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Organic Precipitants for Potassium. I. 2-Chloro-3-nitrotoluene-5-sulfonic Acid and Related Compounds[1]

BY V. H. DERMER AND O. C. DERMER

The use of 2-chloro-3-nitrotoluene-5-sulfonic acid for the determination of potassium has been tested repeatedly,[2] but has not proved very satisfactory, owing to the appreciable solubility of the potassium salt. Efforts have been made[2d,3] to decrease this solubility by using various non-aqueous solvents, but the results are not promising.

The present investigation is a study of the effects of the different functional groups in the compound mentioned on the solubilities of the sodium and the potassium salts, with a view toward developing a better potassium precipitant.

Experimental

Synthesis of Salts.—Several procedures were used in preparing the intermediate sulfonyl chlorides.

I. The amino aryl sulfonic acids were converted to the halogenated acids and thence to the acid chlorides by the procedure of Davies,[4] as modified by Schultz and Lucas.[5]

II. The amines were first changed into aryl halides; then these were sulfonated with fuming sulfuric acid and converted to sulfonyl chlorides with phosphorus oxychloride or chlorosulfonic acid.

III. The aryl halides were sulfonated with chlorosulfonic acid and the crude products fractionally distilled through a 16-inch (41 cm.) Vigreux column at about 5 mm. pressure.

All solid sulfonyl chlorides were recrystallized once from ether or ligroin. Properties are tabulated in Table I.

Nitration and/or hydrolysis of the sulfonyl chlorides was carried out by the procedure of Davies. Portions of the pure sulfonic acids were exactly neutralized with the proper alkalies; the sodium salts were recrystallized from dilute alcohol, the potassium salts from water. All were dried at 120°.

Analysis.—To prove the purity of each salt, it was analyzed for alkali metal by the sulfate method. Simple evaporation with sulfuric acid in open crucibles, however, failed because the initial decomposition was so violent as to cause losses of material. The difficulty was finally overcome by first destroying the organic matter by a Kjeldahl-like digestion in a small flask at about 250°; occasional addition of a drop of nitric acid helped oxidize the carbon. When fluorine-containing compounds were analyzed this preliminary digestion had to be performed in covered platinum crucibles.

Determination of Solubility.—Solutions of each of the salts, mixed with excess solute, were shaken in sealed glass-stoppered bottles for several hours at about 35°, and then placed in a thermostat and further shaken at 30 ± 0.5° until equilibrium was reached. By repeated sampling it was found that twenty-four hours were sufficient to guarantee saturated solutions. Sampling was done by filtering out about 5 ml. of solution, weighing it, evaporating to dryness, and drying the residue to constant weight at 120°. A blank determination gave too small a residue to be weighed.

Discussion of Results

Reagents for the determination of potassium are almost invariably judged by their ability to separate potassium from sodium. It is evident,

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(1) This is an abstract of a thesis submitted by V. H. Dermer in partial fulfilment of the requirements for the degree of Master of Science at the Oklahoma Agricultural and Mechanical College in 1937. The material was presented at the Pittsburgh meeting of the American Chemical Society, September, 1936.

(2) (a) Davies and Davies, *J. Chem. Soc.*, **123**, 2976–2982 (1923); (b) Wiggins and Wood, *J. Inst. Petroleum Tech.*, **21**, 200–203 (1933); (c) Schempf, Bachelor's thesis, University of Wisconsin (1934); (d) Langham, Master's thesis, Oklahoma Agricultural and Mechanical College (1935); (e) Heston, Langham and Smith, paper presented at the 25th meeting of the Oklahoma Academy of Science, December, 1936.

(3) W. H. Langham, private communication.

(4) Davies, *J. Chem. Soc.*, **121**, 785–791 (1922).

(5) Schultz and Lucas, THIS JOURNAL, **49**, 298 (1927).

TABLE I

PREPARATION AND PROPERTIES OF INTERMEDIATE SULFONYL CHLORIDES

Sulfonyl chloride	Made by procedure	M. p., °C.	M. p. (lit.)	M. p. of nitro deriv., °C.	M. p. (lit.), °C.
2-Fluorotoluene-5-	III	< −10	.....	37–38	...
2-Chlorotoluene-5-	I, II, III	59–61	60–65[a], 64–66[b], 65[c], 64[d]	49	49–50[b]
2-Bromotoluene-5-	I, III	56–57	61[a]	64–64.5	...
2-Iodotoluene-5-	I, II	63.5–64.5	61–62[e]	....[p]	...
p-Fluorobenzene-	II	32	36[f]	< −10	...
p-Chlorobenzene-	II	52–53	53[g], 53.3[h], 50.5–51.5[i]		40–41[o]
p-Bromobenzene-	II	74–74.5	75–76[j,k], 74.5[h]	57	56–57[g]
p-Iodobenzene-	II	80–81	86–87[l], 84[h,m], 81.5–82[i], 83–84[n]	....[p]	...

