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Ground-State Quenching of ($^2T_1/^2E$)Cr(NN)$_3^{3+}$. Anion and Temperature Dependence

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The emission lifetimes of $(2T_1/^2E)Cr(NN)_3^{3+}$*, where NN is bpy (2,2′-bipyridine) and phen (1,10-phenanthroline), in aqueous solutions in the presence of 1.0* M $HClO_4$*,* KNO_3*,* $NaBr$*,* $NaBrO_3$*,* HCl*,* Na_2SO_4*,* H_2SO_4 *and neat water media have been determined as a function of the concentration of ground state* $Cr(NN)_3^{3+}$ *in order to quantify the ground-state quenching phenomenon. This process is described by* $^2k_{obs} = {}^2k_o + {}^2k_g[Cr(NN)_3^{3+}]$*, where* ^2k_o $(=1/^2\tau_o)$ *is the first-order rate constant for decay of* $^2T_1/^2E$ *and* ^2k_g *is the second-order rate constant for ground-state quenching. In neat water,* $^2\tau$ *is invariant, 0.25 ± 0.03 ms for* $Cr(phen)_3^{3+}$*, but in the presence of anions* $^2\tau$ *decreases with increase in* $[Cr(phen)_3^{3+}]$*;* ^2k_g *values decrease as the anion varies* $ClO_4^- > NO_3^- > Br^- > BrO_3^- \sim SO_4^{2-} > Cl^- > HSO_4^-$*. For* $Cr(bpy)_3^{3+}$*,* $^2\tau$ *is 0.068 ± 0.008 ms in neat water, and the presence of anions have no effect in 1.0* M *media at 22 °C. Anion mediation of ground-state quenching is proposed as arising from encounters of excited-state and ground-state ion pairs to form the 'ion-bridged excimer',* $^*\{Cr(NN)_3^{3+}\cdots X^-\cdots Cr(NN)_3^{3+}\}$*. Temperature dependence studies of these encounters give* $\Delta H_g^\# = 4.2$ *kcal/mol and* $\Delta S_g^\# = -9$ *eu for* $Cr(phen)_3^{3+}$ *in the temperature range 13–42 °C. At ~15 °C, ground-state quenching is observed for* $Cr(bpy)_3^{3+}$ *in 1.0* M *NaCl medium as a result of lowering* ^2k_o*.*

Introduction

The lowest metal-centred excited states ($^2T_1$/^2E) of chromium(III) polypyridyl complexes, Cr(NN)$_3^{3+}$, are known [1] to be sufficiently long-lived that they can engage in excited-state electron transfer reactions in fluid media. Moreover, ($^2T_1/^2E$)-Cr(NN)$_3^{3+}$ is a powerful oxidizing agent, with $^*E^o$-$[^*Cr(NN)_3^{3+}/Cr(NN)_3^{2+}]$ = 1.2–1.5 V *vs.* NHE [2, 3]. The utilization of Cr(NN)$_3^{3+}$ complexes in solar energy conversion schemes has been discussed [4, 5] and it has been demonstrated [6, 7] that Cr(NN)$_3^{2+}$ reduces water to dihydrogen. It is imperative to know the lifetime ($^2\tau_{obs}$) of ($^2T_1/^2E$)Cr(NN)$_3^{3+}$ under specific experimental conditions in order to evaluate the photophysics and photochemistry of these species. Inasmuch as Cr(NN)$_3^{3+}$ complexes exhibit relatively stable thermal and photochemical behaviour in acidic media (pH < 6), many lifetime measurements have been carried out in 1 *M* HCl [1]. Previous studies [1, 8] in our laboratory have shown that $^2\tau_{obs}$ for several Cr(NN)$_3^{3+}$ complexes is dependent on the Cr(NN)$_3^{3+}$ concentration in the presence of 1 *M* HCl and 1 *M* NaCl. Also, we often note that the concentrations of substrates are not cited in the literature when lifetime data are reported. In this paper, we report the dependence of $^2\tau_{obs}$ for ($^2T_1/^2E$)Cr(bpy)$_3^{3+}$ and ($^2T_1/^2E$)Cr(phen)$_3^{3+}$ (bpy is 2,2′-bipyridine and phen is 1,10-phenanthroline) upon ground-state concentration in aqueous media containing various anions to determine if the ground-state quenching phenomenon observed in the presence of chloride ion is a general one for Cr(NN)$_3^{3+}$

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TABLE I. Medium Dependence of Lifetimes of $(^2T_1/^2E)Cr(bpy)_3^{3+}$ and $(^2T_1/^2E)Cr(phen)_3^{3+}$ in Argon-Purged Aqueous Solutions at 22 °C.

