Apparently, when oxalic acid is heated in glycerol, two simultaneous reactions take place—(1) decarboxylation, a very fast reaction, and (2) a much slower reaction, probably esterification. Above 150° the decarboxylation appears to be completed before the esterification can become appreciable. Below this temperature a portion of the oxalic acid apparently combines with the glycerol to form a stable compound, since no matter how long the solution is heated at temperatures below 150° no further increase in gas volume can be detected. This observation is at variance with the proposed mechanism for the decomposition of oxalic acid in glycerol.[2]

When points on the isotherms in Fig. 1 are inserted in the equation for a first-order reaction the values obtained for the specific reaction velocity are constant for each temperature as shown by the typical example given in Table I. These results indicate that the decomposition of oxalic acid in glycerol is a first order reaction.

TABLE I

DECOMPOSITION OF OXALIC ACID IN GLYCEROL, SPECIFIC REACTION VELOCITY CONSTANT

(Temperature 154.2 ± 0.01°.)

Time, sec.	Vol. CO_2 at STP, ml.	Completion of reaction, %	Specific reaction vel.
90	18.7	46.75	0.00700
120	23.7	59.25	.00747
150	27.4	68.50	.00768
180	30.2	75.50	.00780
210	32.1	80.25	.00770
240	33.7	84.25	.00768
270	35.0	97.50	.00770
300	35.8	89.50	.00750

Kinetic Data.—Figure 3 shows a plot of log k *versus* $1/T$ for the decomposition of oxalic acid dihydrate and the decomposition of oxalic acid in glycerol.

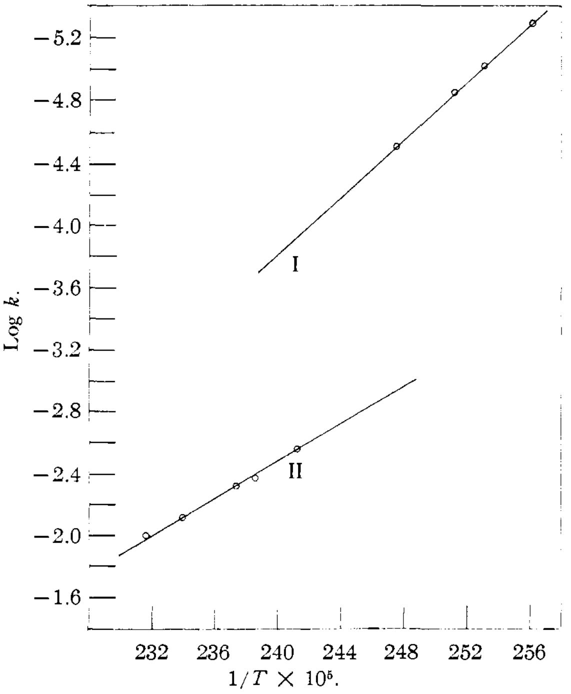

Fig. 3.—Arrhenius plot, log k *vs.* $1/T$: I. decomposition of oxalic acid dihydrate; II, decomposition of oxalic acid in glycerol.

For the decomposition of oxalic acid dihydrate the energy of activation is found to be 40,400 cal., and for the decomposition of oxalic acid in glycerol it is 27,400 cal. The enthalpy of activation, the entropy of activation and the free energy of activation at 125°, for the decomposition of the molten dihydrate, is 39,400 cal., +26.8 e.u., and 28,800 cal., respectively; for the decomposition of oxalic acid in glycerol the corresponding values are 26,400 cal., +42.5 e.u., and 9,500 cal., respectively.

The temperature coefficient (the increase in rate per each 10° rise in temperature) is 3.62 for the molten dihydrate, and 1.90 for the reaction in glycerol.

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Note on the Complexes of Ferric Chloride with Phosphorus Oxychloride

BY V. V. DADAPE AND M. R. A. RAO

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Walden and Oddo[1] reported that sublimed ferric chloride formed a yellowish brown solution with phosphorus oxychloride and subsequently Ruff and Einbeck[2] described a yellow compound having the composition $2FeCl_3 \cdot POCl_3$. During the course of our investigations on the chlorination of ferruginous phosphatic minerals, we observed a reddish brown crystalline deposit in the colder regions of the reaction tube which did not correspond to the composition given above. On account of this discrepancy a detailed study was undertaken.

