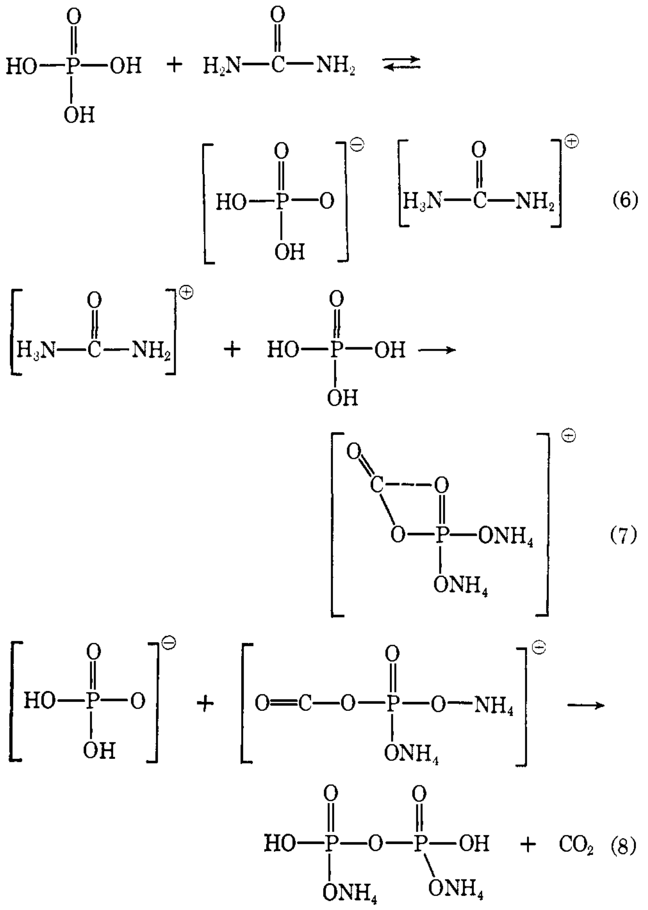
Table VII. Degradation Rate of Ammonium Polyphosphate in 15% Solutions

	100°		60°	
	pH 4.5	pH 6.0	pH 4.5	pH 6.0
First-order rate const, min^{-1}	5.5×10^{-4}	3.3×10^{-5}	4.9×10^{-5}	2.6×10^{-6}



maintain the water vapor pressure below the APP equilibrium value. This approach was tried by heating a thin layer of monoammonium orthophosphate to 350° under a flow of dry ammonia gas for a period of a week, and indeed, some form II APP was found in the product.

The use of urea as a dehydration and ammoniating agent to condense polybasic acids seems to have wide applicability. Urea is a good fluxing agent and often forms a low-temperature eutectic melt with salts. For a reaction involving solids, this property can speed up the usual slow diffusional rate-controlling step.

One conceivable mechanism for such reactions is eq 6–8, using the condensation of H_3PO_4 as an example. In any case, it seems probable that the mechanism is something other than the reaction of urea with free water to drive a simple condensation between molecules of acid because these reactions proceed at much lower temperatures than the simple acid condensations. Indeed, form I APP was prepared during this investigation by heating $NH_4H_2PO_4$ and urea at 118° in a covered dish. Other examples of these low-temperature condensations are the preparation of alkyl ammonium polyphosphate from alkyl dihydrogen phosphate and urea at 120–200°[28] and the preparation of ammonium pyrosulfate from sulfuric acid and urea at 140°.[29]

Acknowledgment. The help of Tom Taulli in obtaining the thermochemical data is appreciated.

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The Solid-State Deamination of Tris(ethylenediamine)- and Tris(propylenediamine)chromium(III) Thiocyanate

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Abstract: The solid state deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ to the corresponding dithiocyanato compounds has been studied isothermogravimetrically. The reaction is catalyzed by ammonium thiocyanate and amine hydrothiocyanates and is first order in catalyst over a wide range of catalyst/salt ratios. Activation energies for the uncatalyzed and catalyzed deamination of $[Cr(en)_3](NCS)_3$ are 47.4 ± 2.4 and 33.1 ± 1.6 kcal/mol, respectively, while those for the deamination of $[Cr(pn)_3](NCS)_3$ are 55.2 ± 2.8 and 44.6 ± 2.2 kcal/mol. The mechanism of the deamination is discussed in terms of the acid catalysis and kinetic observations.

