BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1602—1609 (1973)

Excited States and Intermediates in the Photochemistry of Chromium(III) Complexes Studied by Flash Method

Takeshi OHNO and Shunji KATO

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

(Received September 19, 1972)

Photoreactions of $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ were investigated by means of a flash technique. At low temperature (−87 °C), the lowest excited doublet states (^2E_g) of the complexes were easily observed on d–d excitation in acetone, the yields decreasing rapidly with rising temperature. In methanol–ethyleneglycol–water, ^2E_g states of both complexes were easily observed at dry-ice temperature, but not at −46 °C. Thus, the lowest excited quartet state ($^4T_{2g}$), the precursor of ^2E_g state, should rapidly undergo photolysis at room temperature before being converted into the ^2E_g state. The rate of thermal degradation of $^4T_{2g}$ state including chemical reactions was calculated to be *ca.* $10^{10}\ s^{-1}$ at room temperature. The decay rate of ^2E_g state was estimated to be *ca.* $10^5\ s^{-1}$ at room temperature. In the presence of organic compounds having carbonyl group, a strong and sharp absorption band near the UV region was observed at room temperature. Irradiation of UV light produced $(NCS)_2^-$ radical for both complexes.

It is well-known that ligands in some chromium(III) complexes in solution are replaced by solvent molecules on photo-excitation.[1] In such a reaction, it is important to make certain which excited state of the complex ion is reactive. It is possible to estimate the reactivities of the excited states from their electronic configurations. Chromium-ligand bonds might be elongated in the excited quartet states with an electronic configuration of $(t_2)^2(e)$ in view of a strong field approximation. However, the bond length in the excited doublet state with the configuration $(t_2)^2(\bar{t}_2)$, may be similar to that in the ground state. In principle, the broad absorption band and the large separation between the 0–0 bands of the absorption and emission spectra show a deformation of structure in the excited state. Thus, it is inferred that the excited quartet states differ to a great extent from the ground state in conformation, but not the excited doublet state. It is reasonable that the larger the deformation of the excited state, the easier for a solvent molecule to make a new bond with the central metal ion of the complex. On the other hand, ^2E_g with a long natural lifetime ($10^{-1}\sim10^{-3}$ s) will be more favorable for reaction than the short living $^4T_{2g}$ ($10^{-9}\sim10^{-10}$ s).[2,3]

Many reports have appeared dealing with reaction states. Some of them support the view that the doublet state takes part in the reaction. The quantum yields of the photochemical reactions of chromium (III) complexes such as $[Cr^{III}(NH_3)_6]^{3+}$, $[Cr^{III}(NCS)_4(NH_3)_2]^-$, $[Cr^{III}(urea)_6]^{3+}$, and $[Cr^{III}(NCS)_6]^{3-}$ are known to be independent of the excitation wavelength.[4-6] This suggests that the lowest excited states are the reacting species.

---

[1] A. W. Adamson, W. L. Waltz, E. Zinato, D. W. Watts, P. D. Fleischauer, and R. D. Lindholm, *Chem. Rev.*, **68**, 542 (1968).

[2] K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).

[3] H. L. Schläfer, H. Gausmann, and H. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967).

[4] M. R. Edelson and R. A. Plane, *J. Phys. Chem.*, **63**, 327 (1959).

[5] M. R. Edelson and R. A. Plane, *Inorg. Chem.*, **3**, 231 (1964).

[6] E. E. Weger and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).

Plane[5] and Schläfer[7] supposed that the reacting species was the lowest excited doublet state (^2E_g). This inference seemed to be supported by the fact that the yield of the phosphorescence (0.23) at low temperature[2] was close to that of the aquation reaction (0.28) at room temperature for $K_3[Cr^{III}(NCS)_6]$.

Some others support the view that the quartet states are also reactive. In the case of *cis*-$[Cr^{III}(en)_2(OH)_2]^+$, the quantum yield ratio of *cis-trans* isomerization to aquation was dependent on the excitation wavelength (the ratio was 1.5 on excitation to the first excited quartet state $^4T_{2g}$, and 2.8 to the second excited quartet state $^4T_{1g}$, and 9.6 to ^2E_g at 25 °C[8]). In the case of $[Cr^{III}(NCS)(NH_3)_5]^{2+}$, the quantum yield on direct excitation to ^2E_g is not larger than that to $^4T_{2g}$ and $^4T_{1g}$ states.[9] Chen and Porter[10] and Longford *et al.*[11] proposed the participation of $^4T_{2g}$ state as well as ^2E_g state in the photoreactions of Chromium(III) complexes. They stated that photolysis was less effectively quenched by iodide, hydroxyl and $[Cr^{III}(CN)_6]^{3-}$ than phosphorescence was.

The reacting states in the photolysis of chromium complexes remains still unclarified. We tried to solve the problem by means of the technique of flash photolysis. Phosphorescent states (^2E_g) of some chromium complexes such as $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ were observed by the flash method in a rigid solvent (EPA) at −196 °C.[12] Transient intermediates such ^2E_g state were investigated in a wide temperature range for the purpose of clarifying the mechanism of the photochemical reactions.

Experimental

Apparatus and Procedure. Flash experiments at low temperature were carried out with a flash apparatus.[12] A quartz cell was placed in a Dewar filled with methanol which was cooled with dry ice or liquid nitrogen. Temperature was measured with a copper-constantan thermojunction inserted in the sample solution.

For flash experiments at room temperature, the following flash apparatus was used. Two lamps were placed 5 cm apart in parallel. The sample cell was made of a glass tube, 100 mm long and 10 mm in inner diameter with silica windows at the end. It was located between the two lamps.

