[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Inorganic Chemistry in Trifluoroacetic Acid[1]

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In the investigation of inorganic reactions in anhydrous trifluoroacetic acid, the effects of anhydrous HCl, H_2S, $HClO_4$, H_2SO_4, SO_3, H_3PO_4, HPO_3, Cl_2, CrO_3, $KMnO_4$ and SO_2 upon 25 dissolved trifluoroacetates of metals were studied. The reactions obtained from H_2S closely paralleled those obtained in acidic aqueous systems. More chlorides, perchlorates and bisulfates were preciptated from trifluroacetic acid than from water. The reactions with H_2SO_4 were in most cases rapid and complete. By contrast, the reactions with SO_3 were slow and only partially complete. Orthophosphoric acid produced precipitates slowly. Many of these precipitates were in the form of gels, suggesting polymer formation. The reagents CrO_3, Cl_2 and $KMnO_4$ acted as oxidizing agents, but more slowly than in water. Hydrogen peroxide decomposed in the presence of dissolved trifluoroacetates of metals to form water and oxygen. It also reduced Mn(VII) to Mn(II), and reacted with CrO_3 forming a blue-green solution of a peroxy–chromium compound. The slow reaction of $KMnO_4$ with trifluoroacetic acid produced the gases: CO_2, CF_3COF and COF_2, while Mn(VII) was reduced to Mn(III).

Trifluoroacetic acid is a good solvent for a wide variety of organic compounds, both aliphatic and aromatic.[2,3] Inorganic compounds also dissolve in trifluoroacetic acid[4] but in general to a lesser degree than in water. The solubility of inorganic salts in trifluoroacetic acid must be considered high, particularly when the low dielectric constant, 8.22 at 30°,[5] is taken into account. The low electrical conductivities[6] of salts when dissolved in trifluoroacetic acid illustrate that the acid is not a good ionizing solvent. Ionic type reactions do occur, however, and this study deals largely with such reactions.

Experimental

(I) **Reactions Occurring in the Solvent Trifluoroacetic Acid.**—The solvent, trifluoroacetic acid, as supplied by the manufacturer (Minnesota Mining and Manufacturing Co.) was used without further purification. The metal trifluoroacetate solutions were prepared from salts synthesized by Hara and Cady in their solubility studies.[4] Solutions of $AsOCF_3CO_2$ and the trifluoroacetates of NH_4^+, Sb(III), Bi(III), Cr(III), Fe(III), Pb(II), Li, Mn(II) and Hg(I) were prepared by the authors. Either the carbonates or oxides of the metals were caused to react with trifluoroacetic acid containing enough trifluoroacetic anhydride to combine with water formed by the reaction. The trifluoroacetates were then obtained as solids by evaporating away the solvent. With the exception of $AsOCF_3CO_2$ the products were crystalline solids. The arsenic compound formed a clear, colorless gel which took on a milky white appearance after standing for several weeks. When the temperature of the milky solid was raised to a few degrees above that of the room it again became colorless. No definite melting point could be observed. When possible, 0.1 *m* solutions were used. Saturated solutions were employed for substances of lower solubility than 0.1 *m*.

The reactants were either gases or compounds dissolved in trifluoroacetic acid. The gaseous reactants were HCl, H_2S, SO_3, Cl_2 and SO_2. Except for SO_3 the gases were dried by passage through concentrated sulfuric acid or by passage through a trap cooled with a Dry Ice–acetone bath. Sulfur trioxide was carried from a storage bulb to the reaction solution by dry N_2. The reactants which were dissolved in trifluoroacetic acid were reagent grade $HClO_4$, H_2SO_4, H_3PO_4, HPO_3, CrO_3, H_2O_2 and $KMnO_4$.

With H_2SO_4, H_3PO_4 or H_2O_2 an anhydrous solution was prepared by first dissolving an aqueous solution of known concentration in trifluoroacetic acid. A calculated amount of trifluoroacetic anhydride was then added to just react with the water present. A slight excess of trifluoroacetic anhydride was added to all solutions to maintain the anhydrous state. No anhydride was added to the perchloric acid solution. The anhydride was added, however, to the reaction mixtures either just before the addition of the perchloric acid solution or just after. The order of addition produced no observed effect upon the final results.

Table I lists the concentrations of the stock solutions of trifluoroacetates used for these studies. Table II lists the concentrations of solutions of the reactants. In the cases of HCl, H_2S, Cl_2 and SO_2 the concentrations were those reached by saturating trifluoroacetic acid with the gases at 26° under a total pressure of one atmosphere.

