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Ligand and Solvent Effects on Emission Lifetimes of Cr(III) Ammines

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

Lifetimes for emission from the first thexi doublet state, D_1° (E_g in O_h symmetry) are reported for $Cr(bipyr)_3^{3+}$, $Cr(en)_3^{3+}$, *cis*- and *trans*-$Cr(en)_2(NCS)_2^+$, $Cr(en)(NCS)_4^-$, $Cr(NH_3)_6^{3+}$, $Cr(ND_3)_6^{3+}$, $Cr(NH_3)_5Cl^{2+}$, $Cr(NH_3)_5(NCS)^{2+}$, $Cr(NH_3)_5(H_2O)^{3+}$, *trans*-$Cr(NH_3)_2(NCS)_4^-$, and $Cr(NCS)_6^{3-}$, in water and in D_2O, acetonitrile, dimethylformamide, dimethyl sulfoxide, and sulfolane solutions at 20 °C. Values range from under 5 ns to 55 μs. The temperature dependence of emission was determined for several systems, the apparent activation energies ranging from 7 to 12 kcal mol^{-1}. Initial emission intensities also show temperature dependence, with apparent activation energies, E_f, ranging from −2 to 4.5 kcal mol^{-1}. It is suggested that emisson lifetimes in room temperature fluid solution are controlled by the rate of chemical reaction from D_1° and that E_f reflects the temperature dependence of the prompt intersystem crossing yield. A set of rules is proposed for estimating emission lifetimes of Cr(III) complexes under photochemical conditions.

The ligand field theory of coordination compounds in general and of Cr(III) complexes in particular is, of course, a highly developed subject. Both historically and today the principal experimental parameters are the transition energies as measured by the positions of the band maxima.[1,2] Ligand fields are characterized in such terms, as in the spectrochemical and nephelauxetic series. It is relevant to the present paper to note that one of the approximations of ligand field theory has been the tacit ignoring of solvent effects on ligand field strengths. Although such effects are small, their existence was recognized early[3] and the subject has been investigated occasionally since.[4]

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A new dimension was added to information about ligand field excited states as the photochemistry and photophysics of Werner type complexes developed to its present status.[5] The important excited states now appear to be those reached after thermal equilibration (thexi states) rather than the Franck-Condon state, Q_{FC}, associated with absorption band maxima. Fig. 1 illustrates the distinction. Thexi states have a characteristic structure and reaction chemistry, including stereochemistry.[6] In the case of Cr(III) complexes, the best photochemically studied family of coordination compounds, the two

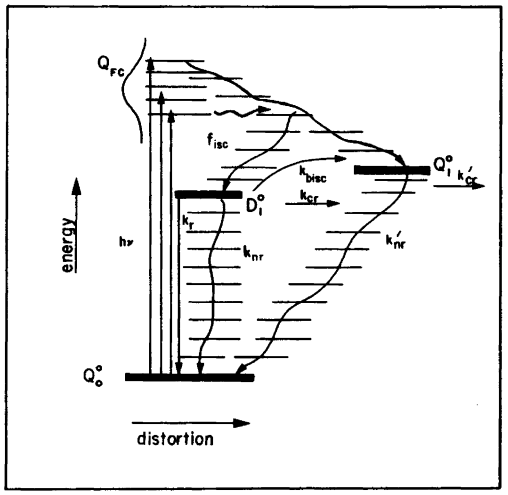

Fig. 1. Energy level diagram for a Cr(III) complex. Q_0^0 is the ground state quartet, Q_{FC} and Q_1° are the Franck-Condon and thexi quartet states, respectively. D_1° is the lowest doublet state.

lowest ligand field thexi states are a doublet, D_1°, and a quartet, Q_1° (^2E_g and $^4T_{2g}$ in O_h symmetry). There has been much interest in determining the role that these states play in the photochemistry of Cr(III) complexes,[7] an interest greatly stimulated in recent years by the ability to observe emission from D_1° under photochemical conditions.[8] Quenching studies[9-11] have suggested that reaction occurs *via* both states in the case of reinecke ion, *trans*-$Cr(NH_3)_2(NCS)_4^-$, (R^-), $Cr(en)_3^{3+}$, and *trans*-$Cr(en)_2(NCS)_2^+$, mostly *via* D_1° in the case of $Cr(bipyr)_3^{3+}$.[12]