Some glass filters (Toshiba) and solution filters were set between the sample cell and the flash lamps. Their transmittances are shown in Fig. 1.

The outputs of a photomultiplier, 1P–28 (Hamamatsu TV.) were recorded with a Hitachi synchroscope V–116. Transient absorption spectra were composed from the oscillographic data of the absorption change observed at various wave numbers. The absorption change in near IR rigion was photographed on Sakura infra-red film. Number of photons absorbed by a chromium complex was measured with a Reineck salt actinometer.[6]

Materials. $K_3[Cr^{III}(NCS)_6]4H_2O$, $NH_4[Cr^{III}(NCS)_4(NH_3)_2]3/2H_2O$, and $[Co^{III}(NCS)(NH_3)_5]SO_4\cdot 2H_2O$, were prepared by the methods reported by Dakin,[13] Roesler,[14] and Werner,[15] respectively.

Potassium iodide was recrystallized three times from water. Ferric nitrate of G. R. grade was used without further purification. Acrylamide of high purity was supplied by Prof. H. Takemura of Nara Women's University. Ethanol was refluxed with silver nitrate, dried over calcium oxide and distilled. Other solvents (G. R. grade) such as methanol, ethyleneglycol, ethylacetate, dimethylformamide, acetophenone, and acetonitril were used without further purification.

Results

General Aspects. The absorption spectrum of $K_3[Cr^{III}(NCS)_6]$ in acetone at room temperature is shown in Fig. 1. Two weak absorption bands in visible region have been assigned to d–d transitions ($^4A_{2g} \rightarrow {}^4T_{2g}$: 17.8 kK, $^4A_{2g} \rightarrow {}^4T_{1g}$: 24.2 kK) and a strong absorption in near UV region to ligand excitation.[16]

When a 2.0×10^{-3} M acetone solution of $K_3[Cr^{III}(NCS)_6]$ was flashed with visible light (filter–24) below −30 °C, the transient spectrum observed agreed with that in EPA solution at −196 °C (Fig. 2). Hence, it is safe to regard it as the ^2E_g state of $K_3[Cr^{III}(NCS)_6]$. With temperature rise, the production of ^2E_g became smaller and could not be detected at 0 °C. A sharp band appeared near the UV region (28.2 kK) above −30 °C. At room temperature, only this band was prominent. The intermediate showing it is denoted by "X".

A flashing on the acetone solution with no filter

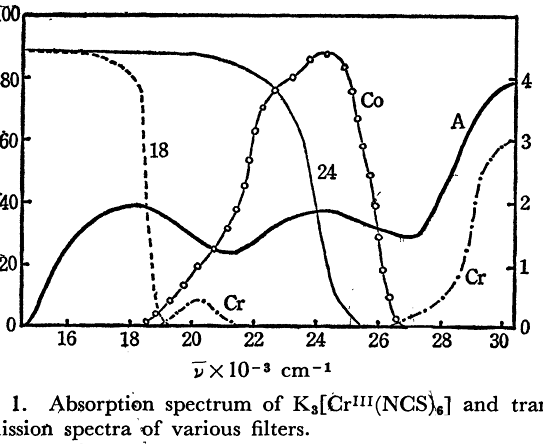

Fig. 1. Absorption spectrum of $K_3[Cr^{III}(NCS)_6]$ and transmission spectra of various filters.
A: $K_3[Cr^{III}(NCS)_6]$ in acetone,
Cr: solution filter of chromium alum aqueous solution,
Co: solution filter of $K_2[Co^{II}(NCS)_4]$ tertiarybutylalcohol solution,
18: glass filter, Toshiba V-O52,
24: glass filter, Toshiba V-Y42.

---

[7] H. J. Schläfer, *Z. Physik. Chem.* (Frankfurt), **11**, 65 (1957).

[8] A. W. Adamson, "Mechanisms of Inorganic Reactions", Advances in Chemistry Series, No 49, American Chemical Society, Washington, D. C., 1965.

[9] R. D. Lindholm, E. Zinato, and A. W. Adamson, *J. Phys. Chem.*, **71**, 3713 (1967).

[10] S. Chen and G. B. Porter, *Chem. Phys. Lett.*, **6**, 41 (1970).

[11] C. H. Langford and L. Tipping, *Can. J. Chem.*, **50**, 887 (1972). N. A. P. Kane-Maguire and C. H. Longford, *J. Amer. Chem. Soc.*, **94**, 2125 (1972).

[12] T. Ohno and S. Kato, This Bulletin, **43**, 8 (1970),

[13] H. D. Dakin, "Organic Syntheses" Vol. 15, p. 74 (1935).

[14] J. Roesler, *Ann.* **141**, 185 (1867).

[15] A. Werner and A. Muller, *Z. Anorg. Chem.*, **22**, 102 (1900).

[16] C. K. Jørgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, Ltd., London (1962), p. 116.

