[Contribution from McPherson Chemical Laboratory, The Ohio State University]

Spectrophotometric Investigation of a Mixed Complex of Copper(II) Ion with Oxalate Ion and Ethylenediamine

By Robert DeWitt and James I. Watters[1,2]

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A mixed complex, $[Cu(C_2O_4)en]^0$, has been identified in solutions containing the corresponding ratios of its constituents. The equilibrium of this mixed complex with both bis-(ethylenediamine)-copper(II) and bis-(oxalato)-cuprate(II) ions was investigated spectrophotometrically by varying the ratios of the concentrations of the three complexes through pH adjustments. In the presence of about 0.1 M excess of both ligands it was possible to shift the equilibrium so the ethylenediamine complex predominated at pH value above about 6.5, the mixed complex predominated in the pH range of about 6.5 to 6.0, and the oxalate complex predominated at lower pH values. From the proportions of the three complexes found in the various solutions by spectrophotometric measurements a complexity constant of $10^{15.44} \pm 10^{0.14}$ was calculated for the mixed complex. At 648 mμ, the ethylenediamine and oxalate complexes have the same molar extinction coefficient of 25.3 molar^{-1} cm.$^{-1}$ while the corresponding value for the mixed complex is 47 molar^{-1} cm.$^{-1}$. The mixed complex has a maximum molar extinction coefficient of 50 molar^{-1} cm.$^{-1}$ at 630 mμ. It has an isosbestic with the oxalate complex at 700 mμ where the molar extinction coefficient is 34.3 molar^{-1} cm.$^{-1}$ and an isosbestic with the ethylenediamine complex at 600 mμ where the molar extinction coefficient is 46.0 molar^{-1} cm.$^{-1}$.

This is the third paper of a series on mixed complex formation in aqueous solution. In previous papers the complexes of copper with both pyrophosphate and ammonia[3] or ethylenediamine[4] ions have been considered. The present system was studied because ethylenediamine and oxalate ion differ greatly in their tendency to associate with hydrogen ions yet both form stable chelate complexes. This difference permitted a variation in the equilibrium from predominantly the ethylenediamine complex to a mixed complex, $[Cu(C_2O_4)en]^0$, and finally to the oxalate complex by the addition of acid to solutions containing copper ion with an excess of both ligands. Most of the experimental details and the derivation of equations are given in a previous paper.[4] A stock solution of 1 M potassium oxalate was prepared by weighing $K_2C_2O_4 \cdot H_2O$, reagent grade, and its concentration was verified by titrating with standard permanganate solution. The ionic strength was always adjusted to unity with $NaNO_3$ and the experiments were performed at 25°.

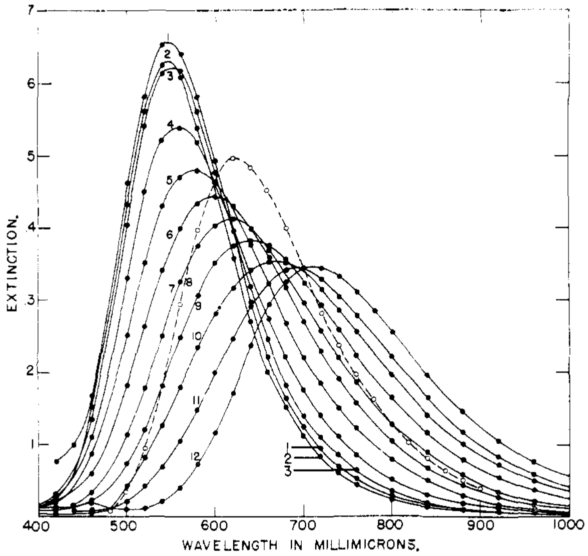

Fig. 1.—Effect of varying the ratio $[Cu^{2+}]:[C_2O_4^{2-}]:[en]$ by varying the amount of ethylenediamine added. All solutions contained 10^{-2} M $CuSO_4$, 0.25 M $K_2C_2O_4$, and the ionic strength was adjusted to unity with $NaNO_3$; extinction = $\log_{10} I_0/I$; 1-cm. cells used. 1, 1:250:3; 2, 1:0:3; 3, 1:250:2; 4, 1:250:1.75; 5, 1:250:1.5; 6, 1:250:1.25; 7, 1:250:1.00; 8, calculated for $[CuC_2O_4\ en]^0$; 9, 1:250:0.75; 10, 1:250:0.5; 11, 1:250:0.25; 12, 1:250:0.

