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Charge transfer photochemistry of Reinecke's salt and of some of its analogues containing organic amines [1]

Bernadette Mainusch [a], A. Karocki [b], D.M. Guldi [c], Z. Stasicka [b], F. Wasgestian [a]

[a] University of Cologne, Institute of Inorganic Chemistry, D-50939 Köln, Germany
[b] Jagiellonian University, Faculty of Chemistry, PL-30-060 Kraków, Poland
[c] University of Notre Dame, Radiation Laboratory, Notre Dame, IN 46556-0579, USA

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Abstract

N-substituted Reineckates of the compositions $[CrA_2(NCS)_4]^-$ (A = NH_3, aniline, n-propylamine, morpholine) and $[Cr(A\text{-}A)(NCS)_4]^-$ (A-A = en, tn) have been prepared. The ligand field absorption maxima were slightly shifted to longer wavelengths in the order NH_3 < en, tn < n-propylamine < morpholine < aniline. All complexes dissociated NCS^- on charge-transfer excitation (254 nm). With exception of the aniline complex they were also decomposed to some extent, yielding Cr(II) and $(NCS)_2^{\bullet -}$ radicals. Approximately 10% of the photochemically formed Cr(II) was oxidised to chromate(VI) in air saturated methanol as was shown by comparison with chemically and radiolytically reduced $[Cr(NH_3)_2(NCS)_4]^-$. $(NCS)_2^{\bullet -}$ radical formation was observed by flash photolysis as well as by pulse radiolysis. Photochemical quantum yields for continuous irradiations of air saturated methanolic solutions were determined for the disappearance of the starting material, ranging from $\Phi_{Cr} = 0.16$ (aniline) to $\Phi_{Cr} = 0.31$ (en), for NCS^- release ranging from $\Phi_{NCS} = 0.17$ (aniline) to 0.52 (n-propylamine) and for chromate(VI) formation ranging from $\Phi_{CrO_4} < 0.001$ (aniline) to 0.009 (NH_3, n-propylamine).

Keywords: Photochemistry; Charge transfer; Chromium complexes; Thiocyanato complexes; Alkylamine complexes

1. Introduction

$K[Cr(NH_3)_2(NSC)]_4$, potassium Reineckate, was introduced as a chemical actinometer by Wegner and Adamson [1] in 1966. It has been widely used for quantum yield determinations in the visible region [2,3]. Its ligand field photochemistry has been studied several times [1,4–10], while studies on the charge transfer photochemistry of Reineckates are less frequent. Apart from a study of the solvent effect in alcoholic solutions, which included some experiments performed at 256 nm [5] and a preliminary communication of this work [11] no other reports are known to us. The photolysis of organo Reineckates has not been studied before.

The present paper focuses on the charge transfer photochemistry of Reinecke's salt and its analogues. In Reinecke's salt (ammonium Reineckate) the *trans* configuration has been established by X-ray diffraction [12]. In contrast the bidentate ligands 1,2-diaminoethane (en) and 1,2-diaminopropane (tn) force the *cis* configuration. n-Propylamine was chosen as an example of a primary alkylamine and morpholine of a secondary amine. Aniline was selected as a representative of the arylamines.

2. Experimental

Reinecke's salt $NH_4[Cr(NH_3)_2(NCS)_4]\cdot H_2O$ [13] and the aniline analogue $NH_4[Cr(aniline)_2(NCS)_4]$ [14] were prepared by literature methods.

The n-propylamine Reineckate was prepared by a modification of the method of Ganescu et al. [15]. 30 ml of the amine (Fluka), freshly distilled over KOH, and 8.1 g (15.6 mmol) $K_3[Cr(NCS)_6]$ (Alfa-Productions), dehydrated for 4 h at 110–120°C, were refluxed for 5 h. The mixture was poured into 300 ml of 10% ice cold acetic acid that had been precooled to 0°C. The pink flaky precipitate was separated by filtration.

The crude Reineckate was transformed into the tetrabutylammonium salt by dissolving it in acetonitrile and subsequent dropping into a 3% aqueous solution of tetrabutylammonium thiocyanate of 0°C. The oily product was separated and washed with toluene. This product was chromatographed

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[1] Dedicated to the 75th anniversary of Frau Professor Dr Marianne Baudler.

