5G_J) + N_2O	-541.2 ± 8.7[a] -142.2 ± 18.8[b]	78 ± 8	233	3.0
Cr(a^5D_J) + N_2	$+321.7 \pm 18.8$[b]	15 ± 2	253	17

[a] Values of $\Delta_rH^0_{298}$ for the CrO formation are derived from D^0_{298}(OX)$-D^0_{298}$(CrO). Using the recent D^0_0(Cr$-$O) value obtained by Hedgecock et al. (ref 14), gives D^0_{298}(Cr$-$O) = 460.8 ± 8.7 kJ/mol. The OX and N_2 bond energies are derived from data given in JANAF table. [b] $\Delta_rH^0_{298}$ for formation of CrN. D^0_{298}(Cr$-$N) = 377.8 ± 18.8 kJ/mol as given in the following: Srivastara, R. D.; Farber, M. *High Temp.* **1973**, *5*, 489.

TABLE 4: Rate Constants for Cr and Mo Upon the Interactions with O_2, No, N_2O, and N_2 (10^{-12} cm^3 s^{-1})

metal	term	energy/cm^{-1}	configuration	O_2	NO	N_2O	N_2
Cr	a^7S_3	0	$3d^54s^1$	1.6 ± 0.3[a,b]	0.03 ± 0.005[a,b]	0.010 ± 0.001[b]	NR
	a^5S_2	7593.2	$3d^54s^1$	27 ± 11[c]	36 ± 4[c]	92 ± 18[d]	NR[e]
	a^5D_J	8090.2[f]	$3d^44s^2$	62 ± 14[c]	115 ± 29[c]	50 ± 20[d]	NR[e]
	a^5G_J	20521.4[f]	$3d^54s^1$	119 ± 12	124 ± 12	78 ± 8	15 ± 2
Mo	a^7S_3	0	$4d^55s^1$	100 ± 30[g]	0.64 ± 0.07[a,h]	<0.001[h]	NR
	a^5S_2	10768.3	$4d^55s^1$	100 ± 30[g]	33 ± 13[h]	250[h]	23 ± 7[h]
	a^5D_J	11832[f]	$4d^45s^2$	9.3 ± 1.8[g]	30 ± 12[h]	9.5 ± 2.2[h]	16 ± 8[h,i]
	a^5G_J	16747[f]	$4d^55s^1$	180 ± 40[g]			

[a] Rate constant at 0.7 Torr of Ar. Because only a termolecular process is possible, rate constants are pressure dependent. [b] Reference 17. [c] Reference 11. [d] The decay profiles for Cr(a^5S_2, a^5D_J) + N_2O were analyzed by a double exponential function and the faster decay components are listed. [c] Instead of depletion, formation of the state was observed. [f] Statistical averaged energies. [g] Reference 14. [h] Reference 15. [i] The rate constant for Mo(a^5D_0) and the other spin$-$orbit levels give an identical and much smaller rate constant, $(0.13 \pm 0.04) \times 10^{-12}$ cm^3 s^{-1}.

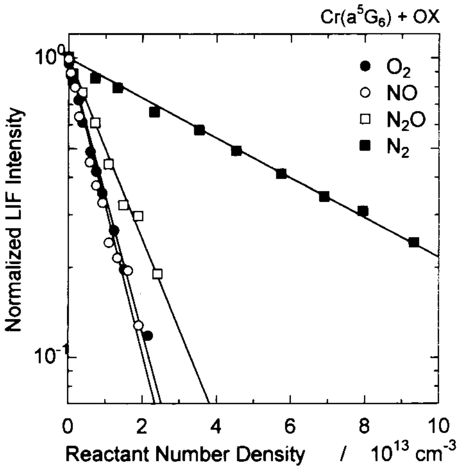

Figure 1. Semilogarithmic plots of normalized LIF intensities, $I(n_X)/I_0$, for Cr(a^5G_6) vs number densities of reactant molecules. The reaction time of these measurements is 1.0 ms. The solid lines are optimized least-squares fits of eq 4 to the data.

depletion processes occur without high energy barriers. In the interaction with N_2, the depletion is not so efficient as those by three oxidants and more than 10 collisions are required.

