

Kinetics of Ti(a^3F , a^5F) and V(a^4F , a^6D) Depletion by NH_3 and H_2S

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The kinetics of depletion of ground-state Ti(a^3F) and V(a^4F) and excited-state Ti(a^5F) and V(a^6D) upon interactions with NH_3 and H_2S are studied in a fast-flow reactor at a He pressure of 0.70 Torr. No depletion of ground-state Ti(a^3F) and V(a^4F) was observed upon interaction with NH_3 . Depletion of Ti(a^3F) and V(a^4F) by H_2S did occur but inefficiently, with measured effective 300 K bimolecular rate constants of $(0.44 \pm 0.12) \times 10^{-12}$ and $(4.0 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. In contrast to the ground-state metals, depletion of excited-state metal atoms Ti(a^5F) and V(a^6D) by NH_3 and H_2S occurred efficiently. The measured effective rate constants for depletion of Ti(a^5F) by NH_3 and H_2S are $(39 \pm 11) \times 10^{-12}$ and $(142 \pm 13) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively. The measured rate constants for depletion of V(a^6D) with these respective gases are $(95 \pm 8) \times 10^{-12}$ and $(69 \pm 5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The reactive differences between the ground and excited states as well as between metals provide important clues about N–H and S–H bond activation in these systems.

Introduction

Information about the gas-phase kinetics for the reactions of simple molecules with transition-metal atoms provides fundamental information about catalytic bond activation. Since the report that transition-metal cations could aggressively activate hydrocarbon bonds,¹ a large number of studies involving the reactivity of transition-metal cations with simple hydrocarbons,² NH_3 (and other simple amines),^{3–7} and H_2O and other alcohols^{8–11} have been carried out, and a detailed understanding of what is necessary to activate C–C, C–H, N–H, and O–H bonds has been gained.² Recently, several studies of the kinetics associated with activation of hydrocarbons and a few other small species by ground-state 3d-series neutral transition metals have shown that these species are relatively inert compared with their cationic counterparts.^{12–19} In general, though, much less is known about bond activation by neutral transition-metal atoms. In this work, we have studied the activation of NH_3 and H_2S by neutral titanium and vanadium atoms. In addition to the gas-phase interest, the activation of σ bonds involving nitrogen and sulfur is of topical interest in the condensed phase.^{20–26}

A controlling factor in the rich chemistry observed for transition metals is the high density of low-lying electronic states, which results from the near degeneracy of the valence s and d orbitals. Many reaction systems involving bond activation by metal cations show drastic differences in efficiency, depending upon the initial state of the metal.²⁷ It is clear that a true understanding of the catalytic role that the metal ion plays can only be obtained if its initial state is well characterized. It seems likely that similar characterizations of the electronic states of neutral metal atoms will also be necessary to understand the reactivity of these systems.

The only reaction systems in which the reactivity of different electronic states of neutral metal atoms has been studied in detail are the reactions of neutral Ti and V with NO , O_2 , and N_2O . These studies show that the first excited states of these metal atoms [Ti(a^5F) and V(a^6D)]^{28–30} react more efficiently than the ground states [Ti(a^3F) and V(a^4F)]^{31–33} by more than 2 orders of magnitude. In order to explain the state-specific behavior,

two reaction mechanisms have been proposed: direct abstraction and electron transfer. In the first mechanism, the oxygen atom is directly abstracted by the neutral metal atoms. In this mechanism, low-lying metal oxide product states have electron configurations that can correlate to the Ti($4s^13d^3$) and V($4s^13d^4$) excited states but not to the Ti($4s^23d^2$) and V($4s^23d^3$) ground states. Consequently, reaction barriers may arise along the surfaces for the ground-state metal atoms, explaining the inefficiency of the reaction.

In the electron-transfer (ET) mechanism, the potential energy surfaces evolving from the ground and excited neutral metal atom states cross an ion-pair surface. In this mechanism, the metal transfers an electron to the reagent gas and the efficiency of the reaction is controlled by the distance at which the electron is transferred [or the difference between the ionization energy (IE) of the metal and the electron affinity (EA) of the reagent gas]. Because the effective ionization energies of the excited states are reduced (compared with the ground states), the potential energy surfaces evolving from these states cross the ion-pair surface at longer ranges, and thus, the reactions occur more efficiently.

Both the direct and ET mechanisms can explain the reactive differences between the ground and excited metal atom states. However, when the reactivities of the different metal systems, Sc, Ti, and V with a single oxidant gas are compared, the direct mechanism predicts that the ground-state reaction rate constants should increase as $k(\text{Sc}) < k(\text{Ti}) < k(\text{V})$, because the energy differences of the $4s^23d^{n-2}$ (where n is the number of valence electrons) ground state and $4s^13d^{n-1}$ first excited state are 1.43, 0.81, and 0.26 eV, respectively. However, the measured rate constants for a single oxidant gas are fairly similar for all three metals and the actual ordering is $k(\text{Ti}) < k(\text{V}) < k(\text{Sc})$. Thus, the direct mechanism cannot account for the ordering between systems. On the other hand, the experimental ordering of the rate constants correlates with the ionization energies of the metals. Thus, the ET mechanism can account for the qualitative reactive differences observed.

In this work, we have studied the activation of NH_3 and H_2S by the ground and first excited states of neutral titanium and vanadium atoms [i.e., Ti(a^3F), Ti(a^5F), V(a^4F), and V(a^6D)]. We have chosen to study the present systems for several reasons. First, both molecules possess lone pairs of electrons that can

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enhance bonding. Therefore, products such as MS and MNH should be formed exothermically at 300 K. (Product formation is discussed in detail below.) Second, the NH_3 and H_2S reagents are isoelectronic (in the sense that the central heavy atom has the same number of valence electrons with the same sp^3 hybridization).³⁴ Therefore, if NH_3 and H_2S are activated by the same mechanism, then the reactive differences between the Ti and V metals should be similar for both gases. For the metal cations, there are many similarities in the reactivity along the isoelectronic CH_4 ,³⁵⁻³⁷ NH_3 ,^{5,6} and H_2O ^{8,38} series, and the reactive ordering of the metals is the same for all of these simple systems (i.e., the reaction rate constants increase as $V^+ < Ti^+ < Sc^+$ for all three of these systems as well as other related ones). However, although NH_3 and H_2S are isoelectronic, they have very different electron affinities. None of the low-lying states of NH_3 will bind an electron, while $EA(H_2S) = 1.1$ eV.³⁹ Therefore, these systems provide an ideal case for testing whether or not the ET mechanism (which appears to control the oxidation of these metals by NO , O_2 , and N_2O) can influence a rather complex bond activation process such as dehydrogenation. Finally, we have studied the present systems because no kinetic data have been reported for the reactions of specific states of Ti and V with NH_3 and H_2S . Thus, our results will extend the kinetic data base available for neutral metal atom reactions.

