The main products are isoprene and ethyl *p*-hydroxybenzoate, which are produced by cleavage. 2,2,3-Trimethyl-5-carbethoxy-coumaran was also obtained, and its occurrence among the pyrolysis products is attributed to cyclization of an abnormal rearrangement product. The abnormal rearrangement manifested in this case is consistent in character with those previously recorded.

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NOTES

The Lead Chloride–Ethylene Glycol–Water System at 25°

BY A. B. GARRETT, M. V. NOBLE, GEORGE KIEFER AND RUSKIN BRYANT

In a thermodynamic study of lead chloride in mixed solvents[1,2,3] some interesting variations were observed in the solubility of lead chloride in solutions of ethylene glycol–water. These are shown in Fig. 1; the data are tabulated in Table I. The solubility of lead chloride in ethylene glycol was found to be 0.0309 (±0.0002) mole per 1000 g. of solvent, as averaged from nine determinations using lead chloride prepared and washed with conductivity water as well as lead chloride prepared and washed with pure ethylene glycol.

TABLE I

SOLUBILITY OF $PbCl_2$ IN ETHYLENE GLYCOL–WATER SOLUTIONS

Glycol (by weight), %	N_2, mole fraction of glycol (water and glycol) $N_2 = n_2/(n_1 + n_2)$	Moles of $PbCl_2$ per 1000 g. of solvent
0.00	0.00	0.03905
5.44	.01642	.0386
6.54	.01992	.0386
7.62	.0234	.0384
8.72	.0300	.0383
9.80	.0306	.0383
10.00	.0313	.0381
10.00	.03125	.0380
10.88	.0342	.0384
11.97	.0380	.0383
13.07	.0418	.0384
20.00	.0677	.0383
21.75	.0747	.0383
30.00	.1106	.0388
40.00	.1621	.0398
42.57	.1772	.0340
50.00	.2251	.0411
60.0	.3034	.0426
60.0	.3034	.0419
62.4	.3234	.0430
70.0	.4039	.0441
80.0	.537	.0457
81.6	.563	.0465
85.4	.630	.0477
87.3	.666	.0479
89.4	.710	.0459
91.7	.762	.0427
93.3	.802	.0406
94.8	.841	.0385
96.5	.889	.0360
100	1.000	Av. .0309

TABLE II

SOLUBILITY OF LEAD CHLORIDE IN 1,2-PROPYLENE GLYCOL-WATER SOLUTION AT 25°

Glycol (by weight), %	N_2, mole fraction of glycol (water and glycol) $N_2 = n_2/(n_1 + n_2)$	Moles of $PbCl_2$ per 1000 g. of solvent
0.000	0.000	0.03905
20.5	.0577	.0292
40.8	.140	.0218
60.8	.270	.0173
80.5	.495	.0124
100.0	1.000	.0091

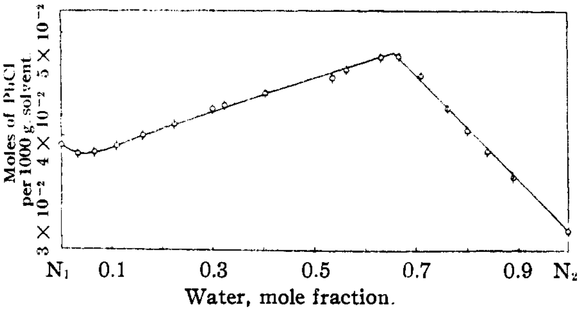

Fig. 1.

The general method of measuring the solubility was similar to that used in other work.[4,5]

The ethylene glycol used was from three different sources, namely, (a) Eastman Kodak best grade, (b) C. P. grade redistilled at low pressure and (c) C. P. grade dried over calcium oxide and redistilled at low pressure.

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(1) M. V. Noble, Ph. D. Thesis, The Ohio State University, 1941.

(2) George Kiefer, M. S. Thesis, The Ohio State University, 1941.

(3) Ruskin Bryant, M. S. Thesis, The Ohio State University, 1941.

(4) Hogge and Garrett, THIS JOURNAL, **63**, 1089 (1941).

(5) Garrett, Vellenga and Fontana, *ibid.*, **61**, 367 (1939).

Since it seemed obvious that a solvate of lead chloride with ethylene glycol was being formed at high concentration of ethylene glycol, the samples in the range of high glycol concentration were prepared from lead chloride which was precipitated and washed with conductivity water as well as from lead chloride precipitated and washed in pure ethylene glycol.

