

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 $I(\text{CH}_3\text{S})$ which is independent of the direct measurement of this ionization potential given above. From the relationships

$$A_1 = \Delta H_f(\text{CH}_3\text{S}^+) + \Delta H_f(\text{CH}_3) - \Delta H_f(\text{CH}_3\text{SCH}_3)$$

$$A_2 = \Delta H_f(\text{CH}_3\text{S}^+) + \Delta H_f(\text{CH}_3\text{S}) - \Delta H_f(\text{CH}_3\text{SSCH}_3)$$

one can derive

$$I(\text{CH}_3\text{S}) = 2A_1 - A_2 - 2\Delta H_f(\text{CH}_3) + 2\Delta H_f(\text{CH}_3\text{SCH}_3) - \Delta H_f(\text{CH}_3\text{SSCH}_3)$$

$$= 8.01 \text{ v.}$$

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 $\text{C}_6\text{H}_5\text{SCH}_3$ was found to be 12.1 ± 0.1 v. When combined with $I(\text{C}_6\text{H}_5\text{S})$ this appearance potential leads to a value for $D(\text{C}_6\text{H}_5\text{S}-\text{CH}_3)$ which is about 20 kcal./mole higher than the 60 kcal./mole proposed for this bond by Back and Sehon.¹⁸ Evidently this appearance potential corresponds to the formation of a $\text{C}_6\text{H}_5\text{S}^+$ ion with a considerable amount of excitation energy. The ionization efficiency curve for $\text{C}_6\text{H}_5\text{S}^+$ 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 $\Delta H_f(\text{C}_6\text{H}_5\text{S}^+)$ or $\Delta H_f(\text{C}_6\text{H}_5\text{S})$.

[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

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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

$$\text{Rate of proton exchange} = 8.8 \times 10^{10}[\text{MeOH}_2^+] + 1.85 \times 10^{10}[\text{MeO}^-] \text{ mole l.}^{-1} \text{ sec.}^{-1}$$

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 $8.4 \Omega^{-1} \text{ cm.}^2$ 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 measurements³ 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 results³ 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. Slichter,

TABLE I
THEORETICAL CALCULATIONS FOR EXCHANGE-BROADENED
SPIN-SPIN DOUBLETS

r	Ratio, for t			
	0.050	0.075	0.100	0.150
1.5	1.003	1.001
2.0	1.246	1.210	1.180	1.129
2.5	1.655	1.574	1.504	1.386
3.0	2.157	2.012	1.888	1.687
3.5	2.734	2.504	2.312	2.011
4.0	3.365	3.037	2.765	2.348
4.5	4.051	3.603	3.240	2.690
5.0	4.784	4.197	3.727	3.034
5.5	...	4.812	4.224	3.376
6.0	...	5.445	4.730	3.714
6.5	5.240	4.048
7.0	4.379
7.5	4.702

except that at fast exchange rates a quantum correction was made.⁵ The treatment assumes that the chemical shift is large compared to the spin-spin interaction. Since a detailed description of the rate calculations has not been given previously, we wish to do so now.

The rate of proton spin inversion will be characterized by a time τ , defined as

$$1/\tau \equiv 2 \times \frac{\text{rate of proton spin inversion of the OH group}}{[\text{MeOH}]} \quad (1)$$

There are two contributions to the spin inversion rate: chemical exchange, and spontaneous inversion. The latter can be characterized by the relaxation time T_1 of the OH protons. Hence

$$1/\tau = 1/T_1 + R/[\text{MeOH}] \quad (2)$$

where R is the rate of the proton exchange.⁶

The procedures used for obtaining τ from the observed spectra depend on whether the CH_3 resonance is a broadened doublet or a single peak. For the following it is convenient to introduce two dimensionless parameters

$$r = J\tau \quad (3)$$

$$t = 2/T_2J \quad (4)$$

Here J is the spin-spin interaction (in radians sec^{-1}) and T_2 the transverse relaxation time (line width parameter) of the CH_3 resonance, *i.e.*, the T_2 which would apply if the broadening caused by OH spin inversion were zero.⁸ In practice T_2 is obtained from measurements of samples for which r is small enough for this broadening to be neglected.

ter, *J. Chem. Phys.*, **21**, 279 (1953); (d) H. M. McConnell, *ibid.*, **28**, 430 (1958).

