$$+ 2Na_2Se\ (aq.) + 3H_2O + 72.78\ \text{kcal.}$$
$$+ 2(88.12) + 3(68.4) = 72.78$$
$$-x = 1.33\ \text{kcal. or}$$
$$Si + 2Se \longrightarrow SiSe_2 - 1.33 \pm 0.5\ \text{kcal.}$$

Thomsen[9] investigated the reaction between aqueous sodium hydroxide and aqueous silicic acid; he found the heat of reaction for aqueous sodium metasilicate to be +5.23 kcal., at the exact equivalence point. Excess reagents produced different results so that the figure is of uncertain reliability. However, it is the only figure available and the calculation of the heat of formation of $Na_2SiO_3(aq)$ when compared to that of $Na_2SiO_3(s)$ is a reasonable one, giving a negative heat of solution of about 6 kcal. per mole.

$$2NaOH\ (aq.) + SiO_2 \longrightarrow Na_2SiO_3\ (aq.) + H_2O + 5.23\ \text{kcal.}$$
$$-2(112.04) - 201.34 + x + 68.4 = 5.23$$
$$x = 362.25$$

To account for the differences between the figures obtained by this calculation and those of Sabatier, the latter's equation must be considered.

$$SiS_2 + 2H_2O \longrightarrow SiO_2(diss) + 2H_2S(g) + 38\ \text{kcal.}$$
$$-x - 2(68) + 201 + 10 = 38$$

in round figures using recent values $-x = -37$ kcal. Sabatier considered the heat of solution of silica a negligible quantity and failed to consider the formation of a saturated solution of hydrogen sulfide. It is also possible that the dissolved silica was a mixture of silicic acids. The use of 6 *M* sodium hydroxide in this study resulted in the formation of dissolved salts of predictable composition, especially since a large excess of sodium hydroxide was always present.

Properties of Silicon Diselenide.—The freshly sublimed silicon diselenide was a white, crystalline solid, which was deposited in a hard compact mass on the wall of the tube.

Silicon diselenide reacts with the oxygen of the air at room temperature in a simple replacement reaction.

$$SiSe_2 + O_2 \longrightarrow SiO_2 + 2Se\ (\text{red}).$$

It reacts vigorously with water, forming hydrogen selenide and silica. With strong bases, the corresponding selenides and silicates are formed. Evidence of the reaction in the crude material was obtained by the formation of zinc selenide and the odor of hydrogen selenide immediately evident when the material was in contact with moist air. Due to its instability and the nature of its decomposition products, extreme caution should be exercised in its preparation and handling.

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(9) J. Thomsen, "Thermochemische Untersuchingen," Vol. II, Johan Ambrosius Barth, Leipzig, 1882, p. 413.

DEPARTMENT OF CHEMISTRY
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RECEIVED JUNE 11, 1951

Preparation of Radioactive Sodium Metal by Exchange of Na^{23} and $Na^{22}Cl$

BY NORMAN H. NACHTRIEB, JOHN A. WEIL AND EDWARD CATALANO

In the course of investigating diffusion phenomena among the alkali metals, we have found it convenient to prepare metallic radioactive sodium by means of the reaction

$$Na^{23}(l) + Na^{22}Cl(s) \longrightarrow Na^{22}(l) + Na^{23}Cl(s)$$

The distribution of Na^{22} between the metal and salt should stand in the approximate ratio of the weights of sodium in the two phases. Under the conditions of our experiments, when the ratio of sodium to sodium chloride was about 10^4, essentially quantitative conversion was obtained. No effort was made to determine the distribution coefficient. On the face of it, it looks as if the reaction occurs between solid sodium chloride and liquid sodium metal, but the detailed nature is not known. The high conversion rate rules out the possibility that the reaction involves only the contact surfaces. Conceivably, the sodium chloride may dissolve in the metal; alternatively, reaction may take place by diffusion of sodium through sodium chloride.

Experimental

The exchange reaction and the subsequent distillation of the metal took place in a specially designed Pyrex tube. An iron thimble made from a 6″ length of 7/8″ dia. seamless tubing, with a bottom plug pressed into place, was sealed into one end of the tube. Adjacent to the thimble was a U shaped section with a seal-off tube connected at the bottom. The other end of the tube led to a vacuum line. 1.00 ml. of a tracer solution,[1] having an activity of 1.13×10^7 disintegrations min.^{-1} and containing a total of 2.39 mg. of carrier sodium chloride, was transferred to the thimble. The water was removed by evacuation of the tube with an oil diffusion pump through an intervening liquid nitrogen trap. A quantity of freshly cut sodium, estimated to weigh about 10 g., was then placed in the thimble and the system was again evacuated. A cylindrical electric furnace was slipped over the end of the tube and the contents of the thimble maintained at 250° overnight.

