

# Equilibrium Deuterium Isotope Effects on the Ionization of Thiol Acids<sup>1</sup>

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**Abstract:** Isotope effects on the ionization of the thiol groups of pentafluorothiophenol, thioacetic acid, 4-nitrothiophenol, thiophenol, methyl mercaptoacetate, mercaptoethanol, and mercaptoacetate in water and deuterium oxide range from  $K_{RSH}/K_{RSD} = 2.0$ – $2.5$  and approximately follow the equation  $\Delta pK = 0.26 + 0.012pK_a$ . Bending as well as stretching frequencies contribute significantly to the isotope effects for reactions of thiols. The increase in the isotope effect with decreasing acidity of the thiol and the magnitude of the difference in the isotope effects for the ionization of RSH and ROH provide evidence that isotope effects on the interaction of  $RS^-$  and  $RO^-$  with the solvent contribute significantly to the observed effects.

We report here a series of determinations of the solvent deuterium isotope effect on the ionization of thiol acids. It has been shown previously that the difference in zero point energies corresponds to a 2.3-fold smaller isotope effect in the RSH–RSD system compared to the ROH–ROD system, because of the low stretching and bending frequencies of the S–H bond.<sup>2,3</sup> Aside from the information provided about the ionization process itself, knowledge of the isotope effect on thiol ionization should aid in the interpretation of kinetic isotope effects of reactions involving general acid or base catalysis by thiol acids or anions; in particular, the considerably smaller isotope effect on the

thiophenol (Aldrich Chemical Co.) was dissolved in hot 5% sodium hydroxide and filtered through a fine sintered glass filter into cold dilute hydrochloric acid.<sup>4</sup> The product was collected, washed with 0.01 M hydrochloric acid, dried over phosphorus pentoxide *in vacuo*, and stored in the freezer under argon (mp 77–78°). Water and deuterium oxide were distilled; for experiments above neutral pH they were boiled before use.

Stock solutions of thiol were made up shortly before use in water (deuterium oxide) or dilute potassium hydroxide which had been previously flushed with argon. In some cases concentrated solutions were first prepared in acetonitrile, but the final concentration of acetonitrile was always well below 1%. Ethylenediaminetetraacetic acid was generally added to alkaline solutions to give a final concentration of  $10^{-4}$  M.

The experimental conditions are summarized in Table I. The experiments were carried out in a series of 3-ml solutions of water or

Table I. Experimental Conditions for pK Determinations in Water and Deuterium Oxide

Thiols	Wavelength, nm	End points		Buffer
		KOH, M	HCl, M	
Mercaptoacetate	250	0.09	0.05	0.05 M proline
Mercaptoethanol	240	0.02	0.05	0.03 M glycine
Methyl mercaptoacetate	240	0.007	0.05	0.03 M tris(hydroxymethyl)aminomethane
Thiophenol	263	0.003	0.1	0.03 M phosphate
4-Nitrothiophenol	410	0.003	0.1	0.05 M acetate
Thioacetic acid	246	0.003	0.1	0.05 M formate
Pentafluorothiophenol	251	a	0.24	0.05 M glycine

<sup>a</sup>0.05 M acetate buffer, 80% base.

ionization of thiol compared to oxygen acids may be useful in attempting to evaluate the state of the proton in the activated complex as a function of the  $\alpha$  or  $\beta$  value for such reactions. The small magnitude of these isotope effects may also provide a useful method for distinguishing thiol from oxygen or nitrogen acids in the active sites of enzymes, from determinations of pH-rate profiles in water and deuterium oxide.

