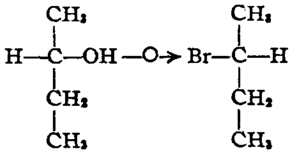
It is, however, more difficult to calculate the amount of racemization that occurred during the alkylation step. Such a value must depend upon the correctness of the values assumed for the rotation of the optically pure compounds. For the over-all reaction using the highest value reported for the rotation of 2-butanol ($[\alpha]^{25}\mathrm{D}$ 13.63°)[4] and 2-methylbutyric acid ($[\alpha]^{25}\mathrm{D}$ 20.5°)[5] there appears to have been a 55.3% retention of activity. In this sequence, only in the preparation of the alkyl halide and the subsequent reaction with pyrrylmagnesium bromide was the asymmetric center involved. Skell, Allen and Helmkamp[6] have demonstrated the following relationship between optically pure 2-butanol and 2-bromobutane by inversion of configuration at the optically active center



$$\begin{array}{c}CH_3\\ |\\ H{-}C{-}OH\\ |\\ CH_2\\ |\\ CH_3\end{array} \xrightarrow{\ \ O\ \ } \begin{array}{c}CH_3\\ |\\ Br{-}C{-}H\\ |\\ CH_2\\ |\\ CH_3\end{array}$$

$[\alpha]^{25}\mathrm{D}$ −13.65° $[\alpha]^{25}\mathrm{D}$ + 39.4°

Thus, the starting 2-bromobutane was 16.65/39.4 or 42.3% resolved and the recovered 2-methylbutyric acid was 8.81/20.5 or 43.0% resolved. Since these calculations are based on specific rotation values from three different laboratories and complex experimental relationships, the apparent 0.7% discrepancy is not significant. *Thus the alkylation at both the 2- and 3-positions occurs with complete inversion of configuration.*

A general method for determining the optical purity of alkyl halides with the halogen at the asymmetric center may be the conversion to alkylpyrroles and oxidation to the corresponding carboxylic acid, as indicated above. This method should prove particularly valuable with secondary, tertiary and benzyl-type halides.

Experimental

(+)-2-Butanol.—2-Butanol was resolved through the brucine salt of the half-ester of phthalic acid by the method of Hauser and Kantor.[7] The (+)-2-butanol prepared had $[\alpha]^{25}\mathrm{D}$ + 10.6°.

(−)-2-Bromobutane.—Hydrogen bromide was bubbled through 31.05 g. of (+)-2-butanol, $[\alpha]^{25}\mathrm{D}$ + 10.6°, cooled in an ice-bath until the theoretical weight had been taken up. The product was sealed in several tubes and heated to 110° for 3 hours. After the tubes were cooled in ice, they were opened and the product separated from the heavy acid layer. The upper layer was extracted with a concentrated solution of calcium chloride to remove unreacted alcohol and then dried over calcium chloride. The bromide was distilled to give a yield of 42.7 g. (73%), $[\alpha]^{25}\mathrm{D}$ −16.65°.

Reaction of (−)-2-Bromobutane with Pyrrylmagnesium Bromide.—To 0.5 mole of pyrrylmagnesium bromide, prepared from 33.5 g. of pyrrole and methylmagnesium bromide, was added 41.4 g. of (−)-2-bromobutane, $[\alpha]^{25}\mathrm{D}$ −16.65°, and 19.6 g. of (±)-2-bromobutane. After refluxing for 33 hours, the reaction was hydrolyzed with dilute phosphoric acid and worked up as usual. The product was distilled under reduced pressure and the distillate carefully fractionated through a Podbielniak Mini-Cal column to give 6.15 g. of pyrrole, b.p. 49° (36 mm.), $n^{25}\mathrm{D}$ 1.5070; 16.95 g. of 2-*sec*-butylpyrrole, b.p. 96° (36 mm.), $n^{25}\mathrm{D}$ 1.4900, $[\alpha]^{25}\mathrm{D}$ +7.63°; and 7.20 g. of 3-*sec*-butylpyrrole, b.p. 100° (36 mm.), $n^{25}\mathrm{D}$ 1.4878, $[\alpha]^{25}\mathrm{D}$ + 8.13°.