Discussion

If ethylenediamine is added to a solution containing copper(II) ions and a moderate excess of oxalate ions the extinction curve shifts from that for bis-(oxalato)-cuprate(II) toward shorter wave lengths until, with an excess of ethylenediamine, it coincides with the extinction curve for bis-(ethylenediamine)-copper(II) ion. When the ratio of copper ion to ethylenediamine is close to unity the extinctions in the wave length range of 600 to 700 mμ are greater than those due to either the oxalate or ethylenediamine complex or calculated for mixtures of the two, indicating the presence of a new specie. By analogy with previous results, its formula is anticipated to be $[Cu(C_2O_4)en]^0$.

In Fig. 1 is shown a series of extinction curves obtained by adding decreasing concentrations of ethylenediamine, indicated by the symbol, en, to solutions containing 0.010 M Cu^{2+} and 0.25 M $C_2O_4^{2-}$. It is observed that curve 3 for the solution containing exactly the stoichiometric concentration of ethylenediamine required to form $[Cuen_2]^{2+}$, nearly coincides with curve 2 which is due to $[Cu(en)_2]^{2+}$. With an excess of ethylenediamine and 0.25 M oxalate as shown in curve 1 the extinction is slightly greater than that in the absence of oxalate ion as shown in curve 2. However, the maximum extinction occurs at exactly the same wave length of 550 mμ and by reducing the oxalate concentration to 0.1 M the two curves coincide. The cause of this slight enhancement of the extinction in solutions containing high oxalate concentrations has not been established. It may be due to a slight tendency of the ethylenediamine complex to accept an oxalate ion in an outer sphere or in extra inner coördination positions as already discussed for ammonia[3] or it may be due to a change in the

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[1] To whom communications should be directed.

[2] Presented before the Division of Physical and Inorganic Chemistry at the convention of the American Chemical Society at Kansas City, Mo., April 1, 1954.

[3] J. I. Watters, A. Aaron and J. Mason, This Journal, **75**, 5212 (1953).

[4] J. I. Watters and E. D. Loughran, *ibid.*, **75**, 4819 (1953).

dielectric constant of the solvent. The complication was eliminated by reducing the oxalate concentration to 0.1 *M*. There are fairly well defined isosbestics at 600 and 700 mμ which are evident from the data in Table I for curves approaching those of the simple oxalate and ethylenediamine complexes. The failure of curves 6, 7, 9 and 10 to pass through these isosbestics indicates, as will be proved, that the equilibrium in this composition range actually involves appreciable concentrations of three species.

The addition of standardized 0.735 *M* nitric acid to solutions containing 0.01 *M* Cu^{2+}, 0.1 *M* ethylenediamine and 0.1 *M* $K_2C_2O_4$ with the ionic strength adjusted to unity with $NaNO_3$ produced a series of curves similar to those of Fig. 1, obtained by varying the ethylenediamine concentration. When the *p*H was reduced from about 7.5 to 5.3 the equilibrium shifted from essentially the pure ethylenediamine to predominantly the oxalate complex. These results are summarized in Table I. The fact that similar extinction curves could be obtained independently of *p*H eliminated the possibility that the complex might contain hydroxyl or hydrogen ions. A continuous variation[4] experiment using 0.005 *M* $[Cuen_2]^{2+}$ and 0.005 *M* $[Cu(C_2O_4)_2]^{2-}$ yielded as shown in Fig. 2 a distinct maximum or minimum in the enhancement of the extinction at $x = 0.5$ at several wave lengths. This indicated the formation of a neutral mixed complex having the empirical formula $[Cu(C_2O_4)en]^0$. The following equilibria were accordingly postulated

TABLE I

EFFECT OF VARYING THE RATIO $[en]/[C_2O_4^{2-}]$ THROUGH *p*H ADJUSTMENTS BY ADDING HNO_3

All solutions 0.1 *M* $K_2C_2O_4$, 0.1 *M* ethylenediamine, HNO_3 varied; $\mu = 1.0$ with $NaNO_3$, $T = 25°$, $E = \log_{10} I_0/I$, 1-cm. cells.