(5) (a) I. Solomon and N. Bloembergen, *ibid.*, **25**, 261 (1956); (b) J. Kaplan, *ibid.*, **28**, 278 (1958).

(6) Note that the defining eq. 1 for $1/\tau$ contains the factor 2. In eq. 2 this factor cancels out because of a factor 0.5 in the relation between T_1 and the transition probability⁷ and also a probability of 0.5 that exchange leads to spin inversion.

(7) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Company, Inc., New York, N. Y., 1959, p. 24.

(8) Perhaps it should be stressed that the T_2 introduced here is not the "natural" relaxation time of the CH_3 protons, but rather an effective T_2 , ideally observed under conditions which differ only in the elimination of the broadening due to spin inversion from those existing during the rate determinations. Specifically, in slow passage measurements T_2 includes contributions from such factors as field inhomogeneity and radiation damping.

In the cases where the CH_3 resonance is a broadened doublet, the ratio of the maximum amplitude of the doublet to the central minimum is a convenient index for τ . Assuming slow passage and negligible saturation, the variation of this ratio with r and t was calculated on the basis of the Bloch equations.^{4,9} The results are given in Table I. The table can be extended to larger values of r by using the asymptotic equation

$$\text{Ratio} = \frac{1 + 1.5t^2 + 3.5tr^{-1} + 0.75r^{-2}}{2t^2 + 6tr^{-1} + 4r^{-2}} \quad (5)$$

For values of r higher than those given in the table, the accuracy of eq. 5 is better than 1%.

When the CH_3 resonance is a single peak, the width of the exchange-broadened line provides a suitable measure for the exchange rate. It is convenient to express the observed width in the form of a relaxation time T_2' , as

$$1/T_2' = \pi \times (\text{full width of the line at half maximum height, in c.p.s.}) \quad (6)$$

In the limiting case of fast exchange, so that $(1/T_2' - 1/T_2) \ll J$, the relationship to τ is given by⁵

$$(1/T_2' - 1/T_2) = \frac{J^2\tau}{4} \left(1 + \frac{1}{1 + \delta^2\tau^2}\right) \quad (7)$$

Here δ is the chemical shift (in radians sec^{-1}) between the two kinds of protons causing the spin-spin splitting J . (In the present problem δ is the chemical shift between the CH_3 and OH protons.) It is assumed throughout that δ is large compared to J . If $\delta/J > 20$, eq. 7 holds to better than 1% in τ for $\tau J < 0.2$.

The last factor in eq. 7 is a quantum correction. This factor is absent in the corresponding "classical" expression^{4,9} derived from the Bloch equations.

For greater values of τ the line width can be obtained from tables of calculated line shapes.^{4b,10} It turns out that the tables and eq. 7 can be condensed conveniently into the single equation

$$(1/T_2' - (1-a)/T_2) = \frac{J^2\tau}{4} f \left(1 + \frac{1}{1 + \delta^2\tau^2}\right) \quad (8)$$

Here f and a are correction factors depending only on r ($\equiv \tau J$) and are given in Table II. The ap-

TABLE II
CORRECTION FACTORS f AND a IN THE TREATMENT OF DATA
FOR A COLLAPSED SPIN-SPIN DOUBLET

$r = J\tau$	f	a
1.5	1.408	0.56
1.4	1.403	.53
1.2	1.366	.41
1.0	1.242	.21
0.8	1.155	.10
.65	1.105	.04
.5	1.064	.01
.35	1.029	.00
.25	1.016	.00

proximation (8) is accurate to 1% or better, provided $\delta/J > 20$. In calculating r (and τ) from

(9) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(10) The "classical" theory is sufficiently accurate for this purpose because it will be applied only in the range where $r\delta \gg 1$ and the quantum correction is therefore negligible.

TABLE III
N.M.R. CONSTANTS FOR LIQUID METHANOL

Temp., °C.	$\delta(\pm 0.5\%)$ (radians/ sec.)	$J(\pm 1\%)^a$ (radians/ sec.)	$-1/T_1$ (sec. ⁻¹) ^b	
			CH ₃	OH
24.8	591	32.4	0.300	0.299
- 0.1	..	32.3
-40.3	801	31.7
-60.3	857	31.2
-81.6	910	31.2	1.45	2.10

^a Corrected for $1/T_2$ and $1/\tau$ effects, H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1229 (1956). ^b Air-saturated. At -81.6° , $1/T_1$ for outgassed methanol is 0.98 sec.⁻¹ for the CH₃ protons and 1.63 sec.⁻¹ for the OH protons.

an experimental line width, applicable values of f and a are obtained by successive approximations.