Oxidation of (+)-2-*sec*-Butylpyrrole to 2-Methylbutyric Acid.—(+)-2-*sec*-butylpyrrole (5.10 g.) was slowly added with stirring to a cold solution of 51 g. of sodium permanganate in 500 ml. of water. The temperature was kept below 10° by cooling the reaction in ice. After all of the pyrrole had been added, the reaction was stirred an additional hour and, while still in an ice-bath, sulfur dioxide was bubbled through the solution to destroy the manganese dioxide. The solution was acidified and extracted ten times with ether to remove the organic acid. The combined ether extracts were dried over sodium sulfate and then over Drierite. The ether was removed by distillation through a short glass-helices packed column, and the residue (about 3 ml.) distilled. The fraction boiling between 160 and 180° was collected, $n^{25}\mathrm{D}$ 1.4020. The specific rotation of the 2-methylbutyric acid was $[\alpha]^{26}\mathrm{D}$ +5.99°.

Oxidation of (+)-3-*sec*-Butylpyrrole to 2-Methylbutyric Acid.—The (+)-3-*sec*-butylpyrrole (5.10 g.) was oxidized as above. The product had a specific rotation of $[\alpha]^{25}\mathrm{D}$ + 5.97°.

---

(4) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911); **103**, 1923 (1913); see P. J. Leroux and H. J. Lucas, *J. Am. Chem. Soc.*, **73**, 41 (1951).

(5) K. B. Wiberg and T. Hutton, *ibid.*, **78**, 1640 (1956); see footnote 6.

(6) P. S. Skell, R. G. Allen and G. K. Helmkamp, *ibid.*, **82**, 410 (1960).

(7) C. R. Hauser and S. W. Kantor, *J Chem. Soc.*, **75**, 1744 (1953).

[CONTRIBUTION FROM THE DIVISION OF PURE CHEMISTRY, NATIONAL RESEARCH COUNCIL, OTTAWA, CANADA. ISSUED AS NRC No. 7050]

Free Radicals by Mass Spectrometry. XXVIII. The HS, CH_3S, and Phenyl-S Radicals: Ionization Potentials and Heats of Formation

BY T. F. PALMER[1] AND F. P. LOSSING

RECEIVED MAY 12, 1962

The vertical ionization potentials of the HS, CH_3S and phenyl-S radicals have been measured by electron impact to be 10.50 ± 0.1, 8.06 ± 0.1 and 8.63 ± 0.1 volt, respectively. From appearance potentials of the radical ions from derivatives, these estimates for the heats of formation of the radicals and ions (in kcal./mole) were obtained: $\Delta H_f(HS^+) \leq 276$, $\Delta H_f(HS) \leq 33.7$, $\Delta H_f(CH_3S^+) \leq 218$, $\Delta H_f(CH_3S) \leq 31.8$. A calculation of $I(CH_3S)$ from the appearance potentials of CH_3S^+ ion from CH_3SCH_3 and CH_3SSCH_3 is in good agreement with the directly measured value. No heats of formation for C_6H_5S ion or radical were obtained.

Introduction

The HS radical has been investigated by a number of workers using spectroscopic methods. It has been observed in absorption in a radio frequency discharge through H_2S[2] and in emission in Schüler-type discharges containing H_2S.[3,4] It has also been observed in emission in flames

---

[1] National Research Council of Canada Postdoctorate Fellow 1960–1962.

(2) M. N. Lewis and J. U. White, *Phys. Rev.*, **55**, 894 (1939).

(3) S. Leach, *Compt. rend.*, **230**, 2181 (1950).

(4) S. Leach, *Discussions Faraday Soc.*, **9**, 81 (1950).

containing H_2S[5] and in fluorescence following irradiation of H_2S with vacuum ultraviolet radiation.[6] The HS and DS radicals were observed by Porter[7] in the flash photolysis of H_2S and D_2S. He obtained vibrational constants and an estimate of 84.9 ± 4 kcal./mole for the H–S bond dissociation energy. A similar investigation of HS and DS by Ramsay using a higher resolving power led to elucidation of further details of the spectrum and an estimate of 82.8 ± 11 kcal./mole for D(H–S).[8] A more recent investigation by Johns and Ramsay[9] led to a value of 81.4 ± 3 kcal./mole for D(H–S), using a shorter Birge–Sponer extrapolation.