The break in the solubility curve is no doubt due to the fact that the solid phase changed to a solvate of lead chloride. A crystalline product was obtained by washing the solvate with ether or acetone and drying it over sulfuric acid or anhydrous calcium sulfate. The lead chloride content of nine samples so prepared ranged from 68.5 or 71.8% and gave an average of 70.0%; this corresponds to the compound di-ethylene glycol lead (II) chloride, $PbCl_2 \cdot 2C_2H_4(OH)_2$ (theoretical per cent. of lead chloride is 69.1%). Evidence concerning the presence or absence of other solvates was inconclusive.

Information about the stability of the solvated product was obtained from cell data.[3,6] The measured potential for the cell

$$Pb(Hg),\ PbCl_2(\text{solvent}),\ AgCl,\ Ag$$

at saturation of lead chloride is 0.4842 volt in water[7] as well as in 20, 40, 60 and 80% (by weight) ethylene glycol–water solutions[3] but is 0.4963 volt in 100% ethylene glycol.[3] This corresponds to a free energy difference of only 520 calories and indicates a low stability of the solvate.

At the present time there seems to be no direct clue to the interpretation of the minimum.

1,2-Propylene glycol does not give these effects at 25° (see Table II).

Work is now in progress on the measurement of the electrical conductivity of lead chloride–ethylene glycol–water solutions.

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(6) Results to be published soon.

(7) Carmody, THIS JOURNAL, **51**, 2905 (1929).

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p-Toluidine Salts of Monoaryl Sulfates

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Since 1876, when Baumann[1] isolated potassium phenyl sulfate from urine, it has become evident that compounds of this type are formed in the animal body from many phenolic substances. Many monoaryl sulfates are unstable in the free acid form and they are usually prepared in the form of their alkali-metal salts. Such salts are unsatisfactory for identification purposes. They do not melt sharply, and only with difficulty can they be freed from inorganic impurities. In the hope of facilitating biochemical investigations involving the isolation and identification of monoaryl sulfates, a study of the preparation and properties of the organic base salts of monoaryl sulfates was undertaken.

A method for the preparation of the *p*-toluidine salts of *o*- and *p*-cresyl sulfates has been described.[2] In the present work a more convenient method of preparing *p*-toluidine salts of monoaryl sulfates has been developed, since preliminary experiments had shown that among the bases tested, *p*-toluidine consistently yielded crystalline derivatives which melted sharply.

Materials.—The potassium aryl sulfates were prepared by the method of Burkhardt and Wood.[3] Chlorosulfonic acid (1.4 moles) was added to a chilled solution of dimethylaniline (3.7 moles) in 500 ml. of carbon disulfide. The phenolic compound (1 mole) was then added and the mixture was stirred for one hour and allowed to stand overnight. The carbon disulfide was distilled off and the oil which remained was poured into aqueous potassium hydroxide (4 moles). The dimethylaniline was separated and the crude potassium aryl sulfate obtained by evaporation of the aqueous solution was crystallized from 80% ethanol and then from water. With the exception of potassium *p*-nitrophenyl sulfate, which crystallized as bright yellow prisms, the potassium salts were obtained in the form of colorless plates.

The *p*-toluidine hydrochloride was prepared by adding an excess of concentrated hydrochloric acid to a solution of *p*-toluidine in ethanol. The mixture was stirred thoroughly and chilled. The crystalline product was filtered off, and recrystallized from ethanol.

Procedure.—Solutions of equimolar portions of the potassium aryl sulfate and of *p*-toluidine hydrochloride in the minimum amounts of water at 60° were mixed quickly and chilled. The *p*-toluidine salt of the aryl sulfate separated almost immediately and was removed by filtration. The crude product was washed on the filter with a small amount of ice-water and crystallized from water, using charcoal, if necessary, to remove any colored impurities. The material was then crystallized once more from water and finally from aqueous ethanol, yielding in every case colorless needles.

The melting points and analyses of the *p*-toluidine salts of a series of monoaryl sulfates are given in the table.

Sulfate was determined gravimetrically as barium sulfate after acid hydrolysis of the *p*-toluidine salt. The equivalent weight was determined by titration with standard sodium hydroxide solution.

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(1) E. Baumann, *Pflügers Arch.*, **13**, 285 (1876).

(2) G. N. Burkhardt and A. Lapworth, *J. Chem. Soc.*, 684 (1926).

(3) G. N. Burkhardt and H. Wood, *ibid.*, 141 (1929).