Kinetics of Neutral Transition-Metal Atoms in the Gas Phase: Oxidation of Ti(a³F) by NO, O_2 , and N_2O

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We describe a general technique for measurement of the kinetics of ground-state neutral transition-metal atoms in a fast flow reactor with 0.75 Torr of He buffer gas using a laser vaporization source and a laser-induced fluorescence detection. For the oxygen atom transfer reactions $Ti(a^{3}F) + OX \rightarrow TiO + X$, with $OX = NO, O_{2}$, and $N_{2}O$, we obtain 300 K effective bimolecular rate constants of $(7.8 \pm 0.6) \times 10^{-12}$, $(1.5 \pm 0.4) \times 10^{-12}$, and $(4.0 \pm 1.4) \times 10^{-13}$ cm³ s⁻¹, respectively. All three reactions are exothermic yet inefficient at 300 K, indicating the presence of activation barriers. For the secondary reaction TiO(X³ Δ) + NO \rightarrow products, we obtain the effective bimolecular rate constant (2.2 ± 0.4) × 10⁻¹² cm³·s⁻¹. A correlation argument based on separated fragments Ti + O + X can explain the inefficiency of the Ti($3d^24s^2$, a^3F) reactions by the need to switch electron configurations along low-energy adiabatic paths from ground-state reactants to energetically accessible TiO + OX product states. The argument should apply to many reactions of metal atom ground states having chemically inert ns^2 configurations.

Introduction

The chemistry of gas-phase transition-metal atomic cations M⁺ has been characterized extensively in the past 10 years by using the full complement of sophisticated mass spectrometric techniques.¹ A good understanding of how M⁺ electronic structure controls reactivity is gradually emerging. In contrast, the gasphase chemistry of neutral transition-metal atoms is much less well explored. The electronic structure of neutral first transition series metals differs qualitatively from that of the cations.² In the neutrals, the lower energy of the 4s orbital relative to 3d results in ground states of primarily 3dⁿ⁻²4s² configuration and low-lying $3d^{n-1}4s$ excited states; $3d^n$ states, which play a crucial role in M⁴ chemistry, lie very high in energy for neutral M. Our goal is to determine how these differences affect the chemistry of neutral metal atoms and to seek unifying concepts that can explain both neutral and cationic chemical reactivity.

Gas-phase metal species play a role in diverse chemical systems. Atoms such as Na, Mg, Sc, Ti, and Fe and the corresponding metal monoxides occur in the earth's atmosphere, apparently due to meteor ablation.³ TiO dominates the absorption spectrum of M-type stars, yielding information about their temperature and age.⁴ Gas-phase oxidation of TiCl₄ is a commerical process used to produce 725000 tons of $TiO_2(s)$ annually.⁵

There is a long history of kinetics and dynamics measurements on reactions of alkali-metal and alkaline-earth-metal atoms with the oxidants NO, O₂, N₂O, O₃, and NO₂. For some reactions, rate constants have been measured;6 for others, chemiluminescence spectra have revealed details of the partitioning of electronically excited products into vibrational states.⁷ Among the transition

metals, oxidation of the neutral atoms Sc and Ti by O₂, NO₂, N₂O, and O₃ was studied by Gole and co-workers,⁸ who dispersed visible chemiluminescence from excited state MO* products. Parson and co-workers9 carried out crossed beam chemiluminescence studies of Ti and V atom reactions with O_2 . In all such single collision studies using oven sources of metal atoms, it is difficult to assess the role of reactant electronic excitation. Flow tube kinetics studies of neutral Zn¹⁰ and Sn¹¹ oxidations have been reported. In early cation work, Ferguson and Fehsenfeld¹² measured the 300 K rate constant for $Fe^+ + O_3 \rightarrow FeO^+ + O_2$. Armentrout, Halle, and Beauchamp¹³ used the ion beam technique to study the kinetic energy dependence of O-atom abstraction cross sections for the cations Cr⁺, Mn⁺, Fe⁺, Co⁺, and Ni⁺ in collisions with O₂ and N_2O . All of the N_2O reactions are exothermic yet exhibit barriers, with the possible exception of $Fe^+ + N_2O$. A recurring theme of all the kinetics work is the slow oxidation of metal atoms by N_2O , in spite of the weak N_2-O bond.⁶⁻¹¹ In work closely related to the present report, Johnsen, Castell, and Biondi¹⁴ measured $Ti^+ + O_2 \rightarrow TiO^+ + O$ and $Ti^+ + NO \rightarrow TiO^+ + N$ rate constants of $(5 \pm 1) \times 10^{-10}$ and $(9.5 \pm 2.0) \times 10^{-11}$ cm³·s⁻¹, respectively, at 300 K.

