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Photoredox Reactions of Polypyridyl Chromium(III) Complexes with Arylthioacetic Acids in Acetonitrile and Aqueous Media

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Abstract: The reductive quenching reactions of $^*Cr(NN)_3^{3+}$ (NN = 2,2′-bipyridyl, 4,4′-dimethyl-2,2′-bipyridyl and 1,10-phenanthroline) with arylthioacetic acids in acetonitrile and arylthioacetate ions in aqueous media have been studied. The substantial difference in k_q values between the acetonitrile and aqueous media is traced to the difference in the origin of electron for the reduction of Cr(III) complexes i.e., sulphur in acetonitrile and carboxylate ion in aqueous medium.

Introduction

Though photoinduced electron transfer reactions of arylthioacetic acids with organic sensitizers like benzophenone and other aromatic ketones[1] have been studied in detail such reactions have not been investigated for these substrates with inorganic complexes. The <u>para</u>-substituents in phenyl ring of $PhSCH_2COOH$ have profound influence towards radiation and electron-donating groups give protection while the electron-withdrawing groups offer sensitization and the effect is in the order of the Hammett σ constants.[2] Recently we reported our results on the reductive quenching of excited states of polypyridyl complexes of chromium(III) with several aryl methyl and alkyl phenyl sulphides.[3] Phenylthioacetic acid (PTAA) and its derivatives are analogous to their corresponding sulphides particularly in oxidation reactions.[4-7]

While the redox reactions of organic sulphides can be studied only in the presence of nonaqueous solvent arylthioacetic acids provide an opportunity to study the photoinduced electron transfer in the nonaqueous medium and in aqueous medium as arylthioacetare ions. When the arylthioacetic acids are used, the origin of electron may be either sulphur with unionized acid or COO^- if thioacetate ions are used as quenchers. Thus the change of the nature of the quencher from undissociated thioacid to thioacetate ion is expected to lead to more interesting redox chemistry than with sulphides and therefore the redox reactions of Cr(III)-polypyridyl complexes with several meta- and para-substituted phenylthioacetic acids in aqueous and acetonitrile media have been investigated with luminescence quenching technique in the present work.

Results and Discussion

The structure of the ligands and the abbreviations of Cr(III) complexes used in the present system are given in Figure 1. The excited state lifetime τ values of these complexes in aqueous, and acetonitrile media are collected in Table 1.

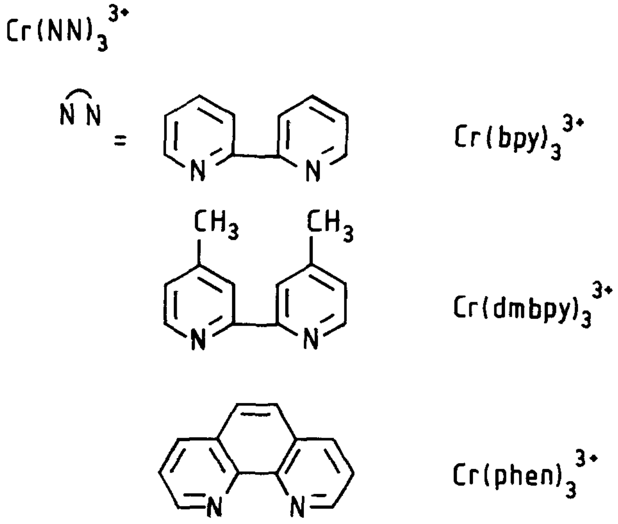


Fig. 1. Structure of ligands and abbreviations of Cr(III) complexes.