The present experiments involving the state-specific reactions of Ti and V with ammonia are closely related to the spin-specific reactions of Ti^+ and V^+ with ammonia reported by Clemmer, Sunderlin, and Armentrout (CSA).^{5,6} CSA found that the ground [high spin, $Ti^+(a^4F)$ and $V^+(a^5D)$] state could dehydrogenate ammonia exothermically to form M^+NH . Their results for the excited, low-spin, doublet states of Ti^+ and triplet states of V^+ showed that these states reacted more efficiently than the high-spin states by more than 2 orders of magnitude. The energy ordering of the high-spin and low-spin states of neutral Ti and V is the opposite of that observed for their cationic counterparts. That is, the ground states of neutral Ti and V are low-spin a^3F and a^4F , respectively, while the excited states we have chosen are the high-spin a^5F and a^6D states, respectively. Thus, this study should provide insight into the reactive differences between neutrals and cations.

Experimental Section

General. The flow tube/LIF instrument used in these experiments has been discussed in detail previously.²⁸ The basic idea is simple in concept. Metal atoms are reacted for a well-defined time period (at 300 K) with a reagent gas of known concentration. Then LIF is used to measure the intensity of unreacted metal atoms in a specific state by probing a known atomic transition.

A flow tube 45 cm long and having an i.d. of 4.5 cm was used in this study. He carrier gas was introduced at the end, directly into the source region. Metal atoms were created in a dc discharge source (described below) and carried downstream in the He buffer gas. The reagent gas (either NH_3 or H_2S) was introduced 24 cm downstream from the source. All gas flow rates were monitored by flowmeters (KOFLOC Model 3710) with flows being pumped from the instrument by a Roots blower. A small amount of Ar (always less than 5% of the He pressure) was added in order to stabilize the discharge. He (99.9999%), Ar (99.999%), NH_3 (99.99%), and H_2S (99.99%) 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.

TABLE 1: Configurations and Energies of the Low-Lying States of Ti and V^a

	config	term	J	energy, cm ⁻¹
Ti	3d ² 4s ²	a ³ F	2	0.000
			3	170.132
			4	386.874
	3d ³ 4s ¹	a ⁵ F	1	6 556.828
			2	6 598.749
			3	6 661.003
			4	6 742.757
			5	6 842.964
	3d ² 4s ²	a ¹ D	2	7 255.369
			0	8 436.618
	3d ² 4s ²	a ³ P	1	8 492.421
			2	8 602.340
			2	11 531.760
	3d ³ 4s ¹	b ³ F	3	11 639.804
			4	11 776.806
2			11 776.806	
V	3d ³ 4s ²	a ⁴ F	³ / ₂	0.000
			⁵ / ₂	137.38
			⁷ / ₂	323.44
	3d ⁴ 4s ¹	a ⁶ d	⁹ / ₂	552.96
			¹ / ₂	2 112.28
			³ / ₂	2 153.21
			⁵ / ₂	2 220.11
			⁷ / ₂	2 311.76
	3d ⁴ 4s ¹	a ⁴ D	⁹ / ₂	2 424.78
			¹ / ₂	8 413.06
			³ / ₂	8 476.23
			⁵ / ₂	8 578.53
			⁷ / ₂	8 715.76

^a Data are taken from ref 40.

Metal Atom Source. Metal atoms were produced in a dc discharge source where the cathode was made of either titanium or vanadium metal (Nilaco, 99.5%). A flow of ~95–99% He and 1–5% Ar was passed over the metal cathode that was biased from -2.0 to -3.5 keV with respect to the flow tube. Ar^+ and He^+ created in the discharge were accelerated toward the metal cathode, and metal atoms were sputtered off. The resulting metal atoms underwent $\sim 2 \times 10^4$ collisions with He, and ~ 500 collisions with Ar before reaching the reaction region. Table 1 lists the low-lying electronic states, configurations, and energies of Ti and V.⁴⁰ Because the transitions between the low-lying excited states are spin and parity forbidden, the radiation lifetimes of these excited states are expected to be on the order of seconds long.^{41,42}

General Flow Characteristics. According to the pressures and flow rates used in our flow tube, the distance necessary for He to develop a characteristic parabolic velocity profile is ~ 8 cm. Because the reagent inlet is located 24 cm downstream from the end of the flow tube, the flow should be fully developed before metal atoms reach the reaction region. The reaction region temperature was measured to be 296 K (essentially room temperature) at a discharge voltage of 2.5 keV and a total pressure of 0.70 Torr. Because the temperature in our laboratory may have fluctuated during the several months over which these experiments were carried out, rate constants are reported at 300 K.