In this paper, we introduce a general technique for measurement of ground-state transition-metal reaction rates under well-characterized conditions at 300 K. Reactant metal atoms created by laser vaporization of a metal target upstream in a fast flow reactor with He buffer gas at 0.75 Torr are probed downstream by using laser-induced fluorescence (LIF). The decay of specific metal atom electronic states vs reagent number density yields effective bimolecular rate constants. Here we report on the kinetics of oxidation of ground-state $Ti(a^{3}F)$ by NO, O₂, and N₂O to form TiO at 300 K. Subsequent reactions of the TiO product with the same three oxidants are also monitored by LIF. All three Ti(a³F) reactions are exothermic yet quite inefficient, which we explain by the necessity of changing overall electron configuration along adiabatic paths from ground-state reactants to low-energy products.

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Experimental Section

The apparatus is essentially the same fast flow reactor previously used for several transition-metal ion kinetics studies in this group.^{15,16} To study the kinetics of neutral Ti decay and TiO formation and decay, we replace the previous quadrupole mass spectrometric detection of reactant and product ions by laserinduced fluorescence (LIF) detection of neutrals.

The flow reactor is a 7.3 cm i.d. stainless steel tube made of modular sections. The sections are joined by end flanges sealed by O-rings. The flow tube has been used at lengths varying from 30 cm to 2 m. The helium buffer gas is introduced upstream through an effusive inlet in the end flange. A flow rate of about 14.7 STP L·min⁻¹, controlled by a feedback mass flow controller system, maintains the pressure in the reaction region at 0.75 Torr. The He is removed downstream by a Roots blower.

A pulsed laser (XeCl excimer, 308 nm, $\sim 10 \text{ mJ/pulse}$, 10 pulse/s, 15 ns fwhm) is focused by a 30-cm quartz lens through a 1-cm opening in the tube to a ~ 0.1 cm diameter spot on a rotating (0.6 rev/min) 1 cm diameter target protruding into the flow tube 30 cm downstream of the He inlet. The laser pulse vaporizes target metal (titanium, Alfa, 99.7% metallic purity), creating a dense packet of electrons and hot metal neutrals and ions. We estimate that $\sim 2 \times 10^{13}$ Ti neutral atoms are vaporized per laser shot. The packet expands and is quickly cooled translationally and entrained in the 0.75 Torr of He carrier gas. The average He flow speed is 6240 ± 160 cm·s.

A pair of stainless steel meshes between the metal source and the detector floated at +23 V dc strip ions from the flow while allowing the neutral species to pass unimpeded through the reaction zone. The oxidant gas is added midstream through "showerhead" inlets oriented upstream relative to the He flow. Flows of oxidant are regulated by a needle valve and monitored by a mass flow system. The helium carrier gas is purified by passage through a series of three traps containing zeolite sieve material at 77 K. The reactant oxidant gases, N₂O (Matheson, 99.0%), O₂ (Matheson, 99.8%), and NO (Matheson, 99.0%), are passed through a trap at 195 K.

Both Ti reactant and TiO product are detected via LIF. A pulsed dye laser (Quanta Ray, Nd:YAG DCR-2 pumped PDL-1, Exciton DCM dye) is triggered so that the beam intersects the flow at the maximum density of the metal packet. The laser is frequency doubled to the near-UV region (305-340 nm) for Ti studies. The laser beam enters and exits the flow reactor through Suprasil windows at the Brewster angle, traveling through 63 cm long baffle arms to minimize scattered light. The total fluorescence is collected by a 5 cm diameter f/2 quartz lens system and focused onto a crossed pair of 5 mm wide slits before striking an EMI photomultiplier tube (PMT, Model 9813B for Ti and Model 9658R for the TiO). The fluorescence is not spectrally resolved. We detect as many as 7×10^5 photons/shot and estimate that up to 2×10^7 photons/shot are created in the 3 mm \times 3 mm \times 3 mm viewing region of the flow tube. The PMT current is dropped over a 50- Ω load to create a voltage pulse that is integrated by an SRS boxcar integrator (Model SR-250). The gate is opened just prior to the laser pulse because scattered light is not a significant fraction of the signal. The slit widths and the voltage applied to the PMT were adjusted to avoid PMT and boxcar saturation.

Results

Characterization of Metal Pulses. Ground-state Ti is detected with spin-orbit level resolution using $w^3G_J^0 \leftarrow a^3F_J$ transitions (Table I). Each of these atomic lines is well isolated and easily assigned.² At distances of 35-45 cm downstream of the source, LIF wavelength scans indicate¹⁷ that at least 90% of the Ti atoms are in the ground term a³F. We can easily detect the much smaller LIF signals originating from the low-lying excited terms a⁵F, a¹D,

TABLE I: Laser-Induced Fluorescence Transitions Used To Probe Ti and TiO

species	transition ^a	energy, cm ⁻¹	
Ti	$w^3G_4^0 \leftarrow a^3F_2$	31,374	
Ti	$w^{3}F_{4}^{0} \leftarrow a^{3}F_{3}$	31,319	
Ti	$w^3G_5^0 \leftarrow a^3F_4$	31,242	
TiO	$B^3\Pi_1 \leftarrow X^3\Delta_1$	16,260	
TiO	$B^3\Pi_0 \leftarrow X^3\Delta_1$	16,234	
TiO	$B^3\Pi_2 \leftarrow X^3\Delta_2$	16,194	
TiO	$B^3\Pi_1 \leftarrow X^3\Delta_2$	16,162	

^aTi transitions from ref 2; TiO transitions to subband heads from ref 18.



