Methyl ethyl ether was obtained as a fraction distilling at 7–14° (75% at 7–9°). Identification was made by a molecular weight determination and a comparison of the infrared absorption spectrum in the 2–15 μ region with that of an authentic sample. An additional amount was identified in the vaporous product by mass spectrometric comparison with the authentic sample (for example, the ratio of the intensity for ions of $m/q = 31$ to that for ions of $m/q = 60$ was 0.68 for both the reaction product and the known).

The amounts of the various products obtained, in moles per mole of peroxide decomposed, were: $(CH_3)_2CO$ (0.78), CH_3OH (0.29), H_2CO (0.25), C_2H_6 (0.21), CO (0.12), n-C_4H_{10} (0.11), $CH_3COC_2H_5$ (0.093), $C_2H_5C(CH_3)_2OH$ (0.086), *$CH_3OC_2H_5$ (0.078)*, C_2H_4 (0.077), C_3H_8 (0.061), H_2 (0.039), CH_4 (0.036) and C_4H_8 (0.007).

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The Ternary System Thallous Sulfate–Sodium Sulfate–Water at 25 and 45°

BY JOHN E. RICCI AND JACK FISCHER

The solubility isotherms at 25 and 45° for the system Tl_2SO_4–Na_2SO_4–H_2O were determined for comparison with the corresponding system Ag_2SO_4–Na_2SO_4–H_2O.[1] In contrast with the continuous solid solution of silver sulfate and anhydrous sodium sulfate, the thallous salt forms no solid solution with the sodium salt at these temperatures.

The materials and the procedure used were those already described in a report on a number of other systems involving thallous sulfate.[2] Complexes prepared from pure Tl_2SO_4 and C.P. Na_2SO_4 were brought to equilibrium and the saturated solution was then analyzed for total solid and for thallium. The mixtures at 25° were seeded with $Na_2SO_4 \cdot 10H_2O$ after the first 24 hours of stirring. In this connection it was noted that the solutions had to be saturated with the sodium sulfate, prior to the seeding with the decahydrate, in order to initiate the precipitation of the new phase, the seed otherwise dissolving without effect. The mixtures were stirred for 7 to 38 days before analysis of the solution, and attainment of equilibrium was proved by constancy of composition on reanalysis after further stirring.

The measurements, in terms of weight percentage, are listed in Table I for the two temperatures studied, and those for 45° are plotted in the usual fashion in Fig. 1. According to the tie-lines the only solid phases formed are the pure salts, Tl_2SO_4 and $Na_2SO_4 \cdot 10H_2O$ at 25°, Tl_2SO_4 and Na_2SO_4 at 45°. The average absolute error from the compositions of the pure solids, calculated by algebraic extrapolation of the 14 tie-lines involved, is only 0.23% (with 0.77 maximum) on the phase diagram.

The solubility of $Na_2SO_4 \cdot 10H_2O$ at 25° is seen to be hardly affected by the Tl_2SO_4, although that of the anhydrous Na_2SO_4 at 45° does suffer the expected decrease. The solubility of Tl_2SO_4 at both temperatures, on the other hand, is distinctly increased by Na_2SO_4, suggesting the formation of some complex involving thallous sulfate and sulfate ion. Potassium oxalate similarly increases the solubility of thallous oxalate.[3]

TABLE I

SYSTEM $Tl_2SO_4(A)$–$Na_2SO_4(B)$–$H_2O(W)$

Complex % A	Complex % B	Solution % A	Solution % B	Density	Solid phase
		Temperature: 25°			
...	0.00	5.222	0.00	1.046	A
19.49	4.89	6.24	5.69	1.112	A
14.97	9.98	7.32	10.87	1.178	A
12.45	15.21	8.06	15.95	1.245	A
14.99	16.98	8.27	18.34	1.275	A
13.99	21.97	8.48	21.23	1.313	A + B·10W
7.98	27.99	8.42	21.34	1.315	A + B·10W
5.47	25.37	6.59	21.50	1.290	B·10W
3.51	25.98	4.36	21.56	1.256	B·10W
1.41	26.11	1.77	21.58	1.219	B·10W
0.00	...	0.00	21.66	1.210	B·10W
		Temperature: 45°			
...	0.00	7.73	0.00	1.064	A
20.02	7.00	9.62	8.00	1.166	A
20.22	13.07	10.86	14.65	1.254	A
17.94	16.96	11.32	18.39	1.308	A
20.03	19.96	11.41	22.11	1.356	A
18.02	27.00	11.05	28.80	1.434	A + B
11.68	32.43	11.04	28.78	1.435	A + B
10.02	35.07	10.95	28.75	1.434	B
7.50	37.50	8.46	29.57	1.399	B
4.96	39.89	5.74	30.42	1.362	B
0.00	...	0.00	32.05	1.308	B

