almost equally simple equation

$$E_s = e^2(\epsilon_0^{-1} - \epsilon_*^{-1})\left(\frac{1}{a} - \frac{1}{R}\right) +$$
$$e^2(\epsilon_*^{-1} - \epsilon_s^{-1})\left\{\Lambda^{-1} - \frac{1}{R}\left[1 - \exp\left(-\frac{R}{\Lambda}\right)\right]\right\} \quad (11)$$

Solvent structural features are now incorporated and gives in this simple form two new parameters for each solvent, namely the correlation length and the short-range dielectric constant. Ways of extracting these quantities from experimental data and of associating them with microscopic models are available in several recent reports.[17,20,26,28b,29]

The data in ref 18 would be in line with solvent nonlocality by the following consideration, which has to be rather qualitative in view of our lacking precise structural information for most of the solvents. As a first crude approach, the aprotic solvents can be regarded as structurally correlated broadly as the parameter $\epsilon_0^{-1} - \epsilon_s^{-1}$. All the points on the $h\nu_{max}/(\epsilon_0^{-1} - \epsilon_s^{-1})$ plot would then be shifted toward smaller $\epsilon_0^{-1} - \epsilon_s^{-1}$, and more so the larger $\epsilon_0^{-1} - \epsilon_s^{-1}$. This would give a larger slope and a smaller intercept,

perhaps better in line with the expected small structural differences between the two oxidation states of ruthenium. To bring water closer to the other solvents, a weaker polarization correlation around the solute ions than for the other solvents is needed. There is no direct evidence for such an effect, but large ions sometimes do exert a "geometric" structure-breaking effect on the water hydrogen-bond network.[30] Also, in a previous analysis of interionic interactions around large alicyclic ions in water, by means of nonlocal dielectic theory, these ions were found to give much smaller correlation lengths than those extracted from solute aliphatic ions.[20,26]

In conclusion, two solvent effects can be suggested as possible origins of the different behavior of water and polar aprotic solvents, namely solute hydrophobicity or solvent nonlocality combined with solvent "structure breaking". These two effects should be distinguishable in principle. Hydrophobic effects would thus lead to a tighter hydrogen-bond structure, reflected in increased librational and molecular deformational vibrational frequencies and decreased O–H stretching frequencies and dielectric relaxation times.[25] Nonlocality and structure breaking would lead to the opposite effects.

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Gas-Phase Chemistry of NF(a¹Δ): Quenching Rate Constants

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The reaction of excess F atoms with HN_3 in a halocarbon-coated flow reactor has been used to generate and study the quenching reactions of NF(a¹Δ,v'=0) at 300 K. Fifteen reagents, selected to represent a variety of chemical interactions, were tested in order to provide a survey of quenching rate constants that could be compared to O_2(a¹Δ$_g$) and NH(a¹Δ). A range of rate constants was found which varied from $\sim 1.0 \times 10^{-11}$ cm³ s⁻¹ for N(CH$_3$) to $\sim 1.0 \times 10^{-15}$ cm³ s⁻¹ for N_2, H_2, and NO. The NF(a¹Δ) molecule is much less reactive than NH(a¹Δ), and it seems to more closely resemble O_2(a¹Δ$_g$). However, the quenching rate constants for NF(a¹Δ) generally are larger than for O_2(a¹Δ$_g$) and show a greater variation from one reagent to another. The self-quenching rate constant for NF(a¹Δ) is $(2.2 \pm 1.2) \times 10^{-12}$ cm³ s⁻¹ with energy pooling to give NF(b¹Σ⁺) being a small component of the total self-quenching reaction.

