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Solvent Dependence of Ligand to Metal Charge-Transfer Oscillator Strength: Outer-Sphere Perturbation of the Ruthenium(III)–Cyanamide Bond

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A study of the effect of the nature of the solvent on the $b_1^* \leftarrow b_1$ LMCT oscillator strength of the complex $[(NH_3)_5Ru((2,3\text{-dichlorophenyl})\text{cyanamide}(1-))][ClO_4]_2$ is reported. A plot of LMCT oscillator strength vs donor number gives a linear relationship with intercept 0.186, slope −0.00294/DN, and $R = 0.998$. Weak and strong coupling approaches to donor and acceptor interactions are used to evaluate this novel effect. The strong coupling approach, in which oscillator strength is proportional to the square of the donor and acceptor wave function overlap, appears to be consistent with all experimental data. Thus, the outer-sphere hydrogen-bonding interactions of the donor solvent with the ammine protons perturbs the ruthenium(III) π-acceptor wave function, reducing its overlap with the π-donor wave function of the cyanamide group.

Introduction

The rate of thermal intramolecular electron transfer between fixed donor and acceptor redox sites is largely determined by kinetic and electronic parameters and can be expressed by

$$k_{et} = \kappa\nu_n \exp(-\Delta G^*_{et}/RT) = \kappa k_0 \qquad (1)$$

where κ is an adiabaticity factor that depends on the extent of coupling between donor and acceptor, ν_n, the nuclear frequency factor, is $(1-10) \times 10^{12}\ s^{-1}$ at 25 °C, and ΔG^*_{et} is the activation barrier to electron transfer. The kinetic dependence of electron-transfer rates has been treated classically by the Marcus theory[1] and modified with some later semiclassical[2] and quantum-mechanical approaches.[3] The electronic dependence of electron-transfer rates arises from the necessity that both donor and acceptor wave functions must interact to some extent for electron transfer to occur.

For mixed-valence complexes, if donor and acceptor wave functions can strongly couple with the bridging ligand's HOMO or LUMO, a delocalized state will result in which the odd electron is shared equally between both redox sites. If one could decrease the coupling in this system (i.e. by changing the nature of the bridging ligand), theory predicts[4] the formation of an activation barrier to electron transfer that would localize the odd electron on a specific redox site. Thermal electron transfer within this localized state would be entirely dependent on kinetic factors (adiabatic electron transfer) provided the extent of electronic coupling is sufficient such that $\kappa = 1$. If electronic coupling is very small, $\kappa < 1$, then both electronic and kinetic factors determine thermal electron-transfer rates (diabatic electron transfer).

One final condition for thermal electron transfer arises when donor and acceptor wave functions are so far apart that overlap between them is not significant. In this case, it is necessary to invoke electron tunneling to model electron-transfer rates[5]

$$k_{et} = k_0 \exp[-\beta(r - r_0)] \qquad (2)$$

where r is the separation between donor and acceptor wave functions, r_0 is the separation at van der Waals contact, and β is proportional to the square root of the potential barrier to electron tunneling.[6] The magnitude of β is expected to depend on the nature of the medium between the redox sites, being small when the energy differences between the medium's HOMO or LUMO and the donor and acceptor wave functions are also small. A few model systems have been developed to explore both distance and medium effects on electron-tunneling processes.[5b,7]

It is clear from the above that the extent of electronic coupling determines the form of the expression used to calculate thermal electron-transfer rates. In this regard, it is important that the influence of the bridging medium between redox sites be quantitatively evaluated. There are some recent theoretical attempts[8] to do just that, but experimental justification is still lacking.

Optical[9] and thermal[2] electron-transfer theories have been successful in treating the solvent as a dielectric continuum when a direct interaction between inner-sphere ligands and solvent molecules does not occur. In a study[10] of asymmetric mixed-valence dimers, made up of ruthenium(III) ammine and ruthenium(II) bipyridine moieties, it was determined that preferential hydrogen bonding to the ammine ligands bound to ruthenium(III)[11] resulted in a solvent donor number[12] dependent contribution to the Frank–Condon barrier of approximately 48 cm^{-1}/donor number that completely overwhelms the dielectric continuum theory derived solvent dependence. Recent studies[13] of the above complexes in mixed solvents have revealed a dependence of electronic coupling between redox sites on preferential solvation of the acceptor redox site.

