Summary

Omega substituted derivatives of 4-arsonoacetophenone were prepared and identified.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Temperature–Concentration Equilibria in the System Dimethylaniline–Sulfur Dioxide[1]

BY J. RUSSELL BRIGHT[2] AND W. CONARD FERNELIUS[3]

Hill and Fitzgerald[4] studied pressure–composition equilibria in the system: sulfur dioxide-dimethylaniline. Although they obtained no solid phase even by cooling to −10° and seeding with crystals of the sulfur dioxide-*o*-toluidine compound, the marked heat of absorption, the red color, and the positive deviation from Henry's law indicated that compound formation was probable. Gleason and Loonan[5] claim that dimethylaniline and sulfur dioxide give no solid products at 0°. The present study of temperature–concentration equilibria in the system sulfur dioxide–dimethylaniline shows the existence of the compound $C_6H_5(CH_3)_2N:SO_2$.

Experimental

The System $C_6H_5(CH_3)_2N:SO_2$.—The apparatus and technique were essentially that used by Booth and Germann[6] with the following modifications: purification of commercial sulfur dioxide was effected by drying (P_4O_{10}) and careful fractional distillation[7]; dimethylaniline, dried over sodium, was added directly to the melting point tube; pressures were measured by means of an absolute manometer[8,9]; and temperatures were measured by means of a carefully calibrated, two-junction copper–constantan thermocouple. Cooling curves were obtained directly by using a Leeds and Northrup Micromax recording potentiometer, Model S-4000. The probable accuracy of the temperature readings is ±0.4°. The temperature-concentration data are summarized in Table I.

Preparation of $C_6H_5(CH_3)_2N:SO_2$.—When dry sulfur dioxide gas was passed into a petroleum ether solution of dimethylaniline, a red oil settled out. The oil was separated from the solution by means of a separatory funnel: d^{27}_4 1.08, m. p. 12.0°.

TABLE I

TEMPERATURE–COMPOSITION DATA OF THE SYSTEM $C_6H_5(CH_3)_2N–SO_2$

Concentration mole fraction $NC_6H_5(CH_3)_2$	Temp., °C.	Curve (Fig. 1)
0.000	−75.0[a]	A. (Solid SO_2, liq., vapor)
.091	−77.5	
.133	−81.1	AB. (Solid SO_2, satd. soln., vapor)
.161	−85.1	
.178	−90.1	B. (Eutectic: solid SO_2, solid $C_6H_5(CH_3)_2N:SO_2$, satd. soln., vapor)
.198	−72.5	
.221	−59.1	
.248	−44.6	
.251	−41.3	
.274	−30.1	
.288	−24.4	
.314	−17.1	
.334	−10.5	
.349	−8.5	
.376	−1.1	
.424	+7.1	
.435	+10.7	
.474	+12.1	
.504	+12.4	BCD. (Solid $C_6H_5(CH_3)_2N:SO_2$, satd. soln., vapor)
.587	+12.6	
.649	+11.5	
.651	+11.9	
.669	+10.9	
.695	+9.2	
.749	+5.3	
.781	+2.3	
.838	−4.5	
.857	−6.8	D. (Eutectic: solid $C_6H_5(CH_3)_2N:SO_2$, solid $NC_6H_5(CH_3)_2$, satd. soln., vapor)
.885	−3.8	
.918	−0.5	
.934	−0.8	
1.000	+2.0	DE. (Solid $NC_6H_5(CH_3)_2$, satd. soln., vapor)
		E. (Solid $NC_6H_5(CH_3)_2$, liq., vapor)

[a] W. F. Giauque and C. C. Stephenson (THIS JOURNAL, 60, 1389 (1938)) give the value −75.46°.

The System $C_6H_5(CH_3)_2N:SO_2–NC_6H_5(CH_3)_2$.—Both liquids were added to the melting point tube from microburets and temperatures recorded as noted above. The data are summarized in Table II.

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[1] Abstracted from a portion of a thesis presented by J. Russell Bright to the Graduate School of The Ohio State University, June 1940, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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[4] A. E. Hill and T. B. Fitzgerald, THIS JOURNAL, **57**, 250–254 (1935).

[5] G. H. Gleason and A. C. Loonan, U. S. Patent 2,186,453, Jan. 9, 1940.

[6] H. S. Booth and A. F. O. Germann, *J. Phys. Chem.*, **30**, 369 (1926).

[7] For method see H. S. Booth and A. R. Bozarth, *Ind. Eng. Chem.*, **29**, 470 (1937).

[8] A. F. O. Germann, THIS JOURNAL, **36**, 2456 (1914).

[9] A. F. O. Germann, and H. S. Booth, *J. Phys. Chem.*, **21**, 8 (1917).