For the actual calculation of τ from the above equations, the values of J , δ and T_1 have to be known. Our measurements of these quantities for methanol are summarized in Table III.

Experimental

N.m.r. Spectrometer.—The spectrometer was a modified Varian HR60 high resolution spectrometer. All proton spectra were taken at 60 Mc. Field homogeneity was carefully adjusted and checked at frequent intervals. The contribution to $1/T_2$ due to field inhomogeneity was never greater than 1.0 sec.⁻¹. The spectrometer was in an air-conditioned room, the temperature of which did not vary by more than 1°. Even so, it was often necessary to make final measurements in the evening or at night in order to assure sufficient stability of magnetic field magnitude and homogeneity.

The modifications introduced in the basic Varian spectrometer will be mentioned here only briefly. A detailed description is planned for publication at a later date. A modification we have found extremely useful is the time-division pulse scheme.¹¹ In this method the transmitter is gated on in short pulses, while the receiver is gated off during the transmitter pulses. Typically the transmitter "on" pulses are 20 μ sec. long and are repeated 1000 times a second. The receiver is "on" 95% of the total time between the transmitter pulses. It is essential that the radio frequency of the transmitter pulses be coherent. But if this condition is fulfilled, ordinary slow passage spectra are obtained, the pulsing being evident only in the appearance of sidebands spaced at multiples of the pulse repetition rate (1000 c.p.s.). The major advantage of the system is excellent base line stability and the elimination of critical probe balancing. These features made it possible to use a simple variable temperature probe instead of the standard Varian probe. The probe consists of an L-shaped evacuated Dewar tube, 2.5 cm. o.d. and 1.3 cm. i.d. The receiver coil and sample tube are in the vertical leg of the Dewar tube. Attached to the top of this leg is a small air turbine for spinning the sample tube. The transmitter coil is glued to the outside of the Dewar tube. The horizontal part of the Dewar tube contains an electrical heater and the leads of a thermocouple, the junction of which is in the bend of the L just below the sample. Dry nitrogen gas, precooled in Dry Ice or liquid nitrogen if low temperatures are desired, is blown through the inside of the Dewar tube flowing first over the heater and then over the sample tube. The temperature is measured and controlled by the thermocouple, a Leeds and Northrup type K3 potentiometer, and a Leeds and Northrup No. 9834 electronic galvanometer. The output of the latter is fed through a Brown servo amplifier to a motor which turns a Variac in the heater circuit of the probe. The system will control the temperature of the sample within $\pm 0.05^\circ$ at temperatures between 0 and 100°, and within $\pm 0.5^\circ$ down to -160° .

The spectrometer was provided with pulse generators (Tektronix types 161 and 162) so arranged that T_1 and T_2 measurements could be made by a modified Carr-Purcell scheme¹² and also by Alexander's method.¹³

(11) As far as we can ascertain this method was originally suggested by J. T. Arnold in 1956 but was not published.

About halfway through this research an additional major modification was made to the spectrometer. Very briefly, this consisted of the introduction of a control probe, providing locking-in of the transmitter frequency with the magnetic field. Two major features of relevance here are: (1) excellent frequency stability, so that slow passage became practicable even for very narrow lines and (2) frequency sweep (instead of the previous field sweep), providing direct frequency calibration of the traces with an electronic counter, without the need of the sideband technique used previously.

Measuring Techniques.—Whenever applicable, ratio measurements were made. These are straightforward and accurate. However, in the majority of cases the exchange was so fast that a single line was observed, and accurate line width measurements, or alternatively T_2 measurements, had to be made. Before the introduction of the frequency stabilization, slow-passage width measurements were sufficiently accurate only on rather wide lines ($1/T_2' > 4$). For narrower lines we measured the decay of the "wiggles" following fast passage, as recorded on a fast (Sanborn) recorder. This method largely eliminates troubles due to field instability. The maxima of the wiggles were read and an exponential decay was fitted by least squares, the necessary calculations being done on a digital computer.

