Summary

1. The isotherm for the quaternary system $MgCl_2$–$CaCl_2$–KCl–H_2O has been determined at 0°.

2. The solid phases occurring in the quaternary isotherm are KCl, $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 6H_2O$ and the double-salt hydrate carnallite, $MgCl_2 \cdot KCl \cdot 6H_2O$.

3. The isotherm at 0° is characterized by the extreme insolubility of potassium chloride and of carnallite in solutions saturated for magnesium chloride. This was noted previously[1] in studying the 0° isotherm of the system $MgCl_2$–KCl–H_2O. Both potassium chloride and carnallite are more soluble, within a restricted concentration range, in magnesium chloride solutions containing calcium chloride. Carnallite, however, cannot exist at 0° in contact with solutions containing less than 3.3% magnesium chloride or more than 33.4% calcium chloride.

4. All quaternary solutions saturated for carnallite are incongruently saturated.

5. Schreinemakers' method of residues was used for identification of the solid phases in this isotherm.

6. A method is suggested for extending the method of residues to quaternary systems containing metathetical components.

SEATTLE, WASHINGTON RECEIVED APRIL 23, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Solubility of Cupric Oxide in Alkali and the Second Dissociation Constant of Cupric Acid. The Analysis of Very Small Amounts of Copper

BY LEON A. MCDOWELL AND HERRICK L. JOHNSTON

The blue solutions produced when either cupric oxide or cupric hydroxide is treated with alkali have been objects of investigation[1–3] for more than a century. They were thought by some investigators[2] to be colloidal but have been shown, more recently, to represent true cases of chemical solution.[3] The most decisive work in support of this conclusion is that of Müller,[3] who obtained reproducible values of solubility and determined solubility curves, both for the oxide and for the hydroxide, between five normal and about twenty normal sodium hydroxide concentrations. At about fifteen normal alkali maxima were obtained in the solubility curves and at concentrations above these maxima the stable solid phase consisted of dark blue crystals whose analysis corresponded to the formula Na_2CuO_2. Aldridge and Applebey[4] have identified similar copper salts of the alkaline earths.

Müller observed that the solubility of the hydroxide exceeds that of the oxide several fold, which represents a case of metastable equilibrium since the hydroxide solubility diminishes with time and, simultaneously, the solid phase is converted to what appears to be a solid solution of hydroxide with oxide. The oxide solubility does not change with time. An apparently permanent difference between the solubility of the oxide and that attained, after several days, by the hydroxide is not explained.

The present investigation, at lower alkalinities than those employed by Müller, was carried out to obtain additional information on the nature of the copper-bearing ions present in solution and to determine dissociation constants of cupric acid.

Experimental

The method employed was similar to that followed by Johnston, Cuta and Garrett[5] in a similar study with silver oxide, and the solubility apparatus and general manipulations were the same.

Cupric oxide was prepared by dropping 0.06 *N* solutions of copper sulfate and of potassium hydroxide, simultaneously, into an initial 500 cc. of boiling conductivity water in a Pyrex reaction vessel. The entire process including subsequent washings (15 to 20 in number) was carried out in an atmosphere of nitrogen. The wash water gave no test for sulfate ion (barium chloride test) after seven or eight washings and the final product gave no test for sulfate when dissolved in nitric acid and the solution diluted.

Potassium hydroxide at concentrations below 1 *N* was prepared from pure amalgams in the manner described by Johnston, Cuta and Garrett. Potassium and sodium hydroxides at concentrations above 1 *N* were prepared from solutions of the reagent quality hydroxides by the addition

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(1) Proust, *J. Phys.*, **59**, 395 (1804); Low, *Z. anal. Chem.*, **9**, 463 (1870); Donath, *ibid.*, **40**, 137 (1901).

(2) Fischer, *Z. anorg. Chem.*, **40**, 39 (1904); Chatterji and Dhar, *Chem. News.*, **121**, 253 (1920).

(3) (a) Creighton, THIS JOURNAL, **45**, 1237 (1923); (b) Melbye, *Vetenskapsakad, Nobelinst*, **4**, No. 8 (1922); (c) E. Müller, *Z. physik. Chem.*, **105**, 73 (1923).

(4) Aldridge and Applebey, *J. Chem. Soc.*, **121**, 238 (1922).

