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Substitution Reactions of Reinecke's Salt

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The solvolysis of $Cr(NH_3)_2(NCS)_4^-$, the ion of Reinecke's salt, whereby thiocyanate is replaced by solvent, has been studied in a number of non-aqueous solvents. It was found that the first step was in general rate determining but was usually followed by the more rapid elimination of one or two additional thiocyanates. The apparent first-order specific rate constant, k_{app}, was of the order of 0.01 min.$^{-1}$ at 60° for solvents of the ROH type (H_2O, CH_3OH, C_6H_5OH), was reduced by 50% in D_2O and was negligible in non-hydrogen bonding solvents such as nitromethane. Activation energies were essentially the same in all cases, and about 28 kcal./mole. No direct bimolecular substitution reactions were found in methanol as solvent where cyanide, azide or iodide were the potential substituents, although in the presence of cyanide ion the amount of thiocyanate released in steps subsequent to the initial, rate determining one, was increased. In methanol-nitromethane mixtures k_{app} was not changed in the presence of azide ion but was increased by such basic ions as cyanide, hydroxide and acetate. The data are interpreted to indicate that the solvolysis reactions proceeded through a front side bimolecular displacement process involving coöperative hydrogen bonding interaction between the anion and the solvent. This mechanism, designated as SN2 FS, is discussed in relation to substitution reactions of octahedral complexes in general.

The mechanism of substitution reactions of octahedral complex ions has been a topic of considerable interest in recent years. In particular, it has been supposed that such reactions should be essentially SN1 in type, involving a five-coördinated intermediate which then reacts competitively with potential ligands, or essentially SN2 in type, involving a seven-coördinated transition state. The distinction has been difficult to make experimentally since substitution reactions in aqueous media have appeared always to go through an aquo complex intermediate so that the first-order kinetics which is in fact observed would be predicted by either mechanism.[1-4] Attempts have been made to develop indirect evidence through a study of specific anion effects on the aquation rates of positively charged complexes and of steric and other changes in the nature of the ligands neighboring the displaced group. Such indirect evidence, unfortunately, is susceptible to more than one interpretation. Attempts have been made to eliminate the aquation reaction entirely, by the use of non-aqueous solvents such as methanol[4]; it will be seen however, that there is no assurance in such situations that one type of solvation process has not merely been replaced by another. In addition, the use of positively charged complex ions in media of low dielectric constant has greatly increased the likelihood that the kinetics of anion substitution will be complicated by ion-pair formation effects. The so-called SN2 IP mechanism which is possible in this last case leads to second-order kinetics without implying a transition state involving seven groups in the primary coördination sphere. Finally displacement reactions involving highly basic substituents such as hydroxide or methoxide ions, while second order, very likely take place through a counter base mechanism in those cases where the complex ion contains ligands having at least slightly acidic hydrogens.[3]

The seven-coördinated transition state for an SN2 reaction has been thought of as a *cis* or *trans* approach of the displacing ligand[5] or in terms of the conceptually similar "edge displacement" process.[4] An alternative hypothesis is one which specifically recognizes interactions between the departing ligand and the entering species, an interaction that actually can hardly fail to be present since one of the groups is generally a solvent molecule. Thus in the solvation reaction, the entering solvent molecule is pictured as interacting, through hydrogen bonding, with both an adjacent amine hydrogen and the departing acido group, in the case of acidoamine complexes.[6] Three aspects, rather than one, are thus involved, *i.e.*, the metal-acido group or M–X interaction, the metal–solvent or M–S interaction and the X–S interaction. This picture seemed necessary to account satisfactorily for the effects of deuteration on the aquation of $Co(NH_3)_5Cl^{+2}$ and for the general data on aquation or solvation of Co(III) complexes, especially the stereochemical aspects.

The present investigation was undertaken to examine more critically the role of solvent and of hydrogen bonding effects on substitution reactions. It was for this reason desirable to choose a complex that would be soluble in a variety of non-aqueous solvents and at the same time one that would be unlikely to become involved in ion-pairing effects. This last requirement indicated that neutral or negatively charged complexes should be chosen, and several were subjected to preliminary study. Neutral species such as $Cr(NH_3)_3Cl_3$, $Cr(NH_3)_3O_4$ and $Co(NH_3)_3(NO_2)_3$ were found to be too insoluble, however, not only in organic solvents, but also in water. Reinecke's salt, $KCr(NH_3)_2(NCS)_4$, or KR, was found to meet the above criteria quite well, however. In particular, it was quite soluble in the non-hydrogen bonding solvent nitromethane, and other work[7] had shown that it was completely dissociated in this medium.

Experimental

Preparation of Materials.—Potassium reineckate was purified by recrystallization from potassium nitrate solution and then from warm water, using C.P. starting material. The thiocyanate content was determined by digesting a weighed sample in potassium hydroxide solution and then measuring the free thiocyanate concentration by means of a colorimetric method previously described[2]; 150 mg. of complex was found to contain 1.69 mmoles of thiocyanate, corre-

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[1] A. W. Adamson, J. P. Welker and W. B. Wright, THIS JOURNAL, **73**, 4786 (1951).

[2] A. W. Adamson and R. G. Wilkins, *ibid.*, **76**, 3379 (1954).