It has been known for many years that $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ (where en = ethylenediamine and pn = propylenediamine) each lose a molecule of ligand on heating in the solid state and are converted to *trans*-$[Cr(en)_2(NCS)_2]NCS$ and *trans*-$[Cr(pn)_2(NCS)_2]NCS$, respectively.[1,2] The study by Rollinson and Bailar showed that the solid-state reaction is catalyzed by ammonium thiocyanate. This has been,

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(2) C. L. Rollinson and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **66**, 641 (1944).

in fact, the usual method of preparing these dithiocyanato complexes.[3] Bear and Wendlandt studied these reactions as well as the deamination of the corresponding chloro complexes by thermogravimetric and differential thermal analysis.[4] They reported activation energies of 34 ± 3 and 53 ± 5 kcal/mol for the deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$, respectively, in the absence of a catalyst and 18 ± 2 and 41 ± 3.5 kcal/mol, respectively, when NH_4SCN was present. Other workers investigating the deamination of $[Cr(en)_3]Cl_3$ found that while this reaction is catalyzed by NH_4Cl, amine hydrochlorides are also effective as catalysts.[5] These studies were made by heating a suspension of the solid in a boiling inert organic solvent and showed that the deamination is catalyzed by the acidic ion of the protonated amine. The rate at which the liberated ethylenediamine is swept out of the reaction vessel also affects the rate of deamination.

This report describes the results of some kinetic studies on the deamination of solid $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$.

Experimental Section

Preparation of Compounds. The compounds $[Cr(en)_3]_2(SO_4)_3$ and $[Cr(pn)_3]_2(SO_4)_3$ were prepared by the method of Rollinson and Bailar.[6] The $[Cr(en)_3](NCS)_3$ was prepared from the sulfate by dissolving 100 g of the sulfate in 275 ml of warm water and adding 147 g of solid ammonium thiocyanate. The product was recrystallized from water, washed with alcohol and ether, and air dried. *Anal.* Calcd for $[Cr(en)_3](NCS)_3 \cdot H_2O$: Cr, 12.27; C, 25.50; H, 6.13; N, 29.65; S, 22.68. Found: Cr, 12.73; C, 25.43; H, 6.13; N, 29.66; S, 22.85.

The $[Cr(pn)_3](NCS)_3$ was prepared by dissolving 100 g of $[Cr(pn)_3]_2(SO_4)_3$ in warm water, filtering, and adding 110 g of solid ammonium thiocyanate. The product was recrystallized from water, washed with alcohol, acetone, and ether, and air dried. *Anal.* Calcd for $[Cr(pn)_3](NCS)_3$: Cr, 11.58; C, 32.13; H, 6.74; N, 28.10. Found: Cr, 11.86; C, 32.02; H, 6.80; N, 27.63.

The amine hydrothiocyanate catalysts were prepared by a procedure similar to that of Mathes, Stewart, and Swedish.[7] Piperidine hydrothiocyanate was prepared by heating 17 g (0.20 mol) of piperidine with 15.4 g (0.20 mol) of ammonium thiocyanate added in small portions while stirring the piperidine. After the addition was complete, the mixture was heated at 85° for 2 hr. After the evolution of ammonia ceased and the mixture was cooled, the product was recrystallized from acetone and washed with cold acetone. A white solid melting at 94–95° was obtained. *Anal.* Calcd for $C_6H_{12}N_2S$: C, 49.96; H, 8.32; N, 19.43. Found: C, 49.95; H, 8.37; N, 19.04.

Ethylenediamine dihydrothiocyanate was prepared by heating 12.4 g (0.21 mol) of ethylenediamine with 33 g (0.43 mol) of ammonium thiocyanate, added in small portions. After the addition was complete, the mixture was heated at 125° for several minutes. After cooling, the product was recrystallized twice from alcohol and washed with cold ethanol. The white crystalline product melts at 144–145° and darkens slowly on exposure to light. *Anal.* Calcd for $C_4H_{10}N_4S_2$: C, 26.95; H, 5.62; N, 31.43. Found: C, 27.29; H, 5.69; N, 31.85.

