the production of 15 g. of 4-*t*-amyl diphenyl ether, b. p. 190–200 (23 mm.).

Anal. Calcd. for $C_{17}H_{20}O$: C, 85.00; H, 8.33. Found: C, 84.42, 84.67; H, 8.15, 8.23.

Summary

The mercuration of diphenyl ether has been described and a number of the mercurated products have been isolated and analyzed. These substances give the normal reactions of organic mercury compounds except that they react with certain halides giving carbon–carbon syntheses. This reaction has been observed with only a few organic mercurials.

LAWRENCE, KANSAS RECEIVED NOVEMBER 15, 1937

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

Reflection and Absorption of Visible Radiation in the System Potassium Chloride–Cupric Chloride

BY GEO. GLOCKLER AND R. E. DIETMEIER[1]

The blue color of cupric salts is due to a region of transmission at about 4900 Å., located between two large absorption bands, one situated in the ultraviolet and another one in the infrared. All blue or green colored copper compounds are hydrated whereas anhydrous copper compounds are colorless or reddish-brown to red. The latter must transmit or reflect red light and should therefore show a reflection or transmission maximum in this region. The system KCl–CuCl$_2$ was studied in powder form by measuring the reflection coefficient with a Keuffel and Esser color analyzer. The two anhydrous salts were melted together and the percentage of reflected light was determined as a function of wave length, using a magnesium carbonate block as a standard. Since during the process of melting some cupric chloride is decomposed, certain of the mixtures were also prepared in the wet way and dehydrated at 132° (asterisk in Table I). No difference in behavior was found. It is seen that all samples containing a sufficient amount of cupric chloride show a maximum of reflection at 6390 ± 20 Å. as does anhydrous cupric chloride (6404 ± 8 Å.). This maximum of reflection is interpreted to correspond to a maximum of transmission or to a minimum of absorption of radiation, since the light from the analyzer passes through the crystal powder before it is finally reflected from the heterogeneous crystalline mass. The minimum of absorption at 6400 Å. is produced by the approach of two large absorption bands as in the case of the hydrated copper salts.

TABLE I

Mole fraction KCl	Absorption max., Å.	Reflection max., Å.	Mole fraction KCl	Absorption max., Å.	Reflection max., Å.
0.0	..	6404 ± 8[a]	0.6	5350	6400
.1	..	6460		5350	6360
	..	6380	.67	5500	6400
.2	5300	6380		5450	6360
	5500	6420		5350*	6360*
.3	5350	6400		5350*	6400*
	5350	6400	.7	5350	6400
.4	5350	6360		5450	6410
	5300	6400	.8	5350	6400
.5	5600	6430		5300	6360
	5400	6360	.9	5400	6400
	5450*	6380*		5400	6380
	5340*	6380*	1.0	..	..
	5350*	6370*		..	..
			Av.	5387 ± 63	6390 ± 20

[a] Pure anhydrous CuCl$_2$ (13 measurements).

* Prepared in wet way and dehydrated at 132°.

More interesting and important is the absorption maximum (reflection minimum) discovered at 5387 ± 63 Å. (Table I and Fig. 1). This absorption region has been subtracted from the large band which reaches into the ultraviolet by drawing in the line AB (Fig. 1). Above the point A and below B, the same difference of ordinate exists between the actual reflection curve and the dotted line. Hence the curve C starts and ends in a horizontal line. The maximum is clearly shown in all the experiments where the mole fraction of potassium chloride is greater than twenty per cent.

Since the absorption at 5387 Å. is not observed in anhydrous cupric chloride, but is found in mixture of this salt with potassium chloride, the agency responsible for the light absorption must be a complex between the two substances. It is

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(1) Based on a thesis presented to the faculty of the Graduate School of the University of Minnesota by R. E. Dietmeier in partial fulfilment of the requirements for the degree of Master of Science, 1937.

