

Depletion Kinetics of Nickel Atoms by Sulfur Dioxide

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Received: September 3, 1998; In Final Form: October 22, 1998

The gas-phase depletion kinetics of Ni(a^3F_J , a^3D_J) in the presence of SO₂ are reported. Nickel atoms were produced by the 248 nm photodissociation of nickelocene and detected by laser-induced fluorescence. The ground term of Ni, a^3F_4 , and the two lowest energy spin–orbit states, a^3D_3 and a^3D_2 , were found to react termolecularly (and with identical rate constants) with SO₂, an indication of rapid interconversion between these states. The limiting low-pressure third-order rate constant, measured over the temperature range 296–612 K, can be expressed as $k_0(T) = 7.455 - 24.41(\log T) + 3.993(\log T)^2 \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. A binding energy of 47 kcal mol⁻¹ was estimated by combining the kinetic results with unimolecular rate theory and density functional methods. The limiting high-pressure second-order rate constant over the temperature range is on the order of the collision rate. The other spin–orbit states of both terms depleted quite rapidly in the presence of SO₂, with rate constants also on the order of the collision rate.

Introduction

There have been several recent investigations of bimolecular reactions of transition-metal (TM) atoms with SO₂.^{1–5} These reactions are of interest, in part, because of the importance of SO₂ in acid rain and in the corrosion of metals. Many of the gas-phase reactions have been observed to proceed with little or no barriers. In most cases, the relatively fast rates have been attributed to an electron-transfer mechanism whereby an electron is transferred from the TM atom to the SO₂. Due to the relatively large ionization energies of TM atoms, valence interactions are expected to play a role in their reactions; i.e., the reactions are driven not only by an electron transfer, but also by the type of orbital occupancies of the TM atoms.

In this paper, the depletion of Ni(a^3F_J , a^3D_J) by SO₂ is reported. Unlike the previous work on TM + SO₂ reactions where abstraction mechanisms were indicated, an abstraction reaction is not thermodynamically feasible for the ground state of Ni. The Ni + SO₂ reaction is endothermic at relatively low temperatures^{6,7} and, therefore, a termolecular mechanism is the only viable reaction channel at room temperature. This work provides information on the efficiency of 1:1 adduct formation between Ni and SO₂. It also allows one to determine if the Ni excited states deplete at appreciable rates in the presence of SO₂, as observed in other TM + SO₂ systems. Density functional theory (DFT)⁸ and Troe's factorization method⁹ are combined with the kinetic results to estimate the binding energy of the NiSO₂ adduct.

Experimental Section

Details of the experimental arrangement have been described in detail elsewhere¹⁰ and are only summarized here. The laser-photolysis/laser-induced fluorescence (LP/LIF), slow-flow technique was used in this work. The reaction chamber was a stainless steel cross with gas inlet and outlet ports, a viewport for LIF detection, and windows for passage of the laser beams; the chamber was contained in a convection oven capable of attaining temperatures up to 628 K. Nickelocene, the nickel precursor, was entrained in a flow of argon gas. The buffer gas

TABLE 1: Atomic States of Ni and LIF Information^a

Ni state ^b	energy (cm ⁻¹)	λ (nm) of excitation ^c
a^3F_4	0	343.728
a^3F_3	1332.153	346.750
a^3F_2	2216.519	348.377
a^3D_3	204.786	341.476
a^3D_2	879.813	349.296
a^3D_1	1713.080	345.846

^a The detection filter was centered at 350 nm and had fwhm = 10 nm. ^b Reference 11. ^c Reference 12.

(argon), diluted precursor, and SO₂ passed through separate mass flow controllers after which they combined into one line and entered the reaction chamber. A slow flow of argon passed over the windows in order to minimize the deposition of the precursor and photofragments. Total flows were between 150 and 8500 sccm, depending on the total pressure. Partial pressures of the individual components were determined by their relative flows and the total pressure in the reaction chamber. Pressures were measured by Baratron manometers, and temperatures were measured with a thermocouple attached to the reaction chamber.

