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13. ABSTRACT (Maximum 200 words)

The $Cl + N_3$ reaction was used to provide a source of $NCl(a^1\Delta)$ molecules in a room temperature flow reactor. The total quenching rate constants were measured for 40 molecular reagent species and for F, N, O and H atoms. In most cases, rate constants were obtained for both $NF(a^1\Delta)$ and $NCl(a^1\Delta)$ so that the data could be confirmed by comparison with earlier studies of $NF(a^1\Delta)$). The quenching rate constants for $NCl(a^1\Delta)$ range from ~1×10^{-15} to 4×10^{-11} cm^3 molecule^{-1} s^{-1}. Except for H, F, O, CH_3Cl, HBr, HCl and HI, the rate constants for the $NCl(a^1\Delta)$ molecule are generally smaller than or comparable to those for $NF(a^1\Delta)$, and $NCl(a^1\Delta)$ is not especially reactive at 300 K. Small rate constants were obtained for common gases, such as H_2, CO_2 and CH_4; the rate constants are larger for unsaturated hydrocarbons and they increase with the number of carbon atoms in the molecule. A correlation was found between the basicity of a series of amines and the magnitudes of quenching rate constants of $NF(a^1\Delta)$ and $NCl(a^1\Delta)$; the rate constants for $NCl(a)$ were smaller than for $NF(a)$ indicating a less acidic nature for $NCl(a^1\Delta)$.

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FINAL TECHNICAL REPORT

for a grant

from AFOSR

to Kansas State University

CHEMICAL REACTIONS OF NCl(a$^1\Delta$): GENERATION AND REMOVAL

AFOSR Grant: F48620-96-1-0110

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Report Period: September 1, 1996 - March 15, 1999

Objectives:

The objectives of this work were to develop and characterize an efficient, gas-phase, chemical source of metastable $NCl(a^1\Delta)$ molecules and then to use this source to measure total quenching rate constants for the $NCl(a^1\Delta)$ molecules at room temperature. The $NCl(a^1\Delta)$ state is the first excited state of the NCl molecule. The ground state, $NCl(X^3\Sigma^-)$ is expected to be reactive and it cannot be used as a precursor to $NCl(a^1\Delta)$. Thus, a reaction that directly gives $NCl(a^1\Delta)$ was needed. Characterization of the chemical source included identifying the elementary chemical steps and measuring their rate constants in the generation mechanism for $NCl(a^1\Delta)$ molecules. After characterizing the $NCl(a^1\Delta)$ chemical source, systematic measurement of a set of quenching rate constants for $NCl(a^1\Delta)$ with a variety of molecules and atoms was done. The focus for the rate constant measurements was on reagents that might be components in the energy extraction schemes from the $NCl(a^1\Delta)$ chemical systems that are under study at the Phillips Laboratory of the US Air Force. The final objective was to study the interactions of $NF(a^1\Delta)$ molecules with $NCl(a^1\Delta)$ molecules and NF(a) molecules with $NCl(X^3\Sigma^-)$ molecules. Throughout our study, we have maintained close interaction with the research groups that are participating in the effort to develop the $NCl(a^1\Delta)$ chemical system into a useful, gas-phase, energy-storage device.

Status of Effort:

The research effort has been completed. The majority of the experiments with $NCl(a^1\Delta)$ were successful and the objectives mentioned above have been achieved. Six papers (*J. Phys. Chem. A* or *Chem. Phys. Lett.*) and one PhD thesis are either published

or accepted for publication. The research effort was extended to demonstrate that the method developed as the source for $NCl(a^1\Delta)$ molecules also could be applied to generate $NBr(a^1\Delta)$ molecules. It also is worth mentioning that the PhD student supported by this grant subsequently won a National Research Council Postdoctoral Fellowship and he has worked at the Phillips Laboratory on further development of the $NCl(a^1\Delta)$ chemical system. The undergraduate research assistant also wrote a Senior Thesis on the research that he did while supported by this grant. Since all the results have been published in readily accessible journals, this Final Report is brief.