Franklin and Lumpkin,[10] using the indirect electron inpact method on ethyl, propyl and butyl mercaptans, found D(HS–H) to be 95.3 kcal./mole. A similar investigation by Stevenson[11] gave (D(HS–H) as 92.2 ± 2 kcal./mole.[11] These measurements are in reasonable agreement with D(HS–H) = 89 ± 4 kcal./mole derived from the decomposition rates of methyl, ethyl and benzyl mercaptan using the toluene carrier technique.[12,13]

From appearance potentials, the heat of formation of the CH_3S radical has been estimated to be 33 kcal./mole, corresponding to D(CH_3S–H) = 89 kcal./mole.[10] From a study of the thermal decomposition of benzyl methyl sulfide, D(benzyl–SCH_3) was found to be 51.5 ± 2 kcal./mole.[14] Using this value and a recent measurement of the heat of formation of benzyl methyl sulfide, Mackle and Mayrick[15] obtained $\Delta H_f(CH_3S) = 30.5 \pm 5$ kcal./mole. They also pointed out that on the basis of more recent values for the heats of formation of $(CH_3)_2S$ and $(CH_3S)_2$, Franklin and Lumpkin's data[10] lead to $\Delta H_f(CH_3S) = 36$ kcal./mole.

The formation of the phenylsulfide radical, C_6H_5S, in the thermal decomposition of phenyl methyl sulfide, has been investigated by Back and Sehon.[16] The main products of the reaction were methane and thiophenol. The activation energy for the decomposition was estimated to be 60 kcal./mole. Using this value and their measured value for $\Delta H_f(C_6H_5SCH_3)$, Mackle and Mayrick[15] calculated $\Delta H_f(C_6H_5S)$ to be 51 kcal./mole. No estimates of the heat of formation of this radical or ion are available from electron impact.

Experimental

The radicals were produced by pyrolysis of suitable derivatives in a fused-silica capillary furnace leading to the ionization chamber of a mass spectrometer.[17] The method of comparison of the ionization efficiency curve for the radicals with that of an added standard gas was the same as employed formerly.[18]

The HS radical was produced in abundance by the pyrolysis of allyl mercaptan at 1000°. Other products were allyl radicals and a rather large amount of H_2S. Since no appreciable amount of allene was formed, the H_2S must have been produced by a reaction of HS radicals with substances adsorbed on the walls of the reactor and ionization chamber. Using 50-v. electrons, a net ion current of 6×10^{-13} amp. was obtained for the HS radical, after subtraction of the contribution of H_2S to the mass 33 peak. Using electrons of energy less than A(HS^+) from H_2S, a large increase in the ion current at mass 33 was found as the furnace temperature was raised to 1000°.

The CH_3S radical was produced by the pyrolysis of methyl benzyl sulfide. Some difficulty was encountered in obtaining a sufficient concentration of the radicals. At 925°, the temperature required to decompose methyl benzyl sulfide more or less completely, a large fraction of CH_3S radicals was decomposed to thioformaldehyde. Using 50-v. electrons, the net ion current for the radical at mass 47 was 2.5×10^{-13} amp. under optimum conditions of temperature.

The C_6H_5S radical was produced in good yield by the pyrolysis of phenyl allyl sulfide at 925°. Allyl radicals were also formed in abundance, as well as the dimer $(C_6H_5S)_2$ and thiophenol. Above 925° the C_6H_5S radical began to decompose, with the formation of cyclopentadienyl radical and (presumably) CS. This reaction is analogous to the decomposition of phenoxy radical to cyclopentadienyl radical and CO.[19] At 925° no difficulty was encountered in obtaining a net radical peak of 8×10^{-13} amp.

Materials.—Allyl mercaptan and benzyl methyl sulfide were commercial samples of good purity. Phenyl allyl sulfide was prepared by the reaction of thiophenol with sodium ethoxide and allyl iodide.[20] The product was distilled and a middle fraction was used. Samples of H_2S and CH_3SCH_3 used for the appearance potential measurements were commercial samples purified by bulb-to-bulb distillation.