## Experimental Section

The thiols were commercial preparations which were redistilled under nitrogen and stored in the freezer under argon. 4-Nitro-

deuterium oxide to each of which had been added a small volume of the same concentrated buffer solution in water. Thus, the buffer composition was identical in water and deuterium oxide. The concentration of water introduced into the deuterium oxide by this procedure was 1% (2% for the thiophenol and 1.7% for the pentafluorothiophenol experiments). A series of five different buffer ratios selected to cover the range of ionization of the thiol was used in each experiment. The absorption was measured at or near the absorption maximum of the thiol anion with a Zeiss spectrophotometer shortly after the addition of a constant amount of thiol to each solution. The absorption was also measured in solutions of dilute hydrochloric acid and potassium hydroxide or alkaline buffer to determine the absorption of the acidic and anionic forms of the thiol, respectively. Duplicate measurements were carried out for each buffer solution and the acid and alkaline end points were determined in triplicate or quadruplicate. In the case of mercaptoethanol and methyl mercaptoacetate it was necessary to carry out a small extrapolation of the readings in alkaline solution to zero time to correct for decomposition of the thiol anion. Measurements of pH were carried out with a Radiometer Model

(1) This work was supported by grants from the National Science Foundation (GB 5648) and the National Institute of Child Health and Human Development of the National Institutes of Health (HD 01247).

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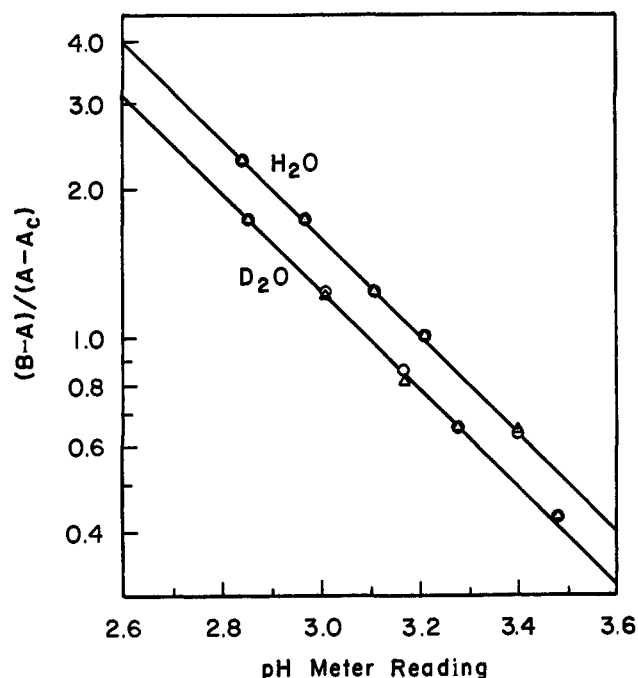


Figure 1. Spectrophotometric determination of the ionization constants for thioacetic acid in water and deuterium oxide in a series of formate buffers at 25°, ionic strength 1.0, maintained with potassium chloride. The triangles and circles represent the results of duplicate determinations.

4 or 26 pH meter. Values of pD were obtained by adding 0.40 to the pH meter readings for deuterium oxide solutions;<sup>5</sup> the validity of this correction was verified by measurement of the pH readings for solutions of 0.01 M HCl (DCI) in each experiment. All concentrations are based on the molarity scale.

## Results

The pK determinations were carried out with a differential method, as described in the Experimental Section, in which the same buffer solution was used to maintain the pH (pD) of the water and deuterium oxide solutions and the entire experiment was carried out in a single day, in order that the differences in pK in the two solvents could be determined as accurately as possible. Typical results, for the spectrophotometric determination of the pK<sub>a</sub> of thioacetic acid in a series of formate buffers, are shown in Figure 1. The ratio  $(B - A)/(A - A_c)$ , in which  $A$  is the observed absorbance and  $B$  and  $A_c$  are the absorbances of the basic and acid forms of the thiol, respectively, is plotted semilogarithmically against the observed pH meter reading and the pK values are obtained from the intercepts of lines of slope 1.0 with the value 1.0 on the ordinate scale, adding 0.40 to the pK value obtained from pH meter readings in deuterium oxide.<sup>5</sup> The results are summarized in Table II. The pK<sub>a</sub> and  $\Delta pK_a$  values of the buffers were also calculated from the results and are shown in the table along with some previously determined values that were obtained under somewhat different experimental conditions.

