

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

The Association of  $\text{SCN}^-$  with  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ ,  $\text{Cr}(\text{NH}_3)_6^{+3}$ , and  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{++}$  in Aqueous Solution<sup>1</sup>BY ARTHUR L. PHIPPS<sup>2</sup> AND ROBERT A. PLANE

RECEIVED DECEMBER 3, 1956

Measurements of ultraviolet absorption spectra were made which indicate that there is slight association of  $\text{SCN}^-$  with  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ ,  $\text{Cr}(\text{NH}_3)_6^{+3}$  and  $\text{Cr}(\text{NH}_3)_5\text{Cl}^{++}$  in aqueous solutions. Limits were assigned to equilibrium constants for the associations and for all three cases the constant lay between  $10^{-1}$  and  $10^{-3}$ . For the  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  and  $\text{Cr}(\text{NH}_3)_6^{+3}$  measurements were made over the temperature range 3 to 26°. From such measurements the enthalpy change on association was found to be  $0 \pm 1$  kcal. mole<sup>-1</sup> and the entropy change at 25° was limited to the range  $-1.2$  to  $-17$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> for  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  and  $-1.2$  to  $-14$  cal. deg.<sup>-1</sup> mole<sup>-1</sup> for  $\text{Cr}(\text{NH}_3)_6^{+3}$ . This entropy decrease is primarily responsible for the fact that  $\text{SCN}^-$  shows less tendency to associate with complex cations than do other anions (such as halides) which have previously been studied. The entropy decrease could arise from the loss of rotational entropy of  $\text{SCN}^-$  on association.

The association in solution of complex cations of the type  $\text{Co}(\text{NH}_3)_6^{+3}$ ,  $\text{Cr}(\text{NH}_3)_6^{+3}$ , etc., with various anions has in recent years received considerable investigation.<sup>3-13</sup> For practically all of the systems studied association constants were found to lie between about ten and a thousand. Yet in most studies the total ionic strength was maintained constant by addition of sodium perchlorate, and it was assumed that there was no association of  $\text{ClO}_4^-$  with the highly charged cation. From the consistencies of the individual investigations this was apparently a valid conclusion, however a possibly surprising one in view of results that all other anions showed a marked tendency toward association. It seemed of interest to establish more directly the specificity of "outer sphere" association and if possible to determine factors which are responsible for specificity.

Of the methods used for detection and study of outer sphere complexes probably the most direct involves measurement of ultraviolet absorption spectra. It is generally found that in the ultraviolet region, ionic association is usually accompanied either by the appearance of a new absorption band, or by a shift of an existing band. These spectral changes can be attributed either to the introduction of a new electronic transition (for example the transfer of an electron from anion to cation), or to the perturbation of an existing electronic transition. The present authors found no spectral changes with changing concentration in solutions of  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  and  $\text{ClO}_4^-$ , even when  $\text{ClO}_4^-$  concentration was greater than 4 *M*. (The

cation  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  was picked on solubility considerations and is suitable since it undergoes substitution reactions quite slowly.<sup>14</sup>) Such results do not necessarily indicate lack of association between these ions since the spectrum might remain unchanged by association, or accompanying changes might occur in the far ultraviolet. It was necessary therefore to pick a system in which a spectral change could be noted, but one in which association might be expected to be slight. From earlier work,<sup>10,12</sup> thiocyanate ion seemed to be suitable on both counts.

## Experimental

The general experimental procedure involved rapidly mixing temperature equilibrated solutions to give a final solution of known composition. This solution was immediately placed in a thermostated cell of a Beckman DU quartz spectrophotometer and absorption measurements begun. The entire process, from mixing to measurement, required but 45 seconds. The time was kept short in order to minimize substitution reaction and other side reactions. The most serious such side reaction is a decomposition of thiocyanate in acidic solution to give an unknown species which is highly absorbing in the ultraviolet region. (Solutions containing  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  were made acidic, 0.05 or 0.10 *M* in order to suppress hydrolysis). At the wave lengths and temperatures used, the rate of change of the spectra amounted to several per cent. per minute, so that readings were taken periodically and extrapolated to time of mixing.

