Inorganica Chimica Acta, 119 (1986) 25–28

Isotope Effect on the Nonradiative Decay in Mixed Amminechromium(III) Complexes

M. MVELE and F. WASGESTIAN*

Institute of Inorganic Chemistry, University of Cologne, Greinstrasse 6, 5000 Cologne 41, F.R.G.

(Received February 12, 1986)

Abstract

Mixed amminechromium(III) complexes of the general formula $[Cr(NH_3)_{6-n}X_n]^m$ ($X = H_2O, SCN^-$) have been prepared and deuterated in the presence of a base. Phosphorescence decay times have been measured at *ca.* 77 K and the isotope effect on the nonradiative deactivation is discussed using Kupka's theory.

Introduction

In previous papers, the exchange of hydrogen for deuterium has been shown to markedly lengthen the lifetime of amminechromium(III) complexes [1–8].

Theoretically, the role of the hydrogen vibrations as accepting modes in the nonradiative decay is rather well understood [9–12]. In particular, the formalism developed by Kupka [13] allows a satisfactory description of the nonradiative transition probability in terms of intramolecular distributions that can be accurately calculated.

Fucaloro *et al.* [5] reported on the isotope effect on the luminescence of amminechromium(III) complexes containing heteroligands. They found H_2O to be a better quencher than NH_3 or SCN^-. In their attempt to deuterate aquoamminechromium(III) complexes in acetate buffer, a side-reaction could not be totally avoided.

Different deuteration procedures have therefore been probed in order to achieve a more efficient hydrogen exchange. The present paper reports on the deuteration of some mixed amminechromium(III) complexes. The isotope effect on the radiationless decay is discussed using Kupka's formalism.

Experimental Section

Materials

Cr(III) amminecomplexes of the general formula $[Cr(NH_3)_{6-n}X_n]^m$ ($X = H_2O$, SCN^-) were prepared using methods reported in the literature. The following compounds were synthesized: $[Cr(NH_3)_6]^{3+}$ [14], $[Cr(NH_3)_5OH_2]^{3+}$ [15], $[Cr(NH_3)_5SCN]^{2+}$ [16]. *cis-* and *trans-*$[Cr(NH_3)_4(OH_2)_2]^{3+}$ [17, 18], *cis-* and *trans-*$[Cr(NH_3)_4(SCN)_2]^+$ [19–21], and $K[Cr(NH_3)_2(SCN)_4]$ [22]. Cationic complexes were used as perchlorates. Deuterated reagents were purchased from Merck Darmstadt.

Deuteration Procedure

The deuteration was carried out in the presence of a base. NaOD (Art. 2911) and/or Na_2CO_3 analytical grade (Art. 6392 E) were used for this purpose. The amminecomplexes were dissolved in D_2O (Art. 2919); drops of NaOD were added to alkalise the solution. An excess of DCl (Art. 2906) was then used to neutralise NaOD and the final solution was mixed with an equal volume of DMSO (Art. 2931). Upon addition of NaOD, the colour of the Cr(III) aquocomplex solutions changed; the original absorption spectra of the solutions were however recovered after the solutions had become acid enough, indicating that no side-reaction had occurred. No shift of the 0–0 emission band was noticed. A DMSO/D_2O (1:1 *v*/*v*) mixture was used for partial deuterations.

Phosphorescence Measurements

The solutions were immersed in liquid nitrogen for 10 min. Phosphorescence spectra and decay times were then recorded from glassy solutions at *ca.* 77 K. The excitation of the samples for the lifetime measurements was performed at 595 nm by means of a dye-laser (Rhodamin CG) constructed in the Institute of Nuclear Physics of the University of Cologne.

Results

According to Palmer and Basolo [23], the deuterium exchange in transition metal ammine complexes is base catalyzed. In CrN_6 systems, the basicity of the dimethylsulfoxide (DMSO) was found to be sufficient for complete exchange [3]. In contrast, the exchange

---

*Author to whom correspondence should be addressed.

0020-1693/86/$3.50

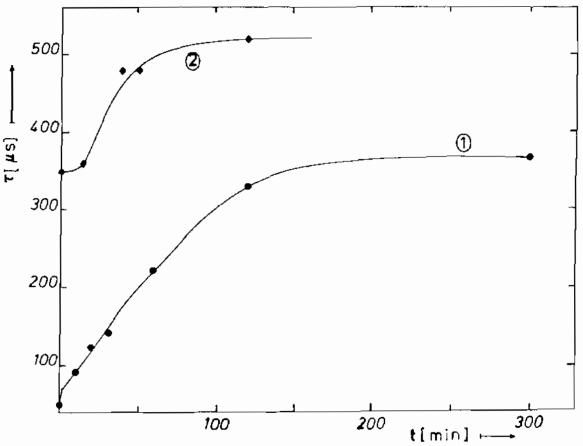

Fig. 1. Dependence of the average phosphorescence decay time on the deuteration time of ①: $[Cr(NH_3)_5OH_2]^{3+}$ and ②: *trans*-$[Cr(NH_3)_2(SCN)_4]^-$.

