

N- β -Bromoethylaniline Hydrobromide

BY WILLIAM M. PEARLMAN

Although a product designated^{1,2} as N- β -bromoethylaniline hydrobromide has been reported to be formed by converting N-phenylethanamine into its hydrobromide at 100° with gaseous hydrobromic acid and then heating to 150–160°, no identification was made and no yields were given. In addition, the indicated procedures are cumbersome. It was found that the desired product could be obtained in 85% yield from β -hydroxyethylaniline and hydrobromic acid by a slight modification of the procedure of Cortese.³

Experimental

β -Hydroxyethylaniline (100 g.) was precooled to 0° and 310 ml. of precooled (0°) 48% hydrobromic acid was added dropwise with stirring and cooling. When all of the hydrobromic acid had been added the mixture was distilled with an efficient fractionating column until a constant boiling distillate was reached. The residue was cooled slightly, placed in a large, open dish in a vacuum desiccator and evacuated with a water jet overnight. The resulting slurry was filtered and the solid recrystallized from absolute ethanol. The yield of nearly colorless needles was 180 g. (85.5%), m. p. 136–139°. A sample recrystallized from benzene was colorless, m. p. 137–138°.

Anal. Calcd. for C₈H₁₁Br₂N: C, 34.19; H, 3.95; N, 4.99. Found: C, 33.87; H, 4.16; N, 4.97.

(1) French Patent 800,369; abstracted in C. A., 30, 8241^a (1936).

(2) Julius v. Braun, *Ber.*, 70, 979 (1937).

(3) "Organic Syntheses," Coll. Vol. II, 91, ed. by Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943.

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Oxidation-Reduction Potentials and Ionization Constants of the Reversible Series: Hexahydroxybenzene - Tetrahydroxyquinone - Rhodizonic Acid

BY PAUL W. PREISLER, LOUIS BERGER AND EDGAR S. HILL

Professor G. Schwarzenbach of the Universität at Zürich has recently called our attention to omission of reference in our publication⁷ to the prior work and publication by Schwarzenbach and Suter⁶ with the same substances. The oxidation-reduction potentials and ionization constants of this series of related compounds has been reported on several occasions.¹⁻⁷ It is regretted that there was no discussion of the work of Schwarzenbach and Suter^{4,6} in our publications,^{5,7} which oversight

(1) P. W. Preisler, E. S. Hill, E. Ronzoni and L. Young, *J. Biol. Chem.*, 123, XCV (1938).

(2) G. E. Carpeni, Thesis, Paris, 1938.

(3) P. W. Preisler, *Cold Spring Harbor Symposia on Quantitative Biology*, 7, 94 (1939).

(4) H. Suter, Thesis, Zürich, 1940.

(5) P. W. Preisler and L. Berger, paper presented at the meeting of the American Chemical Society, April, 1941; *THIS JOURNAL*, 64, 67 (1942).

(6) G. Schwarzenbach and H. Suter, *Helv. Chim. Acta*, 24, 617 (1941).

(6a) *Chemical Abstracts*, 35, 7806 (1941).

(7) P. W. Preisler, L. Berger and E. S. Hill, *THIS JOURNAL*, 69, 326 (1947).

resulted from their being no abstract of the thesis of Suter⁴ in *Chemical Abstracts* and no indication in the abstract^{6a} of their joint publication⁶ that they had worked with any compound of the rhodizonic acid series oxidation-reduction systems.

The two reports^{6,7} differ mainly in the estimation of the ionization constants of rhodizonic acid. Our constants of $pK_1 = 4.1$ and $pK_2 = 4.5$ should be rejected in favor of those of Schwarzenbach and Suter, who found $pK_1 = 3.15$ and $pK_2 = 4.9$, since our values were estimated from the E'_0 - pH curve of the rhodizonic acid-tetrahydroxyquinone system in a range where the curve is quite flat, while their values were determined by colorimetric and photometric methods.

Accepting their constants, 3.15 and 4.9, curves of $E'_0 - pH$ may be drawn which fit our experimentally determined points reasonably well. These changes do not affect the tetrahydroxyquinone-hexahydroxybenzene curve; the estimated ionization constant of tetrahydroxyquinone being unchanged at $pK_1 = 4.8$. Our E'_0 values at $pH = 0$ become altered: for rhodizonic acid-tetrahydroxyquinone to $E'_0 = +0.426$ volt (increase of +0.016) and for tetrahydroxyquinone-hexahydroxybenzene to $E'_0 = +0.388$ volt (increase of +0.008).

These extrapolated values for $pH = 0$ and our measured potentials agree as well as may be expected for systems of this type with the potentials of Schwarzenbach and Suter. However, we experienced no difficulties in obtaining rapidly adjusting stable potentials in the entire pH range studied from 3.5 to 9.9. Therefore, where the slopes of our E'_0 - pH curves are sufficiently well established, as for the tetrahydroxyquinone-hexahydroxybenzene system, we consider the ionization constants reported,⁷ for tetrahydroxyquinone $pK_2 = 6.8$ and for hexahydroxybenzene $pK_1 = 9.0$, to be reliably estimated.

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Freezing Point Depression of Sulfuric Acid by Siloxanes

BY FRASER P. PRICE

Since sulfuric acid is used as an equilibrating agent in the preparation of silicones,¹ it is of interest to investigate the kinds of particles produced when siloxanes are dissolved in this acid. It was hoped that such an investigation would shed some light on the mechanism of siloxane rearrangement.