*p*H	E_{480}	E_{600}	E_{640}	E_{646}	E_{700}	E_{800}	$-\log f_{en}$[a]
11.12[b]	0.282	0.460	0.280	0.260	0.115	0.025	
11.21	.273	.460	.285	.265	.119	.030	
7.28	.256	.460	.294	.271	.124	.029	
7.14	.247	.459	.296	.275	.127	.030	
6.92	.235	.461	.315	.293	.147	.039	
6.85	.224	.461	.320	.298	.155	.039	3.73
6.73	.202	.460	.333	.312	.172	.047	3.95
6.66	.187	.460	.346	.326	.192	.056	4.07
6.56	.162	.460	.365	.349	.207	.069	4.27
6.47	.140	.455	.380	.364	.230	.080	4.42
6.37	.112	.450	.402	.387	.260	.096	4.61
6.28	.087	.432	.400	.390	.271	.107	4.78
6.19	.070	.414	.400	.392	.288	.119	4.95
6.08	.045	.376	.390	.386	.310	.142	5.17
5.90	.034	.327	.369	.370	.329	.170	5.52
5.81	.020	.285	.343	.345	.327	.181	5.68
5.72	.014	.250	.320	.327	.332	.195	5.86
5.61	.015	.225	.302	.312	.336	.202	6.08
5.50	.012	.179	.275	.285	.337	.225	6.30
5.29	.007	.142	.250	.265	.335	.235	6.72
5.20	.008	.135	.246	.264	.341	.250	6.90
5.12	.010	.129	.244	.256	.345	.244	
5.11[c]	.101	.117	.227	.245	.343	.242	

[a] $f_{en} = [en]/([en] + [Hen^+] + [H_2en^{2+}])$. [b] No oxalate added. [c] No ethylenediamine or nitric acid added.

$$[Cuen_2]^{2+} + C_2O_4^{2-} \rightleftharpoons [Cu(C_2O_4)en]^0 + en \qquad (1)$$

$$K_p = \frac{[[Cu(C_2O_4)en]^0][en]}{[[Cuen_2]^{2+}][C_2O_4^{2-}]} = \frac{K_m}{K_{en}} \qquad (2)$$

$$[Cu(C_2O_4)en]^0 + C_2O_4^{2-} \rightleftharpoons [Cu(C_2O_4)_2]^{2-} + en \qquad (3)$$

$$K_q = \frac{[[Cu(C_2O_4)_2]^{2-}][en]}{[[Cu(C_2O_4)en]^0][C_2O_4^{2-}]} = \frac{K_{ox}}{K_m} \qquad (4)$$

where K_{en}, K_{ox}, and K_m are the complexity constants of the ethylenediamine, the oxalate and the mixed complex, respectively.

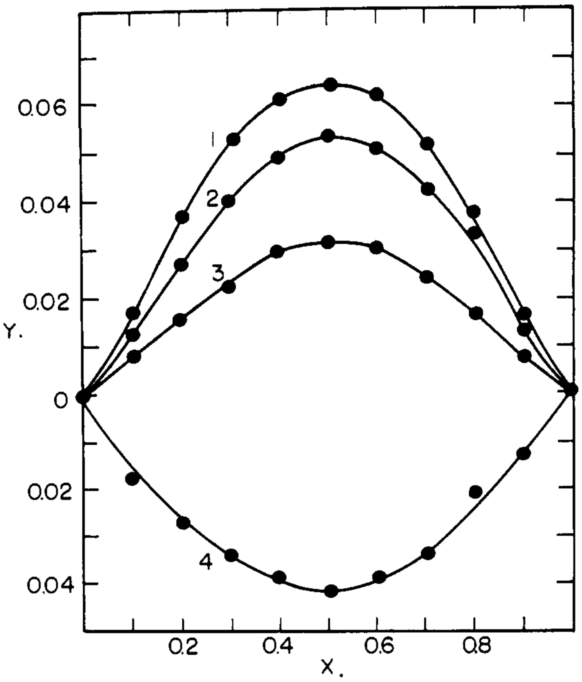

Fig. 2.—Continuous variations of $1 - x$ volumes of 0.005 *M* $[Cu(en)_2]^{2+}$ with x volumes of 0.005 *M* $[Cu(C_2O_4)_2]^{2-}$ at different wave lengths. *Y* is the enhancement of the extinction due to mixed complex formation. 1-cm. cells were used. 1, 646 mμ; 2, 600 mμ; 3, 700 mμ; 4, 480 mμ.