Experimental Procedure

A. Preparation of the Complexes. (i) **Materials Used.**—Phosphorus oxychloride (B.D.H.) was subjected to fractional distillation in an all-glass apparatus, the fraction distilling between 103 and 104° (690 mm. pressure) was employed. *Anal.* Calcd.: P, 20.19; Cl, 69.39. Found: P. 20.08; Cl. 68.64.

(ii) **General Procedure.**—The reaction of ferric chloride with excess phosphorus oxychloride was carried out at 95° in an all-glass apparatus. The unreacted $POCl_3$ was driven off by evacuation (20 mm. pressure). The deep red solution left behind was warmed (35°) under reduced pressure when red crystals separated. The crystals were freed from the mother liquor and dried in a current of dry air. During the entire procedure, care was taken to avoid contamination with atmospheric moisture. A weighed amount of the crystals was dissolved in water and the total P and Cl present in the solution estimated by the ammonium phosphomolybdate and Volhard's methods, respectively. The iron was estimated volumetrically. The analytical data (mean of six determinations) showed that the crystals had the composition $2FeCl_3 \cdot 3POCl_3$. *Anal.* Calcd.: Fe, 14.25; Cl, 67.79; P, 11.84. Found: Fe, 14.35; Cl, 66.94; P, 11.64.

Preparation of the Complex $FeCl_3 \cdot POCl_3$.—The red crystals of $2FeCl_3 \cdot 3POCl_3$ were subjected to further evacuation in a flask (2–3 mm.) at 50° with periodic weighing. In the initial stages there was a rapid loss in weight due to loss of $POCl_3$. After about an hour, loss of $POCl_3$ was not noticed and the pressure of the system remained constant at about 4 mm. The color of the crystals had in the meanwhile changed from red to brown. The average results of analysis of the crystals from six independent experiments were: Fe, 17.63 (theor. 17.72); Cl, 66.73 (theor. 67.41);

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(1) P. Walden and G. Oddo, *Z. anorg. Chem.*, **25**, 212 (1900).

(2) O. Ruff and H. Einbeck, *Ber.*, [IV] **37**, 4518 (1904).

and P, 9.74 (theor. 9.78). The average deviation from the mean value was ±0.4%.

The two compounds $2FeCl_3 \cdot 3POCl_3$ and $FeCl_3 \cdot POCl_3$ were also prepared by the alternative method of passing $POCl_3$ vapor over anhydrous $FeCl_3$ at 200°. Ferric chloride crystals were packed over a length of 3 inches in a Pyrex glass tube maintained at 200° in an electric furnace and nitrogen saturated with $POCl_3$ at 25° was passed over the crystals when reaction took place and a small amount of deep red deposit ($2FeCl_3 \cdot 3POCl_3$) was observed in the colder portions of the reaction tube, while a dark brown solid ($FeCl_3 \cdot POCl_3$) was noticed in the hotter portions. The residue left in the reaction zone showed a variable composition, *viz.*, $POCl_3$:$FeCl_3$ as 1:2.50.

B. Melting Points.—The melting points were determined by the method of cooling curves, employing the following molar ratios of $FeCl_3$:$POCl_3$ (1) 2.06:1, (2) 1.64:1, (3) 1:1, (4) 1:1.4, (5) 1:1.5, and (6) 1:2. Definite melting points were obtained only for the compositions $FeCl_3$:1.5-$POCl_3$ (98 ± 0.2°) and $FeCl_3$:$POCl_3$ (119 ± 0.2°).