[a] Wynne, *J. Chem. Soc.*, **61**, 1036–1073 (1892). [b] Davies.[4] [c] Schultz and Lucas.[5] [d] Dosser and Richter, THIS JOURNAL, **56**, 1132–1133 (1934). [e] Barber and Smiles, *J. Chem. Soc.* 1141–1149 (1928). [f] Lenz, *Ber.*, **12**, 581 (1879). [g] Goslich, *Ann.*, **180**, 98–106 (1876). [h] Mummery, *Proc. Roy. Soc.* (London), **A90**, 455 (1914). [i] Olivier, *Rec. trav. chim.*, **33**, 246 (1914). [j] Hübner and Alsberg, *Ann.*, **156**, 326 (1870). [k] Böeseken, *Rec. trav. chim.*, **32**, 9 (1913). [l] Lenz, *Ber.*, **10**, 1136 (1877). [m] Zincke and Jorg, *Ber.*, **43**, 3450 (1910). [n] Willgerodt and Klinger, *J. prakt. Chem.*, [2] **85**, 190 (1912). [o] Fischer, *Ber.*, **24**, 3190 (1891). [p] Nitration gave only water-soluble decomposition products.

TABLE II

ANALYSES AND SOLUBILITIES OF SALTS

Salt, -5-sulfonate	Metal, %			Soly., g./100 g. H_2O		Mean soly., moles/100 g. H_2O	Soly. Na salt / Soly. K salt
	Calcd.	Found					
Na 2-fluorotoluene-	10.85		11.00	27.5	27.3	0.129	1.6
K 2-fluorotoluene-	17.14		17.07	18.4	18.2	.0811	
Na 2-chlorotoluene-	10.06[a]	10.05	10.24	8.07	8.16	.0355	0.84
K 2-chlorotoluene-	15.98[a]	16.18	16.21	10.2	10.4	.0422	
Na 2-bromotoluene-	8.43[b]	8.36	8.52	6.92	7.04[c]	.0256	.67
K 2-bromotoluene-	13.53[b]	13.38	13.60	10.9		.0377	
Na 2-iodotoluene-	7.19	7.20	7.29	4.99	4.99	.0156	.78
K 2-iodotoluene-	11.63	11.75	11.83	6.73	6.81	.0201	
Na 2-fluoro-3-nitrotoluene-	8.95	8.86	8.93	22.7	22.7	.0890	22
K 2-fluoro-3-nitrotoluene-	14.32	14.17	14.31	1.11	1.11	.00408	
Na 2-chloro-3-nitrotoluene-	8.41	8.49	8.54	20.2	20.4[d]	.0739	35
K 2-chloro-3-nitrotoluene-	13.50	13.68	13.75	0.61	0.61[e]	.00211	
Na 2-bromo-3-nitrotoluene-	7.23	7.23	7.24	17.2	17.7	.0549	34
K 2-bromo-3-nitrotoluene-	11.71	11.59	11.65	0.44	0.54	.00162	
Na 2-fluoronitrobenzene-	9.47	9.49	9.51	23.4	23.5	.0965	8.6
K 2-fluoronitrobenzene-	15.10	15.01	15.07	2.91		.0112	
Na 2-chloronitrobenzene-	8.86	8.87	8.89	19.2	19.6	.0748	10
K 2-chloronitrobenzene-	14.22	13.96	14.15	2.04	2.07[f]	.00744	
Na 2-bromonitrobenzene-	7.57	7.64	7.65	40.9	41.1	.135	18
K 2-bromonitrobenzene-	12.19	12.16	12.24	2.36	2.42[g]	.00747	

[a] It has been reported by Hübner and Majert, *Ber.*, **6**, 791 (1873), and by Wynne, reference *a*, Table I, that these salts exist as hydrates, the potassium salt containing one-half molecule of water and the sodium salt either one-half or one molecule of water per molecule of salt. This water is said to be expelled by drying at 140–190°; but since our analyses showed no water present, the dehydration must occur even at 120°. [b] Hübner, Retschy, Müller and Post, *Ann.*, **169**, 34 (1873), reported that these salts also exist as hemihydrates. As before, we must conclude that the water is completely driven off at 120°. [c] Hübner, Retschy, Müller and Post[b] gave the value 5.3 for 14°. [d] Davies and Davies (reference 2a) gave the value 20.0 for 30°. [e] Davies and Davies gave the value 0.57 for 30°. [f] Ullmann and Kuhn[6] gave the value 1.83 for 20°. [g] Goslich, reference *g*, Table I gave the value 1.006 for 8.75°.

therefore, that essential characteristics of a good precipitant for potassium are (1) minimum solubility of the potassium salt and (2) maximum value of the ratio: solubility of the sodium salt/solubility of the potassium salt.