[3] F. Basolo, *Rec. Chem. Progr.*, **18**, 1 (1957), and preceding papers.

[4] R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956), and preceding papers.

[5] F. Basolo, B. D. Stone and R. G. Pearson, THIS JOURNAL, **75**, 819 (1953).

[6] A. W. Adamson and F. Basolo, *Acta Chem. Scand.*, **9**, 1263 (1955).

[7] H. L. Friedman, THIS JOURNAL, **76**, 2060 (1954).

sponding to 65.3% SCN. The chromium analysis consisted of fuming down with sulfuric acid, then taking up the residue in dilute sulfuric acid, adding silver nitrate and ammonium persulfate to form dichromate and then boiling to remove excess oxidant. A known amount of ferrous ammonium sulfate was then added, followed by back titration with standard permanganate. Calcd. for $KCr(NH_3)_3(NCS)_4$: SCN, 65.1; Cr, 14.6. Found: Cr, 13.7.

The methanol was of reagent grade, dried over magnesium and then distilled over magnesium perchlorate. C.P. ethanol and dioxane were employed without further purification, and the nitromethane was the middle cut. Other reagents were of C.P. grade.

Procedures.—The rate measurements were carried out as follows. The solution was placed in a stoppered volumetric flask which was then immersed up to the neck in an oil thermostat and protected from light. Aliquots were withdrawn periodically for analysis. Free thiocyanate was determined by the ferric thiocyanate colorimetric method[2]; in some cases complete absorption spectra were taken periodically, by means of a Cary recording spectrophotometer. For certain runs the amount of KR remaining also was determined. This was done by precipitating the trimethylammonium salt by means of an excess of trimethylammonium chloride; the precipitate was then filtered off, washed with dilute quaternary amine salt solution, dissolved in nitromethane and the concentration determined spectrophotometrically.

In the case of the systems containing iodide and azide ions, the ferric perchlorate reagent could not be used in the normal manner since these ions formed colored complexes quite similar to that with thiocyanate. In the case of the iodide–thiocyanate mixtures, a few tenths of a cc. of the solution was added to 10 cc. of 0.5 M ferric perchlorate in 0.5 M perchloric acid, and the optical density was then measured at two wave lengths. The concentration of thiocyanate was given by the equation $C = (D_{532} - 0.30\ D_{460})/620$. With azide-thiocyanate mixtures, the near identity of the spectra of the respective Fe(III) complexes precluded the use of two wave lengths; instead, two reagent solutions, one 0.5 M in Fe(III), and the other 0.02 M, were used, to take advantage of the fact that at the lower Fe(III) concentration very little azide complex formed. The concentration of thiocyanate was obtained from the optical densities at 460 mμ of equal dilutions of the reaction mixture into the two reagent solutions, by means of the equation $C = (12.7D_{0.02M} - D_{0.5M})/28450$.

Although the presence of small amounts of moisture appeared to have little effect, moderate precautions were taken to keep the methanol solutions dry. The solvent was dispensed from a storage bottle equipped with a drying tube, and was added directly to the volumetric flask containing the weighed salt, which was then immediately stoppered.

On plotting the rate data as fraction of one thiocyanate per chromium released *vs.* time, there was generally a non-zero intercept, amounting to a few per cent. at the most, and either positive or negative. The data plotted in Figs. 1, 3 and 6 have been corrected so as to show a zero intercept, to facilitate comparisons. The apparent first-order specific rate constants, k_{app}, given in Fig. 2, give the fraction of one thiocyanate released per chromium, per minute; if divided by four, they would give the fraction of total thiocyanate released per minute.

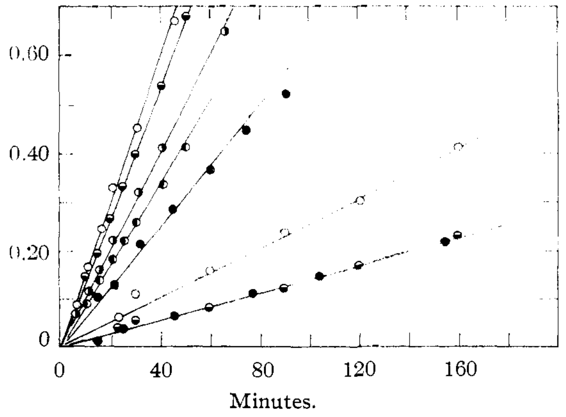

Fig. 1.—Solvation rates for 0.01 M KR at 60.3° in various solvents: ⊖, H_2O; ◐, D_2O; O, CH_3OH; ◑, 75% CH_3OH-25% CH_3NO_2; ●, 50% CH_3OH-CH_3NO_2; O, 20% CH_3OH-80% CH_3NO_2; ⊖, 10% CH_3OH-90% CH_3NO_2; ●, 50% CH_3OH-dioxane (last three symbols are for the bottom two lines of points).