Table 1. Excited State Lifetime (τ) Values (μs) of $Cr(NN)_3^{3+}$ in Aceonitrile and Aqueous Media.

complex	τ values, Acetonitrile*	μs water#
$Cr(bpy)_3^{3+}$	73	35.4
$Cr(dmbpy)_3^{3+}$	200	23.0
$Cr(phen)_3^{3+}$	330	63.7

* Values collected from literature[3]

\# Values measured in the present study

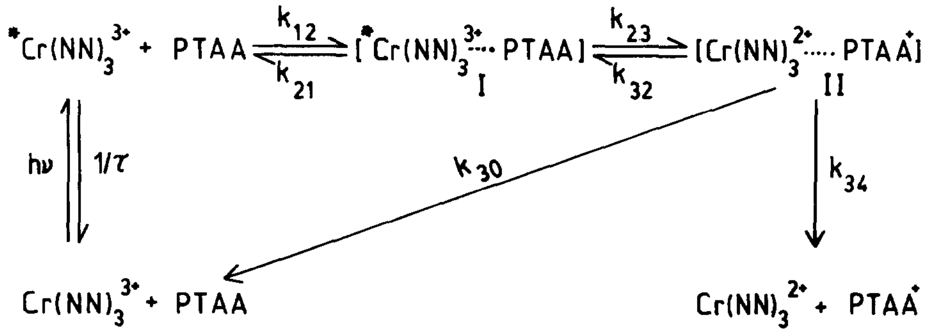
QUENCHING OF $^*Cr(NN)_3^{3+}$ WITH ARYLTHIOACETIC ACIDS IN ACETONITRILE

The quenching rate constant, k_q, values estimated from the luminescence quenching technique for the various substituted phenylthioacetic acids in the case of three $^*Cr(NN)_3^{3+}$ are presented in Table 2. The quenching process in acetonitrile can be discussed in terms of an electron transfer mechanism as shown in Scheme 1 which is similar to the mechanism postulated for Cr(III) and other metal complexes and also in our earlier studies with $^*Cr(NN)_3^{3+}$ and sulphides.[3]

Table 2. Quenching Rate Constants, k_q, for $^*Cr(NN)_3^{3+}$ with $XC_6H_4SCH_2COOH$ and XC_6H_4SMe in Acetonitrile at 298 K$^{\#}$.

No	Substituent (X)	$Cr(bpy)_3^{3+}$		$Cr(dmbpy)_3^{3+}$		$Cr(phen)_3^{3+}$	
1	H	2.3x10^{6}	(7.1x10^{7})	5.5x10^{5}	(2.9x10^{6})	1.7x10^{6}	(7.4x10^{6})
2	p-Me	1.6x10^{7}	(3.9x10^{8})	1.4x10^{6}	(1.4x10^{7})	1.3x10^{7}	(8.1X10^{7})
3	m-Me	6.4x10^{6}	(1.1x10^{8})	9.5x10^{5}	(9.3x10^{6})	5.1x10^{6}	(1.9x10^{6})
4	p-Cl	4.4x10^{5}	(1.3x10^{7})	7.7x10^{4}	(1.7x10^{6})	2.0x10^{5}	(1.9x10^{6})
5	p-F	1.3x10^{6}	(3.0x10^{7})	3.2x10^{5}	(2.4x10^{6})	6.3x10^{5}	(3.7x10^{6})
6	p-Br	5.6x10^{5}	-	1.0x10^{5}	-	2.9x10^{5}	-
7	p-OMe	5.6x10^{7}	(2.5x10^{9})	4.6x10^{6}	(5.3x10^{7})	2.6x10^{7}	(3.2x10^{8})
8	m-OMe	1.3x10^{6}	(3.5x10^{7})	2.4x10^{5}	(2.2x10^{6})	6.1x10^{5}	(5.0x10^{6})

$^{\#}$Values given in the parenthesis are the k_q values for aryl methyl sulphides.[3]



Scheme 1.

The reactants, $^{*}Cr(NN)_3^{3+}$ and PTAA, form an encounter complex I with the diffusion rate constant k_{12} and this is followed by electron transfer within the encounter complex with rate constant k_{23} to give the successor complex II. There are three options for the complex II, $[Cr(NN)_3^{2+}...PTAA^{+}]$. It may decompose to give products due to electron transfer or it may give back the reactants either in the ground state or excited state.