C. Vapor Pressure–Composition Data of the System $FeCl_3$–$POCl_3$.—The studies on the vapor pressure–composition of the system $FeCl_3$–$POCl_3$ were carried out by employing an all-glass Bourdon gage[3] as a differential pressure meter with a sensitivity of ±0.01 mm. Mixtures of $FeCl_3$ and excess $POCl_3$-($FeCl_3$:$POCl_3$ = 1:2.25; 1:2.9; 1:3.7; and 1:1.42) were heated to 95° to complete the reaction and the vapor pressures determined at 40°. The composition of the system was changed by pumping off known amounts of $POCl_3$, employing a liquid air trap to condense $POCl_3$ and the vapor pressure of the new composition determined. The colorless condensate left no solid residue on evaporation indicating the absence of $FeCl_3$ in the vapor phase. The vapor pressure attained a constant value of 12.2 mm. when the composition corresponded to the formula $2FeCl_3 \cdot 3POCl_3$. Similar studies with other mixtures ($FeCl_3$:$POCl_3$ = 1:1.13; 1:1.21; 1:1.42; and 1:1.38) indicated a constant vapor pressure of 1.2–1.3 mm. when the composition of the compound was equimolar with respect to each of the two constituents. The relationship between $1/T$ and $\log p$ (p in mm.) could be represented by the equations $\log p = -(3225/T) + 11.38$ and $\log p = -(4167/T) + 13.53$ for the compounds $2FeCl_3 \cdot 3POCl_3$ and $FeCl_3 \cdot POCl_3$, respectively. The calculated heats of dissociation employing Clausius–Clapeyron equation are 14.56 kcal./mole for $2FeCl_3 \cdot 3POCl_3$ and 18.16 kcal./mol. for $FeCl_3 \cdot POCl_3$.

D. Fractional Crystallization.—Fractional crystallization of heated mixtures of $FeCl_3$ and $POCl_3$ (in the ratios $FeCl_3$:$POCl_3$ as 2:3 and 1:1, respectively) was carried out without exposure to atmospheric moisture. The percentage composition of the three crops of crystals in each case confirmed the existence of the compounds $2FeCl_3 \cdot 3POCl_3$ and $FeCl_3 \cdot POCl_3$.

E. Crystallization of the Compounds from Carbon Tetrachloride.—Crystallization of the two complexes from carbon tetrachloride did not indicate any change in the composition of the solid phase which confirmed the existence of the two complexes. However, when excess of ferric chloride was heated with phosphorus oxychloride in presence of carbon tetrachloride, it was noticed that only the complex $FeCl_3 \cdot POCl_3$ dissolved in the solvent leaving behind the excess ferric chloride. On cooling, the carbon tetrachloride layer yielded crystals of the complex as indicated in Table I and the results confirm the formation of the compound $FeCl_3 \cdot POCl_3$.

TABLE I

Molar ratio $FeCl_3$:$POCl_3$ taken for heating	Molar ratio of $FeCl_3 \cdot POCl_3$ in — Mother liquor	Crystals from mother liquor	Residue
2:1.0	1:1.1	1:1.01	Practically pure $FeCl_3$ with trace of $POCl_3$ (<0.1%)
2:0.5	1:1.02	1:0.90	
2:0.98[a]	1:1.01	1:1.02	

[a] ($FeCl_3$ + $POCl_3$) was heated at 340° in a sealed tube before extraction.

F. Molecular Weight, Conductivity and Absorption Characteristics of the Complexes in Nitrobenzene. (i) **Molecular Weight.**—The molecular weights of the complexes were determined cryoscopically employing nitrobenzene as the non-aqueous solvent. "Chemically pure" nitrobenzene was subjected to fractional distillation and the fraction distilling between 205 and 206° (690 mm. pressure) was collected and used for this work. The molecular weights for the two compounds and for $FeCl_3$ and $POCl_3$ have been recorded in Table II.

TABLE II

DETERMINATION OF THE MOLECULAR WEIGHTS IN NITROBENZENE

Substance	Wt. of subst. 100 g. of solvent, g.	Lowering of f.p., °C.	Mol. wt. Obsd.	Mol. wt. Calcd.
	1.709	0.385	313.0	
Fe_2Cl_6	1.330	.283	331.3	325.0
	0.9508	.180	372.4	
	5.075	1.96	182.5	
$POCl_3$	1.233	0.470	184.9	153.5
	0.9561	0.365	184.6	
$FeCl_3 \cdot POCl_3$	1.904	0.390	344.0	316.0
$2FeCl_3 \cdot 3POCl_3$	2.066	0.47	310.0	785.5

