

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OKLAHOMA AGRICULTURAL AND MECHANICAL COLLEGE]

Solubilities of Sodium and Potassium Salts of Nitrophenols and Related Acids¹

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Aqueous solubilities of salts of 2-chloro-3-nitrotoluene-5-sulfonic acid and some similar acids already have been determined in a search for a better precipitant for potassium.² The present paper reports results of a like study of salts of a variety of other organic acids, chosen because their potassium salts were either known or hoped to be slightly soluble.

Experimental

Synthesis of Salts.—Picric acid, 2,4,6-trinitro-*m*-cresol (methylpicric acid), picrolonic acid, 5-nitrobarbituric acid, and 2,4-dinitronaphthol-7-sulfonic acid were Eastman Kodak Co. products. Styphnic acid, dipicrylamine, N,2,4,6-tetranitroaniline, 3-chloro-2,4,6-trinitrophenol (chloropicric acid), 2,3,4,6-tetranitrophenol, and nitrilic acid were made by nitrating resorcinol, 2,4-dinitrodiphenylamine,³ picramide,⁴ *m*-chlorophenol,⁵ *m*-nitrophenol,⁶ and diacetylhydroquinone,⁷ respectively. 1-Phenylbarbituric acid was prepared by condensing malonic acid with phenylurea⁸ and was nitrated according to the directions given in "Organic Syntheses" for 5-nitrobarbituric acid.⁹ Efforts to prepare pure 1,5-dinitronaphthol-7-sulfonic acid derivatives by nitrating sodium 2-naphthol-7-sulfonate according to the meager directions of Volochneva¹⁰ were abandoned after several failures. 2-Chloro-1,4-dimethyl-3-nitrobenzene-5-sulfonic acid (2-chloro-3-nitro-*p*-xylene-5-sulfonic acid) was prepared from *p*-xylene by the general method described in the first paper of this series;² most of the steps were also those employed by Wahl.¹¹ The successive intermediate stages were 2-chloro-1,4-dimethylbenzene, 2-chloro-1,4-dimethylbenzene-5-sulfonic acid, the corresponding sulfonyl chloride (m. p. 47°, Wahl gave 50°), and 2-chloro-1,4-dimethyl-3-nitrobenzene-5-sulfonyl chloride. 2-Chloro-3-nitrotoluene-5-arsonic acid was synthesized by arsonating *o*-toluidine,¹² introducing a chlorine atom by the Sandmeyer reaction, and nitrating the product.

The salts were made by neutralizing the acid with the calculated amount of the appropriate alkali and recrystallizing the product repeatedly from alcohol or water. The

di-metal salts of flavianic acid had to be recrystallized from dilute alkali to prevent hydrolysis, and those containing only one metallic atom per molecule could not be obtained pure. This verifies the statement of Clark and Willits¹³ that the dipotassium salt is the one precipitated, but casts some doubt on Volochneva's¹⁰ report that monopotassium 1,5-dinitronaphthol-7-sulfonate is the stable form.

Salts of N,2,4,6-tetranitroaniline, 2,3,4,6-tetranitrophenol, 2-chloro-3-nitrotoluene-5-arsonic acid, and 1-phenyl-5-nitrobarbituric acid were not investigated further after qualitative tests showed their potassium salts to be too soluble to precipitate readily. The others were dried at 105° in a vacuum oven, to reduce the danger of an explosion.¹⁴

Analysis and Determination of Solubility.—The purity of each salt was tested and the solubility determined by the methods previously used.²

Discussion of Results

Table I shows the results of our experimental work. The only reagents in this group useful as potassium precipitants have already been suggested for that purpose: dilituric acid¹⁵ and especially dipicrylamine.¹⁶ Little relation can be traced between structure and solubility of salts; dilituric acid is useful, but the addition of a phenyl group destroys its value. The substitution of a methyl group in the 5-position on the ring in 4-chloro-3-nitrobenzenesulfonic acid makes the potassium salt far less soluble,² but addition of another methyl group to the ring yields 2-chloro-1,4-dimethyl-3-nitrobenzene-5-sulfonic acid, which is worthless as a potassium precipitant. The same ruinous effect of a methyl group, or indeed of any group at all in this case, is seen among relatives of picric acid, including also 3,3'-azo-bispicric acid (3,3'-dihydroxy-2,4,6,2',4',6'-hexanitroazobenzene).¹⁷ It is improbable, therefore, that substituted dipicrylamines would exceed or even equal the parent compound in usefulness.

Summary

The sodium and potassium salts of ten possible potassium precipitants, mostly nitrophenols, have been synthesized and their solubilities at 30°

(1) Most of the material in this paper was presented at the Rochester meeting of the American Chemical Society, September, 1937.

(2) Dermer and Dermer, *THIS JOURNAL*, **60**, 1 (1938).

(3) Marshall, *J. Ind. Eng. Chem.*, **12**, 336 (1920).

(4) Jones and Willson, *J. Chem. Soc.*, 2277 (1930).

(5) Tijmstra, *Rec. trav. chim.*, **21**, 292 (1902).

(6) Blanksma, *ibid.*, **21**, 256 (1902).

(7) Gutzeit, *Helv. Chim. Acta*, **12**, 726 (1929).

(8) MacBeth, Numan and Traill, *J. Chem. Soc.*, 1248 (1926).

(9) Hartman and Sheppard, "Organic Syntheses," Vol. XII, John Wiley and Sons, Inc., New York, 1932, p. 58.

(10) Volochneva, *J. Applied Chem. (U. S. S. R.)*, **11**, 369 (1938).

(11) Wahl, *Ann. chim.*, (11) **5**, 5 (1936).