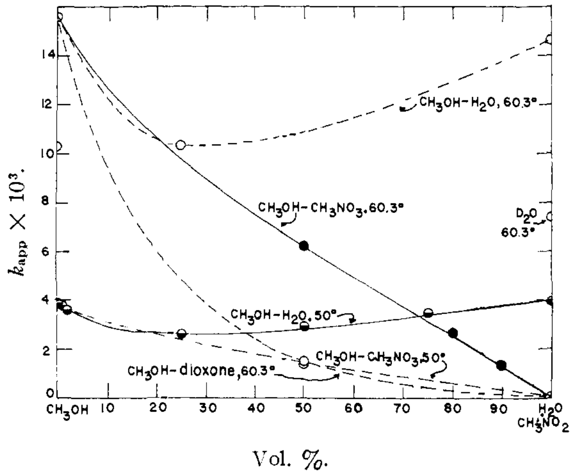

Fig. 2.—Summary of rate of solvation data for various solvents.

Solubilities.—Solubilities were determined by agitating solvent plus excess KR in a thermostat at 25°. The results are given in Table I. Compositions of mixed solvents are given here and throughout the paper in terms of 100 × [volume of first name solvent]/[total volume of solution], *i.e.*, as volume per cent., if volume changes on mixing are neglected.

TABLE I

SOLUBILITY OF POTASSIUM REINECKATE IN VARIOUS SOLVENTS AT 25°

Solvent	Solubility, M	Solvent	Solubility, M
H_2O	0.060	25% CH_3OH-75% H_2O	0.063
CH_3OH	.360	50% CH_3OH-H_2O	.150
C_2H_5OH	.018	75% CH_3OH-25% H_2O	.346
CH_3NO_2	.099		

Results and Conclusions

Initial Rates of Solvation in Various Solvents.—As illustrated in Fig. 1, plots of the fraction of one thiocyanate per chromium, F_{SCN}, *vs.* time were linear up to about 0.5 in F_{SCN}. In most cases the concentration of KR was 0.01 M, but separate series of experiments in which it was varied from 0.01 to 0.02 M showed that, in water and in methanol, k_{app} did not depend on the complex concentration (see Fig. 6).

It can be seen from Fig. 2 that relatively little variation in k_{app} occurred as composition was varied in the methanol–water system, while a nearly linear variation took place in the methanol–nitromethane mixtures. Here, k_{app} increased from zero in pure nitromethane to 15.6 × 10^{-3} min.$^{-1}$ in pure methanol, at 60.3°. The rate in ethanol was 66% of that in either methanol or water, at 60.3°, while the rate in 99% D_2O was only 53% of that in ordinary water, at this same temperature. The complex was insufficiently soluble in pure dioxane for this to be used as a solvent, but a value was obtained for k_{app} in 50% methanol–dioxane, and its probable variation with composition is given by the dotted line in Fig. 2. Similarly, although only one intermediate point was obtained for the methanol–water system at 60.3°, the k_{app} *vs.* composition curve is assumed to parallel that at 50.0°. Again, the nearly linear variation of rate with composition in the methanol–nitromethane system at 60.3° was assumed to hold at 50.0° as well.

A few runs were made with nitromethane containing small amounts of added water, at 70°, but the results were somewhat erratic. Qualitatively, there was little change from the very low rate in the pure solvent.

The temperature dependence of the solvation rate was obtained for four systems, water, methanol, 75% methanol–25% water and 50% methanol–nitromethane, for either two or three temperatures. The apparent activation energies were 27.0, 28.3, 28.5 and 31.0 kcal., respectively (*i.e.*, slope of ln k_{app} *vs.* $1/T$ plot, multiplied by $-R$).

It should be noted that the solvation reaction is strongly photocatalyzed in water, methanol and nitromethane.[8] The high quantum yield for release of thiocyanate in nitromethane is of particular interest in view of the lack of corresponding thermal reaction.

Products of the Solvation Reactions.—To facilitate their presentation, the results are anticipated somewhat by noting that the reaction sequence in a solvent, S, consisted of one or more stages of progressive replacement of thiocyanate by solvent, according to the following equations. No displacement of ammonia occurred, since even

$$\underset{\text{(KR)}}{\mathrm{Cr(NH_3)_2(NCS)_4^-}} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{\text{I}}{\mathrm{Cr(NH_3)_2(S)(NCS)_3}} + \mathrm{SCN^-} \quad (1)$$

$$\mathrm{Cr(NH_3)_2(S)(NCS)_3} + \mathrm{S} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \underset{\text{II}}{\mathrm{Cr(NH_3)_2(S)_2(NCS)_2^+}} + \mathrm{SCN^-} \quad (2)$$

$$\mathrm{Cr(NH_3)_2(S)_2(NCS)_2^+} + \mathrm{S} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \underset{\text{III}}{\mathrm{Cr(NH_3)_2(S)_3(NCS)^{++}}} + \mathrm{SCN^-} \quad (3)$$

$$\mathrm{Cr(NH_3)_2(S)_3(NCS)^{++}} + \mathrm{S} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \underset{\text{IV}}{\mathrm{Cr(NH_3)_2(S)_4^{+++}}} + \mathrm{SCN^-} \quad (4)$$

after long times the solutions remained neutral, although eventually some cloudiness appeared. The above equations are intended to give the over-all stoichiometry rather than to indicate any particular mechanism; nonetheless, since no ion pairing should be present, the forward reactions should be first order and the reverse, second order in species other than solvent regardless of whether an SN1 or an SN2 type mechanism were involved.