Introduction

The metastable NF(a¹Δ;1.42 eV) molecule is one of the few electronically excited states that can be generated in high concentration and with high efficiency by gas-phase chemical reaction.[1-4] In order to utilize the NF(a¹Δ) as an energy storage system, it is necessary to know the quenching rates by other molecules, with itself, and with ground-state NF(X³Σ⁻). We have initiated a program to characterize the quenching and reactive properties of NF(a¹Δ), and we now report quenching rate constants for several types of molecules. With the aid of this survey, comparison can be made to the isoelectronic molecule O_2(a¹Δ$_g$;0.98 eV), which is generally unreactive and quenches by electronic-

to-vibrational (E–V) energy transfer, and to the more reactive NH(a¹Δ;1.56 eV) and O(¹D;1.97 eV) cases. Ultimately, such comparisons will elucidate the chemistry of these excited states.

The experimental method is based upon the generation of NF(a) by the F + HN$_3$ reaction system in a flow reactor ($\sim$10 m s⁻¹ flow velocity):

$$F + HN_3 \rightarrow HF + N_3 \quad (1)$$
$$F + N_3 \rightarrow NF(a^1\Delta) + N_2 \quad (2)$$
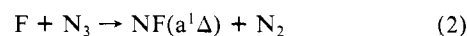
Most experiments were done with excess [F] in order to maximize [NF(a)]. However, reaction 2 is sufficiently rapid that NF(a) can be generated and studied with [F]$_0 \sim$ [HN$_3$]$_0$. With excess [F], the HN$_3$ is converted to NF(a,v'=0) with an efficiency greater than 0.8.[1] The NF(a,v'=1) population is insignificant. The quenching studies were done by adding reagents to the downstream part of a flow reactor after reactions 1 and 2 were completed. The [HN$_3$] concentration was limited to <10¹² molecules cm⁻³ so that the heat released by reactions 1 and 2, $\sim$80 kcal mol⁻¹, does not raise the temperature of the Ar carrier gas and to prevent loss of NF(a) by self-quenching or by quenching from excess F atoms. For these operating conditions, the [NF(a)] was effectively con-

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stant for 0.2 s in the absence of added reagents.

If reaction of F atoms with the added reagent caused no complication and if the reagent did not induce a surface quenching rate, pseudo-first-order decay of NF(a) was observed and quenching rate constants were obtained. Successful experiments were done for 15 reagents (HF, F_2, H_2, D_2, O_2, N_2, CO, NO, CF_4, CF_3NO, NH_3, $(CH_3)_3N$, C_3H_8, C_2H_4, and CH_3Cl) which were selected to illustrate a range of quenching behavior for comparison to O_2(a) and NH(a). For a few cases (Cl_2, HCl, and OCS) difficulties were encountered that prevented measurement of rate constants. Some experiments also were done with higher F and NF(a) concentrations to study quenching by F atoms and self-quenching, respectively.

Experimental Techniques

Reactions 1 and 2 have been characterized recently in our laboratory, and they need no further discussion.[1] The rate constants ($k_1 = (1.1 \pm 0.2) \times 10^{-10}$ and $k_2 = (5 \pm 2) \times 10^{-11}$ cm^3 s^{-1}) are sufficiently large that for 100% excess of [F] relative to [NF(a)], i.e., [F] = 3[HN_3], reaction 2 is complete in ~25 ms for [HN_3] = 1 $\times$ 10^{12} molecules cm^{-3}. Thus, NF(a) can be generated in a flow reactor of moderate flow velocity and the quenching can be studied by adding reagents in the downstream part of the reactor. A 6.5-cm-diameter Pyrex glass reactor pumped with a 1500 L m^{-1} mechanical pump was used for these experiments. The reactor was coated with halocarbon wax (Halocarbon Products Corp.) to inhibit the loss of F atoms and the surface-induced decomposition of N_3. The decomposition of N_3 was negligible, as verified by the absence of the $N_2(B^3\Pi_g-A^3\Sigma_u^+)$ emission.[1,5] The F atoms were prepared by microwave discharge in a dilute (8%) CF_4/Ar flow; titration experiments showed that the [F] was equivalent to ~2[CF_4] for most operating conditions.