Absorption spectra of solutions of  $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$  plus  $\text{HClO}_4$ , of  $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$ , and of  $\text{Cr}(\text{NH}_3)_5\text{Cl}(\text{ClO}_4)_2$  were measured, individually and after being mixed with solutions containing NaSCN in the wave length region 2,600 to 2,900 Å. Every solution containing thiocyanate was also checked at 4750 Å., the wave length of maximum absorption of  $\text{FeSCN}^{++}$ , to ensure absence of ferric ion.

**Materials.**—Chromic perchlorate was made by reducing  $\text{CrO}_3$  in  $\text{HClO}_4$  with 30%  $\text{H}_2\text{O}_2$ . Excess  $\text{H}_2\text{O}_2$  was destroyed by heating in the presence of platinum. The solution was evaporated to crystals and these were recrystallized from 0.5 *M*  $\text{HClO}_4$ . Chromic analyses were performed spectrophotometrically following oxidation to chromate. Mallinckrodt AR 70%  $\text{HClO}_4$  was used without purification. Reagent grade NaSCN was twice recrystallized from redistilled water.  $\text{NaClO}_4$  was made by exactly neutralizing analytical reagent NaOH with analytical reagent  $\text{HClO}_4$  and crystallizing.  $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$  was prepared by dissolving anhydrous  $\text{CrCl}_3$  in liquid  $\text{NH}_3$  in the presence of a bit of dissolved sodium.<sup>15</sup> The residue was dissolved in water, filtered, and  $\text{Cr}(\text{NH}_3)_6(\text{ClO}_4)_3$  precipitated from the filtrate by addition of concentrated  $\text{HClO}_4$ . The product was washed with alcohol and ether and dried under vacuum in the dark. Chloropentamminechromium(III) chloride was obtained as a by-product and was purified by dissolving it in warm water, filtering and precipitating with concen-

(1) From the thesis submitted by Arthur L. Phipps to the Graduate School of Cornell University in partial fulfillment of the requirements for the degree of Master of Science.

(2) Westvaco Mineral Products Division, P. O. Box 920, Modesto, California.

(3) C. W. Davies, *J. Chem. Soc.*, 2421 (1930).

(4) M. Linhard, *Z. Elektrochem.*, **50**, 224 (1944).

(5) E. H. Katzenellenbogen, Paper No. 23, Division of Physical and Inorganic Chemistry, American Chemical Society meeting, September, 1950.

(6) M. Linhard and M. Weigel, *Z. anorg. allgem. Chem.*, **266**, 73 (1951).

(7) H. Taube and F. A. Posey, *THIS JOURNAL*, **75**, 1463 (1953).

(8) M. G. Evans and G. H. Nancollas, *Trans. Faraday Soc.*, **49**, 363 (1953).

(9) R. E. Connick, Paper No. 8, Division of Physical and Inorganic Chemistry, American Chemical Society meeting, Spring, 1953.

(10) A. W. Adamson and R. G. Wilkins, *THIS JOURNAL*, **76**, 3379 (1954).

(11) H. Yoneda, *Bull. Chem. Soc. of Japan*, **28**, 125 (1955).

(12) C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955).

(13) F. A. Posey and H. Taube, *THIS JOURNAL*, **78**, 15 (1956).

(14) J. P. Hunt and R. A. Plane, *ibid.*, **76**, 5960 (1954).

(15) W. E. Henderson and W. C. Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., New York, N. Y., 1935, p. 130.

trated HCl. The salt was filtered, washed with alcohol and ether, and dried under vacuum. The water used in all experiments was redistilled in a Barnstead block tin still.

