

TABLE I

R_f VALUES OF SOME COMMON PHENOLS IN VARIOUS SOLVENT SYSTEMS

The solvent systems were prepared by equilibrating at room temperature (approximately 23°) the proportions by volume of the solvents indicated. The organic phase was employed as the descending solvent and the aqueous phase was placed within the chamber to maintain equilibrium conditions.

Phenol	n -C ₆ H ₁₁ OH-Solvent systems		
	H ₂ O (mutually saturated)	n -C ₆ H ₅ OH- C ₆ H ₆ -H ₂ O 1:9::10	n -C ₆ H ₅ OH- C ₆ H ₆ -H ₂ O 1:19::20
Hydroquinone	0.80	0.43	0.078
Resorcinol	.83	.54	.13
Catechol	.86	.70	.38
Tolhydroquinone	.85	..	.23
Phloroglucinol	.61	..	.00
Pyrogallol	.65	..	.025
α -Naphthol	.90	..	.83
β -Naphthol	.92	..	.85

descending solvent face of the alcohol-benzene-water system to drip from the lower boundary of the paper, greater resolution was obtained in some instances. For example, with butyl alcohol-benzene-water (1:19:20), it was found possible to resolve completely a mixture of the first six phenols listed in the table. By continuing development until the most rapidly moving component (catechol) was about to pass from the paper, the following relative rates of migration were found: (hydroquinone = 1.00), phloroglucinol, 0.00; pyrogallol, 0.33; resorcinol, 1.45; tolhydroquinone, 2.4; catechol, 4.7.

The following systems were tested with the listed phenols but found unsatisfactory because of poor resolution: cyclohexanone-water, hexane-acetonitrile, chloroform-formamide and benzene-formamide.⁷ Butyl alcohol-water effected some resolution as did benzene-water but these systems were comparatively unsatisfactory for the compounds listed.

A serious limitation of the method may be the volatility of phenols of interest. For example, *o*-cresol completely evaporates during the interval necessary for the development and drying of the chromatogram.

Acknowledgment.—The author wishes to thank Dr. Alejandro Zaffaroni for his helpful advice.

(7) A. C. Zaffaroni, R. B. Burton and E. H. Keutmann, *Science*, **111**, 6 (1950).

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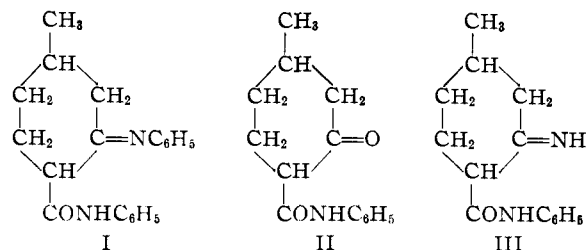
2-Keto-4-methylcyclohexanecarboxyanilide

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Kötz and Merkel¹ reported the preparation of the "anilinoanilid," I, by heating ethyl 2-keto-4-

(1) A. Kötz and B. Merkel, *J. prakt. Chem.*, [2] **79**, 115 (1909).

methylcyclohexanecarboxylate with aniline. In connection with other work,² we attempted to re-



peat their preparation. We obtained a product with the reported melting point, but the analysis corresponded to the ketoanilide, II. It was converted to the corresponding iminoanilide, III, which reacted with aniline to evolve ammonia, as expected.³ The product of this reaction, presumably I, was not isolated in a pure state. These results are compatible with the results of Sen and Basu⁴ who obtained analogs of II, but were unable to obtain any analogs of I from ethyl 2-ketocyclohexanecarboxylate, and with the work of Thomson and Wilson,⁵ who prepared analogs of I under different conditions. Hence, it would appear that the analytical data on the compound reported by Kötz and Merkel was in error.

Experimental⁵

2-Keto-4-methylcyclohexanecarboxyanilide (II).—Equimolar amounts of ethyl 2-keto-4-methylcyclohexanecarboxylate and aniline were heated at 140° for 2 hours. The crude product was obtained in 24% yield, m. p. 123–127°. Recrystallizations from benzene-petroleum ether and ethanol gave a pure material, m. p. 129–130°.

Anal. Calcd. for C₁₄H₁₇O₂N: C, 72.70; H, 7.42. Found: C, 72.73; H, 7.36.

2-Imino-4-methylcyclohexanecarboxyanilide (III).—This compound was prepared according to Thomson and Wilson⁵ and recrystallized from ammoniacal ethanol: m. p. 128–129°; m. p. of mixture with the above compound, 98–108°.

Anal. Calcd. for C₁₄H₁₈ON₂: C, 73.01; H, 7.88; N, 12.17. Found: C, 72.61; H, 7.55; N, 12.09.

When this compound was heated with aniline in petroleum ether (b. p. 100–140°), ammonia was evolved over a period of several hours. The oil which separated on cooling was difficult to crystallize. A sample which melted at 95–99° was obtained, but further attempts to purify it resulted in hydrolysis to compound II.

(2) R. M. Roberts and M. B. Edwards, *THIS JOURNAL*, **72**, 5537 (1950).

(3) J. K. Thomson and F. J. Wilson, *J. Chem. Soc.*, 111 (1935).

(4) H. K. Sen and U. Basu, *J. Ind. Chem. Soc.*, **6**, 309 (1929).

(5) Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill.

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The Osmotic and Activity Coefficients of Cobalt Bromide and Cobalt Iodide

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Osmotic and activity coefficients of a high order of accuracy have been obtained for calcium chlo-

ride¹ and cobalt chloride² while the values for calcium bromide³ are known with a moderate degree of accuracy and those of calcium iodide⁴ to a lesser degree. Since there is some resemblance be-

of use in studies of the complexes formed by these salts in concentrated solution.