Medium^a	$Cr(bpy)_3^{3+}$		$Cr(phen)_3^{3+}$		
	$^2\tau_{obs}$ (ms)	$^2k_{obs} \times 10^{-4}$ (s^{-1})	$^2\tau_o$ (ms)	$^2k_o \times 10^{-3}$ (s^{-1})	$^2k_g \times 10^{-6}$ ($M^{-1}\ s^{-1}$)
$HClO_4$	–	–	0.49	2.0 ± 0.01^c	4.7 ± 0.3^c
KNO_3	0.079	1.3	0.29	3.5 ± 0.05	4.1 ± 0.1
NaBr	0.072	1.4	0.30	3.3 ± 0.04	3.3 ± 0.04
$NaBrO_3$	0.068	1.5	0.25	4.0 ± 0.04	3.0 ± 0.1
HCl^b	0.073	1.4	0.33	3.0	2.3
Na_2SO_4	0.076	1.3	0.26	3.8 ± 0.1	2.9 ± 0.2
H_2SO_4	0.094	1.1	0.36	2.8 ± 0.02	2.1 ± 0.1
H_2O^b	0.068	1.5	0.25	4.0 ± 0.4	–

^{a}Concentration, 1.0 *M*. ^{b}Ref. 8. ^{c}Standard error from the least squares analysis reflects the sactter in the data.

complexes. Further, the temperature dependence of this phenomenon is reported to throw light on the energetics of the ground-state quenching process for $Cr(phen)_3^{3+}$.

Experimental

The perchlorate salts of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ complex ions were available from previous studies [1]. Solutions were prepared from reagent grade chemicals that were used without further purification; water was monodistilled and de-ionized. Emission lifetimes were determined using a 1-kW nitrogen laser (4 ns pulses, 337 nm) as described by Demas and Flynn [9]. The luminescence decay curves were photographed from a Tektronix 7633 oscilloscope equipped with a 7A15A amplifier and a 7B80 time base.

To measure these emission lifetimes, $Cr(NN)_3^{3+}$ solutions of the desired concentrations were prepared in the appropriate medium and deaerated with pre-purified argon for ~30 min at 22 °C immediately prior to measurement. Samples were handled in dim, red light to prevent photodecomposition. Values of $^2\tau_{obs}$ at 22 °C were determined by monitoring the first-order decay of the emission from $(^2T_1/^2E)$ at 727 nm. The values of $^2\tau_{obs}$ (= $1/k_{obs}$) within a single experimental set were reproducible to within 10%; the standard deviation from replicate experiments was of the order of 10–15%.

Tenperature dependence studies of $^2\tau_{obs}$ of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ were carried out under the following conditions: for $Cr(bpy)_3^{3+}$, concentration 1×10^{-3}–1×10^{-5} *M*, pH 9.48, 0.008 *M* Britton–Robinson buffer [10], ionic strength was maintained by 1.0 *M* NaCl; for $Cr(phen)_3^{3+}$, 1×10^{-3}–1×10^{-5} *M*, pH 10.0, 0.008 *M* Britton–Robinson buffer, ionic strength 1.0 *M* NaCl. In both cases, the temperature range was 13–42 °C controlled to ±0.1 °C from a Lauda circulating water bath.

Results and Discussion

We earlier noted [8] that for $Cr(phen)_3^{3+}$ in 1 *M* HCl, $^2\tau_{obs}$ decreases by an order of magnitude when $[Cr(phen)_3^{3+}]$ is increased from 1×10^{-5} to 1×10^{-2} *M*. By comparison, $^2\tau_{obs}$ is invariant (0.25 ± 0.03 ms) over the substrate concentration range 1.2×10^{-5} to 1.2×10^{-3} *M* in the absence of HCl. In contrast, $^2\tau_{obs}$ values for $Cr(bpy)_3^{3+}$ in 1 *M* HCl and neat water are virtually indistinguishable $^2\tau_{obs}$ = 0.073 (±0.008) ms in 1 *M* HCl and 0.068 (±0.008) ms in neat water over the concentration range 1.0×10^{-5}–1.0×10^{-3} *M*. Ground-state quenching for the bpy complex is, however, observed in 5 *M* HCl [8]. In light of these results, attributed to the presence of Cl^- anions, we have undertaken an investigation of the effects of various other anions in aqueous media on the $^2T_1/^2E$ lifetimes of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$.