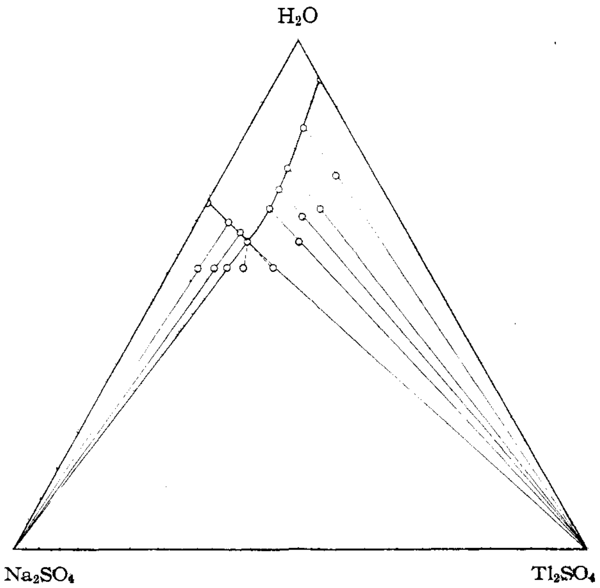

Fig. 1.—System Tl_2SO_4–Na_2SO_4–H_2O at 45°.

Silver and thallous sulfates form solid solutions, besides a 1:1 compound, in their binary system at the melting curve.[4] At room temperatures, however, the argentous salts form solid solutions with various corresponding sodium salts (sulfate,[1] bro-

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(1) E. L. Simons and J. E. Ricci, THIS JOURNAL, **68**, 2194 (1946).

(2) J. E. Ricci and J. Fischer, *ibid.*, **73**, 1443 (1951).

(3) R. Abegg and J. F. Spencer, *Z. anorg. Chem.*, **46**, 406 (1905).

(4) S. I. Sokolov, *J. Russ. Phys. Chem. Soc.*, **62**, 2319 (1930); from *C. A.*, **25**, 4772 (1931).

mate,[5] chlorate,[6] nitrate,[7] for example) but not with potassium and ammonium salts,[1,6,8] while the thallous salts form solid solution with corresponding potassium and ammonium salts (sulfate,[2] chlorate,[9] primary orthophosphate,[10] for example) but not, at least in the present case, with the sodium salt.[11] According to the ionic radii usually listed[12] (Na^+, 0.95, K^+, 1.33; NH_4^+, 1.48; Ag^+, 1.26; Tl^+, 1.44), one would not quite expect this difference between argentous and thallous salts. The values listed by Sidgwick[13] (Na^+, 0.98; K^+, 1.33; Ag^+, 1.13; Tl^+, 1.49), on the other hand, would be in better agreement. While the sulfates of all of these five cations are orthorhombic, moreover, the axial ratios (a:b:c) fall into two groups.[14] For Na_2SO_4 and Ag_2SO_4 they are 0.598:1:1.252 and 0.570:1:1.235, respectively. In the other group we have 0.573:1:0.742 for K_2SO_4, 0.563:1:0.732 for $(NH_4)_2SO_4$, and 0.555:1:0.733 for Tl_2SO_4.

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(7) D. J. Hissink, *Z. physik. Chem.*, **32**, 537 (1900).

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(9) H. W. B. Roozeboom, *ibid.*, **8**, 531 (1891).

(10) Mme. Bruzau, *Bull. soc. chim. France*, 1177 (1948).

(11) According to V. A. Palkin, $TlNO_3$ forms no solid solution with $AgNO_3$, $NaNO_3$ or KNO_3, *Doklady Akad. Nauk. S. S. S. R.*, **66**, 651 (1949), from *C. A.*, **44**, 9232 (1950); *J. Gen. Chem., U. S. S. R.*, **19**, 367 (1949), from *C. A.*, **44**, 9237 (1950).

(12) L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1948, pp. 346, 350.

(13) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. I, Oxford Univ. Press, 1950, p. xxix.

(14) A. N. Winchell, "Microscopic Characters of Artificial Minerals," John Wiley and Sons, Inc., New York, N. Y., 1931, pp. 216–217; R. W. G. Wyckoff, "The Structure of Crystals," Supplement to 2nd Edition, Reinhold Publishing Corp., New York, N. Y., 1935, p. 64.

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Formylation during Nitrolysis in Chloroform

BY JOHN H. ROBSON[1] AND GEORGE F WRIGHT

It has been shown[2] that the nitrolysis of N,N′-dicyclohexylimidazolidine in acetic anhydride–nitric acid yields mainly N-nitro-N,N′-dicyclohexyl-1,2-diaminoethane mononitrate (I), although some N-nitro-N′-aceto-N,N′-dicyclohexyl-1,2-diaminoethane is also formed, presumably by acetylation of I. When chloroform is included in the nitrolysis medium neither of these products can be isolated. Instead a mixture is obtained which, when partially purified, shows by its X-ray diffraction powder pattern that it contains N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane (II). Destruction of this component by potassium persulfate–absolute nitric acid mixture leaves a compound for which analysis indicates the formula $C_{15}H_{27}N_3O_3$. This substance gives a positive Franchimont nitramine test and a negative lanthanum nitrate test for an aceto group. It has been proven to be N-nitro-N′-formyl-N,N′-dicyclohexyl-1,2-diaminoethane (III) by its synthesis *via* formylation of I.