(12) Lewis and Cheetham, "Organic Syntheses," Vol. III, John Wiley and Sons, Inc., New York, 1923, p. 13.

(13) Clark and Willits, *Ind. Eng. Chem., Anal. Ed.*, **8**, 209 (1936).

(14) Berger, *Arbeitsschutz*, No. 3, 73 (1936); *Chimie et Industrie*, **36**, 1140 (1936).

(15) Fredholm, *Z. anal. Chem.*, **104**, 400 (1936).

(16) Kolthoff and Bendix, *Ind. Eng. Chem., Anal. Ed.*, **11**, 94 (1939); see also Sheintzis, *J. Applied Chem. (U. S. S. R.)*, **11**, 1012 (1939); Shapiro, *Zavodskaya Lab.*, **7**, 790 (1938).

(17) Elbs and Schiephake, *J. prakt. Chem.*, **104**, 282 (1922).

TABLE I
 ANALYSES AND SOLUBILITIES OF SALTS

Anion	Na salt				K salt				
	% Metal calcd.	% Metal found ^a	Soly. at 30°, g./100 g. H ₂ O ^b	Soly., milli-moles/100 g. H ₂ O	% Metal calcd.	% Metal found ^a	Soly. at 30°, g./100 g. H ₂ O ^b	Soly., milli-moles/100 g. H ₂ O	Soly. Na salt/soly. K salt
2-Chloro-3-nitro- <i>p</i> -xylene sulfonate	8.95	8.90	93.4	325	14.32	14.24	9.21	30.4	10.7
Methyl picrate	8.68	8.61	3.15	11.8	13.91	13.93	3.78	13.4	0.88
Chloropicrate	8.06	8.04	31.2	110	12.94	12.94	1.82	6.03	18
Styphnate	8.61	8.72	8.43	31.5	13.81	13.76	1.54	5.42	5.8
Flavianate ^c	12.83	12.91	9.8	27	19.12 ^d	19.22	1.03	2.5	10.8
Picrate	8.55 ^d	8.62	5.58 ^e	20.8	14.61	14.53	0.755 ^f	2.84	7.3
Nitranilate	16.79	16.92	0.724	2.64	25.54	25.62	.567	1.85	1.4
Picolonate	8.01	8.04	0.285	1.00	12.90	12.97	.338	1.12	0.89
Dipicrylamide ^g	4.96	5.05	11.6	25.2	8.20	8.17	.146 ^h	0.304	83
Diliturate	11.79	11.80	1.034	5.31 ⁱ	18.52	18.69	.086	0.40 ^j	13

^a Average of two values with a mean deviation of 0.3%. ^b Average of two or three values with a mean deviation of 1.4%. ^c Dibasic. ^d Monohydrate. ^e Perhaps the best literature value is given by Fischer, *Z. physik. Chem.*, **92**, 581 (1918), as 4.30 at 25°. ^f Fischer gives 0.645 at 25°. ^g There is disagreement on the names for salts of dipicrylamine; this one is sometimes called "potassium dipicrylamine." We prefer the name "potassium dipicrylamide" as best indicating the structure of a substituted potassium amide. ^h Kielland, *Ber.*, **71**, 220 (1938), gives the solubility as 0.0025 molar at 25°, which is equivalent to 0.12 g./100 g. H₂O. Kolthoff and Bendix (ref. 16) give the value 0.088 for the same temperature. ⁱ Fredholm (ref. 15) gives the value as 0.049 molar at 18°. ^j Fredholm gives 0.0022 molar at 18°.

determined. The most sensitive reagents in the group were dipicrylamine and dilituric acid. Introduction of additional groups into the molecules of such potassium reagents as picric acid,

dilituric acid, and 2-chloro-3-nitrotoluene-5-sulfonic acid is more likely to decrease than to increase their value.

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Hydrogenation of 1,3-Diketones to Ketols

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Sprague¹ obtained the ketol (CH₃)₃CC(O)CH₂-CHOHCH₃ in 68% yield by the hydrogenation of (CH₃)₃CC(O)CH₂C(O)CH₃. This rather unexpected result was no doubt due to the relative resistance to hydrogenation of a carbonyl group adjacent to a tertiary butyl group. The study reported herewith was directed toward finding conditions under which other ketols, less resistant to hydrogenation, could be obtained by the partial hydrogenation of the corresponding 1,3-diketones.

Eight diketones, in which R was methyl, ethyl, a propyl or a butyl radical in compounds of the formula RCOCH₂COCH₃, were prepared and subjected to hydrogenation over Raney nickel under various conditions in attempting to obtain the optimum yield of the various ketols.

Hydrogenation at 100° over Raney nickel of the diketones dissolved in methanol gave in general the highest yield of ketols. The yields of ketol

were where R was methyl 35%, ethyl 51%, *n*-propyl 58%, isopropyl 50%, *n*-butyl 66%, isobutyl 49%, *s*-butyl 64%. Hydrogenation of the diketone dissolved in ether, dioxane or ethanol gave in several cases lower yields, though this difference may have been due more to differences in the losses during isolation rather than to the effect of the solvent upon the rate or course of hydrogenation. The differences between solvents were in most cases negligible, as for example where R was *t*-butyl the yields of the ketol were 66, 68 and 70% in methanol, ether and ethanol, respectively. The 68% yield in ether confirms the yield reported by Sprague referred to above.

The most important consideration, for a given diketone, in determining the yield of ketol is the amount of hydrogen which is absorbed before the reaction is stopped. In order to obtain the yields given above, the shaking of the reaction vessel was stopped after 0.9 to 1.0 mole of hydrogen per

(1) Sprague and Adkins, *This Journal*, **56**, 2669 (1934).