In the following sections, we are going to discuss each system in a little more detail. The rate constants of other states of Cr and corresponding systems of another group 6 metal, Mo, are summarized in Table 4.[23]

Cr(a^5G_J) + N_2. Because the CrN formation is highly endothermic, only electronic energy transfer is energetically accessible for Cr(a^5G_J) + N_2, and three products, Cr(a^7S_3), Cr(a^5D_J), and Cr(a^5S_2), are possible. One useful piece of information has been provided by the kinetic study of Cr(a^5S_2, a^5D_J) + N_2. In the previous study, we observed that the interaction of N_2 with both Cr(a^5D_J) and Cr(a^5S_2) showed no depletion but an increase of the population of both states.[11] This observation was ascribed to the quenching of higher lying excited states, eq 5, producing Cr(a^5S, a^5D).

$$\mathrm{Cr^{**}} + \mathrm{N_2} \rightarrow \mathrm{Cr(a^5S_2,\ a^5D_{\mathit{J}})} + \mathrm{N_2} \tag{5}$$

The formation kinetics was analyzed by a model where two higher lying states show different quenching rates, k_5 and k_5'. That is, the time-integrated concentration of Cr(a^5S_2) or Cr(a^5D_J) can be given by eq 6,

$$[\mathrm{Cr}(n_X)/\mathrm{Cr}_0] = 1 + [\mathrm{Cr^{**}}_0/\mathrm{Cr}_0][1 - \exp(-k_5 n_X t_{rxn})] + [\mathrm{Cr^{***}}_0/\mathrm{Cr}_0][1 - \exp(-k_5' n_X t_{rxn})] \tag{6}$$

and the best fit rate constants were given as 0.43×10^{-12} and 26×10^{-12} cm^3 s^{-1}, for Cr(a^5S_2). Interestingly, the latter rate constant is similar to the rate constant of Cr(a^5G_J) + N_2, $(15 \pm 2) \times 10^{-12}$ cm^3 s^{-1}. Because the formation of Cr(a^5S_2, a^5D_J) is characterized by two rate constants, at least two higher excited states participate the quenching. The similarity of the rate constants may indicate that Cr(a^5G_J) is one of the states responsible for forming Cr(a^5S_2, a^5D_J) by collisions with N_2 as eq 5a. It is noted that this conclusion is valid only in the case where no direct quenching

$$\mathrm{Cr(a^5G_{\mathit{J}})} + \mathrm{N_2} \rightarrow \mathrm{Cr(a^5S_2,\ a^5D_{\mathit{J}})} + \mathrm{N_2} \tag{5a}$$

from Cr(a^5G_J) to the ground state occurs. This could be reasonable because the quenching to the ground state is expected to be less probable than the quenching, Cr(a^5G_J) + N_2 → Cr(a^5D_J) + N_2.

The occurrence of the latter process is explained by the scheme of curve crossing between repulsive potentials described in the previous paper.[6] In this scheme, two potential curves evolved from Cr(a^5G_J) + N_2 and Cr(a^5D_J) + N_2 cross each other as the Cr$-N_2$ distance lessens, because the filled 4s orbital makes the lower curve from Cr(a^5D_J) + N_2 become repulsive at longer Cr$-N_2$ distance. The energy transfer from Cr(a^5G_J) to Cr(a^5D_J) can occur via this curve crossing. Either of the curves evolved from Cr(a^5S_2) + N_2 or the ground state could not cross with the surface from Cr(a^5G_J) + N_2, because these two states have the same electron configuration as Cr(a^5G_J). Thus, direct quenching from Cr(a^5G_J) to Cr(a^5S_2) or the ground state are expected to be inefficient. One explanation for the formation of Cr(a^5S_2) is the near resonant conversion from Cr(a^5D_J) to Cr(a^5S_2) by collision with N_2.

$Cr(a^5G_J) + O_2$. The effective rate constant for $Cr(a^5G_J) + O_2$ is $(119 \pm 12) \times 10^{-12}$ cm^3 s^{-1}, which is 2−4 times larger than those for $Cr(a^5S_2, a^5D_J) + O_2$. Except for the ground state which has no energetically accessible bimolecular process, the effective rate constants increase with the electronic energy of Cr.

As a bimolecular process, an oxidation reaction, eq 7, and electronic energy transfer are both possible for the interaction of $Cr(a^5G_J)$ with O_2.

$$Cr(a^5G_J) + O_2(X^3\Sigma_g^-) \rightarrow CrO + O \tag{7}$$

Among the electronic energy transfer, the following electronic to electronic energy-transfer processes are also possible:[24]

$$Cr(a^5G_J) + O_2(X^3\Sigma_g^-) \rightarrow Cr(a^7S_3, a^5S_2, a^5D_J) + O_2(a^1\Delta_g) \tag{8}$$

$$Cr(a^5G_J) + O_2(X^3\Sigma_g^-) \rightarrow Cr(a^7S_3) + O_2(b^1\Sigma_g^+) \tag{9}$$

As we discussed in the previous section, the electronic energy transfer could be observed by the kinetic behavior of low-lying states. Because of a large difference in concentrations between $Cr(a^5G_J)$ and $Cr(a^7S_3)$, it is difficult to discriminate a small increase or decrease in the intense LIF signal of the ground state. For $Cr(a^5S_2, a^5D_J)$, it could be possible to see some indication of the energy transfer. However, as we described in the previous paper, the depletion features of these two states were single-exponential functions which suggested simple first-order decay process.[11] Therefore, it can be concluded that the electronic energy transfer processes are not important in the depletion of $Cr(a^5G_J)$. This conclusion could be reasonable if we consider the rate constant for $Cr(a^5G_J) + N_2$ as one typical value for the energy transfer to form $Cr(a^5S_2, a^5D_J)$. This is almost 1 order of magnitude smaller than the rate constant for the depletion of $Cr(a^5G_J)$.