### Results

$\text{Cr}(\text{H}_2\text{O})_6^{+3} + \text{SCN}^-$ .—The results of a typical series of experiments are shown in Fig. 1, which gives the optical density ( $\log I_0/I$ ) for one cm. light path lengths of 0.040  $M$   $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$ , 0.40  $M$

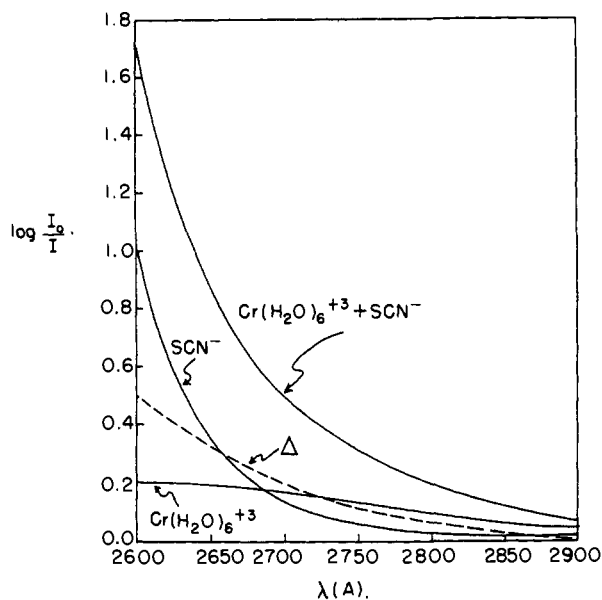


Fig. 1.—Absorption spectra of various ions in acidic solution at 3° for 0.04  $M$   $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$  and 1  $M$  NaSCN in 0.1  $M$   $\text{HClO}_4$ .

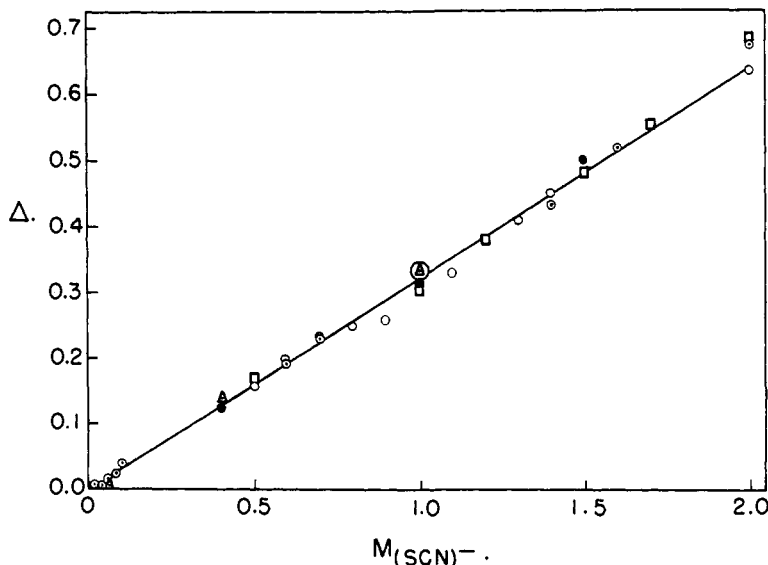


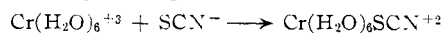
Fig. 2.—The interaction of 0.04  $M$   $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  and various concentrations of  $\text{SCN}^-$ . Data obtained from optical density measurements at 2750  $\text{A}$ . Circles represent points obtained at 3°; squares, at 15°; triangles, at 26°. Open symbols designate solutions containing 0.05  $M$   $\text{HClO}_4$ ; symbols with dots, solutions containing 0.1  $M$   $\text{HClO}_4$ ; blackened symbols, solutions containing sufficient  $\text{NaClO}_4$  to make total ionic strength 2  $M$ .