Research Accomplished:

A.   Generation of NCl(a) and NBr(a) Molecules

The reaction of chlorine atoms with azide radicals (N_3) was utilized as a chemical source of $NCl(a^1\Delta)$ molecules in a room temperature flow reactor. The Pyrex glass reactor was coated with halocarbon wax to inhibit reactions of the atoms, NCl(a) and NF(a) with the walls. The azide radicals are generated from the reaction of F atoms with HN_3 with a branching fraction ≥ 0.96. The azide radicals in turn react with chlorine atoms to produce $NCl(a^1\Delta)$ with a product branching fraction ≥ 0.5. This branching fraction was determined by comparing the intensity of the $NCl(a^1\Delta\text{-}X^3\Sigma^-)$ transition, for an assumed radiative lifetime of 2 s, with that from the $NF(a^1\Delta\text{-}X^3\Sigma^+)$ transition. This radiative lifetime of $NCl(a^1\Delta)$ could be longer and, if so, the branching fraction would increase. A manuscript was published in *J. Phys. Chem. A.* that described the mechanism and the room temperature rate constants in the $F/Cl/HN_3$ reaction system. The most important steps in the mechanism are those for (1) the $F + HN_3$ reaction, (2) the $Cl + N_3$ reaction,

(3) the F + NCl(a) quenching reaction and (4) the Cl + NCl(a) quenching reaction. As part of this research effort, we developed a gas-phase titration scheme for chlorine atom concentrations. Either a microwave discharge in CF_2Cl_2 or the reaction of F with HCl used as a source of Cl atoms. The F atoms were generated by the standard technique of a microwave discharge in CF_4. The key to the success of our systematic experimental study of $NCl(a^1\Delta)$ was the capability of monitoring the NCl(a) concentration by observing the fluorescence intensity of the NCl(a-X) transition with a monochromator using a S-1 response, cooled photomultiplier tube. With this detector, we could simultaneously monitor the relative concentrations of both $NCl(a^1\Delta)$ and $NF(a^1\Delta)$ in the $F/Cl/HN_3$ reaction system. Since the absolute NF(a) concentration could be assigned from the initial $[HN_3]$, we also could estimate the [NCl(a)] from the relative NCl(a)-NCl(X) and NF(a)-NF(X) intensities.

The milestones with regard to characterizing the chemical source of NCl(a) molecules are enumerated below. The flow-reactor source provides NCl(a) concentrations up to $\sim 2 \times 10^{12}$ molecules cm^{-3}.

(i) Dr. Hewett demonstrated that the branching ratio for N_3 radical formation from the $F + HN_3$ reaction was $\geq 96\%$ by monitoring the alternative product HNF by laser induced fluorescence.

(ii) The rate constant for Cl + N_3 was directly measured, using laser-induced fluorescence of N_3 to monitor the $[N_3]$, to be $(1.2\pm0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is two times slower than the F + N_3 reaction.

(iii)   As part of his PhD Dissertation, Jerry Manke developed a titration method for measuring Cl atom concentrations in the flow reactor. With this capability the competition between $F + N_3$ and $Cl + N_3$ could be studied and the <u>relative</u> NF(a-X) and NCl(a-X) emission intensities could be used to establish the product branching ratio for NCl(a) formation from the known branching ratio for NF(a) formation. The NCl(a) formation branching fraction was ≈ 0.5. Another important discovery was the fact that F atoms react to remove NCl(a) 20-30 times more rapidly than they remove NF(a). Thus, the [F] must be carefully controlled in the flow reactor. Fortunately, the reaction rate of NCl(a) with Cl atoms is relatively slow.

(iv)   The bimolecular energy-pooling reactions between NCl(a) with itself and with NF(a) were characterized. The NF(a) + NCl(X) reaction was shown not to generate NCl(a) for the NCl(X) concentrations available in the flow reactor.

