[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY OF LOUISIANA STATE UNIVERSITY]

Catalysis of Schiff Base Hydrolysis by Metal Ions[1,2]

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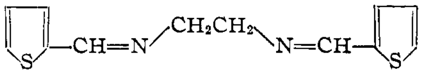
Rate constants have been evaluated, at various temperatures in a 50% water–ethyl alcohol solvent, for the decomposition of the 1:1 copper(II) and nickel(II) complexes of bis-(2-thiophenal)-ethylenediamine into the corresponding ethylenediamine complexes and thiophenaldehyde. The activation energies calculated from the Arrhenius equation are 11.3 and 12.5 kcal. for copper and nickel, respectively. The difference in these values is in accord with the theory that the ability of a metal ion to act as a catalyst in such a decomposition is related to the strength of the coördinate covalent bonds which the metal ion can form.

Introduction

It has been shown in a recent publication[3] that bis-(2-thiophenal)-ethylenediamine



forms an unstable complex with copper ion, and then rapidly decomposes into 2-thiophenaldehyde and the copper complex of ethylenediamine. It was proposed that the formation of the copper–nitrogen bond weakens the carbon–nitrogen double bonds, thus rendering the latter more susceptible to hydrolytic cleavage.

If this theory is correct, there should be a correlation between the ability of a metal ion to catalyze such a hydrolytic reaction and the strength of the bond between that metal and the nitrogen atoms. A more careful investigation of the kinetics of such processes should therefore prove to be of some interest, if it could lead to experimental evidence for the postulated relationship between bond strength and catalytic activity.

It was decided to test this theory through comparative studies with divalent copper and nickel complexes. These metal ions were chosen because they frequently form complexes of similar structure, and because they are relatively easy to handle experimentally. It is well known that copper forms stronger complexes than nickel.[4,5] A quantitative measure of the relative catalytic effect of the two metal ions is the activation energy required for the hydrolysis of the Schiff base. According to our theory, since copper forms stronger bonds than nickel with the nitrogen atoms, the activation energy for the decomposition of the copper complex should be lower than the activation energy in the catalysis with nickel ion.

Experimental

Determination of Rate Constants in the Decomposition of the Copper Complex of Bis-(2-thiophenal)-ethylenediamine.—To determine the rate constants for this decomposition, standard solutions of copper(II) nitrate and bis-(2-thiophenal)-ethylenediamine were mixed in 1:1 molar ratios, the resulting reaction mixture was rapidly transferred to an absorption cell, and the change in absorption with time was measured by means of a Beckman model DU spectrophotometer. Since the Schiff base complex of copper absorbs appreciably at 425 mμ, where the ethylenediamine complex is transparent, the optical density at this wave length is proportional to the concentration of the initial complex.

The Schiff base was prepared according to Eichhorn and Bailar,[3] and dissolved in 50% water–ethyl alcohol to produce a 0.025 *M* solution. A solution of copper sulfate of the same concentration was made up in the mixed solvent.

Since the reaction under investigation would proceed in the cell chamber of the spectrophotometer the temperature of this chamber was maintained constant to ±0.1° by utilizing thermospacers which surround the cell and through which is pumped water from a constant temperature bath.

Samples were prepared containing 2 ml. of the standard $CuSO_4$ solution and 2 ml. of the mixed solvent; they were placed in the temperature bath and allowed to come to reaction temperature. Freshly prepared Schiff base solution was placed in the same bath. The reaction temperature was obtained in the cell chamber by circulating water from the temperature bath through the thermospacers for at least one hour prior to the initiation of the reaction. Two matched Corex absorption cells, 1.00 cm. in width, were employed; the mixed solvent was used as the blank.

The copper solution was removed from the bath immediately before the reaction was initiated. Two ml. of the base solution was added rapidly to the copper sample, and the timing started when approximately half of the base had drained from the transfer pipet. The sample was shaken vigorously for 15 seconds. The cell holder containing the cells was removed from the instrument, and the empty cell was detached from the holder, rinsed once with solution, filled, capped and replaced in the holder, which was then returned to the instrument. The time that elapsed from the removal of the sample from the temperature bath to the replacement of the filled cell in the instrument was 1.5 min. Since the sample unavoidably was held at room temperature during this interval, some time must be allowed for the temperature equilibrium to become re-established. The time required for equilibrium to be attained varied, depending upon the difference between room temperature and reaction temperature.