TABLE I

CONCENTRATIONS OF TRIFLUOROACETATES

Solute[a]	Molal concn. (mole/1000 g.)	Solute	Molal concn. (mole/1000 g.)
NH_4[a]	0.1	Mg	0.1
As(III)[a]	.015	Mn(II)	.025
Sb(III)	.015	Hg(II)	.1
Ba	.1	Hg(I)	.1
Bi(III)	.04	Ni(II)	.1
Cd	.1	K	.1
Ca	.09	Ag(I)	.1
Cr(III)	.06	Na	.1
Co(II)	.1	Sr	.1
Cu(II)	.1	Sn(IV)[a]	.1
Fe(III)	.03	Sn(II)	.06
Pb(II)	.1	Zn	.03
Li	.1		

[a] All the solutes are trifluoroacetates except As(III) and Sn(IV) which are $AsOCF_3CO_2$ and $SnCl_4$.

TABLE II

APPROXIMATE CONCENTRATION OF REACTANTS IN TRIFLUOROACETIC ACID

Reactants	Molal concn.	Reactants	Molal concn.
HCl	0.1	HPO_3	0.5
H_2S	0.2	Cl_2	.2
$HClO_4$	2	CrO_3	.008
H_2SO_4	15	H_2O_2	1.3
SO_3	?	$KMnO_4$	0.04
H_3PO_4	0.3	SO_2	0.6

The reactions were carried out at 25 to 26° in 10 × 75 mm. test-tubes using in each case between 0.5 to 1.5 ml. of a solution of a metal trifluoroacetate. The reactant solutions were added to the trifluoroacetate solutions dropwise until about a two-fold excess was present or until further addition ceased to yield an observable reaction. Gaseous reactants were bubbled through the trifluoroacetate solution until all observable reaction ceased. The reactions were carried out with a small drop of trifluoroacetic anhydride

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[1] Presented at Minneapolis meeting of the American Chemical Society, September 16, 1955. From the Ph.D. thesis of G. S. Fujioka, 1956.

[2] Booklet, "Trifluoroacetic Acid," Minnesota Mining and Manufacturing Co., Saint Paul, Minnesota, 1950.

[3] J. J. Katz, *Nature*, **174**, 509 (1954).

[4] R. Hara and G. H. Cady, THIS JOURNAL, **76**, 4285 (1954).

[5] W. Dannhauser and R. H. Cole, *ibid.*, **74**, 6105 (1952).

[6] J. H. Simons and K. E. Lorentzen, *ibid.*, **74**, 4746 (1952).

(*ca.* 0.05 g.) added to the reaction vessel to ensure anhydrous conditions at all times.

Precipitates formed by the reactions were concentrated by centrifugation, washed with trifluoroacetic acid by decantation, and dried in an oven at 105°. The remaining solid was analyzed in most cases. The supernatant liquid was evaporated, and the residue, if any, was dissolved in water and qualitatively analyzed for both the anion and cation. A designation of "Complete," "Nearly Complete" or "Partial" was placed on the extent of a particular precipitation reaction depending upon whether the qualitative tests showed the metallic ion in question to be (a) absent, (b) present in trace quantity, (c) present in appreciable amount.

Table III lists the precipitates obtained in the reactions of hydrogen chloride, hydrogen sulfide and perchloric acid and the solutes listed in Table I. It is possible that some of the precipitates may have contained trifluoroacetic acid of solvation.

Many analyses of the precipitates resulting from reactions with anhydrous sulfuric acid indicated the presence of both acid and normal sulfates. It appears unlikely that two sulfate species were precipitated from the reaction mixture. It is more probable that some of the precipitated acid sulfates were partially converted to normal sulfates while being washed with pure trifluoroacetic acid. Table IV lists the solutes that gave a sulfate precipitate. The table also gives the mole percentages of acid and normal sulfate found by analysis.