Preparation of Samples and Kinetic Measurements. Samples of complex containing known amounts of catalyst were prepared by adding the desired volume of an acetone solution of known catalyst concentration to a weighed sample of crystalline complex. The acetone was then removed by evaporation under reduced pressure in a vacuum desiccator. This procedure partially dehydrates the $[Cr(en)_3](NCS)_3 \cdot H_2O$, and the extent of dehydration has been taken into account in calculating the theoretical weight loss percentages corresponding to complete conversion of the samples to *trans*-$[Cr(en)_2(NCS)_2]NCS$. Acetone solutions of piperidine hydrothiocyanate and potassium thiocyanate were used in the same way to add these materials to the samples of complexes. Ethylenediamine dihydrothiocyanate was added as a solution in ethanol.

The rates of deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$ were followed by determining the loss of weight of samples suspended in an oil bath at the desired temperature. The method is essentially an isothermal thermogravimetric method. The progress of the reaction was followed from several samples of the same initial composition which were removed from the oil bath at the desired time intervals. The desired number of 0.10–0.15-g samples of the material to be used in a run were weighed into carefully cleaned 12 × 75 mm Pyrex tubes. These were placed in an aluminum holder, and the entire assembly was suspended in the oil bath. Zero time was taken as the time of immersion. The bath temperature remained constant to within about ±0.2°. Sample tubes were removed at the desired intervals, carefully cleaned with benzene, and the weight loss determined. The fraction of $[Cr(en)_3](NCS)_3$ or $[Cr(pn)_3](NCS)_3$ deaminated was calculated by comparing the actual weight loss with that calculated for complete conversion of the sample to the dithiocyanato compound.

Treatment of Kinetic Data. The usual form of the rate expression for an acid-catalyzed reaction[8] can easily be modified for the solid-state reaction studied here to give

$$-\ln(1 - \alpha) = (k_0 + k_1c)t \qquad (1)$$

which has the form of a frequently encountered expression for solid-state reactions.[9,10] In eq 1, α is the fraction of the complex deaminated, k_0 is the rate constant for the uncatalyzed reaction, k_1 is the rate constant of the catalyzed reaction, and c is the concentration of the acid catalyst. The simple expression of eq 1 does not fit the data for the reactions studied here over a large extent of reaction. No attempt was made to find empirical expressions which would exactly fit the data for reactions proceeding 70–80% toward completion.

If α is fairly small (less than about 0.5), $-\ln(1 - \alpha) \simeq \alpha$ and a plot of α *vs.* t should be linear. Accordingly, plots of α *vs.* t, for a given amount of acid catalyst, have been found to be linear up to 50–60% completion. The plots of α *vs.* t have been used to determine which data were to be used in determining the initial rate for a given run. The method of initial rates has been used, and these were calculated using a least-squares routine programmed for an IBM 1620 computer. Initial rates were fitted to the rate laws by this least-squares routine, as well as the rate data to an Arrhenius plot for calculation of the activation energies. Errors were estimated by the procedures of Benson to be about ±6% for the initial rate determinations and about ±5% for the activation energy determinations.[11]

Results

The amount of hydrate water remaining in the $[Cr(en)_3](NCS)_3$ after the addition of the catalyst varies but all samples used in a given run were identical in water content. The calculated weight loss for samples of the monohydrate converted completely to *trans*-$[Cr(en)_2(NCS)_2]NCS$ is 18.4% and for the conversion of anhydrous $[Cr(en)_3](NCS)_3$ to the dithiocyanato salt, 14.7%. The weight loss in all runs varied between these limits and averaged about 15–16% when deamination was complete. The $[Cr(pn)_3](NCS)_3$ was found to be anhydrous; complete conversion to *trans*-$[Cr(pn)_2(NCS)_2]NCS$ corresponds to a weight loss of 16.5%.

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Table I. Initial Rates of Deamination of $[Cr(en)_3](NCS)_3$ at Several $NH_4SCN/[Cr(en)_3](NCS)_3$ Mole Ratios, C/S[h]

$10^2C/S$	Initial rate[a] × 10^5, sec^{-1} 130°	125°	110°
0.00[b]	0.647		
0.00[c]	0.628		
0.00[d]	0.617		
0.367	0.733	0.268[e]	
0.700	0.803	0.383[e]	
1.52	1.24	0.525	0.278[f]
2.05	1.64	1.24[e]	0.739[f]
2.57	2.61	1.88	0.708[f]
2.87	3.19		
3.00[g]	3.81	2.98	0.853
3.51	4.68	3.85	1.02
4.40	6.05	4.11	1.10
5.50[g]	8.26	5.13	1.31
6.68	10.5	7.46	1.67