$\text{NaSCN}$  and a mixture of the two, all solutions 0.10  $M$  in  $\text{HClO}_4$ , and at 3°. The dotted line in the figure represents the optical density of the mixture minus that of the separate chromic and thiocyanate solutions (hereafter called  $\Delta$ ). Al-

though the chromic spectrum is *not* affected by change of acidity or temperature in the ranges covered by these experiments, the  $\text{SCN}^-$  spectrum was somewhat affected—increasing both with increasing acidity and with increasing temperature. In every case the  $\Delta$ s were obtained by subtracting the contribution of the  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  and that of a  $\text{NaSCN}$  solution identical with the final mixture except that  $\text{Cr}(\text{H}_2\text{O})_6(\text{ClO}_4)_3$  was absent.

Because of the decrease of  $\Delta$  and of the optical density of  $\text{SCN}^-$  with increasing wave length, measurements at low  $\text{SCN}^-$  concentration were most precise at shorter wave length, and those at high  $\text{SCN}^-$ , at longer wave length. The shortest wave length at which the entire range of  $\text{SCN}^-$  concentration from 0.02 to 2.0  $M$  could be precisely studied was 2750  $\text{A}$ . The results of experiments at this wave length are given in Fig. 2. Values of  $\Delta$  are plotted *versus* formal concentration of  $\text{SCN}^-$ , and the plot shows that experiments at two acidities, three temperatures, with and without added  $\text{NaClO}_4$  (to make total ionic strength 2  $M$ ) form a single curve, which is essentially a straight line. Experiments at other wave lengths give similar results.

If the association between  $\text{SCN}^-$  and  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  is governed by the equilibrium



as seems to be true of all other cases studied,<sup>3-13</sup> then within the accessible range of  $\text{SCN}^-$  concentrations a significant fraction of the chromic ion is never converted to the associated species. Significant conversion would cause the plot of  $\Delta$  *vs.*  $\text{SCN}^-$  concentration to approach zero slope; on the other

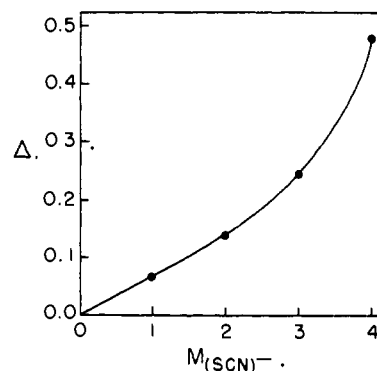


Fig. 3.—The interaction of 0.04  $M$   $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  and  $\text{SCN}^-$ . Data obtained at 2900  $\text{A}$ , 3° and in solutions containing 0.05  $M$   $\text{HClO}_4$ .

hand only slight association requires the plot to approach a straight line of finite slope. From an assessment of errors and precision of the present experiments, it is found that an association equilibrium constant greater than 0.1 would cause detectable de-

viation from the straight line described by the points in Fig. 2. In addition to this upper limit placed on the value of  $K$ , a lower limit can be assigned by assuming a maximum value for the extinction coefficient of the associated species. If this coefficient is assumed to be  $10^4$  at 2750 Å., it follows from the data plotted in Fig. 2 that at 1.0  $M$   $\text{SCN}^-$ , the concentration of the ion pair would be  $3.2 \times 10^{-5}$  and  $K$  would be  $8 \times 10^{-4}$ .

It might seem somewhat curious that even if the association constant for this system is small, points at various ionic strengths (both those in which the total ionic strength was allowed to vary from 0.36 to 2.34 and those in which the total ionic strength was maintained constant at 2.00 by addition of  $\text{NaClO}_4$ ) describe a straight line. This would seem to indicate that over the concentration range investigated, the pertinent activity coefficients ratios of individual species are nearly constant. It is perhaps significant that the activity coefficients ( $\gamma_{\pm}$ ) for  $\text{NaSCN}$  which comprises the bulk concentration in most experiments vary by less than  $\pm 5\%$  in the ionic strength range of these experiments, and those of  $\text{NaClO}_4$ , which comprises the bulk concentration in the remaining experiments are almost equally constant and differ from the  $\text{NaSCN}$  coefficients by about 10%.<sup>16</sup>