In a manner already described[4] a combination of expressions for Beer's law, the conservation of copper ions and equation 2 yields the following expression

$$\frac{[C_2O_4^{2-}]/[en]}{(e_{en} - \bar{e})} = \frac{1}{(e_{en} - e_m)K_p} + \frac{[C_2O_4^{2-}]/[en]}{(e_{en} - e_m)} \qquad (5)$$

where e_{en} and e_m are the molar extinction coefficients of the ethylenediamine complex and the mixed complex, respectively, while $\bar{e}$ is the observed mean molar extinction coefficient of copper ion in all forms.

The term $[C_2O_4^{2-}]/[en]/(e_{en} - \bar{e})$ is plotted along the *y*-axis *versus* $[C_2O_4^{2-}]/[en]$ along the *x*-axis to yield a straight line having a slope of $(e_{en} - e_m)^{-1}$ and an intercept $(e_{en} - e_m)^{-1}K_p^{-1}$. If the ratio of oxalate to ethylenediamine is sufficiently large so that the equilibrium shifts until equation 3 becomes important the following expression must replace equation 5

$$\frac{R}{(e_{en} - \bar{e})} = \frac{1 + K_pR + K_pK_qR^2}{(e_{en} - e_m)K_p + (e_{en} - e_{ox})K_pK_qR} \qquad (6)$$

where R is the ratio $[C_2O_4^{2-}]/[en]$, and e_{ox} is the molar extinction coefficient of the oxalate complex.

It is accordingly important to work in a range where the quantity $K_pK_qR^2$ is, as indicated by Landauer and McConnell,[5] small compared to K_pR and the last term in the denominator drops if the data are obtained at 650 mμ where $e_{en} = e_{ox}$. Of greater importance is the choice of a wave length where the difference between the extinction coefficients of the two dominant species reaches a maximum. If the measurements are made below about 580 mμ the extinction coefficient of known species, e_{en}, is large compared to that of the postulated species, e_m.

In the *p*H range where the oxalate and the mixed complex predominate a combination of Beer's law, the expression for the conservation of copper ions, and equation 3 yields

$$\frac{[en]/[C_2O_4^{2-}]}{(e_{ox} - \bar{e})} = \frac{K_q}{(e_{ox} - e_m)} + \frac{[en]/[C_2O_4^{2-}]}{(e_{ox} - e_m)} \quad (7)$$

The term $[en]/[C_2O_4^{2-}]/(e_{ox} - \bar{e})$ is plotted along the *y*-axis *versus* $[en]/[C_2O_4^{2-}]$, along the *x*-axis. The slope of the linear portion of the curve is equal to $(e_{ox} - e_m)^{-1}$ and the intercept has the value $K_q/(e_{ox} - e_m)$. When the ratio $[en]/C_2O_4^{2-}]$ becomes sufficiently large so that an appreciable concentration of the ethylenediamine complex is present, the above limiting expression must be replaced by one analogous to equation 6. The intercept divided by the slope yields K_q and permits an independent evaluation of K_m *vs.* K_{ox}, according to equation 4. The molar extinction coefficient of the mixed complex can be calculated from the reciprocal slope since e_{ox} can be measured but more accurate values were obtained by the isosbestic method. The best value for K_q should be obtained near 800 mμ where the difference between the extinction coefficients, e_m and e_{ox}, reaches a maximum.