Attempts to determine the dissociation constant of thiobenzoic acid were unsuccessful because of interference from an absorption at 295 nm which was reversibly converted to an absorption at 265 nm in solutions more acid than the pK of thiobenzoic acid. It is not known whether this is a property of thiobenzoic acid itself or an

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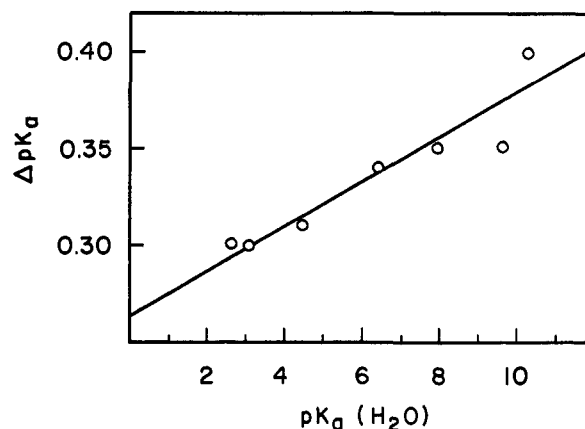


Figure 2. The isotope effect on the ionization of thiol acids,  $\Delta pK_a$ , as a function of the acidity of the thiol.

impurity that was not affected by distillation or by recrystallization of the diisobutylammonium salt of the acid.

Table II. Ionization Constants in Water and Deuterium Oxide at 25° and Ionic Strength 1.0<sup>a</sup>

	$\overline{pK_a}$ H <sub>2</sub> O	$\overline{pK_a}$ D <sub>2</sub> O	$\Delta pK$	$K_{H_2O}/K_{D_2O}$
<b>Thiols</b>				
Mercaptoacetate	10.25	10.65	0.40	2.5
Mercaptoethanol	9.61	9.96	0.35	2.2
Methyl mercaptoacetate	7.91	8.26	0.35	2.2
Thiophenol	6.43	6.76	0.34	2.2
4-Nitrothiophenol	4.50	4.81	0.31	2.0
Thioacetic acid	3.20	3.50	0.30	2.0
Pentafluorothiophenol	2.68	2.98	0.30	2.0
<b>Buffers</b>				
Proline	10.58	11.23	0.65	4.5
Glycine (NH <sub>3</sub> <sup>+</sup> )	9.71	10.30	0.59	3.9
			0.53, <sup>b</sup> 0.63 <sup>c</sup>	
Tris(hydroxymethyl)aminomethane	8.19	8.75	0.56	3.6
Phosphate	6.85	7.37	0.52	3.3
			0.56, <sup>d</sup> 0.54, <sup>e</sup> 0.46 <sup>b</sup>	
Acetic acid	4.65	5.14	0.49	
			0.52, <sup>e,f</sup> 0.51 <sup>g</sup>	
Formic acid	3.67	4.13	0.46	2.9
			0.46, <sup>f</sup> 0.40, <sup>b</sup> 0.45 <sup>h</sup>	
Glycine (COOH)	2.47	2.85	0.38	2.4
			0.39, <sup>c</sup> 0.40 <sup>b</sup>	

<sup>a</sup> Maintained with potassium chloride. All constants are based on the molar scale. <sup>b</sup> G. Schwarzenbach, A. Epprecht, and H. Erlenmeyer, *Helv. Chim. Acta*, **19**, 1292 (1936). <sup>c</sup> N. C. Li, P. Tang, and R. Mathur, *J. Phys. Chem.*, **65**, 1074 (1961). <sup>d</sup> C. K. Rule and V. K. La Mer, *J. Amer. Chem. Soc.*, **60**, 1974 (1938). <sup>e</sup> R. A. Robinson, M. Paabo, and R. G. Bates, *J. Res. Nat. Bur. Stand., Sect. A*, **73**, 299 (1969). <sup>f</sup> Reference 6. <sup>g</sup> V. Gold and B. M. Lowe, *J. Chem. Soc. A*, 1923 (1968). <sup>h</sup> Reference 5.