The k_q values obtained for arylthioacetic acids are lower than the corresponding k_q values of aryl methyl sulphides (cf.Table 2). This is not surprising as the presence of carboxyl group reduces the electron density on the sulphur atom of the phenylthioacetic acid and therefore phenylthioacetic acid is a poor electron donor compared to phenyl methyl sulphide. Similar lower reactivity of phenylthioacetic acid compared to phenyl methyl sulphide has been observed in several other redox reactions.[4,5]

The data in Table 2 show that the rate of luminescence quenching is accelerated by electron-releasing groups and retarded by electron-withdrawing substituents present in the phenyl ring of $PhSCH_2COOH$ with all Cr(III) complexes. The Hammett plot of log k_q versus σ is linear in

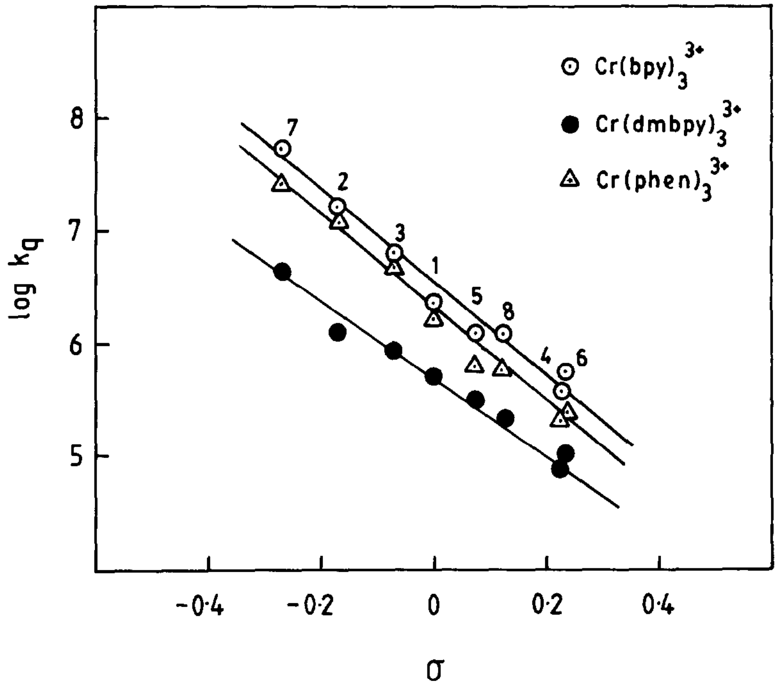


Fig. 2. Hammett plot of log k_q vs σ in acetonitrile medium at 298 K. The points in the figure referred to by the same numbers in Table 2.

all three cases (Figure 2). The reaction constant (ρ) and correlation coefficient (r) values for $Cr(bpy)_3^{3+}$, $Cr(dmbpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ are -4.02(r = 0.989), -3.28(r = 0.993) and -4.28(r = 0.990) respectively. The ρ values obtained under similar conditions for aryl methyl sulphides are -3.64, -2.78 and -3.96 respectively.[3] Thus the ρ values obtained for arylthioacetic acids are slightly higher than those observed for aryl methyl sulphides. The reactivity of arylthioacetic acids (k_q values) is lower than that of corresponding aryl methyl sulphides but the selectivity, indicated by the ρ values, is higher for thioacetic acids. These results are in accordance with the reactivity-selectivity principle.[8] The comparison of the k_q data obtained for aryl methyl sulphides and arylthioacetic acids clearly shows that the quenching reactions of arylthioacetic acids with $Cr(NN)_3^{3+}$ complexes in acetonitrile are analogous to those of organic sulphides.