At higher  $\text{SCN}^-$  concentrations, a plot of  $\Delta$  vs. concentration of  $\text{SCN}^-$  does not give a straight line. Data obtained at 2900 Å. are plotted in Fig. 3. The curvature is in the opposite direction demanded by that for the "saturation" of an association. In this concentration region the activity coefficients of  $\text{NaSCN}$  increased markedly,<sup>16</sup> and may quite possibly account for the deviation. Similar deviations are noted in experiments in which the concentration of  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  ( $\text{ClO}_4$ )<sub>3</sub> is varied with consequent wide variation in total ionic strength. The data in Table I

TABLE I  
VARIATION OF  $\Delta$  AT 0.5  $M$   $\text{SCN}^-$  AND VARIOUS CONCENTRATIONS OF  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$

Temperature 3°; wave length 3090 Å.			
$\text{Cr}(\text{H}_2\text{O})_6^{+3}$ , $M$	0.5	1.0	1.5
Ionic strength, $M$	3.6	6.6	9.6
$\Delta$	0.054	0.196	0.509

show that in this case,  $\Delta$  is not directly proportional to chromic concentration. Again the explanation could well lie in the fact that at high ionic strength, activity coefficients of  $\text{SCN}^-$  increase, which should cause the apparent association constant (based on concentrations not activities) to increase with increasing ionic strength.

It was noted earlier that the effect of temperature on observed values of  $\Delta$  is quite small. If the assumption is made that the absorption process (*i.e.*, extinction coefficient of the associated species) is not affected by temperature, then any change in  $\Delta$  with temperature is due to a change in the extent of association. From a comparison of duplicate points at the temperatures 3, 15 and 26°

(16) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

of Fig. 2, it is found that the change in equilibrium constant within this temperature range is less than 10% so that the enthalpy change for the association is within 1 kcal. mole<sup>-1</sup> of 0. With this value for  $\Delta H$  and the two limits previously placed on the equilibrium constant, it is possible to place limits on the entropy change for the association. At 25°, the entropy change lies in the range  $-1.2$  to  $-17$  cal. deg<sup>-1</sup> mole<sup>-1</sup>.

$\text{Cr}(\text{NH}_3)_6^{+3} + \text{SCN}^-$ .—Experiments with  $\text{Cr}(\text{NH}_3)_6^{+3}$  and  $\text{SCN}^-$  were similar in design and results to those with  $\text{Cr}(\text{H}_2\text{O})_6^{+3} + \text{SCN}^-$ . Values of  $\Delta$  at 2750 Å. are plotted in Figs. 4 and 5. Comparable results were obtained at other wave lengths. There is again a linear relation between  $\Delta$  and both  $\text{SCN}^-$  and  $\text{Cr}(\text{NH}_3)_6^{+3}$ , and the points in Fig. 5 show the absence of temperature dependence. In this case there seems to be much less deviation from linearity at high  $\text{SCN}^-$ . A comparison of the optical density of solutions of  $\text{Cr}(\text{NH}_3)_6^{+3}$  plus  $\text{SCN}^-$  with solutions of  $\text{Cr}(\text{H}_2\text{O})_6^{+3}$  plus  $\text{SCN}^-$  at comparable concentrations, shows that the value of  $\Delta$  is greater by about a factor of 5 in the case of  $\text{Cr}(\text{NH}_3)_6^{+3}$  plus  $\text{SCN}^-$ . This could mean that either the association constant or the extinction coefficient of the associated species is somewhat greater for  $\text{Cr}(\text{NH}_3)_6^{+3}$ - $\text{SCN}^-$ . It seems probable that a stronger interaction would cause both to increase. By the methods used previously, limits set on the association constant are  $1 \times 10^{-1}$  to  $4 \times 10^{-3}$ ; the enthalpy change,  $0 \pm 1$  kcal. mole<sup>-1</sup>; and the entropy change,  $-1.2$  to  $-14$  cal. deg<sup>-1</sup> mole<sup>-1</sup>.