[a] Estimated error is about ±6%. [b] $[Cr(en)_3](NCS)_3 \cdot H_2O$ with no treatment. [c] $[Cr(en)_3](NCS)_3 \cdot H_2O$ after dehydration. [d] $[Cr(en)_3](NCS)_3 \cdot H_2O$ dehydrated after addition of acetone. [e] Runs at 123°. [f] Runs at 115°. [g] Different batch of $[Cr(en)_3](NCS)_3$ used in these runs. [h] Catalyst/salt.

Table II. Initial Rates of Deamination of $[Cr(pn)_3](NCS)_3$ at Several $NH_4SCN/[Cr(pn)_3](NCS)_3$ Mole Ratios, C/S

$10^2C/S$	Initial rate[a] × 10^5, sec^{-1} 175°	165°	155°
0.00	2.96	0.653	
1.48	3.64	0.764	
2.69	5.17	1.00	0.389[b]
2.74	4.59	1.03	
4.40	7.39	2.15	0.603[c]
5.40	9.21	3.11	
5.83	9.33	2.96	
6.97	11.2	4.71	1.18
7.35		4.24	1.26
7.90		4.49	1.36
8.20	13.6		

[a] Estimated error is about ±6%. [b] For this run, $10^2C/S = 2.67$. [c] For this run, $10^2C/S = 4.49$.

Table III. Initial Rates of Uncatalyzed Deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$

Complex	Temp, °C	Initial rate[a] × 10^5, sec^{-1}
$[Cr(en)_3](NCS)_3$	135	0.647
$[Cr(en)_3](NCS)_3$	140	1.41
$[Cr(en)_3](NCS)_3$	145	2.39
$[Cr(en)_3](NCS)_3$	150	5.31
$[Cr(pn)_3](NCS)_3$	165	0.653
$[Cr(pn)_3](NCS)_3$	170	1.51
$[Cr(pn)_3](NCS)_3$	175	2.96
$[Cr(pn)_3](NCS)_3$	180	5.46

[a] Estimated error is about ±6%.

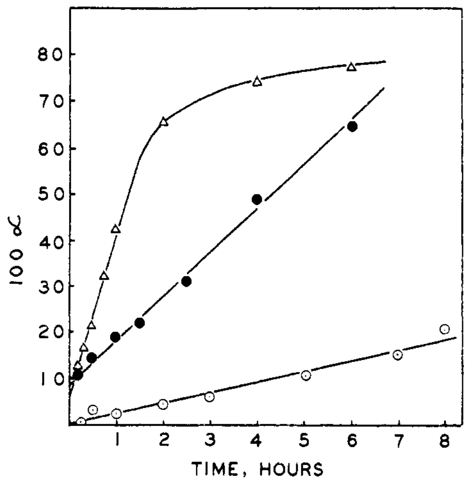

Figure 1. Typical rate plots for deamination of $[Cr(en)_3](NCS)_3$ catalyzed by NH_4SCN. Mole ratios of catalyst to salt are as follows: ○, 0.00; ●, 0.0257; △, 0.0668.

Typical curves of 100α (α = fraction of complex deaminated) *vs.* time for the deamination of $[Cr(en)_3](NCS)_3$ at 130° using different $NH_4SCN/[Cr(en)_3](NCS)_3$ mole ratios are shown in Figure 1. Some of the plots deviate from linearity after a short period of heating. In general, the plots are linear over several hours of reaction using the lower catalyst concentrations and temperatures. The linear portion of the curve for each run (in some runs the first few points and in others, all the points) have been used to calculate the initial rates, $d\alpha/dt$. The initial rates obtained using several $NH_4SCN/[Cr(en)_3](NCS)_3$ mole ratios are shown in Table I. Similar data for the deamination of $[Cr(pn)_3](NCS)_3$ are shown in Table II.

The rates of deamination of the complexes without a catalyst present are shown in Table III.

Rate data showing the effects of piperidine hydrothiocyanate, ethylenediamine dihydrothiocyanate, oxalic acid, and potassium thiocyanate on the deamination of $[Cr(en)_3](NCS)_3$ are shown in Table IV.