Nickel atoms were produced from Ni(C₅H₅)₂ by the unfocused output of an excimer laser operating on KrF (248 nm) at 21 Hz. Rate-constant measurements did not depend on the photolysis fluences, which were approximately 200–400 mJ cm⁻² in the reaction chamber. Detection of nickel atoms was by LIF using laser light from an excimer-pumped dye module. The photolysis and dye beams counterpropagated through the chamber. Neutral density filters were used to ensure that the dye laser fluence (less than 1 mJ/pulse) did not affect the kinetic results. The Ni states studied and the corresponding excitation wavelengths are listed in Table 1.^{11,12} A photomultiplier tube and lens focusing system, situated 90° to the laser beams, collected the LIF signal, which was subsequently sent to a gated boxcar sampling module, and the boxcar's output was stored and analyzed by a computer.

All kinetic results are based on the disappearance of Ni atoms under pseudo-first-order conditions, where the number density of Ni was much less than the number density of SO₂ and Ar. Reaction time was taken as the delay time between the laser

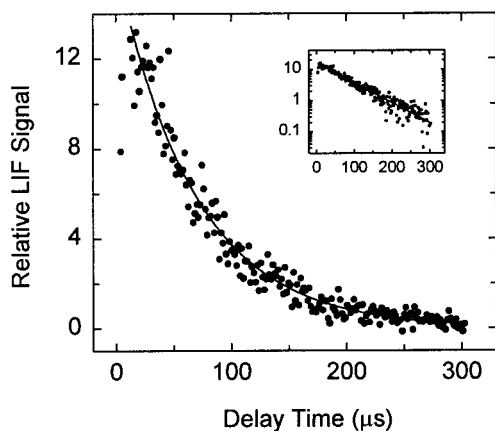


Figure 1. Typical decay profile of Ni in the presence of SO₂. Data are for Ni(a³D₃). $T = 296$ K, $P_{\text{tot}} = 40$ Torr, $P_{\text{SO}_2} = 16.8$ mTorr. The solid line through the data is an exponential fit with $\tau = 68.0$ μs . The inset is the same data in semilogarithmic form; note the linearity.

pulses. For a given experimental run, the delay time was varied by a digital delay generator controlled by a computer. Minimum delay times were typically 1–10 μs in order to prevent overlap of the prompt emission with the LIF signal. The trigger source for these experiments was scattered pump laser light incident upon a fast photodiode. LIF decay traces consisted of 200–500 points, each point averaged over 2–10 laser shots. LIF intensities were proportional to Ni number densities.

Reagents. The following reagents were used as received: Ni-(C₅H₅)₂ (Strem Chemicals, Inc., 99%), Ar (Potomac Airgas, Inc., 99.998%), SO₂ (MG Industries, 99.98%).

Data Analysis and Results

A typical decay trace is shown in Figure 1. It represents the decay of Ni(a³D₃) in the presence of added SO₂. Partial pressures of the precursor nickelocene are not accurately known in these experiments. However, based on the carrier flow rate and pressure, total flow rate, and total pressure, nickelocene's partial pressure in the reaction chamber is estimated to be less than 0.5 mTorr for all experiments. The solid line through the data is an exponential fit to the equation

$$I = I_0 \exp(-t/\tau) \quad (1)$$

where I and I_0 are the LIF signals at time t and time $t = 0$, respectively, and τ is the lifetime from which the pseudo-first-order rate constant, $1/\tau$, is obtained. $1/\tau$ is given by

$$1/\tau = 1/\tau_0 + k[\text{SO}_2] \quad (2)$$

where τ_0 is the lifetime of Ni without added SO₂, k is the second-order rate constant, and $[\text{SO}_2]$ is the partial pressure of SO₂. τ_0 represents the lifetime of Ni in the presence of species other than SO₂ in the reaction chamber and diffusion out of the detection zone. τ_0 was usually long compared to τ . Second-order rate constants were obtained from the slopes of plots of $1/\tau$ vs SO₂ partial pressure such as that shown in Figure 2. Note that the intercept ($1/\tau_0$) is relatively small so that interference from photofragments and diffusion was minimal.