## Discussion

The deuterium isotope effects,  $\Delta pK_a$ , for the ionization of thiols in water and deuterium oxide are plotted in Figure 2 as a function of the pK<sub>a</sub> of the thiol. The two principal conclusions are as follows. (1) The absolute magnitudes of the isotope effects,  $\Delta pK = 0.30$ – $0.40$  corresponding to  $K_{H_2O}/K_{D_2O}$  ratios of 2.0–2.5, are

considerably smaller than those for the ionization of oxygen or nitrogen acids of comparable acidity, which generally exhibit isotope effects in the range  $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = 2.5\text{--}4.5$ . (2) There is a small, but definite increase in the isotope effect with decreasing acidity of the thiol; the line in the figure follows the equation

$$\Delta pK_a = 0.26 + 0.012pK_a \quad (1)$$

This may be compared with the corresponding equation that is approximately followed for oxygen acids<sup>6</sup> which

$$\Delta pK_a = 0.44 + 0.017pK_a \quad (2)$$

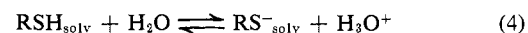
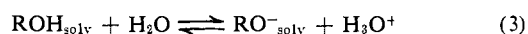
appear to exhibit a somewhat larger sensitivity of their isotope effect to acid strength.

The relatively small magnitude of the isotope effect for the ionization of thiol acids is expected as a consequence of the low stretching and bending frequencies of the S-H bond. It has been suggested previously that the large fractionation factor of 2.32 for the distribution of deuterium between ethanethiol and water (favoring the S-H and O-D bonds)<sup>2</sup> and the solvent deuterium isotope effect of  $K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = 2.27$  for hemithioacetal formation, in which an S-H is converted to an O-H bond,<sup>3</sup> may be accounted for most satisfactorily if bending as well as stretching and perhaps other frequencies are taken into account, although there has been some uncertainty as to the assignment of these frequencies.<sup>2,7</sup> Bending vibrations (in the transition state) have also been shown to be significant for reactions of H-F.<sup>8</sup> The difference in zero point energies,  $\frac{1}{2}h\nu$ , of the stretching vibrations, based on observed values of the X-H (X-D) frequency of 3640 (2670)  $\text{cm}^{-1}$  for monomeric methanol<sup>9</sup> and 2550 (1854)  $\text{cm}^{-1}$  for monomeric methanethiol,<sup>10</sup> gives a difference of  $\Delta pK = 0.28$  between the isotope effects for the ionization of ROH and RSH. However, this difference will be considerably smaller in aqueous solution because hydrogen bonding to the solvent causes a decrease in the frequency of the O-H stretching vibration, but has little or no effect on the S-H frequency because of the small tendency of the S-H group to form hydrogen bonds.<sup>11</sup> Based upon reported stretching frequencies of 3330 and 2476  $\text{cm}^{-1}$  for hydrogen-bonded ROH and ROD, respectively,<sup>12</sup> and allowing a generous estimate of 50  $\text{cm}^{-1}$  for the shift of the RSH frequency upon hydrogen bonding to oxygen<sup>13</sup> the calculated difference in isotope effects between RSH and ROH is only  $\Delta pK = 0.16$ . Based upon the stretching frequency of 3074  $\text{cm}^{-1}$  for acetic acid in water estimated by Bunton and Shiner<sup>14</sup> the calculated difference in isotope effects for the ionization of acetic and thioacetic<sup>13</sup> acids is only 0.10. Although there are uncertainties in the calculations, these differences are probably significantly smaller than the