The time that the metal atoms spend in the reaction region was determined to be 2.0×10^{-3} s by using a pulse laser to vaporize the metal and measuring the time delay for observation of chemiluminescence at the detection region. For this chemiluminescence detection, we used same optics as the LIF detection. The optics is designed to collect the emission from only a limited region such that the detection region is smaller than the laser excitation region. Therefore, we believe that the chemiluminescence detection provides the time for metal atoms reaching the LIF detection region. The metal atom velocity is significantly higher than the bulk flow velocity calculated for

TABLE 2: LIF Transitions Used To Probe Ti(a³F), Ti(a⁵F), V(a⁴F), and V(a⁶D)^a

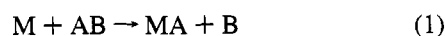
species	transition	energy, cm ⁻¹	wavelength, nm
Ti(a ³ F)	y ³ F ₂ -a ³ F ₂	25 107.417	398.29
	y ³ F ₃ -a ³ F ₃	25 057.085	399.09
	y ³ F ₄ -a ³ F ₄	25 001.460	399.98
Ti(a ⁵ F)	x ³ D ₀ -a ⁵ F ₁	23 272.269	429.70
	x ³ D ₁ -a ⁵ F ₂	23 256.499	429.99
	x ³ D ₂ -a ⁵ F ₃	23 246.270	430.18
	x ³ D ₃ -a ⁵ F ₄	23 243.428	430.23
	x ³ D ₄ -a ⁵ F ₅	23 217.364	430.71
V(a ⁴ F)	y ⁴ F _{3/2} -a ⁴ F _{3/2}	25 930.55	385.65
	y ⁴ F _{5/2} -a ⁴ F _{5/2}	25 866.85	386.60
	y ⁴ F _{7/2} -a ⁴ F _{7/2}	25 798.64	387.62
	y ⁴ F _{9/2} -a ⁴ F _{9/2}	25 618.96	390.34
V(a ⁶ D)	y ⁶ D _{3/2} -a ⁶ D _{1/2}	24 325.36	411.09
	y ⁶ D _{5/2} -a ⁶ D _{3/2}	24 352.72	410.63
	y ⁶ D _{7/2} -a ⁶ D _{5/2}	24 384.69	410.09
	y ⁶ d _{7/2} -a ⁶ D _{7/2}	24 293.04	411.64
	y ⁶ D _{9/2} -a ⁶ D _{9/2}	24 313.54	411.29

^a Energies and wavelengths are derived from data in ref 40.

He. This indicates that the metal atom density is largest in the center of the flow tube where the He axial velocity is largest. Sticking of metal atoms to the flow tube surface is expected to be efficient.^{32,43}

LIF Detection. Metal atom number densities in specific states were measured by using unsaturated LIF, as verified by linearity in the LIF signal with laser power. The transitions and energies used for detection Ti(a³F), Ti(a⁵F), V(a⁴F), and V(a⁶D) are given in Table 2. A frequency-doubled Nd:YAG (10 Hz, 10 ns FWHM) laser (Continuum NY-82) was used to pump a tunable titanium-sapphire laser (Continuum TS-60) capable of generating intense light from ~740 to 900 nm. To obtain the wavelengths of light used in these studies, light from the titanium-sapphire laser was frequency doubled by using a KDP crystal. A band-pass filter (HOYA CM-500) was used to eliminate fundamental radiation. Over several hours, the intensity of the laser was stable to within ±20%. Spectrally unresolved fluorescence was collected by a lens system and focused through a 2.0-mm slit into 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 time-integrated rate expression for the simple bimolecular process 1 involving depletion of a metal atom (M) by a reagent gas (AB) is given by eq 2. Here, $M(n_{AB})$ is the metal atom concentration, M_0 is



$$\ln[M(n_{AB})/M_0] = -k_{rxn}t_{rxn}n_{AB} \quad (2)$$

the metal atom concentration when no reactant gas is present, k_{rxn} is the bimolecular rate constant, t_{rxn} is the mean reaction time, and n_{AB} is the reactant number density. For excited-state metal atoms (M*) such as Ti(a⁵F) and V(a⁶D), quenching, process 3, might also deplete the reactant M* signal. In such



a case, the time-integrated rate expression is given by eq 4, where k_q is the quenching rate constant for processes 4. It is

$$\ln[M(n_{AB})/M_0] = -(k_{rxn} + k_q)t_{rxn}n_{AB} \quad (4)$$

conceivable that termolecular association reactions that lead to the formation of an MAB adduct could deplete the measured

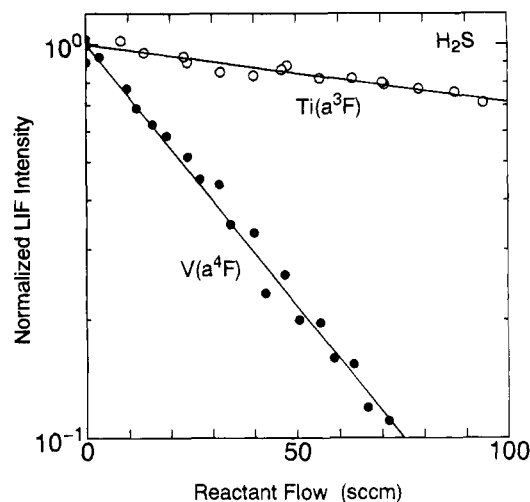


Figure 1. Semilogarithmic plots of the $M(n_{AB})/M_0$ LIF intensities for Ti(a³F) and V(a⁴F) vs flow of H₂S. The solid lines are optimized least-squares fit of eq 2 to the data.

M atom signal. However, as discussed previously (and shown below),²⁸ adduct formation is expected to be very inefficient and is not important in these studies.

Because the depletion signal that we measure could be affected by reactions 1 and 3, our reported rate constants are referred to as *effective* values rather than absolute values. Effective state-specific 300 K bimolecular rate constants were derived by fitting semilogarithmic plots of the data using a least-squares routine. We report 2σ uncertainties for the precision of the fits to multiple data sets. The absolute accuracies of the rate constants are estimated to be ±30% for Ti(a³F), V(a⁴F), and V(a⁶D) and ±40% for Ti(a⁵F). A comparison of our rate constants for the reactions of NO and O₂ with ground-state Ti(a³F) and V(a⁴F) and excited-state V(a⁶D) to rate constants measured by other groups shows that the present instrument is capable of making highly accurate measurements on these types of systems.²⁸ The accuracies are limited mainly by fluctuations in laser power and source atom production. 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 $\sim 5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ based on our ability to easily observe a 5% decrease in our signal at a reagent gas flow rate of 100 sccm.