As the reaction mechanism, the importance of ionic potential surfaces was proposed.[3,6,9,11] That is, an electron transfer from Cr to O_2 leads the system to an attractive ionic surface which directly correlates to the product, CrO + O. The electron transfer occurs at a crossing region between the ionic, $Cr^+ + O_2^-$, and covalent, $Cr + O_2$, surfaces. For electronically excited states of Cr, their electronic energies raise covalent surfaces and the electron transfer can occur at a larger $Cr-O_2$ distance. If we assume that the crossing radius provides a measure of the occurrence of the depletion, a higher energy excited state is expected to give a larger rate constant. If we estimate the crossing radius by the equation $R_X = 14.4/(IP(Cr) - EA(O_2))$,[25] R_X are given as 2.67, 2.70, 3.81 Å for $Cr(a^5S_2)$, $Cr(a^5D_J)$, and $Cr(a^5G_J)$, respectively.[26] Rate constants estimated from these values are 127, 130, and 258 $\times 10^{-12}$ cm^3 s^{-1}, for $Cr(a^5S_2)$, $Cr(a^5D_J)$, and $Cr(a^5G_J)$, respectively. Although they are 2−5 times larger than the observed rate constants, the general trend agrees quite well with the observed one. The electronic structure of CrO also suggests the importance of the ionic surface in the reaction mechanism. The theoretical study has proposed that the low-lying electronic states of CrO are quite ionic, Cr^+O^-, and there are significant contributions from both $Cr^+(^6S)$ and $Cr^+(^6D)$.[27] Hence, the ionic surface can directly correlate to the products. Recent density functional study of CrO_2 also suggests that the electron transfer occurs to form an septet complex.[28]

In the electron-transfer mechanism, another important factor is probabilities of nonadiabatic transitions from covalent to ionic surfaces. Definitely, electron configurations of both surfaces play an important role in the electronic part of the transition probabilities. From this viewpoint, $Cr(a^5D_J) + O_2$ may be less favorable for the crossing with the ground-state ionic surface than $Cr(a^5S_2) + O_2$. The ground state of the ion, $Cr^+(^6S_{5/2})$, has the 3d^5 configuration.[12] This is accessible from $Cr(a^5S_2)$ by a single electron transfer, while the configuration change of more than two electrons are required for the transition from $Cr(a^5D_J$, 3d^{4}4s^2) + O_2 to $Cr^+(a^6S_{5/2}$, 3d^5) + O_2^-. The same is true for $Cr(a^5G_J$, 3d^{5}4s^1) if the ground-state ion is taken into account. Although the loss of one 4s electron seems to convert it to the ground state of Cr^+, the 3d^5 configuration in $Cr(a^5G_J)$ has a term of ^4G which is different from ^6S of Cr^+. That is, the change of m_l is required for the transition from covalent to ionic surfaces. However, the lowest excited state of the ion, $Cr^+(a^6D_J$, 3d^4(^{5}D)4s), is accessible by the one-electron jump. By using the electronic energy of this state, 12277.87 cm^{-1}, R_X is given as 2.71 Å. The rate constant estimated by this value is 131×10^{-12} cm^3 s^{-1}, which is similar to the value we determined. This result may suggest that the excited ionic surface participates and the harpoon mechanism via this surface works in the interaction of $Cr(a^5G_J)$ with O_2.

$Cr(a^5G_J)$ + NO. The effective rate constant for $Cr(a^5G_J)$ + NO is $(124 \pm 12) \times 10^{-12}$ cm^3 s^{-1} which is again larger than those for $Cr(a^5S_2, a^5D_J)$ + NO. Except for the ground state, which has no energetically accessible bimolecular process, the effective rate constants increase with the electronic energy of Cr.

