kieselguhr to 5-aminophthalide (85% conversion), and sodium-α-hydroxy-*o*-toluate (phthalide dissolved in aqueous sodium hydroxide) yielded *o*-toluic acid (80%) on hydrogenation over nickel-on-kieselguhr.

The hydrogenation of phthalic anhydride, pthalide and various phthalide derivatives is summarized in Table I.

## Experimental Part

**Apparatus.**—The apparatus used in this work consisted of a shaking device, high pressure steel tubes connected to recording gages, electrical pyrometers for temperature control and a source of high pressure hydrogen. The tube capacity was approximately 400 cc. In operation, the material and catalyst were charged into the tube which was then made tight with a plug and a threaded nut. A thermocouple well extended through the plug into the inner space of the tube, and a hydrogen inlet line, valve and flexible line connected to the gas manifold completed the assembly. The tube was heated and agitated mechanically, and hydrogen absorption was measured by the pressure drop in the closed system. The time of reaction given in Table I was measured from the beginning of the hydrogenation to the conclusion of the run.

**Catalysts.**—Nickel-on-kieselguhr catalyst was prepared from the nitrate by precipitation of the carbonate followed by hydrogen reduction according to well-known methods[3] (p. 1651). Unsupported pyrophoric nickel was prepared according to the method of Raney,[5] and copper chromite and promoted copper chromite catalysts[6] were prepared according to the standard procedures.

**Isolation of Products.**—Water-soluble solvents were evaporated, replaced by benzene, and the acidic components extracted with aqueous sodium carbonate. The alkaline solution was separated and acidified to give *o*-toluic acid or hexahydro-*o*-toluic acid. Phthalide was obtained by evaporation of the organic solvent and may be further purified by crystallization from alcohol or benzene. Phthalic acid, when isolated, was found in the catalyst fraction and was recovered by solution and reprecipitation from sodium carbonate solution. All of the materials isolated were characterized by means of their melting points or boiling points and by comparison with authentic specimens.

## Summary

Phthalide has been obtained in excellent yields by the hydrogenation of phthalic anhydride (a) with copper chromite in benzene, (b) with Raney catalyst in ethanol and (c) with nickel-on-kieselguhr in ester or alcohol solvents. The novel use of alcohol as a solvent for this reduction has been investigated and a mechanism for the hydrogenation has been proposed. Hexahydrophthalide, 5-aminophthalide and *o*-toluic acid have been obtained in high yields by further hydrogenation of phthalide or appropriate derivatives.

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[5] Raney, U. S. Patent 1,628,190; *C. A.*, **21**, 2116 (1927).

[6] Lazier, British Patent 301,806, June 12, 1926; *C. A.*, **23**, 4306 (1929); U. S. Patent 1,746,783, Feb. 11, 1930; *C. A.*, **24**, 1649 (1930); U. S. Patent 1,964,000, June 26, 1934; Adkins and Connor, THIS JOURNAL, **53**, 1091 (1931); Connor, Folkers and Adkins, *ibid.*, **54**, 1138 (1932).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

# The Ternary Systems $KClO_3$–KBr–$H_2O$, $KClO_3$–KI–$H_2O$ and $KIO_3$–KI–$H_2O$ at 25°

BY JOHN E. RICCI

The solubility isotherms reported in this paper were studied during the course of more extensive investigations; while no complex formation, in the form either of double compounds or of solid solutions, was found in all three systems, the results are nevertheless presented as solubility determinations which may have some interest and value. In connection with the system $KIO_3$–KI–$H_2O$, it may be mentioned that although a double compound or complex of some sort of these two salts might have been expected on the basis of the compounds known to form between sodium iodate and sodium iodide,[1] the results show no tendency at all toward compound formation between the potassium salts at 25°.