(5) H. L. Johnston, F. Cuta and A. B. Garrett, THIS JOURNAL, **55**, 2311 (1933).

of sufficient barium hydroxide to precipitate the carbonate.

Salts, except potassium ferrocyanide as noted later, were twice recrystallized from "reagent quality" products.

Conductivity water which even after several weeks' storage had a conductivity no higher than 2 × 10^{-6} mho was employed in the preparation of all solutions and in the washing and purification of materials.

Equilibrium was approached both from the cold and from the hot side. For approach from the cold side samples were agitated at 25 ± 0.01° for from fourteen to fifty days. For approach from the hot side samples were first agitated at 45° for four days, then transferred to the 25° thermostat for an additional fourteen days. The shorter period appeared adequate in every instance. Seven days were allowed for *sedimentation.* A portion of the clear solution was then siphoned from each flask and *filtered* through a No. 1 sintered Jena glass filter, preparatory to analysis for total alkali and for copper. The first portions of the solutions which passed through the filter were discarded.

Analytical Procedure

After testing various methods which have been used for the determination of small concentrations of copper, including colorimetric methods and the polarigraph, electrometric titration with potassium ferrocyanide as precipitant was employed.

There have been several previous attempts to determine copper electrometrically but none were entirely satisfactory for very small amounts. Dutoit and von Weisse[6] concluded that a copper electrode is unsuitable for cupric copper because of irregularities in the change of its potential. By using a polarized platinum electrode they were able to titrate 0.01 N copper solutions with potassium sulfide, potassium ferrocyanide or sodium thiosulfate to a precision of about 1% but the low sensitivity of the method and the deposit of some copper by the polarizing current render the method unsuitable for determinations in which the copper concentration falls as low as 1 × 10^{-4} M. Titration as cuprous thiocyanate, with a copper electrode,[7] or reduction with an excess of titanous chloride followed by back titration with either potassium dichromate or potassium bromate,[8] is not sufficiently accurate for our requirements.

After unsatisfactory trials of a copper electrode in titrations with either sodium sulfide or potassium ferrocyanide, in which our experience was similar to that of Dutoit and von Weisse, we substituted an electrode of platinum foil. With sodium sulfide results were still unsatisfactory due to the fact that the end-point depended to too great an extent on the *p*H value of the solution. With ferrocyanide as precipitant,[9] and a technique similar to that employed by Johnston, Cuta and Garrett, high sensitivity and good accuracy were obtained. Titration of 10 cc. of a standard copper solution 6 × 10^{-4} M in cupric ion with potassium ferrocyanide which had a copper equivalence of 1 × 10^{-6} mole of copper per cc. led to an inflection of from 10 to 16 mv. per drop (0.02 cc.) at the equivalence point and the end-point could usually be located to within one or two drops. It was found best to clean the electrode with pumice after each titration; otherwise the sensitivity was continuously reduced. The position of the end-point was independent of the dimensions of the platinum foil (absence of adsorption). Titrations were carried out in a 250-cc. beaker which was connected by a bridge of potassium nitrate set in agar-agar to a calomel half cell. The copper solution was made just acid to methyl orange indicator. Readings of electromotive force were taken at three-minute intervals and near the end-point the standard ferrocyanide solution was added one drop at a time from a microburet.

The ultimate standard for the determination of copper was an approximately 0.06 M solution of copper sulfate which was analyzed for copper by electrolytic deposition and then diluted one hundred fold. Potassium ferrocyanide solutions, of copper equivalences varying from 1 × 10^{-6} to 6 × 10^{-6} mole of copper per cc. were prepared from Baker and Adamson reagent quality potassium ferrocyanide without recrystallization. These were standardized by titration against the standard copper solutions under conditions closely identical with those employed in the analysis of samples (*i. e.*, acidity, salt concentrations, total volume, temperature, etc.).

Total alkalinity was determined by titration with standard sulfuric acid to the first sharp color change with methyl orange.

Our experience with the use of the ferro-ferricyanide couple for the titration of copper differs from that of Müller and Takegami,[10] who found no sharp inflection in the e. m. f. curve and concluded that the difficulty lay in some secondary reaction such as

$$3Cu_2Fe(CN)_6 + K_4Fe(CN)_6 = 2K_2Cu_3Fe_2(CN)_{12}$$

We found, in titrations which employed weighed amounts of the reagent quality potassium ferrocyanide, that the sharp break in the e. m. f. curve came at a position within 5% of the stoichiometric value for the assumed formation of $Cu_2Fe(CN)_6$. This approximate 5% deviation was reproducible. With our method of standardization described above, this reproducible deviation from the stoichiometric end-point did not introduce error into the analyses.