As Table II shows, 2-bromo-3-nitrotoluene-5-sulfonic acid is slightly better than the chlorine derivative in the first respect, and slightly poorer in the second. This does not agree with the findings of O'Leary and Papish,[7] who reported that

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(6) Ullmann and Kuhn, *Ann.*, **366**, 102–104 (1909).

(7) O'Leary and Papish, *Ind. Eng. Chem., Anal. Ed.*, **6**, 108 (1934).

the bromine compound is relatively insensitive to potassium, but gave no details of preparation or testing procedure. None of the other compounds tested at all approaches these two reagents in value.

Among the substituent radicals, the nitro group seems to be most important in rendering a compound effective, since without it solubilities of potassium salts increase tenfold and ratios decrease to less than one. This might have been predicted in view of the almost universal presence of the nitro or the nitrite group in potassium precipitants. Yet, curiously enough, 2,6-dinitrochlorobenzene-4-sulfonic acid gives a potassium salt more than twice as soluble as the salt of the mononitro derivative.[6] We have spent some time attempting to prepare the halogen-free compound, 3-nitrotoluene-5-sulfonic acid, for comparison with the other acids studied, but have not been able to obtain it free from isomers.

Summary

In an effort to improve 2-chloro-3-nitrotoluene-5-sulfonic acid as a precipitant for potassium, the sodium and the potassium salts of nine closely related acids have been synthesized and their solubilities at 30° determined.

Of these acids, only 2-bromo-3-nitrotoluene-5-sulfonic acid is equal in value to the chlorine compound.

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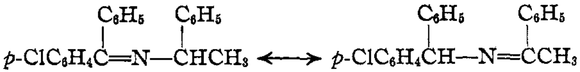
[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Tautomerization of an Optically Active Azomethine

BY GERALD T. BORCHERDT AND HOMER ADKINS

Probably no one today seriously questions the concept of dynamic equilibrium in tautomerization, *i. e.*, that if A is in equilibrium with B, A is being converted to B and B is being converted to A. However, all the known *facts* bearing on this point *could* be rationalized on the assumption that the rate of conversion of A to B is progressively slowed up by the accumulation of B (and *vice versa*) so that at equilibrium A is not being converted to B, but is in a state which Michael called a "static" equilibrium.[1] It has seemed to us worth-while to ascertain by experiment whether in a given case, A is actually being converted to B at the rate predicted by the classical theory. This may be done by following the rate of a reversible rearrangement of an optically active substance by two methods, one of which depends upon the loss of optical activity and the other upon the concentration of the optically active compound plus the optically inactive compound resulting from the reversal of the reaction. If the rate of reaction calculated from the loss in optical activity is less than that found by the second method, support would be given to the concept of static equilibria. At the time these studies were begun (1930) no one, so far as we are aware, had ever determined the rate of a reversible reaction involving an optically active component, by two such methods. Since that time Ingold and his associates have made such measurements, having in mind objectives quite different from our own. However, their published data did not seem to us adequate for our purpose, since we were especially interested in the rate of reaction in the vicinity of equilibrium.

The rate of tautomerization of *l*-*p*-chlorobenzhydrylidene-α-phenylethylamine (I) to α-phenylethylidene-*p*-chlorobenzhydrylamine (II) has been measured by two independent methods. The



$$p\text{-ClC}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\text{C}}\text{=N—}\overset{\text{C}_6\text{H}_5}{\text{C}}\text{HCH}_3 \longleftrightarrow p\text{-ClC}_6\text{H}_4\overset{\text{C}_6\text{H}_5}{\text{C}}\text{H—N=}\overset{\text{C}_6\text{H}_5}{\text{C}}\text{CH}_3$$

I II

tautomerization of I was made at 85° in alcohol using sodium ethoxide as a catalyst. The rate was determined (a) by noting the loss in rotatory power of the reaction mixture and (b) by determining with a polarograph the ratio of *p*-chlorobenzophenone to acetophenone resulting from the hydrolysis of the mixture of the two azomethines.

The rate of tautomerization of I was recently determined by Ingold and Wilson[2] who observed, first, the rotatory power of the α-phenylethylamine, and second, the chloride content of the mixture of hydrochlorides of α-phenylethylamine and *p*-chlorobenzhydrylamine, resulting from hydrolysis of the mixture of azomethines.

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(1) Michael and Leupold, *Ann.*, **379**, 263 (1911).

(2) Ingold and Wilson, *J. Chem. Soc.*, 1495 (1933); 92 (1934).