Results

Reactions of Ground-State Ti(a³F) and V(a⁴F). Depletion of ground-state Ti(a³F₂) and V(a⁴F_{3/2}) upon interaction with NH₃ was not observed for flow rates up to 100 sccm. This indicates that the bimolecular reaction rate constant is less than $0.05 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and that adduct formation is insignificant (as discussed above).

Depletion of the ground-state metal atoms by H₂S was observed. Figure 1 shows semilogarithmic plots of the $M(n_{AB})/M_0$ signals for depletion of Ti(a³F₂) and V(a⁴F_{3/2}) at H₂S flow rates from 0 to 100 sccm and a He pressure of 0.70 Torr. Clearly, V(a⁴F_{3/2}) is depleted more rapidly than Ti(a³F₂). The plots for the three *J* levels of Ti(a³F_{*J*}) and four *J* levels of V(a⁴F_{*J*}) are indistinguishable within the uncertainty of the data. This is shown for V(a⁴F_{*J*}) in Figure 2. Analysis of the data lead to effective bimolecular rate constants for depletion of Ti(a³F_{*J*}) and V(a⁴F_{*J*}) of (0.44 ± 0.12) and $(4.0 \pm 0.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively.

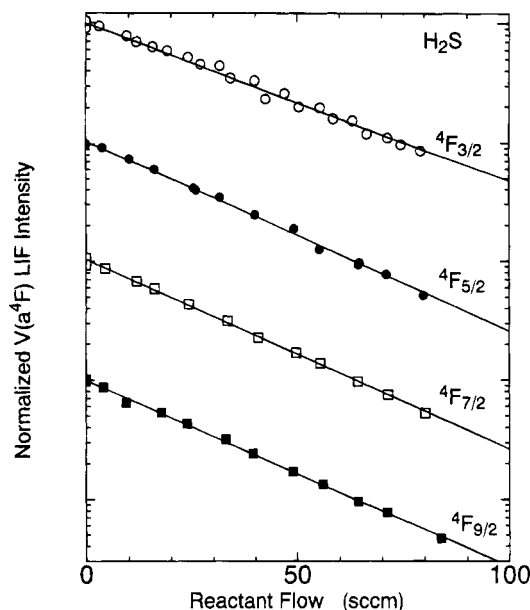


Figure 2. Semilogarithmic plots of the $M(n_{AB})/M_0$ LIF intensities for four J levels of $V(a^4F_j)$ vs flow of H_2S . The solid lines are optimized least-squares fits of eq 2 to the data.

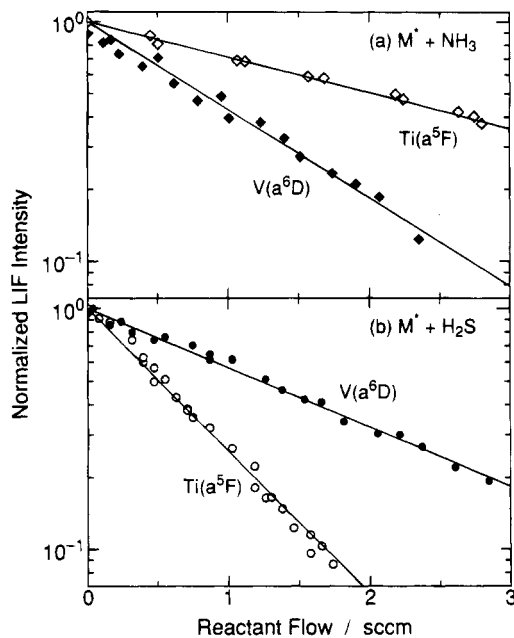


Figure 3. Semilogarithmic plots of the $M(n_{AB})/M_0$ LIF intensities for $Ti(a^4F)$ and $V(a^6D)$ vs flow of NH_3 (a) and H_2S (b). The solid lines are optimized least-squares fits of eq 2 to the data.

Reactions of Excited-State $Ti(a^5F)$ and $V(a^6F)$. Figure 3 shows semilogarithmic plots of the $M(n_{AB})/M_0$ signals for depletion of excited-state $Ti(a^5F_2)$ and $V(a^6D_{1/2})$ by NH_3 and H_2S (over a range of 0–3 sccm) at a He pressure of 0.70 Torr. All of the spin-orbit states listed in Table 2 were studied, and no differences in the depletion rates are observed. The most striking difference between these data and those for the ground-state metal atoms is that rapid depletion of both excited-state $Ti(a^5F)$ and $V(a^6D)$ is observed upon interaction with both of the reagent gases. It is also clear that excited-state $Ti(a^5F)$ is depleted more rapidly than excited-state $V(a^6D)$ by H_2S , while the reverse is true for depletion by NH_3 . The effective bimolecular rate constants derived for the depletion of $Ti(a^5F)$ from interactions with NH_3 and H_2S are (39 ± 11) and $(142 \pm 13) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, respectively, and the rate constants for

TABLE 3: Effective Bimolecular Rate Constants for Reactions of $Ti(a^3F)$, $Ti(a^5F)$, $V(a^4F)$, and $V(a^6D)$ with NH_3 and H_2S at 300 K

reactants	k , $10^{-12} \text{ cm}^3 \text{ s}^{-1}$, (0.7 Torr He)	k_{HS}/k_{exp}^a	E_{max}^b , kcal/mol
$Ti(a^3F_2) + NH_3$	NR ^c		
$Ti(a^3F_2) + H_2S$	0.44 ± 0.12	582	3.8
$Ti(a^5F_1) + NH_3$	39 ± 11	7.3	1.2
$Ti(a^5F_1) + H_2S$	142 ± 13	1.8	0.4
$V(a^4F_{3/2}) + NH_3$	NR		
$V(a^4F_{3/2}) + H_2S$	4.0 ± 0.2	61	2.4
$V(a^6D_{3/2}) + NH_3$	95 ± 8	2.9	0.6
$V(a^6D_{3/2}) + H_2S$	69 ± 5	3.5	0.7

^a Calculated by comparison of our experimental k 's to k_{HS} (see ref 48). ^b Values of E_{max} are estimated from the Arrhenius equation, $E_{max} = -RT \ln(k_{300}/k_{HS})$. ^c No reaction was observed. This implies that $k \leq 5 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ as discussed in the text.

depletion of $V(a^6D)$ by these respective gases are (95 ± 8) and $(69 \pm 5) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. These values are tabulated in Table 3.