Values of the optical density were then recorded at regular intervals. The first few points were known to be in error, since temperature changes were occurring in the samples. Measurements were made for a sufficient time to permit the decomposition to proceed to completion.

Rate Constants in the Catalysis with Nickel.—The system in which nickel ion serves as a catalyst for the decomposition of the base is not so favorable for rate studies as the copper system, because initial and final complexes both absorb throughout the entire visible range of the spectrum. 620 mμ was arbitrarily chosen for the measurements, and the modified King method[6,7] was used to calculate the rate constants.

Samples containing 4.0 ml. of 0.075 *M* nickel(II) nitrate were prepared along with a Schiff base solution of the same concentration. To initiate the reaction 4.0 ml. of the base was added to the nickel sample; the remainder of the procedure was identical with that described for the investigation of the copper system.

Results

Reaction with Copper.—Optical density measurements as a function of reaction time were obtained on the decomposition of the mono-(bis-2-

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[1] Presented at the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, Dec. 4–6, 1952.

[2] Taken in part from a master's thesis by Isaac M. Trachtenberg, Louisiana State University, 1952.

[3] G. L. Eichhorn and J. C. Bailar, Jr., THIS JOURNAL, **75**, 2905 (1953).

[4] D. P. Mellor and L. Maley, *Nature*, **159**, 370 (1947).

[5] H. Irving and R. J. P. Williams, *ibid.*, **162**, 746 (1948).

[6] E. L. King, THIS JOURNAL, **74**, 563 (1952).

[7] G. L. Eichhorn and I. M. Trachtenberg, *ibid.*, **76**, 4734 (1954).

thiophenal-ethylenediamine)-copper(II) complex over a temperature range extending from 10.0 to 30.5°. At each temperature the logarithm of the optical density was plotted against reaction time, and a straight line was drawn, ignoring the first few points because of the noted temperature adjustments, and the last points, since the reaction had then proceeded almost to completion. The slopes of the lines were then determined and converted to rate constants by means of the equation

$$\text{slope} = -k/2.303$$

Two typical curves for the determination of rate constants are shown in Fig. 1, and the constants determined at various temperatures have been gathered in Table I.

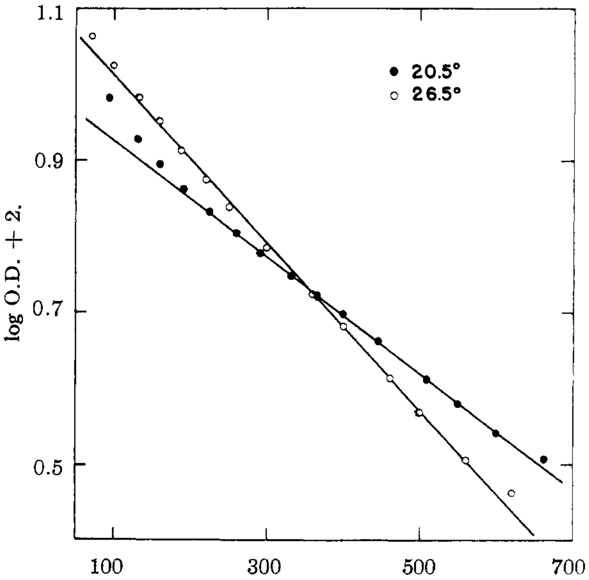

Fig. 1.—Rate constant determination: copper(II) system.

TABLE I

RATE CONSTANTS FOR DECOMPOSITION OF COPPER COMPLEX

Temp., °C.	$k \times 10^3$,[a] sec.$^{-1}$
10.0	0.832 ± 0.008 (3)
20.5	1.80 ± .04 (5)
24.0	2.35 ± .06 (4)
26.5	2.46 ± .10 (4)
30.5	3.25 ± .07 (3)

[a] Parentheses indicate number of experiments.