The measured rate constants are listed in Table 2. The uncertainties resulting from the linear regression fits, such as that in Figure 2, were approximately 3% ($\pm 1\sigma$) in precision. The overall uncertainties, estimated at $\pm 30\%$ at the 95% confidence limit, include statistical scatter in the data, the

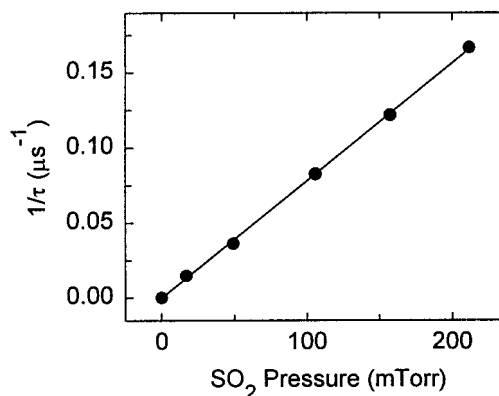


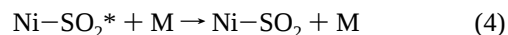
Figure 2. Typical plot for determining second-order rate constants. The conditions are the same as in Figure 1, except the partial pressures of SO₂ are changing. Each point represents an average of 2–3 measurements. The slope gives $k = (2.40 \pm 0.06) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹, where the uncertainty is $\pm 2\sigma$ from the linear regression.

TABLE 2: Measured Second-Order Rate Constants for the Depletion of Ni (a³F_J, a³D_J) by SO₂^a

state	P (Torr)	k (10^{-11} cm ³ molecule ⁻¹ s ⁻¹)				
		296 K	349 K	399 K	498 K	612 K
a ³ F ₄	10	0.760				
	20	1.39		0.494		
	120	4.83		2.41		
a ³ F ₃	10	17.9				
a ³ F ₂	10	15.5				
a ³ D ₃	10	0.799	0.416	0.299	0.138	
	20	1.49	0.718	0.489	0.243	0.107
	40	2.40	1.17	0.891	0.399	0.176
	80	3.82	2.38	1.52	0.792	0.336
	120	4.63	3.21	2.07	1.10	0.476
	200	5.79	4.07	2.83	1.70	0.737
	300	6.79	5.54	3.89	2.18	1.06
a ³ D ₂	400	8.27	6.01	4.59	3.10	1.41
	500	8.97	7.33	5.16	3.19	1.52
	600	9.32	7.51	5.85	4.01	1.95
	10	0.793				
a ³ D ₁	40	2.19				
	10	13.2				

^a Buffer = argon. Overall uncertainties are $\pm 30\%$ at the 95% confidence limit.

reproducibility of k , and instrumental uncertainties such as digital delay and flow measurements. The rate constants for the depletion of the a³F₄, a³D₃, and a³D₂ states are identical. These rate constants increase with increasing total pressure and decrease with increasing temperature, an indication of the termolecular reaction mechanism



The third body M was predominantly argon. The partial pressures of the other gaseous components were too low to contribute significantly to the stabilization of the NiSO₂* adduct. Data were not collected above 600 Torr and 612 K because of a low signal-to-noise ratio under such conditions. Since the depletion rate constants of the a³F₄, a³D₃, and a³D₂ states are identical, a thorough pressure and temperature-dependence study was undertaken for only Ni(a³D₃), because it had the largest LIF signal.