Results and Discussion

The HS Radical.—The vertical ionization potential found for HS radical, 10.50 ± 0.1 v., is given in Table I. It is interesting to note that the radical has nearly the same ionization potential as the S atom, 10.357 v.,[21] and H_2S, 10.47 v.[22–24] This value is appreciably lower than an estimate[25] of 11.1 v. for I(HS), based on appearance potentials of fragment ions. The appearance potential for HS^+ fragment ion formation from H_2S was found in this work to be 14.43 ± 0.1 v. This is considerably lower than the result of earlier workers, 15.2 ± 0.5 v.[26] Part of this discrepancy arises from the fact that Neuert and Clasen evaluated

Table I

Ionization and Appearance Potentials of HS, CH_3S and C_6H_5S Radicals and Ions

Transition	Energy (volts) This work	Energy (volts) Lit.
$HS \rightarrow HS^+$	10.50 ± 0.1	11.1[25]
$CH_3S \rightarrow CH_3S^+$	8.06 ± .1	8.2[25]
$C_6H_5S \rightarrow C_6H_5S^+$	8.63 ± .1	...
$H_2S \rightarrow HS^+ + H$	14.43 ± .1	15.2 ± 0.5[26]
$CH_3SCH_3 \rightarrow CH_3S^+ + CH_3$	11.24 ± .1	11.38[10]
$CH_3SSCH_3 \rightarrow CH_3S^+ + CH_3S$	11.12 ± .1	11.38[10]

---

(5) A. G. Gaydon and G. W. Whittingham, *Proc. Roy. Soc.* (London), **A189**, 313 (1947).

(6) P. J. Dyne and D. W. G. Style, *Nature*, **167**, 899 (1951).

(7) G. Porter, *Discussions Faraday Soc.*, **9**, 60 (1950).

(8) D. A. Ramsay, *J. Chem. Phys.*, **20**, 1920 (1952).

(9) J. W. C. Johns and D. A. Ramsay, *Can. J. Phys.*, **39**, 210 (1961).

(10) J. L. Franklin and H. E. Lumpkin, *J. Am. Chem. Soc.*, **74**, 1023 (1952).

(11) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

(12) A. Sehon, *J. Am. Chem. Soc.*, **74**, 4722 (1952).

(13) A. Sehon and B. de B. Darwent, *ibid.*, **76**, 4806 (1954).

(14) E. H. Braye, A. H. Sehon and B. de B. Darwent, *ibid.*, **77**, 5282 (1955).

(15) H. Mackle and R. G. Mayrick, *Trans. Faraday Soc.*, **58**, 33 (1962).

(16) M. H. Back and A. H. Sehon, *Can. J. Chem.*, **38**, 1076 (1960).

(17) J. B. Farmer and F. P. Lossing, *ibid.*, **33**, 861 (1955).

(18) J. B. de Sousa and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 281 (1959).

(19) A. G. Harrison, L. R. Honnen, H. J. Dauben, Jr., and F. P. Lossing, *ibid.*, **82**, 5593 (1960).

(20) C. D. Hurd and H. Greengard, *ibid.*, **52**, 3357 (1930).

(21) C. E. Moore, *National Bur. Standards Circ.* **467**, Vol. II, 1952.

(22) W. C. Price, J. P. Teegan and A. D. Walsh, *Proc. Roy. Soc.* (London), **A201**, 600 (1950).

(23) J. D. Morrison, *J. Chem. Phys.*, **19**, 1305 (1951).

(24) K. Watanabe, *ibid.*, **26**, 542 (1957).

(25) F. H. Field and J. L. Franklin, "Electron Impact Processes," Academic Press, Inc., New York, N. Y., 1957.

(26) H. Neuert and H. Clasen, *Z. Naturforsch.*, **7a**, 410 (1952).