A thin iridescent metal mirror appeared on the walls of the tube beyond the thimble. Since its thickness did not increase with time, it was assumed to be a trace of potassium and was flamed out of the tube. When the temperature was raised to 525°, all of the sodium distilled from the thimble and condensed in the U section. Careful flaming transferred almost all of the metal into the seal-off tube. The 7.60 g. of sodium thus recovered was found to have a specific activity of 1500 disintegrations $\text{min.}^{-1}\ \text{mg.}^{-1}$. The possibility that $Na^{22}Cl$ was carried over mechanically was ruled out by the fact that redistillation did not diminish the activity of the metal. Some discoloration of the U section appears to be unavoidable, but can be minimized by care in flaming. Five preparations have been carried out in this manner.

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(1) Supplied by Isotopes Division, United States Atomic Energy Commission, Oak Ridge, Tennessee.

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Thallous Salts as Derivatives of Sulfonic Acids. II

BY HENRY GILMAN AND H. SMITH BROADBENT

The present report is an extension of previous preliminary studies[1] on the use of thallous salts for the characterization of some sulfonic and other acids or their soluble salts. Several advantages of these salts as derivatives of sulfonic acids were mentioned in the earlier reports.[1] Among the salts now reported is found additional support

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(1) (a) Gilman and Abbott, THIS JOURNAL, **65**, 123 (1943); (b) Gilman and Abbott, *ibid.*, **71**, 659 (1949).

TABLE I

THALLOUS SALTS OF SUBSTITUTED BENZENESULFONATES

No.	Substituents	M.p., °C.	Rel. solubility	Formula	Tl analyses, % Found	Tl analyses, % Calcd.
1	2,5-Dimethyl-[a]	217–219	Extremely sol.	$C_8H_9O_3STl$	52.8	52.5
2	3-Biphenyl-[b,c]	454–457 dec.	Quite insol.	$C_{18}H_{13}O_3STl$		
3	4-Biphenyl-[b,c]	> 532	Very insol.	$C_{18}H_{13}O_3STl$		
4	4-Chloro-[b]	258–260	Moderately sol.	$C_6H_4O_3ClSTl$	52.0	51.6
5	2,5-Dichloro-[a]	326–328	Quite insol.	$C_6H_3O_3Cl_2STl$	47.4	47.5
6	3,4-Dichloro-[b]	273–275	Moderate	$C_6H_3O_3Cl_2STl$	47.65	47.5
7	3-Chloro-4-methyl-[b]	198–200	Moderate	$C_7H_6O_3ClSTl$	49.45	49.9
8	4-Chloro-3-methyl-[b]	227–229	Moderate	$C_7H_6O_3ClSTl$	50.2	49.9
9	4-Hydroxy-[b,d]	266	Very sol.	$C_6H_5O_4STl$	54.6	54.2
10	4-Hydroxy-5-isopropyl-2-methyl-[e] [Thallous thymolsulfonate]	243–244	Very sol.	$C_{10}H_{13}O_4STl$	49.2[e]	47.2
11	2-Hydroxy-3,4-dichloro-[b]	270–272	Moderate	$C_6H_3O_4Cl_2STl$	45.8	45.8
12	2-Nitro-[a,f]	226–228	Moderate	$C_6H_4O_5NSTl$	49.95	50.3
13	4-Nitro-[a]	284–285	Moderate	$C_6H_4O_5NSTl$	50.7	50.3
14	2,4-Dinitro-[a]	241	Moderate	$C_6H_3O_7N_2STl$	44.9	45.3
15	2-Methyl-5-nitro-[b]	305–308 dec.	Moderate	$C_7H_6O_5NSTl$	48.5	48.6
16	2-Chloro-5-nitro-[a]	323–324 dec.	Quite insol.	$C_6H_3O_5NClSTl$	46.3	46.4
17	4-Bromo-3-nitro-[a]	308–309	Quite insol.	$C_6H_3O_5NBrSTl$	41.7	42.1
18	4-Chloro-3-methyl-5-nitro-[b]	363–364	Quite insol.	$C_7H_5O_5NClSTl$	44.62[g]	44.9
19	2-Amino-[a]	169–171	Quite sol.	$C_6H_6O_3NSTl$	54.1	54.3
20	5-Amino-2-methyl-[a]	187–188	Quite sol.	$C_7H_8O_3NSTl$	52.5	52.35
21	4-Amino-3-methyl-[a]	212–213	Moderate	$C_7H_8O_3NSTl$	51.8	52.35
22	2-Amino-5-(4-aminophenyl)-[a] [Thallous benzidine-3-sulfonate]	269–271	Moderate	$C_{12}H_{11}O_3N_2STl$	44.1[g]	43.7
23	2-Anilino-5-nitro-[b] [Thallous 4-nitrodiphenylamine-2-sulfonate]	277–280 dec.	Very insol.	$C_{12}H_9O_5N_2STl$	40.7[g]	41.1
24	4-Hydrazo-[a]	Dec. *ca.* 245	Moderate	$C_7H_7O_3N_2STl$	52.0	52.2
25	4-(4-Aminonaphthylazo)-[b]	Darkens 268 Dec. 275–280	Very insol.	$C_{16}H_{12}O_3N_3STl$	38.2[g]	38.5