reaction in mixed complexes was much slower. Figure 1 shows the average phosphorescence decay of aquopentaamminechromium(III) as a function of the deuteration time in DMSO/D_2O. After 5 h, a plateau is reached. Extrapolation to infinite reaction time by linear regression (τ *versus* $1/t$) based on the final three points leads to lifetime values of 409 and 578 μs for $[Cr(NH_3)_5OH_2]^{3+}$ and *trans*-$[Cr(NH_3)_2(SCN)_4]^-$, respectively. The reaction obviously does not lead to a complete deuteration.

In the aquo complexes, the reaction scheme is complex, because the deuteration of the coordinated water may be expected to be much faster than that of the ammonia ligands [5]. Extrapolation to zero deuteration time yields a value of 75 μs for $[Cr(NH_3)_5OH_2]^{3+}$. This is longer than the lifetime of the perprotonated complex, but equal to a value of 79 μs that was obtained from a solution frozen immediately after the perprotonated complex had dissolved in the DMSO/D_2O solvent mixture. The same deuteration procedure yielded 110 and 130 μs for *cis*- and *trans*-$[Cr(NH_3)_4(OH_2)_2]^{3+}$, respectively. We assume that under these conditions, only the aquo protons have exchanged.

Fucaloro *et al.* used sodium acetate as base [5]. They observed that the original colour did not always return upon acidification. Some of our preliminary experiments showed that $[Cr(NH_3)_5OH_2]^{3+}$ dissolved in 0.1 mol sodium acetate for 3 h and afterwards acidified had its absorption maxima shifted by 5 nm relative to fresh solution. This indicated an appreciable degree of substitution during the deuteration.

We therefore decided to use a stronger base and a shorter reaction time. OD^- and CO_3^{2-} are strong bases; none of them coordinated to central Cr(III) ion under our experimental conditions. For this reason, NaOD and/or Na_2CO_3 should be appropriate means to increase the pH-values of the complex solutions for deuteration purposes. Thiocyanatoammine complexes were already satisfactorily deuterated in the presence of Na_2CO_3. The aquoammine complexes had to be treated with NaOD.

The phosphorescence decay times at 77 K are presented in Table I. At this temperature, the splitting components of the doublet state are in thermal equilibrium [5]. Single exponential decay was observed.

Our data of the perdeuterated complexes agree well with the literature values, despite the different deuteration methods. Although Fucaloro *et al.* [5] encountered a side-reaction with the acetate method, it obviously did not affect their results. In contrast, our decay times of partially deuterated complexes disagree with those reported by Fucaloro *et al.*

Discussion

The radiative lifetimes of the doublet states of chromium(III) complexes average 10 ms [24, 25]. Since the decay times of the perdeuterated complexes lie between 2 and 6 ms, the radiative decay process must play an important role in these com-

TABLE I. Phosphorescence Decay Times[a]

Cr(III)-complex	τ_H[b] (μs)	τ_D[c] (ms)	Base	τ_D Reference (ms)
$[Cr(NH_3)_6]^{3+}$	69	5.30	DMSO	4.35 [1, 2]/5 20 [3] 5.40 [5]
$[Cr(NH_3)_5OH_2]^{3+}$	49	3.40	NaOD	3.57 [5]
$[Cr(NH_3)_5SCN]^{2+}$	70	3.20	Na_2CO_3	
cis-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	39	2.40	NaOD	2.46 [5]
trans-$[Cr(NH_3)_4(OH_2)_2]^{3+}$	39	2.41	NaOD	2.32 [5]
cis-$[Cr(NH_3)_4(SCN)_2]^+$	123	2.50	Na_2CO_3	
trans-$[Cr(NH_3)_4(SCN)_2]^+$	140	2.50	Na_2CO_3	
trans-$[Cr(NH_3)_2(SCN)_4]^-$	349	2.20	NaOD	2.80 [1, 2]

[a] Experimental error ±10%. [b] Decay times of perprotonated forms [27]. [c] Decay times of perdeuterated forms (this work).

pounds. The radiative rate, however, can only be estimated from absorption intensities obtained at room temperature. Hence, its contribution to the deactivation escapes our knowledge at present. Nevertheless, the data show that the deuterium stretching modes do not act as accepting modes.