TABLE II

HEATS OF FORMATION AND BOND DISSOCIATION ENERGIES

Species	ΔH_f(R)	ΔH_f(R$^+$)	Bond	Dissociation energy This work	 Lit.
HS	≤ 33.7	≤ 275.9	D(HS–H)	≤ 90.6	92.2 ± 2^{11} $89 \pm 4^{12,13}$ 95.3^{10a}
			D(CH$_3$–SH)	≤ 71.6	74.2^{10a} 67^{13}
			D(H–S)	≤ 84.6	84.9 ± 5^{7} 81.4 ± 3^{9}
CH$_3$S	≤ 31.8	≤ 217.7	D(CH$_3$S–H)	≤ 89.3	88.8^{10a} 93.3^{10b} 88 ± 5^{15}
			D(CH$_3$S–CH$_3$)	≤ 73.3	73.2^{10a} 77.3^{10b} 72 ± 5^{15}
			D(CH$_3$S–SCH$_3$)	$\leq 69.4^{c}$	73.2^{10a} 77.3^{10b} 67 ± 6^{15}
			D(CH$_3$–S)	≤ 66.9	69 ± 5^{15}

[a] From ref. 10 without recalculation. [b] Recalculated using $\Delta H_f(CH_3SH) = -5.4$ kcal./mole (ref. 28), $\Delta H_f(CH_3SCH_3) = -8.98$ kcal./mole (ref. 32), $\Delta H_f(CH_3SSCH_3) = -5.75$ kcal./mole (ref. 33). [c] Based on $\Delta H_f(CH_3S) \leq 31.8$. By the direct method, $D(CH_3S–SCH_3) \leq A(CH_3S^+)_{CH_3SSCH_3} - I(CH_3S) = 70.6$ kcal./mole.

their appearance potential using the "linear extrapolation" method which is unreliable for fragment ions. Evaluation of the appearance potential from the curves for HS$^+$ and A$^+$ given in Fig. 1 of their paper, using the "vanishing-current" method, gives about 14.7 for A(HS$^+$), a value much closer to that found in the present work. Evaluation of our data by the "vanishing-current" and "extrapolated voltage difference" methods[25] gave 14.45 ± 0.1 and 14.55 ± 0.1 v., respectively, in good agreement with the "semi-logarithmic" method. $A(HS^+) = 14.43$ v., together with $\Delta H_f(H_2S) = -4.82$ kcal./mole[27] gives $\Delta H_f(HS)^+ \leq 275.9$ kcal./mole. Subtracting $I(HS) = 10.50$ v. gives $\Delta H_f(HS) \leq 33.7$ kcal./mole. This corresponds to $D(HS–H) \leq 90.6$ kcal./mole. As shown in Table II, this result is in excellent agreement with the earlier values of $D(HS–H) = 92.2 \pm 2$ kcal./mole and 89 ± 4 kcal./mole given above and is only slightly lower than the value obtained by Franklin and Lumpkin.[10] The value of D(CH$_3$–SH) given in Table II was calculated using $\Delta H_f(CH_3SH) = -5.4$ kca./mole[28] and $\Delta H_f(CH_3) = 32.5$ kcal./mole.[29]

To calculate D(H–S) in HS radical requires ΔH_f(S)g which is not known with certainty. From spectroscopy three values for D(S–S) are possible, 76.1, 83.0 and 101.5 kcal./mole.[30] Using $\Delta H_f(S_2) = 30.8$ kcal./mole,[27] these values correspond to $\Delta H_f(S)_g = 53.5$, 56.9 and 66.2 kcal./mole. Consequently the sum $D(HS–H) + D(H–S)$ has one of the values 162.5, 165.9 or 175.2 kcal./mole. If D(HS–H) is about 91 kcal./mole, as indicated above, then D(H–S) would have the possible values 72, 75 or 84 kcal./mole. Of these, only the latter is in good agreement with $D(H–S) = 84.9 \pm 5$ or 81.4 ± 3 kcal./mole as found by Porter[7] and Johns and Ramsay,[9] respectively. The present data therefore are consistent with $D(S–S) = 101.5$ kcal./mole. Support for this value for D(S–S), based on a mass spectrometric study of the vapor phase above CaS, has recently been put forward by Goldfinger, *et al.*[31]

The CH$_3$S Radical.—The observed vertical ionization potential of the CH$_3$S radical, 8.06 ± 0.1 v. (Table I) is close to a value of 8.2 v. derived[25] from the appearance potentials of fragment ions in (CH$_3$)$_2$S and (CH$_3$)$_2$S$_2$.[10] It is interesting to note that although the addition of a hydrogen atom to a sulfur atom causes little change in the ionization potential (see above), the addition of a CH$_3$-group to S atom reduces the ionization potential by 2.4 v.