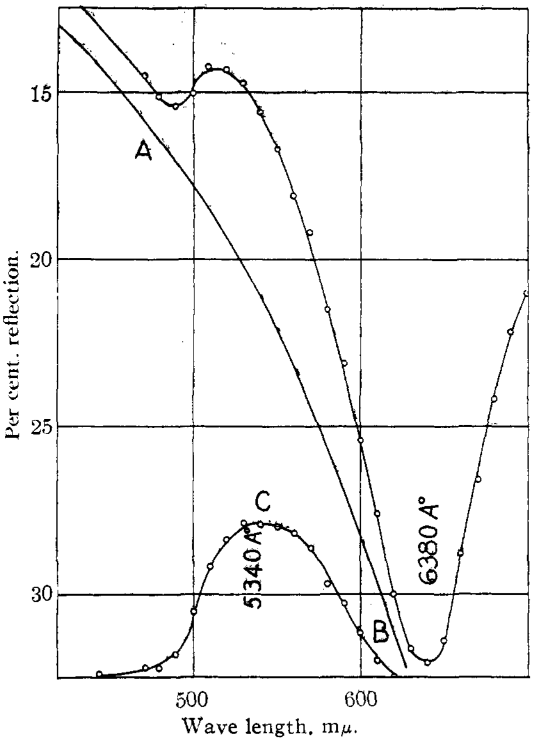

Fig. 1.—Reflection coefficient of the system KCl-$CuCl_2$ as a function of wave length (mμ).

most likely the trichlorocuproate ion since the potassium salt of this anion is known.[2] The trichlorocuproate ion does not exist in solid anhydrous cupric chloride for this substance does not show the absorption band under discussion.

Little can be said from these measurements regarding the mechanism of light absorption.

The fraction of light reflected depends on the state of subdivision of the substance and is not of any special significance. The dry powders used showed the reflections given in Fig. 2. It appears that at the reflection maximum (6400 Å.) the two salts ($CuCl_2$ and $KCuCl_3$) have about the same reflection coefficient and that no free, uncombined potassium chloride exists in the crystalline mass below mole fraction 0.5, indicating a complex KCl–$CuCl_2$ or K[$CuCl_3$].

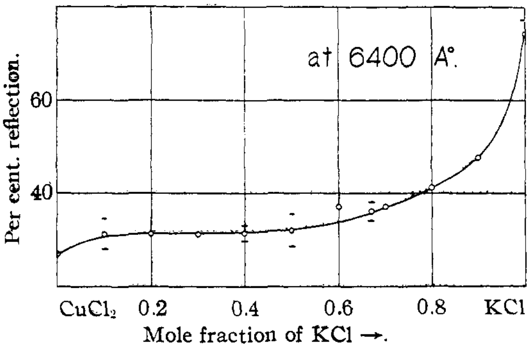

Fig. 2.—Reflection of light as a function of composition (system KCl-$CuCl_2$).

Summary

Solid anhydrous cupric chloride shows a maximum of reflection at 6404 Å. as do mixtures with dry potassium chloride. The mixtures have an absorption maximum at 5387 Å. which is ascribed to the trichlorocuproate ion.

MINNEAPOLIS, MINN.

RECEIVED JANUARY 10, 1938

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(2) Gmelin-Kraut, "Handbuch der anorganischen Chemie," 7th Edition, V. I. C. Winter, Heidelberg, 1909, p. 1094.

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Transition Temperature of Sodium Sulfate Heptahydrate

BY E. ROGER WASHBURN AND W. JACK CLEM

T. W. Richards[1] suggested the use of transition temperatures of hydrated salts as fixed points in thermometry and in subsequent years he and his students[2] investigated many of these. Subsequent workers have verified these results[3] and added others.[4] The transition temperature of sodium sulfate decahydrate to anhydrous sodium sulfate and solution, 32.384°, is now considered to be one of the best established secondary standards of thermometry.

It would be of considerable advantage to have a secondary standard in the range near 25° but the nearest well established transition temperatures are those of sodium sulfate decahydrate (mentioned above) and of sodium chromate decahydrate to sodium chromate hexahydrate and solution[5] at 19.525°. This latter salt possesses the disadvantage of being difficult to obtain in

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(1) Richards and Churchill, *Z. physik. Chem.*, **26**, 690 (1898); Richards and Churchill, *Proc. Am. Acad. Arts Sci.*, **34**, 277 (1899).

(2) Richards and Yngve, THIS JOURNAL, **40**, 89 (1918).

(3) Dickinson and Mueller, *ibid.*, **29**, 1381 (1907).

(4) Wells and McAdam, *ibid.*, **29**, 721 (1907).

(5) Richards and Kelley, *ibid.*, **33**, 847 (1911); Richards and Kelley, *Proc. Am. Acad. Arts Sci.*, **47**, 171 (1911).