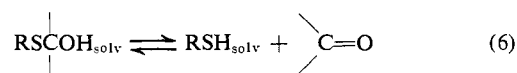
difference in  $pK$  of 0.23 between oxygen and thiol acids of  $pK$  10 and 0.20 for acids of  $pK$  4. The differences in the bending frequencies of O-H and S-H bonds are more than adequate to account for this discrepancy and also make a significant contribution to the isotope effect for hemithioacetal formation and hydrogen-deuterium fractionation between RSH and ROH, for which  $\log K_{\text{H}}/K_{\text{D}} = 0.35$ . A conservative estimate of this contribution corresponds to a difference in isotope effect of  $\Delta \log K = 0.13$ , based upon observed in-plane deformation frequencies of 804 and 624  $\text{cm}^{-1}$  for  $\text{CH}_3\text{-SH}$  and  $\text{CH}_3\text{SD}$ , respectively,<sup>10</sup> and of 1210 and 900  $\text{cm}^{-1}$  for ROH and ROD, respectively (from an average value of 900  $\text{cm}^{-1}$  for several deuterated alcohols and of 1.35 for the ratio  $\nu_{\text{OH}}/\nu_{\text{OD}}$ ).<sup>9</sup> A maximum, and probably more realistic, estimate of the contribution of bending frequencies to the difference in isotope effect is  $\Delta \log K = 0.20$ , based upon a value of 1420  $\text{cm}^{-1}$  for a hydrogen-bonded alcohol<sup>7</sup> and assuming a constant ratio  $\nu_{\text{OH}}/\nu_{\text{OD}} = 1.35$ .<sup>9</sup>

Two observations provide evidence that interactions of  $\text{RO}^-$  and  $\text{RS}^-$  with the solvent make a significant contribution to the observed isotope effects for the ionization of ROH and RSH. First, the increase in isotope effect with decreasing acidity of the thiol cannot be accounted for by a change in stretching frequency of the thiol acid because there is no regular effect of thiol acidity on this frequency<sup>13,15</sup> and even the maximum observed frequency difference of 40  $\text{cm}^{-1}$ , between alkylthiols and thioacetic acid,<sup>13a</sup> would give only an insignificant change of 0.01 in the isotope effect. Since hydrogen bonding to the weakly basic sulfur atom of a free thiol is not expected to be significant, this change must reflect a  $pK$ -dependent change in the interaction of  $\text{RS}^-$  with the solvent. According to the treatment of Bunton and Shiner,<sup>14</sup> the major part of the  $pK$  dependence of the isotope effect for the ionization of oxygen acids is a consequence of the dependence on the basicity of  $\text{RO}^-$  of the H-O stretching frequencies of three or four hydrogen-bonded solvent molecules and Salomaa, *et al.*,<sup>16</sup> have reached a similar conclusion regarding the importance of the solvent isotope effect on  $\text{RO}^-$  solvation, which is treated in terms of an activity coefficient effect.

Second, the observed difference between the isotope effects on the  $pK_a$  of oxygen and of thiol acids of 0.18–0.24 (eq 3–5) is significantly smaller than the difference of 0.35 that is attributable to the RSH and ROH groups



themselves, as measured by the isotope effect on the hemithioacetal equilibrium (eq 6) or hydrogen-deuterium fractionation.<sup>2,3</sup> Since HOH and  $\text{H}_3\text{O}^+$  are



common to the ionization reactions of RSH and of ROH (eq 3 and 4), this difference must be a conse-