We have been interested in the study of solvent and temperature effects on emission lifetimes as a means of understanding the nature of the rate controlling process. The results in the case of R^- ion suggested that this process might be that of direct chemical reaction from D_1°.[13] The present paper extends the investigation to other Cr(III) complexes.

EXPERIMENTAL

Materials. The various complexes were prepared by standard procedures, as described below. Chemicals generally were of reagent grade, including the solvents acetonitrile (AN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), sulfolane, and pyridine.

$[Cr(en)_3](ClO_4)_3$. Tris(ethylenediamine)chromium(III) chloride.$3H_2O$ was prepared according to a literature procedure.[14] The corresponding perchlorate salt was obtained by adding concentrated $HClO_4$ dropwise to a cooled aqueous solution of the chloride salt, and recrystallized from a cooled aqueous solution. The spectrum in 10^{-2} M $HClO_4$ was in excellent agreement with the literature.[15]

trans-$[Cr(en)_2(NCS)_2]NCS$. *trans*-Diisothiocyanatobis(ethylenediamine)chromium(III) thiocyanate was prepared from $Cr(en)_3(NCS)_3$ according to a literature procedure.[14] This material was recrystallized as the perchlorate salt. The absorption spectrum was in excellent agreement with that of Bifano and Linck.[16]

$[Cr(NH_3)_6](Cl)_3$. Hexaamminechromium(III) chloride was prepared by a modified literature procedure.[17] Sublimed $CrCl_3$ was added to condensed liquid NH_3 to which had been added a small amount of Na metal and ferrous ammonium sulfate. A light red solid was collected upon evaporation of the excess liquid NH_3. Recrystallization of this material as the nitrate salt produced a yellow crystalline solid whose absorption spectrum was in excellent agreement with that reported in the literature.[15] The nitrate salt is not soluble in acetonitrile. However the trichloroacetic acid salt is quite soluble in that solvent and was prepared by a simple metathesis with the nitrate salt in aqueous CCl_3COO^- solution. The yellow crystalline solid was recrystallized from dilute aqueous trichloroaceitic acid solution cooled to ice water temperature. Again the absorption spectrum was in excellent agreement with that reported for $Cr(NH_3)_6^{3+}$.[15] Perdeuteriohexaminechromium(III) nitrate, $[Cr(ND_3)_6](NO_3)_3$, was prepared by bringing a concentrated solution of the perproteo salt in D_2O to pH = 9 for 3 min at 25 °C, and then reacidifying with D_2SO_4 to about pH = 1. Cooling the solution to ice water temperature produced a yellow solid material whose doublet absorption displayed the expected shift reported for the perdeutero salt.[18]

$[Cr(en)(NCS)_4]^-$. Ethylenediaminetetraisothiocyanatochromate(III) was prepared *in situ* by adding ethylenediamine to a solution of $Cr(NCS)_6^{3-}$. The product solution displayed an absorption spectrum in excellent agreement with that reported for this complex.[19]

trans-$[Cr(NH_3)_4(NCS)_2]NCS$ was prepared as described by Kirk and Wong.[20].

trans-$[Cr(NH_3)_4Cl_2]^+$, *trans*-$[Cr(NH_3)_4ClH_2O]^{2+}$, and $Cr(NH_3)_5H_2O^{3+}$ were prepared as described by Hoppenjans, Hunt and Gregoire.[21] The deuterio-aquo pentaamminechromium salt was prepared simply by dissolving the aquo species in D_2O and allowing exchange of the water protons for deuterons.