Figure 1. Arrival time distributions from source to laser-induced fluorescence probe for $Ti(a^3F)$ and for $TiO(X^3\Delta)$ at source-probe distances as shown. The Ti curve at 117.5 cm is displaced vertically for clarity.

and $a^{3}P$. However, collisional cascade of these electronically excited states has negligible effect on the $a^{3}F$ kinetics, as evidenced by the observed exponential decays of $a^{3}F$ vs oxidant flow (vide infra). Ground-state TiO is detected with spin-orbit sublevel resolution using different subbands of the $B^{3}\Pi \leftarrow X^{3}\Delta$ band system¹⁸ (Table I).

The metal atom pulses have been characterized at various distances downstream of the laser vaporization source. By measuring integrated LIF signal vs delay time between source and probe lasers, we map out the arrival time distribution of Ti and TiO states from source to probe laser volume. Figure 1 displays typical signal intensity vs time data at distances of 90.5 and 117.5 cm from target to center of LIF viewing region. A plot of delay to the *peak* of the arrival time distribution vs distance from source to detector yields a straight line with slope (mean Ti atom axial speed) of $(v_{Ti}) = 9070 \pm 250$ cm·s⁻¹. The speed based on *mean* arrival times is the same within experimental error.

Similar asymmetric distributions, skewed toward long detection times, are characteristic of the Ti(a³F) ground state, the Ti*(a³P) excited state, $Ti^+(a^4F)$ ions, and $TiO(X^3\Delta)$ products. The asymmetric broadening of the metal packet as it flows down the tube is a result of the coupling of radial and axial diffusion.¹⁹ The fact that Ti, Ti*, and TiO neutrals and Ti+ cations all move at larger average speeds than the bulk He speed indicates that the metal species number densities peak at the center of the tube where He axial velocity is largest. Apparently wall losses are comparably efficient and diffusion coefficients are quite similar for all three atomic species. Howard and co-workers^{6a} found that wall collisions remove Na and NaO molecules from the gas phase with near unit efficiency. The intensity maxima for all species occur at the same time at every distance along the tube from 30 to 140 cm. The TiO packet broadens slightly less than the atom packets. This suggests a somewhat smaller TiO diffusion coefficient, but the comparison is complicated by the fact that TiO is a reaction product formed continuously in the reaction zone while the atomic species are created further upstream in the laser vaporization source.

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Figure 2. Semilogarithmic plot of $Ti(a^3F)$ laser-induced fluorescence signal vs flow of oxidant for NO, O₂, and N₂O reactions; reaction zone length is fixed at 55 cm.

TABLE II: Effective Bimolecular Rate Constants^a for Reactions of $Ti(a^{3}F)$ and $TiO(X^{3}\Delta)$ with Oxidants at 300 K in 0.75 Torr of He

reaction ^a	$-\Delta H^{\circ}_{298}$, ^b kcal·mol ⁻¹	$k, 10^{-12} cm^3 s^{-1}$	$\langle \sigma \rangle, ^{c}$ Å ²	collision no. ^d
$Ti(a^{3}F) + NO$	10 ± 4	7.8 ± 0.6	1.34	32
$Ti(a^3F) + O_2$	41 ± 3	1.5 ± 0.4	0.26	170
$Ti(a^{3}F) + N_{2}O$	121 ± 3	0.40 ± 0.14	0.07	640
$TiO(X^{3}\Delta) + NO$	-6 ± 6	2.2 ± 0.4	0.45	120

^aTermolecular contributions to these rate constants have not been ruled out experimentally. In the Ti + OX reactions, the bimolecular TiO product has been detected by LIF, although termolecular TiO₂ would go undetected. In the TiO + NO reaction, we do not detect products; the exothermicity given assumes the products TiO₂ + N. ^bSee ref 20 and 21. ^cAverage cross section $\langle \sigma \rangle = k/\langle v \rangle$, where $\langle v \rangle$ is the mean relative velocity at 300 K. ^dRatio of estimated hard-sphere collision cross section $\sigma_{hs} = \pi(d_1 + d_2)^2$ to $\langle \sigma \rangle$, with d_1 and d_2 the estimated diameters of each collision partner. Hard-sphere-diameter estimates were 4.00, 4.20, 3.47, 3.43, and 3.88 Å for Ti, TiO, NO, O₂, and N₂O, respectively. See ref 23.