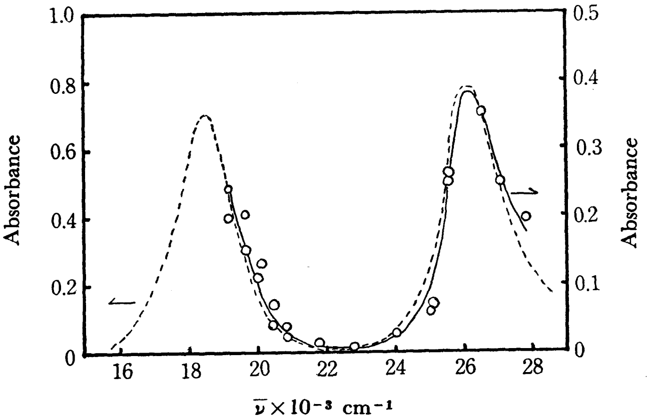

Fig. 2. Transient absorption spectra for $K_3[Cr^{III}(NCS)_6]$ 30 μs after flashing at low temperature.
-O-: 2×10^{-3} M acetone solution of $K_3[Cr^{III}(NCS)_6]$ at −61±5 °C, 200J flash with filter-18,
……: 10^{-3} M EPA solution of $K_3[Cr^{III}(NCS)_6]$ at −196 °C, 100J flash with filter-24.

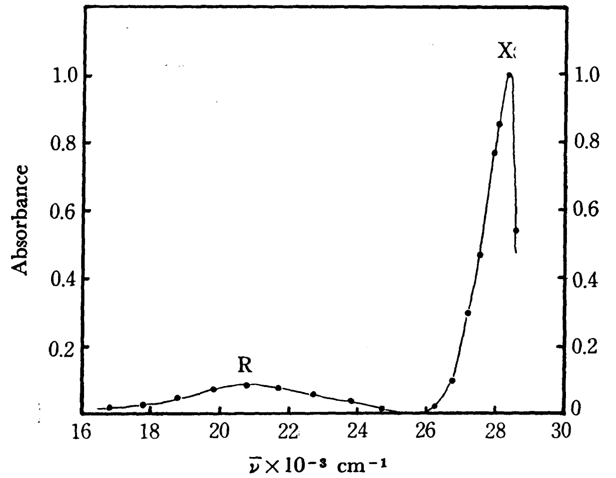

Fig. 3. Transient absorption spectrum when a 10^{-3} M acetone solution of $K_3[Cr^{III}(NCS)_6]$ in a glass cell with 200J flash at room temperature.

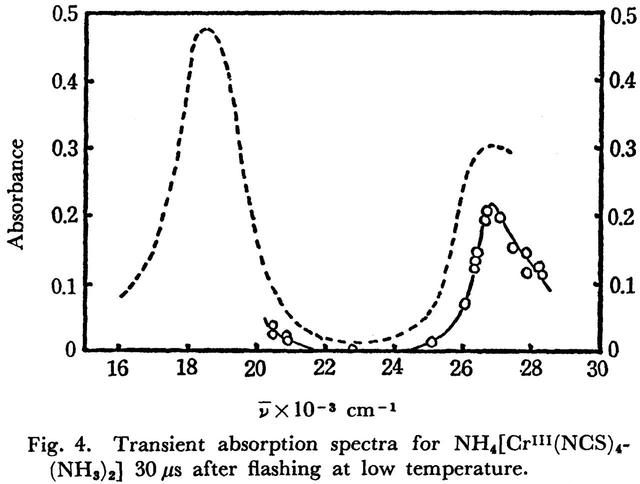

Fig. 4. Transient absorption spectra for $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ 30 μs after flashing at low temperature.
-O-: 5×10^{-3} M acetone solution of the complex at −61±5 °C, 200J flash with filter-18,
……: 10^{-3} M of the complex in polymethylmethacrylate at −196 °C 100J flash with filter-24.

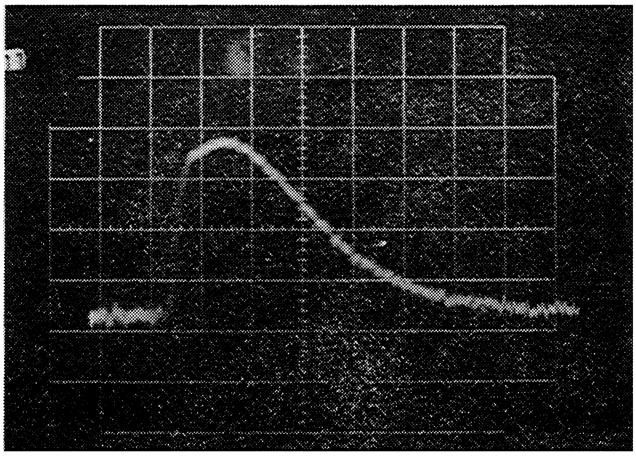

Fig. 5. A typical oscilogram of a transient absorption, observed at 26.3 kK, when a 10^{-3} M acetone solution of $K_3[Cr^{III}(NCS)_6]$ was flashed with filter-24 at −78°C. One large division is 10 μs.

produced transiently a broad band in addition to the sharp band of X at room temperature (Fig. 3). The broad absorption spectrum in visible region is due to a third intermediate denoted by "R". R vanished several milliseconds after flashing, while X survived a few seconds after the disappearance of R.

A single flash with filter-24 on $K_3[Cr^{III}(NCS)_6]$ at room temperature produced 4×10^{-5} M of free thiocyanate ion which was analyzed as ferric thiocyanate.

As in the case of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, three intermediates were detected depending on experimental conditions. As shown in Fig. 4, a transient absorption observed at −61±5 °C can be assigned to ^2E_g state referring to the absorption spectrum of ^2E_g state at −196 °C in polymethylmethacrylate. With rise in temperature the yield of ^2E_g state decreased, R and X becoming observable. The absorption maximum and the decay rate of X for $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ were similar to those of X for $K_3[Cr^{III}(NCS)_6]$.

