to room temperature and opened. The presence of carbon monoxide was detected by suspending a palladium chloride-phosphomolybdic acid solution[3] in a medicine dropper over the reaction mixture. In the presence of carbon monoxide the yellow solution turned blue. The crystals of quaternary salts were collected on a filter and washed with boiling anhydrous isopropyl alcohol; tetramethylammonium bromide (III) was insoluble in this solvent. It did not melt at 350°. Concentration of the isopropyl alcohol washings yielded white needles of dimethylammonium bromide (IV), m.p. 131–131.5°.

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Ionization Constant of Hexanethiol from Solubility Measurements

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The ionization constant of hexanethiol has been determined from measurements of its solubility in aqueous solutions of varying *p*H. This method of determining the ionization constant is not in common use, even though it follows straightforwardly from well known principles. Potentiometric titration is the means most often used for determining ionization constants, but this method can be applied to most organic compounds only in mixed-solvent systems because of solubility limitations. The solubility method, on the contrary, can best be applied to sparingly soluble compounds and gives the value of the ionization constant in water.

When this investigation was begun, the only values for the ionization constants of alkanethiols in water had been reported by Yabroff.[1] This investigator examined the mercaptans from ethyl to butyl by potentiometric titration (*pK* 10.64 and 10.78, respectively) and the mercaptans from ethyl to heptyl (excepting hexyl) by partitioning between isooctane and $0.5M$ sodium hydroxide (*pK* 10.60 to 10.75; hexyl was not measured, but interpolation of the other data gives 10.7). Recently, Danehy[2] has reported the value 10.50 for ethanethiol. In 23% *tert*-butyl alcohol Fletcher[3] found 11.51 for butanethiol and 11.72 for octanethiol. In aqueous ethanol, Maurin and Paris[4] reported 12.0 for ethanethiol and 13.5 for hexanethiol. The last results are of uncertain significance, because they were estimated from the extent of reaction with indicators in aqueous ethanol, using the indicator constants determined in *water*. It seems unlikely that the difference between ethanethiol and hexanethiol would be as large as was reported by those investigators.

In addition to determining the ionization constant for hexanethiol in water by solubility measurements, the constant was determined by titration in 44.4% aqueous ethanol, and similar measurements were carried out for ethanethiol. Their significance will be discussed after the description of the experimental procedure.

EXPERIMENTAL

Materials. Hexanethiol (I) used in the solubility measurements was an American Petroleum Institute standard sample obtained from the Chemical and Petroleum Research Laboratories, Carnegie Institute of Technology, Pittsburg, Pa., and certified to contain less than 0.1 mole % impurities. It was transferred to a number of smaller bulbs in the following way: the bulbs, of about 0.5-ml. capacity with long capillary necks, were placed in a vacuum desiccator, which was first evacuated and then filled with nitrogen; the bulbs were then placed neck down in the opened ampule of hexanethiol, the whole was put in the vacuum desiccator, and the procedure repeated. The pressure of nitrogen forced the hexanethiol into the bulbs, the capillary ends of which were then sealed.

Hexanethiol (II) used in the titrations was an Eastman Kodak White Label product which was redistilled under nitrogen; the middle one-third, boiling at 133–135° and 740 mm., was stored in small bulbs as described above. Iodimetric titration[5] indicated a purity of 88%.

Ethanethiol was an Eastman Kodak technical-grade product; it was redistilled and the fraction collected that boiled at 30–31° and 741 mm. The purity was 94%. It was stored like hexanethiol (II).

Nitrogen was a commercial product, passed through three successive gas washing bottles containing vanadous ion to remove oxygen[6] and one bottle containing ascarite to remove any acid vapors that could be carried over from the washing bottles.

The water used in the preparation of all solutions was doubly distilled, deaerated by boiling, and cooled with a stream of nitrogen bubbling through it. It was stored under nitrogen and dispensed with the aid of nitrogen under slight pressure.

Ethanol, 95% was diluted with an equal volume of water; such a mixture contains 44.4% ethanol by weight. It was deoxygenated by bubbling nitrogen through it, which had been passed through a solution of vanadous ion, ascarite, and a washing bottle containing 44.4% ethanol.

Absorbancy coefficients. Approximately 0.1 g. of hexanethiol (I) was weighed accurately and dissolved in 250 ml. of $0.1M$ sodium hydroxide; this was diluted fifty times, giving about a 5×10^{-5} M concentration of mercaptan.

The absorbance was determined at 240 mμ with a Beckman Model DU spectrophotometer in a 1-cm. silica cell; the blank cell was filled with $0.1M$ sodium hydroxide. Six determinations gave an average value of 5290 ± 50.

The absorbance of hexanethiol in water at 240 mμ is negligible.