(ii) **Conductivity.**—The measurements of conductivity were carried out at 25 ± 0.05° in a Washburn cell protecting the solution from the atmospheric moisture. The specific conductivity of the purified nitrobenzene at 25° was found to be 2.6×10^{-7} mho cm.$^{-1}$. This value is midway between those of Kahlenberg,[4] *et al.* (3.5×10^{-7}), and Payne[5] (1.0×10^{-7}) and could be considered satisfactory since the conductivities of the solutions of the complexes were of the order of 1.0×10^{-4} mho cm.$^{-1}$. The specific conductivity was determined for the following systems at various dilutions: (i) $FeCl_3$, (ii) $POCl_3$, (iii) mixture of $2FeCl_3 + 3POCl_3$, (iv) mixture of $FeCl_3 + POCl_3$, (v) $2FeCl_3 \cdot 3POCl_3$ complex and (vi) $FeCl_3 \cdot POCl_3$ complex. The results are given in Table III.

Conductometric Titrations.—Nitrobenzene solutions (0.3 *M* $FeCl_3$) containing varying amounts of $POCl_3$ were heated to 95° for 15 minutes and their specific conductivities determined at 25°. Two points of inflection corresponding to the compositions $FeCl_3 \cdot POCl_3$ and $2FeCl_3 \cdot 3POCl_3$ were obtained, thus confirming the formation of the two complexes. When the $FeCl_3$ concentration in the mixture was 0.2 *M* and lower, the point of inflection was distinct only for the complex $2FeCl_3 \cdot 3POCl_3$.

TABLE III

SPECIFIC CONDUCTIVITY DATA AT 25° FOR $FeCl_3$–$POCl_3$ SYSTEMS

	Sp. cond. ohm^{-1} × cm.$^{-1}$ × 10^{-4}			Sp. cond. ohm^{-1} × cm.$^{-1}$ × 10^{-4}		
Concn. mole/l.	$2FeCl_3 \cdot$-$3POCl_3$ (complex)	$2FeCl_3 + 3POCl_3$ (mixture)	$2FeCl_3 + 3POCl_3$ (mixture) calcd.[a]	$FeCl_3 \cdot$-$POCl_3$ (complex)	$FeCl_3 + POCl_3$ (mixture)	$FeCl_3 + POCl_3$ (mixture) calcd.[a]
0.20	17.1	17.0	7.42	8.4	8.35	5.15
.15	13.5	13.35	6.39	7.32	7.25	4.38
.10	9.8	9.7	5.16	6.3	6.2	3.52
.075	7.85	7.8	4.4	5.7	5.6	3.02
.050	6.15	6.2	3.53	4.95	4.9	2.46
.025	4.55	4.6	2.47	3.8	3.8	1.71
.010	3.2	3.25	1.56	2.6	2.6	1.15

[a] Values were calculated from the individual specific conductivities of the two components in nitrobenzene.

(iii) **Absorption Characteristics.**—The absorption spectra have been studied with the help of a "Coleman Universal Spectrophotometer" between the wave lengths 400 and 800 mμ. Two absorption maxima at 500 and 720 mμ were obtained for the ferric chloride solution while in the case of each of the two complexes, only one maximum at 500 mμ was noticed. $POCl_3$ solutions did not indicate any absorption in the above range.

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(3) J. R. Partington and A. L. Whynes, *J. Phys. Chem.*, **53**, 500 (1949).

(4) L. Kahlenberg and A. T. Lincoln, *ibid.*, **3**, 26 (1899).

(5) D. S. Payne, *J. Chem. Soc.*, 1052 (1953).

Discussion

It is strange to find that with $FeCl_3$ the molecular weight increases with a diminution in the concentration of the solute. Similar results were also noticed by Kahlenberg and Lincoln.[4] The molecular weight obtained for the compound $FeCl_3 \cdot POCl_3$ is 344, while the calculated value is 316. The difference between the observed molecular weight (310) and the calculated value (785.5) for the compound $2FeCl_3 \cdot 3POCl_3$ is quite considerable. This may be due to the dissociation of the complex.

$$2FeCl_3 \cdot 3POCl_3 \rightleftarrows 2(FeCl_3 \cdot POCl_3) + POCl_3 \quad (1)$$

This also explains the equality in conductivity of the two complexes for a given concentration of ferric chloride.