[a] Prepared from the free sulfonic acid. [b] Prepared from the sodium salt of the acid. [c] Both *p*-terphenyl derivatives are very insoluble and highly refractory, particularly the *p*-terphenyl-4-sulfonate. Even heating with fuming nitric acid at 400° for 72 hours in a sealed tube failed to completely decompose the organic matter making a satisfactory analysis for thallium virtually impossible by this method. [d] The dithallous salt is not formed quantitatively. It seems best to use two equivalents of thallous formate and isolate the monothallous salt by recrystallizing it from ethanol–water (2:1). Otherwise products analyzing low for the monothallous salt are obtained. [e] The starting sulfonic acid was the Eastman Kodak Co. white label product (m.p. for the anhydrous product was 114–115°). Stebbins, THIS JOURNAL, **3**, 111 (1881), gives the melting point of the monohydrate as 91–92°. It is very difficult to prepare this very soluble thallous salt with a satisfactory melting point. An acceptable analysis was not obtained. Several values varying from 2 to 4% high for thallium were obtained. Some thallous sulfate was also isolated from the reaction. It appears likely that the sample of the sulfonic acid was impure. [f] A mixture of two types of crystals is obtained if the solution is boiled too long in the course of evaporation. One type is the bright, yellow crystals of the thallous sulfonate, and the other is the fine, white needles of thallous sulfate (m.p. 632°). The former is soluble in 95% ethanol while the latter is not. Both No. 13 and 14 would also likely undergo hydrolysis giving thallous sulfate under similar conditions. [g] These analyses required preliminary destruction of the organic matter by heating with fuming nitric acid at 300° in a sealed tube.

for the suitability of these derivatives for the separation and characterization of isomers.

As a result of the present more extensive study, it appears that about 20% of the thallous salts now reported are so high melting as to require temperatures above those conveniently attained with ordinary melting point apparatus (*ca.* 300–350°). However, in such cases one of the conventional melting point blocks described in the literature[2] may be used satisfactorily. Furthermore, we were unable to prepare pure, crystalline thallous salts from two acids (metanilic acid and 4-amino-3-hydroxynaphthalenesulfonic acid) and two sulfonates (sodium 3,4-dimethylbenzenesulfonate and sodium 2,4-dimethylbenzenesulfonate). The difficulty in the latter case appeared to be the only slightly lower solubility of the thallous sulfonates compared to the sodium salts from which they were obtained.

The results are summarized in Tables I and II.

The authors are grateful to R. K. Abbott, Jr., Gene Mock and Keith Brinker for assistance.