The molal freezing point depressions and the van't Hoff " i " factors in approximately 100% sulfuric acid were determined by the method of Hammett and Deyrup.² The only departure from their method was that the weight of solvent

(1) Patnode and Wilcock, *ibid.*, 68, 358 (1946).

(2) Hammett and Deyrup, *ibid.*, 55, 1900 (1933).

was determined by weighing the freezing point tube containing the solute and acid at the end of the run and subtracting the weight of solute and tube.

The nomenclature used in this paper is a modification of that developed in this Laboratory for the simplified representation of polymethylpolysiloxane structures³: M = (CH₃)₃Si, D = (CH₃)₂Si, T = CH₃Si, Q = Si. The results of the study are given in Table I.

TABLE I

VAN'T HOFF "i" FACTORS FOR SEVERAL SILOXANES IN 100% SULFURIC ACID

Solute	[Solute]	[H ₂ O]	θ(°C.)	i	i (av.)
MOM	0.0368	0.066	0.947	4.29	
	.0802	.066	2.053	4.27	4.28
(DO) ₄	.148 × 10 ⁻³	.134	0.277	11.88 ^a	
	.487 × 10 ⁻³	.134	0.965	12.60	
(MO) ₃ T	1.01 × 10 ⁻³	.134	1.951	12.58	12.59
	8.59 × 10 ⁻³	.092	0.425	8.20	
	21.0 × 10 ⁻³	.092	1.035	8.25	
(MO) ₄ Q	39.0 × 10 ⁻³	.092	1.874	8.23	8.23
	7.84 × 10 ⁻³	.092	0.449	9.48	
	15.66 × 10 ⁻³	.092	0.889	9.46	
	26.6 × 10 ⁻³	.092	1.507	9.57	9.50

^a This figure rejected as it is too far out of line.

Previous work with silyl sulfates⁴ shows that only the normal sulfate is isolated when hexamethyldisiloxane is treated with sulfuric acid. However, the freezing point data for this siloxane indicate that the major reaction is

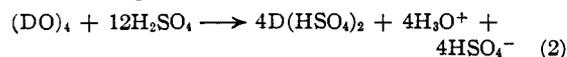


which gives an "i" of 4. The slightly higher value observed is presumably due to the partial ionization of the MHSO₄. If the formation of the normal sulfate were the major reaction, then an "i" of only 3 would be observed or it would be necessary to assume that the reaction



went to completion in order to explain the observed value. Furthermore, it seems highly improbable that in this acid medium anything other than the acid sulfate could exist in appreciable quantity. It is more likely that the previous workers' results are due to the normal sulfate having a much higher solubility than the bisulfate in the extracting solvents. Hence, any small amount of sulfate that was formed would be removed and the equilibrium would shift to make up the deficiency.

The result obtained with the cyclic tetramer (DO)₄ is explained by the reaction



The deviation from the integral value of 12 is probably due to ionization of the D(HSO₄)₂.

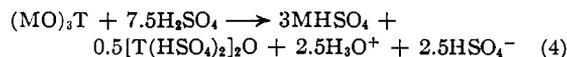
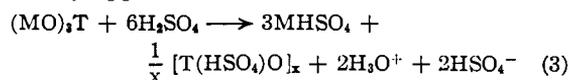
(3) Sauer, THIS JOURNAL, 68, 954 (1946).

(4) Sommer, Pietrusza, Kerr and Whitmore, *ibid.*, 68, 156 (1946).

The deviations of the "i" factors from integers for both MOM and (DO)₄ are 0.28 and 0.59, respectively. However, when these deviations are made comparable by dividing by the number of silicon atoms, practically identical values are obtained. It then appears that the ionizations of MHSO₄ and D(HSO₄)₂ both proceed to about the same extent and that the replacement of methyl by bisulfate has little effect.

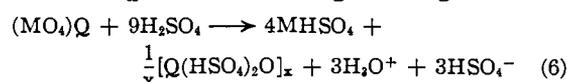
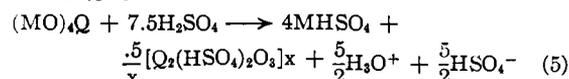
The two remaining siloxanes contain units capable of producing a three dimensional network. Furthermore, these networks, if they form, will be quite insoluble in the acid. If these siloxanes reacted in a manner analogous to the two discussed above, the "i" factors should be 10 and 13 for (MO)₃T and (MO)₄Q, respectively. Since the observed values are much lower, it is obvious that some type of polymerization must have occurred to remove T or Q units.

For the (MO)₃T case the equations which most closely approximate the observed "i" value are



Assuming that x in Equation 3 is large, these equations give values of "i" of 7 and 8.5 for Equations 3 and 4, respectively. It is, therefore, probable that both these reactions take place.

Consideration of the possible reactions for the (MO)₄Q system leads to



with "i" factors of 9 and 10 for Equations 5 and 6, respectively. Whereas in the case of the (MO)₃T the reaction lay between the cyclic polymer, [T(HSO₄)O]_x and the dimer, [T(HSO₄)₂O]₂, here it lies between the three-dimensional gel and the cyclic polymer. In no case, however, does the number of HSO₄ radicals attached to silicon exceed two.

When freshly prepared polysiloxane hydrolysates are equilibrated with sulfuric acid, catalytic amounts, ca. 5%, of 95% acid are used. Hence, the conditions observed in the freezing point experiments are not exactly those prevailing during equilibration. In spite of these differences, in view of the non-integral values of "i" for MOM and (DO)₄ a probable active intermediate in the rearrangement is a positive siliconium ion which attacks the oxygen of the unreacted siloxane, forming a new Si-O bond and ejecting a new siliconium ion which repeats the process.

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