Plots of the second-order rate constants (for a³D₃) as a function of total pressure at all temperatures are shown in Figures 3 and 4. The lack of any true bimolecular component

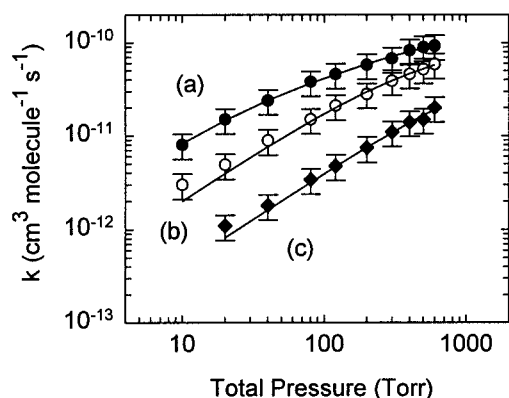


Figure 3. Pressure dependence of Ni(a³D₃) + SO₂ at (a) 296, (b) 399, and (c) 612 K. The solid line through the data at 296 is a fit to eq 6, and the solid lines through the other data are fits to eq 7. See Table 3 for results of fits.

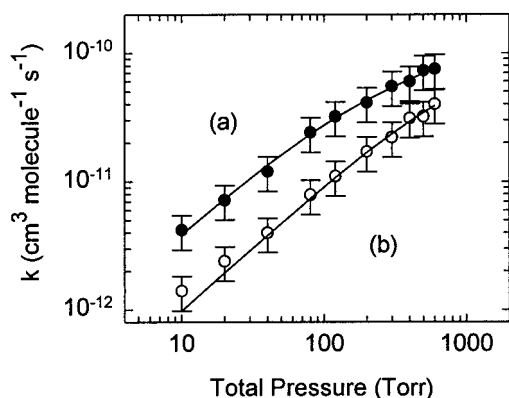


Figure 4. Pressure dependence of Ni(a³D₃) + SO₂ at (a) 349 and (b) 499 K. The solid lines through curves (a) and (b) are fits to eqs 6 (with fixed k_{∞}) and 7, respectively. See Table 3 for results of fit.

to the rate is consistent with the thermochemistry of the ground state, bimolecular channel



being thermodynamically inaccessible at relatively low temperatures. The solid line through the 296 data is a fit using Troe's formalism⁹

$$\log k = \log \frac{k_0[M]}{1 + (k_0[M]/k_{\infty})} + \frac{\log F_c}{1 + [\log(k_0[M]/k_{\infty})]^2} \quad (6)$$

where k_0 is the limiting low-pressure third-order rate constant, k_{∞} is the limiting high-pressure second-order rate constant, $[M]$ is the buffer gas number density, and F_c is the broadening factor. Large uncertainties (>100%) in the fitted parameters were obtained when the higher temperature data were fitted to eq 6. Thus, for the 349 K data, k_{∞} was fixed at $1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in eq 6. The simplified Lindemann–Hinshelwood expression¹³

$$k = k_0 [M] / (1 + k_0 [M] / k_{\infty}) \quad (7)$$

was used for the higher temperature data. Results of the fits are given in Table 3. k_0 decreases with increasing temperature, as shown in Figure 5, and can be expressed as

$$k_0(T) = 7.455 - 24.41(\log T) + 3.993(\log T)^2 \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \quad (8)$$

TABLE 3: Falloff Modeling Parameters for the Reaction of Ni (a⁶D_{1/2}, a⁴F_j) with SO₂

T (K)	k_0 (cm ⁶ molecule ⁻² s ⁻¹)	k_{∞} (cm ³ molecule ⁻¹ s ⁻¹)	F_c
296	$(3.3 \pm 0.3) \times 10^{-29}$	$(1.7 \pm 0.4) \times 10^{-10}$	0.64 ± 0.10
349	$(1.6 \pm 0.2) \times 10^{-29}$	1.5×10^{-10} (fix)	0.79 ± 0.07
399	$(0.84 \pm 0.08) \times 10^{-29}$	$(1.1 \pm 0.2) \times 10^{-10}$	a
498	$(0.51 \pm 0.08) \times 10^{-29}$	$(1.1 \pm 0.5) \times 10^{-10}$	a
612	$(0.26 \pm 0.05) \times 10^{-29}$	$(0.84 \pm 0.47) \times 10^{-10}$	a

^a The simplified Lindemann–Hinshelwood mechanism, eq 7, was used to fit the data. The uncertainties represent two standard deviations (precision).