Table III indicates that the specific conductivity of the complex $FeCl_3 \cdot POCl_3$ is invariably higher than the sum of the conductivities of the individual components. This increase in the conductivity can be explained by assuming the dissociation of the complex as

$$FeCl_3 \cdot POCl_3 \rightleftarrows FeCl_4^- + POCl_2^+ \quad (2)$$

The studies described above indicate the formation of the two complexes $2FeCl_3 \cdot 3POCl_3$ and $FeCl_3 \cdot POCl_3$. The existence of the compound $2FeCl_3 \cdot POCl_3$ reported in the literature, however, could not be confirmed.

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An Aqueous Synthesis of Barium Titanate

BY STEWARD S. FLASCHEN

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High temperature calcination and reaction of titanium dioxide and barium as the oxide, nitrate, carbonate or hydroxide, or as the mixed oxalates are the usual bases for the preparation of barium titanate ($BaTiO_3$). In the method reported herein crystalline barium titanate as well as various titanate solid solutions are synthesized directly from aqueous solution. This method is based upon the precipitation of barium titanate upon addition of a titanium ester to an aqueous solution of a soluble barium salt. Analogous to the solution chemistry of the zirconates, vanadates and chromates, a strongly alkaline environment is found to be essential for the formation of the "meta" salt. Precipitation from neutral and acid solutions result in the formation of hydrated titanium dioxide only.

In this method a dilute propyl alcohol solution of a titanium ester such as tetrapropyltitanate or an ester of a higher alcohol is added dropwise and with vigorous stirring to a degassed water solution of barium hydroxide, *p*H 11 to 14. Reaction in a KOH solution is used where a controlled *p*H is desirable. No chemical or physical differences in the nature of the product could be detected by reaction in the presence of potassium ion or as a function of the *p*H over this range. Sufficient excess of the ester is added to result in a final 1:1 or greater molar ratio of BaO to TiO_2. A white, fine grained (1 to 5 μ), homogeneous phase readily precipitates on mixing over the temperature range 20 to 100°. Reaction above 80° yields a crystalline product directly. The low temperature precipitate must be aged for from one to two hours at the boiling point. The precipitate is filtered and then washed with hot, degassed distilled water to remove excess barium salt.

The X-ray diffraction pattern of the product is identical to that characteristic of the tetragonal modification of $BaTiO_3$ as synthesized by means of high temperature solid state reaction. This method has also been used successfully for the introduction of trace impurities and for the synthesis of homogeneous solid solutions in which partial substitution has been made for the barium ion.

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Basicity of the Amide Bond[1,2]

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During the course of an investigation of the ultraviolet absorption spectra of amides and peptides it was observed that these compounds showed a marked lowering of the molar extinction coefficient (ϵ) in concentrated sulfuric acid solutions. The shape of the curves, ϵ *vs.* concentration of sulfuric acid, suggested that we were measuring the proton binding ability of the amide and peptide structures. Cryoscopic measurements[3,4] in 100% H_2SO_4 have indicated that amides and carboxylic acids bind one proton. Hall[5] using potentiometric methods, measured the acid dissociation constant for the acetamidonium ion and found pK_a[6] values of −0.5 in water and −1.65 in glacial acetic acid. More recently Lemaire and Lucas[7] determined the thermodynamic pK_a values of a number of weak bases, including acetamide, by use of an indicator method. The value of pK_a determined in the last instance was about −0.04. We have made a study of a series of acetamide derivatives, using a spectrophotometric method, to determine the effect of substituent on the nitrogen and of adjacent charge on the basicity of the amide bond.

Experimental

Materials.—Acetic acid, acetamide, methyl- and dimethylacetamide, glycinamide and acetylglycine were commercially available materials which were purified by fractional distillation or crystallization. The butylacetamides were prepared by mixing acetic anhydride (2 moles) with the

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[1] Supported by Grant #NSF-G617 from the National Science Foundation.

[2] Reported, in part, at the Meeting of the American Chemical Society held in New York during March of 1954.

[3] A. Hantzsch, *Ber.*, **64**, 667 (1931).

[4] J. L. O'Brien and C. J. Niemann, THIS JOURNAL, **72**, 5348 (1950).

[5] N. F. Hall, *ibid.*, **52**, 5115 (1930).

[6] $pK_a = -\log K_a$. K_a = (acetamide)(H+)/(acetamide H+).

[7] H. Lemaire and H. J. Lucas, THIS JOURNAL, **73**, 5198 (1951).