The experimental procedure was that usually employed for similar measurements. Definite mixtures of the components were stirred in a bath thermostatically controlled at 25 to ±0.02°, sufficient time (at least two days) being allowed for the attainment of equilibrium. The method of analysis of the saturated solution varied for the different systems, as follows: for the first system, the potassium bromide was determined by titration with standard silver nitrate solution, using Mohr's method; the total solid was determined by evaporation at 100° followed by 250°; and the potassium chlorate was then calculated by difference. In the second system, the potassium iodide was likewise titrated argentometrically, by Fajans' method, using eosin as the

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[1] Ricci, THIS JOURNAL, **56**, 295 (1934).

adsorption indicator, and titrating actually to the clear-point; the potassium chlorate was then calculated similarly by means of the total solid determination. In the third system, the titration of the iodide was avoided because of the insolubility of silver iodate; the potassium iodate was consequently determined directly by adding excess potassium iodide, acidifying, and titrating the liberated iodine with standard sodium thiosulfate; the determination of total solid then allowed the calculation of the original potassium iodide by difference.

The solid phases, already known in every case, were identified and verified by algebraic extrapolation of the tie-lines on the ternary diagrams, the average deviation of these extrapolations for all three systems being 0.26% from the composition of the pure solid phase. The densities reported were calculated from the weight delivered by a volumetric pipet calibrated for delivery.

The experimental results for the three systems are presented in Tables I, II and III. Figure 1 shows the isotherm for the system $KClO_3$–$KBr$–$H_2O$; the isotherms for the other two systems are very similar to this and need not be added here. The data and the plotted results show clearly that the only solid phases in the systems at this temperature are the anhydrous salts themselves, and that there is no evidence of any complex formation in the various pairs of salts.

TABLE I

SYSTEM $KClO_3$–$KBr$–$H_2O$ AT 25°

| Original complex, wt. % | | Satd. solution, wt. % | | Density | Solid phase |
|---|---|---|---|---|---|
| $KClO_3$ | KBr | $KClO_3$ | KBr | | |
| ... | 0.00 | 7.905 | 0.00 | 1.047 | $KClO_3$ |
| 20.55 | 7.73 | 4.59 | 9.30 | 1.100 | $KClO_3$ |
| 19.60 | 14.07 | 3.21 | 16.99 | 1.160 | $KClO_3$ |
| 19.06 | 20.00 | 2.41 | 24.20 | 1.216 | $KClO_3$ |
| 18.98 | 26.09 | 1.87 | 31.66 | 1.292 | $KClO_3$ |
| 18.99 | 32.38 | 1.42 | 39.47 | 1.376 | $KClO_3$ |
| 18.98 | 33.47 | 1.43 | 40.00 | 1.385 | $KClO_3$ + KBr |
| 7.50 | 45.50 | 1.42 | 40.01 | 1.386 | $KClO_3$ + KBr |
| 1.39 | 50.95 | 1.37 | 40.06 | 1.387 | $KClO_3$ + KBr |
| Average | (of 5) | 1.42 | 40.01 | 1.385 | $KClO_3$ + KBr |
| 0.00 | ... | 0.00 | 40.63 | 1.380 | KBr |

TABLE II

SYSTEM $KClO_3$–$KI$–$H_2O$ AT 25°

| Original complex, wt. % | | Satd. solution, wt. % | | Density | Solid phase |
|---|---|---|---|---|---|
| $KClO_3$ | KI | $KClO_3$ | KI | | |
| ... | 0.00 | 7.905 | 0.00 | 1.047 | $KClO_3$ |
| 23.15 | 7.52 | 5.04 | 9.33 | 1.103 | $KClO_3$ |
| 22.03 | 15.09 | 3.35 | 18.74 | 1.178 | $KClO_3$ |
| 21.49 | 23.06 | 2.30 | 28.72 | 1.275 | $KClO_3$ |
| 20.97 | 31.52 | 1.60 | 39.26 | 1.400 | $KClO_3$ |
| 20.68 | 40.06 | 1.10 | 49.94 | 1.555 | $KClO_3$ |
| 20.01 | 46.98 | 0.82 | 58.34 | 1.702 | $KClO_3$ |
| 19.98 | 48.22 | .81 | 59.27 | 1.724 | $KClO_3$ + KI |
| 12.01 | 57.93 | .84 | 59.30 | 1.723 | $KClO_3$ + KI |
| 2.99 | 66.06 | .84 | 59.26 | 1.725 | $KClO_3$ + KI |
| Average | (of 3) | .83 | 59.28 | 1.724 | $KClO_3$ + KI |
| 0.59 | 67.99 | .67 | 59.36 | 1.724 | KI |
| .00 | ... | .00 | 59.76 | 1.718 | KI |