There is no difficulty in preparing good specimens of cobalt bromide or iodide from the carbonate and the corresponding acid. They do, however, decompose slowly in solution, this being particularly true of the iodide in dilute solution; for this reason we do not claim a high degree of accuracy for these results and, in the case of iodide, we did not make measurements in solutions more dilute than 0.5 *m*. An estimate has been made for these dilute solutions by comparison with magnesium iodide and zinc perchlorate, the isopiestic data for these salts being comparable with those of cobalt iodide.

Calcium bromide was used as a reference salt for equilibration with cobalt bromide solutions; in the case of cobalt iodide, calcium chloride was the reference salt. The experimental data are given in Table I and, with the aid of the osmotic and activity coefficients of the calcium salts,^{1b} the data given in Table II have been evaluated.

TABLE I
MOLALITIES OF ISOPIESTIC SOLUTIONS OF COBALT BROMIDE AND CALCIUM BROMIDE AT 25°

CoBr ₂	CaBr ₂	CoBr ₂	CaBr ₂	CoBr ₂	CaBr ₂	CoBr ₂	CaBr ₂
0.1593	0.1617	0.3435	0.3524	0.5503	0.5676	0.7491	0.7769
1.068	1.115	1.658	1.749	2.085	2.191	2.446	2.554
2.694	2.791	3.107	3.182	3.516	3.565	3.768	3.785
3.930	3.922	4.589	4.435	5.672	5.144		

MOLALITIES OF ISOPIESTIC SOLUTIONS OF COBALT IODIDE AND CALCIUM CHLORIDE AT 25°

CoI ₂	CaCl ₂	CoI ₂	CaCl ₂	CoI ₂	CaCl ₂	CoI ₂	CaCl ₂
0.5610	0.6407	0.6945	0.8035	0.7260	0.8445	0.9445	1.122
1.121	1.348	1.404	1.702	1.746	2.134	1.926	2.362
2.501	3.089	2.528	3.124	3.201	3.966	3.535	4.384
3.930	4.870	4.775	5.880	4.981	6.113	5.074	6.196
5.945	6.986	6.448	7.336	6.502	7.377	7.096	7.752
7.439	7.973	8.164	8.413	9.229	9.172	10.10	9.874

TABLE II
OSMOTIC AND ACTIVITY COEFFICIENTS OF COBALT BROMIDE AND IODIDE AT 25°

<i>m</i>	CoBr ₂			CoI ₂		<i>m</i>	CoBr ₂		CoI ₂	
	ϕ	γ	γ calcd.	ϕ	γ		ϕ	γ	ϕ	γ
0.1	0.871	0.546	0.549	(0.89)	(0.58)	2.0	1.678	1.478	1.90	2.4
.2	.894	.513	.517	(0.92)	(.56)	2.5	1.921	2.25	2.24	4.4
.3	.922	.509	.511	(0.96)	(.57)	3	2.149	3.42	2.56	7.7
.4	.955	.517	.518	(1.00)	(.59)	3.5	2.358	5.10	2.87	13.6
.5	.992	.532	.532	1.05	.62	4	2.564	7.62	3.17	24
.6	1.029	.554	.552	1.10	.66	4.5	2.737	11.02	3.41	40
.7	1.068	.580	.578	1.15	.71	5	2.880	15.36	3.59	62
.8	1.109	.612	.608	1.21	.77	5.5	2.990	20.6	3.63	83
.9	1.152	.648	.644	1.26	.84	6	3.61	102
1.0	1.196	.690	.687	1.32	.91	6.5	3.54	115
1.2	1.286	.789	.794	1.43	1.09	7	3.46	130
1.4	1.382	.914	.932	1.54	1.31	8	3.28	150
1.6	1.482	1.069	...	1.65	1.59	9	3.17	174
1.8	1.580	1.255	...	1.78	1.95	10	3.10	214

tween the osmotic coefficients of calcium and cobalt chloride, at least up to the concentration (about 2.5 *m*) at which the rose color of the latter is changing to violet or blue (after which some form of complex formation reduces the osmotic coefficients below those of calcium chloride), some interest is to be found in corresponding data for cobalt bromide and cobalt iodide, which are now reported as a result of isopiestic measurements and which can be compared with the corresponding values for the calcium salts. No activity coefficients seem to have been determined for either of these salts and the values now recorded may be

The activity coefficients of cobalt bromide given in the column headed γ calcd. of Table II have been calculated by the "hydration" equation of Stokes and Robinson,⁵ using the following parameters: $n = 16$, $\text{Å} = 5.35$. The "hydration" equation also holds for cobalt iodide up to 0.9 *m*, using $n = 20$ and $\text{Å} = 5.93$. The necessary density data are to be found in the literature for cobalt bromide but not for cobalt iodide; a density of 1.3139 for a 1.260 *m*. solution of the latter was measured giving a value of 46.1 cc. per mole for the apparent molal volume of the iodide at this concentration.

(1) (a) R. H. Stokes, *Trans. Faraday Soc.*, **41**, 637 (1945); (b) **44**, 612 (1949).

(2) R. A. Robinson and J. B. Brown, *Trans. Roy. Soc. (New Zealand)*, **77**, 1 (1948), see also ref. 1b.

(3) R. A. Robinson and H. C. McCoach, *THIS JOURNAL*, **69**, 2244 (1947).

(4) R. A. Robinson, *Trans. Faraday Soc.*, **38**, 445 (1942), see also ref. 1b.

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(5) R. H. Stokes and R. A. Robinson, *THIS JOURNAL*, **70**, 1870 (1948).