The appearance potential found in this work for CH$_3$S$^+$ from CH$_3$SCH$_3$ is 11.24 ± 0.1 v., in close agreement with that found by Franklin and Lumpkin[10] (Table I). From $\Delta H_f(CH_3SCH_3) = -8.98$ kcal./mole[32] this appearance potential gives $CH_3S^+ \leq 217.7$ kcal./mole. Subtracting $I(CH_3S) = 8.06$ v. gives $\Delta H_f(CH_3S) \leq 31.8$ kcal./mole. This value is significantly lower than the value of 36 kcal./mole recalculated[15] from Franklin and Lumpkin's appearance potentials[10] using more recent heats of formation for CH$_3$SCH$_3$[32] and CH$_3$SSCH$_3$ (−5.75 ± 0.2 kcal./mole).[33] The CH$_3$S–R bond dissociation energies based on these heats of formation and on $\Delta H_f(CH_3S) \leq 31.8$ kcal./mole are given in Table II, together with other values from the literature. The present results are in agreement with the conclusions of Mackle and Mayrick[15] that D(CH$_3$S–CH$_3$) is stronger than D(CH$_3$S–SCH$_3$) by about 4 kcal./mole. A redetermination of the appearance potential of CH$_3$S$^+$ from CH$_3$SSCH$_3$ (A_2) gave a value slightly lower than that of CH$_3$S$^+$ from CH$_3$SCH$_3$ (A_1) as shown in Table I, in contrast to the earlier results.[10]

---

(27) W. H. Evans and D. D. Wagman, *J. Research Nat. Bur. Standards*, **49**, 141 (1952).

(28) T. L. Allen, *J. Chem. Phys.*, **31**, 1039 (1959).

(29) H. A. Skinner, "Modern Aspects of Thermochemistry," Lectures, Monographs and Reports No. 3, The Royal Institute of Chemistry, London, 1958.

(30) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules," 2nd Ed., Chapman and Hall, London, 1953.

(31) R. Colin, P. Goldfinger and M. Jeunehomme, *Nature*, **187**, 408 (1960).

(32) J. P. McCullough, W. N. Hubbard, F. R. Frow, I. A. Hossenlopp and G. Waddington, *J. Am. Chem. Soc.*, **79**, 561 (1957).

(33) W. N. Hubbard, D. R. Douslin, J. P. McCullough, D. W. Scott, S. S. Todd, J. F. Messerly, I. A. Hossenlopp, A. George and G. Waddington, *ibid.*, **80**, 3547 (1958).

This difference, although small, is probably significant. It corresponds to a difference of 2.8 kcal./mole in the bond dissociation energies.

From the appearance potentials A_1 and A_2, it is possible to derive by the indirect method a value for $I(CH_3S)$ which is independent of the direct measurement of this ionization potential given above. From the relationships

$$A_1 = \Delta H_f(CH_3S^+) + \Delta H_f(CH_3) - \Delta H_f(CH_3SCH_3)$$
$$A_2 = \Delta H_f(CH_3S^+) + \Delta H_f(CH_3S) - \Delta H_f(CH_3SSCH_3)$$

one can derive

$$I(CH_3S) = 2A_1 - A_2 - 2\Delta H_f(CH_3) + 2\Delta H_f(CH_3SCH_3) - \Delta H_f(CH_3SSCH_3) = 8.01 \text{ v.}$$

The good agreement of this indirect value with the direct value of 8.06 v. shows that the two appearance potentials and the vertical ionization potential are self-consistent within ± 0.05 v.