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in chloroform on silica gel 60 (grain 0.062–0.2 mm) Merck. Three fractions were obtained. The first fraction was a light violet colour and contained the starting material $[Cr(NCS)_6]^{3-}$. This solution was discarded. The second fraction was red–violet and yielded the desired tetrathiocyanato complex. The third fraction was a red colour caused by the tristhiocyanatotris-n-propylamine complex. The second fraction was concentrated and separated from colloidal silica by centrifugation. After evaporation of the solvent the still oily product was dissolved in ~10 ml of an ethanol/acetonitrile mixture (10:1 vol./vol.) and injected into 100 ml of cold water by pipette. The products could be filtered more easily if the suspension was frozen and rethawed again. The purified product was sufficiently free of uncomplexed NCS^- ($\leq 3\%$). The yield of the tetrabutylammonium salt after the chromatographic purification amounted to 0.96 g. *Anal.* Found: Cr, 8.0; C, 48.1; H, 8.3; N, 14.9. Calc.: Cr, 8.1; C, 48.5; H, 8.4; N, 15.2%

The morpholine Reineckate was prepared by the same method.

$K[Cr(en)(NCS)_4]$ was obtained in a three-step synthesis worked out by Weinmann [16]. (i) $[Cr(ox)(en)_2]$-$[Cr(ox)_2(en)]$: 100 g (0.21 mol) $K_3[Cr(ox)_3] \cdot 3H_2O$, prepared according to the literature [17], was dissolved in 120 ml of hot water. Then 30 ml of freshly distilled ethylenediamine were added. The solution was stirred for 2 h at 60°C. During that time a pink solid was formed which was separated by filtration and washed with ether (yield 51 g). (ii) $[CrCl_2(H_2O)_2(en)]Cl$: 48 g (0.09 mol) $[Cr(ox)(en)_2]$-$[Cr(ox)_2(en)]$ was dissolved in 72 ml conc. HCl and was vigorously stirred until the salt was completely dissolved. During that time the temperature increased to 40°C. Then the solution was cooled to 5°C and kept for 2 days at this temperature. The dark violet crystals of $[CrCl_2(en)_2]Cl$ were removed by filtration. Afterwards the solution was cooled below −12°C in an ice sodium chloride bath and HCl gas was introduced until the colour changed from red–violet to blue–violet. The solution was kept for another 2 days at 5°C and separated from the solid chromium chloride. Several days later the blue–violet product crystallized from the cold solution. (iii) $K[Cr(en)(NCS)_4]$: 5 g (80.02 mol) $[CrCl_2(H_2O)_2(en)]Cl$ was dissolved in 10 ml H_2O and filtered. Then a solution of 8 g (0.08 mol) KNCS in ~5 ml H_2O was added. The mixture was warmed to 45°C and kept at this temperature until the colour changed to dark red. A red product was formed upon cooling. It was recrystallized from methanol. Yield 1 g. *Anal.* Found: Cr, 14.8; C, 18.9; N, 22.7. Calc.: Cr, 13.6; C, 18.8; N, 21.9%.

$K[Cr(tn)(NCS)_4]$ was obtained by a preparation analogous to that of $K[Cr(en)(NCS)_4]$.

The potassium salts were transformed into the tetrabutylammonium salts by dropping a solution of the Reineckates into an ice cold saturated aqueous solution of tetrabutylammonium thiocyanate.

UV–Vis spectra were recorded with Cary 2300 and Shimadzu 2100 instruments. IR spectra were obtained on a Nicolet 5PC FT-IR spectrometer.

Ligand field irradiations were performed using equipment described before [18]. 3 ml samples were irradiated at 23°C with 436 nm light of a high pressure mercury lamp (HBO 100) in combination with a Schott interference filter. The charge transfer excitation (254 nm) was carried out with a low pressure mercury lamp (Philips PLS9 WTUV) without filtering. The absorbed quanta were determined either with a bolometer [18] or by iron oxalate actinometry [19].

Flash photolysis was done with the flash spectroscopic equipment of the Chemical Faculty of the Jagiellonian University [20,21]. The unfiltered light from a xenon lamp was used with flashes characterised by 400 J energy per pulse and 25 μs duration.

For the continuous γ-irradiations the ^{60}Co source of the Institute of Physical Chemistry, University of Cologne, was used. The dose rate was determined by Fricke dosimetry and amounted to 1.35×10^5 rad/h.