It was clear that more than the first stage reaction was in general present since, as illustrated in Fig. 3, the amount of thiocyanate released perchromium, F_{SCN}, exceeded unity after long times. In water solution, it approached a limiting value of 3.2, so that the final mixture consisted of a mixture of predominantly species III and IV. A similar terminal ratio would be expected in the analogous aquothiocyanato series.[9]

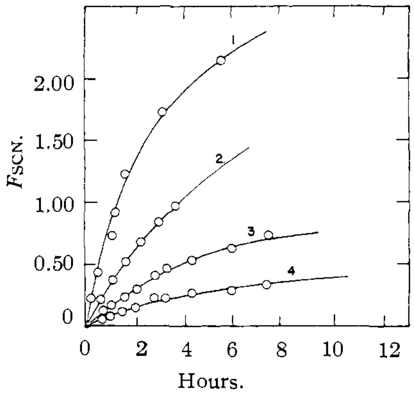

Fig. 3.—Solvation of 0.01 *M* KR in mixed CH_3OH–CH_3NO_2 solvents at 60.3°: 1, CH_3OH; 2, 50% CH_3OH–CH_3NO_2; 3, 20% CH_3OH–80% CH_3NO_2; 4, 10% CH_3OH–90% CH_3NO_2.

It was necessary to consider two extreme possible kinetic situations, namely, that reaction 1 was rate controlling at all times, with the product species I promptly reacting further to give a kinetically controlled equilibrium mixture of products, or that the sequence was one of steadily decreasing rates. In this last case there would be a continued appearance of free thiocyanate after all the original KR had reacted, while in the first case the ratio, R, of thiocyanate released per KR reacted would remain constant.

This point was investigated by determining both the amount of free thiocyanate formed at various times, and the amount of KR remaining in solution. As shown in Fig. 4, with water as solvent, R was constant over the first 50% of reaction and had

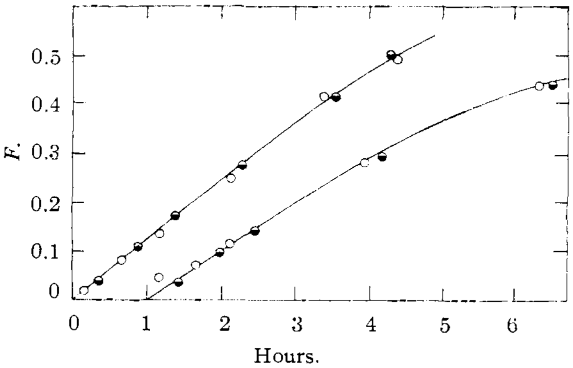

Fig. 4.—True rates of solvation of 0.01 *M* KR in H_2O and in CH_3OH at 50.0°. (Lower curve displaced by one hour, for clarity). Upper curve, water as solvent; ○, *F* of KR reacted (direct analysis), ◒, $F_{\mathrm{SCN}}/2.25$; Lower curve, CH_3OH as solvent; ○, *F* of KR reacted (direct analysis), ◒, $F_{\mathrm{SCN}}/2.75$.

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[8] A. W. Adamson and A. H. Sporer, paper presented at the Third International Symposium on Coördination Chemistry, Rome, 1957.

[9] C. Postmus and E. L. King, *J. Phys. Chem.*, **59**, 1208 (1955), and earlier references cited.

the value 2.25. It may thus be concluded that the rate-determining step 1 is followed by prompt equilibration of the product species I to a mixture of II and III. The value of k_1 is then $k_{app}/2.25$, or 1.75×10^{-3} min.$^{-1}$ at 50°. On the other hand, since an eventual ratio of 3.2 was reached (after 24 hr.), a slow further reaction also must have taken place. The successive spectra, displayed in Fig. 5ab, confirm the presence of more than one species of product since computations of the ratio $(D_0 - D)/(D_0 - D_\infty)$ for 300 and 520 mμ gave different values for the apparent amount of reaction.

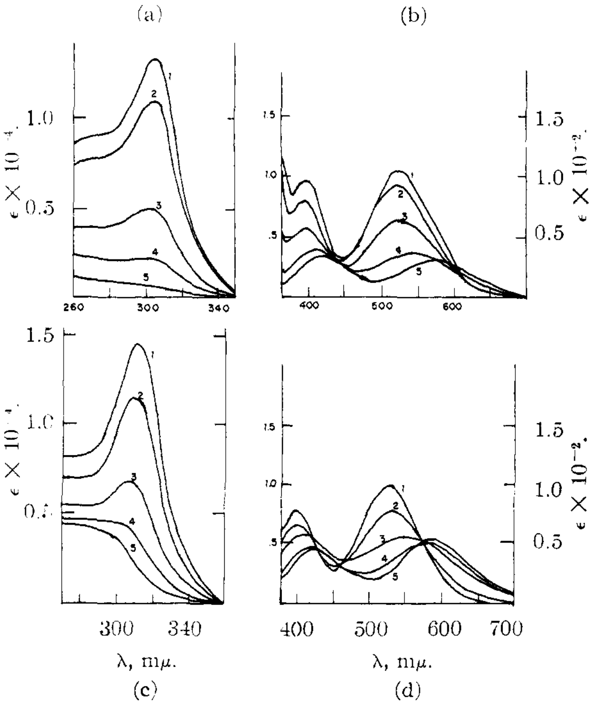

Fig. 5.—Sequence of absorption spectra during solvation of 0.01 M KR in H_2O and in methanol at 60.3°. Fig. 5ab.—H_2O as solvent; curve 1, initial spectrum; curve 2, 1.58 hr., F_{SCN} = 0.56; curve 3, 3.08 hr., F_{SCN} = 1.58; curve 4, 6.33 hr., F_{SCN} = 2.87; curve 5, 24 hr., F_{SCN} = 3.21. Fig. 5cd.—CH_3OH as solvent; curve 1, initial absorption spectrum; curve 2, 1.97 hr., F_{SCN} = 0.86; curve 3, 2.92 hr., F_{SCN} = 1.64; curve 4, 5.50 hr., F_{SCN} = 2.15; curve 5, 26 hr., F_{SCN} = 2.43.