The situation changes when protons are bonded to the coordinating atoms (active hydrogen atoms). In this case, the hydrogen stretching modes provide the efficient energy acceptors. For the perprotonated complexes, Kupka's theory [13] has been shown to adequately describe the nonradiative transitions [3, 4, 26, 27]. We use this theory to calculate the rates of the partially deuterated complexes. Assuming that only the proton modes (N–H and O–H modes) contribute to the nonradiative deactivation, we can calculate the transition probability as a function of the number of active hydrogen atoms. The deactivation constant k_{NR} is given by

$$k_{NR} = k_{N-H} + k_{O-H} \qquad (1)$$

where k_{N-H} and k_{O-H} are the rates of the nonradiative decay induced by N–H and O–H stretching modes, respectively. These rates are proportional to Kupka's intramolecular distributions I_k that depend

$$k = AI_k(n, \beta, \Delta) \qquad (2)$$

on n, the number of vibrational quanta to bridge the energy gap, on β, the ratio of the ground and excited state vibrational frequencies, and finally on Δ, the displacement of the minima of the potential energy surfaces. The index k indicates the number of degenerate oscillators that is equal to the number of N–H or O–H stretching modes. A is a proportionality factor containing the promoting modes and the electronic matrix elements.

Figure 2 shows the dependence of the nonradiative rates on the number of the N–H modes calculated for the H_2O-, HDO-, and the D_2O-pentaammine chromium(III) ions. The parameter set previously obtained for the perprotonated complex was used for the calculation [27].

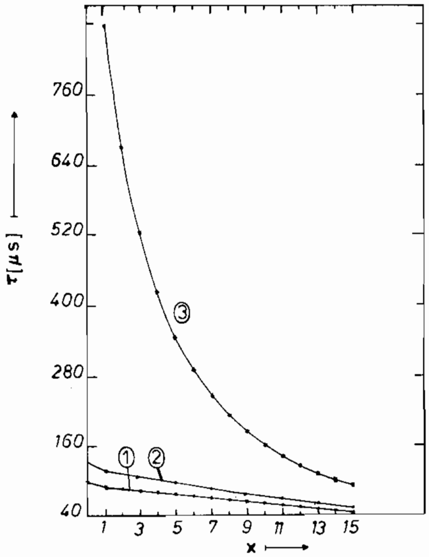

Fig. 2. Profiles of theoretical nonradiative decay times of partially deuterated aquopentaamminechromium(III) $[Cr(N_5H_xD_{15-x})L]^{3+}$ ①: L = H_2O; ②: L = HDO; ③: L = D_2O. A = 6.43×10^{10}; $\beta = 0.96$; $\Delta = 0.20$.

Experimentally, the rate of the nonradiative decay induced by the hydrogen modes is given by

$$k_{NR} = 1/\tau_H - 1/\tau_D \qquad (3)$$

The decay time τ_D of the perdeuterated complex comprises all other deactivation processes [4]. These rates are presented in Fig. 2.

The experimental lifetime of $[Cr(NH_3)_5OH_2]^{3+}$ dissolved in DMSO/D_2O and immediately frozen agrees fairly well with the theoretical value calculated for $[Cr(NH_3)_5OD_2]^{3+}$. Besides, the limiting lifetime for long deuteration times in DMSO/D_2O corresponds to a value of x close to 4 (see Fig. 2). In the series $[Cr(NH_3)_{6-n}(OD_2)_n]^{3+}$, the N–H

TABLE II. Deactivation Constants k_{NR} of Partially Deuterated Cr(III) Aquoammine Complexes[a]

n	$[Cr(NH_3)_{6-n}(OD_2)_n]^{3+}$ $10^{-4} \times k_{NR}$ (s^{-1})			$[Cr(ND_3)_{6-n}(OH_2)_n]^{3+}$ $10^{-4} \times k_{NR}$ (s^{-1})	
	Calculated	Experimental[b]	Reference 5	Calculated	Reference 5
1	1.10	1.24	1.72	1.00	0.13
2 (*cis*-)	0.80	0.87	1.88	1.66	0.34
2 (*trans*-)	0.80	0.73	1.85	1.66	0.59
3	0.55			2.51	
4	0.35			3.56	
5	0.19			4.81	

[a] $k_{NR} = \tau_H^{-1} - \tau_D^{-1}$. [b] This work.