Pulse radiolysis experiments were performed by utilising either 500 ns pulses of 1.55 MeV electrons from a Van de Graaff accelerator or 50 ns pulses of 15 MeV electrons from a linear electron accelerator (LINAC). Basic details of the used equipment and the data analysis have been described elsewhere [22,23]. Dosimetry was based on the oxidation of NCS^- to $(NCS)_2^{\bullet -}$, which takes place in aqueous solution with $G \approx 6$ (G denotes the number of species per 100 eV or the approximate μM concentration per 10 J absorbed energy). The radical concentrations generated per pulse amounted to $(1–3)10^{-6}$ M for all the investigated systems. Reductive conditions were obtained in N_2 saturated solutions containing 1 vol.% of 2-propanol or t-butanol, i.e. hydrated electrons and α-hydroxy alkyl radicals. On the other hand, saturation with N_2O in the absence of other additives exclusively led to the formation of the highly oxidative OH radicals.

The amount of liberated NCS^- was spectrophotometrically determined with Fe^{3+} by monitoring the absorbance at 460 nm in H_2O/MeOH 4:1 (vol./vol.) [1,24] (apparent molar absorbancy 4.30×10^3 M^{-1} cm^{-1}). The unreacted starting material was removed prior to the analytical determinations. The fact that the tetrabutylammonium Reineckates are only sparingly soluble in water was used to precipitate them from the methanolic solutions by adding water. 1 ml aliquots were mixed with 4 ml of water. If the suspensions were frozen (−18°C) and rethawed, they were easier to filter. The potassium Reineckate was precipitated as described for $[Cr(NCS)_6]^{3-}$ by Wegner and Adamson [1]. By these methods the starting materials were precipitated quantitatively whereas the reaction products remained in solution. Tests with solutions that contained tetrabutylammonium Reineckate of the same concentration as used in the photochemical experiments and known concentrations of NCS^- (1.3×10^{-5} to 2.6×10^{-4} M) gave the same results as in the absence of the Reineckate (experimental error

Table 1
UV–Vis spectral data of Reineckate complexes $[Cr(A)_2(NCS)_4]^-$ (A = amine)

Amine	Solvent	Absorption maxima, λ (nm) (ϵ (l mol^{-1} cm^{-1}))
2 NH_3	H_2O	519 (105), 391 (89), 308 (14.9×10^3)
	CH_3CN	522 (101), 396 (83)
	MeOH	523 (110), 396 (91), 308 (18.3×10^3), 235 (26.5×10^3)
2 aniline	CH_3CN	549 (164), 400sh
	MeOH	548 (165), 400sh, 313 (28.2×10^3), 249 (45.0×10^3)
2 n-propylamine	CH_3CN	529 (114), 402 (87)
	MeOH	527 (122), 401 (95), 310 (19.2×10^3)
2 morpholine	CH_3CN	544 (140), 410 (110)
	MeOH	544 (150), 410 (112), 318 (23.4×10^3)
en	CH_3CN	528 (135), 399 (96)
	MeOH	526 (140), 399 (100), 310 (14.8×10^3)
tn	CH_3CN	527 (128), 396 (91)
	MeOH	525 (139), 394 (107), 309 (16.7×10^3)

± 3%). The filtrates of the freshly prepared solutions were completely transparent in the region of the ligand field bands, whereas filtrates of irradiated solutions and of samples that had been kept in the dark for several hours did not absorb in this region.

Deaerated solutions were obtained by the freeze pump technique or by bubbling nitrogen through the solutions. They were transferred to the irradiation cells with a nitrogen purged syringe.

3. Results and discussion

The UV–Vis spectral data are compiled in Table 1. In contrast to the ammine-halogeno-chromium complexes the geometry of the ligand arrangements does not affect the spectral properties seriously. The en and tn complexes, being in the *cis* configuration, have a slightly stronger ligand field absorbance than the respective NH_3 and n-propylamine complexes. The *cis* complexes, lacking a centre of symmetry, are expected to absorb more intensively than the analogous *trans* complexes [25]. Since the molar absorbance of the n-propylamine complex is significantly lower than the absorbance of the en and tn complexes, we assume that the n-propylamine complex is in the *trans* configuration. The ligand field strength decreased in the order: $NH_3 <$ en $\sim$ tn $\sim$ n-propylamine $<$ morpholine $<$ aniline. The corresponding nephelauxetic series showing the decrease in the interelectronic repulsion parameter B was: aniline $>$ tn $>$ en $>$ NH_3 $>$ morpholine $>$ n-propylamine. With the exception of the aniline and morpholine complexes the wavelength of the first charge transfer maximum (309 ± 1 nm) remained almost unaffected by the ligand variation with an average molar absorbance of $(17\pm2)\times10^3$ M^{-1} cm^{-1} in methanol. This absorption has been assigned to derive from a ligand to metal charge transfer transition [26].

