p-BROMOANILINE SALTS OF MONOARYL SULFATES

Monoaryl sulfate	Crystalline form	Solubility[a] at 8°	Solubility[a] at 25°	Formula	Analytical data[b] Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Sulfate, % Calcd.	Sulfate, % Found	Equiv. wt. Calcd.	Equiv. wt. Found
Phenyl	Plates	1.04	2.21	$C_{12}H_{12}NO_4SBr$	41.63	41.78	3.50	3.67	4.05	4.15	27.8	27.4	346	343
o-Methoxyphenyl	Needles	1.92	3.26	$C_{13}H_{14}NO_5SBr$	41.50	41.57	3.75	3.79	3.72	3.95	25.5	24.5	376	376
p-Bromophenyl	Plates	0.37	0.77	$C_{12}H_{11}NO_4SBr_2$	33.90	34.01	2.61	2.53	3.30	3.49	22.6	22.0	425	421
p-Cresyl	Plates	.24	.62	$C_{13}H_{14}NO_4SBr$	43.35	43.60	3.92	4.05	3.89	3.79	26.7	26.6	360	360
α-Naphthyl	Plates	.60	.89	$C_{16}H_{14}NO_4SBr$	48.49	48.45	3.56	3.73	3.53	3.82	24.2	24.0	396	394

[a] Grams of derivative per 100 ml. of solution. [b] The micro-analyses were performed by Mr. Michael Edson.

with phenols.[2] Experiments with *p*-bromoaniline suggested that this base might serve as a useful precipitant for monoaryl sulfates. For example, at 8° the solubility of potassium phenyl sulfate is 12.85 g. per 100 ml. of solution, whereas the solubility of *p*-bromoaniline phenyl sulfate is 1.04 g. per 100 ml. of solution. Several potassium monoaryl sulfates were prepared by the method of Burkhardt and Wood,[3] and were converted to their *p*-bromoaniline salts (see table) by the above method.[1] Although these derivatives are fairly insoluble, they are somewhat unstable, and their melting points are ill-defined.

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[2] D. H. Laughland and Leslie Young, *Trans. Roy. Soc., Can.*, Series III, **36**, 166 (1942).

[3] G. N. Burkhardt and H. Wood, *J. Chem. Soc.*, 141 (1929).

DEPARTMENT OF BIOCHEMISTRY
UNIVERSITY OF TORONTO
TORONTO, ONTARIO, CANADA

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The Action of Ammonia on Allophanic Azide

BY WERNER L. LIPSCHITZ

In contrast to Thiele and Uhlfelder[1] we were not able to prepare tetruret by the action of ammonia on allophanic azide, but, under the varied reaction conditions herein described, always obtained the normal amide, biuret, and in no experiment was a significantly different product formed which could be claimed to be tetruret.

(1) **Concentrated Ammonia.**—A suspension of allophanic azide (prepared from 41 g. of aminobiuret hydrochloride and 18.3 g. of sodium nitrite. *Anal.* Calcd. for $C_2H_3N_5O_2$: C, 18.6; H, 2.32. Found: C, 18.55; H, 2.34) in 30 cc. of water was treated with 250 cc. of 28% aqueous ammonia and, after the initial spontaneous reaction subsided, the mixture was maintained at 55–60° until a clear solution was obtained. The product (21 g.) separated from the concentrated and cooled solution was recrystallized from 100 cc. of boiling water and yielded 18 g. of pure biuret, which melted at 192° and did not depress the melting point of an authentic specimen. *Anal.* Calcd. for $C_2H_5N_3O_2$: C, 23.3; H, 4.86; N, 40.78. Found: C, 23.43; H, 4.45; N, 39.9.

(2) **Dilute Ammonia.**—The azide (3 g.) was added, during an hour and a quarter, to 31 cc. of 2% ammonia at 0° and stirring was continued for a half hour at room temperature. More 2% ammonia (15 cc.) was added, the mixture was shaken overnight at room temperature and, when heated to 70°, gave a clear solution which, when cooled, deposited 1.48 g. of crystalline product and, after concentration, yielded 0.87 g. more of the same material. The combined solids were recrystallized three times from ethanol and yielded pure biuret. *Anal.* Calcd. for $C_2H_5N_3O_2$: C, 23.3; H, 4.86. Found: C, 23.16; H, 4.76.

(3) **Liquid Ammonia.**—The azide (3 g. *Anal.* Calcd. for $C_2H_3N_5O_2$: C, 18.6; H, 2.32; N, 54.26. Found: C, 18.1; H, 2.84; N, 53.87) was dissolved in 125 cc. of liquid ammonia and, after one hour, the solvent was evaporated. The residue (3.84 g.), twice recrystallized from ethanol, gave 1.02 g. of pure biuret. *Anal.* Calcd. for $C_2H_5N_3O_2$: C, 23.3; H, 4.86; N, 40.78. Found: C, 22.78, 23.33; H, 4.53, 4.16; N, 40.0, 41.2.

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[1] J. Thiele and E. Uhlfelder, *Ann.*, **303**, 93 (1898).

LEDERLE LABORATORIES
PEARL RIVER, N. Y.

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On the Cryoscopic Constant of Camphor

BY JOHN E. RICCI

If the heat of fusion of camphor is 10.74 ± 0.40 cal. per g., then the limiting molecular freezing point depression for solutions in equilibrium with pure solid camphor must be $K_f = RT^2/1000\ l_f = 37.7 \pm 1.4$ deg. per mole as calculated by Frandsen,[1] who also measured the heat of fusion. Meldrum, Saxer and Jones[2] have reported, in some careful and well-planned experiments, that a cryoscopic constant of 39.7 (in sufficiently close agreement with the calculated value) is actually obtained in solutions of four different solutes in camphor; but that the molecular depression apparently increases, in every case, as the concentration of the solute decreases (below ~ 0.2 *m*) and approaches zero.

This would constitute a serious anomaly, if the facts are real. Deviations from the calculated depression are caused either by (A) deviation of the liquid solution from ideality in the positive or in the negative sense, or by (B) precipitation of a solid solution of camphor rather than of pure camphor.

(A) The deviations from ideality, in either direction, must vanish to zero with increasing dilution. Hence the observations cannot be the result either of repulsion, since the molecular depression should in that case start as the theoretical and then fall short of it, or of attraction, which should again give the theoretical depression in limiting dilution, with subsequent increase above the calculated value.

Solid solution would lead always to values lower than the theoretical (even to negative values) but never to values higher than the theoretical cryoscopic constant. For, in the ideal and limiting case, the apparent molecular depression then becomes

$$K_f' = K_f(1 - k)$$

where *k* is the distribution constant of the solute

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[1] B. S. Frandsen, *J. Res.*, **7**, 477 (1931).

[2] Meldrum, Saxer and Jones, THIS JOURNAL, **65**, 2023 (1943).