$[Cr(NH_3)_5Cl](NO_3)_2$. Chloropentaamminechromium(III) chloride was purchased from Alfa Inorganics, Inc. The corresponding nitrate salt was prepared by recrystallizing the chloride salt from a fairly concentrated solution of KNO_3, and then again from a dilute solution of KNO_3. The dark red crystalline material displayed an absorption spectrum in excellent agreement with that in the literature.[15]

$K_3[Cr(NCS)_6]$. Potassium hexathiocyanatochromate was purchased from Alfa Inorganics, Inc., and recrystallized twice from aqueous solution.

trans-$K[Cr(NH_3)_2(NCS)_4]$. Ammonium Reineckate was purchased from Matheson Coleman and Bell, and recrystallized as the potassium salt.[22]

cis$[Cr(en)_2(NCS)_2]NCS$ was prepared using a procedure analogous to that used to prepare the *cis*-tetraammine species.[23] The absorption spectrum is in excellent agreement with that reported in the literature.[15] Also the IR spectrum shows the expected absorptions for the *cis* isomer.[24,25]

Since emission properties were to be studied, low level impurities, if strongly emitting, could be important. The absence of any significant such contribution to emission was tested by checking that additional recrystallization of a compound had no

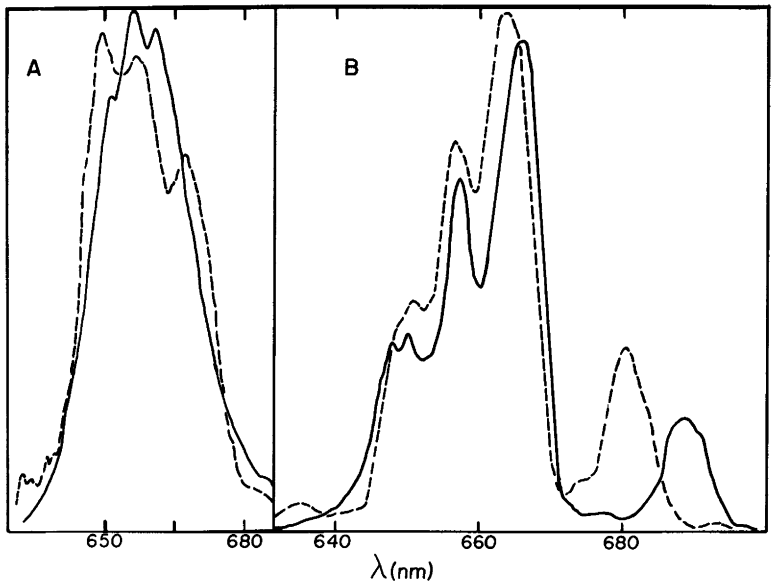

Fig. 2. Mass effect on D_1° emission. A. Solid line: $Cr(NH_3)_5(H_2O)^{3+}$ in H_2O. Dashed line: $Cr(ND_3)_5(D_2O)^{3+}$ in D_2O. B. Solid line: $Cr(NH_3)_6^{3+}$ in H_2O. Dashed line: $Cr(ND_3)_6^{3+}$ in D_2O.

effect on the emission behavior. In addition, our emission decay plots were first order over at least two lifetimes in all cases.

Equipment and procedures. The pulsed laser and detection equipment was that previously described,[13] as was the vidicon detector and multichannel analyzer used in obtaining emission spectra. The procedures were also essentially as previously followed. Absorption spectra were obtained by means of a Beckman Acta recording spectrophotometer, and the emission yield of $Cr(en)_3^{3+}$ was estimated from intensity data obtained with the use of an Aminco spectrofluorimeter. The emission spectrum was compared with that of a known, matching emitter, thionine.[26]

RESULTS

Emission spectra. Fig. 2 shows the emission spectra for $Cr(NH_3)_6^{3+}$ and $Cr(NH_3)_5(H_2O)^{3+}$, including the effects of deuteration. The former pair agree satisfactorily with those previously published.[27] The results for $Cr(NH_3)_5(H_2O)^{3+}$ are new.