With methanol as solvent, R was constant at 2.75 over the first 40% of reaction, as shown in Fig. 4. Again, the formation of product species I must have been followed by a prompt equilibration with II and III, and k_1 is then $k_{app}/2.75$ or 1.44×10^{-3} min.$^{-1}$ at 50°. This figure of 2.75 is higher than the final value approached after long times, which was 2.4 thiocyanates per chromium. In methanol, then, unlike the water system, there was no residual slow reaction; the regression in the value of the ratio was presumably due to repression of the equilibria 2 and 3 by the increasing thiocyanate concentration. The sequence of spectra, given in Fig. 5cd, shows an approximate isosbestic point, as would be expected if the solution contained KR plus a nearly constant ratio of product species. Moreover, the ratios $(D_0 - D)/(D_0 - D_\infty)$ determined at 310 and 520 mμ gave values of the amount of KR reacted consistent with each other and those calculated from the amount of free thiocyanate present.

The ratio R should in general be temperature dependent, and at 60° in methanol the data of Fig. 3 are fitted by the equation

$$y/a = R\exp(-k_1t) \qquad (5)$$

where y denotes the amount of free thiocyanate at time t, and a, the initial complex concentration. The solid line in the figure is computed using R = 2.40 and k_1 = 0.00692. The true activation energy is then somewhat larger than the 28.3 kcal. computed from the k_{app} values.

For mixed methanol–nitromethane solvents there was a progressive decrease in the limiting ratio of free thiocyanate to chromium as the methanol content was lowered, as illustrated in Fig. 3. The data for 50% methanol–nitromethane are fitted by equation 5 with R = 2.0 and $k_1 = 3.25 \times 10^{-3}$, as shown by the solid line. In 20% methanol–nitromethane and 10% methanol–nitromethane, the back reaction of equation 1 cannot be neglected since the low terminal ratios of thiocyanate released to total chromium indicates that some KR was always present. The integrated rate law for a first-order forward and a second-order reverse reaction, adapted to the present situation, is

$$k_1t(2aR/y_\infty - 1) = \ln\left[\frac{1 + (y/y_\infty)(1 - y_\infty/aR)}{1 - y/y_\infty}\right] \qquad (6)$$

where y_∞ denotes the equilibrium concentration of free thiocyanate. The data in Fig. 3 are fitted by equation 6, using R and k_1 values of 1.5 and 0.002 min.$^{-1}$, and 1.0 and 0.0014 min.$^{-1}$, respectively, as shown by the solid lines. Decreasing methanol content thus resulted in decreased equilibrium amounts of reaction as well as in decreased k_1 values.

Some attempts were made to isolate solid products. A 0.1 M solution of KR in methanol was kept at 60° until a ratio of 2.4 free thiocyanates per chromium was reached; the solution remained neutral, so no loss of ammonia occurred. It was then evaporated to dryness and the residue taken up in nitromethane, leaving a white solid which tested for potassium thiocyanate and which contained close to one thiocyanate per original chromium. The nitromethane solution on evaporation gave very hygroscopic blue-green crystals which contained one free thiocyanate per chromium, and, on being subjected to a cycle of mild digestions with potassium hydroxide and sulfuric acid, yielded an additional two thiocyanates. The blue-green product was thus the thiocyanate salt of a dithiocyanato complex, *i.e.*, $[Cr(NH_3)_2(S)_2(NCS)_2]SCN$. If S were methanol, the molecular weight would be 384, as compared to the observed weight per three thiocyanates of 360; the difference may have been due to some loss of solvent on drying. Since the original solution contained 2.4 free thiocyanates per chromium, the monothiocyanato complex present must have been converted to the dithiocyanato species by the evaporation treatment.

Bimolecular Substitution Reactions.—Since cyanide ion is a very nucleophilic species, it was thought possible that a direct bimolecular substitution reaction might take place, *i.e.*

$$Cr(NH_3)_2(NCS)_4^- + CN^- = Cr(NH_3)_2(NCS)_3(CN)^- + SCN^- \quad (7)$$

The presence of such a reaction should show up as an increased rate of thiocyanate release in the presence of cyanide ion, and, accordingly, a search was made for this effect using KR in methanol solution at 50.0°. As shown in Fig. 6, the rate of appearance of free thiocyanate, which corresponded to a k_{app} of 3.94×10^{-3} min.$^{-1}$ in methanol alone, increased to 6.40×10^{-3} min.$^{-1}$ in the presence of 0.01 *M* cyanide. It was at first thought that reaction 7 was indeed occurring, but, as shown in the figure, exactly the same increased rate was obtained for *any* cyanide ion concentration in the range studied (0.01 to 0.08 *M*). An additional run was then made, in which the methanol solution, initially free of cyanide, was divided into three portions. The thiocyanate release, of course, followed the lower line in Fig. 5 for all three. After 40 minutes, portion 1 was made 0.015 *M* in cyanide, whereupon the amount of free thiocyanate immediately increased up to the value *for that time* as given by the upper line (see the dotted arrow in the figure), and then followed the *upper* line thereafter. After 70 minutes, portion 2 was made 0.015 *M* in cyanide, and, again, the amount of free thiocyanate present immediately increased to the value given by the upper line and thereafter followed that line.