Table IV. Effects of Amine Hydrothiocyanates, Oxalic Acid, and Potassium Thiocyanate on the Initial Rate of Deamination of $[Cr(en)_3](NCS)_3$

Added compd	$10^2A/S$[a]	Temp, °C	Initial rate[b] × 10^5, sec^{-1}
KSCN	3.15	130	0.861
KSCN	6.40	130	0.964
$H_2C_2O_4$	4.76	130	7.15
PipHSCN[c]	2.75	130	3.59
PipHSCN	2.79	130	4.40
PipHSCN	5.32	130	6.87
PipHSCN	2.75	120	1.84
PipHSCN	2.79	120	1.84
PipHSCN	5.32	120	4.04
PipHSCN	2.75	110	0.975
PipHSCN	2.79	110	0.667
PipHSCN	5.32	110	1.20
$en(HSCN)_2$[d]	2.57	130	4.85
$en(HSCN)_2$	2.57	120	2.06
$en(HSCN)_2$	2.57	110	1.16

[a] A/S = mole ratio of added compound to complex. [b] Estimated error is about ±6%. [c] PipHSCN = piperidine hydrothiocyanate. [d] $en(HSCN)_2$ = ethylenediamine dihydrothiocyanate.

The rate data shown in Table I for runs at 130° were used to prepare Figure 2, which shows the relationship between rate and catalyst concentration. It is obvious from this figure that above a mole ratio of $NH_4SCN/[Cr(en)_3](NCS)_3$ of about 2×10^{-2}, the rate of deamination is proportional to the amount of catalyst. Similar first-order plots are obtained at the other temperatures. The linear portion of these plots of initial rate *vs.* catalyst/salt ratio have been used to evaluate the rate constants, k_1 of eq 1, by the method of least squares. These rate constants were used to evaluate activation energies for the deamination of $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3]$-

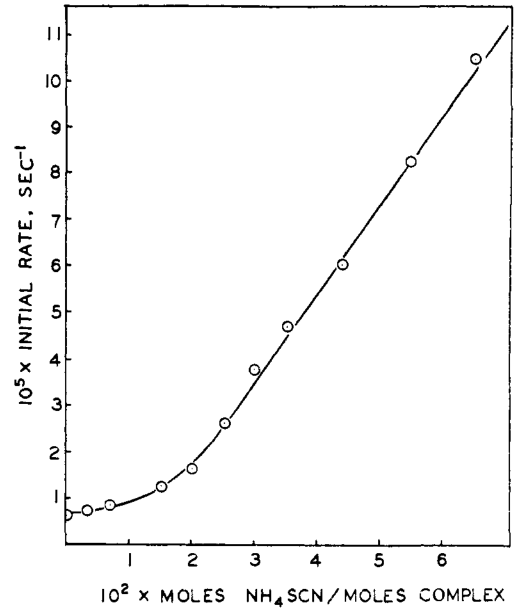

Figure 2. The rate of deamination of solid $[Cr(en)_3](NCS)_3$ at 130° as related to the $NH_4SCN/[Cr(en)_3](NCS)_3$ mole ratio.

$(NCS)_3$ both catalyzed by NH_4SCN and uncatalyzed. The results of these evaluations are shown in Table V.

Table V. Activation Energies for the Deamination of Solid $[Cr(en)_3](NCS)_3$ and $[Cr(pn)_3](NCS)_3$

Complex	Catalyst	Activation energy, kcal/mol This work[a]	Activation energy, kcal/mol Bear and Wendlandt[4]
$[Cr(en)_3](NCS)_3$	None	47.4 ± 2.4	34 ± 3
$[Cr(en)_3](NCS)_3$	NH_4SCN	33.1 ± 1.6	18 ± 2
$[Cr(pn)_3](NCS)_3$	None	55.2 ± 2.8	53 ± 5
$[Cr(pn)_3](NCS)_3$	NH_4SCN	44.6 ± 2.2	41 ± 3.5

[a] Errors are estimated to be ±5%.

For the NH_4SCN-catalyzed deamination of $[Cr(pn)_3](NCS)_3$, the rate at 155° for a catalyst/salt ratio of 2.67×10^{-2} does not lie in line with the other data at this temperature. Because of this, the rate constant for 155° is probably too low. Since this one point changes the rate constant at 155° considerably, the resulting change in the slope of the Arrhenius plot is fairly large. Ignoring this one point lowers the activation energy about 6 kcal/mol from the value obtained when all the data are used. When no catalyst is used, the initial rates at several temperatures were used directly to evaluate the activation energies. Rates of these uncatalyzed reactions are shown in Table III.