The Ar carrier gas, the HN_3, and the F atom flows were introduced at the entrance to the reactor. The reagent flow was introduced 15 cm (25 ms) further downstream via a ring inlet. Experiments were done at either ~2.5- or ~5-Torr total pressure. The higher pressure was used for reagents with small quenching rate constants, which required high partial pressure of reagent. The Ar flow, purified by passage through cooled (195 K) molecular sieve filled traps, was measured with a calibrated triflat flowmeter. The HN_3 was prepared by the reaction of stearic acid with NaN_3 and stored as a 15% Ar mixture in a 10-L reservoir. Relatively high reagent flows were necessary, and the reagents were used without purification, except for routine degassing. Reagents with large rate constants were added as preprepared dilute mixtures in Ar and stored in 10-L glass reservoirs. For F_2, HF, and some other cases with small quenching rate constants, the gases were metered directly from tanks by using a passivated stainless steel gas handling system. The flow rates for HN_3, CF_4, and reagents were measured from the pressure rise in calibrated volumes with pressure transducers.

The NF(a) relative concentration was monitored via the relative emission intensity of the NF(a–X) transition at 874 nm, which was observed with a 0.5-m Minuteman monochromator fitted with a grating blazed at 500 nm and a cooled RCA-C31034 photomultiplier tube. The signal was recorded with a photon counting system and displayed on a strip chart recorder. The NF(b–X) transition at 528 nm was monitored to record the NF(b) relative concentration for a few experiments.

Experimental Results

Characterization of the NF(a) Source. Figure 1 shows the variation of [NF(a)] vs distance (time) in the flow reactor for several sets of operating conditions: (b)–(e) [HN_3] ≈ 0.5 × 10^{12} molecules cm^{-3} with [F]$_0$ increasing from [F]$_0$ = [HN_3] to [F]$_0$ = 7[HN_3] and (a) [HN_3] = 2.9 × 10^{12} molecules cm^{-3} and [F]$_0$ = 2.3[HN_3]. For the low range of [HN_3] with [F] ≤ 2[NF(a)], the decay of NF(a) over the length of the reactor (0.2 s) was negligible. The NF(a) radiative decay rate is not well established,
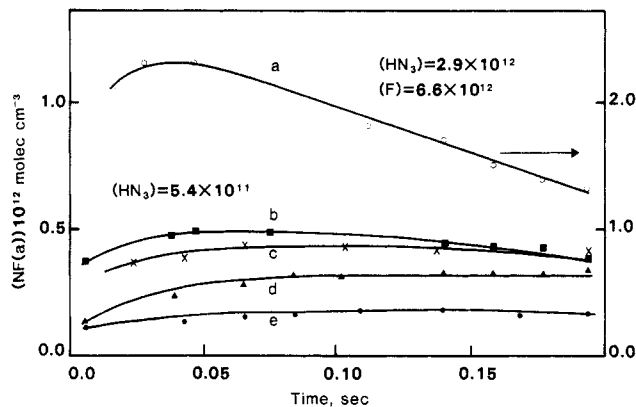

Figure 1. NF(a) concentration as a function of reaction time is shown for several [F]$_0$ and two different [HN_3]. Plot a shows the NF(a) decay due to self-quenching. Plot b shows a small degree of quenching of NF(a) by a large excess of F atoms, [F]$_0$ ≃ 7[HN_3]. A twofold excess of F atoms ([F]$_0$ ≈ 4[HN_3]) as well as stoichiometric conditions ([F]$_0$ ≈ 2[HN_3]) gives no appreciable NF(a) decay as shown in curves c and d, respectively. Curve e with [F] ≈ [HN_3] illustrates the fact that reaction 2 can compete with (1) in the generation of NF(a).

but the experimental value,[4] ~5 s, has been supported by recent calculations,[6,7] and radiative decay is not important in the reactor. The low-[F] experiments set a limit for wall quenching in our halocarbon coated reactor of $k_w \le 0.2$ s^{-1}. Experiment with [F] < [HN_3] can be used to set a limit on k_2 relative to k_1 by comparing the yield of NF(a) to the maximum value for large [F]; such experiments give $k_2 \sim 5 \times 10^{-11}$ cm^3 s^{-1} in agreement with our earlier report.[1]

The plots in Figure 1 show that NF(a) does decay at higher CF_4 flows. Since CF_4 has a very small quenching rate constant (vide infra) and since the $CF_2(\tilde{X}^1A_1)$ excitation energy, 2.4 eV,[8] is well above the NF(a) energy and since the quenching rate by CF_3 is slow,[9] the observed quenching was assigned to F atoms. Data in which the [F] was systematically changed for constant HN_3 suggest a quenching rate constant of ~2 × 10^{-14} cm^3 s^{-1}.