The Solubility Data

The results obtained are given in the following tables in which all concentrations are expressed in moles per 1000 g. of water. These are also illustrated in the accompanying figure. Samples were always run in pairs to obtain approach to equilibrium both from the side of undersaturation and from that of supersaturation. In the tables, the data obtained with individual samples are shown separately[11] while, in the figures, the circles

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[6] Dutoit and von Weisse, *J. chim. phys.*, **9**, 578 (1911).

[7] Treadwell and Weiss, *Helv. Chim. Acta*, **2**, 694 (1919).

[8] Zintl and Wattenberg, *Ber.*, **55**, 3366 (1922).

[9] The electromotive force of the cell depends on the ferro-ferricyanide couple. Bichowsky [*Ind. Eng. Chem.*, **9**, 668 (1917)] obtained success with the use of the ferro-ferricyanide couple in the titration of zinc. *Cf.* also Kolthoff and Verzijl, *Rec. Trav. Chim.*, **43**, 380 (1924).

[10] Müller and Takegami, *Z. anal. Chem.*, **73**, 284 (1928).

[11] Alkalinities were separately determined for each sample. When significant differences were found for the two samples constituting a pair the data were corrected to a common alkalinity.

represent the means of the results obtained from under- and from supersaturation.

TABLE I

SOLUBILITY OF CUPRIC OXIDE IN AQUEOUS POTASSIUM HYDROXIDE

Alkali molality	Moles of copper per 1000 g. $H_2O \times 10^5$ Undersaturated	Supersaturated
0.0417	0.07	0.07
.0513	.08	.08
.0586	.151	.158
.0600	.132	.241
.0741	.196	.189
.0832	.172	.162
.0932	.409	.414
.0968	.302	.282
.1027	.145	.184
.1150	.324	.308
.1175	.300	.273
.1385	.398	.371
.1608	.489	.604
.1705	.608	.563
.1772	.534	.518
.2035	1.02	.83
.2165	0.96	.73
.2238	.93	.84
.2637	1.34	1.25
.2761	...	1.56
.3163	4.04	3.72
.3244	4.66	3.44
.544	4.91	5.36
.650	4.66	3.72
.753	11.7	11.0
.860	11.2	9.8
1.000	16.1	16.2
1.337	26.1	24.4
1.633	32.4	34.3
1.963	71.0	65.7
2.333	82.7	79.6
2.495	80.1	73.1
2.848	91.8	94.1
3.180	117.2	121.4
3.380	132	87.0
4.015	171	144
4.151	144	150
4.227	164	156
5.065	184	167
5.253	203	181
6.05	297	...
8.38	...	435

TABLE II

SOLUBILITY OF CUPRIC OXIDE IN AQUEOUS SODIUM HYDROXIDE

Alkali molality	Moles copper per 1000 g. $H_2O \times 10^5$ Undersaturated	Supersaturated
2.212	70.1	71.4
3.247	92.5	...
4.227	185	176

Data obtained by Müller[3] are included in Fig. 1, in which the curve is empirical. The solid curves in Figs. 2 and 3 are calculated from equation (4). The basis of this calculation and the significance of the broken lines will be referred to later.

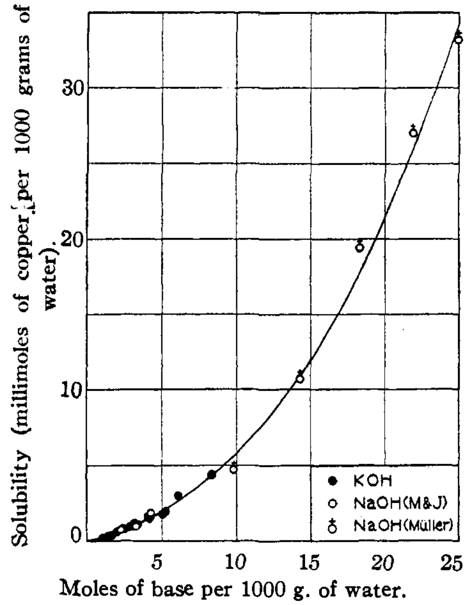

Fig. 1.—Solubility of cupric oxide in strong alkali.