The above results made it clear that the additional thiocyanate released in the presence of cyanide came from a reaction of the latter with *products* of some rate-determining step which itself was not affected. It was necessary to conclude, therefore, that the rate of the direct bimolecular substitution reaction 7 was undetectably small in methanol.

A few runs were carried out in 10% methanol–nitromethane as solvent. Using 0.1 *M* potassium cyanide, the value of k_{app} increased from 1.3×10^{-3} min.$^{-1}$ to 4.0×10^{-3} min.$^{-1}$ at 60.3°. Again, cyanide may have been reacting with a reaction product, but an additional possibility was that it might have been acting as a base relative to the pseudo-acid nitromethane, *i.e.*

$$CH_3NO_2 + CN^- = CH_2NO_2^- + HCN \quad (8)$$

in which case the actual reactant might have been $CH_2NO_2^-$. In aqueous media, the neutralization of nitromethane is nearly complete at the *p*H of 0.1 *M* potassium cyanide.[10] If the above explanation were correct, then other basic anions should similarly affect k_{app}, and this was found to be the case. With 0.1 *M* potassium hydroxide, k_{app} was again 4.0×10^{-3} min.$^{-1}$, while in 50% methanol–nitromethane, the presence of 0.1 *M* sodium acetate increased k_{app} from 6.2×10^{-3} min.$^{-1}$ to 0.01 min.$^{-1}$ at 60.3°. The course of these reactions was not studied in detail, so it is not known how the products differed from those in methanol solution alone.

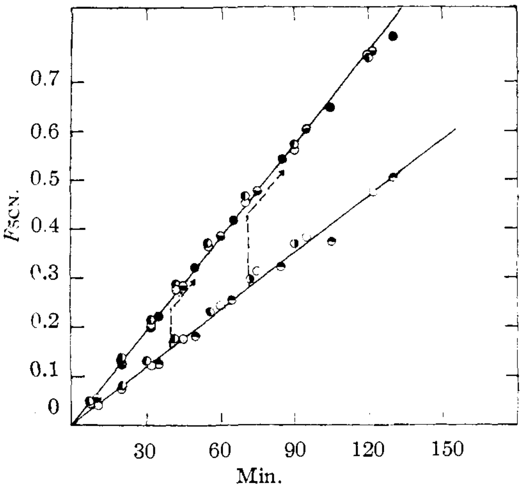

Fig. 6.—Rate of solvation of KR in methanol at 50.0° as a function of cyanide concentration. Upper line: ●, 0.01 KR; 0.01 KCN; ◒, 0.02 KR, 0.02 KCN; ○, 0.01 KR, 0.03 KCN; ◐, 0.01 KR, 0.08 KCN. Lower line: ◐, ◒, 0.01 KR; ○, 0.02 KR. Dotted lines: sequence taken on addition of KCN after initial periods of 40 to 70 minutes.

Since Brown, *et al.*,[11] believed that azide ion underwent a direct bimolecular substitution reaction with *cis*-$Coen_2Cl_2^+$ in methanol, this ion was tested in our system. With 0.01 *M* KR and 0.032 *M* NaN_3, in water at 50.5°, there was no significant change in the rate of thiocyanate release or in the total free azide concentration. The same observation was made for pure methanol as solvent and for 50% methanol–nitromethane. Similarly, in the case of 0.01 *M* KR and 0.03 *M* KI, either in water or in methanol, at 50°, there was no change in the rate of thiocyanate release and no change in free iodide concentration.

In summary, no evidence for direct bimolecular substitution could be found either in water or in methanol, in the case of cyanide, azide or iodide ions. In nitromethane containing media, cyanide, hydroxide and acetate but not azide increased k_{app}, so the effect correlated better with the basicity of the ion than with its nucleophilic character.

Discussion

The principal observations concerning the solvation reactions may be summarized as follows. The reactions followed the sequence 1. . .4, with the first step being accompanied by a prompt equilibration of the product species I with species II and III. The extent to which this occurred was about the same in water as in methanol but decreased with decreasing methanol content in the case of mixed methanol–nitromethane media. The rates, either in terms of k_{app} or k_1, were remarkably similar in all ROH type solvents, *i.e.*, water, methanol and ethanol, and extremely small in other solvents, *i.e.*, dioxane and nitromethane. The difference in behavior was related to the presence or absence of the –OH function, rather than to general solvent quality. Thus nitromethane is a better solvent than water for KR, while dioxane is a much poorer solvent. The importance of the –OH function in the solvent was also demonstrated by the observation that k_{app} was affected more by replacing H_2O by D_2O than by whether R in ROH was H, CH_3 or

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[10] E. W. Miller, A. P. Arnold and M. J. Astle, THIS JOURNAL, **70**, 3971 (1949).