 $Ti(a^{3}F)$ Kinetics and Mechanism. Ground-state Ti(a³F) effective bimolecular reaction rate constants were obtained from least-squares fits to plots of the logarithmic decay of the state-selected LIF signal vs calibrated flow of oxidant (Figure 2) at various fixed reaction lengths by using the relation

$$\ln \left[\text{Ti}(n_{\text{OX}}) / \text{Ti}_0 \right] = -kt_{\text{rxn}} n_{\text{OX}}$$

Here $Ti(n_{OX})$ is the time-integrated fluorescence signal as a function of oxidant number density; Ti_0 is the signal with no oxidant flowing; t_{rxn} is the mean reaction time calculated as $z/\langle v_{Ti} \rangle$ from the measured average Ti velocity and the reaction distance z; n_{OX} is the oxidant number density obtained from the calibrated mass flow meters. All kinetics measurements were obtained by using unsaturated LIF, as verified by the linearity of signal with dye laser intensity.

We have measured the state-specific effective bimolecular rate constants of the reactions

$$Ti(a^{3}F) + NO \rightarrow TiO + N$$
 (1)

$$Ti(a^{3}F) + O_{2} \rightarrow TiO + O$$
 (2)

$$Ti(a^{3}F) + N_{2}O \rightarrow TiO + N_{2}$$
(3)

in 0.75 Torr of He at 300 K. Reaction exothermicities ΔH°_{298}



Figure 3. Semilogarithmic plot of $Ti(a^3F_J)$ laser-induced fluorescence signal vs NO flow at fixed reaction length of 106 cm, showing decay rates independent of the spin-orbit level probed.



Figure 4. Semilogarithmic plot of $TiO(X^{3}\Delta)$ laser-induced fluorescence signal vs NO flow at fixed reaction length of 106 cm. Solid line is nonlinear least-squares fit to the two-exponential function gives in the text.

are -9.6 ± 4.0 , -41.4 ± 3.0 , and -120.6 ± 3.0 kcal·mol⁻¹, respectively.²⁰ The pseudo-first-order reaction conditions produced linear semilog plots of Ti LIF signal vs concentration of oxidant (Figure 2). We obtain the respective rate constants (7.8 ± 0.6) $\times 10^{-12}$, (1.5 ± 0.3) $\times 10^{-12}$, and (0.40 ± 0.14) $\times 10^{-12}$ cm³·s⁻¹ for the disappearance of Ti(a³F) via reactions 1–3. The uncertainties represent the precision of the data as two standard deviations (Table II). The absolute accuracy of the observed rate constants is estimated at $\pm 30\%$ for NO and O₂ and $\pm 50\%$ for N₂O, limited by the many small uncertainties, random noise in the data, etc.

For all three reactions, we observe no systematic dependence of the observed reaction rate on the spin-orbit level probed by LIF, either J = 2, 3, or 4 of the Ti(a^3F_J) atom (Figure 3). Either the J-specific rate constants k_J are equal within our precision, or collisional interconversion among spin-orbit levels is fast compared to reaction in all cases. In the latter limit, we would measure a 300 K Boltzmann average over the individual k_J 's.

 $TiO(X^3\Delta)$ Kinetics and Mechanism. For each of the three oxidants, we have also measured $TiO(n_{OX})$, the LIF signal from specific sublevels of $TiO(X^3\Delta)$ as a function of oxidant flow. The data of Figures 4 and 5 show that TiO is not the final product, but an intermediate in a sequence of reactions. We do not detect the final product from the disappearance of the TiO, but assume it is TiO_2 as follows:

$$TiO + NO \rightarrow TiO_2 + N$$
 (4)

$$TiO + O_2 \rightarrow TiO_2 + O$$
 (5)

$$TiO + N_2O \rightarrow TiO_2 + N_2 \tag{6}$$

Reaction 4 is approximately thermoneutral, with $\Delta H^{\circ}_{298} = 6 \pm 6 \text{ kcal·mol}^{-1}$; reactions 5 and 6 are exothermic with $\Delta H^{\circ}_{298} = -25$

⁽²⁰⁾ $\Delta H_{f}^{\circ}_{298}(\text{TiO}) = 12 \pm 2 \text{ kcal·mol}^{-1} \text{ from: Pekley, J. B.; Marshall, E. M. J. Phys. Chem. Ref. Data$ **1983** $, 12, 983; values of <math>\Delta H_{f}^{\circ}_{298}$ for other molecules from: Stull, B. R.; Prophet, H. JANAF Thermochemical Tables, 2nd ed.; 1971, NSRDS-NBS37.



Figure 5. Semilogarithmic plot of $TiO(X^3\Delta)$ laser-induced fluorescence signal vs N₂O and O₂ flows at fixed reaction length of 85 cm. The dashed lines are extensions of straight lines drawn tangent to the curves at large flows; note the inflection points on the falling side of both curves.

 \pm 5 and -105 \pm 5 kcal·mol⁻¹, respectively.²¹ Termolecular contributions to the TiO reactions have not been ruled out; these are more likely important in reactions 4-6 than in reactions 1-3 because one additional atom is present in the bimolecular complex. The TiO(n_{OX}) data are indistinguishable when the dye laser probes either the X³ Δ_1 or X³ Δ_2 sublevels, again indicating either identical removal rates from these two sublevels or rapid collisional equilibration on the time scale of the secondary reactions.