In this paper, we establish a spectroscopic method by which the extent of electronic coupling between a π-acceptor metal and a π-donor ligand can be evaluated and varied in a predictable manner by changing the nature of outer-coordination-sphere interaction with the ammine ligands bound to Ru(III). When this type of chromophore is incorporated into a mixed-valence complex, it will act as a probe of the extent of acceptor wave function interaction with the bridging ligand.

The system in this study, $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ (where 2,3-Cl$_2$pcyd = (2,3-dichlorophenyl)cyanamide anion), contains a Ru(III)–cyanamide anion LMCT chromophore. In a previous paper,[14] we have shown that the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition for a series of pentaammineruthenium(III) complexes of phenylcyanamide anion ligands increases with increasing π basicity of the cyanamide ligand. We will demonstrate that the nature of the outer coordination sphere can perturb the Ru(III) acceptor orbital and its interaction with the cyanamide anion group and that the perturbation can be evaluated by the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition. We will show that the interaction between Ru(III) and the cyanamide anion group should not be treated with a weak coupling approach and suggest that a direct relationship exists between the magnitude of donor and acceptor wave function

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Table I. Spectroscopic Data for the $b_1^* \leftarrow b_1$ LMCT Transition of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ in Various Solvents

solvent	DN[a]	E[b]	ϵ_{max}[c]	$\bar{\nu}_{1/2}$[d]	f[e]
dimethyl sulfoxide	29.8	16.32	5120	4260	0.100
dimethylformamide	26.6	16.11	5490	4280	0.108
tetrahydrofuran	20	14.86	6330	4280	0.125
acetone	17	14.85	6560	4480	0.135
acetonitrile	14.1	14.41	6850	4580	0.144
nitromethane	2.7	13.71	7160	5450	0.180

[a] Donor number.[5] [b] LMCT band energy at ϵ_{max}, $\times 10^{-3}$ cm^{-1}. [c] In M^{-1} cm^{-1}; at least two quantitative measurements (weight and volume to four significant figures) were performed in each solvent; average percent deviation in measurements was 1.2%. [d] Bandwidth in cm^{-1}. [e] Oscillator strength was calculated from eq 3.

overlap and the oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition.

Experimental Section

The synthesis of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ has been previously described.[15] Accusolv grade dimethyl sulfoxide, tetrahydrofuran, acetone, and acetonitrile were purchased from Anachemia. Spectrograde dimethylformamide and nitromethane (99+%) were purchased from Aldrich. All solvents were stored over 4-Å molecular sieves. UV–vis spectra were recorded on a Perkin-Elmer Lamda 4b spectrophotometer.

Results and Discussion

The crystal structure[14] of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$ has shown the cyanamide group to be coordinated to ruthenium(III) via the nitrile nitrogen. The cyanamide anion has two pairs of nonbonding electrons of π symmetry that can interact with π-symmetry d orbitals on ruthenium(III). These give rise to two LMCT transitions in the visible region of the complex's electronic absorption spectrum. The lower energy LMCT band has been assigned[15] to an allowed $b_1^* \leftarrow b_1$ transition and is completely separated from any other absorption. This allows accurate determination of the band's oscillator strength using the expression[16]

$$f = 4.6 \times 10^{-9} \epsilon_{max} \bar{\nu}_{1/2} \qquad (3)$$

where ϵ_{max} is the extinction coefficient at maximum band height in M^{-1} cm^{-1} and $\bar{\nu}_{1/2}$ is the band width at half the band height. In addition to the solvents listed in Table I, piperidine and triethylamine were tested. However, low solubility combined with decomposition of the complex in these solvents made oscillator strength determination unreliable. No dependence of the $b_1^* \leftarrow b_1$ LMCT oscillator strength on complex concentration was found over a concentration range 3×10^{-4} to 5×10^{-5} M in the solvents studied.[17] The data are compiled in Table I, and a plot of oscillator strength vs donor number is given in Figure 1.