Emission lifetimes. The data for 20 °C are summarized in Table 1. Deuteration, either of coordinated ammonia in $Cr(NH_3)_6^{3+}$ or of solvent make independent 15 to 30 % increases in the D_1° lifetime. Further, as shown in Fig. 3, the change in lifetime, τ, for $Cr(NH_3)_6^{3+}$ is linear in solvent H_2O-D_2O composition, or essentially in composition of the solvation shell. We found the same behavior for R^- ion for acetonitrile (AN)–water mixtures.[13]

In general, solvent deuteration significantly increases the longer lifetime cases, but tends not to affect strongly the shorter lifetime ones. Thus τ for *trans*-$Cr(en)_2(NCS)_2^+$ increases from 6.0 to 7.8 μs on solvent deuteration, while the τ's for *cis*-$Cr(en)_2(NCS)_2^+$, $Cr(NH_3)_5(NCS)^{2+}$, R^-, and *trans*-$Cr(NH_3)_4(NCS)_2^+$ show little to no change.

Change to a non-aqueous solvent also affects the emission lifetime. The effects are not as large as those reported for R^- ion;[13] we were restricted in choices of solvent, however, because of the need to use polar solvents in order to have sufficient solubility. These complexes with τ's of 0.5 μs or more show solvent effects that are relatively small and variable, while those with small τ tend to show greatly increased lifetimes in the non-aqueous media – note especially the cases of R^- and $Cr(NCS)_6^{3-}$.

Temperature dependencies. Table 2 summarizes the results on temperature dependence. As illustrated in Fig. 4, emission lifetimes obey an Arrhenius plot within experimental error; we judge

Table 1. Phosphorescence lifetimes for Cr(III) complexes. (20 °C; τ, μs).

Complex	Solvent H_2O	D_2O	AN	DMF	DMSO	Sulfolane[a]
$Cr(bipyr)_3^{3+}$ [b]	53[c]		38			
$Cr(en)_3^{3+}$	1.85	2.27	1.23	1.61	1.64	2.00
trans-$Cr(en)_2(NCS)_2^+$	6.0[d]	7.8	6.3	4.75	3.6	6.5
cis-$Cr(en)_2(NCS)_2^+$	0.52	0.56	0.15	0.37	0.50	0.40
$Cr(en)(NCS)_4^-$	0.040[e]					
$Cr(NH_3)_6^{3+}$	2.2	3.6	1.5[f]	3.0	4.2	3.0
$Cr(ND_3)_6^{3+}$	3.0	3.8				
$Cr(NH_3)_5(NCS)^{2+}$	0.26	0.30	[g]	0.51	0.92	[g]
trans-$Cr(NH_3)_4(NCS)_2^+$	0.56	0.53	[g]	0.85	0.44	[g]
trans-$Cr(NH_3)_2(NCS)_4^-$	0.005[h]	0.005[h]	0.12	0.080	0.090	0.25
$Cr(NH_3)_5(H_2O)^{3+}$	<0.005					
$Cr(NH_3)_5(D_2O)^{3+}$		<0.005				
$Cr(NH_3)_5Cl^{2+}$	<0.005					
trans-$Cr(NH_3)_4Cl_2^+$	<0.005				<0.005	
trans-$Cr(NH_3)_4(H_2O)Cl^{2+}$	<0.005				<0.005	
$Cr(NCS)_6^{3-}$	0.005[i]		0.03	0.12	0.10	0.14

[a] Glass. [b] Pyridine: 14 μs. [c] Literature value: 51 μs at 22 °C.[12] [d] Literature value: 10.5 μs at 15 °C.[11] [e] Maximum value because of possible impurities. [f] Solubilized as the CCl_3COO^- salt. [g] Not sufficiently soluble. [h] Extrapolated from lower temperatures. These values for R^- agree within experimental error with those previously reported.[13] [i] Rise in D_1° absorption.[28]

the reported apparent activation energies, E_p, to have an uncertainty of ± 1 kcal mol^{-1} or less. Solvent effects are small, with the notable exception of $Cr(bipyr)_3^{3+}$, for which the range is from 3.7 kcal mol^{-1} in AN to 7.9 kcal mol^{-1} in DMSO, including the data of Ref. 8.