The k_q values are higher for $^*Cr(bpy)_3^{3+}$ with all arylthioacetic acids compared to the complexes $^*Cr(dmbpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ as observed with aryl methyl sulphides. The lower k_q values obtained with $^*Cr(dmbpy)_3^{3+}$ is probably due to the unfavourable $E_{1/2}$ value and by the bulky nature of the ligand 4,4'-dimethyl-2,2'-bipyridine. The k_q values with $Cr(phen)_3^{3+}$ are only slightly lower compared with $Cr(bpy)_3^{3+}$. As the difference in the size between 2,2-bipyridne and 1,10-phenanthroline is negligible, the smaller k_q value with $Cr^*(phen)_3^{3+}$ may be attributed to slightly lower $E_{1/2}$ value.

QUENCHING OF $Cr(NN)_3^{3+}$ WITH ARYLTHIOACETATE IONS IN AQUEOUS MEDIUM.

The k_q values for the quenching of $^*Cr(NN)_3^{3+}$ with arylthioacetate ions and thiodiglycollate ion in aqueous solutions are collected in Table 3. By mixing equal concentrations of acids and sodium hydroxide in water, arylthioacetate ions are produced. The comparison of k_q values collected in Table 3 with those in Table 2 indicates the operation of different mechanisms in different media. The k_q values of all substituted phenylthioacetate ions in aqueous solution are 2-3 orders higher than the corresponding k_q values of thioacetic acids in acetonitrile. To check the validity of Hammett equation to this photoredox reaction in aqueous medium, log k_q values of several substituted phenylthioacetate ions have been plotted against σ (Figure 3), The correlations are good with all complexes and the ρ values along with correlation coefficient values for the redox reactions respectively are $Cr(bpy)_3^{3+}$,ρ=-2.64 (r=0.990); $Cr(dmbpy)_3^{3+}$,ρ=-2.21 (r=o.996); $Cr(phen)_3^{3+}$, ρ =-2.54(r=0.989). The comparison of ρ values obtained in aqueous solution with those in acetonitrile medium proves that ρ values are substantially lower in aqueous medium. An interesting feature is that in aqueous medium, the k_q values for $Cr(phen)_3^{3+}$ are larger than those of $Cr(bpy)_3^{3+}$. These results are contrary to those observed in acetonitrile medium. Higher k_q value for $Cr(phen)_3^{3+}$ compared to $Cr(bpy)_3^{3+}$ has been observed in the quenching of these complexes with iodide ion.[9] The large difference in k_q values in different media cannot be attributed to solvent effect as less polar and low viscous acetonitrile will favour electron transfer reactions compared to aqueous medium.[10] Thus the possible explanation for this enormous difference in k_q values in two different media is the difference in the source of electron. As the carboxylate ion can easily donate an electron compared to sulphide function in $ArSCH_2COO^-$, the reaction in aqueous solution is initiated by electron transfer from $-CO_2^-$ to $Cr(NN)_3^{3+}$ to form $-CO_2^{\cdot}$ and $Cr(NN)_3^{2+}$. Carbon dioxide can easily be removed from $ArSCH_2CO_2^{\cdot}$ to form $ArSCH_2^{\cdot}$ which can react with aqueous medium to form stable $ArSCH_3$. The analysis of product after quenching reaction confirms the formation of PhSMe as the major product when phenylthioacetate ion is used as the quencher. Therefore, we present the following mechanism, Scheme 2, tentatively for the reductive quencing of $Cr(NN)_3^{3+}$ complexes with arylthioacetate ions in aqueous medium.

Table 3. Quenching Rate Constant, k_q, Values for $Cr(NN)_3^{3+}$ with $XC_6H_4SCH_2CO_2^-$ Ions and Thiodiglycollate Ion in Aqueous Medium at 298 K.