[11] D. D. Brown and C. K. Ingold, *J. Chem. Soc.*, 2680 (1953).

C_2H_5 (see Fig. 2). Moreover, in mixed ROH–non-ROH solvents (methanol–nitromethane and methanol–dioxane), the solvation rate was approximately proportional to the ROH content, *i.e.*, reaction 1 was essentially first order in ROH. The lack of importance of the nature of the R group and of general solvent quality was further borne out by the uniformity in activation energies for the solvation reaction in various media.

The above observations appear to rule out the pure SN1 type of mechanism, *i.e.*, unimolecular dissociation to a pentacoördinated intermediate. The transition state would not contain solvent in such a case, contrary to the important kinetic role of solvent actually observed. Nor could this role be attributed to general solvent effects since, if this were the case, a parallel should have been observed with the solubility of KR in the various media.

The data also appear to rule out a pure SN2 or direct bimolecular substitution mechanism. Reactions by such a mechanism should be favored in proportion to the nucleophilic character of the displacing agent, and if the solvation reaction 1 were occurring merely by virtue of the nucleophilic character of the solvent molecule, then such strongly nucleophilic ions as cyanide and azide should have been able to compete successfully with the solvation process, contrary to observation. In the case of cyanide, it is particularly significant that while this ion was able to displace thiocyanate from the *products* of the rate-determining step 1, it was unable to do so directly from KR. In other words, the action of cyanide must have been to compete with thiocyanate for the displacement of *solvent* from product species rather than to compete with solvent for the displacement of thiocyanate, *i.e.*, the process must have been of type (9) rather than (10).

$$Cr(NH_3)_2(S)_2(NCS)_2{}^+ + CN^- = Cr(NH_3)_2(S)(CN)(NCS)_2 + S \quad (9)$$

$$Cr(NH_3)_2(S)_2(NCS)_2{}^+ + CN^- = Cr(NH_3)_2(S)_2(CN)(NCS)^+ + SCN^- \quad (10)$$

Our findings thus do not support the presence of a general bimolecular displacement process, but only of the very specific one in which an acido group is displaced by solvent, or *vice versa*. This is essentially the conclusion reached by Adamson and Basolo[6] in the case of $Co(NH_3)_5Cl^{++}$, namely, that while the aquation was bimolecular, it occurred by virtue of specific hydrogen bonding interaction between the –OH function of the solvent (water in this case) and the acido group, leading to a *front side* displacement.[12] The transition state in the present case would by this hypothesis be of the type shown in Fig. 7, in which hydrogen bond bridging by ROH between an ammine hydrogen and a thiocyanate group serves to facilitate the opening up of the octahedral configuration. The need for the –OH function in one of the two interchanging ligands is thus apparent, as is the explanation for the relatively large effect of replacing hydrogen by deuterium, as contrasted with the relatively small one of varying the R group. This picture is also consistent with the lack of dependence of the activation energies on the nature of the R group in ROH type solvents. Furthermore, the slowness of substitution reactions in nitromethane is now understandable, while it would not be expected if an SN1 mechanism prevailed. In the latter case, the formation of a pentacoördinated intermediate should be about as favorable in nitromethane as in methanol (the solubility ratios of KR and of $Cr(NH_3)_3(NCS)_3$ are about the same in the two solvents), and substitution by nucleophilic ions should have occurred. If, however, the actual mechanism is as depicted in Fig. 7, then nitromethane would be expected to be inert in that it would not form hydrogen bond bridges nor would it constitute a good ligand. The acido group-solvent displacement process would thus not be expected to take place, and the reaction path 12, 13 discussed below would not be available for the introduction of nucleophilic substituents such as azide.

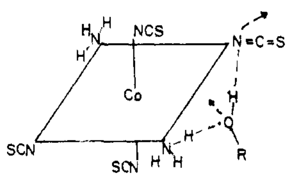

Fig. 7.—Intermediate for the SN2 FS mechanism.

The front side displacement mechanism, which for convenience will be designated SN2 FS, together with the SN2 IP ("ion pair") and the SN2 CB ("counter base") paths accounts fairly well for the general observations on substitution reactions in octahedral complexes. In particular, the net displacement reaction where neither group is of the

$$M\text{-}X + Y^- = M\text{-}Y + X^- \quad (11)$$

ROH type can take place *via* the SN2 FS process, by virtue of competitive displacement of S by X^- and Y^-

$$M\text{-}X + S \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} M\text{-}S + X^- \quad (12)$$

$$M\text{-}S + Y^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M\text{-}Y + S \quad (13)$$

where S now denotes a solvent or other molecule of the ROH type. Where the amount of MS present is small, S acts essentially as a catalyst for the displacement of X^- by Y^-, and steady state kinetics may be applied, giving the rate law

$$d(MY)/dt = \frac{k_1k_2(MX)(Y)}{k_{-1}(X) + k_2(Y)} \quad (14)$$

Where k_2 is large, the rate of substitution of Y^- for X^- will be independent of the concentration or nature of Y^-, and the mechanism will *appear* to be SN1. Where k_{-1} is large, there will be a progressive retardation of the reaction as X^- builds up in concentration. It is this situation, for example, which exists in the case of positively charged complex ions in methanolic media—very little solvation product develops and consequently equation 14 applies. In particular, precisely the same effects used to argue an SN1 mechanism for anion substitution in $Coen_2Cl_2{}^{++}$ in methanol[11] would equally well sup-

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[12] F. Basolo does not agree with this interpretation; see, for example, ref. 3.

port an SN2 FS process with solvent. Clearly, in situations of this type, the use of non-aqueous solvents obscures without in any way eliminating the importance of the solvent as a catalyst for net displacement reactions.