Experimental

Procedure.—In the preparations from the sulfonic acids, 0.01 mole of acid dissolved in the minimum amount of water is titrated with thallous hydroxide,[1,3] or the requisite amount of base is merely added to a weighed quantity of acid. In the preparations from the sodium sulfonates, a weighed quantity of sodium sulfonate dissolved in a small amount of water is treated with an equivalent quantity of thallous formate or malonate dissolved in a few drops of water. In either case, on cooling, the thallous sulfonate crystallizes out on standing. With the more soluble salts, evaporation to a smaller volume or to dryness may be necessary. The product is recrystallized from water or mixtures of ethanol and water. The principal point of importance in preparing the more soluble of these salts lies in adjusting the amount and ratio of these two recrystallizing solvents quite accurately to the properties of the sulfonate being prepared. No extensive study was made of other solvents, but none of the more common ones appeared to be more suitable.

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[2] Berl and Kullmann, *Ber.*, **60**, 811 (1927).

[3] Care must be taken not to expose the solution of thallous hydroxide unduly to light and air which oxidizes it slowly, precipitating the insoluble thallic hydroxide and oxide on the walls of the container, thus changing the titer of the solution.

TABLE II

THALLOUS SALTS OF OTHER SULFONIC ACIDS

No.	Thallous salt	M.p., °C.	Rel. solubility	Formula	Tl analyses, % Found	Calcd.
1	4-Methyl-1,3-benzenedisulfonate[b,c]	272–276[c] 295–297	Fairly insol.	$C_7H_6O_6S_2Tl_2$	60.5[c]	62.0
2	Benzidine-3,3′-disulfonate[a]	Chars above 350	Moderate	$C_{12}H_{10}O_6N_2S_2Tl_2$	54.8	54.4
3	D,L-Camphor-β-sulfonate[a,d]	259–260	Extremely sol.	$C_{10}H_{15}O_4STl$	46.7	46.9
4	D-Camphor-β-sulfonate (Reychler's)[a,d]	259–260	Extremely sol.	$C_{10}H_{15}O_4STl$	46.9	46.9
5	4-Amino-1-naphthalenesulfonate[a]	240–241	Quite insol.	$C_{10}H_8O_3NSTl$	47.9	47.9
6	8-Hydroxy-5,7-dinitro-2-naphthalenesulfonate[a] (dithallous salt)	Dec. *ca.* 376 explosively	Quite insol.	$C_{10}H_4O_8N_2STl_2$	56.95	56.7
7	1-Anthraquinonesulfonate[e]	475–480 dec	Moderate	$C_{14}H_7O_5STl$		
8	2-Anthraquinonesulfonate[b]	384–386	Quite insol.	$C_{14}H_7O_5STl$	41.9[g]	41.6
9	5-Nitro-1-anthraquinonesulfonate[a]	348–350	Fairly insol.	$C_{14}H_6O_7NSTl$	38.45	38.1
10	8-Nitro-1-anthraquinonesulfonate[a]	339–341	Fairly insol.	$C_{14}H_6O_7NSTl$	37.7	38.1
11	8-Hydroxy-5-quinolinesulfonate[a] (monothallous salt)	292–295	Quite insol.	$C_9H_6O_4NSTl$	47.3[g]	47.7
12	8-Hydroxy-5-quinolinesulfonate[a] (dithallous salt)	Darkens 400 Dec. 425	Quite insol.	$C_9H_5O_4NSTl_2$	64.8[g]	64.7
13	8-Hydroxy-7-iodo-5-quinolinesulfonate[a,f]	Dec. *ca.* 300	Quite insol.	$C_9H_4O_4NISTl_2$	56.0[f,g]	53.9