$\text{Cr}(\text{NH}_3)_5\text{Cl}^{++}-\text{SCN}^-$ .—Experiments with solutions of  $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  and  $\text{NaSCN}$  are plotted as the lower line in Fig. 5. The linear relation is again shown so that the association constant is small also in this case. As with the other cases, this relation holds equally well at other wave lengths. At comparable concentrations of complex cation and  $\text{SCN}^-$ , the values of  $\Delta$  are only very slightly less than those observed for  $\text{Cr}(\text{NH}_3)_6^{+3}$  with  $\text{SCN}^-$ . It therefore seems likely that the extent of association is about the same in the two systems.

## Discussion

The small tendency of  $\text{SCN}^-$  to associate with complex cations, shown by the present study, seems somewhat unusual when compared with the results of previous studies.<sup>3-13</sup> In those cases, association constants were found which are orders of magnitude greater than that for  $\text{SCN}^-$ . The unique position of  $\text{SCN}^-$  is probably not entirely due to its relatively low charge and large size. Comparison of the present results with those obtained for tripositive cobaltamines plus  $\text{SO}_4^{--}$ ,<sup>13</sup>  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ,<sup>8</sup> show that the enthalpy of association for  $\text{SCN}^-$  is as favorable as that for any of the other cases. (The values of  $\Delta H$  obtained in the previous studies range from 0 to +3.7 kcal./mole). The significant difference between  $\text{SCN}^-$  and other anions is the entropy change which accompanies association. Whereas the entropy term for the associations noted above are all positive by 10 or more calorie mole<sup>-1</sup> degree<sup>-1</sup>, that for  $\text{SCN}^-$  is negative. Of the anions previously

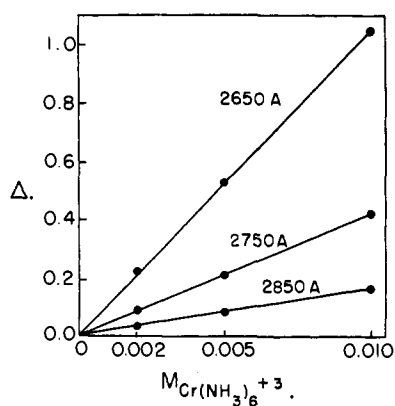


Fig. 4.—The interaction of 1.0  $M$   $\text{SCN}^-$  with various concentrations of  $\text{Cr}(\text{NH}_3)_6^{+3}$  at  $3^\circ$ .

studied, only  $\text{N}_3^-$  shows a similar entropy loss on association.<sup>8</sup> The unique characteristic of  $\text{N}_3^-$  and  $\text{SCN}^-$  is that each is a linear ion which might possess rotational entropy which would be lost on association. Unfortunately, no data exist on the entropy of either of these anions from which it would be possible to decide whether the ions in aqueous solution possess rotational entropy. However, for gas phase association, Evans and Nancollas estimate rotational entropy loss for  $\text{N}_3^-$  of 11 cal. degree<sup>-1</sup> mole<sup>-1</sup>.<sup>8</sup> A similar calculation for  $\text{SCN}^-$  shows its gas phase rotational entropy loss to be 16 cal. degree<sup>-1</sup> mole<sup>-1</sup>. This value is sufficiently large to change the total entropy of