The observation of no systematic dependence of the depletion of different J levels for ground-state metal atoms $Ti(a^3F_j)$ and $V(a^4F_j)$ is similar to the results of these metal atoms by NO , O_2 , and N_2O .^{12,28,32,33} These results indicate that either the reaction rate constants for individual J levels are the same within the experimental sensitivity or the reaction rate is much slower than the interconversion of J levels from collisions with He or Ar or the reactant gas. The dearth of J dependence for the excited-state metal atoms also indicates either that the reaction rates for different J levels are the same or that the reaction rate is much slower than the interconversion rates. However, in the latter case, collisional interconversion must come from interactions with He or Ar since collisions with NH_3 or H_2S deplete the excited-state signal with high efficiency (Table 3).

Discussion

Collisional Quenching of Excited-State $Ti(a^5F)$ and $V(a^6D)$.

Because the LIF signals for electronically excited metal atoms could be depleted by collisional quenching (process 3), it is important to consider the efficiencies of the quenching processes. A good place to begin is to consider the kinetics of depletion of M^* by N_2 since no bimolecular chemical processes are thermodynamically feasible. The rate constant for quenching $Ti(a^5F)$ with N_2 is $k_q = (6.5 \pm 2.2) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, as we reported previously. We have also measured the rate constant for quenching $V(a^6D_{3/2})$ by N_2 to be $k_q = (0.50 \pm 0.03) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, in good agreement with the very precise value $k_q = (0.562 \pm 0.083) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, measured previously by a laser photolysis/LIF technique.³⁰ These quenching rates are slow, however, polyatomic NH_3 and H_2S may be much more efficient quenchers than diatomic N_2 .

A more direct test of whether or not quenching is important in the depletion of M^* by NH_3 and H_2S can be obtained by considering LIF signal for ground-state $V(a^4F)$. By comparing the LIF intensities of all of the $V(a^4F)$ and $V(a^6D)$ transitions we have observed, we estimate that population of excited-state $V(a^6D)$ atoms to be $\sim 10\%$ as large as the population of $V(a^4F)$ atoms.⁴⁴ If the quenching of $V(a^6D)$ is dominant in the depletion of NH_3 and H_2S , it should be possible to detect an increase of the LIF signal of $V(a^4F)$ with an increase of the reactant flow rate. Because no increase in the ground-state $V(a^4F)$ LIF signal was observed upon addition of NH_3 and H_2S , we are certain that quenching cannot account for the large depletion rate constants measured in the $V(a^6D)$ systems.⁴⁵ Assuming that values of k_q for the $Ti(a^5F)$ and $V(a^6D) + NH_3$ and H_2S systems

TABLE 4: Pertinent Reagent 298 K Thermochemistry (kcal/mol)^a

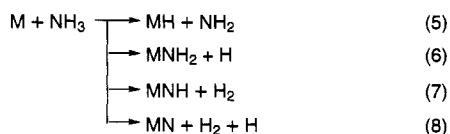
bond	D ⁰	M-L	D ⁰ (Ti-L)	D ⁰ (V-L)
H-H	104.106(0.003) ^b	M-H	48.9(2.1) ^c	41(4) ^d
H ₂ N-H	108.3(0.3) ^e	M-NH ₂	66 ^f	79 ^f
HN-H ₂	100.4(0.3)	M-NH	86 ^f	99 ^f
N-H	79.7(0.3)	M-N	114(8) ^g	114(2) ^h
HS-H	91.1(1.0) ⁱ	M-SH	NA	NA
S-H ₂	70.5(1.0)	M-S	99.9(0.7) ^j	115(2) ^k

^a All values except where noted are from the JANAF Tables: Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *J. Phys. Chem. Ref. Data* **1984**, *14 Suppl. 1*. Uncertainties are in parentheses. ^b Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure, IV. Constants of Diatomic Molecules*; van Nostrand Reinhold: 1979. ^c Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *95*, 1228. ^d Chen, Y.-M.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1993**, *98*, 4929. ^e Derived from thermochemistry given in: Anderson, W. R. *J. Phys. Chem.* **1989**, *93*, 530. ^f Estimated from ionic bond energies; see detail in text. ^g Sterarns, C. A.; Kohl, F. J. *High Temp. Sci.* **1970**, *2*, 146. ^h Farber, M.; Srivastava, R. D. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 390. ⁱ McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493. ^j Edwards, J. G.; Franklin, H. F.; Gilles, P. W. *J. Chem. Phys.* **1971**, *54*, 545. ^k Botor, J. P.; Edwards, J. G. *J. Chem. Phys.* **1984**, *81*, 2185.

are similar to those measured for the N₂ systems shows that quenching accounts for less than 5% of the signal decrease in all the systems, with the exception of Ti(a⁵F) + NH₃, where quenching could account for as much as 15%.

The large differences in the depletion rate constants that we have measured for H₂S and NH₃ compared with the quenching rate constants for N₂, combined with our inability to observe an increase in the signal for ground-state V(a⁴F) upon addition of the reagent gases, suggest that M* reacts with the reagent gases. Therefore, we assume for the remaining portion of this work that the primary depletion processes for Ti(a⁵F) are via reaction rather than quenching. This assumption is reasonable since the quenching of the excited states of other metal atoms by polyatomic molecules has been reported to be inefficient.⁴⁶ However, it is worth noting that we are cautious in this assumption since we cannot rule out the possibility that quenching is the dominant depletion pathway.

Consideration of Reaction Products. There is no existing experimental information about the products for the reactions of neutral Ti and V with NH₃ or H₂S.⁴⁷ However, progress in understanding the neutral systems can be made by comparison to the cation reaction systems (where product information is available) and by considering which reactions are exothermic at 300 K. For the reactions of Ti⁺ and V⁺ with NH₃ and H₂O (the H₂O results should be similar to the H₂S system studied here), only singly ligated ML⁺ products are observed under bimolecular reaction conditions. Assuming that only single ligand products are formed in the neutral systems, then only reactions 5–8 are possible for interaction of Ti and V with NH₃.