		k_q values, $M^{-1}s^{-1}$		
No	X	$Cr(bpy)_3^{3+}$	$Cr(dmbpy)_3^{3+}$	$Cr(phen)_3^{3+}$
1	H	$2.4x10^9$	$5.2x10^8$	$9.5x10^9$
2	p-Me	$1.1x10^{10}$	$1.2x10^9$	$3.6x10^{10}$
3	m-Me	$5.9x10^9$	$7.2x10^8$	$1.8x10^{10}$
4	p-Cl	$1.1x10^9$	$1.8x10^8$	$3.2x10^9$
5	p-F	$1.6x10^9$	$3.4x10^8$	$6.7x10^9$
6	p-Br	$1.4x10^9$	$2.2x10^8$	$6.3x10^9$
7	p-OMe	$1.8x10^{10}$	$1.8x10^9$	$5.3x10^{10}$
8	m-OMe	$1.6x10^9$	$2.7x10^8$	$5.3x10^9$
9	p-NO_2	$2.5x10^7$	$8.3x10^6$	$1.0x10^8$
10	Thiodiglycollate ion	$1.1x10^6$	$3.0x10^5$	$1.9x10^6$

$$Cr(NN)_3^{3+} + h\nu \text{ -----> } {}^*Cr(NN)_3^{3+}$$

$$^*Cr(NN)_3^{3+} + ArSCH_2CO_2^- \text{ -----> } Cr(NN)_3^{2+} + ArSCH_2CO_2^{\bullet}$$

$$ArSCH_2CO_2^{\bullet} \text{ -----> } ArSCH_2^{\bullet} + CO_2$$

$$ArSCH_2^{\bullet} + H_2O \text{ -----> } ArSCH_3 + {}^{\bullet}OH$$

$$Cr(NN)_3^{3+} \text{ or } ArSCH_2CO_2^- + {}^{\bullet}OH \text{ -----> } \text{Products}$$

Scheme 2.

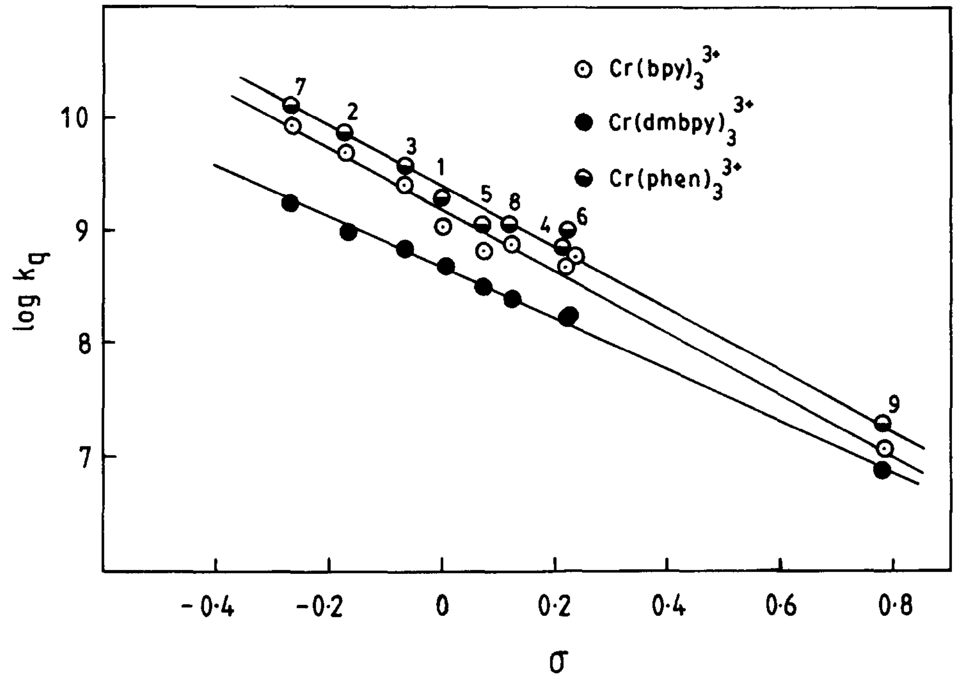


Fig. 3. Hammett plot of log k_q vs σ in aqueous medium at 298 K. The points in the figure referred to by the same numbers in Table 3.