The Arrhenius frequency factors, A, defined as $A=(1/\tau)\exp(E_p/RT)$, are included in Table 2. The data fit approximately the same linear plot of ln A *vs.* E_p as found to hold for R^- in various solvents.[13]

A second kind of temperature dependence is included in Table 2. Extrapolation of the emission

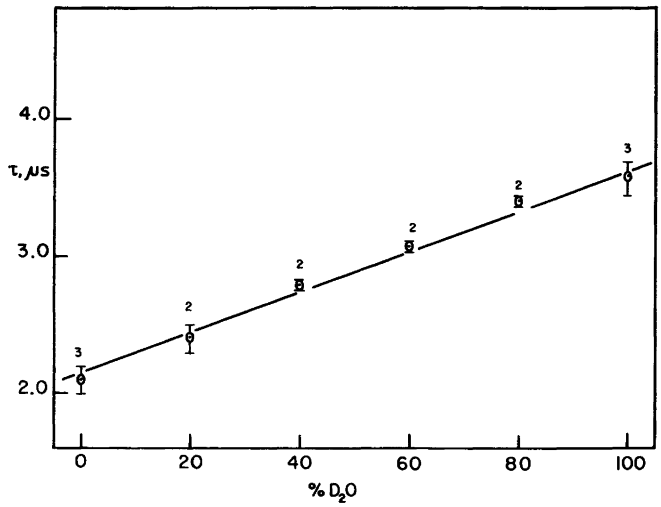

Fig. 3. D_1° emission lifetime for $Cr(NH_3)_6^{3+}$ as a function of solvent D_2O composition at 20 °C. Number of determinations shown above each point.

Table 2. Apparent activation energies for emission from Cr(III) complexes[a] (in kcal mol^{-1}).

Complex	Solvent H_2O			D_2O			AN		
	E_p	ln A	E_f	E_p	ln A	E_f	E_p	ln A	E_f
$Cr(bipyr)_3^{3+}$ [b]	7.0	22					3.7		
$Cr(en)_3^{3+}$	10	30	4.5	11.7	33	3.2			
trans-$Cr(en)_2(NCS)_2^+$	7.6	25	0.0						
$Cr(NH_3)_6^{3+}$ [c]	10	30	4.6	10.8	31				
$Cr(ND_3)_6^{3+}$	12.5	34	5.2						
trans-$Cr(NH_3)_2(NCS)_4^-$	10	36	−2.3	9.0	35		10.5	34	−2.3
$Cr(NCS)_6^{3-}$							11.8	38	

[a] E_p: from temperature dependence of the phosphorescence lifetime; E_f: from temperature dependence of V_0 (see text). [b] Literature values for E_p are 7.5 (H_2O), 6.8 (DMF), and 7.9 (DMSO) (Ref. 8), and 9.1 (H_2O) (Ref. 12). E_p is 5.0 in pyridine (this work). [c] Literature values for E_p are 10.4 (H_2O), 10.8 (D_2O), 12.8 (DMF), 14.0 (DMSO) (Ref. 8).

intensity to zero time, that is, to the inflection point of the rise of emission gave an initial reading V_0, on the oscilloscope trace. We can write $V_0 = \alpha I_0$, where I_0 is the absolute emission rate in $E\ s^{-1}$ per E of excitation quanta absorbed and α consists of various apparatus and geometry factors. For any one system, the variation of V_0 with temperature (corrected for the $\pm 10\%$ variations in exciting pulse energy as determined from the photodiode trace[13]) should also give the variation in I_0. That is, α should not be temperature dependent. The V_0 values could not be determined as precisely as the τ's but, as illustrated in Fig. 4, appear to fit the Arrhenius equation. The apparent activation energies, E_f, are given in Table 2. Note that the values range from 4.6 kcal mol^{-1} to −2.3 kcal mol^{-1}; that is, in some cases V_0 decreased with increasing temperature.