The thermal solvolysis of the parent compound is well documented [4,27–32]. Room temperature rate constants for aqueous and alcoholic solutions were found in the range of 10^{-6} to 10^{-5} s^{-1}. Hence, the dark reaction did not interfere with the time scale of the photoreaction (≤ 1 h). The organo Reineckates were less stable in aqueous solution. In methanol, however, their solvolysis rate was sufficiently reduced to permit photochemical studies. A solution kept in the dark for 1 h decomposed less than 1%. The following order of stability was observed:

$NH_3 >$ en $\sim$ tn $>$ n-propylamine $>$ morpholine $>$ aniline

Upon ligand field excitation of Reineckates, NCS^- substitution is the main reaction path [1,5,6,10]. The spectral changes are shown in Fig. 1. The reaction caused a bathochromic shift accompanied by a decrease in absorbance of both spin allowed ligand field bands. The charge transfer band at 308 nm was not shifted but displayed a stronger decrease relative to the bleaching of the ligand field bands. The CT absorption band at 220 nm was shifted hypsochromically with an intermediate decrease in absorbance.

Irradiation into the charge transfer bands produced different spectral changes (Fig. 2). The wavelength shift of the ligand field bands was smaller and additional absorption appeared in the region of the second ligand field band around 380 nm. The new absorption obviously derived from the formation of chromate(VI) in a reaction with O_2 as was also observed in the CT photolysis of hexacyanochromate(III) [33–35]. Chromate(VI) has an intense band at 372 nm and its formation was confirmed by its colour reaction with diphenylcarbazide. In deaerated solutions the chromate(VI) formation was significantly reduced. We attribute the remaining formation to the presence of traces of oxygen.

Ammonia release was checked by observing the pH change in aqueous solution. Liberated ammonia should increase the pH. Irradiation with 254 nm light, however, resulted in a slight decrease in pH from pH 6.2 ± 0.1 to pH 5.6 ± 0.2 (3 ml of a 2×10^{-3} M solution irradiated for 8 min with 1.5×10^{-3} einstein l^{-1}). Ammonia release might have been obscured by decomposition products of NCS^-. Sole NCS^- release, however, is predicted by Adamson's rules [36]. In the case of *trans*-$[Cr(en)_2(NCS)_2]^+$ Bifano and Linck [37]

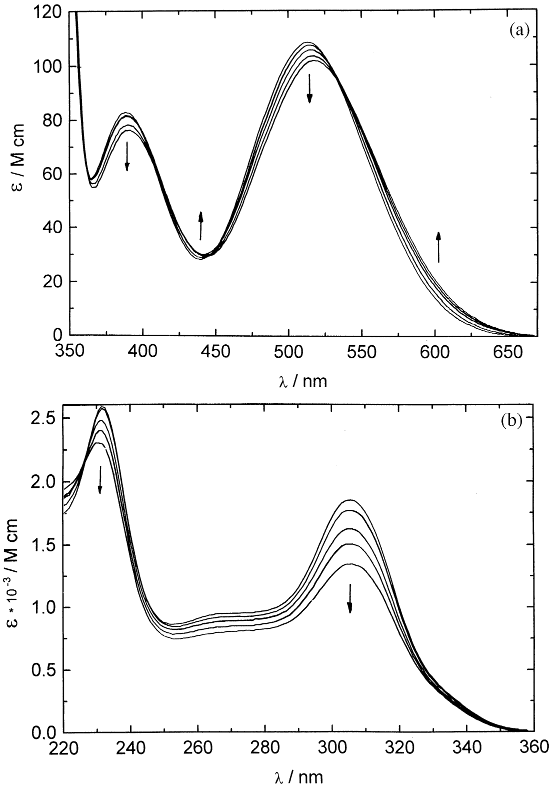


Fig. 1. Spectral changes upon irradiation into the ligand field region of $Bu_4N[Cr(NH_3)_2(NCS)_4]$ after 0, 4, 8, 12 and 16 min of irradiation of a 2×10^{-3} M methanolic solution with 1.4×10^{-4} einstein min^{-1} l^{-1} at 436 nm at 23°C: (a) ligand field bands; (b) charge transfer bands.