Representative data for $^2\tau_{obs}$ and $^2k_{obs}$ of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ in 1.0 *M* Br^- and 1.0 *M* SO_4^{2-} are depicted in Fig. 1; the quenching phenomenon is described by $^2k_{obs} = {}^2k_o + {}^2k_g[Cr(NN)_3^{3+}]$, where ^2k_o is the first-order rate constant for $^2T_1/^2E$ decay at infinite substrate dilution and ^2k_g is the second-order rate constant for quenching of $^2T_1/^2E$ by the ground state $(^4A_2)Cr(NN)_3^{3+}$ substrates. $^2k_o = {}^2k_{rad} + {}^2k_{rx} + {}^2k_{nr}$ for which k is the first-order rate constant for radiative (rad), reactive (rx), and nonradiative (nr) decay modes. Inasmuch as the

TABLE II. Redox Potentials (*vs.* NHE) of X/X^- Couples and Absorption Spectral Properties.

X/X^-	E°, V	Species	λ_{max}, nm[f]
$^*Cr(bpy)_3^{3+}/Cr(bpy)_3^{2+}$	1.44[a]	$({}^4A_2 \rightarrow {}^4T_2)Cr(NN)_3^{3+}$	400[g]
$^*Cr(phen)_3^{3+}/Cr(phen)_3^{2+}$	1.42[a]	$({}^4A_2 \rightarrow {}^2T_1/{}^2E)Cr(NN)_3^{3+}$	695, 727[h]
F/F^-	3.6[b]	ClO_4^-	<180
Cl/Cl^-	2.6[c]	Cl^-	175
Br/Br^-	2.0[c]	Br–	199
SO_4^-/SO_4^{2-}	3.4[d]	HSO_4^-	<200
$NO_3\cdot/NO_3^-$	~1.9[c]	SO_4^{2-}	175
SCN/SCN^-	<1.62[e]	NO_3^-	303
I/I^-	1.42[c]	SCN^-	222
		I^-	227
		BrO_3^-	<200

[a] Refs. 2, 3. [b] B. M. Berdinikov and N. M. Bazhim, *Zh. Fiz. Khim.*, *44*, 712 (1970). [c] J. F. Endicott, in A. W. Adamson and P. D. Fleischauer, (Eds.), 'Concepts in Inorganic Photochemistry', John Wiley, New York, N.Y., 1975. [d] R. Memming, *J. Electrochem. Soc.*, *116*, 785 (1969). [e] G. Nord, B. Pedersen and O. Farver, *Inorg. Chem.*, *17*, 2233 (1978). [f] M. J. Blandamer and M. F. Fox, *Chem. Rev.*, *70*, 59 (1970). [g] Ref. 2. [h] Ref. 5.

quantum yield of luminescence is small, ${}^2\phi_{rad} < 10^{-3}$ [2, 11] and ${}^2\phi_{rx} \sim 0.13$ [5] the contribution of ${}^2k_{rad}$ and ${}^2k_{rx}$ to ${}^2k_o$ is negligible; that is, ${}^2k_{rad} + {}^2k_{rx} \ll {}^2k_{nr}$ and ${}^2k_o \cong {}^2k_{nr}$. Rate constants ${}^2k_o$ and ${}^2k_g$, and lifetimes for all the media (1 *M* X^{n-}: ClO_4^-, NO_3^-, Br^-, BrO_3^-, Cl^-, SO_4^{2-}, HSO_4^-; and neat water) studied are collected in Table I. Clearly, these results show a parallel of ${}^2\tau_{obs}$ as demonstrated in Cl^- media [8]. In the presence of I^- and SCN^-, the emission lifetimes are totally quenched. It must be emphasized that the use of different samples of the recrystallized complexes, reagent grade chemicals, and purified water has no effect on the results. Also, the presence of up to 1 × 10^{-3} *M* of free phenanthroline or 5 × 10^{-3} *M* free bipyridine in 5 × 10^{-5} *M* $Cr(phen)_3^{3+}$ or $Cr(bpy)_3^{3+}$ in HCl medium does not quench the luminescence from ${}^2E$ [8]. Moreover, the quenching phenomenon illustrated in Figure 1 cannot be attributed to any quenching by the anions. Table II summarizes the redox potentials of the X/X^- couples as well as those of $^*Cr(NN)_3^{3+}/Cr(NN)_3^{2+}$; also shown are the spectral absorption maxima of the X^- anions and $^*Cr(NN)_3^{3+}$. It is evident from these data that both electron-transfer quenching and energy-transfer quenching are energetically unfavourable processes.