We attempted to determine the solubility of the oxide in pure water and to locate accurately the position of the minimum on the solubility curve. In this we were faced with the difficulty that the solutions usually came out colloidal unless the alkalinity exceeded about 0.03 normal. It was thought best not to include data obtained for several alkalinities below 0.04 normal because of non-reproducibility. But we may conclude from the solubility product of hydroxide or oxide in pure water that the minimum on the solubility curve must lie at an alkali concentration below 0.01 normal.

We were successful in obtaining a rough value for the solubility of the oxide in pure water. This value is 2.9×10^{-5} mole/liter at 25° and is the mean of four determinations (2.5, 3.5, 3.7 and 1.7×10^{-5}, respectively) in which colloidal material was not visible. Three other samples, which were similarly handled, were definitely colloidal and were not analyzed. This result is represented by the triangle in the border of Fig. 2. While we do not regard this value as particularly accurate, we do not believe that the solubility of the oxide can be appreciably higher than this since the nature of the experimental difficulties were such as would lead to high rather than to low results. This constitutes the only value in the literature based on a direct analytical determination. Jellinek and Gordon[12] obtained 1.7 × 10^{-13} for the solubility product of the hydroxide at 20° by concentration cell measurements, in the presence of excess alkali. This result, which is not corrected for the changing activity coefficients of the ions, corresponds to a solubility about double that which we have determined. There is probably a real difference between the oxide and the hydroxide solubilities in water, as there is in alkali,[3] so that this value probably corresponds to a more soluble form than the stable oxide. Remy and Kuhlmann[13] obtained 6.7 × 10^{-5} mole/liter for the oxide at 20°, by conductimetric methods.

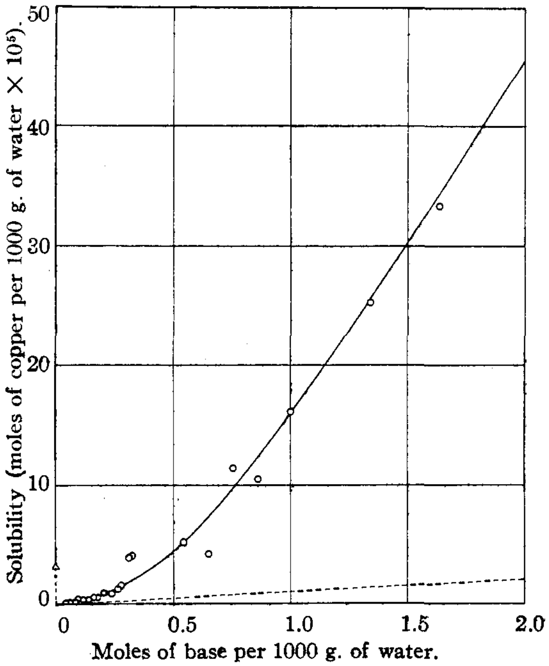

Fig. 2.—Solubility of cupric oxide in potassium hydroxide of moderate concentration: ————, total copper (calculated by Eq. 4); — — — — —, bicuprate ion concentration; Δ, water solubility.

Discussion and Interpretation of Results

Solution of copper oxide in alkali may be represented by the reactions

$$CuO + OH^- = HCuO_2^- \qquad (1)$$

$$K_1 = (m_{HCuO_2^-}/m_{OH^-})\,(\gamma_{HCuO_2^-}/\gamma_{OH^-})$$

$$CuO + 2OH^- = CuO_2^{=} + H_2O \qquad (2)$$

$$K_2 = (m_{CuO_2^=}/m^2_{OH^-})\,(\gamma_{CuO_2^=}/\gamma^2_{OH^-})a_{H_2O}$$

with their corresponding equilibrium constants. In these equations the m's represent stoichiometrical molalities of the ions; the γ's their corresponding activity coefficients and a_{H_2O} the activity of water from the solutions. For practical purposes this latter may be replaced by p/p^0, the ratio of the vapor pressure to that of pure water.[14] The total solubility of copper at concentrations of alkali too great to permit the existence of Cu^{++} ions is thus given by the relationship

$$S_{Cu} = m_{Cu(OH)_2} + K_1 m_{OH^-}(\gamma_{OH^-}/\gamma_{HCuO_2^-}) + K_2 m^2_{OH^-}(\gamma^2_{OH^-}/\gamma_{CuO_2^=})(p^0/p) \qquad (3)$$