The TiO reaction with NO shows simpler behavior than the reactions with O_2 and N_2O . The peak intensity of the TiO (n_{OX}) signal occurs at ~ 3 times greater flow of oxidant for NO than for O_2 and N_2O . In addition, the TiO (n_{NO}) curves can be accurately fit to a sum of two exponentials, one rising and one falling vs n_{OX} , while the O_2 and N_2O data cannot.

For the NO reaction sequence, eq 1 and 4 yield the integrated expressions

$$Ti(t) = Ti_0 \exp[-k_1 n_{NO} t]$$
$$TiO(t) = [k_1/(k_1 - k_4)]Ti_0[\exp[-k_1 n_{NO} t] - \exp[-k_4 n_{NO} t]$$

where k_1 and k_4 refer to the corresponding equations. These expressions correctly predict the linear semilog plots of Ti(n_{NO}) vs n_{NO} (Figure 2) as well as the two exponential form of the TiO(n_{NO}) behavior (Figure 4). In the nonlinear least-squares fits to the TiO(n_{NO}) data, both parameters k_1 and k_4 were allowed to float. The faster of the two best fit rate constants matches the observed rate constant for Ti decay within the uncertainty of the parameters. We can therefore unequivocally assign the slower decay rate to k_4 , the rate constant for the TiO + NO reaction. The decay of Ti provides the most accurate measure of k_1 . From the TiO(n_{NO}) data we obtain $k_4 = (2.2 \pm 0.4) \times 10^{-12} \text{ cm}^3 \text{s}^{-1}$ (Table II) as an average over fits to six separate TiO(n_{NO}) curves; data from X³ Δ_1 and X³ Δ_2 kinetics are combined. Each curve comprises 20-50 data points.

The TiO(n_{OX}) curves for the O₂ and N₂O reactions are more complex (Figure 5), exhibiting distinct inflection points in the decay that cannot be adequately fit to a sum of only two exponentials. We have tried to fit these curves to several models more complicated than eq 2, 3, 5, and 6 without success. In one model, we introduced a single phenomenological excited-state species TiO* along with its formation rate k^*n_{OX} , its secondary reaction rate $k^*_r n_{OX}$, and a quenching rate $k_q n_{OX}$ from TiO* to TiO ground state. The model could not mimic the inflections of Figure 5. Addition of a reasonable quenching rate of TiO* by He can produce inflections, but none so sharp as observed. Finally, we tried a model including a termolecular step TiO + OX + OX \rightarrow

TABLE III: Low-Lying TiO Electronic States^a

state	energy, cm ⁻¹	approx confign ^b	
$\overline{X^{3}\Delta}$	0	9018	
$a^{1}\Delta$	3440	9σ1δ	
$d^1\Sigma^+$	5655	$9\sigma^2$	
E ³ II	12,025	$9\sigma 4\pi$	
$A^{3}\Phi$	14,090	$4\pi 1\delta$	
b¹Π	14,762	$9\sigma 4\pi$	
В ³ П	16,293	$4\pi 1\delta$	
$C^{3}\Delta$	19,427	11σ1δ	
c ¹ Φ	21,330	$4\pi 1\delta$	

^aReference 33. For comparison, the exothermicities of the Ti($a^{3}F$) + NO, O₂, and N₂O reactions are 3500, 14 300, and 42 300 cm⁻¹, respectively (ref 20). The N₂O reaction has sufficient energy to form many higher energy TiO states as well. ^bElectron configurations from the configuration interaction calculations of ref 31. All states have the common core configuration (1-7) $\sigma^{2}1\pi^{4}2\pi^{4}8\sigma^{2}3\pi^{4}$. The 9 σ orbital is a Ti(4s) orbital with some Ti(4p) admixture; 1 δ is Ti(3d); 4 π is almost entirely Ti(3d_{π}); and 11 σ is a Ti(3d_{σ}) and Ti(4p_{σ}) mixture.

TiO(OX) + OX but again failed to fit the data with reasonable values of termolecular rate constants. The LIF spectra indicate >90% a³F Ti atoms in the reaction zone, but it is possible that fast reaction of the <10% excited-state population could contribute to the TiO curves of Figure 5. Clearly models involving several reactant or product excited states and a concomitant proliferation of adjustable parameters would be necessary to fit the data. The simple model succeeds for the fastest, least exothermic reaction (that of NO), which can populate only two electronic states of TiO (Table III). Direct formation of TiO as a reactant from laser vaporization of solid TiO₂ and use of a nonreactive electronic quencher will prove a better technique for obtaining ground-state TiO rate constants.