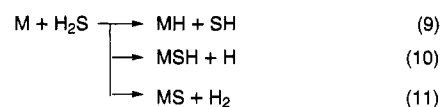


From the known MH, MN, and ammonia thermochemistry given in Table 4, and the electronic excitation energies given in Table 1, we calculate that reaction 5 for Ti(a³F), Ti(a⁵F), V(a⁴F), and V(a⁶D) is endothermic by 59 ± 2, 41 ± 2, 67 ± 4, and 61 ± 4 kcal/mol and reaction 8 is endothermic by 62 ± 8, 43 ± 8, 62 ± 3, and 56 ± 3 kcal/mol for these respective metal systems. Thus, we rule out the possibility that MH or MN is formed in

these experiments. Although the thermochemistry for neutral MNH₂ has not been measured experimentally, a reasonable estimate of the bond strength can be obtained from the intrinsic⁴⁸ bond energy for the ionic M⁺NH₂ species, ~85 kcal/mol, determined for early transition metals.⁴⁹ When these values are corrected for the promotion energies of neutral Ti and V, the bond energy estimates for M-NH₂ given in Table 4 are obtained. These M-NH₂ bond energies (which are strictly upper limits to the upper values) can be combined with other thermochemistry in Tables 1 and 4 to calculate that reaction 6 for Ti(a³F), Ti(a⁵F), V(a⁴F), and V(a⁶D) is endothermic by at least 42 ± 2, 24 ± 2, 29 ± 4, and 23 ± 4 kcal/mol. Clearly, even if large uncertainties were accrued upon our estimation of the M-NH₂ bond energy it is likely that this reaction is still endothermic. Therefore, we rule out reaction 6 as a possible means of explaining our data.

The only remaining process is dehydrogenation, reaction 7. For the ionic systems, the bond energies for M⁺-NH are stronger than those for M⁺-NH₂ by ~20 kcal/mol. If we assume that the same is true of the neutral systems, then the bond energies listed in Table 4 are obtained. In the titanium system, these values show that reaction 7 for ground-state Ti(a³F) is endothermic by ~14 kcal/mol and exothermic by ~5 kcal/mol for excited-state Ti(a⁵F). Therefore, according to this calculation, ground-state Ti(a³F) should not undergo reaction 7 while the excited state should, consistent with our experimental results (Table 3). The same is true for the vanadium system. Reaction 7 is calculated to be endothermic by ~1 kcal/mol for ground-state V(a⁴F) and exothermic by ~5 kcal/mol for excited-state V(a⁶D). Again these values are consistent with our experimental results (Table 3). We note that the uncertainty associated with our estimation of the thermochemistry for the process between V(a⁴F) and NH₃ is at least 3 kcal/mol. However, our inability to observe this process may support that this overall process is slightly endothermic.

Proceeding in the same manner for the M + H₂S system, three reactions are possible, reactions 9–11. By using the



thermochemistry given in Tables 1 and 4, we calculate that reaction 9 for Ti(a³F), Ti(a⁵F), V(a⁴F), and V(a⁶D) is endothermic by 42 ± 2, 23 ± 2, 50 ± 4, and 44 ± 4 kcal/mol, respectively. Thus, MH is not formed in these experiments. As for the MNH₂ molecule, the thermochemistry for MSH is not well established. Unfortunately, an intrinsic M⁺-SH bond energy has not been determined. Thus, it is difficult to proceed further in determining whether or not reaction 10 is important in these studies. However, the thermochemistry for MS is well established, and the data in Tables 1 and 4 allow us to calculate that reaction 11 for Ti(a³F), Ti(a⁵F), V(a⁴F), and V(a⁶D) is exothermic by 29 ± 1, 48 ± 1, 45 ± 2, and 50 ± 2 kcal/mol, respectively. Thus, we are certain that dehydrogenation is thermodynamically allowed for both the NH₃ and the H₂S systems.

Reaction Efficiencies and Activation Energies. The kinetic information, summarized in Table 3, shows that depletion of ground-state metal atoms by H₂S and NH₃ is inefficient while depletion of the excited-state metal atoms occurs quite efficiently for both molecules. One way to compare the efficiencies of the reactions studied here is to compare the measured rate constants to calculated hard-sphere rate constants, *k*_{HS}.⁵⁰ This comparison, given as *k*_{HS}/*k*_{exp} in Table 3, shows that dehydro-

generation of ammonia occurs on average in about seven collisions for Ti(a^5F) and three collisions for V(a^6D). For H_2S , the excited states Ti(a^5F) and V(a^6D) react very efficiently, roughly on every two or three collisions, respectively, while dehydrogenation by the ground-state atoms Ti(a^3F) and V(a^4F) requires ~ 580 and ~ 60 collisions, respectively.

Assuming that these systems are governed by an Arrhenius behavior [i.e., $k(T) = Ae^{-E/kT}$], the hard-sphere rate constants can be used as upper limits for the A factor (A_{max}), and upper limits for the activation energy (E_{max}) can be calculated. These results are also listed in Table 3 and range from 0.3 to 1.2 for Ti(a^5F) and V(a^6D). The E_{max} values for activation of H_2S by the ground-state metal atoms are larger, 3.8 and 2.4 kcal/mol, for Ti(a^3F) and V(a^4F), respectively.

Reaction Mechanisms. Dehydrogenation of NH_3 . In order to understand the mechanism for the dehydrogenation of NH_3 by neutral Ti and V, it is instructive to consider the detailed work that has been done for dehydrogenation of ammonia by Ti^+ and V^+ by CSA.^{5,6} As mentioned above, excited low-spin states of both metal ions were found to dehydrogenate ammonia more efficiently than the ground states by factors of 100 and ~ 160 for Ti^+ and V^+ , respectively. CSA explained this result by suggesting that the reaction proceeds through a HM^+NH_2 intermediate where the metal ion has inserted into an ammonia NH bond, followed by elimination of H_2 via a four-centered transition state.