The same flow reactor and detection scheme that were used for the $F/Cl/HN_3$ system was employed to investigate the $Br + N_3$ reaction as a source of $NBr(a^1\Delta)$ molecules. The electronic energy of $NBr(a^1\Delta)$ is nearly identical with that for $NCl(a^1\Delta)$. A microwave discharge in CF_2Br_2 served as the Br atom source. The experiments were successful and this experimental design can be used to systematically study the chemical and physical reactions of $NBr(a^1\Delta)$. The preliminary work suggests that the rate constant for $Br + N_3$ is similar to those for F and Cl atoms with N_3; however, the branching fraction for $NBr(a^1\Delta)$ formation from $Br + N_3$ probably is less than for $NCl(a^1\Delta)$ formation from $Cl + N_3$. This claim is based on observation of similar, but somewhat weaker $NBr(a^1\Delta\text{-}X^3\Sigma^-)$ emission intensity, relative to the $NCl(a^1\Delta\text{-}X^3\Sigma^-)$ intensity, for the same initial $[HN_3]$, plus

the expectation that the radiative lifetime of $NBr(a^1\Delta)$ will be significantly shorter than for $NCl(a^1\Delta)$. Another observation was that Br atoms seem to cause significant quenching of $NBr(a^1\Delta)$. These two observations suggest that $NBr(a^1\Delta)$ molecule will be a less desirable energy storage system than the $NCl(a^1\Delta)$ molecule. However, the trends in reactivity for NF(a), NCl(a) and NBr(a) definitely are worth further investigation. A paper published in *Chem. Phys. Lett.* describes these experiments with $NBr(a^1\Delta)$.

B.   Quenching Rate Constants of $NCl(a^1\Delta)$ Molecules

The major experimental effort during the last year of the grant was to obtain a set of reliable quenching rate constants for $NCl(a^1\Delta)$ at room temperature using the flow reactor. Dr. Hewett checked (usually confirmed) the preliminary experiments of Jerry Manke. Room temperature rate constants were obtained for 40 reagents, and upper limits to rate constants were obtained for HN_3, CF_4 and CF_2Cl_2. Considerable time and effort were spent in obtaining reliable rate constants for HF, F_2, ClF and HI, since these molecules are likely components in the iodine atom energy extraction scheme of the NCl(a) chemical system. The table of rate constant that will be published in the paper describing the quenching measurements is attached. For most reagents, the quenching of NF(a) was observed in the same experiment and new rate constant measurements for $NF(a^1\Delta)$ are included in the table. In general, good agreement exists between our new rate constant measurements for $NF(a^1\Delta)$ and those that are in the literature. This agreement gives confidence in the $NCl(a^1\Delta)$ results. Inspection of the Table shows that the reactivity of $NCl(a^1\Delta)$ is similar to that for $NF(a^1\Delta)$ with a few exceptions. One significant difference is the larger rate constant for quenching of NCl(a) by O_2. This is

attributed to greater ease of electronic energy exchange giving $O_2(a)$, because of the smaller energy defect for the $NCl(a^1\Delta)$ reaction. Another difference is that ethers, alcohols and alkanes seem to induce a concentration dependent, wall deactivation rate for $NCl(a^1\Delta)$, but not for $NF(a^1\Delta)$, i.e., the halocarbon wax coating in the reactor failed. Thus, obtaining the gas-phase quenching rates for $NCl(a)$ was very difficult and sometimes impossible for these reagents.

As noted in our very first experiments in 1996, the rate constants measured in the flow reactor usually do <u>not</u> agree with those measured by pulsed laser (ultraviolet) photolysis of ClN_3. Our quenching rate constants are <u>much</u> smaller for H_2, HF, HCl, F_2, Cl_2 and Br_2. Dr. Henshaw (Phillips Lab) also has confirmed the smaller rate constants measured in the flow reactor vs. the pulsed experiments. In our opinion, the flow reactor experiments have fewer potentials difficulties. We believe the pulsed laser photolysis of ClN_3 gives data that are unreliable with respect to $NCl(a)$ quenching processes. Several of these rate constants in the above list could be important in the energy extraction schemes from the $NCl(a^1\Delta)$ system that have been contemplated for application. Since these rate constants have the potential to be important in applications, most of our measurements were done in two different reactors with different sources of the reagents. The rate constants from the two flow reactors are quite reproducible, and we believe that these rate constants are correct to within ±30%.