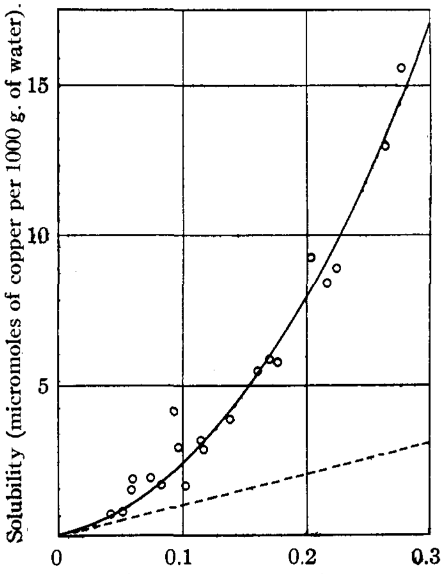

Fig. 3.—Solubility of cupric oxide in dilute potassium hydroxide: ————, total copper (calculated by Eq. 4); — — — — —, concentration of bicuprate ion.

in which $m_{Cu(OH)_2}$ is included to represent a probable low concentration of undissociated hydroxide in equilibrium with the solid phase. This might ordinarily be evaluated from the intercept of the solubility curve on the solubility axis but in this case, as is evident from Fig. 3, the value of this term must be quite low and the data do not permit its evaluation. For this reason we

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(12) Jellinek and Gordon, *Z. physik. Chem.*, **112**, 207 (1924).

(13) Remy and Kühlmann, *Z. anal. Chem.*, **65**, 161 (1925).

(14) These expressions represent cupric oxide as the solid phase in equilibrium with the saturated solutions. If, in reality, this phase is a solid solution of cupric hydroxide in cupric oxide, as the data of Müller seem to indicate, reactions (1) and (2) may be rewritten

$$(XCuO, yCu(OH(_2)\ \text{solid} + OH^- = HCuO_2 + yH_2O \qquad (1a)$$

$$K_{1a} = K_1 a^y_{H_2O}$$

$$(XCuO, yCu(OH)_2)\ \text{solid} + 2OH^- = CuO_2^= + (1 + y)\ H_2O \qquad (2a)$$

$$K_{2a} = K_2 a^y_{H_2O}$$

Since Müller's data show that the mole fraction of the hydroxide cannot exceed 0.1 at most (*i. e.*, y cannot exceed 0.1) K_{1a} and K_{2a} will not differ from K_1 and K_2 by more than 1% even in 3 N alkali. It should be noted also that the solid solution, rather than pure copper oxide, is taken as the standard state in defining K_{1a} and K_{2a}. This defines the significance of the standard free energy change computed from these constants.

have chosen to neglect it. This will introduce no appreciable error into the evaluation of the constants K_1 and K_2.

At low and moderate ionic strengths, equation (3) may be considerably simplified, since the several activity coefficients will approach the values given by the Debye–Hückel interionic attraction theory and the ratio $(\gamma_{OH^-}/\gamma_{HCuO_2^-})$ may be expected to remain near unity even in solutions for which the theory no longer correctly evaluates the separate activities. In the analogous case of silver oxide dissolved in alkali it was found[5] that the ratio $(\gamma_{OH^-}/\gamma_{AgO^-})$ did not depart appreciably from unity even in 1 N alkali. A further simplification comes in the final term. Here $(\gamma^2_{OH^-}/\gamma_{CuO_2^-})$ may be accurately replaced by $(\gamma^4_{KOH}/\gamma^3_{K_2CuO_2})$ and $\gamma^3_{K_2CuO_2}$ may be, in turn, replaced[15] by $\gamma^6_{KHCuO_2}$. Introduction of unit ratio between hydroxide and bicuprate ions now completes the simplification in this term and we have

$$S_{Cu} = K_1 m_{OH^-} + K_2 m^2_{OH^-}(p^0/p\gamma^2_{KOH}) \qquad (4)$$

The parenthetical expression in the last term of (4) is easily evaluated from reliable data.[16] On the assumption that equation (4) remains valid to an ionic strength of unity we have evaluated the two constants of this equation, by an empirical "best fit" to the data recorded in Table I. We have obtained for these constants: $K_1 = 10.3 \times 10^{-6}$, $K_2 = 81 \times 10^{-6}$. The solid lines in Figs. 2 and 3 are calculated with these constants in equation (4). The excellent agreement with the experimental results both at high and low concentrations of alkali is regarded as confirmation both of the assumptions on which (4) is based and on the reliability of the chosen constants. The constants cannot be varied more than a few per cent. without destroying this agreement.