Discussion

Since we have not necessarily identified all the reaction products, it is possible that termolecular reactions with He as third body contribute to the effective bimolecular rate constants for $Ti(a^{3}F)$ in Table II. Ion-molecule termolecular M⁺ + diatomic or triatomic association reactions in rare gases are very slow,²² typically $\sim 3 \times 10^{-30}$ cm⁶·s⁻¹ for alkaline-earth-metal cations such as Mg⁺, Ca⁺, and Ba⁺ combining with O₂, CO, or CO₂ using He as third body. If we take such an ion-molecule rate constant as a plausible upper bound on analogous neutral rate constants, then the termolecular contributions to effective bimolecular rate constants measured in 0.75 Torr of He would be less than 7×10^{-14} cm³·s⁻¹, only 15% of the slowest Ti + OX bimolecular rate constant in Table II. Barring highly attractive chemical forces between Ti(a³F) and OX, which are unlikely in view of the small observed reaction rates, we expect bimolecular processes to dominate in our conditions.

The efficiencies of the O-atom abstraction reactions of $Ti(a^3F)$ with the three oxidants NO, O_2 , and N_2O are quite small at 300 K. On average, a successful oxygen atom transfer to ground-state Ti requires about 32 hard-sphere collisions with NO, 170 collisions with O_2 , and 640 collisions with N_2O ,²³ in spite of the exothermicities of 10, 41, and 121 kcal/mol, respectively. This indicates that all three reactions encounter substantial barriers or steric constraints. The inverse relationship between reaction rates and exothermicities suggests that the electronic factors underlying the inefficiency of the reactions vary substantially among the three oxidants. However, even subtle energetic differences in the entrance channel could cause the observed factor of 20 range of rate constants at 300 K. If we assume equal Arrhenius A factors, the range in 300 K bimolecular rate constants corresponds to only a 2 kcal-mol⁻¹ difference in activation energy.

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⁽²³⁾ Ti diameter estimated from 2(r) for the 4s orbital of the a³F Hartree-Fock wave function; TiO diameter is a rough estimate. See: Fischer, C. F. *The Hartree Fock Method for Atoms*; Wiley: New York, 1977. Other diameters from: Hirschfelder, J. O.; Curtiss, C. F.; Bird, R. B. *Molecular Theory of Gases and Liquids*; Wiley: New York, 1954; Table I-A.

The electron jump ("harpoon") mechanism²⁴ responsible for the large cross section of the Ba + NO₂ reaction, 7a for example, cannot explain the magnitudes or the ordering of the observed Ti + OX reaction rates. Electron jump cross sections calculated from the crossing point of the diabatic neutral Ti + OX and ion pair Ti⁺ + OX⁻ one-dimensional curves²⁵ are 14, 16, and 13 Å² for Ti + NO, O₂, and N₂O, respectively. These are smaller than the estimated hard-sphere collision cross sections of $\sim\!45$ Ų, yet 10-200 times larger than the observed average reaction cross sections $\langle \sigma \rangle = k / \langle v \rangle$ (Table II). Harpooning does not increase the cross section for close encounters beyond the usual hard-sphere estimate. This does not preclude ionic Ti⁺-OX⁻ character from playing an important role along successful reaction paths. It does indicate that the onset of covalent, chemical forces and of ion pair formation would occur at similar Ti + OX separations.

Electronic state correlation diagrams^{26,27} connecting reactant states to intermediate states to product states are often useful in explaining the size of reaction cross sections and the product branching ratios for electronically simple reactions such as Ar⁺ + H_2 or He^+ + H_2 . However, they are less obviously useful for reactions involving the electronically more complex transitionmetal atoms. Ti(a³F) brings substantial spin and orbital angular momentum to the collision. Ground-state reactants thus tend to correlate adiabatically with many, if not all, energetically accessible product channels, resulting in few symmetry restrictions on ground-state reactivity. For example, no less than 84 potential energy surfaces, including quartet and doublet $\Delta,\,\Phi,\,and\,\,\Gamma$ terms in $C_{\infty v}$ symmetry, emanate from Ti(a³F) + NO(x²\Pi) ground state reactants. In gas-phase transition-metal cation chemistry, we now know that the surfaces that provide the low-energy paths to products frequently correlate diabatically with excited-state reactants; surface intersections are therefore crucial in the ground-state chemistry.1 This is almost surely the case for most neutral transition-metal atoms as well, since we expect $3d^{n-2}4s^2$ ground states to be chemically inert due to the large spatial extent of the closed 4s subshell. In addition, we know nothing about the electronic structure of chemical intermediates of stoichiometry TiNO, TiO₂, and TiN₂O. In more favorable circumstances,²⁷ the known structure of the intermediate would guide arguments about the qualitative behavior, either attractive or repulsive, of diabatic surfaces arising from different reactant asymptotes.