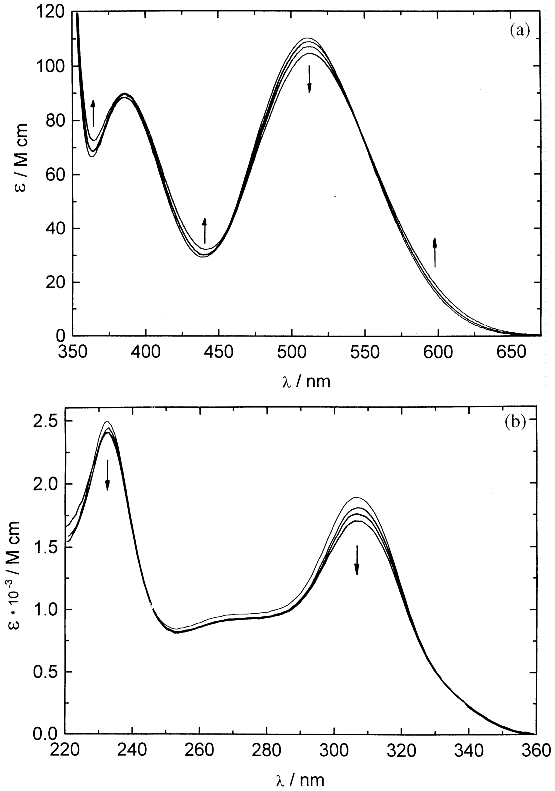
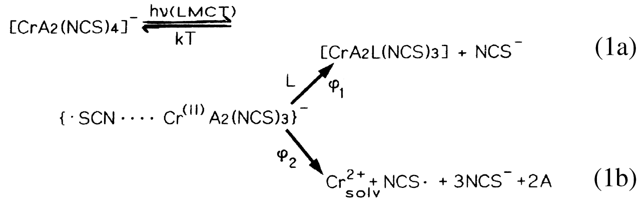


Fig. 2. Spectral changes upon irradiation into the charge transfer region of $Bu_4N[Cr(NH_3)_2(NCS)_4]$ after 0, 2, 4 and 6 min of irradiation of 3 ml of a 2×10^{-3} M methanolic solution with 1.9×10^{-4} einstein min^{-1} l^{-1} at 254 nm at 23°C: (a) ligand field bands; (b) charge transfer bands.

and Balzani and co-workers [38] found H^+ consumption against Adamson's rules. The labilisation of the chromium amine bond has been explained by a stronger Cr–NCS bond due to π-bonding [37].

Since the absorption at 254 nm originates from a ligand to chromium transition, the immediate reaction product is supposed to be a chromium(II) species. Thus we assume the following mechanism:



$$NCS^{\bullet} + NCS^- \rightarrow (NCS)_2^{\bullet-} \tag{2}$$

$$Cr^{2+}_{solv} + O_2 + 4OH^- \rightarrow CrO_4^{2-} + 2H_2O \tag{3}$$

$$2Cr^{2+}_{solv} + 1/2O_2 + H^+ \rightarrow 2Cr^{3+}_{solv} + OH^- \tag{4}$$

$$(NCS)_2^{\bullet-} \xrightarrow{e^-} 2NCS^- \tag{5a}$$

$$2(NCS)_2^{\bullet-} \rightarrow (NCS)_2 + 2NCS^- \tag{5b}$$

The radical pair may either produce $^{\bullet}NCS$ radials or NCS^-. Reaction (1a) may proceed either via internal conversion into the ligand field system or by back electron transfer within a solvent separated radical pair. The labile Cr(II) complex is supposed to be solvolysed completely before it is reoxidised. The $^{\bullet}NCS$ radical is stabilised by forming the dimer radical (Eq. (2)). The fate of the dimer radical cannot be established beyond doubt. Baxandale et al. [39] found disproportionation (Eq. (5b)). Simple reduction (Eq. (5a)), however, cannot be ruled out on account of its high reduction potential [40] ($E_0 = 1.33$ V versus NHE). If it is reduced, four NCS^- will be found in solution. In the other case, there will be three NCS^-.