The fact that many of the curves in the intermediate *p*H range did not pass through either isosbestic indicated an equilibrium among all three complex species, thus

$$2[Cu(C_2O_4)en]^0 \rightleftarrows [Cu(C_2O_4)_2]^{2-} + [Cuen_2]^{2+} \quad (8)$$

$$K_s = \frac{[[Cu(C_2O_4)_2]^{2-}][[Cuen_2]^{2+}]}{[[Cu(C_2O_4)en]^0]^2} = \frac{K_{ox}K_{en}}{K_m^2} \quad (9)$$

From equation 9 it is evident that the magnitude of the dismutation constant, K_s, is independent of the concentrations of ethylenediamine or oxalate ions and can be calculated from the concentrations of the three complex species alone. Its relation to the three complexity constants thus permits a completely independent evaluation of K_m on the basis of spectrophotometric measurements alone. The concentrations of the three complex species can be obtained by the isosbestic method proposed by Watters and Loughran.[4] At the 600 mμ isosbestic where the molar extinction coefficients, e_{i_1}, of both the amine and the mixed complex have the value 46.0 molar^{-1} cm.$^{-1}$, the corresponding value e_{ox_1} for the oxalate complex is 11.7 molar^{-1} cm.$^{-1}$. Thus any decrease in the observed mean molar extinction coefficient, $\bar{e}_1$, below 46.0 molar^{-1} cm.$^{-1}$ is due to the presence of the oxalate complex for which the mole fraction, x_{ox}, is readily calculated thus

$$x_{ox} = \frac{e_{i_1} - \bar{e}_1}{e_{i_1} - e_{ox_1}} \quad (10)$$

At the 700 mμ isosbestic, where the molar extinction coefficients of both the oxalate and the mixed complex, e_{i_2}, are 34.3 molar^{-1} cm.$^{-1}$ and the value for the ethylenediamine complex is 11.5 molar^{-1} cm.$^{-1}$, any decrease in the observed mean molar extinction coefficient, $\bar{e}_2$, is due to the presence of the amine complex for which the mole fraction, x_{en}, is calculated thus

$$x_{en} = \frac{e_{i_2} - \bar{e}_2}{e_{i_2} - e_{en_2}} \quad (11)$$

Finally these data were used to calculate the extinction curve for the pure mixed complex, curve 8 in Fig. 1, from the data for any curve thus

$$e_m = \frac{(\bar{e} - x_{en}e_{en} - x_{ox}e_{ox})}{(1 - x_{en} - x_{ox})} \quad (12)$$

After e_m had been calculated at a wave length other than the isosbestics the concentrations of all three species were readily calculated by determinants using three equations of the following form for three wave lengths

$$\bar{e} = x_{ox}e_{ox} + x_{en}e_{en} + x_me_m \quad (13)$$

where

$$\log_{10} I_0/I = \bar{e}[Cu^{2+}]_0 \quad (14)$$

and $[Cu^{2+}]_0$ is the concentration of copper ion in all forms. These data permitted calculations of K_p and K_q by substitution of data from individual experiments into equations 2 and 4.

In the *p*H variation experiments a large variation in [en] was readily obtained by *p*H adjustments and [en] was readily calculated as previously described.[4] Oxalic acid,[6] having pK_1 and pK_2 values of about 1.14 and 3.85, is a sufficiently strong acid to remain dissociated throughout the entire effective *p*H range. The isosbestic value of 46.0 molar^{-1} cm.$^{-1}$ at 600 mμ is evident from the extinctions of the first 8 solutions at 600 mμ while the isosbestic value of 34.3 at 700 mμ is evident from the extinctions of the last six solutions at 700 mμ.

In this study it was possible to obtain fairly accurate preliminary values for K_p and e_m by applying this graphic method to equation 5 without correcting for the concentration of oxalate and ethylenediamine bound in the complexes because the total concentrations of these species in all forms were fairly large compared to those of the complex species. In Fig. 3, curves 1 and 2, respectively, show the results obtained at 480 mμ without and with this correction. For the uncorrected data in curve 1 the slope of 4.0 × 10^{-2} molar cm. and the intercept of 7.8 × 10^2 molar cm. yield a value of 4.29 for pK_p. After estimating the concentrations of complexes on the basis of this value of pK_p and equation 2, the calculations were repeated after applying a correction for the bound ligands. For the corrected data in curve 2, Fig. 3, the slope of 4 × 10^{-2} molar cm. the intercept of 9 × 10^2 molar cm. yield a value of 4.35 for pK_p and 3.3 molar^{-1} cm.$^{-1}$ for e_m. Similar calculations at 560 and 700 mμ yielded final values of 4.66 and 4.58 for pK_p.