The data of Table I reveal that concentration quenching does not occur in the absence of anions (*cf.* results in Table I for water); this phenomenon is mediated by the presence of the anions [8]. Further confirmation of anion-mediation is obtained from the parallel behaviour shown on replacing the cation: HCl *vs.* NaCl [8] and H_2SO_4 *vs.* Na_2SO_4 (Table I). In this regard, ${}^2k_g$ is greater in 1 *M* NaCl

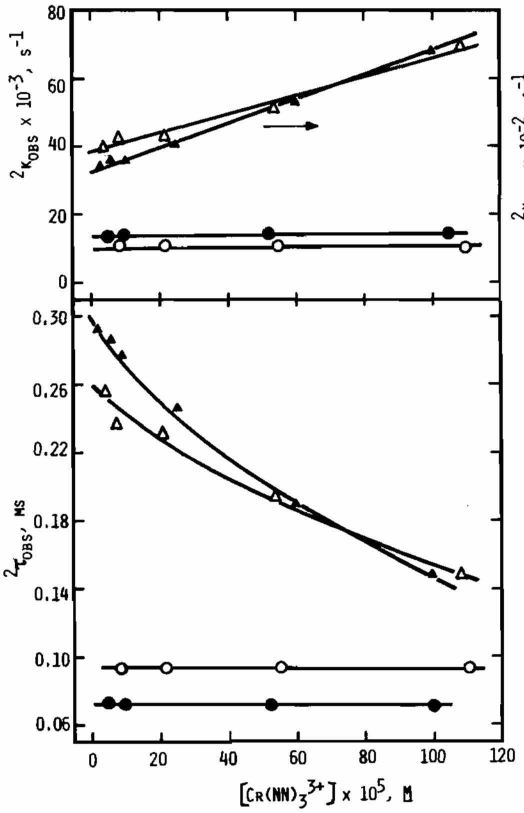


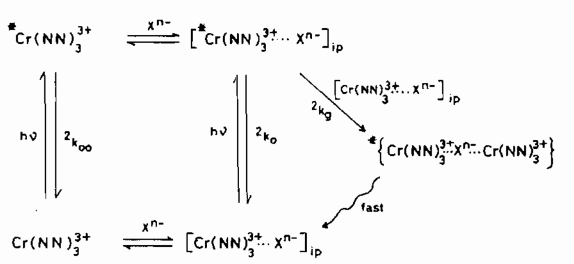
Fig. 1. (Upper) Quenching plot of the data for $({}^2T_1/{}^2E)$-$Cr(NN)_3^{3+}$ in argon-purged solutions at 22 °C. (Lower) Lifetime of $({}^2T_1/{}^2E)Cr(NN)_3^{3+}$ as a function of substrate concentration in argon-purged solutions at 22 °C. (○) NN = bpy, 1.0 *M* H_2SO_4; (●) NN = bpy, 1.0 *M* NaBr; (△) NN = phen, 1.0 *M* Na_2SO_4; (▲) NN = phen, 1.0 *M* NaBr.

than in 1 *M* HCl, and it is also greater in 1 *M* Na_2SO_4 than in 1 *M* H_2SO_4. Similar observations have been made for a whole series of $Cr(NN)_3^{3+}$ complexes [1]. Evidently, interaction between anion and complex ion (in both ground state and excited state) is affected by the nature of the cation; it is well known that the activity coefficient of 1 *M* HCl is larger than that of 1 *M* NaCl, as is the case also for H_2SO_4 and Na_2SO_4, although the possibility that HSO_4^- and SO_4^{2-} affect ground-state quenching differently cannot be precluded. Furthermore, one may be tempted to ascribe variations in $^2\tau_o$ for $(^2T_2/^2E)Cr(phen)_3^{3+}$, ranging from 0.49 to 0.25 ms, to variations in the concentrations of quenching impurities present in the various media; however, we have pointed out earlier [8] that such variations in $^2\tau_o$ do not fit this presumed pattern in a quantitative way.

The lack of observable ground-state quenching for the $Cr(bpy)_3^{3+}$ complex ion in the various 1 *M* X^- media arises from the failure of the medium to sufficiently decrease ^2k_o; observation of ground-state quenching depends on low values of ^2k_o and high values of ^2k_g [8]. However, 5 *M* HCl sufficiently decreases ^2k_o such that the phenomenon is observed for the bpy complex.