Solubility of hexanethiol. An excess of hexanethiol (I) was added to the buffer solution in a glass-stoppered flask and the air was displaced by nitrogen. The mixture was shaken by hand for 5 min. and put in a thermostat at 25 ± .05° for 0.5 hr. This procedure was repeated once. After shaking a third time, the mixture was allowed to stand in the thermo-

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stat for 2 to 3 hr. Most of the undissolved thiol came to the surface during this time, but some remained suspended in the aqueous layer. A 10-ml. sample was withdrawn from the bottom of the flask with a hypodermic syringe and a 6-in #18 needle, transferred to two test tubes, and centrifuged for 4 min. An aliquot portion of the solution was withdrawn with another syringe from the middle of the test tubes and a suitable amount of it was added to sodium hydroxide solution so the final hydroxyl ion concentration was 0.1*M* and the total thiol concentration about $5 \times 10^{-5}M$. The solubility was then calculated from the optical density and the molar absorbancy coefficient at 240 mμ.

The operations of transfer and dilution were performed in about 6 min., and loss of mercaptan by oxidation in this time was negligible. However, losses of 5 to 10% were observed if the operations were prolonged unduly.

The *p*H of the aqueous layer after equilibration with the mercaptan was measured with a Beckman Model G *p*H meter, with a type E-2 high *p*H glass indicator electrode and a calomel reference electrode. It was standardized with borax buffer of *p*H 9.18.

Titration of hexanethiol and ethanethiol. A quantity of the mercaptan was accurately weighed and dissolved in sufficient solvent to give a concentration between 2×10^{-2} and $2 \times 10^{-3}M$. This solution was then titrated in a thermostated beaker (25 ± 0.1°) with standard carbonate-free sodium hydroxide delivered from a microburet. During the titration nitrogen was made to flow over the surface of the solution.

DISCUSSION

For the ionization of a mercaptan in water one can write the equation:

$$RSH + H_2O \rightleftharpoons H_3O^+ + RS^-$$

and the thermodynamic equilibrium constant is given by

$$K_t = \frac{[H_3O^+][RS^-]}{[RSH][H_2O]} = \frac{[H_3O^+](RS^-)\gamma RS^-}{[H_2O](RSH)\ \gamma RSH}$$

where the quantities in square brackets represent the activities, those in parentheses the molal concentrations, and γ the activity coefficients of the chemical species involved.

In the experiments described, the solubility of hexanethiol was determined in solutions containing 0.1, 0.3, and 0.5*M* potassium chloride. In these solutions, the ionization of mercaptan can be neglected, and the experimental solubility *s* set equal to (RSH). The solubility was then determined in buffer solutions containing the same concentrations of potassium chloride as well as 0.02*M* bicarbonate-carbonate buffers; in these cases, the experimental solubility s = (RSH) + (RS^-).

If one assumes (a) that the solubility of RSH is not affected by the presence of the buffer components and (b) that the experimental *p*H measurements correspond to the hydronium ion activity, one can calculate a "practical constant" *K* by means of the equation

$$K = \frac{[H_3O^+](RS^-)}{(RSH)} = K_t \frac{\gamma RSH}{\gamma RS^-} [H_2O] \qquad (1)$$

At a given potassium chloride concentration, the activity of water and the activity coefficients of RS^- and RSH should be nearly constant, and *K* should also be constant.

TABLE I

*p*K OF HEXANETHIOL FROM SOLUBILITY MEASUREMENTS

*p*H	Ionic Strength	Solubility × 10^4 Moles/Liter	*p*K
7.00	0.10	3.61	—
9.98	0.10	5.72	10.21
10.25	0.10	6.72	10.31
10.54	0.10	9.24	10.35
7.00	0.30	3.03	—
9.92	0.30	4.42	10.26
10.32	0.30	6.07	10.32
10.70	0.30	9.50	10.37
7.00	0.50	2.72	—
9.95	0.50	3.89	10.32
10.40	0.50	5.25	10.33
10.80	0.50	9.91	10.38

The results are listed in Table I, and it can be seen that the values of *pK* determined at varying *p*H values differ by an amount greater than experimental error, which should be about 0.05 units. This indicates that the assumptions and approximations made are not strictly correct, but the differences are within 0.2 units, and the errors which attach to the use of Equation 1 are therefore not large. As the concentration of potassium chloride is increased, it tends to "swamp" the other effects, and it is observed that the variation in *pK* is smallest for the 0.5*M* solution.

The activity coefficient of RSH is inversely proportional to its solubility,[7] and hence it is seen that it increases by a factor of about 1.3 as the potassium chloride is increased from 0.1 to 0.5*M*. On the other hand, the activity coefficient of RS^- should decrease; the two changes partly compensate, and hence it is reasonable to expect that the *pK* values would not vary much in this range, as is observed. A reasonable estimate for γRS^- at 0.1 ionic strength is 0.83[8] while γRSH and $[H_2O]$ are nearly 1; pK_t can be estimated on this basis to be 10.4 ± 0.1.