The activation energy for the decomposition was determined by plotting the logarithms of the average rate constants *vs.* $1/T$°K. (Fig. 2), using the equation

$$\text{slope} = -E/2.303R$$

and was found to equal 11.3 kcal./mole. The entropy of activation calculated from the equation

$$\Delta S^* = R\left(\ln \frac{kh}{KT} + \frac{E}{RT} - 1\right)$$

is −34.7 e.u.

Reaction with Nickel.—The data for the determination of the rate constants in the reaction with nickel were obtained in a manner similar to that which has been described for the copper catalysis, except that changes in optical density, rather than the optical density itself, were plotted, as explained in the experimental section. The τ-values selected varied from −240 sec. for the reaction at 20.0° to 60 sec. for the reaction at 35.0°.

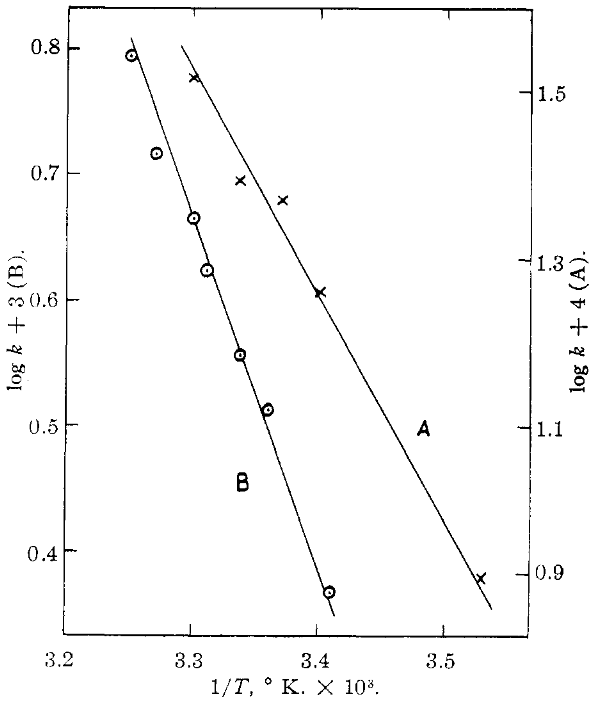

Fig. 2.—Activation energy determination: (A) copper(II) system; (B) nickel(II) system.

The rate constants at various temperatures for this reaction are contained in Table II, and the plot for the determination of the activation energy in Fig. 2. The activation energy was calculated to be 12.5 kcal./mole, and the activation entropy −30.0 e.u.

TABLE II

RATE CONSTANTS FOR DECOMPOSITION OF NICKEL COMPLEX

Temp., °C.	τ, sec.	$k \times 10^3$,[a] sec.$^{-1}$
20.0	−240	2.34 ± 0.05
25.0	−240	3.27 ± .04
26.8	−120	3.61 ± .10
28.5	−120	4.20 ± .01
30.0	−120	4.72 ± .04
32.5	−120	5.21 ± .06
35.0	− 60	6.22 ± .26

[a] Average for three experiments.

A comparison of the data obtained for the copper and nickel complexes leads to the following observations: (1) the activation energy is higher for the decomposition of the nickel complex; (2) the activation entropies are highly negative, the absolute value being lower for nickel; (3) the reaction rates for the decomposition of the nickel complex are higher.

The relative values[8] for the activation energies are in agreement with the supposition that the activation energy is a function of the metal to nitro-

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(8) It should be pointed out that the similarity of these values renders any conclusions concerning them tentative.

gen bond strength, since the copper complexes of amines are more stable than those of nickel. Because the activation entropy, however, counteracts the effect of the activation energy, the catalytic potentials of the two ions, as measured by the reaction rates, are in reverse order from that which had been anticipated.

The negative activation entropies can perhaps be explained by a model in which water molecules are held tightly to the Schiff base double bond, the nucleus of the hydrolytic reaction. The large entropy values may indicate extensive reorientation of solvent molecules as a consequence of the formation of the activated complex. The greater absolute value for the activation entropy in the copper system could result from either greater rigidity of the activated complex or lower rigidity of the unactivated system. The first alternative appears more plausible, since it may be supposed that the greater diminution of electron density in the carbon to nitrogen bond of the copper complex would lead to a greater dipole induced dipole attraction for the water molecules.