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quence of differences in the interaction of  $\text{RS}^-$  and of  $\text{RO}^-$  with solvating water molecules. It is known that  $\text{RO}^-$  is less stable in DOR than in HOR by a factor of about 2,<sup>17</sup> and there is evidence for a similar difference in the stability of the lyoxide ion in deuterium oxide and water.<sup>14,18</sup> These differences, at least in the case of the alkoxide ion, may be attributed to changes in the O-H stretching frequencies of one or more solvent molecules hydrogen bonded to the  $\text{RO}^-$  ion<sup>14</sup> and/or to changes in lower frequency librations.<sup>19</sup> The fact that the difference in the isotope effect on the ionization constants of ROH and RSH is less than that attributable to ROH and RSH themselves means that the sum of these frequencies must be smaller for molecules solvating  $\text{RS}^-$  than for those solvating  $\text{RO}^-$  anions of similar basicity. Both the hydrogen-bonding ability and the basicity of sulfur compounds are less than those of comparable oxygen compounds because of the large size and small electron density of sulfur, but for a given basicity there are indications that sulfur may cause a greater frequency shift of a hydrogen-bonded O-H group than oxygen: (i) for a given  $-\Delta H$  (or  $K_{\text{eq}}$ ) for hydrogen bond formation with phenol, the shift in  $\nu_{\text{OH}}$  is considerably larger for sulfur than for oxygen or nitrogen as

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electron donors<sup>20</sup> and (ii) although oxygen and sulfur anions of the same basicity have similar effectiveness as general base catalysts for reactions with a large  $\beta$  value, sulfur anions are relatively more effective for reactions with a low  $\beta$  value, in which the transition state would be expected to resemble a hydrogen bond between  $\text{RS}^-$  and a proton donor.<sup>21</sup> Both of these observations may reflect the high polarizability of sulfur. Although the libration frequencies of water molecules in the neighborhood of a sulfur anion are not known, librational frequencies are known to decrease with increasing size and "structure-breaking" character of anions,<sup>19</sup> so that a decrease in these frequencies might be expected in the presence of the large sulfur anion. Thus, although direct experimental evidence is not yet available, there is reason to believe that either or both of these frequency shifts may be larger for  $\text{RS}^-$  than for  $\text{RO}^-$  and will provide the additional factor needed to account quantitatively for the observed differences in the isotope effects for the ionization of thiol and oxygen acids. The unusually large increase of 2.59-fold in the activity coefficient of  $\text{SO}_3^{2-}$  in deuterium oxide compared to water<sup>22</sup> may reflect a similar influence of lone pair electrons of the sulfur atom on stretching and/or librational frequencies of solvent molecules.

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## The Structure of Binor-S Established from the Dione Derivative. The Crystal and Molecular Structure of Decahydro[1,2,4:5,6,8]dimetheno-*s*-indacenedione

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**Abstract:** The Binor-S-dione (decahydro[1,2,4:5,6,8]dimetheno-*s*-indacene-3,7-dione) was synthesized *via* the catalytic dimer of 7-*tert*-butoxynorbornadiene and its structure has been determined by a single-crystal X-ray diffraction study. This substance,  $\text{C}_{14}\text{H}_{12}\text{O}_2$ , crystallizes in space group  $P2_1/c$  ( $a = 7.914$ ,  $b = 12.932$ ,  $c = 9.641$  Å,  $\beta = 100.27^\circ$ ) with four molecules per unit cell. The intensities of 1659 reflections were measured on a Picker automatic diffractometer using Cu  $K\alpha$  radiation. The structure was solved by exploiting the  $\Sigma_2$  relationship. Full-matrix least-squares refinement assuming anisotropic thermal parameters for C and O atoms and isotropic parameters for H converged at a conventional  $R$  factor  $R_1 = 4.9\%$  for the 1550 reflections above background. This study establishes that the caged hydrocarbon known as Binor-S is the syn isomer. Bond angles indicate the presence of considerable strain in the nortricyclanone subunits. Bond distances from the carbon atoms directly bonded to the cyclopropyl rings to the ring atoms are significantly shorter than the distances from these carbons to the remaining (apex) carbon atoms.

The caged hydrocarbon known as Binor-S is obtained when norbornadiene is dimerized in the presence of certain multicenter catalysts containing cobalt, rhodium,

and iridium.<sup>2-4</sup> Because the mechanism of catalysis, believed to involve the concerted union of norbornadi-

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