The presence of a formyl group in III may be ascribed either to oxidation of the methylene linkage of the imidazolidine or to formylation of I by mixed formic–acetic anhydride. Such an anhydride might arise from formic acid produced by decomposition of chloroform in the nitrolysis medium. The latter interpretation is preferred because none of III was formed when chloroform was absent. Furthermore a small yield of III could be obtained when formic acid rather than chloroform was used in the reaction mixture. This meager yield was not unexpected in consideration of the instability of formic acid in the nitrolysis medium. Indeed the stability of the disubstituted formamide (III) in this medium was unexpected and is being investigated further.

Experimental[3]

N-Nitro-N′-formyl-N,N′-dicyclohexyl-1,2-diaminoethane (III).—To 21.0 ml. (0.5 mole) of absolute nitric acid at −2 to 0° was added dropwise with stirring, a solution of 5.9 g. (0.025 mole) of N,N′-dicyclohexylimidazolidine in 25 ml. of chloroform (ethanol-free and dry). Then 100 ml. of distilled acetic anhydride was added at 0–5° and the stirred suspension maintained at 35–45° for seven hours. All volatile solvents were removed under reduced pressure. The residual oily solid was thrice-crystallized from ethanol to yield 2.0 g., m.p. 147–148°. This material did not depress the melting point of authentic N-nitro-N′-nitroso-N,N′-dicyclohexyl-1,2-diaminoethane (m.p. 147–148°) and the X-ray (Cu,Kα; Ni filtered) diffraction powder pattern included spacings (Å.) characteristic of pure II. Thus intensities [I/I_0] and spacings for II are: [10] 4.62; [7] 3.12; [6] 5.67, 4.03, 3.70; [5] 8.34, 2.81, 2.38; [4] 2.71, 1.90; [3] 2.59, 2.19; [2] 6.70, 5.15, 2.00, 1.77; [1] 2.27, 2.06, 1.72, 1.65, 1.48, 1.26. The impure 2.0 g. portion gave a comparable pattern: [10] 4.66; [6] 5.67, 3.86, 2.84; [5] 3.12; [4] 4.07, 2.39; [3] 8.18, 3.70, 2.13; [2] 5.15, 3.45, 2.71; [1] 2.55, 2.21, 1.96, 1.92, 1.79, 1.76, 1.51. In order to demonstrate the non-identity with N-nitro-N′-aceto-N,N′-dicyclohexyl-1,2-diaminoethane the powder pattern for the latter substance was also determined: [10] 5.03, 4.57; [7] 5.71; [6] 4.23, 3.42; [5] 3.66, 3.10; [4] 8.42, 2.42; [3] 2.76; [2] 2.26, 2.08; [1] 2.59, 2.23.

Furthermore purification of the 2-g. portion was accomplished firstly by treatment with 7.2 g. of ammonium persulfate in 7.2 g. of absolute nitric acid at 0–5° for four hours to yield a semi-solid oil after drowning in ice. This oil was treated five minutes with 15 ml. of hot 70% nitric acid, the mixture drowned in ice, and the resulting solid crystallized from ethanol or diisopropyl ether to yield 0.94 g. (13%) of III, m.p. 163–164°.

Anal. Calcd. for $C_{15}H_{27}N_3O_3$: C, 60.6; H, 9.17; N, 14.2. Found: C, 60.5; H, 9.05; N, 14.3.

The X-ray diffraction pattern with CuKα (Ni filtered) radiation included spacings in Å. with intensities [I/I_0] as follows: [10] 4.97; [7] 4.15; [6] 3.86; [5] 5.60, 2.83; [3] 3.45, 2.99; [2] 3.23, 2.32, 2.14, 1.79; [1] 2.62, 2.49, 1.76.

If the chloroform was eliminated from the preparative procedure and 10 ml. of formic acid was, instead, added at 0° subsequent to addition of the acetic anhydride, the otherwise identical method gave a 13% yield of I and a 2% yield of III.

When 1.50 g. (0.0047 mole) of I was dissolved in 7 ml. of 99% formic acid, the solution warmed to 50°, and 2.2 ml. (0.0225 mole) of acetic anhydride added dropwise with stirring at 50–55° over a 45-minute interval, subsequent dilution into ice–water mixture gave 0.67 g., m.p. 130–155°. Crystallization from 70% nitric acid and then from ethanol yielded 0.14 g., (48% crude yield, 10% pure), m.p. 162–164°. A mixed melting point with III obtained by nitrolysis was not depressed.

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[2] J. L. Boivin and G. F Wright, *Can. J. Res.*, **B28**, 213 (1950).

[3] All melting points are corrected against reliable standards.