As [NF(a)] was increased for the lowest [F] that was adequate to convert HN_3 to NF(a), the NF(a) decay rate increased. The quenching rates by N_2 and HF are very small (vide infra), and this decay can be assigned to the self-quenching reaction.

$$2NF(a) \rightarrow N_2 + 2F \qquad \Delta H_0° = -6.3 \text{ eV} \qquad (3a)$$

$$\rightarrow NF(b) + NF(X) \qquad \Delta H_0° = -0.5 \text{ eV} \qquad (3b)$$

$$\rightarrow \text{other products} \qquad (3c)$$

The enhanced decay at higher [NF(a)] had been noted before,[1] but could not be assigned to (3) until the HF quenching constant had been measured. The data in Figure 1a for [NF(a)] = 2.9 × 10^{12} molecules cm^{-3} fit second-order decay kinetics, and the rate constant was (2.2 ± 1.2) × 10^{-12} cm^3 s^{-1}. It should be emphasized that, for the experiment depicted in Figure 1a, process 3 must be the dominant NF(a) removal channel, because (1) the excess F atom concentration was kept low and (2) the HF, N_2, CF_2, and CF_3 quenching constants are small. The NF(b) in the first part of the flow reactor is formed from HF(v) + NF(a). This [NF(b)] formed due to the V–E process decays and eventually reaches a steady-state level that correlates with the square of [NF(a)]. Comparing the NF(b) and NF(a) steady-state intensities gives ~2 × 10^{-14} cm^3 s^{-1} as the rate constant for (3b), and this is a minor channel for reaction 3.

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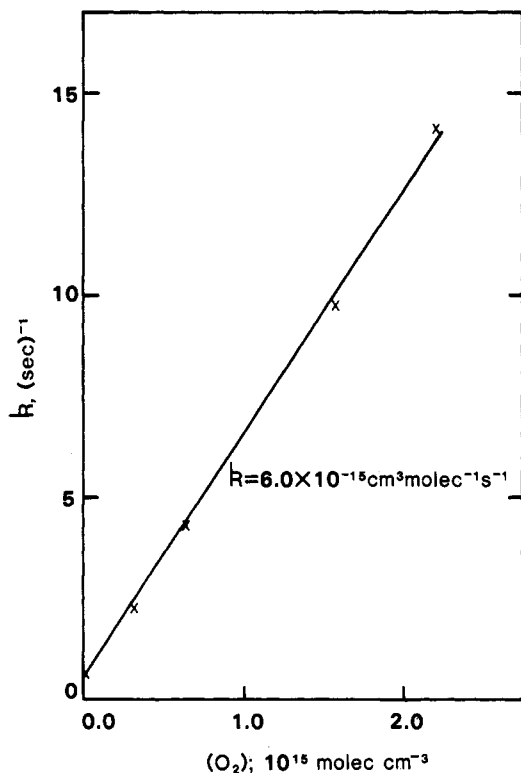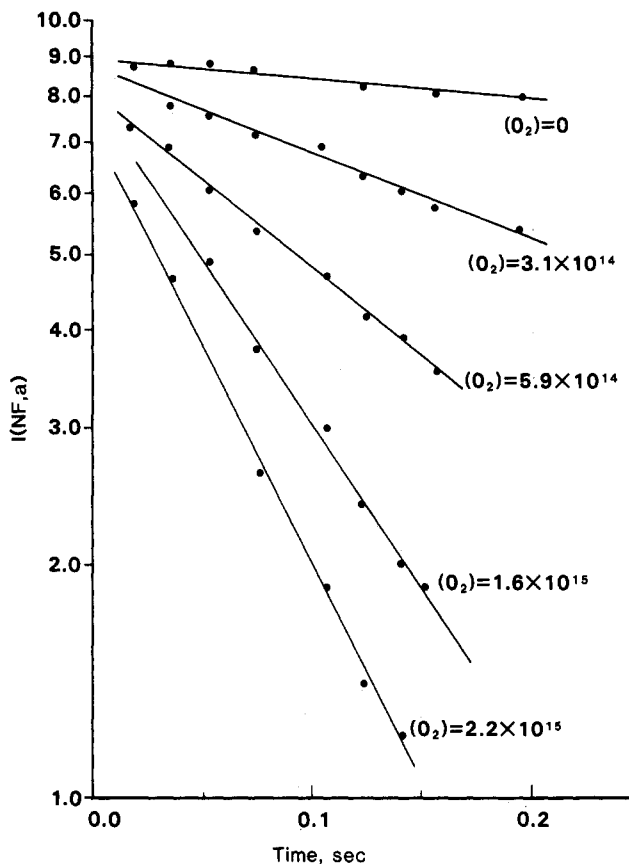
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Figure 3. Quenching plots for $NF(a)$ in a halocarbon-coated reactor: F_2, C_2H_4, and CF_4 are examples of well-behaved reagents. An initial drop in $[NF(a)]$ was observed when a small D_2 or C_3H_8 concentration was added followed by normal quenching as higher concentrations of these reagents were added.