A second independent measurement is included in the Table for F atom removal of $NCl(a^1\Delta)$. This experiment uses a microwave discharge in F_2 as the F-atom source, wherever the earlier measurement (paper #4 in the publication list) used discharges in

CF_4 and SF_6. The large quenching rate constant for F atoms was confirmed. The last set of experiments in the flow-reactor was a measurement of quenching by H, O and N atoms. The removal rates for $NF(a^1\Delta)$ and $NCl(a^1\Delta)$ were compared for the same atom concentration and in the same reactor. The $NCl(a^1\Delta)$ rates were similar, but somewhat larger, than for NF(a); we recommend $k_H = 2.1 \pm 0.5 \times 10^{-12}$, $k_O = 7 \pm 3 \times 10^{-12}$ and $k_N = 0.9 \pm 0.4 \times 10^{-12}$ cm^3 $molec^{-1}$ s^{-1} as the rate constants for $NCl(a^1\Delta)$ at room temperature. As for NF(a), the NCl(a) molecule is not particularly reactive with these atoms at room temperature.

Table 1. Quenching rate constants for NCl(a$^1\Delta$) at room temperature.

Molecule	NCl(a$^1\Delta$) (10^{-14} cm^3 molecule^{-1} s$^-$) Current[a]	Previous	NF(a$^1\Delta$) (10^{-14} cm^3 molecule^{-1} s^{-1}) Current[a]	Previous[b]	O$_2$(a$^1\Delta_g$)[c] (10^{-18} cm^3 molecule^{-1} s^{-1})
O$_2$	280 ± 60	250 ± 20[d]	0.5 ± 0.2	0.70 ± 0.07	1.9 ± 0.5
N$_2$	≲0.10 ± 0.05			≤0.0012	0.1
NO	~0.4 ± 0.2			≤0.15	40 ± 10
H$_2$	≤0.1	68 ± 7[d]		0.007 ± 0.002	4.5 ± 0.5
CO	0.34 ± 0.07		0.6 ± 0.1	0.36 ± 0.04	9.0 ± 3.0
CO$_2$	0.11 ± 0.02			0.006 ± 0.002	< 0.5
SO$_2$	12 ± 3		4.0 ± 0.5		0.004 ± 0.001
CH$_4$	≤0.1		<0.1	≤0.01	1.4 ± 0.3
C$_2$H$_2$	1.4 ± 0.3		18 ± 3	23 ± 2	6.0 ± 0.6
C$_2$H$_4$	2.5 ± 0.5		29 ± 4	32 ± 3	2.0 ± 0.2
C$_3$H$_6$	18 ± 3		145 ± 20	150 ± 20	2.2 ± 0.2
C$_4$H$_6$	62 ± 6		230 ± 30	270 ± 30	10 ± 5
cis-C$_4$H$_8$	134 ± 10		330 ± 30		20 ± 10
trans-C$_4$H$_8$	162 ± 15		310 ± 30		
C$_6$H$_6$	128 ± 15		39 ± 4		5.3
F$_2$	3.4 ± 0.7	25 ± 11[a]	3.4 ± 0.3	3.2 ± 0.3[e]	
Cl$_2$	40 ± 10	1800 ± 300[d] 2900 ± 600[g]	56 ± 4	58 ± 6[f]	
Br$_2$	1400 ± 400	14000 ± 2000[g]	2100 ± 400	3800 ± 600[f]	
ClF	1060[h]		760[h]	760 ± 100[f]	
F	4200 ± 400	2200 ± 700[i]		40 ± 20	

HF	0.5 ± 0.3	82 ± 12^d	0.2 ± 0.1	0.3^e	140 ± 50
HCl	1.5 ± 0.4^j	490 ± 70^d	0.20 ± 0.05	0.16 ± 0.03	4 ± 3
HBr	180 ± 30		9.0 ± 2.0		8 ± 4
HI	2900 ± 500		380 ± 50		< 20
HN_3		$\leq 1.0^i$			
CH_3Cl	10 ± 2		1.1 ± 0.3	1.1 ± 0.2	5 ± 2
CH_2Cl_2	18 ± 2			0.71 ± 0.08	
CF_2Cl_2	≤ 0.1				
CH_3Br	7.2 ± 0.4		20 ± 4	26 ± 4	30 ± 15
CF_2ClBr	0.3 ± 0.1		0.5 ± 0.1	0.59 ± 0.06	
CH_3I	81 ± 8		246 ± 25	230 ± 20	40 ± 20
CF_3I	60 ± 10		25 ± 3	24 ± 3	< 0.5
NH_3	11 ± 2		360^k	360 ± 20	4.41 ± 0.46
NH_2CH_3	240 ± 40		1230 ± 100	1250 ± 200	13 ± 2
$NH(CH_3)_2$	1040 ± 100		1840 ± 200	1750 ± 100	93 ± 6
$N(CH_3)_3$	1960 ± 200		2500 ± 300	2600 ± 200	3200 ± 200
C_2H_6	1			0.07 ± 0.02	
C_4H_{10}	$\leq 0.5^m$		1.5 ± 0.5		
CH_3OH	1		8 ± 2	11 ± 1	
$(CH_3)_2O$	35 ± 6^m		145 ± 30	130 ± 15	
H_2S	2.7 ± 0.4^m		65 ± 10	61 ± 6	2.0 ± 1.5
COS	1		5 ± 1		2 ± 1