For all three reactions, in the limit of weak spin-orbit coupling,²⁸ ground-state Ti($a^{3}F$) + OX reactants in C_s symmetry correlate adiabatically with ground-state products as well as a large fraction of the other product channels energetically accessible (Table III). In order to understand why these oxygen atom abstraction reactions are nevertheless inefficient, we separate the reaction into two conceptual steps: O-X bond breaking and Ti-O bond formation. Following Mahan,²⁷ we ask how the electron configuration and total state symmetry must evolve from specified states of Ti + OX reactants to specified low-energy, separated "atom" states of Ti + O + X to specified TiO + X product states. This kind of correlation argument, based on separated atom rather than intermediate [TiOX] symmetries and orbital occupancies, 29,30 has the advantage that the states and configurations of $\mathrm{Ti}+\mathrm{O}+\mathrm{X}$ are well-known. It is of course improbable that reactive trajectories actually pass through regions of phase space well described by separated atom states. The qualitative argument asserts that if ground-state reactants and a set of specified product states both

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Figure 6. Schematic correlation diagram for Ti + OX \rightarrow TiO + X reaction with OX = NO and O_2 , and N_2O . Solid lines indicate adiabatic correlations; dashed lines (at right) indicate "diabatic" correlations in the sense of conservation of electron configuration. When adiabatic and diabatic correlations coincide, solid lines are used. A barrier on the adiabatic surface connecting ground-state reactants with low-lying products might arise from the need to change electron configuration from $Ti(3d^24s^2, a^3F) + OX$ to low-lying $TiO(...9\sigma^1) + X$ products. Dotted lines (at left) show spin-conserving correlations in the case of $OX = N_2O$. See text for details.

correlate to the same low-energy Ti + O + X asymptote, in both the electron configuration and total electronic state symmetry senses of the word correlate,²⁹ then we expect no barriers on the adiabatic surfaces connecting ground-state reactants to specified product states.

From the point of view of Ti-O bond formation, all three ground-state reactions suffer from the chemically inert Ti- $(3d^24s^2,a^3F)$ configuration. The 9σ molecular orbital of TiO is primarily Ti(4s) with some admixture of Ti(4p) to polarize the orbital away from the negative O ligand.³¹ The ground state and several low-lying excited states of TiO (Table III) have approximate charge distributions Ti⁺O⁻, with atomic Ti population roughly $3d^24s$ (9σ singly occupied). All but one of the low-lying TiO states have 9σ either singly occupied or empty; the only exception is $d^{1}\Sigma^{+}$ (9 σ^{2} occupancy) at excitation energy of 0.7 eV. Thus the 4s² ground state of Ti must correlate orbitally with highly excited products. The lowest energy Ti atom term with 4s singly occupied is $(3d^34s, a^5F)$ at 0.8 eV.² However, to prepare for covalent bonding, a Ti atom must decouple two of its 3d electron spins from the remaining 3d4s electrons to form a mixed state composed of more highly excited low-spin terms such as Ti-(3d³4s,b³F) at 1.5 eV. Analyzed in this fashion, all three reactions will likely have barriers in the entrance channels of the adiabatic surfaces connecting ground-state reactants to low-energy products (Figure 6). The barriers arise from the intersections of repulsive "diabatic" surfaces of Ti(3d²4s²) configuration with chemically attractive diabatic surfaces of Ti(3d³4s¹) character. This orbital correlation argument can explain the fact that all three reactions are slow at 300 K. The argument should be quite general for reactions of ground-state metal atoms having ns^2 configurations.

From the bond-breaking point of view, the O atom released from O-X during the collision must be in the $(2s^22p^4, {}^{3}P)$ ground state, rather than the (2s²2p⁴, ¹D) excited state, in order to optimize bonding with the chemically prepared Ti atom described above. $O(^{3}P)$, with two unpaired 2p electrons, can form one covalent σ bond, one covalent π bond, and one dative π bond with Ti, as required in the $X^{3}\Delta$ state of TiO. In contrast, O(¹D), with its paired 2p electron spins, can form only weaker dative bonds.³²

Nostrand-Reinhold: New York, 1979.

⁽²⁴⁾ Herschbach, D. R. Adv. Chem. Phys. 1966, 10, 319.

⁽²⁵⁾ The simple electron-transfer cross section is πR_x^2 , where $R_x = e^2/(IP)$ EI), IP is the first ionization energy of the metal, and EA is the electron affinity of the oxidant. This expression treats the neutral pair curve as flat as long range. Use of adiabatic electron affinities gives larger cross sections than would use of "vertical" electron affinities, especially for N₂O.
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The ground states of both NO($^{2}\Pi$) and O₂($^{3}\Sigma^{-}$) dissociate adiabatically to ground-state atomic asymptotes, namely $N(^{4}S)$ + $O(^{3}P)$ and 2 $O(^{3}P)$. Therefore, the bond-breaking processes in the Ti + NO, O₂ reactions should cause no electronic constraints in addition to those already arising from $Ti(4s^2)$. However, the N_2O reaction encounters the further difficulty, often noted in previous work,⁷⁻¹¹ that in order to conserve electron spin, the ${}^{1}\Sigma^{+}$ ground state must correlate diabatically to excited-state asymptotes $O(^{1}D) + N_{2}(^{1}\Sigma_{g}^{+}), 2.0 \text{ eV above } O(^{3}P) + N_{2}(^{1}\Sigma_{g}^{+}).$ For N₂O, the lowest energy reaction path requires hopping from reactant surfaces of $O(^{1}D)$ character to separated atom surfaces of $O(^{3}P)$ character in order to access low-energy product states. This further constraint may account for the relatively slow N₂O reactions with Ti and with other neutral and ionic metals as well.