It seemed of interest to compare the ionization constant in water determined as described above with that determined in a mixed solvent by the potentiometric titration method. Accordingly, hexanethiol of about $3 \times 10^{-3}M$ concentration in 44.4% ethanol was titrated with sodium hydroxide. The mercaptan is so weakly acidic that its reaction with sodium hydroxide cannot be considered quantitative, as in the case of stronger acids. In order to calculate the mercaptide concentration from the electroneutrality expression (OH^-) must

$$(RS^-) = (Na^+) - (OH^-)$$

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be known. In order to determine this, very dilute sodium hydroxide solutions of known concentrations were made up in the solvent medium, and the pH measured. At the midpoint in the titration, when $(RS^-) = (RSH)$, Equation (1) reduces to $pH = pK$, as is well known.

The experimental value of the pH at the midpoint in the titration was 11.9. For many reasons, Equation 1 is not exactly applicable in these circumstances and the difference of 1.5 pK units comprises not only the intrinsic difference between the acid strengths in water and 44% ethanol, but also the quantitative consequences of several corrections and approximations. In any case, the difference of 1.5 pK units may usefully be regarded as a correction factor by which the pK values determined in the mixed aqueous organic medium can be transposed to water. To check the applicability of the correction, ethanethiol was titrated both in water and in 44.4% alcohol, and the pK values found at the midpoint of the titration were 10.6 and 12.1; the difference is 1.5.

The pK value for ethanethiol in water accords well with that found by Yabroff[1] and Danehy.[2] The value for hexanethiol is a little lower than that estimated from the data of Yabroff.

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Deoxygenation of Aromatic *o*-Dinitroso Derivatives by Phosphines[1]

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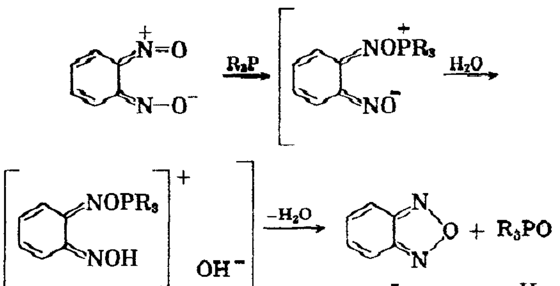
Azoxy derivatives,[4] amine oxides,[4] C-nitroso derivatives,[4] nitrones,[4] isonitrones,[5] nitrous oxide,[6] and nitrogen dioxide[7] have been partially or completely deoxygenated by trialkyl- or triarylphosphines. The present work extends deoxygenation by phosphines to aromatic *o*-dinitroso derivatives.

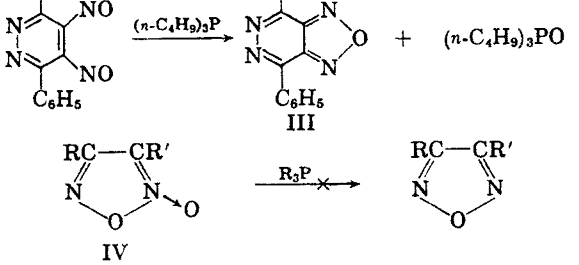
Triphenylphosphine oxide (II. $R = C_6H_5$) is obtained in good yield from equimolar quantities of triphenylphosphine and *o*-dinitrosobenzene in a hydrocarbon solvent. Benzofurazan (I), presumably formed simultaneously, was not isolated; however, after steam distillation of a similar reaction mixture in ethanol both products are isolated in very good yield and excess triphenylphosphine, if present, is recovered. Initial attack by a phosphine at oxygen rather than nitrogen of the nitroso group is not established but presents a plausible explanation for the formation of the product. Intermediate colored materials may be phosphonium zwitterions and/or quaternary bases similar to those postulated for the reaction of other polarizable double bonds and phosphines.[4]



I II

Substitution of tri-*n*-butylphosphine or triethyl phosphite for triphenylphosphine affords benzofurazan in comparable yields. Apparently tri-*n*-butylphosphine is a more powerful reagent than triphenylphosphine since the former but not the latter converts, 1,2-dinitrosonaphthalene to naphthofurazan. In a similar reaction 4,7-diphenylfurazano[*d*]pyrazine (III) is obtained from 3,6-diphenyl-4,5-dinitrosopyridazine.

In the reaction of *o*-dinitrobenzene and triphenylphosphine neither *o*-dinitrosobenzene nor benzofurazan has been detected; however, good yield of triphenylphosphine oxide and a trace of an unidentified solid are isolated in addition to starting materials. *o*-Dinitrobenzene and triethylphosphine are reported to form an unstable 1:1 adduct, m.p. 140° dec., in anhydrous solvents.[8] Color formation takes place in the attempted re-



III

IV

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