The broken lines in the figures were computed with the final term in (4) omitted and so represent the concentration of bicuprate ion alone. It is clear from these curves that even at low concentrations of alkali a considerable portion of the dissolved copper exists as the divalent acid ion. Other authors[17] have considered the divalent ion concentration as negligible in dilute alkali, in their interpretation of other cases similar to this. It appears from this work that such interpretations will warrant further investigation.

Dissociation Constants of Cupric Acid

The first dissociation constant of cupric acid cannot be determined without more information on the concentration of undissociated hydroxide (*i. e.*, a more reliable basis for extrapolation of the solubility curve to zero alkalinity). But the present data permit the evaluation of the constant for the second step in the acid dissociation

$$HCuO_2^- = H^+ + CuO_2^=$$

$$K_5 = (a_{H^+}a_{CuO_2^=})/a_{HCuO_2^-} \qquad (5)$$

by substituting for a_{H^+} its equivalent $K_w(a_{H_2O}/a_{OH^-})$, and substituting for $a_{CuO_2^=}$ and $a_{HCuO_2^-}$ from equations (1) and (2). This gives

$$K_5 = K_w(K_2/K_1) = 7.9 \times 10^{-14} \qquad (6)$$

with K_w taken to be 1.01×10^{-14} at 25°.[18]

We may estimate the first dissociation constant of cupric acid to be of the order of magnitude of 10^{-10} from the generalization that the first and second constants of di- and tri-basic acids of this approximate strength ordinarily differ by a factor of 10^3 or 10^4. This would make the concentration of undissociated hydroxide of the order of magnitude of 10^{-9} mole per liter, which we could not hope to determine by extrapolation of solubility data even if the colloidal difficulties at low alkalinities were entirely avoided.

Summary

The solubilities of cupric oxide in aqueous potassium hydroxide have been determined for the alkaline range 0.04 normal to about 8 normal, and for a few concentrations of sodium hydroxide. The data at high concentrations are in good agreement with the results obtained, in strong alkali, by Müller.[3c] Up to 2 normal alkali the solubility is well reproduced by the relationship

$$S_{Cu} = 10.3 \times 10^{-6} m_{OH^-} + 81 \times 10^{-6} m^2_{OH^-}/(a_{H_2O}\gamma^2_{KOH})$$

which is derived by application of the interionic attraction theory. The two constants in this equation are the thermodynamic equilibrium constants for the respective reactions

$$CuO + OH^- = HCuO_2^-$$

$$CuO + 2OH^- = H_2O + CuO_2^=$$

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(15) This follows from the fact that at low ionic strengths, where the Debye–Hückel limiting law is obeyed, the activity coefficient of a 1–2 electrolyte is the square of that of a 1–1 electrolyte at the same ionic strength and that where ions are of nearly the same size, as must be true with cuprate and bicuprate ions since they only differ by a proton, this relationship will continue to hold when the limiting law has broken down and terms for the ionic radius are included. This relationship was first called to attention by Walker, Bray and Johnston [THIS JOURNAL, **49**, 1235 (1927)] and shown by them to hold quite accurately for carbonate and bicarbonate solutions even to ionic strengths of 2.

(16) (a) Scatchard, *ibid.*, **47**, 648 (1925); Knobel, *ibid.*, **45**, 70 (1923); Harned and Åkerlöf, *Physik. Z.*, **27**, 411 (1926). (b) "The International Critical Tables," Vol. III, p. 373.

(17) Randall and Spencer, THIS JOURNAL, **50**, 1572 (1928); Fuseya, *ibid.*, **42**, 368 (1920); Piater, *Z. anorg. allgem. Chem.*, **174**, 321 (1928).

(18) "International Critical Tables," Vol. VI, p. 152.

From these data we obtain 7.9 × 10^{-14} for the second acid dissociation constant of copper hydroxide

$$HCuO_2^- = H^+ \ CuO_2^=$$

The relative proportions of bicuprate ($HCuO_2^-$) and cuprate ($CuO_2^=$) ions in the solutions are evaluated and it is shown that the second of these predominates even below 0.1 normal alkali.