stretching vibrations provide the most important contribution to the radiationless decay process. Equation (1) then reduces into

$$k_{\mathrm{NR}} \simeq k_{\mathrm{N-H}} \tag{4}$$

In the same manner, the deactivation constant of the species $[Cr(ND_3)_{6-n}(OH_2)_n]^{3+}$ is given by

$$k_{\mathrm{NR}} \simeq k_{\mathrm{O-H}} \tag{5}$$

In this case, according to Kupka, only the O–H stretching vibrations contribute significantly to the radiationless deactivation. We used the above equations to calculate the lifetimes of all partially deuterated compounds. Table II summarizes the results for the two series $[Cr(NH_3)_{6-n}(OD_2)_n]^{3+}$ and $[Cr(ND_3)_{6-n}(OH_2)_n]^{3+}$. The experimental data reported by Fucaloro *et al.* deviate significantly from the theoretical values. Those of the D_2O complexes turned out to be faster and those of the H_2O complexes were found to be smaller than the theoretical values. The authors had prepared their partially-deuterated samples by hydrogen exchange in acid solution (at pH 3). They assumed that at this pH, only the aquo hydrogen should exchange. Provided the calculations are essentially correct, it appears that under those conditions, even the aquo hydrogens have not yet exchanged completely.

Acknowledgements

We thank Dr. H. Kupka (Mülheim/a.d. Ruhr) for the calculation of the intramolecular distributions. Financial assistance by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. One of us (M.M.) thanks the Commission des Communautés Européennes for a scholarship. We also thank Prof. P. von Brentano for the opportunity to use the dye-laser of the Institute of Nuclear Physics. Finally, we are particularly indebted to Dr. Debbie Allen who took time to read the manuscript.

References

1 I. B. Neporent, E. B. Sveshnikova and A. P. Serov, *Izv. Akad. Nauk. SSSR, Ser. Fiz., 39,* 1959 (1975).
2 I. B. Neporent and E. B. Sveshnikova, *Russ. J. Inorg. Chem., 24,* 391 (1979).
3 A. Ditze, *Ber. Bunsenges, 90,* 111 (1986).
4 A. Ditze and F. Wasgestian, *J. Phys. Chem., 89,* 426 (1985).
5 A. F. Fucaloro, L. S. Forster, J. V. Rund and S. H. Lin, *J. Phys. Chem., 87,* 1796 (1983).
6 N. A. P. Kane-Maguire, K. C. Wallace and D. B. Miller, *Inorg. Chem., 24,* 597 (1985).
7 P. K. Miller, W. S. Crippen and N. A. P. Kane-Maguire, *Inorg. Chem., 22,* 696 (1983).
8 J. F. Endicott, T. Ramasami, R. Tamilarasan, R. B. Lessard, Chong Kul Ryu and G. R. Brubaker, *Coord. Chem. Rev.,* in press.
9 G. W. Robinson and R. P. Frosch, *J. Chem. Phys., 37, 1962 (1962);* 38, 1187 (1963).
10 R. Englman and J. Jortner, *Mol. Phys., 18,* 145 (1970).
11 D. J. Robbins and A. J. Thomson, *Mol. Phys., 25,* 1103 (1973).
12 B. R. Henry and W. Siebrand, *Chem. Phys. Lett., 3,* 327 (1969).
13 H. Kupka, *Mol. Phys., 36,* 685 (1979); *37,* 1673 (1979); *39,* 849 (1980).
14 A. L. Oppegard and J. C. Bailar, *Inorg. Synth., 13,* 153 (1950).
15 M. Mori, *Inorg. Synth., 5,* 131 (1957).
16 E. Zinato, R. Lindholm and A. W. Adamson, *J. Inorg. Nucl. Chem., 31,* 449 (1969).
17 D. W. Hoppenjans and J. B. Hunt, *Inorg. Chem., 8,* 505 (1969).
18 J. Springborg and C. E. Schäfer, *Inorg. Synth., 18,* 82 (1978).
19 M. Linhard and M. Weigel, *Z. Anorg. Chem., 15,* 299 (1959).
20 P. Pfeiffer and M. Tilgner, *Z. Anorg. Chem., 55,* 361 (1907).
21 A. D. Kirk and C. F. C. Wong, *Inorg. Chim. Acta, 27,* 265 (1978).
22 A. W. Adamson, *J. Am. Chem. Soc., 88,* 394 (1966).
23 J. W. Palmer and F. Basolo, *J. Inorg. Nucl. Chem., 15,* 279 (1960).
24 G. B. Porter, in A. W. Adamson and P. D. Fleischauer (eds.), 'Concepts of Inorganic Photochemistry', Wiley, New York, 1975, p. 37.
25 L. S. Forster, *Transition Met. Chem., 5,* 1 (1969).
26 K. Kühn, F. Wasgestian and H. Kupka, *J. Phys. Chem., 85,* 665 (1981).
27 M. Mvele and F. Wasgestian, *Spectrochim. Acta, Part. A,* in press.