In the case of other solvents, the behaviors of three

TABLE 1. RELATION BETWEEN INTERMEDIATES AND EXCITATION CONDITIONS IN ACETONE

Complexes	Excited states directly produced	Temp. °C	Intermediates
$K_3[Cr^{III}(NCS)_6]$	LE[a], $^4T_{1g}$, $^4T_{2g}$	25	X, R
	LE	25	R
	$^4T_{1g}$, $^4T_{2g}$	25	X
	$^4T_{1g}$	25	X
	$^4T_{2g}$	25	X
	$^4T_{1g}$, $^4T_{2g}$	−87	^2E_g
	$^4T_{1g}$, $^4T_{2g}$	−196[b]	^2E_g
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	LE, $^4T_{1g}$, $^4T_{2g}$	25	X, R
	$^4T_{1g}$, $^4T_{2g}$	25	X
	$^4T_{1g}$, $^4T_{2g}$	−87	^2E_g
	$^4T_{1g}$, $^4T_{2g}$	−196[c]	^2E_g

a) LE denotes an excited state localized in ligand.
b) The solvent used was EPA.[12]
c) Methylmethacrylate dissolving the chromium complex was polymerized.

intermediates were very similar to those in acetone except that X was not observed in methanol, ethanol, and water.

Observed intermediates under various experimental conditions are listed in Table 1. The excitation in d–d band (to $^4T_{2g}$ and $^4T_{1g}$) produces ^2E_g state below -10 °C and X above -30 °C, the excitation in the ligand band (UV) produces R in acetone.

^2E_g State. When a 10^{-3}M acetone solution of $K_3[Cr^{III}(NCS)_6]$ was flashed at -78 °C, absorbance of the ^2E_g state reached maximum at 10 μs and then decreased rapidly (Fig. 5).

The decay was of first order and the rate constant did not vary in the range from -87 °C to -10 °C. Hence the initial absorbances due to ^2E_g produced by flashing were obtained in high accuracy by analysis of the decay curves. The absorbance was 3.0 at 27 kK for a 1.0×10^{-3} M acetone solution of $K_3[Cr^{III}(NCS)_6]$ at -78 °C, and decreased to 0.66 at -46 °C. In order to avoid experimental errors due to smaller absorbance at higher temperature, more concentrated acetone solution (4.0×10^{-3} M) of $K_3[Cr^{III}(NCS)_6]$ was examined above -54 °C. The values 2.0 at -46 °C and 0.23 at -9 °C were obtained as the initial absorbances of ^2E_g. At 0 °C, production of the ^2E_g state could not be detected even during the course of flash illumination with more concentrated solutions. The effect of temperature upon production is shown in Fig. 6.

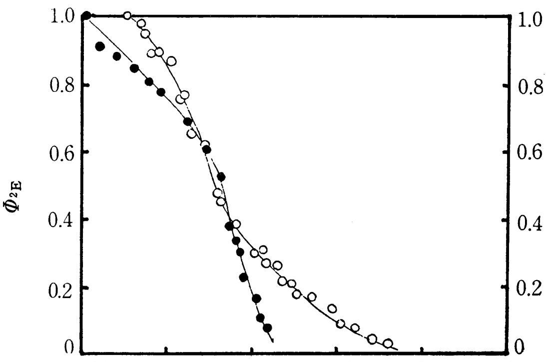

Fig. 6. Effects of temperature upon the yields of ^2E_g state of $K_3[Cr^{III}(NCS)_6]$, when flashed with filter-24.
○: 1—4×10^{-3} M in acetone,
●: 1—4×10^{-3} M in the mixed solvent.

The ordinate gives the quantum yield calculated on the conventional assumption that yield is unity -87 °C. Thus, the calculated yields are the largest possible values.

In the case of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ in acetone, similar behaviors were observed. The lifetime was constant from -87 °C to -18 °C, making the measurement of the relative yield accurate. The quantum yields are calculated also on the assumption that yield is unity at -87 °C. The temperature dependence of the quantum yield is shown in Fig. 7.

In the cases of ethanol and ethanol–ethyleneglycol (1 : 1) solutions of $K_3[Cr^{III}(NCS)_6]$, temperature dependence of the yield of the ^2E_g state was similar to that in acetone solution. Absorbance could still be detected at -30°C for 5.0×10^{-3} M ethanol–ethyl-

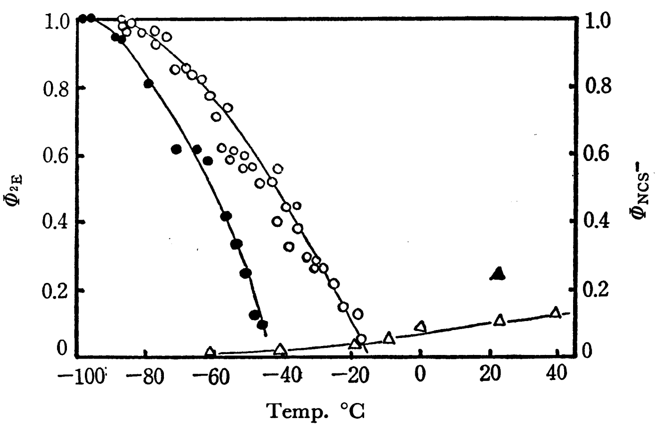

Fig. 7. Effects of temperature upon the yields of ^2E_g state and chemical reactions of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, when flashed with filter-24.
○: the yield of ^2E_g in acetone,
△: the yield for free SCN^- in acetone,
●: the yield of ^2E_g in methanol-ethyleneglycol-water,
▲: the yield for free SCN^- in methanol-ethyleneglycol-water.