The k_q data given in Table 3 for thiodiglycollate ion, an aliphatic thioacid, indicates that quenching by aliphatic acids are inefficient compared to aromatic thioacids. This can be explained in terms of the formation of the resonance stabilised radical $ArSCH_2^{\bullet}$ after the decarboxylation of $ArSCH_2CO_2^{\bullet}$. Thus the formation of relatively stable $ArSCH_2^{\bullet}$ can be taken as the driving force for this efficient reaction compared to aliphatic acids. Though the abstraction of H from water to form $ArSCH_3$ is speculative, under the present experimental conditions it is difficult to visualise alternative routes for the formation of $ArSCH_3$ from $ArSCH_2^{\cdot}$. The abstraction of hydrogen from polypyridyl ligands is highly unlikely. It is pertinent to point out that the formation of $ArSCH_3$ from $ArSCH_2^{\cdot}$ by abstraction of H from H_2O has been shown in the peroxodisulphate ion oxidation of arylthioacetic acids.[5]

The formation of $PhSCH_3$ from the photodecarboxylation of $PhSCH_2CO_2H$ with different sensitizers is also explained by a mechanism similar to the Scheme 2.[11] The observed low ρ values in aqueous medium compared to acetonitrile medium also support the postulated mechanism. As the *para*-substituent is far away from the reactive centre CO_2^- compared to sulphide function, the transmission of electronic effect is less efficient in *p*-$XC_6H_5SCH_2COO^-$ in aqueous medium.

Experimental

The Cr(III) complexes of 2,2′-bipyridine, 4,4′-dimethyl-2,2′-bipyridine and 1,10-phenanthroline have been synthesised by reported methods.[3,9] Arylthioacetic acids have been prepared by refluxing an alkaline mixture of monochloroacetic acid and the corresponding thiophenol in an oil-bath at 120-130°C for five hours.[12] The solution was cooled and extracted with a small amount of ether and the ether layer was rejected. The reaction mixture was acidified (50% HCl) and filtered. The precipitated thioacetic acid was recrystalised from water. A different procedure as advocated by Shaw and Miller was adopted for the preparation of *p*-nitrophenylthioacetic acid.[13] The solvents and other reagents have been purified by reported procedures.[14] The melting points of $XC_6H_4SCH_2CO_2H$ synthesised in the present study and literature values are given below.[12,13,15,16]

X	H	*m*-OMe	*p*-OMe	*p*-Me	*m*-Me	*p*-Cl	*p*-F	*p*-Br	*p*-NO_2
M.P.°C	63.0	61.5	75.5	93-94	66-67	106	77	117	153
Literature Value°C	63.5	62.5	76.0	94.0	67.0	105-107	77	118	151-153

The reaction mixture, after the quenching reaction was completed, was taken up for product analysis. The t.l.c. analysis of the product confirmed the formation of $ArSCH_3$ as the major product. After the photoredox reaction was over, the reaction mixture was extracted with ether, dried with anhydrous $MgSO_4$ and the solvent is evaporated. The IR spectrum of the residue shows no peak at 1080 cm^{-1} confirming out the absence of S=O linkage in the product. The irradiation of the aqueous solution of $PhSCH_2CO_2^-$ in the absence of $Cr(NN)_3^{3+}$ did not give $PhSCH_3$ as the major product which supported our formulation given in Scheme 2.

The excited state lifetime of $Cr(bpy)_3^{3+}$ and $Cr(phen)_3^{3+}$ in aqueous media were measured using laser flash photolysis technique (Applied

Photophysics Ltd. U.K. System). The KrF pulsed excimer laser with gas purifier was used as the excitation source. All the solutions were deoxygenated by purging purified dry N_2 gas for 30 min. before recording emission spectra. Luminescence spectra were recorded using a JASCO FP-770 spectroflurometer using Xenon lamp as the source. The details of measuring quenching rate constant and other experimetal details are given in previous report.[3]

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