TABLE III

SYSTEM $KIO_3$–$KI$–$H_2O$ AT 25°[a]

| Original complex, wt. % | | Satd. solution, wt. % | | Density | Solid phase |
|---|---|---|---|---|---|
| $KIO_3$ | KI | $KIO_3$ | KI | | |
| ... | 0.00 | 8.449 | 0.00 | 1.071 | $KIO_3$ |
| 22.14 | 2.03 | 7.15 | 2.40 | 1.053 | $KIO_3$ |
| 19.87 | 10.11 | 4.33 | 12.04 | | $KIO_3$ |
| 18.03 | 19.00 | 3.27 | 22.38 | 1.227 | $KIO_3$ |
| 16.99 | 35.01 | 2.54 | 41.10 | 1.451 | $KIO_3$ |
| 16.96 | 48.54 | 2.35 | 57.02 | 1.722 | $KIO_3$ |
| 16.96 | 50.06 | 2.36 | 58.54 | 1.749 | $KIO_3$ + KI |
| 8.73 | 58.98 | 2.36 | 58.54 | 1.754 | $KIO_3$ + KI |
| 2.19 | 69.14 | 2.35 | 58.47 | 1.749 | $KIO_3$ + KI |
| Average | (of 3) | 2.35 | 58.51 | 1.751 | $KIO_3$ + KI |
| 1.92 | 64.84 | 2.25 | 58.62 | | KI |
| 0.81 | 69.91 | 1.10 | 59.14 | 1.731 | KI |
| .00 | ... | 0.00 | 59.76 | 1.718 | KI |

[a] Some of the determinations for this isotherm were made by Dr. John H. Wills, formerly of this department.

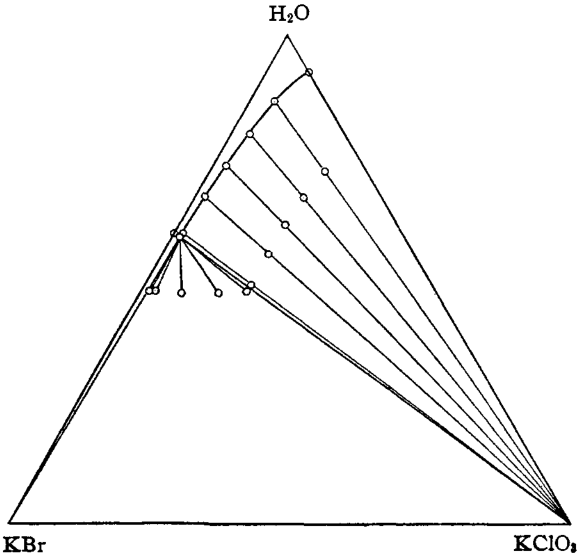

Fig. 1.—25° Isotherm: $KClO_3$–$KBr$–$H_2O$.

## Summary

Solubility measurements are given for the ternary systems $KClO_3$–$KBr$–$H_2O$, $KClO_3$–$KI$–$H_2O$ and $KIO_3$–$KI$–$H_2O$ at 25°. These salt pairs are found to form neither double compounds nor solid solutions at this temperature, the only solid phases being the respective anhydrous salts.

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