TABLE 2. PRODUCTION AND LIFETIME OF ^2E_g STATE UNDER VARIOUS CONDITIONS

Complex	Concentration M	Temperature °C	Solvent	Absorption 10 μs after flashing	Lifetime μs
$K_3[Cr^{III}(NCS)_6]$	1×10^{-3}	−87	acetone	3.1	20
	1×10^{-3}	−60	acetone	1.0	20
	4×10^{-3}	−54	acetone	2.5	20
	4×10^{-3}	−9	acetone	0.23	20
	1×10^{-3}	−100	mixed[a)]	1.9	2500
	4×10^{-3}	−56	mixed	1.3	21
	1×10^{-3}	−196	EPA	—	10000
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	2×10^{-3}	−87	acetone	2.8	20
	5×10^{-3}	−18	acetone	0.49	20
	1×10^{-3}	−100	mixed[a)]	2.2	300
	4×10^{-3}	−62	mixed	1.1	19
	1×10^{-3}	−196	polymer	—	310

a) The "mixed" indicates a mixture of methanol, ethyleneglycol, and water (2 : 2 : 3).

eneglycol (1 : 1) solution of $K_3[Cr^{III}(NCS)_6]$.

For methanol–ethyleneglycol–water solutions (2 : 2 : 3) of $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, transient absorption was easily observed at −100 °C. However, it weakened rapidly with temperature rise, and could not be observed at all above −45 °C. Changes of yields with temperature are shown in Figs. 6 and 7. The accuracy is less satisfactory than in the case of the acetone solution, as the lifetime of the ^2E_g state greatly changes in the range from −100 °C to −50 °C. The absorbances in various conditions are shown in Table 2.

The quantum yield Φ_E is formulated as follows.

$$\Phi_E = \frac{k_i}{k_i + k_d} \tag{1}$$

where k_i and k_d are rate constants of intersystem crossing and thermal deactivation of $^4T_{2g}$ state (precursor of ^2E_g state), respectively. Eq. (1) is rewritten as follows.

$$\ln\left(\frac{1}{\Phi_E} - 1\right) = \ln\frac{k_d}{k_i} \tag{2}$$

$$= \ln\frac{A_d}{A_i} - \frac{E_d - E_i}{RT} \tag{3}$$

where suffixes d and i denote the thermal deactivation process and the intersystem crossing process, respectively, A and E the frequency factor and the activation energy, respectively. When the temperature dependence of quantum yield (Fig. 6) is analyzed by means of Eq. (3), a linear relation with a break at −62 °C is obtained for both complexes in methanol–ethyleneglycol–water (Fig. 8).

The decay processes are of first order with respect to the concentration of the ^2E_g state, and the rate constants are the same for all complexes examined, $5.0 \times 10^{-4}\ s^{-1}$ in acetone, independent of temperature and concentration (Fig. 9). On the other hand, in methanol–ethyleneglycol–water solvent, the decay rates are dependent on temperature as shown in Table 2 and Fig. 10. The apparent activation energy of the deactivation process of the ^2E_g state was obtained to be 11 kcal/mol in a temperature region higher than −70 °C for both complexes.

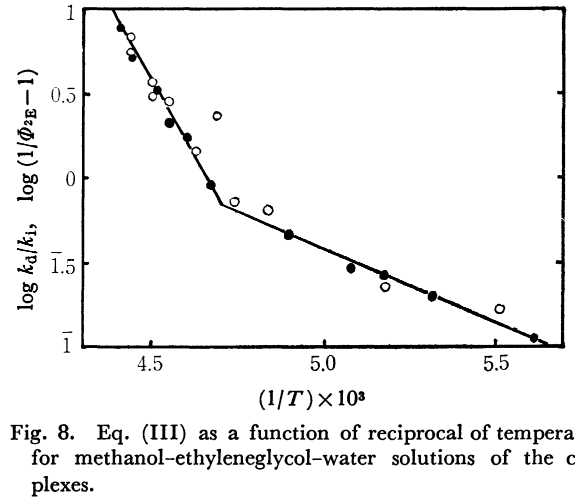

Fig. 8. Eq. (III) as a function of reciprocal of temperature for methanol-ethyleneglycol-water solutions of the complexes.
○: 1–4×10⁻³ M of $K_3[Cr^{III}(NCS)_6]$,
●: 2–5×10⁻³ M of $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$.

Intermediate X. Intermediate X observed in acetone solutions of $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ on d–d excitation at room temperature, has a sharp absorption band near the UV region. Similar spectra were observed in ethylacetate, dimethylformamide, acetophenone and polymethylmethacrylate, but not in ethanol, methanol, aceto-

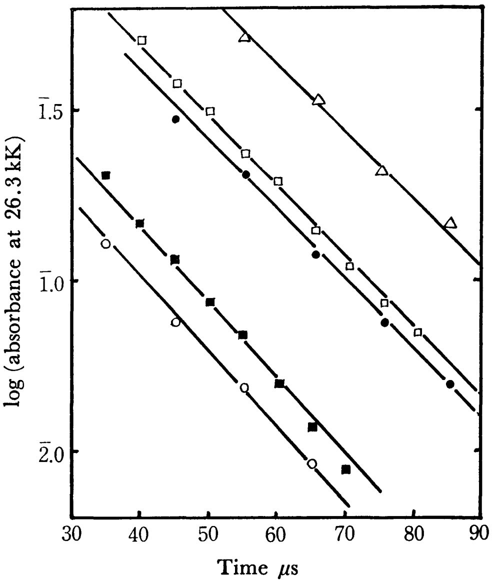

Fig. 9. First order decay of ^2E_g state formed by flashing $K_3[Cr^{III}(NCS)_6]$ in acetone.
△: 4×10⁻³ M at −59 °C,
●: 4×10⁻³ M at −32 °C,
○: 4×10⁻³ M at −14 °C,
□: 1×10⁻³ M at −69 °C,
■: 1×10⁻³ M at −46 °C.