TABLE III

REACTIONS OF TRIFLUOROACETATES IN TRIFLUOROACETIC ACID

Reactant	Product
HCl	Chloride ppt.: Reaction, complete: Cd(II), Cu(II), Pb(II), Hg(II), Hg(I), Ni(II), Zn(II). All the ppt. colors were white except for Ni(II) which was amber Reaction, nearly complete: Bi(III), Co(II), Mn(II), Sn(II). The Co(II) ppt. was light blue, but the others were white Reaction, partial: Fe(II), olive color Colloidal ppt.: Ag(I), white, orange CrO_3 soln. was converted to a red soln. probably CrO_2Cl_2
H_2S	Sulfide ppt.: Reaction, complete: Sb(III), Cd(II), Cu(II), Hg(II), Hg(II) and Hg from Hg(I), Ag(I) Reaction, nearly complete: Fe(II) soln. and S from Fe(III), Sn(II), Zn(II) Reaction, partial: Bi(III) Colloidal ppt.: As(III), orange CrO_3 soln. was converted to a green soln. of Cr(III) and H_2SO_4 The colors of the sulfides were the same as the colors obtained from pptn. from aqueous media
$HClO_4$	Perchlorate ppt.: Reaction, complete: K(I) Reaction, nearly complete: NH_4^+, Cd(II), Hg(I), Ag(I), Na(I), Sr(II), Sn(II), Zn(II) Reaction, partial: Sb(III), Ba(II), Bi(III), Cr(III), Co(II), Cu(II), Fe(III), Pb(II), Mg(II), Mn(II), Hg(II), Ni(II) Colloidal ppt.: As(III) (solid not identified) Cobalt perchlorate was pink, copper perchlorate was light blue, nickel perchlorate was light green. All the other perchlorates were white

Sulfur trioxide precipitated most of the metals which reacted with dissolved sulfuric acid. A few sulfates were precipitated which were not brought down by sulfuric acid. Sulfur trioxide is very soluble in trifluoroacetic acid and is known to react with the acid to produce trifluoroacetic anhydride and sulfuric acid. With a high concentration of SO_3 some of the sulfuric acid may be converted to pyrosulfuric acid. Some of the precipitates were normal sulfates. Others were either acid sulfates or pyrosulfates or mixtures. As a sample was dried in the oven before analysis it had a chance to absorb water which would convert a pyrosulfate to an acid sulfate. On this account the analyses did not clearly characterize all of the precipitates. On the basis of the metal to sulfate ratio and on this alone the compositions of the precipitates are given in Table V in terms of the % of normal sulfate and the % of pyrosulfate. Table V lists: (1) the trifluoroacetates that gave precipitates with SO_3, (2) the weight per cent. of the cation and of the sulfate ion found in the precipitate, (3) the molar ratio of the cation to the sulfate, (4) the possible formula or formulas that could fit this molar ratio (assuming pyrosulfate and not acid sulfates to be present).

Table VI lists the reactions obtained with orthophosphoric acid and Table VII gives the reactions obtained with metaphosphoric acid. The high phosphate content of many of the precipitates suggests that in those cases polyphosphates were formed. The precipitates produced by orthophosphoric acid were generally slow in forming and often they were in the form of gels. The precipitate obtained from stannic chloride and orthophosphoric acid formed a foam and expanded to about 50 times its original volume when it was dried at 105°.

TABLE IV

REACTIONS OF TRIFLUOROACETATES WITH SULFURIC ACID

Trifluoroacetate	Ppt. formula[a]	Ppt. color	Extent of reaction
Sb(III)	$Sb_2(SO_4)_3$	White	Nearly complete
Ba	$BaSO_4$	White	Complete
Bi(III)	$Bi(HSO_4)_3$, 75%; $Bi_2(SO_4)_3$, 25%	White	Nearly complete
Cd	$CdSO_4$, 90%; $Cd(HSO_4)_2$, 10%	White	Complete
Ca	$CaSO_4$	White	Complete
Co(II)	$CoSO_4$	Pink	Complete
Cu(II)	$CuSO_4$, 84%; $Cu(HSO_4)_2$, 16%	White	Complete
Fe(III)	$Fe_2(SO_4)_3$	White	Complete
Pb(II)	$PbSO_4$, 57%; $Pb(HSO_4)_2$, 43%	White	Complete
Li	$LiHSO_4$	White	Partial
Mg	$Mg(HSO_4)_2$	White	Complete
Mn(II)	$MnSO_4$, 50%; $Mn(HSO_4)_2$, 50%	White	Complete
Hg(II)	$HgSO_4$	White	Nearly complete
Hg(I)	Hg_2SO_4	White	Nearly complete
Ni(II)	$NiSO_4$, 55%; $Ni(HSO_4)_2$, 45%	Pale green	Complete
Ag(I)	$AgHSO_4$, 70%; Ag_2SO_4, 30%	White	Partial
Sn(II)	$SnSO_4$	White	Nearly complete
Sr	$SrSO_4$	White	Complete
Zn	$ZnSO_4$	White	Complete

[a] Based on analysis of the precipitate after washing in trifluoroacetic acid and drying at 105°.