Extensive ion-pairing between $Cr(NN)_3^{3+}$ and X^- must surely occur in both the ground state and excited state, as has been demonstrated [12] for ground-state $Fe(NN)_3^{2+}$ and Cl^-. A comparison of the values of $^2\tau_o$ in H_2O to those in HCl, H_2SO_4, and $HClO_4$ reveals a prolongation of the doublet lifetime in the latter media; this has previously been attributed [13] to anion-mediated interference of the critical ligand vibrations that promote the nonradiative deactivation path ($^2k_{nr}$). $^2k_{nr}$ seems to depend on the microstructure of the medium surrounding the $^2T_1/^2E$ state. In some cases, ground-state quenching of $^2T_1/^2E$ lifetimes often masks this prolongation effect. A reduction in the overall positive charge is expected on going from $(^4A_2)$-$Cr(NN)_3^{3+}$ to $[(^4A_2)Cr(NN)_3^{3+}\cdots X^-]_{ip}$, and from $(^2T_1/^2E)Cr(NN)_3^{3+}$ to $[(^2T_1/^2E)Cr(NN)_3^{3+}\cdots X^-]_{ip}$, with the consequence that a reduction in mutual electrostatic repulsion also occurs. Expectedly, the values of ^2k_g reflect the encounter of ion-paired ground-state $[Cr(III)\cdots X^-]$ and excited-state $[^*Cr(III)\cdots X^-]$ species; in the absence of such anion medium, ^2k_g may be several orders of magnitude lower so that ground-state quenching is not observed.

Clearly then, deactivation of the excited state species $[(^2T_1/^2E)Cr(NN)_3^{3+}\cdots X^-]_{ip}$ must occur through collision-induced (with $[(^4A_2)Cr(NN)_3^{3+}\cdots X^-]_{ip}$) nonradiative decay, as illustrated in the Scheme ($^2k_{oo}$ is the inherent decay of the excited state species in the absence of anions). The result of such an encounter between ground-state and



excited-state ion-paired species could be the formation of an 'ion bridged excimer', $\{^*Cr(NN)_3^{3+}\cdots X^-\cdots Cr(NN)_3^{3+}\}$; we have observed no emission attributable to such a species. However, the $\{^*Cr(NN)_3^{3+}\cdots X^-\cdots Cr(NN)_3^{3+}\}$ lifetime is expected to be very short inasmuch as nonradiative decay through coupling of the various vibrational modes must certaining 0.008 *M* Britton–Robinson buffer [10] at iously [8] for ground-state quenching mediated by Cl^-; the presently available data indicate its general application in the various X^- aqueous media of Table I. It must be noted that addition of other substances to the medium affects the values of ^2k_o and ^2k_g; thus, for $Cr(phen)_3^{3+}$ in 1.0 *M* NaCl containing 0.008 *M* Britton–Robinson buffer [10] at pH 9.5, $^2k_o = 4.3 \times 10^3\ s^{-1}$ and $^2k_g = 6.1 \times 10^6\ M^{-1}\ s^{-1}$ (*cf.* results for 1 *M* HCl in Table I) [1]. The change in the nature of the medium clearly causes changes in $^2k_{nr}$.

An additional feature of the data in Table I is the ordering of ^2k_g values as a function of the nature of the anion. Within one standard error, ^2k_g values vary in the order $ClO_4^- > NO_3^- > Br^- > BrO_3^- \sim SO_4^{2-} > Cl^- > HSO_4^-$. In a related study of the thermal racemization of $Cr(phen)_3^{3+}$ [14], the order of effectiveness of anions in retarding racemization is $ClO_4^- > NO_3^- > I^- > Br^- > Cl^-$; such pronounced ability of anions to suppress racemization has been attributed to specific ion interaction. These can in part be understood in light of the model we have suggested for the thermal aquation and photo-aquation of $Cr(phen)_3^{3+}$ and related complexes [1, 15]. The nucleophile, H_2O, directly attacks the metal core with subsequent expulsion of a polypyridine ligand. The presence of anions effectively blocks, through formation of tight ion-pairs, the interligand pockets and thus retards attack by the nucleophile. Comparison of the kinetics and activation parameters of thermal racemization [E_a = 23.5 ± 0.1 kcal/mol and $\Delta S^\# = -10.9 \pm 0.1$ eu] [14] with those of thermal aquation [E_a = 23.9 ± 0.7 kcal/mol and $\Delta S^\# = -8.4 \pm 2.3$ eu] [15] indicates a common mechanism for these two processes. It is also interesting to note that the stability constant between $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ with various anions varies according to $ClO_4^- > NO_3^- > Br^- > Cl^-$ [12]. The order of the ^2k_g values above