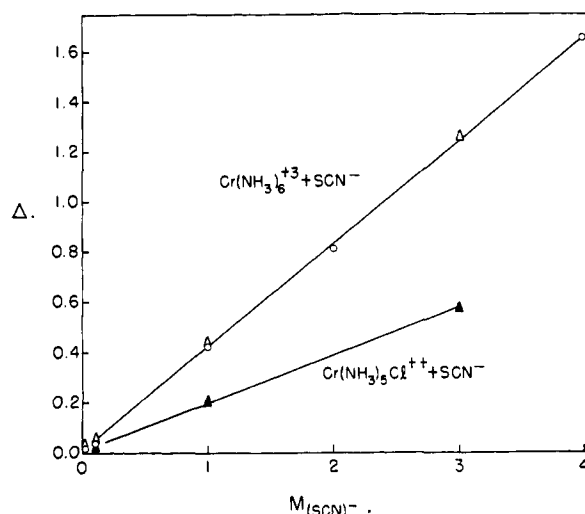


Fig. 5.—The interaction of 0.01  $M$   $\text{Cr}(\text{NH}_3)_6^{+3}$  and 0.005  $M$   $\text{Cr}(\text{NH}_3)_5\text{Cl}^{+2}$  with various concentrations of  $\text{SCN}^-$ . Data obtained from optical density measurements at 2750 Å. Circles represent points obtained at  $3^\circ$ ; triangles, at  $26^\circ$ .

association from a positive value, such as is found for other anions, to a negative value defined by the present experiments, and, hence, can account for the very slight tendency toward association noted for  $\text{SCN}^-$ .

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

## Photoreduction of Eosin in the Bound State<sup>1a,b</sup>

BY JUDITH S. BELLIN AND GERALD OSTER

RECEIVED NOVEMBER 30, 1956

The spectral and photochemical properties of eosin Y bound to polyvinylpyrrolidone differ considerably from those of the free dye. The bound dye exhibits self-quenching of fluorescence at much lower concentrations than does the free dye, whereas for self-quenching of phosphorescence (in rigid media) the opposite is true. Furthermore, *p*-phenylenediamine which quenches the phosphorescence of the free dye is without effect on the bound dye. Nitrobenzene retards the photoreduction of free eosin but inhibits the photoreduction of bound eosin, the duration of the inhibition period being proportional to the concentration of the inhibitor. *p*-Phenylenediamine both inhibits and retards the photoreduction of bound eosin while it only retards the reaction for the free dye. For small dye concentrations the quantum yield of photoreduction of bound eosin increases with increasing dye concentration while for free dye the opposite is the case. These rate studies suggest that a bound dye molecule in the first electronically excited state rapidly exchanges energy with a bound dye molecule in the ground state to produce a long-lived excited species which reacts with the reducing agent (here ascorbic acid). A mechanism is proposed for dye-sensitization in silver halide photography based on photoreduction of bound dye.

### Introduction

The photochemical properties of dyestuffs when bound to substrates are considerably different from those of the free dye in solution. For example, rose bengal (2',4',5',7'-tetraiodo-3,4,5,6-tetrachlorofluorescein) is readily photooxidized in solution whereas the dye when bound to polyvinylpyrrolidone (PVP) resists photooxidation even

(1) (a) This paper represents a part of the dissertation submitted by Judith S. Bellin to the faculty of the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. AF18(600)1182.

when exposed to sunlight for one month.<sup>2</sup> On the other hand, dyes which are bound to high polymeric substrates are more readily photoreduced than are the free dyes.<sup>3-5</sup>

The present paper is concerned with the photoreduction of eosin Y (2',4',5',7'-tetrabromofluorescein) when bound to PVP in solution. The kinetics of photoreduction of free eosin Y have been studied.<sup>6</sup> It has been shown that the kinetics of photoreduction of free fluorescein and its halo-

- (2) G. Oster, *J. Polymer Sci.*, **9**, 553 (1952).
- (3) G. Oster, *Trans. Faraday Soc.*, **47**, 660 (1951).
- (4) G. Oster, *J. Polymer Sci.*, **9**, 553 (1952).
- (5) G. Oster and J. Bellin, *THIS JOURNAL*, **78**, 294 (1957).
- (6) G. Oster and A. H. Adelman, *ibid.*, **78**, 913 (1956).