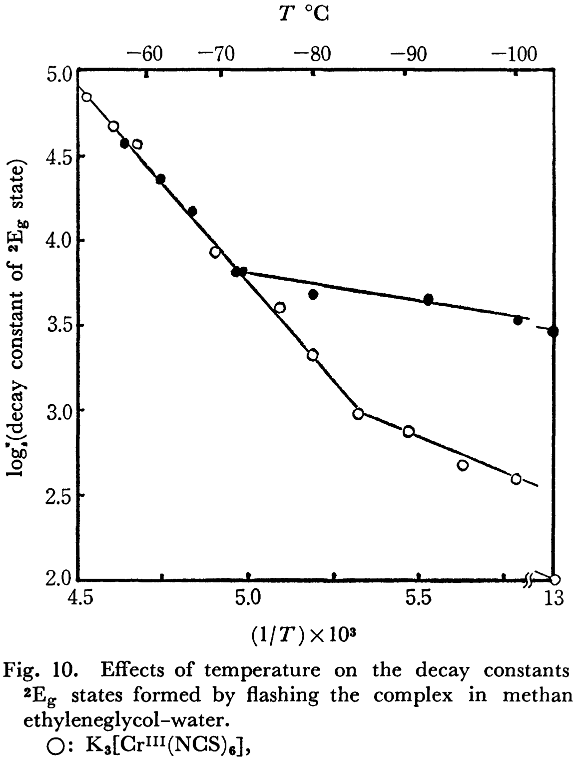

Fig. 10. Effects of temperature on the decay constants of ^2E_g states formed by flashing the complex in methanol-ethyleneglycol-water.
○: $K_3[Cr^{III}(NCS)_6]$,
●: $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$.

Table 3. Behavior of intermediate X at room temperature

Complex	Solvent	Abs. max. kK	Decay constant s^{-1}
$K_3[Cr^{III}(NCS)_6]$	acetone	28.2	0.24
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	acetone	28.6	0.06
$K_3[Cr^{III}(NCS)_6]$	DMF[a]	26.6	8.6×10^4
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	DMF[a]	26.8	7.8×10^4
$K_3[Cr^{III}(NCS)_6]$	polymer[b]	27.2	0.2
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	polymer[b]	27.4	0.2

a) DMF: dimethylformamide.
b) Methylmethacrylate dissolving the chromium complex was polymerized.

Table 4. Production and rate constant of decay process of intermediate X at room temperature

Solvent		Production	Decay constant s^{-1}
Acetone %	Ethanol %		
100	0	0.600	0.25
97.5	2.5	0.511	1.3
95.0	5.0	0.450	2.1
90.0	10.0	0.447	2.9
85.0	15.0	0.477	3.4
10.0	90.0	0.170	8.1
0	100	0	—

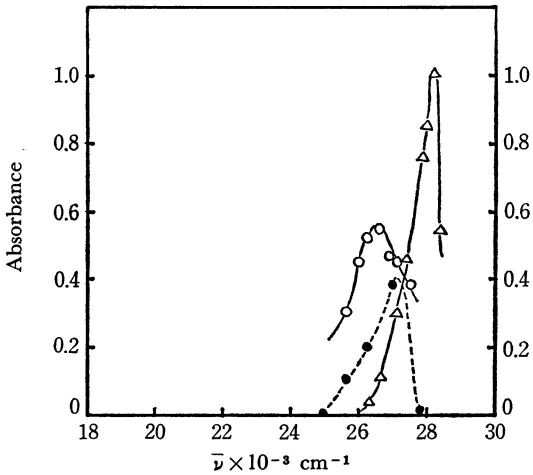

Fig. 11. Transient absorption spectra of various X-intermediates produced by flashing various solutions of $K_3[Cr^{III}(NCS)_6]$ at room temperature.
△: 1×10^{-3} M in acetone,
●: 1×10^{-3} M in polymethylmethacrylate,
○: 4×10^{-3} M in dimethylformamide.

nitril, and water on d-d excitation. It is worth noticing that all solvents in which the intermediate appeared have a carbonyl group, and that the wave number of the absorption maxima does not depend upon the species of the complex but upon the solvent as shown in Table 3 and Fig. 11.

Decay of the intermediate, regarded as of first order process, also depends on the solvent (Table 3). It is very slow except the case of dimethylformamide. Characteristics such as yields, absorption maxima and decay constants differ with solvent. Thus, X is assumed to be a reaction product between solvent and photoproduct of the complex. For the sake of confirmation the behavior of X was studied in mixed solvents of acetone and ethanol (Table 4). Its production and lifetime gradually decrease with increasing fraction of ethanol, but is observable even in 90% ethanol solution.

Intermediate R. When 1.0×10^{-3} M acetone solution of $K_3[Cr^{III}(NCS)_6]$ was irradiated with UV light, a transient species intermediate R with absorption maximum at 21.5 kK was observed. This was also produced from both complexes in other solvents such as ethanol, methanol, and water. A single flash irradiation through UV filter made an absorbance of 0.15 at absorption maximum, and finally gave 180 μM of free thiocyanate ion. The absorption spectrum due to R was also observed in aqueous solution of $[Co^{III}(NCS)(NH_3)_5]SO_4$ on irradiation of full light. Cobalt(III) was reduced to cobalt(II) during the course of photodecomposition of the complex. It is reasonable that NCS^- coordinating to cobalt is oxidized to thiocyanate radical, accompanied by the reduction of cobalt(III), since thiocyanate ion has the highest reducing potential in the system.