TABLE I: Quenching Rate Constants (cm^3 molecule^{-1} s^{-1}) of $NF(a^1\Delta)$

reagent	$10^{15}k_Q NF(a^1\Delta)$	$10^{18}k_Q O_2(a^1\Delta)$	$10^{11}k_Q NH(a^1\Delta)$
N_2	0.13	0.14 ± 0.02^c	$(0.75 \pm 0.06) \times 10^{-2f}$
CO	6.3	9.0 ± 3.0^a	
O_2	6.6	1.56 ± 0.05^b	1.55^d
NO	0.5	50 ± 10^a	
H_2	0.64	5.3 ± 0.9^c	0.46 ± 0.04^d
D_2	0.32		
HF	3.0	140 ± 50^a	0.073 ± 0.026^f
F_2	32		0.063 ± 0.016^f
CF_4	<0.047		0.38 ± 0.04^d
NH_3	1.9×10^3	10 ± 2^a	11.0 ± 0.8^f
CF_3NO	8.0×10^3	$(3.0 \pm 1.0) \times 10^{6\,a}$	
$(CH_3)_3N$	1.3×10^4	3000 ± 500^a	
C_2H_4	3.0×10^2	2.0 ± 0.2^e	8.8 ± 0.8^d
CH_3Cl	25	5 ± 2^a	
C_3H_8	5.9	2.4^e	4.2 ± 0.3^d
HCN	<10	5 ± 2^a	
COS	g	2 ± 1^a	
HCl	g	4 ± 3^a	7.9 ± 0.8^e
Cl_2	g	6 ± 3^a	

^{a}See ref 12. ^{b}See ref 13. ^{c}See ref 14. ^{d}See ref 15. ^{e}See ref 16. ^{f}See ref 17. ^{g}Good first-order plots for these reagents were not obtained; see text.