TABLE III. Temperature Dependence of Lifetimes of $(^2T_1/^2E)Cr(NN)_3^{3+}$ in Aqueous Solutions.[a]

$Cr(bpy)_3^{3+}$ [b]			$Cr(phen)_3^{3+}$ [c]		
Temperature (°C)	$^2k_o \times 10^{-3}$ (s^{-1})	$^2k_g \times 10^{-6}$ (M^{-1} s^{-1})	Temperature (°C)	$^2k_o \times 10^{-3}$ (s^{-1})	$^2k_g \times 10^{-6}$ (M^{-1} s^{-1})
14.9	9.46	1.6	13.5	2.4	4.0
22.0	15.9		22.0	4.0	5.4
29.3	23.3		29.2	6.4	6.5
36.1	32.9		36.1	10	7.5
			42.1	14	8.8

[a] Argon-purged solutions. [b] Concentration, 1×10^{-3}–1×10^{-5} *M*, pH 9.48, Britton–Robinson buffer, 1.0 *M* NaCl. [c] Concentration, 1×10^{-3}–1×10^{-5} *M*, pH 10.0, Britton–Robinson buffer, 1.0 *M* NaCl.

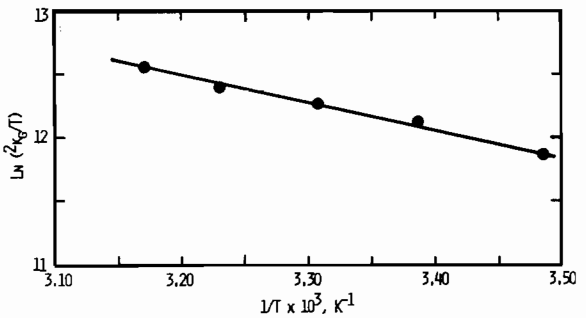


Fig. 2. Eyring activation plot of $\ln(^2k_g/T)$ against T^{-1} for $Cr(phen)_3^{3+}$ (see text for experimental details).

depicts, no doubt, various anion factors (e.g. ion-pairing ability among others) in making the encounters between the ground-state and excited-state ion-pairs more effective, and in promoting decay of the 'ion-bridged excimer'. Obviously, ClO_4^- is most effective and may have to do with the manner in which the perchlorate oxygens penetrate into the interligand pockets (see *e.g.* ref. 16). Oxygen atoms of the perchlorates are wedged in pockets in the structure of these polypyridyl complexes such that in the solid state the cation and ClO_4^- ions form very tight ion-pairs; it is not inconceivable that also in solution the oxygens of these anions are wedged in the pockets.

The temperature dependence data of lifetimes of $(^2T_1/^2E)Cr(NN)_3^{3+}$ (for NN = bpy and phen) in aqueous, argon-purged solutions are summarized in Table III. Where NN is bpy, it is noteworthy that the ground-state quenching phenomenon is observed at ~15 °C, $^2k_g = 1.6 \times 10^6$ M^{-1} s^{-1}; ^2k_o is reduced sufficiently to make the process observable. Figure 2 illustrates the Eyring activation plot of $\ln(^2k_g/T)$ *vs.* T^{-1} from which were obtained $\Delta H_g^{\#} = 4.2$ kcal/mol and $\Delta S_g^{\#} = -9$ eu from the slope and intercept, respectively, for the ground-state quenching process in $*Cr(phen)_3^{3+}$ in Cl^- media. The relatively small enthalpic barrier for the formation of the activated complex in the ground-state quenching process reflects the efficiency of the diffusion process in bringing together two ion-paired but positively charged species. The negative entropic factor can be considered to reflect the coalescence of two species in the transtion state which favours the 'ion-bridged excimer' model.

Concluding Remarks

It is clear from the above discussion that the importance of identifying and characterizing the factors that affect the photochemical and photophysical behaviour of $Cr(NN)_3^{3+}$ complex ions cannot be overemphasized. Investigations of the effects of altering the solution medium on $^2\tau_{obs}$ under specific reaction conditions are necessary (a) for evaluating the photophysics of the $^2T_1/^2E$ state, (b) for calculating quenching rate constants, ^2k_q, from luminescence quenching studies, and (c) for choosing optimum conditions in various photochemical reaction schemes.

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