Discussion

Acid Catalysis of Deamination. Since HSCN is a strong acid, it seemed that the catalytic effects of salts of this acid other than the ammonium salt should be determined. This is especially important since it has been shown that amine hydrochlorides catalyze the deamination of $[Cr(en)_3]Cl_3$.[4,5] The rates shown in Table IV show clearly that piperidine hydrothiocyanate (PipHSCN) and ethylenediamine dihydrothiocyanate ($en(HSCN)_2$) are effective catalysts for the deamination of $[Cr(en)_3](NCS)_3$. The fact that the $en(HSCN)_2$ was prepared by the action of ethylenediamine on NH_4SCN at elevated temperatures shows that when NH_4SCN or PipHSCN is the original catalyst, it is quickly converted to enHSCN or $en(HSCN)_2$ with the evolution of an equivalent amount of ammonia or piperidine. The monohydrothiocyanate would probably form because there is a continuous evolution of ethylenediamine as the reaction proceeds. In either case, the catalytic species is a protonated ethylenediamine molecule.

The rates shown in Tables I and IV further show that when PipHSCN and NH_4SCN are used at comparable mole ratios, the rates of deamination are comparable. Although the same catalyst/salt mole ratios were not used, the approximate rates can be estimated from Figure 2 and a similar plot of the data at 110°. At a catalyst/salt mole ratio of 2.75×10^{-2}, the rates at 130 and 110° are 3.06×10^{-5} and 0.83×10^{-5} sec^{-1} for NH_4SCN as the original catalyst and 3.59×10^{-5} and 0.98×10^{-5} sec^{-1} for PipHSCN as the catalyst. At a catalyst/salt mole ratio of 5.32×10^{-2}, the rates at 130 and 110° are 7.95×10^{-5} and 1.25×10^{-5} sec^{-1} for NH_4SCN and 6.87×10^{-5} and 1.20×10^{-5} sec^{-1} for PipHSCN. These results indicate that there is little if any difference between these two initial catalysts.

It is apparent that when $en(HSCN)_2$ is the catalyst, the rates are higher than when NH_4SCN is used at the same mole ratio. If the rates of deamination are compared when the catalyst/salt ratio is 2.57×10^{-2}, the rate at 130° is about twice as large when $en(HSCN)_2$ is used as the catalyst as when NH_4SCN is used (4.85×10^{-5} and 2.61×10^{-5} sec^{-1}, respectively). The rate when $en(HSCN)_2$ is used should be divided by two to give a comparison based on equivalents of acid rather than moles. However, the rate of the uncatalyzed reaction is 0.63×10^{-5} sec^{-1} at 130°. Subtracting this gives the increase in rate due to catalysis (1.98×10^{-5} and 4.20×10^{-5} sec^{-1}, respectively, when NH_4SCN and $en(HSCN)_2$ are used). Dividing the catalytic rate for $en(HSCN)_2$ by two gives 2.10×10^{-5} sec^{-1} compared to 1.98×10^{-5} sec^{-1} when the same number of equivalents of NH_4SCN is used. One run made with oxalic acid as the catalyst was inconclusive owing to the rapid curvature of the plot α *vs.* time. Oxalic acid appears to be as effective as a monoprotic acid.

Mechanism of Deamination. The kinetic studies clarify some of the features of these thermal deaminations. These reactions are similar to the thermal deaminations of the corresponding chloro compounds in that they are acid-catalyzed solid-state reactions. The fact that *trans* products result from the thiocyanate complexes and *cis* products from the chloro complexes points to a major difference between the two cases. Catalysis by acidic ions implies that protonation of the diamine molecule is an essential feature of loosening it from the chromium ion and, as can be seen from Figure 2, the deamination is first order in catalyst over a wide range of catalyst concentration. The rates obtained when KSCN is present indicate that the thiocyanate ion does not significantly alter the rate of deamination. However, the amount of thiocyanate ion added as KSCN is very small compared to that already present as anion from the complex. The results indicate that the rate-determining step of the reaction depends more on the acid catalyst than on the anion. Avaliability of the anion in the solid lattice may also be a limiting factor in this situation, but it is evident that the effect of the thiocyanate ion added as part of the catalyst is insignificant compared to the effect of the acidic ion.