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(5) L. Landauer and H. McConnell, This Journal, **74**, 1221 (1952).

(6) R. K. Cannan and A. Kibrick, *ibid.*, **60**, 2314 (1938).

The graphs were always perfectly linear in the pH range of 6.8 to 6.4. Below this pH the linear relation failed due to the presence of significant concentrations of $[Cu(C_2O_4)_2]^{2-}$ while the change in extinction was insufficient at higher pH values. Using Bjerrum's[7] value of -20.04 for pK_{en} and the mean value 4.53 ± 0.18 for pK_p yields -15.51 for pK_m.

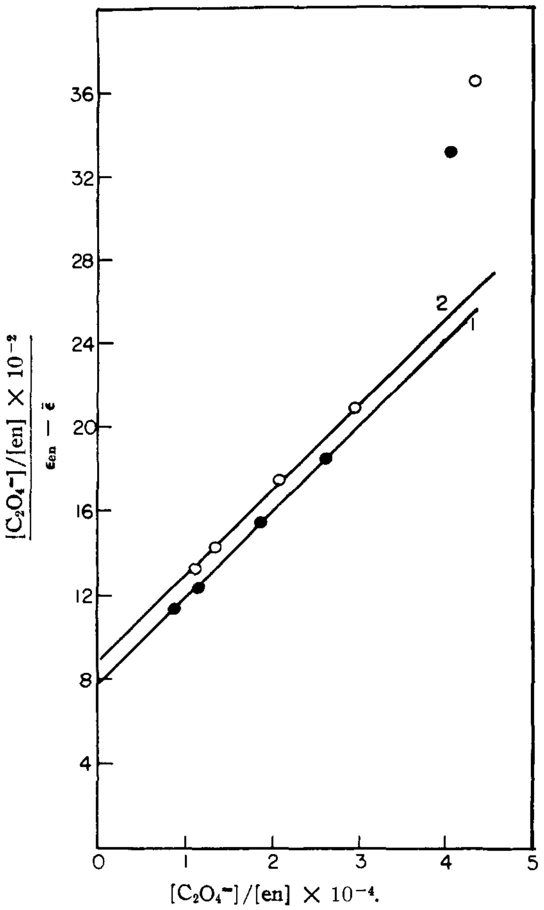

Fig. 3.—Graphic determination of equilibrium constant, K_p at 480 mμ. The five points plotted had pH values of 6.73 to 6.37: 1, not corrected for ligands bound in complex; 2, corrected.

A similar slope intercept treatment of the data at 800 mμ according to equation 7 for solutions having extinctions approaching that of the oxalate complex yielded, as shown in Fig. 4, linear results in the pH range of 5.6 to 6.0. The slope of 10.7×10^{-2} molar cm. and the intercept of 1.4×10^{-5} molar cm. in curve 2 yield a value of 5.88 for pK_q and 14.8 molar^{-1} cm.$^{-1}$ for e_m. To calculate K_m a value of -9.70 was taken for pK_{ox} the negative logarithm of the complexity constant of the oxalate complex at 25° and unit ionic strength as described by Meites[8] except that +0.015 volt *versus* the saturated calomel electrode was used instead of +0.030 volt for the standard potential of aquocopper(II) ion. This value calculated by the authors from polarographic data for bis-(ethylenediamine)-copper(II) is close to that used in most of the polarographic literature.[9] Combining the values of pK_q and pK_{ox} according to equation 4 yields the value -15.58 for pK_m.

