

Intramolecular Hydrogen Bonds. XI.¹⁾ The Intramolecular Hydrogen Bonding Ability of Sulfur

Nobuo MORI, Yoshiharu TAKAHASHI and Yojiro TSUZUKI

Department of Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo

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Although sulfur atom has not been so well recognized as a base in hydrogen bonding as oxygen and nitrogen atoms, several reports have appeared implying this atom as a proton acceptor.²⁾ More recent infrared investigations have indicated that, on the basis of the OH spectral shifts, the sulfur atom in sulfides is a relatively strong proton acceptor in both inter-^{3,4)} and intra-molecular hydrogen bondings;^{3,5)} in the case of some typical proton acceptors such as ethers, sulfides and *t*-amines, the OH spectral shifts increase with the proton acceptor atoms in the order: O < S < N. However, this indication can not always be justified, since, in general, spectral shifts can not be used to compare the strengths, or more exactly the enthalpies, of hydrogen bonds involving different proton acceptors such as halogens.⁶⁾ In order to

clarify this point of problem, the *ω*-ethylmercapto-alkanol series has now been investigated as regards intramolecular hydrogen bonding by means of infrared spectroscopy, by comparing with the corresponding series of compounds which contain oxygen as well as nitrogen as the proton acceptor atom instead of sulfur.

Table 1 summarizes the physical constants of the compounds examined and the apparent infrared data observed in carbon tetrachloride solutions of such low concentrations that any intermolecular hydrogen bonding is negligible.

Each compound, where the number of *n* is 2 or 3, showed two bands due to the free and the bonded OH groups, while the others showed no bonded OH band. The range of *n* allowing the formation of the hydrogen bond is narrower than those in

TABLE 1. SUMMARY OF THE PHYSICAL CONSTANTS AND THE INFRARED DATA OF COMPOUNDS IN THE C₂H₅S-(CH₂)_{*n*}-OH SERIES

<i>n</i>	Bp, °C/mmHg	<i>n</i> _D ²⁵	Molarity × 10 ³	ν _{OH} cm ⁻¹	Δν _{1/2} cm ⁻¹	log <i>I</i> ₀ / <i>I</i>	ε	<i>K</i> _S	<i>K</i> _O *1	<i>K</i> _N *1
2	84—84.5/20 ⁸⁾	1.4839 (20°C)	3.74	3637	30	0.28	68	1.4	12.3	15
				3547	105	0.205	35			
			5.60	3636	30	0.46	68	1.5		
				3548	96	0.34	34			
3	82—83/5 ⁸⁾	1.4830	4.03	3640	30	0.75	68	0.09	1.5	4.7
				3502	127	0.18	180			
4*2	94—95/5	1.4813	2.50	3640	30	0.53	70	—	0.65	3.5
5	133—134/20 ⁹⁾	1.4796	3.20	3642	30	0.65	68	—	*3	0.11

*1 *K*_O and *K*_N are the equilibrium constants in the *ω*-methoxy-⁷⁾ and the *ω*-diethylamino-alkanol series.¹⁾

*2 Found: C, 53.70; H, 10.48%. Calcd for C₆H₁₄OS: C, 53.71; H, 10.52%.

*3 5-Methoxypentanol is internally bonded,¹⁰⁾ but this compound is not described in Lit. 7.

1) Part X: N. Mori, E. Nakamura and Y. Tsuzuki, This Bulletin, **40**, 2191 (1967).

2) G. C. Pimental and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Co., San Francisco, Calif. (1960), p. 201.

3) P. von R. Schleyer and R. West, *J. Am. Chem. Soc.*, **81**, 3164 (1959).

4) R. J. Niedzielski, R. S. Drago and R. L. Midgough, *ibid.*, **86**, 1694 (1964).

5) A. W. Baker and A. T. Shulgin, *J. Am. Chem. Soc.*, **80**, 5358 (1958); E. A. Allan and L. W. Reeves, *J. Phys. Chem.*, **66**, 613 (1962); A. Luttringhaus, S. Karuss, H. Prinzbach and F. Langenbucher, *Ann.*, **653**, 195 (1962); M. P. Mertes, *J. Org. Chem.*, **26**, 5236 (1961); *ibid.*, **28**, 2320 (1963); H. H. Szmant and J. J. Rigau, *ibid.*, **31**, 2288 (1966).

6) R. West, D. Powell, L. Watley, M. Lee and P.

von R. Schleyer, *J. Am. Chem. Soc.*, **84**, 3221 (1962); D. A. K. Jones and J. G. Watkinson, *J. Chem. Soc.*, **1964**, 2366; *ibid.*, **1964**, 2371; H. Bourassa-Bataille, P. Sauvageau and C. Sandorfy, *Can. J. Chem.*, **41**, 2240 (1963); A. W. Baker and A. T. Shulgin, *ibid.*, **43**, 650 (1965); P. J. Krueger and H. D. Mettee, *ibid.*, **42**, 288 (1964); *ibid.*, **42**, 326 (1964); *ibid.*, **42**, 340 (1964).

7) L. P. Kuhn and R. A. Wires, *J. Am. Chem. Soc.*, **86**, 2161 (1964).

8) R. M. McCurdy and J. H. Prager, *J. Polymer Sci.*, **A2**, 1185 (1964).

9) G. M. Bennett and E. G. Turner, *J. Chem. Soc.*, **1938**, 814.

10) A. B. Foster, A. H. Haines and M. Stacey, *Tetrahedron*, **16**, 177 (1961).

the comparative series of nitrogen- and oxygen-containing compounds, and also the equilibrium constants (K_S) between the bonded and the free OH species are much lower than those (K_O and K_N) in the latter series; these indicate that the sulfide-sulfur atom is much lower in intramolecular hydrogen bonding ability than the oxygen and the nitrogen. Further, this suggests that the enthalpy of the OH \rightarrow S hydrogen bond formation is considerably low as compared with that of the OH \rightarrow O as well as OH \rightarrow N hydrogen bond formation, since these different proton-acceptor atoms are expected to bring about nearly the same losses in entropy for the formation of rings with similar geometries through the hydrogen bonding. Accordingly, it may be concluded that (1) the spectral shifts do not provide any significant information on the strengths of the intramolecular hydrogen bonds involving the different proton-acceptor atoms, (2) the sulfide-sulfur atom has an ability to form a ring with at most six members, and (3) the intramolecular hydrogen bonding abilities of these proton-acceptor atoms increase in the order: S<O<N, as can be indicated by the order of the K values ($K_S<K_O<K_N$) and also by the order of the ranges of n allowing the formation of the hydrogen bond.

Experimental

The ω -ethylmercaptoalkanols were prepared by the known method⁹⁾ from the corresponding haloalkanols¹¹⁾ and ethylmarcaptan and then purified by fractional distillation; their physical constants were in complete agreement with those reported in the literature, except for 4-ethylmercaptobutanol which has not hitherto been described.

Determination of the equilibrium constants (K_S) were carried out by the method previously described,¹⁾ on the basis of the intensities of the free OH bands. The molar extinction coefficients (ϵ) were based on the calculated concentrations of the free and the bonded OH species.

The infrared spectra were measured by using a Perkin-Elmer 21 single-beam spectrometer equipped with a lithium fluoride prism and a cell of 3 cm long.

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11) N. Mori, E. Nakamura and Y. Tsuzuki, This Bulletin, **40**, 2189 (1967).