[a] Prepared from the free sulfonic acid. [b] Prepared from the sodium salt of the acid. [c] Part of the product always melted at 272–276° and the main part of it at 295–297° even after several recrystallizations. The analyses were consistently 1.5% low for the dithallous salt. Perhaps the original sulfonate contained a small amount of impurity not separable by the processes of preparation. [d] These thallous salts are exceedingly soluble in water, but they are very readily prepared by evaporating the solution to dryness under reduced pressure and recrystallizing from absolute ethanol. The melting point for thallous D-camphorsulfonate here recorded is somewhat lower than previously reported.[1a] The melting points for both the camphorsulfonates were determined on several different samples of these salts, and they were found to be unchanged after repeated crystallizations from absolute ethanol. The fact that both the D- and the D,L- salts have the same melting point and that a mixed-melting point of the two is undepressed indicates that the D- and L- salts form a continuous series of solid solutions in any proportion. To guarantee the identity of these salts they were examined polarimetrically. For thallous D-camphorsulfonate $[\alpha]^{25}\mathrm{D}$ +11.8 ± 0.2°, in 5–8% aqueous solution. This value corresponds closely on the basis of equivalent D-camphorsulfonate ion concentration with the values reported for free D-camphorsulfonic acid in aqueous solution of +21.5° (Reychler, *Bull. soc. chim. France*, [3] **27**, 982 (1902)) and of +22.60° (Rewald, *Ber.*, **42**, 3137 (1909)). Our sample of thallous D,L-camphorsulfonate was found to be entirely optically inactive and, hence, uncontaminated with optically active salt. [e] It was very difficult to secure a crystalline thallous salt (fine, yellow needles) from the highly insoluble crude potassium sulfonate (Eastman Kodak Co.). This is a case of the initial salt being nearly as insoluble as the thallous salt product making isolation of the desired product very difficult. A satisfactory analysis was never obtained, although the product appeared to be pure. [f] No crystalline material could be isolated using one equivalent of thallous hydroxide. The crystalline dithallous salt decomposed so that no melting point check on purity was available. It was very difficult to analyze the product, but the analysis shown was checked. [g] These analyses required preliminary destruction of the organic matter by heating with fuming nitric acid at 300° in a sealed tube.

Melting Points.—The melting points of all compounds melting below 345° were determined on an electrically heated block similar to the Fisher–Johns melting point apparatus. All such melting points were uncorrected. The melting points of those compounds melting above 345° were determined in a Berl–Kullmann block[2] using a Weston dial type thermometer calibrated with a thermocouple.

Analyses.—Suitable modifications of the method of Meyer and Bertheim[4] were used for determining thallium content.

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(4) Meyer and Bertheim, *Ber.*, **37**, 2051 (1904).

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The Reaction of Dibenzothiophene-5-oxide with *n*-Butyllithium

BY HENRY GILMAN AND DONALD L. ESMAY

The treatment of sulfoxides with organometallic compounds has resulted in reduction,[1] cleavage,[1a,2] cyclization,[1b,3] rearrangement,[3b,4] lateral metalation,[3b] sulfonium salt formation,[5] or complex formation.[3b,6] No nuclear metalation of aryl or heterocyclic sulfoxides has been reported, although metalation of the nucleus has been shown to occur with sulfides such as ethyl phenyl sulfide,[7] diphenylsulfide,[8] thiophene[9] and dibenzothiophene.[8,10]

We are reporting the reaction of dibenzothiophene-5-oxide with *n*-butyllithium[11] in diethyl ether to give upon carbonation 4-dibenzothiophenecarboxylic acid as the major product. The identity of the acid product was established by the method of mixed melting points and by comparison of spectra obtained by infrared absorption measurements.

An initial experiment at the temperature of refluxing ether gave a very small yield of 4-dibenzo-

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(1) (a) K. Fuchs and P. Gross, *Ber.*, **63**, 1009 (1930); (b) C. Courtot, M. Chaix and L. Nicholas, *Compt. rend.*, **194**, 1660 (1932); (c) H. Hepworth and H. W. Clapham, *J. Chem. Soc.*, **119**, 1188 (1921); (d) C. Courtot and C. Pomonis, *Compt. rend.*, **182**, 893 (1926).

(2) (a) E. Bergmann and M. Tschudnowsky, *Ber.*, **65**, 457 (1932); (b) E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1320 (1935).

(3) (a) A. Schönberg, *Ber.*, **56**, 2275 (1923); (b) K. Fuchs and F. Breuer, *Monatsh.*, **53**, 438 (1929); (c) C. Courtot, M. Chaix and J. Kelner, *Compt. rend.*, **194**, 1837 (1932).

(4) A. Schönberg and A. Stephenson, *Ber.*, **66**, 260 (1933).

(5) B. S. Wildi, S. W. Taylor and H. A. Potratz, THIS JOURNAL, **73**, 1965 (1951).

(6) H. Hepworth, *J. Chem. Soc.*, **119**, 1249 (1921).

(7) H. Gilman and F. J. Webb, THIS JOURNAL, **62**, 987 (1940); *ibid.*, **71**, 4062 (1949).

(8) H. Gilman and R. L. Bebb, *ibid.*, **61**, 109 (1939).

(9) H. Gilman and D. A. Shirley, *ibid.*, **71**, 1870 (1949).

(10) (a) H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938); (b) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *ibid.*, **3**, 120 (1938).

(11) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).