NF(a) Quenching Rate Constants. Experiments were done with two model reagents to demonstrate good pseudo-first-order decay kinetics for $[Q] > [NF(a)]$.

$$NF(a) + Q \rightarrow NF(X^3\Sigma^-) + Q$$

$$\rightarrow \text{chemical reaction} \qquad (4)$$

Figure 2a shows data in which the relative $[NF(a)]$ was monitored along the flow reactor for various concentrations of O_2. The pseudo-first-order rate constants for O_2 are plotted vs concentration in Figure 2b to obtain a quenching rate constant. The rate

Figure 2. (a, top) Semilog plot of the $NF(a-X)$ emission intensity as a function of reaction time for different $[O_2]$. The $[HN_3]$ was set at 0.5×10^{11} molecules cm^{-3} and $[F]$ was $(3-4)[HN_3]$ for these quenching experiments. (b, bottom) Psuedo-first-order quenching rate constants obtained from the movable-detector method shown in (a) as a function of the corresponding $[O_2]$. Agreement was found between the values of the $NF(a)$ quenching constant by O_2 calculated by using both the movable-detector ($k = 6.0 \times 10^{-15}$ cm^3 molecules^{-1} s^{-1}) and fixed-point detection ($k = 6.6 \times 10^{-15}$ cm^3 molecules^{-1} s^{-1}) methods, indicating no wall deactivation effects.
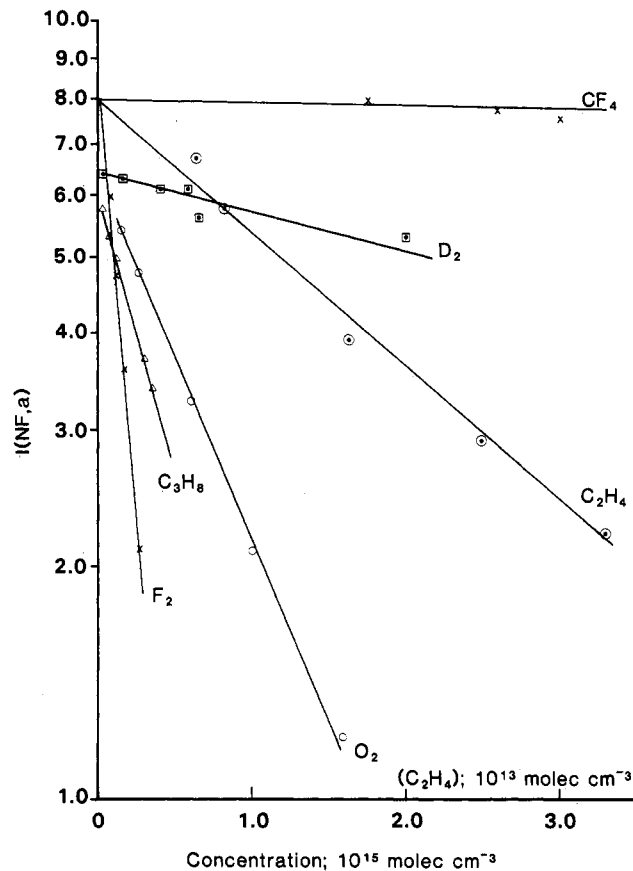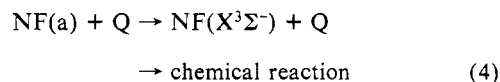
constants from the variable time experiments were 6.0×10^{-15} and 3.4×10^{-13} cm^3 s^{-1} for O_2 and C_2H_4, respectively. Figure 3 shows data obtained for experiments in which the [NF(a)] was monitored at a fixed time for variable [O_2] and [C_2H_4]. The same quenching rate constant was obtained for both methods with [O_2] and [C_2H_4]; see Table I. In general, experiments were done with the fixed point detection method, and plots for some additional reagents are shown in Figure 3. A summary of quenching rate constants from fixed-point observation is given in Table I. Only an upper limit value could be obtained for HCN because we had limited sample available. The NF(a) signal was relatively weak, and high reagent flows were needed for some cases to observe quenching; therefore, the rate constants have more uncertainty, ±30%, than typical measurements in discharge flow reactors.