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A Linear Phosphoryl Absorption Relationship

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There is a linear correlation between the phosphoryl absorption wave length in phosphoryl halides and the sum of the Pauling electronegativity constants of the halogens. This same correlation is found to exist between the Raman shift of the phosphoryl stretching vibration of phosphoryl halides and the sum of the Pauling electronegativities of the halogens in these same molecules. Similarly it has been found that other more complex substituent groups, *i.e.*, alkoxy, hydroxy, etc., influence the stretching absorption of the phosphoryl bond in a constant and additive manner. These groups, therefore, have been assigned derived numerical values comparable in magnitude to a Pauling electronegativity constant. These constants are referred to as phosphoryl absorption shift constants. It is also proposed that the derived constant for each substituent largely represents the Pauling electronegativity of the substituents.

Introduction

In recent years much attention has been devoted to pentavalent organo-phosphorus compounds and their infrared and Raman spectra. The molecules of special interest are tetrahedral in form as represented by Figs. 1a and 1b. V, Y and Z may be individual atoms or substituent groups which vary widely in character and weight. Changing these substituents causes a marked shift in the infrared wave length and Raman frequency of the phosphoryl vibration. The wave lengths, which vary from 7.0 to 8.5 μ, depend on the nature of the substituent groups.

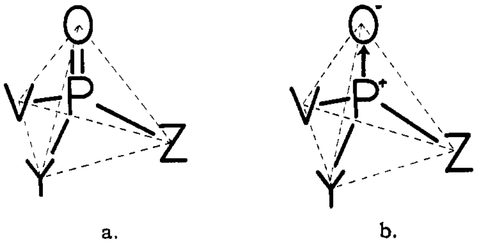

Figure 1.

Several attempts have been made to establish a means of predicting the wave length of the phosphoryl stretching vibration.[1-3] Daasch and Smith in particular have noted that there is a correspondence between the phosphoryl frequency and the "electronegativity" of the substituent groups.

In the work described in this paper we have found (1) that there is a good linear correlation between the Raman shift of the phosphoryl vibration in phosphoryl halides and the sum of the Pauling electronegativity constants of the halogens (Fig. 2); (2) the effects of various substituents upon the infrared wave lengths of the P=O stretching vibrations in many types of phosphoryl compounds are constant and additive; (3) the effect of a substituent upon the infrared wave length may be given a

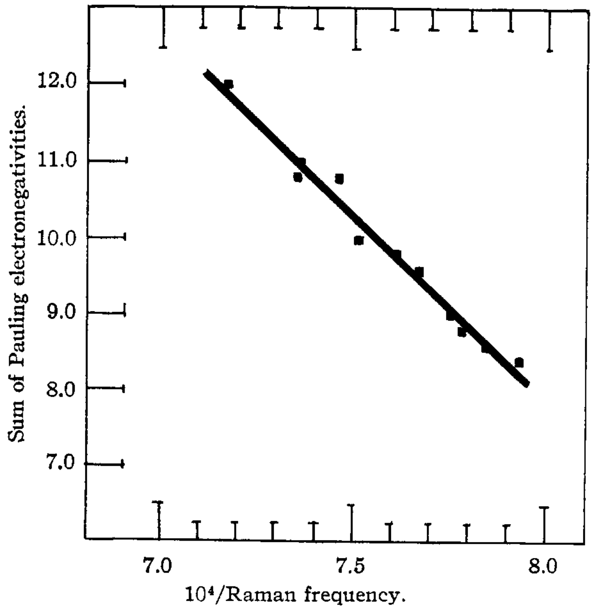

Fig. 2.—Raman data $\mu = (47.31 - \Sigma x)/4.933$.

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(1) M. L. Delwaulle and F. Francois, *J. chim. phys.*, **46**, 87 (1949).

(2) R. C. Gore, *Disc. Faraday Soc.*, **9**, 138 (1950).

(3) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).