Discussion

The data of Table I are plotted in Fig. 1. These data show the formation of the compound $C_6H_5(CH_3)_2N : SO_2$, dimethylaniline–sulfur dioxide, with a congruent melting point near 12.6°. Eutectics

Table II

Temperature–Composition Data of the System $C_6H_5(CH_3)_2N : SO_2$[a]–$NC_6H_5(CH_3)_2$[b]

Concentration, mole fraction $NC_6H_5(CH_3)_2$	Temp., °C.	Apparent molecular weight ($\overline{M}$)[e]
1.0000[c]	+2.0	...
0.9535	0.0	263
.9054	−1.4	303
.8695	−2.4	328
.8204	−4.6	354
.7659	−5.8	363
0.0000[d]	+12.0	
.3549	+7.1	
.5193	+3.2	
.6469	−3.2	
.7074	−6.6 (eutectic)	
.7602	−5.9	
.8002	−4.6	

[a] Formula weight, 185. [b] Molal freezing point constant for dimethylaniline, 5.80, Ampola and Rimatori, *Gazz. Chim. Ital.*, **27**, 51 (1897). [c] $NC_6H_5(CH_3)_2$ = solvent. [d] $NC_6H_5(CH_3)_2$ = solute; [e] $\overline{M}$ is apparent molecular weight of $C_6H_5(CH_3)_2N : SO_2$.

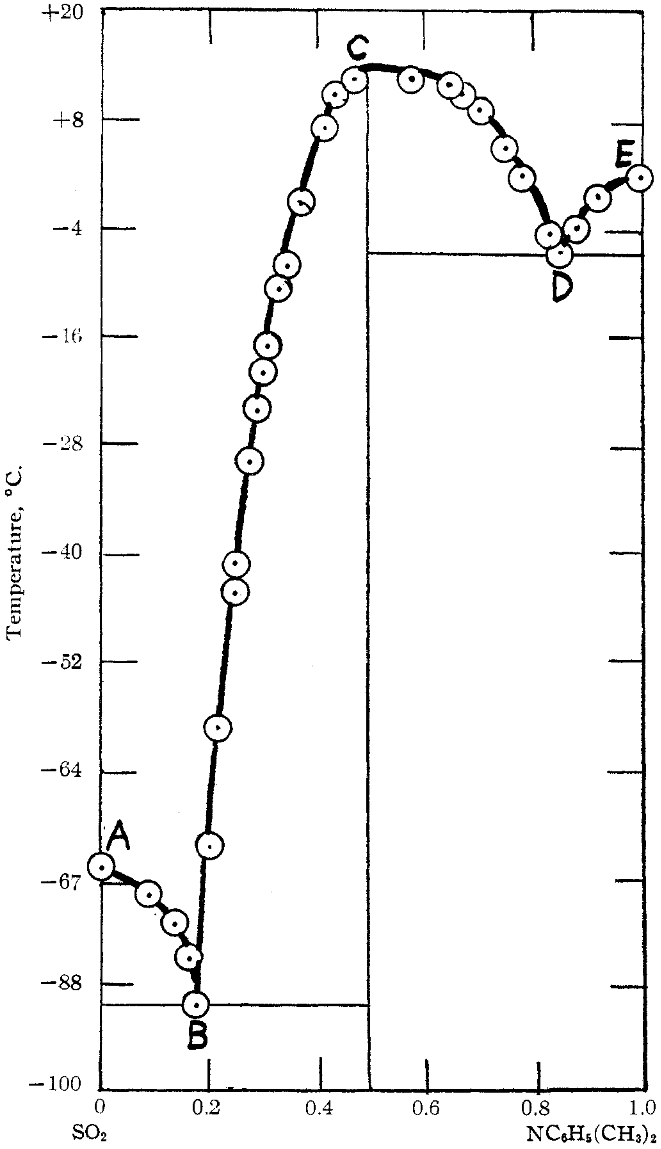

Fig. 1.—Temperature–composition diagram of the system dimethylaniline–sulfur dioxide.