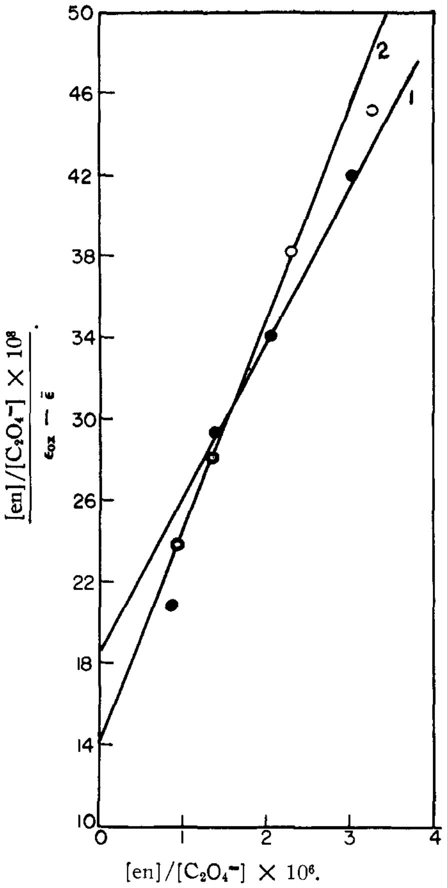

Fig. 4.—Graphic determination of equilibrium constant, K_q at 800 mμ. The points plotted had pH values of 5.61 to 5.90: 1, not corrected for ligands bound in complex; 2, corrected.

In Table II are listed the mole fractions of the copper present as each complex calculated at each pH first in the row indicated by (a) on the basis of equations 10 and 11 and then, in the second row indicated by (b), by determinants using three equations of the form of (11) at the wave lengths 600, 640 and 700 mμ. The ratio $[en]/[C_2O_4^{2-}]$ corrected for the concentrations of ligands bound in the complexes is also included. In the last three columns are given the equilibrium constants based on the individual data. The deviations in the negative logarithms of the constants calculated from the individual data were usually much less than 0.20 except in those calculations involving values where the experimental error in the spectrophotometric measurements was the limiting factor.

The constant K_s is of particular interest for it permits the evaluation of K_m on the basis of spectrophotometric measurements alone. The mean value of 1.00 ± 0.05 for pK_s combined with the values -20.04 and -9.70 for pK_{en} and pK_{ox} according to equation 9 yields -15.37 for pK_m in

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[7] J. Bjerrum and E. N. Nielson, *Acta Chem. Scand.*, **2**, 297 (1948).

[8] L. Meites, THIS JOURNAL, **72**, 184 (1950).

[9] N. C. Li and R. Doody, *ibid.*, **74**, 4184 (1952).

TABLE II

CALCULATION OF EQUILIBRIUM OF CONSTANTS FROM COMPLEX CONCENTRATIONS

At each *p*H the values in the (a) series were solved at isosbestics by equations 10 and 11 while those in the (b) series were solved by determinants using equation 11 at 600, 640 and 700 mμ.

*p*H	$\frac{[\text{en}]}{[C_2O_4^{2-}]} \times 10^6$		X_{ox}	X_m	X_{en}	pK_p	pK_q	pK_s
6.85	183	(a)	0	0.177	0.823	4.41		
		(b)	0	.188	.812	4.38		
6.73	93.5	(a)	0	.253	.747	4.50		
		(b)	0	.271	.728	4.46		
6.66	74.1	(a)	0	.341	.659	4.42		
		(b)	0	.359	.641	4.38		
6.56	47.8	(a)	0	.408	.592	4.48		
		(b)	0	.437	.563	4.40		
6.47	33.8	(a)	0.014	.495	.491	4.47		
		(b)	.018	.490	.492	4.47		
6.37	22.8	(a)	.029	.600	.351	4.41		
		(b)	.035	.597	.371	4.44		
6.28	15.9	(a)	.082	.609	.310	4.51	5.67	1.16
		(b)	.075	.611	.308	4.50	5.71	1.24
6.19	11.0	(a)	.134	.632	.234	4.52	5.63	1.07
		(b)	.147	.614	.257	4.58	5.58	1.00
6.08	6.92	(a)	.244	.593	.137	4.53	5.54	1.02
		(b)	.262	.586	.163	4.60	5.51	.92
5.90	3.25	(a)	.388	.503	.109	4.82	5.60	.78
		(b)	.414	.513	.091	4.74	5.58	.85
5.81	2.33	(a)	.507	.423	.070	4.85	5.56	.71
		(b)	.478	.463	.035	4.51	5.62	1.11
5.72	1.32	(a)	.612	.365	.039		5.66	
		(b)	.589	.371	.032		5.68	
5.61	0.956	(a)	.685	.285	.022		5.64	
		(b)	.685	.285	.023		5.64	
5.50	.595	(a)	.819	.163	.018		5.53	
		(b)	.795	.186	0		5.60	
5.29	.227	(a)	.927	.073	0		5.54	
		(b)	.895	.095	0		5.67	
5.20	.149	(a)	.947	.053	0		5.58	
		(b)	.939	.059	0		5.62	
					Av. (a)	4.54	5.60	.95
					(b)	4.51	5.62	1.04