Emission *yields*, ϕ_p, are given by $I_0\tau$. The yields, however, are not proportional to $V_0\tau$ since α should vary from one complex to the other because of variations in the fraction of the emission spectrum sampled by the detector-monochromator system. Finally, although no strict correlation is expected, it is not surprising that our τ values do vary approximately as do the reported relative emission yields.[8] As one comparison of interest, the emissions from *trans*-$Cr(en)_2(NCS)_2^+$ and *trans*-$Cr(NH_3)_2(NCS)_4^+$ are reported[8] as "moderately strong" and

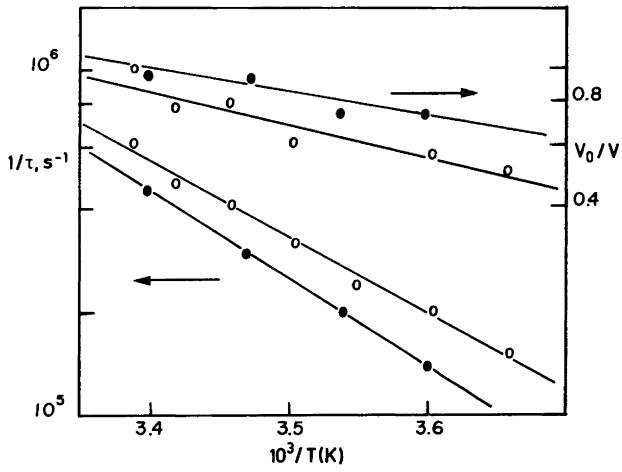

Fig. 4. Temperature dependence of $1/\tau$ and of V_0/V for $Cr(en)_3^{3+}$ in H_2O, open circles, and in D_2O, full circles. V, proportional to the excitation pulse energy, corrects V_0 to the standard pulse.

"weak", respectively, while our lifetimes are 6 μs and 0.56 μs, again respectively. Parenthetically, ϕ_p's are small; thus for the relatively strong emitter, $Cr(en)_3^{3+}$, $\phi_p \simeq 1 \times 10^{-4}$.[26]

DISCUSSION

Emission lifetimes of Cr(III) complexes at around room temperature presumably do *not* reflect k_r, the radiative rate constant. The pure radiative lifetimes of Cr(III) ammines are of the order of ms, as obtained from low temperature measurements.[29] It is conventional to assume that k_r is not highly environment (or temperature) dependent. The theory of spontaneous emission invokes the wave-mechanical, that is, electron, *n*-pole field of the molecule as interacting with the initial and final vibronic states,[30] and thus deals with intramolecular parameters. Alternatively, radiative transition probabilities may be estimated from absorption spectra,[29] and these last are nearly temperature and environment independent.[3,4] Also, of course, the experimental ϕ_p's are small, an indication that $k_r \ll 1/\tau$. Thus while in principle, $1/\tau = (k_r + k_{nr} + k_{cr} + k_{bisc})$, where nr denotes nonradiative relaxation to ground state, *cr*, chemical reaction directly from D_1°, and bisc, back intersystem crossing to Q_1°, it seems safe to neglect k_r as being much smaller than $1/\tau$.

We will also suppose that only some *one* of the remaining rate constants is important for our systems. In the case of R^- in various solvents, it was noted that the data obeyed a Barclay-Butler type of plot, that is, that a plot of ln *A vs.* E_p was linear.[13] Such behavior implies that the set of data pertain to some single rate mechanism. On adding our present data a linear plot again obtains, although the data for R^- and for $Cr(NCS)_6^{3-}$ lie somewhat above the best line for the other complexes. We will draw the same conclusion as before, namely that throughout the series it is some *one* of the rate constants k_{nr}, k_{bisc}, or k_{cr} that is always largest.

The non-radiative process could be the determining one for some of our systems, but in others, quenching studies[9-12,31] indicate that the quantum yield for reaction from or through D_1° is non-negligible, so that if some *one* rate process is to be dominant for the whole series, it is not the non-radiative one. For this and the reasons previously noted,[13] we will not consider the non-radiative process further.

