

p-BROMOANILINE SALTS OF MONOARYL SULFATES

Monoaryl sulfate	Crystalline form	Solubility ^a		Formula	Analytical data ^b									
		8°	25°		Carbon, %		Hydrogen, %		Nitrogen, %		Sulfate, %		Equiv. wt.	
					Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Phenyl	Plates	1.04	2.21	C ₁₂ H ₁₂ NO ₄ SBr	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 ₄ SBr	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 ₄ SBr 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 ₄ SBr	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 ₄ SBr	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.

(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

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The Action of Ammonia on Allophanic Azide

BY WERNER L. LIPSCHITZ

In contrast to Thiele and Uhlfelder¹ 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 C₂H₃N₃O₂: 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 C₂H₃N₃O₂: 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 C₂H₃N₃O₂: C, 23.3; H, 4.86. Found: C, 23.16; H, 4.76.

(3) **Liquid Ammonia.**—The azide (3 g. *Anal.* Calcd. for C₂H₃N₃O₂: 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 C₂H₃N₃O₂: 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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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 $K_f = RT^2/1000 l_f = 37.7 ± 1.4$ deg. per mole as calculated by Frandsen,¹ who also measured the heat of fusion. Meldrum, Saxer and Jones² 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

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

(2) Meldrum, Saxer and Jones, *This Journal*, **65**, 2023 (1943).

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

between solid and liquid phases.³ Since k cannot be negative, the limiting value of K_f' must be smaller than K_f . The unexpected behavior of camphor therefore cannot be caused by solid solution.

Since the theory cannot be satisfied, it seems that the experimental data must be at fault somewhere. The experimental values involved in the calculation of the ideal constant, K_f , are the melting point and the heat of fusion. The melting point, though somewhat uncertain, can hardly be so incorrect, especially as an absolute temperature, as to account for an almost 50% change in K_f . The fusion heat seems to have been measured with great care, and it similarly does not seem possible for it to be wrong by such a factor; Frandsen reports it as 10.74 ± 0.40 cal., and his data seem to justify this estimate.

There are, however, two points in Frandsen's report which indicate that the camphor under observation near its melting point was not absolutely pure; it appears that it may have been slightly impure at the outset or that it underwent some slight decomposition at temperatures at or near its melting point. Thus: (1) the cooling curve for the determination of the melting point shows a degree of rounding-off hardly consistent with purity; and (2) the agreement in the duplicate determinations of heat content for liquid camphor was not very close. Incidentally, the above suggestions about the impurity or the instability of the camphor used are made by Frandsen himself.

Now, while a slight degree of impurity or instability would hardly affect the measured melting point and heat of fusion to the extent here in question, it is possible to account, on such a basis, for the apparently anomalous molecular freezing point depressions reported by Meldrum. Even with initially pure camphor, it may be that the melting, mixing and grinding required in the preparation of the binary mixtures for melting point determinations, caused in each case a small and approximately constant extent of decomposition of the camphor. If this decomposition amounts to m' moles of foreign species per 1000 g. of camphor, then the true molecular depression would be $K_f = \Delta T_f / (m + m')$. If m' is very small, its neglect would have a negligible effect on K_f measured in high concentration, but would cause the apparent K_f' to rise higher and higher as the concentration decreases.

It is sufficient to assume m' equal to only 0.005, in Meldrum's experiments, to derive a molecular depression approximately constant throughout, within the probable experimental error (as shown in Fig. 1), and with an average value of 39.2° per mole, which is sufficiently close to the calculated limiting or ideal value. The constancy is even better than it seems, when it is remembered that

(3) Thus in Glasstone, "Text-Book of Physical Chemistry," D. Van Nostrand Co., New York, 1940, p. 641.

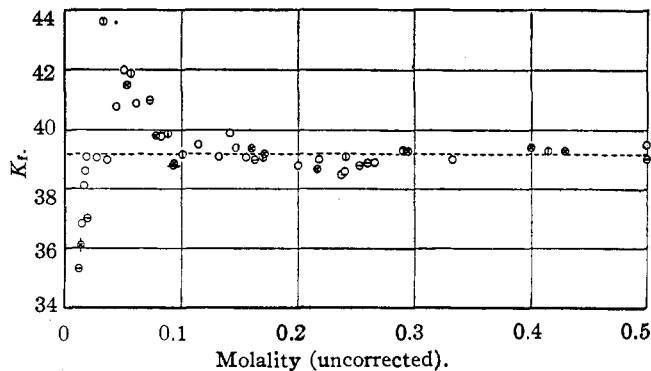


Fig. 1—Solute key: O, naphthalene; ⊕, *p*-bromodiphenyl; ⊖, phenylacetic acid; ⊗, ethylacetanilide.

the points at lowest concentration are likely to be experimentally the most uncertain (as pointed out by Meldrum himself). Since the temperatures in Meldrum's experiments seem to have been measured to a precision of only 0.05° , ΔT is probably dependable only within 0.05 to 0.10° . It follows then that at small values of m , even relatively large variations in the value of the ratio $\Delta T/m$ must be considered insignificant; for example, ± 2 or 3 at $m = 0.05$, and as high as ± 8 at m (uncorrected) = 0.012 . It is significant that the values of K_f now calculated from all the measurements with $\Delta T > 3^\circ$, lie, with one exception, within one unit of the mean, 39.2 , the average deviation being only 0.3 unit.

It should be pointed out that, depending on the molecular weight of the impurity, this value of m' would represent about 0.02 to 0.06% (for molecular weights of 50 to 150) by weight of the camphor used. Such contamination or decomposition would hardly be detectable in the melting point or in the heat of fusion of the substance, but would have the actual effect on the determination of K_f at very low concentrations which was observed by Meldrum.

We have here, in other words, another and very sensitive method for the determination of the purity (or the stability) of a substance. In the absence of solid solution, the molecular depression of the freezing point should approach the value calculated from its melting point and heat of fusion, in limiting dilution.

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NEW COMPOUNDS

N-Substituted Piperonylamides

In a previous communication¹ several new N-substituted piperonylamides have been recorded. Since then, it has

(1) Gertler and Haller, *THIS JOURNAL*, **64**, 1741 (1942).