measured with a variable condenser which was carefully calibrated against a General Radio Precision Condenser (calibrated by the manufacturer at 1000 cycles per second). The cell was of the type described by Doborzynski[4] and the cell constant was obtained by measurements on purified samples of chlorobenzene, ethylene dichloride and benzene whose dielectric constants are known accurately (5.612, 10.36, 2.272 at 25°). Table I summarizes the results.

TABLE I

DIELECTRIC CONSTANTS AND DIPOLE MOMENTS OF ACETYLENIC ETHERS AND PHENYLACETYLENE

Compound, -acetylene	ϵ	M	d^{25}_4	n^{25}_D	MR_D obs.	$(n^2_\infty)^{25°}$	μ
Ethoxy-	8.05	70.1	0.7874	1.3785	20.53	1.853	1.98
Butoxy-	6.62	98.2	0.8078	1.4033	29.66	1.925	2.03
Phenoxy-	4.76	118.1	1.0088	1.5143	35.27	2.216	1.41
Phenyl-	2.98	102.1	0.9243	1.5461	34.99	2.231	0.78

Dipole moments were calculated by the Onsager equation[5,6] and phenylacetylene was included for comparison. The value is in reasonable agreement with 0.77–0.87 found by measurements in benzene solution.[7] The values of n^2_∞ were obtained by extrapolating the molecular refraction to infinite wave length as was done by Böttcher.[8] The observed molecular refractions for the acetyleneic ethers are in close agreement with the calculated values so that no error was introduced by using the latter. Phenylacetylene shows a rather large exaltation, but even here the values for the dipole moment obtained using calculated or observed molecular refractions were not greatly different (0.78 instead of 0.75).

Böttcher[8] has calculated the dipole moments of a number of compounds from the dielectric constants of the pure liquids using Onsager's equation. His results for unassociated substances are in excellent agreement with dipole moments obtained from measurements in solution or in the vapor state except for anisole and diethyl ether, and for these he believed that the equation failed. His calculations appear to be in error for anisole, and the corrected figure lies between values obtained in solution and in the vapor. We have calculated the moments for phenetole and diphenyl ether and found fairly close agreement, so that Onsager's equation appears to give reasonable results with simple aromatic ethers. The values for diethyl ether from the Onsager equation are high as Böttcher reported, but better agreement is found for di-*n*-propyl ether. Table II compares the calculated values for these ethers with values from measurements in solution or in the vapor.

TABLE II[a]

DIPOLE MOMENTS OF ETHERS

Compound	n^2	ϵ	Ref.	μCalcd.	μ_v	μ_s
Diethyl ether	1.798	4.376	9	1.47	1.18	1.2–1.3
Di-*n*-propyl ether	1.873	3.394[b]	10	1.31	1.18	1.16
Anisole	2.214	4.41	11	1.28	1.35	1.2
Phenetole	2.187	4.22	11	1.34	1.4	1.0
Diphenyl ether	2.388	3.686	11	1.17	1.14	1.13–1.17

[a] The values are at 20° unless otherwise stated. The calculated *MR*'s were used, but the exaltations are low with these compounds and μ is lowered but slightly by using *MR* obs. for the calculation. $\mu_{\text{calcd.}}$, μ_v and μ_s designate the dipole moments in Debye units from the calculations and from measurements in the vapor and in solution respectively. All μ_s values are in benzene except di-*n*-propyl ether which is in hexane. The values for the dipole moments in solution were taken from Landolt-Börnstein, "Physikalisch-chemische Tabellen," the second and third supplementary volumes, Julius Springer, 1931–1936. The values from measurements in the vapor phase are from Groves and Sugden, *J. Chem. Soc.*, 1779, 1782 (1937), except for diphenyl ether where their value of 1.35 appears less reliable than that found by Coop and Sutton, *J. Chem. Soc.*, 1869 (1938). [b] At 25.7°.

Despite the simplifying assumptions of symmetrical dipole configurations and non-association made in the derivation of the Onsager equation, the agreement between calculated and measured values is satisfactory in general and, as Wilson[6] has commented, the equation appears to be empirically useful. Certainly the values for acetylenic ethers are not in gross error. No interpretation of the moments of ethers can be made without knowledge of the —C—O— bond angles and these may be quite different in unsaturated ethers as compared with saturated. Nevertheless it is interesting that the dipole moment of phenoxyacetylene is only slightly larger than those of other aromatic ethers while the alkoxyacetylenes give figures which are significantly higher. One interpretation of this difference is that in the latter there is a considerable contribution from resonance forms of the type $R-\overset{+}{O}=C=\overset{-}{C}H$, an idea which is in accord with their greater rate of hydration.[12] An extended study of the dipole moments of vinyl and ethynyl ethers will be undertaken when more time and better equipment are available.

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(4) Doborzynski, *Z. Physik*, **66**, 657 (1930).

(5) Onsager, THIS JOURNAL, **58**, 1486 (1936).

(6) Wilson, *Chem. Rev.*, **25**, 377 (1939).

(7) Smyth and Dornte, THIS JOURNAL, **53**, 1296 (1931).

(8) Böttcher, *Physica*, **6**, 59 (1939); see ref. 6.

(9) LeFèvre, *Trans. Faraday Soc.*, **34**, 1127 (1938).

(10) Pyle, *Phys. Rev.*, **38**, 1057 (1931).

(11) Estermann, *Z. physik. Chem.*, **1B**, 134 (1928).

(12) Jacobs and Searles, THIS JOURNAL, **66**, May (1944).

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p-Bromoaniline Salts of Monoaryl Sulfates

BY D. H. LAUGHLAND AND LESLIE YOUNG

It has been shown[1] that *p*-toluidine salts of a number of monoaryl sulfates can be prepared readily by allowing the alkali metal salt of the monoaryl sulfate to interact with the base hydrochloride in an aqueous medium. With bases which yield relatively insoluble salts of monoaryl sulfates, this reaction is of value in the isolation of monoaryl sulfates from the urine of animals dosed

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(1) A. D. Barton and Leslie Young, THIS JOURNAL, **65**, 294 (1943)

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).

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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).

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).