It is possible using the data in Table I to plot LMCT energy vs donor number and derive a linear relationship with intercept 13 200 cm^{-1}, slope 101 cm^{-1}/DN, and correlation coefficient R = 0.970. This linear relationship is expected[11] and indicates ground-state stabilization of the complex by the solvent. However, the plot of oscillator strength vs donor number also shows a linear relationship with negative slope −0.00294/DN, intercept f = 0.186, which may represent oscillator strength in the absence of solvent donor interaction, and R = 0.998. The normal correction for oscillator strength solvent dependence[18] does not account for the observations, and so further discussion is necessary.

Oscillator strength, f, is a dimensionless quantity that is used to express transition probability and can be calculated theoretically from the expression[19]

$$f = 1.085 \times 10^{11} G \bar{\nu} D^2 \qquad (4)$$

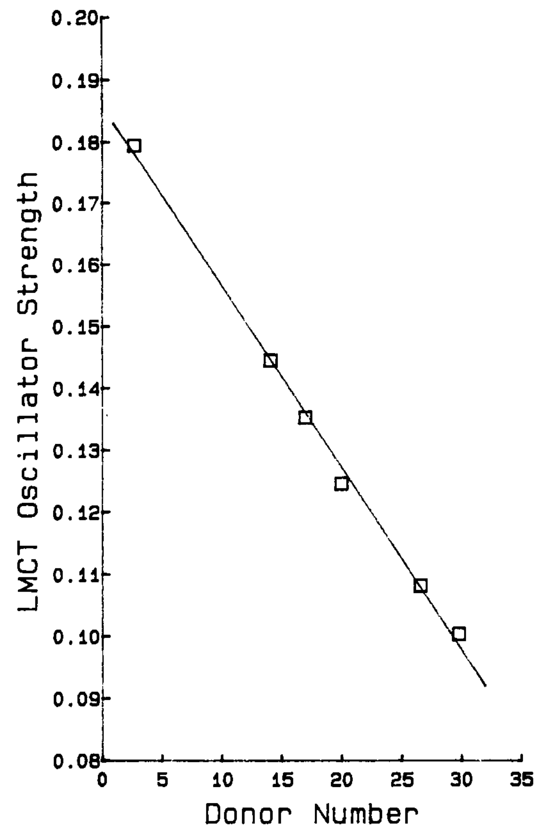

Figure 1. Plot of oscillator strength of the $b_1^* \leftarrow b_1$ LMCT transition of $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ vs solvent donor number.

where G refers to the degeneracy of the states concerned (for the complex, the $b_1^* \leftarrow b_1$ transition is unidimensional and G = 1), $\bar{\nu}$ is the energy at ϵ_{max} in cm^{-1}, and D is the dipole strength for an electric-dipole-allowed transition. For a one-electron system, the dipole strength is related to M, the charge-transfer transition dipole moment, by

$$M = \langle \Psi_g | er | \Psi_e \rangle = eD^{1/2} \qquad (5)$$

where Ψ_g is the ground-state wave function, Ψ_e is the excited-state wave function, and er is the transition moment dipole operator.[19] The square of the electronic charge, e^2, is usually incorporated into the prefactor of eq 4. The form of the transition moment depends on whether the coupling between donor and acceptor wave functions is strong or weak.

Mulliken's charge-transfer theory[20] has been successful in predicting the oscillator strength dependence of weakly interacting organic charge-transfer complexes. The same theoretical approach has formed the basis of the Hush model[21] of intervalence transitions seen for weakly coupled mixed-valence complexes.