[a]This work. Note that the quenching rate constants for $O_2(a)$ are four orders of magnitude smaller than those for NCl(a) and NF(a). The references mentioned below are given in the paper describing these experiments.

[b]Reference 17. [c]Reference 20b if reported, otherwise from reference 20a. [d]Reference 32.

[e]Reference 16. [f]Reference 18. [g]Reference 31.

[h]The rate constants for ClF have been scaled to match the previously determined NF(a) rate constant, see text for details. Even without scaling, $k_{ClF} > 500 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

[i]Reference 1.

[j]The smaller rate constant for HCl reported here is favored over the value given in ref. 33; the rate constant for quenching NBr(a) by HCl given in ref. 33 also may be too large.

[k]The rate constant for NH_3 was set equal to 360×10^{-14} cm^3 molecule^{-1} s^{-1} in order to accurately determine the reaction time. If the time was calculated by assuming plug flow, then the average rate constant was $(320 \pm 20) \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}.

[l]Reproducible data were not obtained.

[m]Two decay processes were observed, an extremely fast decay followed by a slow decay. The listed rate constant is for the slow decay process.

Personnel Supported:

- Dr. Jerry Manke - Jerry completed his PhD work in October 1997 and accepted an NRC Postdoctoral Fellowship at the Phillips Laboratory.

- Dr. Kevin Hewett - Kevin was a postdoctoral fellow who worked on the grant from November 1996 through August 1998.

- Mr. Greg Brewood - Greg worked as an undergraduate assistant from September, 1998 through March, 1999. Greg wrote his senior undergraduate thesis from the work that he did on this project.

Publications:

1. K. B. Hewett and D. W. Setser, "Determination of the Product Branching Fraction for HNF Formation in the Reaction of HN_3 with F", *J. Phys. Chem. A*, 101, 9125 (1997).

2. G. C. Manke II and D. W. Setser, "Measuring Gas-Phase Chlorine Atom Concentrations: Rate Constants for Cl + HN_3, CF_3I and C_2F_5I", *J. Phys. Chem. A*, 102, 153 (1998).

3. K. B. Hewett and D. W. Setser, "Chemical Kinetics of the Azide Radical: Rate Constants for Reactions with Cl, NO, NO_2, O_2, CO, CO_2, Cl_2 and C_3H_6",*J. Phys. Chem. A*, 102, 6274 (1998).

4. G. C. Make II and D. W. Setser, "Kinetics of $NCl(a^1\Delta)$ Generation: The Cl + N_3 Rate Constant, the Product Branching Fraction and Quenching of $NCl(a^1\Delta)$ by F and Cl Atoms", *J. Phys. Chem. A*, 102, 7257 (1998).

5. K. B. Hewett and D. W. Setser "Generation of $NBr(a^1\Delta)$ by the Reaction of N_3 Radicals with Br Atoms: A Flow-Reactor Source for Quenching Rate Constant Measurements", *Chem. Phys. Lett.* 297, 335 (1998).

6. K. B. Hewett, G. C. Manke II, D. W. Setser and G. Brewood, "Quenching Rate Constants of $NCl(a^1\Delta)$ at Room Temperature", *J. Phys. Chem.* Submitted June, 1999.

7. G. C. Manke II, PhD Dissertation, Kansas State University (1997).