Another type of evidence that has been cited in favor of the SN1 mechanism is that the aquation rates of acidoammine complexes increases as the bulkiness of the ammine groups is increased through methyl or other substitution.[13] Here again, however, the same effect would be expected were the process SN2 FS. Thus most of the arguments for an SN1 process do not actually distinguish between it and bimolecular front side displacement. An important exception is the observation by Mathieu[14] that the solvation process is stereospecific; he found that $Coen_2NH_3Br^{++}$ underwent mutarotation to the corresponding monoaquo complex without racemization and with retention of configuration. While this would be expected if the process were SN2 FS, it is difficult to see why the pentacoördinated intermediate demanded by an SN1 mechanism should retain optical activity.

Not only does the available evidence indicate that reactions considered to be SN1 are actually SN2 FS, but, in addition, certain reactions thought to be normal SN2 in type may well belong to the more special category. For example, Basolo[3] considered that the fact that the aquation rate of $Coen_2NO_2Cl^+$ was about normal rather than very slow to be evidence that the mechanism was SN2. Actually the NO_2^- should form good hydrogen bond bridging with water, and the rate would not be expected to be abnormal if the SN2 FS mechanism were involved.

On the other hand, those substitution reactions of type 11 whose rate is first order in Y^- are presumably not SN2 FS. While they could be normal SN2 in type, it probably is significant that they occur only where Y^- is basic (OH^- in water, CH_3O^- in methanol, in the case of acidopentammines and tetrammines, and CN^-, OH^- and $C_2H_3O_2^-$ in the case of KR in nitromethane containing solvents), or under circumstances such that ion pair formation between MX and Y^- is likely (see ref. 6). Such reactions may thus be SN2 CB or SN2 IP in nature; their detailed discussion is beyond the scope of the present paper.

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[13] R. G. Pearson, C. R. Boston and F. Basolo, THIS JOURNAL, **75**, 3089 (1953).

[14] J. P. Mathieu, *Bull. soc. chim. France*, [5] **4**, 687 (1937).

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New Preparation for Chromyl Fluoride and Chromyl Chloride

BY GERALD D. FLESCH AND HARRY J. SVEC

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Uncontaminated chromyl fluoride and chromyl chloride have been prepared by the reaction of dry CrO_3 with CoF_3 or $AlCl_3$. The mixed halide, CrO_2FCl, was produced by the metastatic reaction of the two pure compounds. The equilibrium constant for this reaction and the infrared spectra of the mixed halide are presented.

Methods for preparing chromyl fluoride[1] and chromyl chloride,[2] as well as many of their physical properties, are well described in the literature. Many of these methods of preparation have been attempted here but have been found undesirable for various reasons. The methods often are not adaptable to small scale preparations, involve reactants difficult to handle or involve side reactions which result in mixtures difficult to purify. Simpler, more direct methods of preparation capable of producing a purer product were needed. Methods have been developed which fulfill these needs. Necessary manipulations in these methods are easy, handling of materials is reduced to a minimum, and an uncontaminated product results. The general procedure involves mixing dry CrO_3 with an appropriate dry halogenating agent, heating the mixture in a glass or an all-metal vacuum apparatus and collecting the chromyl halide in a trap cooled in a bath of solid CO_2–trichloroethylene slush.

The mixed halide, CrO_2ClF, was prepared by combining pure CrO_2F_2 with pure CrO_2Cl_2. Its infrared spectrum was determined and a tentative equilibrium constant, K_{liq}, was determined for the reaction

$$CrO_2F_2 + CrO_2Cl_2 \rightleftharpoons 2CrO_2ClF \qquad (1)$$

Experimental

Apparatus.—The vacuum pumping system to which the apparatus was attached consisted of a mechanical pump, mercury diffusion pump, liquid nitrogen cold trap, thermocouple vacuum gage and packless, bellows type valves (Hoke M482). Because of the corrosive nature of the reactants and products, the reaction apparatus was made of copper, nickel, monel and stainless steel. It consisted of three pieces, a monel reaction tube, a copper connecting tube and a copper U-tube fitted with Hoke valves at either end. Stainless steel or monel fittings (Hoke S24) were used to join the three pieces into a unit and connect the unit to the vacuum system. The U-tube served as the sample collector and storage vessel.

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[1] (a) K. Fredenhagen, *Z. anorg. allgem. Chem.*, **242**, 23 (1939); (b) H. V. Wartenburg, *ibid.*, **247**, 135 (1941); (c) K. Wiechert, *ibid.*, **261**, 315 (1950); (d) A. Engelbrecht and A. V. Grosse, THIS JOURNAL, **74**, 5262 (1952).

[2] H. H. Sisler, "Inorganic Syntheses," W. C. Fernelius, ed., Vol. II, 1st Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 205.