In order to check whether O_2 will oxidize chromium(II) to chromate(VI) under our experimental conditions, we reduced $[Cr(NH_3)_2(NCS)_4]^-$ with metallic zinc in deaerated methanolic solution. After exposure to air the absorption at 380 nm gradually developed and chromate(VI) was detected by its reaction with diphenylcarbazide.

Reineckate may also be reduced with methanol radicals and solvated electrons obtained by ^{60}Co-γ-irradiation of methanolic N_2 saturated solutions. The spectral changes were similar to the ones observed under CT excitation of deaerated solutions. In the ligand field region both bands decreased in absorbance. A 2×10^{-3} M solution of potassium Reineckate that was irradiated for 80 min showed a decrease of the first ligand field band of 3.3%. In this solution 3.8×10^{-4} M NCS^- and 6.5×10^{-5} M Cr^{2+} were found. An aliquot of

Table 2
Photochemical quantum yields of Reineckates, tetrabutylammonium salts in air saturated methanolic solutions at 23°C, if not otherwise stated

Amine	Irradiation wavelength (nm)	Φ_{Cr}	Φ_{NCS}	Φ_{CrO_4}	Remarks
2 NH_3	436	0.18	0.19		
	254	0.29	0.44	0.009	
	254		0.60	0.003	deaerated
	254		0.42	0.004	K^+ salt in H_2O
2 aniline	254	0.16	0.17	<0.001	
2 n-propylamine	254	0.30	0.52	0.009	
2 morpholine	254		0.40	0.006	
en	254	0.31	0.46	0.006	
tn	254		0.48	0.005	

the irradiated solution that was exposed to air contained 0.59×10^{-5} M chromate(VI).

These experiments confirmed that Cr(II) is indeed oxidised to chromate(VI) in air saturated methanolic solutions. Its yield is approximately 10%. The formation of free NCS^- is slightly higher than is accounted for by the dissociation of all four NCS^- ligands of the reduced Reineckate ion (2.6×10 M^{-4}). The excess NCS^- in the deaerated solutions might be attributed to Cr(II) catalysed solvolysis of $[Cr(NH_3)_2(NCS)_4]^-$.

Photochemical quantum yields were determined by the following methods:

(i) the chromium content in solution after precipitating the unphotolysed complex (Φ_{Cr});

(ii) the liberated thiocyanate determined with Fe^{3+} (Φ_{NCS});

(iii) chromate(VI) by its colour reaction with diphenylcarbazide (Φ_{CrO_4}).

Table 2 presents the results obtained with irradiation times between 2 and 8 min. It shows that:

(i) the photochemical quantum yields were higher and the ratio of Φ_{NCS}/Φ_{Cr} was larger on charge transfer excitation than on ligand field excitation;

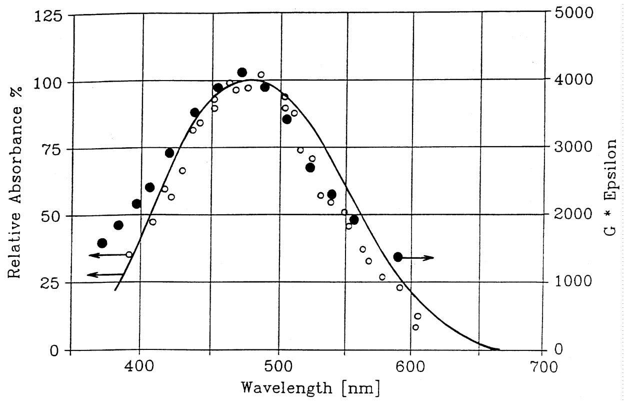


Fig. 3. Spectrum of the $(NCS)_2^{\bullet-}$ radical recorded by: flash photolysis of 5×10^{-5} to 2×10^{-4} M $(Bu_4N)[Cr(NH_3)_2(NCS)_4]$ in methanol (continuous line, average of 7 experimental spectra); pulse radiolysis of 1.0×10^{-4} M aqueous solution of $K[Cr(NH_3)_2(NCS)_4]$, N_2O saturated (black circles); flash photolysis of aqueous 1×10^{-4} M KNCS reported by Dogliotti and Hayon [42] (open circles).