The solubility of the oxide in pure water is found to be approximately 3 × 10^{-5} mole per liter, which is somewhat lower than values now in the literature.

An accurate potentiometric method of determining copper in low concentrations is described.

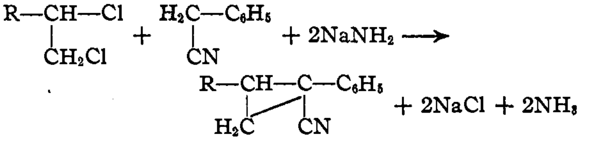
COLUMBUS, OHIO RECEIVED JULY 10, 1936

[CONTRIBUTION FROM THE WALKER CHEMICAL LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

Alkylene and Alkylidene Phenylacetonitriles and Derivatives. 1-Phenyl-2-ethylcyclopropanecarbonitrile, α-Phenyl-β-ethylacrylonitrile and α-Phenyl-β-isopropylacrylonitrile[1]

BY JAMES V. MURRAY AND JOHN B. CLOKE

It has been shown that 1-phenylcyclopropanecarbonitrile and its 2-methyl homolog can be prepared by the alkylenation of phenylacetonitrile with suitable dihalide derivatives, such as ethylene chloride and propylene chloride, in the presence of sodium amide, according to the reaction[2]



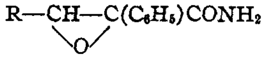
Directions have also appeared for the condensation of acetaldehyde[2] and *n*-butyraldehyde[3] with phenylacetonitrile by the action of sodium ethoxide as generalized below

$$RCHO + H_2C(CN)C_6H_5 = RCH{=}C(CN)C_6H_5 + H_2O$$

This work constitutes an extension of the work of Meyer and Frost[4] on the aromatic aldehydes to the aliphatic group.

The present paper describes the preparation of one alkylene phenylacetonitrile, 1-phenyl-2-ethylcyclopropanecarbonitrile, and two alkylidene phenylacetonitriles, *viz.*, α-phenyl-β-ethylacrylonitrile and α-phenyl-β-isopropylacrylonitrile, together with some of their derivatives.

The proof of the structures of the alkylidene phenylacetonitriles follows from (1) their method of preparation, if aldehydes are used, (2) their reaction with alkaline hydrogen peroxide to give glycidamides,



$R—CH—C(C_6H_5)CONH_2$,[3] although not all α,β-ethylenic nitriles react, and (3) their oxidation with potassium permanganate. On the other hand, the isomeric cyclopropanecarbonitriles may be recognized (1) by their reaction with hydrogen peroxide to give simple amides, if they react at all, and (2) by their stability in the presence of permanganate. In addition, molecular refractivities have been useful in the differentiation of the cyclopropane and ethylenic isomers, although they are less reliable than the chemical methods.

1-Phenyl-2-ethylcyclopropanecarbonitrile.—This nitrile was obtained in yields up to 40% by the interaction of phenylacetonitrile (I), 1,2-dichlorobutane and sodium amide, as indicated in the accompanying flow sheet. In this reaction it is advantageous to deviate from the original procedure of Knowles and Cloke by preparing the sodium amide in liquid ammonia, according to the method of Vaughn, Vogt and Nieuwland,[5] and using this solution in the initial stages of the reaction.

In passing, it may be pointed out that the glycidamide and Radziszewski reactions may be employed for the removal of phenylacetonitrile and α,β-ethylenic nitrile from the 1-phenyl-2-alkylcyclopropanecarbonitriles, since the latter are quite inert to the reagent.

Following the synthesis of 1-phenyl-2-ethylcyclopropanecarbonitrile (VI), it was essential to produce evidence for the presence of the cyclo-

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[1] This paper is based upon a thesis presented by James Vincent Murray, Jr., to the Graduate School of the Rensselaer Polytechnic Institute in June, 1935, in partial fulfilment of the requirements for the degree of Master of Science.

[2] Knowles and Cloke, THIS JOURNAL, **54**, 2028 (1932).

[3] Murray and Cloke, *ibid.*, **56**, 2751 (1934).

[4] Meyer and Frost, *Ann.*, **250**, 157 (1889).

[5] Vaughn, Vogt and Nieuwland, THIS JOURNAL, **56**, 2120 (1934).