If we consider isolated donor ϕ_d and acceptor ϕ_a wave functions to weakly couple, the resulting ground and excited wave functions can be written in the general form

$$\Psi_g = \phi_d + \alpha_{ad}\phi_a \qquad (6)$$

$$\Psi_e = \phi_a + \alpha_{da}\phi_d \qquad (7)$$

As these wave functions must be mutually orthogonal

$$\alpha_{ad} + \alpha_{da} + S_{ad} = 0 \qquad (8)$$

where S_{ad} is the overlap integral between donor and acceptor wave functions. For a weakly coupled system, the assumption S_{ad} = 0 is reasonable and the mixing coefficients are related such that

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$\alpha_{ad} = -\alpha_{da} = \alpha$. Then by perturbation theory

$$\alpha = H_{ad}/E_d - E_a \tag{9}$$

where H_{ad} is the resonance exchange integral in cm^{-1}, which is a measure of the degree of electronic coupling between "pure" donor and acceptor wave functions, and $E_d - E_a$ is the difference in energy in cm^{-1} between donor and acceptor wave functions that can be approximated by the optical energy at ϵ_{max} of the charge-transfer band $\bar{\nu}$. Substituting eqs 6 and 7 into eq 5 yields after simplification[22]

$$M = \alpha e R \tag{10}$$

where R represents the transition dipole length (the distance through which the charge is carried) in cm. Using eqs 9, 10, and 5 to solve for the dipole strength and substituting this value into eq 4 yields

$$f = 1.085 \times 10^{11} G H_{ad}^2 R^2 \bar{\nu}^{-1} \tag{11}$$

It can be readily shown by substituting into eq 11 values of f and $\bar{\nu}$ for $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)]^{2+}$ in acetonitrile from Table I and using an estimated value of $R = 3.15$ Å (the separation between Ru(III) and the center of the cyanamide group[23]) that H_{ad} has a calculated value of 4400 cm^{-1}. This degree of coupling is incompatible with the weak coupling approximation ($S_{ad} = 0$) used to derive eq 11. For example, the delocalized strongly coupled mixed-valence state in the Creutz–Taube ion has an estimated $H_{ad} = 3140$ cm^{-1}.[4] Since it is known that strongly coupled mixed-valence complexes do not obey the Hush model,[4] we feel it more appropriate to treat the π interaction between ruthenium(III) and the cyanamide anion as a strong coupling case in which $S_{ad} > 0$.[24]

Mulliken[25,26] recognized that for an allowed transition between ground and excited charge-transfer states there must be some region of overlap between donor and acceptor. He derived the following expression for the transition dipole moment, using the atomic orbital approximation for interatomic charge transfer between two totally symmetric hydrogen wave functions

$$M = e S_H R \tag{12}$$

where S_H is the overlap integral between two hydrogen 1s orbitals and e and R have the same meaning as before. Other researchers who have investigated the MLCT transitions of Cu(I)[27] and Ru(II)[28] diimine systems have incorporated an adjustable constant k that depends on the orbital type to give the more general expression

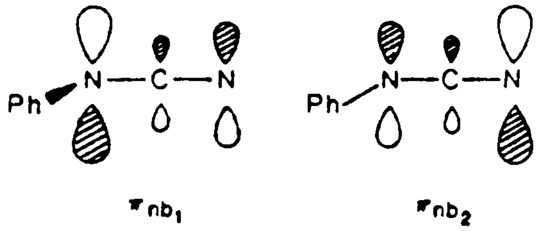
$$M = e k S_{ad} R \tag{13}$$

Using eqs 5 and 13 to solve for the dipole strength and substituting this result into eq 4 yields

$$f = 1.085 \times 10^{11} G \bar{\nu} k^2 S_{ad}^2 R^2 \tag{14}$$

The trend in oscillator strength in Figure 1 can now be explained by a decrease in π overlap between the cyanamide group and ruthenium(III) as the donor number of the solvent increases.