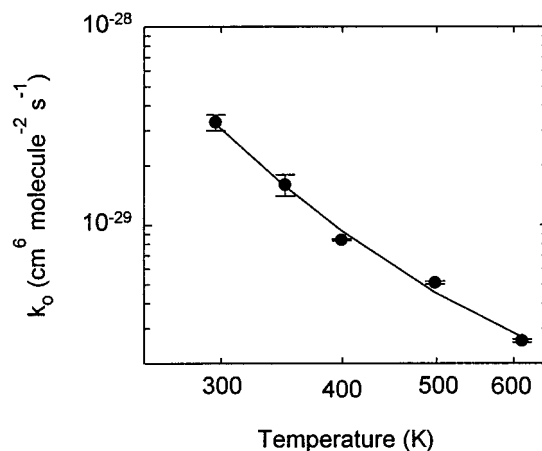


Figure 5. Temperature dependence of k_0 . The solid line through the data is a polynomial fit. See text for results of fit. The error bars represent the $\pm 2\sigma$ uncertainties (precision).

k_{∞} appears to decrease with increasing temperature. However, the relatively long extrapolations of the second-order rate constants to the high-pressure limit as the temperature increases and the combined uncertainties in k_{∞} precluded an accurate assessment of this observation. The k_{∞} values obtained from eqs 6 and 7 are on the order of the gas kinetic rate constant of $\sim 2 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, thus justifying the use of $k_{\infty} = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the 349 K data.

Table 2 shows that the excited states above 880 cm⁻¹ deplete at approximately the gas collision rate, an indication of no activation barrier. The kinetics of these states were not investigated at total pressures above 10 Torr due to decreasing signal-to-noise ratios. A pressure dependence and a positive temperature dependence are not expected since the depletion rate constants are large.

Discussion

The results presented here indicate that the excited states below 880 cm⁻¹ deplete at identical rates and/or the rate of interconversion among them is fast. The thermal energy is 206 cm⁻¹ and the a³D₃ state is only 205 cm⁻¹ above the ground state. Thus, rapid interconversion is likely, at least between the a³F₄ and a³D₃ states. (Ni(a³D₃) and Ni(a³D₂) account for approximately 22% and 3%, respectively, of the thermal population at 296 K.) Ni(a³F₄), Ni(a³D₃), and Ni(a³D₂) were also found to react with NO at identical rates at ~ 1 Torr total pressure, and none of these states reacted with O₂ and N₂O.¹⁴ Rapid interconversion between the states was not indicated in that work. It thus appears that the depletion mechanism of Ni-(a³D₂) in the presence of small oxidants is similar to that of Ni(a³F₄) and Ni(a³D₃). The 3d⁸4s² electron configuration of the ground state does not appear to introduce any barriers to reaction. Since the a³F₄ state is in thermal equilibrium with the

$3d^9 4s^1 a^3D_3$ state, any barriers due to the closed s-subshell could be screened. On the basis of the orbital-occupancy argument presented above, we conclude that the ground state is converted to the a^3D_3 state, which is reactive. k_∞ is close to the gas kinetic rate constant, and k_0 decreases with increasing temperature, indications of no energy barrier to product formation.