Oxidative addition of NH to a metal center can be achieved by donation of electrons in σ -bonding orbitals into empty $4s$ and $3d\sigma$ orbitals on the metal and back-donation of metal $3d\pi$ electrons into σ^* -antibonding orbitals. This increases the electron density between the metal and the molecular fragments and also lengthens the $N-H$ bond. If the HM^+NH_2 intermediate that is formed contains covalent $M-H$ and $M-NH_2$ single bonds, then two of the valence electrons on M^+ are involved in bonding, those remaining are in nonbonding orbitals, and the ground states of HTi^+NH_2 and HV^+NH_2 should have doublet and triplet spins, respectively. The dehydrogenation products $TiNH^+ + H_2$ and $VNH^+ + H_2$ also have doublet and triplet spins, respectively. Thus, the enhanced reactivity of the excited low-spin M^+ states, compared with the high-spin ground states, was attributed to the result that electronic spin is conserved for the low-spin states but not the high-spin states. The inefficient reactivity observed for the high-spin ground states was explained by an inefficient crossing of low-spin and high-spin surfaces. We have redrawn the qualitative potential surfaces proposed by CSA that are associated with dehydrogenation of ammonia from the interaction of the low-lying states of V^+ in Figure 4.

If we proceed by applying the same rationale to our present results for the dehydrogenation of ammonia by neutral Ti and V, we determine that the ground-state potential surfaces for the reaction products $TiNH + H_2$ and $VNH + H_2$ should have triplet and quartet spin states, respectively. Further, these states should correlate to the $HTiNH_2$ and $HVNH_2$ intermediates, which also should have triplet and quartet spin states, respectively. This is shown in Figure 4. Clearly our results, that the low-spin Ti(a^3F) and V(a^4F) ground states are effectively unreactive compared with the high-spin Ti(a^5F) and V(a^6D) excited states, suggest that spin conservation is not the overriding difference between the reactivity of these states, as was observed in the cationic systems.

The dramatic differences in reactivity of the low-spin excited-state cations, $Ti^+(a^3F)$ and $V^+(a^3F)$, and low-spin ground-state neutrals, Ti(a^3F) and V(a^4F), can be understood by considering the electron configurations of these species. The valence electron configuration of neutral Ti(a^3F) and V(a^4F) is $4s^23d^{n-2}$

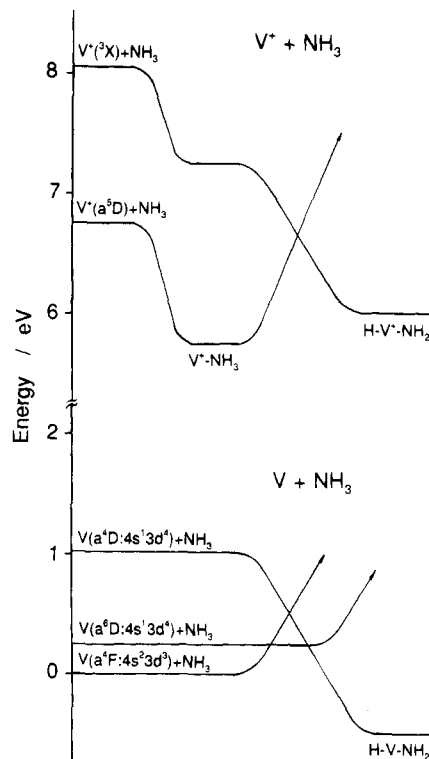


Figure 4. (lower curves) Semiquantitative potential energy surfaces for the interaction of several states of neutral V with NH_3 . (upper curves) Semiquantitative potential energy surfaces determined for interaction of several states of V^+ with NH_3 (taken from ref 6).

(where n is the number of valence electrons) while the valence configurations of the excited low-spin states of the metal cations are either $4s^13d^{n-1}$ or $4s^03d^n$. Because the $4s$ orbital for the neutral metal atoms is filled, it cannot accept electron density from the sigma bond in order to oxidatively add an $N-H$ bond to form $HMNH_2$. Instead, as shown in Figure 4, the interaction of the filled $4s$ orbital with the filled $N-H$ σ -bond should be repulsive and prohibit the reaction of this state.

One question that still remains is the means by which the high-spin Ti(a^5F) and V(a^6D) reactants are coupled to the low-spin $TiNH + H_2$ and $VNH + H_2$ products. From the above ideas, it seems likely that the neutral $HMNH_2$ intermediates correlate directly to highly excited low-spin metal states that have an electron configuration suitable for oxidatively adding the $N-H$ bond. One possibility is that states with a $4s^13d^{n-1}$ configuration can activate the bonds. If this is the case, then states with fairly low electronic energies, Ti(b^3F) at ~ 11500 cm^{-1} and V(a^4D) at ~ 8400 cm^{-1} (Table 1), may provide the necessary crossing with the Ti(a^5F) and V(a^6D) states. This is shown for the vanadium system in Figure 4. A similar insertion mechanism has been discussed in the reaction of neutral Ni atom with H_2O .¹⁹ In the nickel system, insertion occurs via a crossing from the Ni(a^3D , $3d^94s^1$) + H_2O surface to the surface evolved from Ni(a^1D , $3d^94s^1$) + H_2O .

In addition to a mechanism that is analogous to that proposed for the M^+ cation systems, two other mechanisms for dehydrogenation of ammonia are also possible. First, the initial MNH_3 collision complex could undergo a direct 1, 1-elimination of H_2 from the nitrogen to produce $MNH + H_2$. In addition, a triply ligated intermediate, where an NH and two H atoms are bound to the metal atom, may play an important role in the dehydrogenation process. In the cation systems, these mechanisms appear to be less reasonable than the one discussed above. We currently do not have enough information about the neutral

metal reaction systems to speculate about the veracity of these mechanisms.

Dehydrogenation of H₂S. It seems reasonable that the potential energy surfaces discussed above (and shown in Figure 4) for dehydrogenation of ammonia by neutral Ti and V could also be extended to explain the results obtained for dehydrogenation of H₂S by these metal atoms. Clearly, our experimental results, that the excited-state Ti(a⁵F) and V(a⁶D) rate constants are much larger than those measured for the ground-state Ti(a³F) and V(a⁴F) reactants (by factors of ~320 and ~20, respectively), are consistent with these surfaces. Therefore, this mechanism is consistent with our data.