The phenylcyanamide anion is a resonance-stabilized three-atom π system, Ph—N═C═N$^-$ ↔ Ph—N̄—C≡N. There are two pairs of nonbonding electrons that can be delocalized in this π system. Their orthogonal molecular orbitals can be represented by I where the size of an atomic orbital approximates[29] its contribution to the molecular orbital. The π_{nb_1} MO can delocalize into the phenyl ring π system, while the π_{nb_2} MO is restricted to the cyanamide group. The $b_1^* \leftarrow b_1$ transition essentially involves a transition of an electron from the anionic cyanamide π_{nb_2} MO to a ruthenium(III) 4d orbital.[15] The overlap integral for the associated π-bonding interaction is



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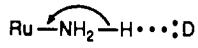
$$S_\pi = C_n \langle \Psi_{4d} | \Psi_{2p} \rangle \tag{15}$$

where C_n represents the electron density coefficient of the terminal nitrogen of the π_{nb_2} MO, Ψ_{2p} is the terminal nitrogen 2p wave function, and Ψ_{4d} is the ruthenium(III) 4d wave function. The magnitude of C_n will depend on the ability of ruthenium(III) to polarize electron density to itself and stabilize the Ph—N═C═N$^-$ resonance structure.

Preresonance Raman studies[30] of metal to ligand charge transfer, in $[(NH_3)_4Ru(2,2'\text{-bipyridine})]^{2+}$, have provided direct evidence for the strengthening of the ammine nitrogen–ruthenium bond with increasing solvent donor number. The net effect of a hydrogen bond between donor solvent and ammine proton is the transfer of electron density from the partially deprotonated ammine to ruthenium(III)



the limiting case being the complete loss of a proton and the formation of an amido ligand (a strong π donor).[11] This sets up a competition with the cyanamide anion for the πd orbitals of ruthenium(III), weakening the ability of Ru(III) to polarize cyanamide π-electron density to itself and increasing the contribution of the resonance form Ph—N̄—C≡N to the π_{nb} MO's in I. The magnitude of C_n and hence S_π is therefore expected to decrease with increasing solvent donor number. On the other hand, the transition dipole moment should increase with increasing solvent donor number. As the effect of this on oscillator strength, calculated by using eq 14, is in opposition to the trend in Figure 1, only a change in π overlap can be used to explain the dependence of the $b_1^* \leftarrow b_1$ LMCT oscillator strength on solvent donor number.

Evidence for the weakening of the Ru(III)–cyanamide bond is shown by the change in LMCT bandwidths with donor number in Table I. For charge-transfer transitions between bonding and antibonding MO's, bandwidth is predicted to decrease as the difference between ground-state internuclear separation and excited-state internuclear separation for both inner and outer coordination spheres becomes smaller (Franck–Condon factors).[16] Since the outer-coordination-sphere contribution to bandwidth is expected to increase with increasing solvent donor number,[11] the overall decrease in bandwidth with solvent donor number (see Table I) must be due to the dominant decrease in π bonding and antibonding character between Ru(III) and the cyanamide anion.

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(23) The cyanamide π_{nb} MO involved in the $b_1^* \leftarrow b_1$ LMCT transition is a three-atom π system localized on the cyanamide group.[15] The transition dipole moment was estimated to be the distance between the cyanamide carbon and Ru(III) by using data from the X-ray crystal structure of the complex $[(NH_3)_5Ru(2,3\text{-}Cl_2pcyd)][SO_4]\cdot C_2H_5OH$ in ref 14.

(24) To reach a weak coupling limit of <1000 cm^{-1} [4] would require $R = 14$ Å. This is even greater than the total length of the Ru(III)–phenylcyanamide group. The phenyl ring will introduce only a second-order effect to the magnitude of the transition dipole moment because it is not coupled to the cyanamide π_{nb} MO involved in the $b_1^* \leftarrow b_1$ LMCT transition.[15] Examples of systems where extended conjugation has resulted in an increase in CT oscillator strength are found in refs 21 and 26.

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It is possible that the decomposition of the complex in strong donor solvents arises from the weakening of the Ru(III)–cyanamide bond, although further study into the mechanism would have to confirm this.

From the above observations, it is clear that outer-sphere interactions with ligands can have a substantial effect on the degree of electronic interaction between donor and acceptor wave functions. Future studies will attempt to derive theoretical estimates of C_n and R as a function of solvent and the nature of the phenylcyanamide ligand. We have prepared the bridging ligand 4-pyridylcyanamide anion and intend to prepare asymmetric ruthenium mixed-valence complexes. The Ru(III)–cyanamide chromophore is a probe of the extent of acceptor wave function interaction with the bridging ligand that will help evaluate the predicted[13] solvent-dependent electronic coupling between donor and acceptor sites.