Physical quenching is the likely depletion channel of the states above 880 cm^{-1} . An abstraction channel is not accessible, and rate constants on the order of $10^{-10}\text{ cm}^3\text{ s}^{-1}$ for a termolecular channel at only 10 Torr total pressure is not expected. $E-V$ energy transfer may take place via the vibrational modes of SO_2 since the energy differences between the Ni states are close to the vibrational modes of SO_2 .⁷

To estimate the binding energy E_b of the NiSO_2 adduct relative to $\text{Ni}(a^3D_3)$, simplified RRKM calculations using the formalism of Troe⁹ were performed at 296 K. In brief, the rate constant for the unimolecular dissociation in the low-pressure limit, k_{uni} , of NiSO_2 was first calculated. k_0 was then calculated from the equilibrium expression $K_{\text{eq}} = k_{\text{uni}}/k_0$, where K_{eq} is the equilibrium constant for $\text{NiSO}_2 \rightleftharpoons \text{Ni} + \text{SO}_2$. The collision efficiency, β_c , of Ar was assumed to be 0.20. β_c can be determined by comparing the experimental and calculated (strong collision) third-order rate constants. However, the uncertainties and adjustable binding energy in the calculations precluded such an approach. The molecular structure and vibrational frequencies of NiSO_2 needed for the RRKM calculations were calculated from density functional⁸ methods. The binding energy was varied until agreement was obtained between the calculated and experimental third-order rate constant. The density functional calculations are not intended to be exhaustive, but instead serve mainly to provide estimates of the molecular parameters.

The molecular parameters of NiSO_2 were calculated by the SPARTAN^{15,16} suite of programs. Calculations were performed with the LSDA/pBP86 model and DN** numerical basis sets. Several triplet isomers were assumed. The "side-on bonded," $\eta^2_{\text{O,O}}$ isomer (C_{2v} geometry) gave the lowest energy. The DFT results are to be taken with caution; numerical errors are likely since calculations involve numerical integration steps. Additionally, the relatively large number of low-lying states of Ni and other TM atoms poses a challenge for the theoretical treatment of transition metals. Pertinent output from the computations are listed in the Appendix.

Agreement between the measured and calculated k_0 at 296 K was obtained for $E_b = 47 \pm 3\text{ kcal mol}^{-1}$; the uncertainty in E_b is based only on the overall uncertainty in k_0 at 296 K. Since there is no activation barrier, significantly smaller E_b values would give association rate constants that are too small because k_0 is a sensitive function of the binding energy.¹³ The presence of several low-lying states in atomic Ni and the possibility of several low-lying bound states in NiSO_2 could lead to additional pathways, thus affecting the calculated results. The equilibrium constant, and hence k_0 , is also affected by the relatively low level of the DFT calculations. Thus, only an estimate of E_b is reported. This estimate is reasonable, however. A comparison of the rates of TM and main-group metals with small oxygen-containing molecules indicates that a bond energy of $40\text{--}50\text{ kcal mol}^{-1}$ is in accord with third-order rate constants of the magnitude measured in this work.^{17–21}

The binding energies of Na-SO_2 and K-SO_2 have been found to lie within the range of the corresponding binding energies of the metal- O_2 superoxides.^{19,20} C_{2v} $\eta^2_{\text{O,O}}$ -type structures, where the alkali-metal atoms are side-bonded to the

oxygen atoms, are observed and calculated. The binding energy of NiSO_2 estimated in this work is approximately equal to the binding energy of C_{2v} $\eta^2_{\text{O,O}}$ Ni-O_2 from an ab initio study: $E_b = 48 \pm 7\text{ kcal mol}^{-1}$.²² This observation suggests that the bonding in C_{2v} NiO_2 and C_{2v} NiSO_2 is similar. Covalent and ionic components are present in NiO_2 . The relatively large limiting low-pressure and high-pressure rate constants for $\text{Ni} + \text{SO}_2$ and the larger electron affinity of SO_2 (than O_2)⁶ suggest an ionic component in NiSO_2 .