The appearance potential of the phenylsulfide ion from $C_6H_5SCH_3$ was found to be 12.1 ± 0.1 v. When combined with $I(C_6H_5S)$ this appearance potential leads to a value for $D(C_6H_5S{-}CH_3)$ which is about 20 kcal./mole higher than the 60 kcal./mole proposed for this bond by Back and Sehon.[16] Evidently this appearance potential corresponds to the formation of a $C_6H_5S^+$ ion with a considerable amount of excitation energy. The ionization efficiency curve for $C_6H_5S^+$ ion formed from phenyl disulfide showed considerable tailing, and no reliable estimate of the appearance potential could be made. The present work therefore yields no value for $\Delta H_f(C_6H_5S^+)$ or $\Delta H_f(C_6H_5S)$.

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY]

Kinetics of Proton Transfer in Methanol and the Mechanism of the Abnormal Conductance of the Hydrogen Ion

BY ERNEST GRUNWALD,[1] CHARLES F. JUMPER AND S. MEIBOOM

RECEIVED JULY 13, 1962

This paper reports a nuclear magnetic resonance study of the rate of proton transfer between methyloxonium ion and methanol, and between methoxide ion and methanol. The measurements were made on buffered solutions and extrapolated to zero buffer concentration. The results at 24.8° can be summarized by the equation

$$\text{Rate of proton exchange} = 8.8 \times 10^{10}[MeOH_2^+] + 1.8_5 \times 10^{10}[MeO^-] \text{ mole l.}^{-1} \text{ sec.}^{-1}$$

The enthalpy of activation for the methyloxonium rate is about 2 kcal. On the assumption of a specific model for the proton transfer a value for the abnormal conductance of the hydrogen ion can be calculated and compared with the experimental value. The models tested are a random walk and various versions of structural diffusion. A good agreement is obtained for two structural diffusion mechanisms; a simple random walk model is unsatisfactory. The abnormal equivalent conductance of the methoxide ion is too small to be estimated from conductance measurements. From the measured rate of proton exchange a value of 8.4 Ω^{-1} cm.^{2} is estimated.

Introduction

In water the abnormal conductance of hydrogen ion and hydroxide ion can be accounted for quantitatively on the basis of proton transfer between H_3O^+ or OH^- and H_2O.[2] In methanol some recent measurements[3] suggest that proton exchange between methyloxonium ion and methanol is too slow to account for the abnormal conductance of hydrogen ion. The present work was undertaken to check this point, because its confirmation would imply that most of the abnormal conductance in methanol is due to the motion of "bare" (or loosely bonded) protons. However, our new measurements show that the previous results[3] were quantitatively in error, and that actually the abnormal conductance in methanol is due to proton jumps involving methyloxonium ions.

The cause of the error in the previous measurements has been traced to the use of unbuffered solutions containing hydrochloric acid at extremely low concentrations. The new measurements were therefore made in buffered solutions containing a carboxylic acid and its sodium salt. Under these conditions there was some proton exchange between methanol and the buffer components, but this contribution to the exchange rate was eliminated by extrapolation to zero buffer concentration.

By using suitable buffers and buffer ratios, we were able to measure the rate constant not only for the proton exchange between methyloxonium ion and methanol, but also for the proton exchange between methoxide ion and methanol. The latter rate constant is smaller than the former by a factor of about 10. On the basis of this result, about one-fifth of the conductance of methoxide ion in methanol at 25° can be ascribed to proton transfer.

Measurement and Calculation of Reaction Rates.—Rate measurements were based on the nuclear magnetic resonance (n.m.r.) spectrum of the CH_3 protons of methanol. Because of spin-spin coupling with the OH proton, the CH_3 resonance is a doublet which, however, is broadened or collapsed into a single line as a result of the chemical exchange of the OH protons. The shape and width of the CH_3 resonance provides a direct measure of the rate of proton spin inversion of the OH proton.

The calculations made use of previously reported equations for an exchange-broadened doublet,[4]

---

[1] Alfred P. Sloan Fellow, 1960–1961.

[2] S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961).

[3] Z. Luz, D. Gill and S. Meiboom, *ibid.*, **30**, 1540 (1959).

[4] (a) A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957); (b) "Tables of Exchange Broadened N-M-R Multiplets," Technical Note No. 2, Contract No. AF 61(052)-03, between the U. S. Air Force and the Weizmann Institute of Science, Rehovoth, Israel, 1958; Astia No. AD-213 032; (c) H. S. Gutowsky, D. W. McCall and C. P. Slich-