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Non-Metal Redox Kinetics: Reactions of Trichloramine with Ammonia and with Dichloramine

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Trichloramine reacts with excess NH_3 and base (B) with the rate expression $-d[NCl_3]/dt = 2k_B[B][NH_3][NCl_3]$, based on the overall stoichiometry $2NCl_3 + 3NH_3 + 3OH^- \rightarrow 3NH_2Cl + N_2 + 3Cl^- + 3H_2O$. The reaction is general-base assisted with k_B values ($M^{-2}\ s^{-1}$, 25.0 °C, $\mu = 0.50$ M) of 4.46×10^3 for OH^-, 3.3×10^3 for PO_4^{3-}, and 22 for NH_3. A water path with $k_{H_2O} = 2.2\ M^{-1}\ s^{-1}$ and an acidic phosphate path for $H_2PO_4^-$ ($k_{HB} = 450\ M^{-2}\ s^{-1}$) are also found. The rate-determining step in the proposed mechanism is a Cl^+ transfer between NCl_3 and NH_3 to give $HNCl_2$ and NH_2Cl. This is followed by N_2 formation in a rapid base-assisted reaction between NCl_3 and $HNCl_2$ with the rate expression $-d[NCl_3]/dt = k_B'[B][HNCl_2][NCl_3]$, based on the stoichiometry $NCl_3 + HNCl_2 + 3OH^- \rightarrow N_2 + 2HOCl + 3Cl^- + H_2O$. Values of k_B' ($M^{-2}\ s^{-1}$, 25.0 °C, $\mu = 0.50$ M) are 2.92×10^4 for HPO_4^{2-} and greater than 4×10^7 for OH^-. The HOCl released in the formation of N_2 reacts with excess NH_3 to give more NH_2Cl, which accounts for the overall stoichiometry of 1.5 NH_2Cl formed per NCl_3. The reaction between NCl_3 and $HNCl_2$ is of critical importance in the explanation of breakpoint chlorination processes.

Introduction

Monochloramine, dichloramine, and trichloramine (nitrogen trichloride) are formed when excess chlorine is added to aqueous solutions that contain ammonia.[1-6] A process known as breakpoint chlorination occurs at Cl/N molar dose ratios greater than 1.6.[5-7] Under these conditions, ammonia is oxidized to N_2 and the active chlorine species (HOCl, NH_2Cl, $HNCl_2$, and NCl_3) are reduced to Cl^-. Chlorination provides the essential disinfection needed in the treatment of potable and waste water. The breakpoint process is vital in order to remove excess chloramines that are toxic to aquatic life. The mechanism of breakpoint chlorination has not been well understood, because many competing reactions can take place with the highly reactive chlorine species. In the past there has not been sufficient information about the kinetics of individual reaction steps that lead to N_2 formation. We have addressed this problem by isolation of several of the reactions where NCl_3 is a reactant.

Table I. Ultraviolet Absorption Spectral Characteristics of Chlorine Species[a]

species	λ, nm	ε, $M^{-1}\ cm^{-1}$
NCl_3	336 (max)	195[b]
	360	130
$HNCl_2$	294 (max)	272[c]
	360	≃3
NH_2Cl	243 (max)	461[c]
	360	≃0
OCl^-	292 (max)	350[d]
	360	≃5
HOCl	228 (max)	120[e]
	360	≃0

[a] This work except where noted. [b] References 17 and 18. [c] Reference 16. [d] References 14 and 15. [e] Calculated from ref 15.

The addition of Cl_2 to water generates HOCl (eq 1), which reacts with NH_3 to form NH_2Cl (eq 2). Monochloramine is

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (1)$$

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \qquad (2)$$

relatively stable in dilute solutions that contain excess ammonia. Hydrazine formation requires highly basic solutions and is a slow process.[8] Dichloramine forms on the addition of more HOCl to monochloramine (eq 3) or by the disproportionation of monochloramine in acidic solutions (eq 4). Dichloramine is not stable

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