Chromium trioxide and potassium permanganate failed to precipitate dichromates or permanganates with the dissolved metal trifluoroacetates. They still retained their oxidizing activities but to somewhat lesser degree than in water. In the reactions with potassium permanganate, the manganese was reduced to the +3 state rather than the +4 or +2 state. The reactions of these substances are summarized in Tables VIII and IX. The oxidation reactions of chlorine are listed in Table X.

Besides the oxidation reactions with some trifluoroacetates, potassium permanganate also reacted slowly with the pure anhydrous solvent. After three hours, a solution of the salt had lost about 3% of its oxidizing power. Mass spectrum analyses of the gaseous products showed the presence of CO_2, CF_3COF and COF_2. In these analyses the major constituent found was carbon dioxide. The presence of some silicon tetrafluoride in the product indicated that part of the carbonyl fluoride reacted with the glass container. A solution of potassium permanganate in trifluoroacetic acid had a green color similar to that of a solution of potassium permanganate in concentrated sulfuric acid. The Mn(VII) was present as a volatile substance, probably Mn_2O_7, which distilled under vacuum with the trifluoroacetic acid. To avoid danger from possible explosions only small amounts of potassium permanganate were used.

(II) **Solubilities of Gases in Trifluoroacetic Acid.**—The concentrations given in Table II for gaseous reactants are those for saturated solutions at 26°. These quantities were

TABLE V

REACTIONS OF TRIFLUOROACETATES WITH SULFUR TRIOXIDE

			Ppt. analysis			
Trifluoroacetate	Color of ppt.	Extent of reaction	% Cation	% SO_4^{-2}	Molar ratio Cation/ SO_4^{-2}	Possible formula(s)
Sb(III)	White	(Colloidal)	43	53	1/1.56	$Sb_2(SO_4)_3$
Ba	White	Complete				$BaSO_4$
Bi(III)	White	Partial	64	30	1/1	?
Cd	White	Partial	52	45	1/1	$CdSO_4$
Ca	White	Complete	18	81	1/1.9	CaS_2O_7, 90% $CaSO_4$, 10%
Co(II)	Pink	Partial	39	60	1/0.9	$CoSO_4$
Cu(II)	White	Complete	35	66	1/1.25	$CuSO_4$, 75% CuS_2O_7, 25%
Pb(II)	White	Partial	56	50	1/1.9	PbS_2O_7, 90% $PbSO_4$, 10%
Mg	White	Complete	11	82	1/1.9	MgS_2O_7
Hg(II)	White	Partial	66	33	1/1	$HgSO_4$
Hg(I)	White	Nearly complete	69	29	1.14/1	HgS_2O_7, 75% Hg_2SO_4, 25%
Ni(II)	Pale green	Partial	23	74	1/2	NiS_2O_7
Ag(I)	White	Partial	67	33	1.8/1	Ag_2SO_4, 80% $Ag_2S_2O_7$, 20%
Sn(IV)[a]	White	Complete	40	32 10% Cl^-	1/1	?
Sn(II)	White	Partial	55	45	1/1	$SnSO_4$
Zn	White	Complete	40	59	1/1	$ZnSO_4$

[a] Sn(IV) is $SnCl_4$ and not a trifluoroacetate.

TABLE VI

REACTIONS OF TRIFLUOROACETATES WITH PHOSPHORIC ACID

			Ppt. analysis			
Trifluoroacetate	Color of ppt.	Extent of reaction	% Cation	% PO_4^{-3}	Molar ratio Cation PO_4^{---}	Possible formula(s)
Sb(III)	White	Partial	38	62	1/2.09	?
Bi(III)	White	Partial	53	48	1/2	?
Cd	White	Partial	28	71	1/3	?
Co(II)	Pink	Partial	38	62	1/1	$CoHPO_4$
Mn(II)	White	Partial	31	64	1/1.2	$MnHPO_4$, 80% $Mn(H_2PO_4)_2$, 20%
Hg(I)	White	Nearly complete	64	35	1/1.1	$Hg(H_2PO_4)_2$
Ag(I)	White	Partial	46	52	1/1.28	?
Sn(IV)[a]	White		43	38	1/1.1	?
Sn(II)	White	Nearly complete	36	60	1/2.08	$Sn(H_2PO_4)_2$
Zn	White		27	78	1/2.0	$Zn(H_2PO_4)_2$

[a] Sn(IV) is $SnCl_4$ rather than a trifluoroacetate.