For some cases, such as D_2 and C_3H_8 in Figure 3, there was an abrupt small drop in [NF(a)] upon addition of $\sim 10^{13}$ molecules cm^{-3} of reagent. Some experiments were done with [F]$_0 \approx$ [HN$_3$] for these cases in order to observe the quenching in the absence of F atoms; the initial drop in [NF(a)] upon addition of reagent seemed to be less serious. Reagents containing hydrogen will react with the excess [F] to give HF and a radical. Although the quenching rate by HF is slow and the small [HF] should cause no difficulty, the radical may cause problems. We believe that this rapid drop in [NF(a)] is associated with products from F atom reactions, but there may be other explanations. For cases showing two-component quenching plots, the slower quenching component was associated with electronic quenching of NF(a).

Obtaining good first-order plots with Cl_2, HCl, and COS proved to be impossible. For these cases there was a very *large* ($\sim$50%) drop of [NF(a)] upon the introduction of even a low concentration of reagent. Furthermore, the [NF(a)] returned to the initial value very slowly (>10 min) after the reagent flow was stopped. This behavior is characteristic for activation of the surface toward quenching by adsorption of the reagent.

There are very few other rate constant measurements available for comparison, but Heidner[10] has reported $k(NF_2) = (2.7 \pm 1.0) \times 10^{-16}$ cm^3 s^{-1} and Pritt and Benard[9] report $k(IF) \cong 1.6 \times 10^{-11}$, $k(CF_3/HF) \lesssim 10^{-13}$, $k(I) \sim 3.8 \times 10^{-12}$, and $k(F/F_2) \leq 10^{-13}$ cm^3 s^{-1} at 300 K. There also is an early report[11] that $k(DF) < 10^{-14}$ cm^3 s^{-1}. These values tend to support the trends of our work.

Conclusions

The large quenching rate constants of CF$_3$NO for both O_2(a) and NF(a) are consistent with prior arguments[12] about excitation transfer to a low-energy triplet acceptor state for CF$_3$NO. The lowest CF$_3$NO singlet state is at 1.69 eV,[17] and the triplet state will be below this energy. Quenching of NF(a) by O_2 also probably occurs by excitation transfer.

$$NF(a^1\Delta) + O_2(X^3\Sigma_g^-) \rightarrow NF(X^3\Sigma^-) + O_2(a^1\Delta_g)$$
$$\Delta H_0^\circ = -0.4 \text{ eV}$$
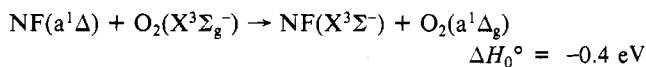
It is surprising that this rate constant is so small. According to Pritt and Benard,[9] the excitation-transfer rate constant to I atoms, with a similar energy defect, is much larger, 3.8×10^{-12} cm^3 s^{-1}.

The magnitudes of the rate constants for the diatomic reagents are indicative of quenching by E–V transfer. The isotope effect for H_2/D_2 is rather small relative to that for most E–V reactions, but this can be explained by energy considerations. Although both are nearly resonant, $D_2(v=4, \Delta H_0^\circ = -0.03$ eV) and $H_2(v=3, \Delta H_0^\circ = 0.04$ eV), the higher vibrational quantum number for $D_2(v=4)$ will reduce the rate constant somewhat. The E–V rate constants for NF(a) are larger than for O_2(a), even though the energy is larger for NF(a) and the molecules must acquire more vibrational energy. This implies that the intermolecular interaction potentials between NF(a) and these reagent molecules are stronger than with O_2(a). The rate constants for C_2H_4, NH$_3$, and (CH$_3$)$_3$N are suggestive of quenching by chemical reaction, even though the rate constants are smaller than for the reactions of NH(a). Except for cases that appear to proceed by chemical reaction, the room-temperature quenching rate constants of NF(a) tend to be approximately an order of magnitude smaller than those for NF(b).[19] Our estimate for the self-quenching rate constant is larger than the 1×10^{-13} cm^3 s^{-1} value favored by Heidner and co-workers,[10] but still much smaller than the 7×10^{-11} cm^3 s^{-1} value reported by Cheah, Clyne, and Whitefield for ground-state NF[3a]. In summary, these preliminary results show that quenching rate constants are small and that the self-quenching rate constant is modest. The NF(a) system continues to show promise as an energy storage medium.

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