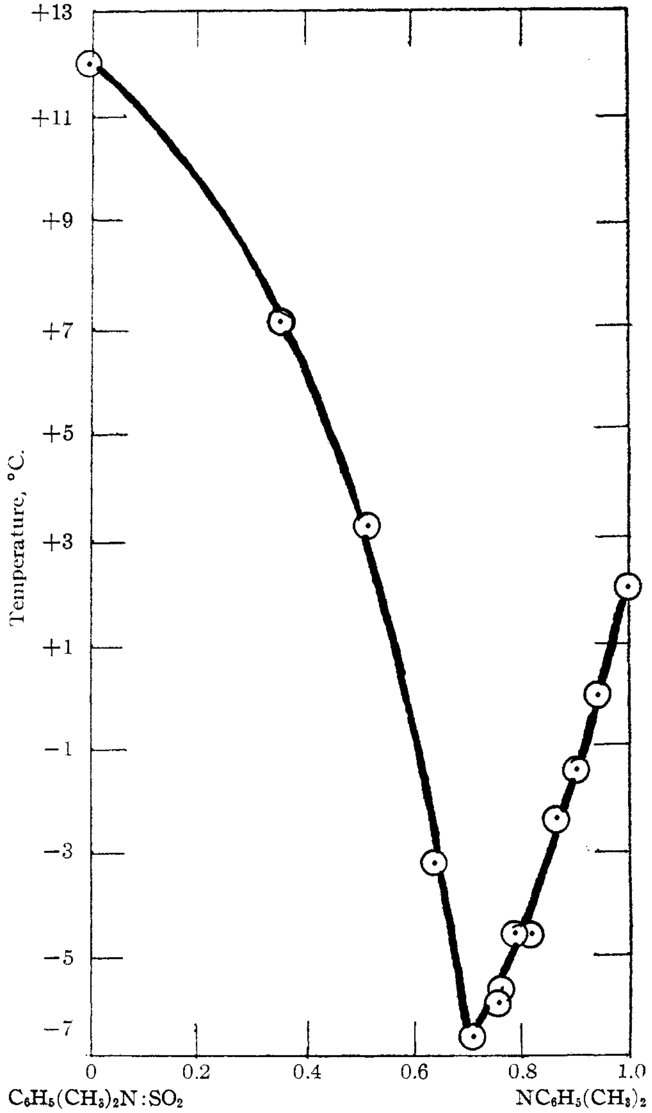

Fig. 2.—Temperature–composition diagram of the system $C_6H_5(CH_3)_2N:SO_2$–$NC_6H_5(CH_3)_2$.

occur at −90.1° (82.2 mole per cent. SO_2) and −6.8° (14.3 mole per cent. SO_2). The broadness of the maximum in the melting point curve indicates considerable dissociation of the compound $C_6H_5(CH_3)_2N:SO_2$ at its melting point. This is confirmed by the fact that the compound prepared in petroleum ether smells strongly of sulfur dioxide. However, the compound is reasonably stable over short periods of time because the values obtained for the system $C_6H_5(CH_3)_2N:SO_2{-}NC_6H_5(CH_3)_2$ check fairly well the corresponding ones obtained for the system $C_6H_5(CH_3)_2N{-}SO_2$.

The data of Table II may be used to calculate the apparent molecular weight of the addition compound in dimethylaniline at several concentrations. The values for the apparent molecular weight indicate some association at the lowest concentration and increasing amount with each increase in concentration. This point is being investigated further.

Summary

1. The temperature–concentration diagram for the system $C_6H_5(CH_3)_2N{-}SO_2$ has been determined.

2. The compound dimethylaniline–sulfur dioxide, $C_6H_5(CH_3)_2N:SO_2$, has been identified and isolated and its congruent melting point determined.

3. Cryoscopic molecular weight measurements for $C_6H_5(CH_3)_2N:SO_2$ dissolved in dimethylaniline indicate association of the solute. The degree of association increases with increasing concentration.

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The Viscosity of Sulfur[1]

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The viscosity of sulfur has long been known to vary in an exceptional manner with temperature. In spite of its unusual irregularity the literature contains but two attempts to measure it. In both papers the published data are far from agreement.

Rotinjanz[1a] by a capillary method measured the viscosity of sulfur throughout its entire liquid range up to its boiling point. He found that the rate of heating varied the values. With heating rates of 0.27 to 1° per minute the sulfur attained a maximum viscosity at 187° of 52,000 relative to water at 17°. Greater heating rates gave lower values for the maximum viscosity and shifted it to higher temperatures. Preheating the sulfur had a profound effect. The higher the sulfur was preheated when the determination was made with falling temperature, the lower was the maximum viscosity and the higher the temperature at which it occurred. Admixture of iodine and ammonia with the sulfur greatly reduced the viscosity values.

Twelve years later Farr and Macleod[2] using a system of rotating cylinders for measuring the viscosity, published data which differed greatly from those given by Rotinjanz. These authors went to much greater lengths to purify their sulfur and experienced great difficulty in obtaining concordant results. Their maximum value for purified gas-free sulfur occurred at about 200° and was 215 poises. Their maximum for purified sulfur (not gas free) after prolonged exposure to air may have a value as high as 800 poises at about 190°.

Rotinjanz assumed that the temperature of his air-bath was the same as that of the sulfur in the capillary tube and that sulfur crystallized from carbon disulfide was pure. Kellas[3] states that the sulfur used in this work was of doubtful purity. Farr and Macleod state that their carefully purified sulfur had a greenish color. This fact indicates that their sulfur was not completely purified in spite of their efforts to make it so.

The wide discrepancy in the published results and the well-founded suspicion that the sulfur used in both cases was impure seemed to warrant further work on the purification of sulfur and its viscosity.

Experimental Methods

The method employed for measuring viscosity above 160° was to impress a definite vacuum on a capillary tube

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(1) Original manuscript received March 7, 1942.

(1a) L. Rotinjanz, *Z. physik. Chem.*, **62**, 609 (1908).

(2) C. Farr and D. B. Macleod, *Proc. Roy. Soc.* (London), (a) **97**, 80 (1920). In a later paper *ibid.*, **118A**, 534 (1928) these authors admitted that their original sulfur preparation was impure. They stated that the impurity was mercury vapor from the pump. In our work several thermometers were accidentally broken in the sulfur. The presence of mercury did not bring about low viscosity values.

(3) A. M. Kellas, *J. Chem. Soc.*, **113**, 903 (1918).