The second possibility is that back intersystem crossing (see Fig. 1) is rate determining, that is, that D_1° exits the excited state system *via* Q_1°. E_p is now assigned to k_{bisc} and should be identified approximately with the $(Q_1^\circ - D_1^\circ)$ energy difference, ΔE°. This difference cannot be obtained with accuracy, but should at least be proportional to ΔE_m,[32] the energy corresponding to the difference between the absorption band maxima for the first ligand field band and the doublet band. Contrary to such expectation, however, there is little correlation between ΔE_m and our ΔE_p values. Thus for $Cr(bipyr)_3^{3+}$, $Cr(en)_3^{3+}$, $Cr(NH_3)_6^{3+}$, *trans*-$Cr(en)_2(NCS)_2^+$, *trans*-$Cr(NH_3)_2(NCS)_4^-$, and $Cr(NCS)_6^{3-}$ the respective ΔE_m values are (in kcal mol^{-1})[33]: 23, 20, 18, 18, 17, and 13. The corresponding E_p values are: 7, 10, 10, 7.6, 10, and 12 (in AN).

While it has been inferred from quenching studies that back intersystem crossing is the principal mode of disappearance of D_1° in the cases of $Cr(en)_3^{3+}$ and *trans*-$Cr(en)_2(NCS)_2^+$,[10,11] the results can accomodate the alternative supposition that k_{cr} is the important rate constant (note also Ref. 31). Further, direct reaction from D_1° has recently been proposed as dominant in the case of $Cr(bipyr)_3^{3+}$.[12] Because of the lack of correlation between ΔE_m and E_p and because k_{bisc} seems not to be important for some systems, we assume it is not important for the set of complexes, and turn to the third possibility.

The supposition that direct chemical reaction from D_1° is the process which generally controls the lifetime of this state in room temperature fluid solution has interesting aspects. Some general implications of this mechanistic scenario were discussed previously.[13] and we consider here a possible explanation of the wide variations in τ for our series of complexes. The sharpest contrast is perhaps between *trans*-$Cr(en)_2(NCS)_2^+$, with $\tau = 6.0$ μs, and *trans*-$Cr(NH_3)_4(NCS)_2^+$, for which τ is only 0.56 μs. Another is between *trans*- and *cis*-$Cr(en)_2(NCS)_2^+$, with τ values of 6.0 and 0.52 μs, respectively. Note also that the series of complexes having six Cr – N bonds, $Cr(bipyr)_3^{3+}$, $Cr(en)_3^{3+}$, $Cr(NH_3)_6^{3+}$, and $Cr(NCS)_6^{3-}$, spans four orders of magnitude in τ.

It appears possible to organize the data qualitatively by means of empirical rules, much as was done earlier for Cr(III) photochemistry.[34] These are:

Rule 1: For complexes with six equivalent Cr – L bands, the emission lifetime in room temperature

fluid solution decreases with decreasing ligand field strength.

Rule 2: If two different kinds of ligands are coordinated, the emission lifetime will be relatively short[35] if that ligand which is preferentially substituted in the *thermal* reaction lies on the weak field axis of the complex.

That the above rules apply may be shown by means of the following examples. The order of τ's for the CrL_6 series is that of the spectrochemical series.[2] The weak field axis of *trans*-$Cr(en)_2(NCS)_2^+$ is the SCN−Cr−NCS one, but the ground state reaction is aquation of ethylenediamine,[16] so rule 2 is violated, and a relatively long emission lifetime is predicted, as observed. In the case of *trans*-$Cr(NH_3)_4(NCS)_2^+$, however, the thermal reaction is almost certainly one of *thiocyanate* aquation,[36] and τ is now small. Rule 2 likewise correctly predicts τ to be small for *cis*-$Cr(en)_2(NCS)_2^+$ and for the $Cr(NH_3)_5X^{2+}$ complexes. $Cr(en)(NCS)_4^-$ and *trans*-$Cr(NH_3)_2(NCS)_4^-$ conform; for both the weak field axis is SCN−Cr−NCS, and for both thiocyanate aquation is the preferred thermal reaction.[19,37]

Rule 2 carries a suggestion that emission lifetimes may tend to vary with solvent according to thermal reactivity. Some information is available on rates of solvolysis in non-aqueous solvents,[38] but more is needed. The case of $Cr(bipyr)_3^{3+}$ may be special. The mechanism of the solvation reaction in water has complexities[39] and could be very solvent dependent, possibly correlating with our results.