As a bimolecular process, an oxidation reaction, eq 10, and an electronic energy transfer are both possible for the interaction of $Cr(a^5G_J)$ with NO, while only the energy transfer is opened for $Cr(a^5S_2, a^5D_J)$.

$$Cr(a^5G_J) + NO(X^2\Pi) \rightarrow CrO + N \tag{10}$$

The nitride formation, eq 11, is near thermoneutral ($\Delta_r H^0_{298} = +7.4 \pm 18.8$ kJ/mol) and could be possible by the use of thermal energy.

$$Cr(a^5G_J) + NO(X^2\Pi) \rightarrow CrN + O \tag{11}$$

For the electronic energy transfer, the same discussion as that for $Cr(a^5G_J) + O_2$ is applicable. That is, the previously measured depletion profiles of $Cr(a^5S_2, a^5D_J)$ showed no sign of the energy transfer, $Cr(a^5G_J) + NO \rightarrow Cr(a^5S_2, a^5D_J) + NO$. However, the very large rate constant of $Cr(a^5D_J)$ + NO suggests that the energy transfer, the only possible process for $Cr(a^5D_J)$, is very efficient in the interaction with NO. This is more than 90% of the rate constant for $Cr(a^5G_J)$ + NO. Therefore, the energy transfer could be still dominant in the depletion process of $Cr(a^5G_J)$. Because of the lack of the sign of the $Cr(a^5S_2, a^5D_J)$ formation, the energy transfer forms the ground state of Cr.

Because the electronic energy transferred has no resonance with vibrational and electronic energies of NO, a direct E−V,E energy transfer is improbable. An intermediate complex may participate in the depletion process. One important characteristics of NO is the presence of a singly occupied π^* orbital. This orbital may be able to interact attractively with the 4s orbital. A long-lived intermediate formed by attractive interaction presumably increases the efficiency of the electronic energy transfer. The chemical reaction, eq 10, may be less probable from this intermediate because the singly occupied π^* orbital with which Cr interacts is localized in N end.

$Cr(a^5G_J) + N_2O$. The effective rate constant for $Cr(a^5G_J) + N_2O$ is $(78 \pm 8) \times 10^{-12}$ cm^3 s^{-1}. As a chemical reaction, the following oxidation and nitride formation are possible for the interaction of $Cr(a^5G_J)$ with N_2O. Although another two-atom transfer reaction could be possible, no thermochemical information is available for CrNO or CrN_2. An electronic energy transfer is also possible.

$$Cr(a^5G_J) + N_2O(X^1\Sigma^+) \rightarrow CrO + N_2 \qquad (12)$$

$$Cr(a^5G_J) + N_2O(X^1\Sigma^+) \rightarrow CrN + NO \qquad (13)$$

From an energetic viewpoint, the following process is also possible, $\Delta_r H^0_{298} = -80.4 \pm 0.5$ kJ/mol:

$$Cr(a^5G_J) + N_2O(X^1\Sigma^+) \rightarrow Cr(a^7S_3) + N_2(X^1\Sigma_g^{\ +}) + O(^3P_J) \qquad (14)$$

As we discussed in the Cr(a^5G_J) + O_2 section, the depletion profiles of Cr(a^5S_2, a^5D_J) provide useful information for the presence of the energy transfer. In the previous paper, we reported that nonexponential decay features were obtained for the depletion of Cr(a^5S_2, a^5D_J) upon the interaction with N_2O.[11] These features strongly suggest the occurrence of the energy transfer to form Cr(a^5S_2, a^5D_J). Because only higher electronic states can be the origin of the energy transfer under room-temperature conditions, the quenching from Cr(a^5G_J) to Cr(a^5S_2, a^5D_J) may be important.

The large rate constant suggests that an intermediate participates in the energy transfer. One mechanism to form such an intermediate is an electron transfer. However, recent density functional study of the interaction of Sc, Ti, V + N_2O suggests that the electron transfer from the metal to N_2O leads to metal oxide formation without an energy barrier.[29] Therefore, the intermediate formation for the energy transfer could be less likely via the electron-transfer mechanism, if one more electron in Cr does not affect the proposed oxide formation mechanism.

Summary

A discharged flow−LIF technique is used to extend the kinetic study to the depletion of excited-state Cr(a^5G_J) having 20000 cm^{-1} electronic energy. The depletion of this high-energy state is studied upon interaction with O_2, NO, N_2O, and N_2 at a He pressure of 0.7 Torr. All oxygen-containing molecules show very efficient depletions whose rate constants are in the same order of the gas kinetics ones. In the interaction with O_2, good correlation is observed between harpoon-type electron-transfer rate constants and observed values, suggesting the importance of the electron-transfer mechanism. More information on electronic transition probabilities from covalent to ionic surfaces is required. In the interaction with NO or N_2O, electronic energy transfer processes via intermediate complexes are suggested. For the interaction with N_2, the electronic energy transfer is identified as Cr(a^5G_J) + N_2 → Cr(a^5S_2, a^5D_J) + N_2.

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(23) Because W has very different electronic level structure, we did not list its rate constants.

(24) The electronic energies of O_2, $a^1\Delta_g$ and $b^1\Sigma_g^{\ +}$ are 7918.1 cm^{-1} (0.982 eV) and 13195.1 cm^{-1} (1.64 eV), respectively.

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