To clarify the character of R, potassium iodide or acrylamide was added as a radical scavenger. Decay of R in all the cases examined was of first order process with respect to R. Addition of the scavenger to an aqueous solution of $K_3[Cr^{III}(NCS)_6]$, reduced the lifetime under aerobic conditions. The decay constant observed (k_{obs}) is given by

$$k_{obs} = k_o + k_S[S] \qquad (4)$$

where k_o denotes the decay constant in the absence of scavenger and k_S the second order rate constant of the reaction between R and a scavenger, and [S] the concentration of the scavenger. From the dependence of decay constants on the concentration of scavenger (Fig. 12), the value of k_S are evaluated as shown in Table 5.

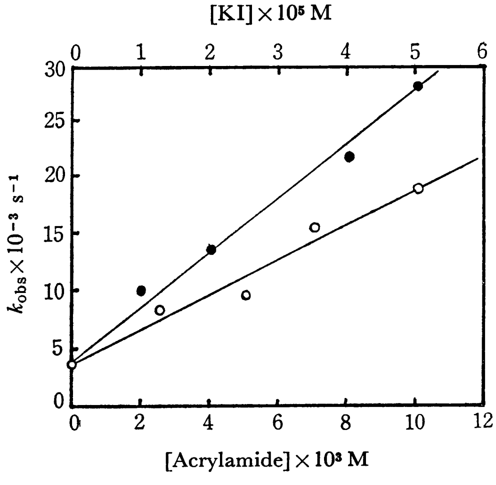

Fig. 12. Relationships between decay constants of R-intermediate and the concentration of potassium iodide and acrylamide added.
○: acrylamide (the bottom scale),
●: potassium iodide (the upper scale).

TABLE 5. REACTION RATE CONSTANTS k_0 AND k_S OF $(NCS)_2^-$ AT ROOM TEMPERATURE

	k_0 s^{-1}		k_S M^{-1} s^{-1}
$K_3[Cr^{III}(NCS)_6]$	2.8×10^3	KI	5.0×10^8
$[Co^{III}(NCS)(NH_3)_5]SO_4$	2.3×10^3	Acrylamide	1.6×10^6

Discussion

Changes of the quantum yields and the lifetimes of ^2E_g states from -100 °C to -10 °C give information on the behaviors of both $^4T_{2g}$ and ^2E_g states. The values of the quantum yields of the ^2E_g state (Table 6) were calculated on the assumption that the quantum yields were unity at -87 °C in acetone and -100 °C in the methanol–etyleneglycol–water. They fall less than 0.1 at -25 °C. The quantum yield at room temperature was extrapolated to be the order of 10^{-3}. However, the quantum yields of decomposition of the complexes are 0.12—0.34 at room temperature. It is worth noticing that they are much higher than the extrapolated yields at room temperature. The quantum yield of decomposition increased but the yields of ^2E_g state decreased with rising temperature (Fig. 7). Thus, it is concluded that the decomposition of the complexes in the $^4T_{2g}$ state competes with the intersystem crossing to the ^2E_g state and that $^4T_{2g}$ decomposes rapidly before being converted into ^2E_g state at room temperature.

The low quantum yield (<0.1) at -25 °C, means that the rate constant of the thermal deactivation (k_d) of $^4T_{2g}$ is at least ten times as large as that of the intersystem crossing (k_i) according to Eq. (1). Because of the fall of Φ_E with temperature, k_d may be much larger at room temperature. The rate constant of the fluorescence process (k_f, the reciprocal of the natural lifetime) is calculated to be about 10^5 s^{-1} using Einstein's equation of spontaneous transition probability.[17] For all complexes examined, no fluorescence has been detected even at -196 °C. Therefore, k_i may be 10^4 times as large as k_f on the ground that fluorometers can detect fluorescence with a quantum yield of 10^{-4}. Accordingly, k_d is estimated to be larger than 10^{10} s^{-1} at room temperature.

On the other hand, the rate constant of phosphorescence process (the reciprocal of natural lifetime) is obtained to be $10\sim10^3$ s^{-1} by Einstein's equation. The observed lifetime of ^2E_g state indicated that the rate constant of thermal deactivation for both complexes was 5.0×10^4 s^{-1} at -9 °C—-87 °C in acetone and at about -50 °C in the mixed solvent. It is surprising that the change of lifetime with temperature was largely dependent on the solvents and not on the complexes. It is inferred that a strong interaction of the fluid solvent with ^2E_g probably causes its degradation to the ground state or $^4A_{2g}$.