The loss of a bidentate ligand and its replacement by two monodentate anions would normally be expected to produce a *cis*-diacido complex. Such complexes are produced by the deamination of $[Cr(en)_3]Cl_3$ and $[Cr(pn)_3]Cl_3$, but the corresponding thiocyanate complexes yield *trans*-dithiocyanato products.[1] The *trans* effect in substitution reactions in square-planar complexes is well known and there have been several attempts to explain substitution in octahedral complexes by the *trans* effect.[12,13] Recently, an infrared study of nitrosylruthenium complexes showed a *trans*-directing influence of several ligands based on the Ru–NO stretching frequency. It was further shown that the *cis* effect was smaller than the *trans* effect, although too large to ignore.[14] Although these studies have dealt with other metals, they may have some validity for chromium(III) systems. Recently, evidence was reported for a *trans* effect in a chromium(III) reaction.[15]

The rate of deamination depends upon the rate at which metal–ligand bonds are broken and may involve electrophilic attack by the protonated amine catalyst; on the other hand, the protonation of the ligand could be subsequent to the breaking of a metal–ligand bond. First-order dependence on the acidic species present indicates that electrophilic attack is involved in the rate-determining step. This accounts for the activation energy of the catalyzed reactions being lower than those of the uncatalyzed reactions where the metal–ligand bond must be broken without the aid of protonation. A thiocyanate ion entering the coordination site vacated by the breaking loose of a protonated end of an ethylenediamine molecule might then exert a strong enough *trans* effect on the position *trans* to it that another ethylenediamine molecule has one end loosened. This would lead to a *trans* product. If the chloride ion exerts a strong *cis* effect or does not exert a strong *trans* effect, the bound end of the protonated ethylenediamine molecule may break loose and the second chloride enter there. This would give a *cis* product.

It is impossible at this time to assess the relative importance of these effects as they apply to the reactions studied here. It is also quite possible that these effects assume different proportions in solid-state reactions than in solution reactions. Structural isomerism of the products can be predicted by the assumption of either a strong *trans* effect by NCS^- or a strong *cis* effect by Cl^-.

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Electrochemical and Spectral Studies of Dimeric Iron(III) Complexes[1]

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Abstract: The electrochemical behavior of the monomeric ($EDTA\text{-}Fe^{III}OH^{2-}$) and dimeric ($(EDTA\text{-}Fe^{III})_2O^{4-}$) complexes present at equilibrium in the Fe^{III}–EDTA system at pH 9 has been characterized. Fast-sweep cyclic voltammetry in pH 9 buffered media reveals two reduction waves and a single anodic wave. Both the monomer and dimer, by a two-electron reduction, are reduced to ferrous monomer. In buffered media, slow-sweep linear voltammetry with thin-layer electrodes produces single cathodic and anodic waves because the dimer dissociates as the monomer is reduced. The rate constant for dissociation of dimer is estimated at 0.5 sec^{-1} from chronocoulometric measurements. A pathway involving solvent assistance is suggested as the mechanism of dimer breakup.

The formation, hydrolysis, and dimerization of ferric complexes of ethylenediaminetetraacetate (EDTA) and related aminocarboxylic acids have received considerable attention. A comprehensive study of the latter two phenomena with references to prior work has been reported by Gustafson and Martell.[3] They have shown that the ferric complexes of EDTA, N-hydroxyethylethylenediaminetriacetate (HEDTA), cyclohexanediaminetetraacetate (CDTA), and nitrilotriacetate (NTA) are hydrolyzed by alkali to give equilibrium mixtures of monohydroxy monomers and binuclear complexes; in a subsequent step, dihydroxo mononuclear complexes are formed. The observed magnetic and spectral properties of the dimer in the $HEDTA\text{-}Fe^{III}$ system led us to formulate its structure as containing an approximately linear Fe–O–Fe bridging unit.[4] The proposed Fe–O–Fe bridging unit in the dimer has been verified by an X-ray structural determination of the salt $[enH_2^{2+}][(HEDTA\text{-}Fe^{III})_2O]\cdot 6H_2O$, where enH_2^{2+} is

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