(ii) in deaerated solutions a further increase of Φ_{NCS} was observed;

(iii) the organo Reineckates behaved similarly to the parent compound;

(iv) the anilino Reineckate did not exhibit any redox photochemistry. In this case the quantum yield for NCS release was the same as that for the disappearance of the starting material.

The charge transfer state probably involves the oxidation of the aniline ligand from which the energy is transferred into the ligand field system.

The reaction mechanism (Eqs. (1)–(5)) postulates the formation of $^{\bullet}NCS$ radicals which react in a diffusion controlled reaction with NCS^- ions to the relatively long lived $(NCS)_2^{\bullet-}$ radicals. The transient differential absorption spectra obtained both by flash photolysis and pulse radiolysis were compatible with each other and showed one band in the visible region with a maximum at about 480 nm. This wavelength was reported for the absorption of the $(NCS)_2^{\bullet-}$ radical [41–48] (Fig. 3). The radical life time, being of the order of hundreds of μs, was increased in the absence of oxygen or in the presence of excess NCS^- and influenced by the nature of the amine ligand or solvent (Table 3). The initial radical concentrations were determined on the basis of a molar absorbance of 7600 M^{-1} cm^{-1} [44]. The permanent decrease in CT absorption at 380 nm after the flash was used to estimate the number of absorbed quanta. Assuming that the photochemical reaction products do not absorb at 308 nm, the decrease in absorbance gives a lower limit for the disap-

Table 3
Efficiency of the $(NCS)_2^{\bullet-}$ radical formation in the flash photolysis of 5×10^{-5} to 1×10^{-4} M $n\text{-}Bu_4N[Cr(amine)(NCS)_4]$ in methanol, if not otherwise stated

Amine	$\Delta c_{rad}/\Delta c_{spec}$	$\tau_{1/2}$ (μs)	Remarks
2 NH_3		230	in water
2 NH_3	0.11	380	
2 NH_3	0.15	540	deaerated
tn	0.05	250	
tn	0.08	350	1.2×10^{-2} M KNCS
2 benzyl		130	
2 n-butyl		135	

pearance of the starting material Δc_{spec}. The ratio of the initial radical concentration to Δc_{spec} is included in Table 3. Δc_{spec} was also determined in the experiments with continuous irradiation at 254 nm. Quantum yields based on those values amounted to $\Phi_{\text{spec}} = 0.26$ and 0.25 for $[Cr(NH_3)_2(NCS)_4]^-$ and $[Crtn(NCS)_4]^-$ in methanol, respectively. Although white light was used in the flash experiments, absorption within the ligand field bands can be neglected on account of their low absorbance. If we assume a constant quantum yield for excitation within the long wavelength CT band, the quantum yield for the radical production Φ_{rad} can be estimated. We obtained $\Phi_{\text{rad}} = 0.03$ and 0.01 from the data of Table 2 for the diamine and tn tetrathiocyanatochromates in methanol, respectively.

Pulse radiolysis under reductive conditions showed the characteristic absorption of the hydrated electron at 720 nm. Its decay ($\tau_{1/2} \approx 1$ μs) concomitantly occurred with ground state bleaching in the LMCT region of the chromium complex. Thus we assign the underlying reaction to the reduction of the Reineckate by the hydrated electron. After the electron initiated reduction was completed (Fig. 4, curve a) the absorption time profiles displayed consecutive CT bleaching resembling the one found upon UV irradiation (Fig. 2). This slower reaction was completed within 30 μs (Fig. 4, curve b). There was no difference between the reaction run in 2-propanol and t-butanol. This rules out reduction by α-alkoxyradicals which might take place in 2-propanol. Hence, we assign this secondary change to NCS^- release from the reduced chromium complex in analogy to Eq. (1b). This reaction brings about a decrease of the NCS → Cr charge transfer absorption. Cr(II) catalysed solvolysis can be ruled out in the μs time scale.

The pulse radiolysis under oxidative conditions (i.e. N_2O saturated aqueous solutions) also produced CT bleaching but in addition a strong absorption appeared around 340 nm. This absorption disappeared within 10 μs after its formation. This transient absorption can be either assigned to an OH adduct with the Reineckate or to a coordinated $^{\bullet}NCS$ radical. Significant absorption, by a monomeric $NCS^{\bullet}$ radical or by its OH adduct, can be ruled out on account of their short life time and their low molar absorptivity [47,49].