good agreement with the values obtained by two different slope intercept methods. On a statistical basis alone the concentration of the mixed complex should be twice that of either simple complex for equal concentrations of the latter two. Thus statistical considerations lead to a value of 0.60 for pK_s compared to the observed value of 1.0. A complete interpretation of the factors responsible for the remaining 0.40 must await further study of other mixed complexes. It is probably due to the absence of the electrical repulsion contribution obtained when two oxalate anions are associated for the effect is larger when the tetravalent pyrophosphate anion replaces the oxalate anion.[4] In the latter case pK_s has the value 1.70.

The values of pK_p and pK_q obtained from the individual data are also in good agreement with those obtained by the slope intercept treatments. In Table III are summarized the mean values of K_m calculated by eight different methods. The mean value of pK_m is -15.44 ± 0.14.

TABLE III

Method	Equations	pK_p	pK_q	pK_s	log K_m
Slope intercept	5	4.53			15.51
Slope intercept	7		5.88		15.58
Isosbestics	10, 2	4.54			15.50
Isosbestics	11, 4		5.60		15.30
Isosbestics	10, 11, 9			0.95	15.35
Determinants	13, 2	4.51			15.53
Determinants	13, 4		5.62		15.32
Determinants	13, 9			1.04	15.39
				Av.	15.44 ± 0.14

COLUMBUS, OHIO

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Hydrogen–Deuterium Exchange on Copper, Silver, Gold and Alloy Surfaces[1]

BY RICHARD J. MIKOVKSY, MICHEL BOUDART AND HUGH S. TAYLOR

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The catalytic activity of copper, silver and gold foils, of a silver–lead (0.69 atom %) alloy foil and of several granular silver catalysts has been studied in the hydrogen-deuterium-exchange reaction. Observed activation energies and temperature ranges of activity of the catalysts have been measured. The data lead to observations on two possible mechanisms of the exchange reaction, to a suggested activation of copper by d-s promotion of the metal, and to a possible unification of "Brillouin zone" and d-band concepts in relation to catalysis.

Introduction

Copper has occupied an anomalous position in the history of hydrogenation catalysts in that while its activity in certain reactions has been studied for many years it has been known that, for the hydrogenation of benzene, it was ineffective in comparison with such catalysts as nickel.[2] It did not conform to the Balandin multiplet hypothesis relating catalytic action to lattice parameter.[3] Latterly, the relative inactivity of copper and of silver and gold has been related to the complete d-bands in their crystals[4] with the possibility that activity in chemisorption is related to d-s promotion.[5] The white color of silver suggests that the d-s promotion energy is greater than in the case of the colored metals copper and gold. That evaporated films of copper are unable to chemisorb N_2 and H_2 in the region 0 to −183° has recently been recorded by Allen and Mitchell.[6] By contrast, in the early literature, chemisorption of hydrogen by reduced copper

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[1] This article is based on a thesis submitted in partial fulfillment of the requirements for the Ph.D. degree in Princeton by R. J. Mikovsky in September, 1951.

[2] J. H. Long, J. C. W. Frazer and E. J. Ott, THIS JOURNAL, **56**, 1101 (1934); V. N. Ipatieff, B. B. Corson and J. D. Kurbatov, *J. Phys. Chem.*, **43**, 589 (1939).

[3] P. H. Emmett and N. Skau, THIS JOURNAL, **65**, 1029 (1943).

[4] D. A. Dowden, *Research*, **1**, 239 (1948); *J. Chem. Soc.*, 242 (1950).

[5] (a) M. Boudart, A.C.S. meeting, New York, September, 1951; (b) THIS JOURNAL, **74**, 1534 (1952); (c) R. J. Mikovsky, Thesis, Princeton, 1951; (d) B. M. W. Trapnell, *Proc. Roy. Soc.* (*London*), **A218**, 566 (1953).

[6] J. A. Allen and J. W. Mitchell, *Discs. Faraday Soc.*, 361 (1950).