TABLE VII

REACTIONS OF TRIFLUOROACETATES WITH METAPHOSPHORIC ACID

			Ppt. analysis			
Trifluoroacetate	Color of ppt.	Extent of reaction	% Cation	% PO_3^-	Molar ratio Cation PO_3^-	Possible formula(s)
Sb(III)	White	Nearly complete	52	34	1/1	$SbOPO_3$
Bi(III)	White	Nearly complete	48	52	1/3	$Bi(PO_3)_3$
Cd	White	Partial	42	53	1/1.8	$Cd(PO_3)_2$
Hg(I)	White	Partial	55	42	1/2	?
Ag(I)	White	Partial	46	53	1/1.55	?
Sn(II)	White	Nearly complete	57	39	1/1	?
Zn	White	Complete	29	66	1/2	$Zn(PO_3)_2$

TABLE VIII

REACTIONS OF SOLUTES WITH CHROMIC ACID ANHYDRIDE[a]

	Products			
Solute[b]	Oxidation	Reduction	Color of final soln.	Extent of reaction
Sb(III)	Sb(V)	Cr(III)	Light green	Partial
Mn(II)	Mn(III)	Cr(III)	Dark orange	?
Hg(I)	Hg(II)	Cr(III)	Light green	Complete
Sn(II)	Sn(IV)	Cr(III)	Light green	
SO_2	H_2SO_4	Cr(III)	Light green	
H_2O_2	Peroxy–chromium soln.		Blue green	

[a] CrO_3 in trifluoroacetic acid is pale orange in color. [b] Except for SO_2 and H_2O_2 all the solutes were trifluoroacetates. All the solutes were colorless.

TABLE IX

REACTIONS OF TRIFLUOROACETATES WITH POTASSIUM PERMANGANATE

	Product			
Solute	Oxidation	Reduction	Color of final soln.	Extent of reaction
Sb(III)[a]	Sb(V)	Mn(III)	Brown-red	Complete
As(III)[b]	As(V)	Mn(III)	Brown-red	Partial
HCl	Cl_2(?)	Mn(III)	Brown-red	Partial
Mn(II)[a]	Mn(III)	Mn(III)	Brown-red	Partial
Hg(I)[a]	Hg(II)	Mn(III)	Brown-red	Partial
Sn(II)[a]	Sn(IV)	Mn(III)	Brown-red	Nearly complete
H_2S	S	Mn(II)	Colorless	
H_2S[c]	H_2SO_4	Mn(III)	Brown-red	
SO_2	H_2SO_4	Mn(III)	Brown-red	Complete

[a] These solutes are trifluoroacetates. [b] $AsOCF_3CO_2$. [c] Reaction with excess $KMnO_4$.

TABLE X

REACTIONS OF TRIFLUOROACETATES WITH CHLORINE

	Product			
Trifluoroacetate	Oxidation	Reduction	Color of product	Extent of reaction
Sb(III)	Sb(V)	Cl^-	Clear soln.	Partial
As(III)[a]	As(V)	Cl^-	White ppt.	Partial
Hg(I)	Hg(II)	Hg_2Cl_2	White ppt.	Nearly complete
Ag(I)[b]	AgCl, CO_2	CF_3Cl	White ppt. (colloidal)	
Sn(II)	Sn(IV)	Cl^-	Clear soln.	Nearly complete

[a] As(III) compound is $AsOCF_3CO_2$. [b] Reaction of $AgCF_3CO_2$ and Cl_2 was reported by Haszeldine.[7]

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(7) R. N. Haszeldine, *J. Chem. Soc.*, 584 (1951).

determined by using a gas measuring tube in such a way that the materials were confined over mercury. First, a sample of gas was placed in the tube and measured. Second, a measured sample of trifluoroacetic acid was added from a hypodermic syringe. The apparatus was then shaken mechanically for several hours until repeated measurements of the volume of gas in the tube indicated that the solution had become saturated. By using the measured changes in the volume of gas and by applying a correction for the partial pressure of trifluoroacetic acid vapor, it was possible to calculate the solubility coefficients given in Table XI. The coefficient given is that of Ostwald. It is the volume of gas (ml.) absorbed in unit volume of solvent (1 ml.), the pressure of the gas being that existing over the solution. The pressure given in the table is the difference between atmospheric pressure and the partial pressure of trifluoroacetic acid. To permit a comparison, the table also gives the corresponding solubility coefficients for aqueous solutions of the same gases as found in the literature[8,9] for a temperature of 25°, and partial pressures of 74 to 76 cm.