One point worth making, however, is that in general the reactivity between metal cations for simple systems such as CH₄, NH₃, and H₂O changes systematically with the metal. That is, in all of these systems, the efficiency of dehydrogenation increases as V⁺ < Ti⁺ < Sc⁺ for both the high-spin ground-state and low-spin excited-state reactivities. Although the ordering of the neutral systems may differ from the cations, if the dehydrogenation mechanisms are similar for NH₃ and H₂S, then we expect that one metal should be more reactive with both neutrals. Table 3 shows that this is not the case. V(a⁶D) is more reactive than Ti(a⁵F) with ammonia, while the reverse trend is true for reaction of these species with H₂S. Thus, it appears that another mechanism may contribute to the reactive differences between these systems.

As mentioned in the Introduction, one mechanism that can influence the H₂S system, but not the NH₃ system, is an electron-transfer process. In this mechanism, a potential surface corresponding to interaction of the ion pair, M⁺ + H₂S⁻, crosses the essentially flat neutral surface, and transfer of an electron can relieve many of the spin and electron configuration constraints associated with the neutral pair interactions. One way to test whether or not the ET mechanism might explain the differences between the NH₃ and H₂S systems is to compare the rate constants measured for the reactions of Ti(a³F), V(a⁴F), Ti(a⁵F), and V(a⁶D) with H₂S to those calculated by the ET mechanism.

The distances at which the ion-pair surface crosses the neutral surfaces are given by eq 12,⁵¹ where IE(M), EA(R), and E_{e1}(M) are the ionization energy of the metal atom, the electron

$$R_x = e^2 / \{IE(M) - EA(R) - E_{e1}(M)\} \quad (12)$$

affinity of the reactant molecule, and the electronic energy of the metal atom, respectively. Equation 12 shows that for the same neutral molecule, the distance at which the electron is transferred, and hence the rate constant, correlates with the effective ionization energy [IE(M) - E_{e1}(M)].⁵² The rate constants of M (or M*) + H₂S are plotted as a function of the effective IE in Figure 5.⁵³ This figure shows the strong correlation expected if the ET mechanism influences this reaction. Also shown in Figure 5 are the rate constants we have measured for the reaction of excited-state metal atoms with NH₃. Clearly the strong dependence observed for the H₂S system is not observed in the NH₃ system. As discussed above, because there are no known states of NH₃ that will bind an electron, this system is not expected to correlate with the effective ionization energy.

Finally, we note that the absolute values of the rate constants for the reaction of excited-state Ti(a⁵F) and V(a⁶D) are in reasonable agreement with those calculated from the electron-transfer mechanism shown in Figure 5. The ET rate constants calculated for the reaction of ground-state Ti(a³F) and V(a⁴F) are somewhat larger than the measured values given in Table 3. One qualitative explanation for the overestimation of the

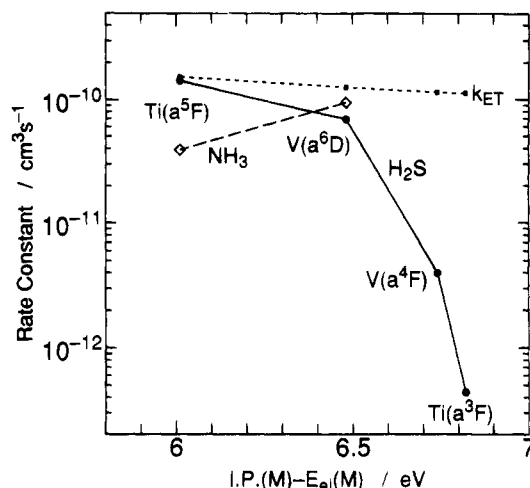


Figure 5. Plots of the rate constants vs the effective ionization potentials, LP(M) - E_{e1}(M), for the reactions M + H₂S and M + NH₃. Also shown are k_{ET} calculated for M + H₂S reactions.

rate constants by the ET mechanism may be that the neutral M + H₂S surfaces become repulsive (due to the fully occupied 4s orbital) before the ET surface crosses the neutral surface. In this case, an additional barrier would arise, decreasing the efficiency of the reaction. Certainly, detailed theoretical calculations would be useful in unraveling the details of the importance of the ET mechanism in this system.

Summary

We have measured the 300 K rate constants for the depletion of Ti and V in their ground and first electronic excited states upon interaction with H₂S and NH₃. The ground-state Ti and V atoms are depleted by interaction with only H₂S, and the rate constants are (0.44 ± 0.12) × 10⁻¹² and (4.0 ± 0.2) × 10⁻¹² cm³ s⁻¹. Although depletion of the ground states is inefficient, depletion of the Ti(a⁵F) and V(a⁶D) excited states occurs efficiently. The measured effective bimolecular rate constants for Ti(a⁵F) are (39 ± 11) × 10⁻¹² and (142 ± 13) × 10⁻¹² cm³ s⁻¹, and those for V(a⁶D) are (95 ± 8) × 10⁻¹² and (69 ± 5) × 10⁻¹² cm³ s⁻¹, with NH₃ and H₂S, respectively.

The large reaction rates for Ti(a⁵F) and V(a⁶D) could not be explained only by collisional quenching processes, and it is proposed that the dehydrogenation is the major reaction channel in all systems. The large enhancement in reactivity observed for the excited states is explained by dehydrogenation to form MNH + H₂ and MS + H₂ for the NH₃ and H₂S systems, respectively. Dehydrogenation of NH₃ is proposed to occur by a mechanism that is analogous to that proposed for the reaction of M⁺ + NH₃. In this mechanism, the metal atom inserts into the N-H bond to form a HMNH₂ intermediate followed by elimination of H₂ from a four-centered transition state. This type of mechanism can be extended to explain the H₂S system. However, the reactive differences observed between the NH₃ and H₂S systems suggest that dehydrogenation of H₂S may proceed via an electron-transfer process.

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