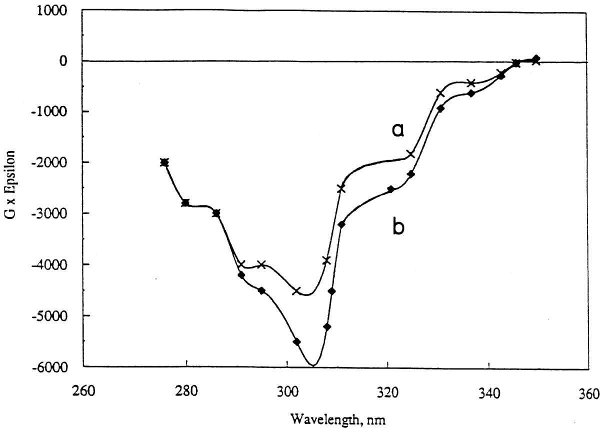


Fig. 4. Transient differential absorption spectrum obtained upon radiolysis of 1.0×10^{-4} M $K[Cr(NH_3)_2(NCS)_4]$ in a nitrogen saturated aqueous solution at pH 7, containing 5 vol.% t-butanol: (a) 1 μs, (b) 30 μs after the pulse.

Simultaneously with the disappearance of the 340 nm transient a strong absorption at 480 nm appeared (Fig. 3). Its spectral features closely resembled those observed in the flash experiments, where the formation of $(NCS)_2^{\bullet -}$ radicals has been established. We tentatively assign the absorption at 340 nm to a coordinated $NCS^{\bullet}$ radical on account of its high absorbance.

$$[Cr^{III}(NH_3)_2(NCS)_3(^{\bullet}NCS)] + 2H_2O \rightarrow (NCS)_2^{\bullet -} + [Cr^{III}(NH_3)_2(NCS)_2(H_2O)_2]^+ \quad (6)$$

The $(NCS)_2^{\bullet -}$ radical could be formed either in an inter- or intramolecular reaction, such as Eq. (6). To investigate a case where any intramolecular contribution could be ruled out, we decided to study the mono-thiocyanato complex. $[Cr(NH_3)_5(NCS)](ClO_4)_2$. Upon pulse radiolysis under similar experimental conditions no absorption was found that might be ascribed to any $(NCS)_2^{\bullet -}$ formation. This result shows that the $(NCS)_2^{\bullet -}$ radical is probably formed from Reineckates via an intramolecular process, if free NCS^- is absent. Kirk and co-workers [50,51] argued similarly with respect to the dithiocyanate radical formation in the UV photochemistry of cobalt thiocyanato complexes.

The quantum yields of the various products may be rationalised in the reaction scheme as outlined in Eqs. (1)–(5). If we assume that the intermediately formed Cr(II) species dissociates before it is reoxidised, the apparent quantum yields are:

$$\Phi_{Cr} = \varphi_1 + \varphi_2; \qquad \Phi_{NCS} = \varphi_1 + n\varphi_2, \quad 3 \leq n \leq 4 \quad (7)$$

where $n = 3$, if $(NCS)_2^{\bullet -}$ disproportionates (Eq. (5b)) and $n = 4$, if it is quantitatively reduced to $2NCS^-$ (Eq. (5a)). The experimentally determined quantum yields for $[Cr(NH_3)_2(NCS)_4]^-$ ($\Phi_{Cr} = 0.29$, $\Phi_{NCS} = 0.44$) give $\varphi_1 = 0.215$ and $\varphi_2 = 0.075$ if $n = 3$ and $\varphi_1 = 0.24$ and $\varphi_2 = 0.05$ if $n = 4$. Since n is unknown, we assume that the true values are in between the extremes and write: $\varphi_1 = 0.23 \pm 0.05$, $\varphi_2 = 0.06 \pm 0.02$. In this scheme the quantum yield for radical formation should be equal to φ_2. The experimental value of $\Phi_{\text{rad}} = 0.03$ is not too far off this estimate. Since on air oxidation approximately 10% of the Cr(II) is oxidised to CrO_4^{2-}, the quantum yield of 0.009 for chromate formation should correspond to $\Phi_{Cr(II)} = \varphi_2 = 0.09$ in reasonable agreement with the postulated mechanism. In the case of the anilino Reineckate, which did not produce radicals on CT excitation, reaction (1b) is inefficient ($\varphi_2 = 0$). Then Φ_{Cr} should be equal to Φ_{NCS} as was observed.

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