TABLE XI

SOLUBILITIES OF GASES IN TRIFLUOROACETIC ACID

Gas	Temp., °C.	Partial pressure of gas, cm.	Ml. of gas dissolved in one ml. of solvent In CF_3COOH	In H_2O_2[8,9]
CO_2	27	65.2	3.5	0.826
CO	26	64.6	0.0	0.0208
Cl_2	25.5	65.6	9.3	1.985
HBr	26	65.7	6.6	580
HCl	26	65.2	4.1	423
H_2S	26	65.7	8.6	2.46
N_2	26	63.6	0.1	0.0156
N_2O	24.5	66.5	4.3	0.65
O_2	27	64.2	0.2	0.0309
PH_3	26	65.3	15.9	?
SO_2	26	66.7	23.4	35.7

Discussion

Although trifluoroacetic acid is not a good ionizing solvent, rapid reactions resembling ionic reactions in water do occur. Many of these changes proceed to completion. The ease with which they occur suggests that the reactants exist as ion pairs. Many precipitation reactions which do not occur in water proceed in trifluoroacetic acid. Generally speaking, precipitation reactions of hydrogen sulfide which take place in acidic aqueous solutions also occur in anhydrous trifluoroacetic acid. An exception to this is the failure of lead sulfide to precipitate in trifluoroacetic acid. A large number of precipitates were obtained in trifluoroacetic acid which are not produced in water. This is especially true for the precipitation of the perchlorates.

The observed high solubilities of gases confirm other studies[2,4] which have indicated the excellence of trifluoroacetic acid as a solvent. Most of the gases tested are considerably more soluble in the acid than in water. The exceptions to this are the hydrogen halides and sulfur dioxide which are highly soluble in water, because they react with the solvent.

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[8] Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 1, 3rd Ed., D. Van Nostrand Co., New York, N. Y., 1940.

[9] "International Critical Tables," Vol. III, McGraw-Hill Book Co., New York, N. Y., 1928, pp. 256-258.

[CONTRIBUTION FROM THE RICHARDSON CHEMISTRY LABORATORY OF TULANE UNIVERSITY]

Inorganic Complex Compounds Containing Polydentate Groups. XII. Cobalt(II) Complexes of Tetraethylenepentamine

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The complexing tendency of tetraethylenepentamine (abbrev. tetren) with the cobalt(II) ion has been determined. The data indicates that all five amino groups of tetren coördinate. The sixth coördinating position can be occupied by H_2O, CH_3OH or the OH^- ion. The complexity constants of $[CotetrenH_2O]^{2+}$ have been determined at 25, 35 and 45°. The complex ion $[CoTetrenOH]^{1+}$ has been shown to oxygenate reversibly with only a slight amount of oxidation.

Introduction

The metal complexes of polyamines containing up to four amino groups have been investigated extensively.[2,3]

The purification of tetraethylenepentamine (abbrev. tetren) the next higher polyamine has only recently been accomplished.[4]

The present study was undertaken to investigate the type of complexes formed between the cobalt(II) ion and tetren.

Experimental

A. **Materials.**—The tetren was obtained from the Carbide and Carbon Corporation and purified as described previously.[4] All other chemicals were C.P. materials.

B. **Instruments.**—The *p*H measurements were made with a Model G *p*H meter standardized with Beckman buffer solutions of *p*H 4, 7 and 10. The solutions were measured in constant temperature baths at 25 ± 0.2°, 35 ± 0.2°, and 45 ± 0.2°. The spectrophotometric measurements were made on a Beckman Model B spectrophotometer with matched Corex cells. The conductometric titrations were performed as described earlier.[5]

C. **Determination of Log *K* Values** of $[CotetrenH_2O](ClO_4)_2$.—The complexity constants of the cobalt tetren complex were determined by the method of Bjerrum[6] at 25,

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[1] Abstracted in part from the Ph.D. dissertation of Fred W. Frey, Tulane University, 1954.

[2] G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 974 (1950).

[3] H. B. Jonassen, G. G. Hurst, R. B. LeBlanc and W. Meibohm, THIS JOURNAL, **56**, 16 (1952).

[4] H. B. Jonassen, F. W. Frey and A. Schaafsma, *ibid.*, **61**, 504 (1957).

[5] H. B. Jonassen, R. E. Reeves and L. Segal, *ibid.*, **77**, 2667 (1955).

[6] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Sons, Copenhagen, 1941.