Biondi and co-workers¹⁴ found that Ti⁺, presumably in its ground state $(3d^34s, a^4F)$, reacts with O₂ at the Langevin collision rate and with NO at about 1/5 of the Langevin rate at 300 K. The X² Δ ground state of TiO⁺ has 9 σ unoccupied, so once again we expect avoided crossings of repulsive diabatic surfaces from ground-state Ti⁺(3d²4s) and attractive diabatic surfaces from excited states of Ti⁺ having 3d³ configurations. Yet the barriers to ground-state reaction are apparently substantially smaller in $Ti^+ + OX$ than in Ti + OX, for X = O and N. One important difference is the smaller promotion energy to atomic states of the optimal configuration.² For the ionic reactions, Ti⁺(3d³,b⁴F) lies at 1030 cm⁻¹ and Ti⁺($3d^3$, a^2G) lies at 9060 cm⁻¹; for the neutral case, $Ti(3d^34s,a^5F)$ lies at 6660 cm⁻¹ and $Ti(3d^34s,b^3F)$ lies at 11 640 cm⁻¹. In addition, the ion-induced dipole force should make the ground-state Ti⁺ + OX diabatic surfaces less repulsive than those of Ti + OX. Both effects will tend to push the location of

Conclusion

In summary, the separated atom, orbital correlation arguments presented here appear useful in explaining the general inefficiency of O atom transfer reactions to the neutral Ti(3d²4s²,a³F) ground state and to other metal atoms with ns^2 configurations as well. Yet much is left unexplained. We have no rationale at present for the intriguing fact that the $Ti(a^{3}F) + NO$ reaction is 5 times faster than $Ti(a^{3}F) + O_{2}$, while $Ti^{+}(a^{4}F) + NO$ is 5 times slower than $Ti^+(a^4F) + O_2$.

Finally, the same orbital considerations suggest, for example, that 3d³4s excited states of Ti such as a⁵F and b³F should abstract oxygen atoms much more efficiently than the 3d²4s² ground state studied here. Accordingly, Dubois and Gole⁸ observed chemiluminescence from reaction of a metastable Ti excited state with O_2 and tentatively identified the reactive state as a^5F based on the TiO states observed in emission. We look forward to direct measurement of the effect of electronic excitation of transitionmetal atoms on the efficiency of gas-phase oxidation reactions.

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Atomization Energies of the Gaseous Molecules LaC and La₂C by High-Temperature **Equilibrium Measurements**

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The Knudsen effusion mass spectrometric technique has been used to determine the thermodynamic properties of the molecules LaC and La₂C. The enthalpies of the reactions La(g) + C(graphite) = LaC(g) and 2La(g) + C(graphite) + La₂C(g) were measured in two runs in the temperature ranges 2286-2609 and 2767-2835 K, respectively, resulting in ΔH_0° (reaction 1) = 253 ± 18 kJ mol⁻¹ and ΔH_0° (reaction 2) = -234 ± 25 kJ mol⁻¹. From these values the atomization energies, $\Delta H_a^{\circ}_{0}$, and standard heats of formation, $\Delta H_{f}^{\circ}_{298.15}$, were obtained as 458 ± 20 and 685 ± 20 kJ mol⁻¹ for LaC and 945 ± 28 and $625 \pm 28 \text{ kJ mol}^{-1}$ for La₂C.

Introduction

Rare-earth monocarbides are not well-known, and only CeC has been measured and characterized, by Gingerich and coworkers.^{1,2} Two actinide metal carbides, UC³ and ThC⁴ have also been investigated recently. This class of compounds is interesting from a scientific point of view to define the strength and the nature of the M-C bond, as well as for the application of the corresponding solid monocarbides as technological materials.

A major problem concerning the measurements by mass spectrometric equilibrium investigation is that their measured ion intensity is mostly due to fragmentation of the corresponding MC₂ molecules, which is the most abundant equilibrium specie in the respective vapor phase. In fact, because of the relative electropositivity of the rare-earth metals and of the pseudo-oxygen character of the C₂ group, the D_0° of the mostly polar Ce-C₂ bond is as high as 680 kJ mol⁻¹ as compared to 441 kJ mol⁻¹ of the CeC bond.² A reverse situation characterizes the platinum-group metal monocarbides where these species are the most abundant in the gas phase and the respective bond enthalpies, D_0° , of the mostly covalent bond between the electronegative transition metal and

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