Comparing the rate constants (10^{10} s^{-1}) of the thermal deactivation of the $^4T_{2g}$ and ^2E_g states (10^5 s^{-1}, it is concluded that the former is influenced by solvent molecules more strongly. It should be pointed out that the temperature dependence of Φ_E does not change with the species of the complexes but with solvent. This shows that the deactivation processes of the $^4T_{2g}$ state consist in the interaction of the solvent molecules, which lead to chemical change in part. It is plausible that long metal-ligand bonds in the $^4T_{2g}$ state induce the interaction of the central metal with solvent which results in bimolecular reaction. A bimolecular reaction is also suggested by the fact that $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ was almost non-reactive at -70 °C (Fig. 7). If a hexa-coordinated complex is dissociated in its excited state and decomposes monomolecularly on irradiation, the yield of photochemical reaction will be independent of temperature. $Cr^0(CO)_6$ is such a case, decomposing photochemically to five coordinated complex with high efficiency even at -196 °C.[18]

TABLE 6. QUANTUM YIELDS OF THE DECOMPOSITION OF COMPLEXES AND ^2E_g STATE FORMATION

Complex	Solvent	Decomposition	^2E_g formation
$K_3[Cr^{III}(NCS)_6]$	acetone	0.12(23°C)	0.03 (−9°C)
	mixed		0.07(−45°C)
	water	0.26(23°C)[a]	
$NH_4[Cr^{III}(NCS)_4(NH_3)_2]$	acetone	0.13(41°C)	0.10(−18°C)
	mixed	0.25(23°C)[b]	0.10(−46°C)
	water	0.34(40°C)[a]	

a) E. E. Wegner and A. W. Adamson, *J. Amer. Chem. Soc.*, **88**, 394 (1966).
b) A. W. Adamson, *J. Phys. Chem.*, **71**, 798 (1967).

It is difficult to say whether the second excited state, $^4T_{1g}$, reacts in its lifetime or not. It is generally believed that the second excited states of aromatic molecules have too short a lifetime (10^{-12} s) to react or fluoresce with a few exception.[19] The situation is assumed to be the same for the $^4T_{1g}$ state of chromium complexes, though, if predissociative, it will decompose in one vibration. From this point of view, one can not deny the view that the chemical reaction would take place during the course of lifetime.

The complexes decomposed at higher temperature. Intermediate X appeared in solvents having carbonyl group such as acetone, but not in ethanol, methanol, acetonitrile, and water. If X were produced in the monomolecular decomposition of the complexes also in ethanol and water but not detected because of the rapid quenching of the solvents, a small amount of ethanol would effectively shorten the lifetime of X. Actually, however, X has a long lifetime of 0.12 s even in 90% ethanol solution. It is not reasonable to consider that X decays too rapidly to be detected in pure ethanol when it has a long lifetime of 0.12 s in 90% ethanol solution. When acetone was added to ethanol by 10%, appreciable amount of X was produced.

---

[17] J. G. Calvert and J. M. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York (1967), p. 173.

[18] W. Strohmeier and K. Gerlach, *Chem. Ber.*, **94**, 398 (1961).

[19] M. Beerand and H. C. Longuet-Higgins, *J. Chem. Phys.*, **23**, 1390 (1955).

It is thus concluded that acetone is required as a reactant to produce X. Data were not sufficient to identify X, but we might guess that the species produced by a reaction between acetone and the complexes on irradiation, is probably either $[Cr^{III}(NCS)_5(CH_3)_2CO]^{2-}$ or $(NCS)^- \cdot (CH_3)_2CO$. The latter, a molecular complex between thiocyanate ion and acetone, is more probable from the fact that ketones form molecular complexes with sodium iodide, lithium iodide, or sodium hydrogensulfide which are similar to thiocyanate salts in chemical aspect. $[Cr^{III}(NCS)_5(CH_3)_2CO]^{2-}$ cannot be considered to have such a short lifetime as observed.

The absorption spectrum of R agrees with that of the transient species found by Adams *et al.*[20] Baxendale and Scott found[21] the same spectrum in the radiolysis of pottassium thiocyanate aqueous solution and attributed it to $(NCS)_2^-$ on the basis of its kinetical dependence on potassium thiocyanate concentration, but no evidence was given to show it to be a radical. It is concluded that R is a radical because it reacts very fast with radical scavengers such as potassium iodide and acrylamide. Formation of acrylamide radical in a reaction between R and acrylamide was confirmed by the fact that the polymerization of acrylamide solution containing $[Co^{III}(NCS)(NH_3)_5](NCS)_2$ is initiated by illumination.[22]

Chromium(II) could not be detected in the photoreactions of $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$ in deaerated solution. Another transient species with very short lifetime (a few μs) was observed in deaerated ethanol solution of the complex, which has a broad absorption spectrum with maximum at 13.6 kK. Since the maximum and lifetime of the transient absorption are similar to those of solvated electron,[23] the following reaction seems to take place,

$$[Cr^{III}(NCS)_6]^{3-} + h\nu \rightarrow [Cr^{III}(NCS)_4]^- + (NCS)_2^- + e_{solv} \quad (5)$$

Summary

Excitation to the d–d excited state $^4T_{2g}$ of $K_3[Cr^{III}(NCS)_6]$ and $NH_4[Cr^{III}(NCS)_4(NH_3)_2]$, is followed by both nonradiative transition to the ^2E_g and the release of one of the ligands (thiocyanate ion). With temperature rise, the release of thiocyanate ion becomes faster and the freshly released thiocyanate ion forms an adduct with carbonyl compound such as acetone and ethylacetate, which decomposes slowly. Irradiation of UV light to the complexes produces a thiocyanate ion radical $(NCS)_2^-$.

Financial support from Fuji Photo Film Co., LTD. is gratefully acknowledged.

---

[20] G. E. Adams, J. W. Boag, and B. D. Michael, *Trans. Faraday Soc.*, **61**, 1674 (1965).

[21] J. H. Baxendale and S. A. Scott, *Chem. Commun.*, **1967**, 699.

[22] H. Takemura, private communication.

[23] L. M. Dorfman and M. S. Matheson, "Progress in Reaction Kinetics," Vol. 3, Pergamon Press, Oxford (1965), p. 284.