The reaction of $\text{Mn}(3d^5 4s^2 a^6S_{5/2})$ with SO_2 was also investigated in this work to determine if a relatively unreactive TM atom would react with SO_2 . An upper limit of $\sim 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ was obtained over the temperature range of $296\text{--}622\text{ K}$. The electron-transfer mechanism has been offered as an explanation for the reactions of TM atoms with SO_2 . The ionization energy of Mn is less than that of Ni.⁶ Thus, the orbital occupancy of the TM atom is the predominant driving force (at least when comparing Mn and Ni).

Summary and Conclusions

Results presented here indicate that Ni is very reactive toward SO_2 . The three lowest states of Ni, a^3F_4 , a^3D_3 , and a^3D_2 , react with SO_2 via a termolecular mechanism. The 1:1 adduct formation is efficient. The kinetic results were combined with DFT and RRKM calculations to provide an estimate of 47 kcal mol^{-1} for the binding energy of NiSO_2 ($\eta^2_{\text{O,O}}$ isomer). A comparison between NiO_2 and NiSO_2 suggest covalent and ionic components to the bonding in NiSO_2 . The a^3F_3 , a^3F_2 , and a^3D_1 states of Ni deplete at approximately the gas collision rate in the presence of SO_2 .

Acknowledgment. This research was supported by the Naval Academy Research Council and a Cottrell College Science Award of Research Corporation.

Appendix

The DFT suite of SPARTAN programs^{15,16} was used to calculate the molecular parameters of NiSO_2 . For the triplet $\eta^2_{\text{O,O}}$ isomer of NiSO_2 (C_{2v} geometry), we found bond lengths of $r(\text{S-O}) = 1.5847\text{ \AA}$ and $r(\text{O-Ni}) = 1.9539\text{ \AA}$. Bond angles are $\angle(\text{O-S-O}) = 100.1412^\circ$, $\angle(\text{S-O-Ni}) = 91.4730^\circ$, and $\angle(\text{O-Ni-O}) = 76.9128^\circ$. Calculated frequencies, in units of cm^{-1} , are 127.12, 301.61, 349.38, 504.62, 836.33, and 841.61.

For the simplified RRKM calculations at 296 K, E_0 was taken as an adjustable parameter. The rate constant for the unimolecular dissociation in the low-pressure limit, k_{uni} , is given by⁹

$$k_{\text{uni}} = \beta_c Z_{\text{LJ}} \frac{\rho(E_0)RT}{Q_{\text{vib}}} \exp(-E_0/RT) F_{\text{anh}} F_E F_{\text{rot}} F_{\text{rotintn}} F_{\text{corr}}$$

where β_c is the collisional efficiency of Ar, Z_{LJ} is the Leonard-Jones rate constant, $\rho(E_0)$ is the vibrational density of states of NiSO_2 at the threshold energy E_0 for dissociation, Q_{vib} is the vibrational partition function of NiSO_2 , F_{anh} is a correction for vibrational anharmonicity, F_E is a correction for the variation of the density of states, and F_{rot} is the molecular rotational correction factor. The corrections for internal rotational modes and the coupling of the F factors, F_{rotintn} and F_{corr} , were taken as one.

A Lennard-Jones collision frequency of $6.38 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ was calculated from reasonable values of the Lennard-Jones parameters. β_c was taken as 0.20. $s = 6$ and $m = 3$, where s is the number of vibrational modes in NiSO_2 and

m is the number of vibrational modes that has disappeared after dissociation. $E_0 = 47 \text{ kcal mol}^{-1}$. Calculated RRKM parameters are $a(E_0) = 0.989$, $F_{\text{anh}} = 1.37$, $F_E = 1.06$, and $F_{\text{rot}} = 22.4$, where $a(E_0)$ is a constant calculated from the energy. Calculated K_{eq} , k_{uni} , and k_0 values are $3.14 \times 10^{-10} \text{ molecule cm}^{-3}$, $5.17 \times 10^{-38} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and $3.30 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, respectively.

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