A rationale for these rules is, of course, desirable, although not necessary to their practical usefulness. First, there is indication that direct excitation of the doublet absorption band leads preferentially to the thermal mode of reaction. This was demonstrated in the case of $Cr(NH_3)_5(NCS)^{2+}$,[40] for example. We now assume this preference to be general, possibly because the D_1° state has or has readily accessible a vacant t_{2g} orbital and a bimolecular substitution reaction of mechanism similar to that of the ground state process is thereby facilitated. It remains to assume that this facilitation occurs primarily for a ligand on the weak field axis and is more effective for a weak field than for a strong field ligand. If the facilitation coincides with the thermal mode of reaction, then reaction from D_1° is relatively fast and the lifetime of the state, relatively short.[41]

As with the earlier rules dealing with Cr(III) photolyses, should the present ones prove to be useful, more detailed theoretical explanations may be worth exploring. These might be along the lines developed by Zink,[46] Vanquickenborne,[47] and perhaps, especially by Wrighton[48] (and their coworkers).

The various deuteration effects should be commented on. As already noted, the shifts in the emission spectra presumably occur because of the vibronic nature of the transition. This aspect is presumably irrelevent to the deuteration effects on our emission lifetimes because of the unimportance of k_p. We assign the increases in τ on deuteration to slower rates of reaction from D_1°. Thermal substitution reaction rates, for example, are generally slower in D_2O than in H_2O as solvent.[19,37] The linear variation of τ with degree of solvent deuteration seems consistent with this interpretation.

We turn lastly to the temperature dependencies of V_0. The initial emission intensity, I_0, to which V_0 is proportional, is given by $f_{isc}k_p$, where f_{isc} is the efficiency of prompt intersystem crossing (see Fig. 1). Since k_p should not be very temperature dependent, our E_f values are presumably those for intersystem crossing. Present indications are that this process can be fast – occurring within short picoseconds.[28] We believe it to occur before complete thermal equilibration to Q_1°.[49] A temperature dependence of f_{isc} thus indicates competition between intersystem crossing and thermal equilibration. Since the intersystem crossing event should not *per se* be temperature sensitive, we should interpret our E_f values in terms of changes in rates of thermal equilibration. To the extent that solvent fluidity is important in allowing the necessary bond length and bond geometry distortions to occur in the equilibration from Q_{FC} to Q_1°, increasing temperature should increase the rate of thermal equilibration and thus decrease f_{isc}. We observe both positive and negative values for E_f, however, and other effects must be present. Reinecke's salt is soluble in a variety of solvents, and may therefore not be solvated in a highly specific way; for R^-, then, the negative E_f may reflect this solvent viscosity effect. The positively charged, ethylenediamine and ammonia containing complexes, however, require polar solvents for solubility and the positive E_f's may have to do with how a highly structured solvation shell is affected by temperature.

In the case of *trans*-$Cr(en)_2(NCS)_2^+$ the lack of variation of V_0 and hence presumably of f_{isc} with temperature raises the possibility that f_{isc} is near its ceiling, that is, unity. The possibility is not

necessarily in contradiction to the quenching data which, in this case, indicated that about 80 % (not 100 %) of chemical reaction was quenched on quenching the emission from D_1°.[11] It is quite possible that quenching encounters with D_1° induce chemical reaction (in this case about 20 % of the time). Thus complete emission quenching does not require complete photochemical quenching even with an f_{isc} of unity.

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