The unavoidable residual inhomogeneity of the magnetic field limits the accuracy of the "wobble" method. In an effort to eliminate this factor, spin-echo measurements using Alexander's method¹⁴ were also made in a number of cases where very narrow lines had to be measured. Comparison of the wiggle and spin-echo methods showed that the wiggle method is often in error, the error ranging up to 20%.

Later measurements, when the frequency stabilization was available, were nearly all made by the slow passage method. Accuracies comparable to those obtained with the spin-echo method could be obtained even on narrow lines.

In interpreting the slow passage line width measurements a correction for saturation was made in the regular manner. This correction was always less than 10%.

Another source of possible error in accurate line width measurements is broadening due to radiation damping.¹⁵ This effect is proportional to the signal amplitude and can be quite appreciable for the strong methanol lines. Our practice has been to detune the receiver coil in the probe so as to reduce the signal by a factor of about three. Under these circumstances the radiation damping could be neglected.¹⁶

Standard thin-walled sample tubes with an outer diameter of 5 mm. were used. In order to obtain high resolution consistently, an initial thorough cleaning is necessary: in the procedure adopted, the glassware was first washed in hot detergent and rinsed. It then was soaked in 2 N HCl for at least one hour, rinsed in water, in dilute ammonia, and again in water.

Chemical Part.—Commercial reagent-grade methanol was dried by treatment with magnesium¹⁶ and distilled, the first and final quarter being discarded. The middle fraction obtained in this way was ca. $10^{-6} M$ in methoxide. A small quantity (ca. 50 mg./l.) of benzoic acid was therefore added and the resulting solution again distilled, only the middle one-half being collected. The methanol purified by this method had a hydrogen ion concentration between 10^{-8} and $10^{-9} M$ (as deduced from a measurement of $1/\tau$), contained no titratable acids or bases, and had a water content that was always less than 0.01 M and usually less than 0.003 M .

Benzoic acid (reagent grade) and *o*-nitrobenzoic acid (Eastman white label) were further purified by three recrystallizations from boiling water. *p*-Nitrobenzoic acid (Eastman white label) was recrystallized from pure methanol, and *m*-nitrobenzoic acid (Eastman white label) from methanol-water. The purified acids were dried *in vacuo* over anhy-

(12) S. Meiboom and D. Güll, *Rev. Sci. Instr.*, **29**, 688 (1958).

(13) S. Alexander, *ibid.*, **32**, 1066 (1961).

(14) A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, New York, N. Y., 1961, p. 73.

(15) Radiation damping is effective also in wiggle decay measurements, but not in spin-echo. Saturation is effective only in slow passage.

(16) N. Bjerrum and L. Zechmeister, *Ber.*, **56**, 894 (1923).

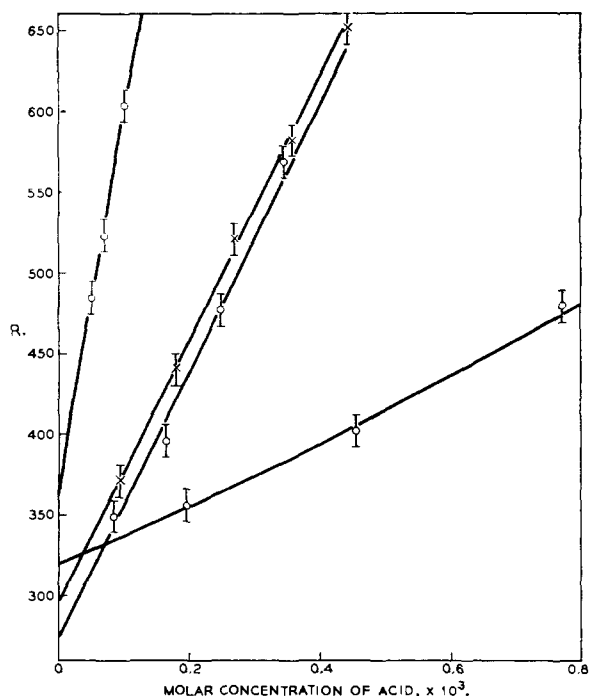


Fig. 1.—Extrapolation of R to zero buffer concentration for (left to right): *o*-nitrobenzoic acid (buffer ratio 0.122), *m*-nitrobenzoic acid (buffer ratio 0.273), *p*-nitrobenzoic acid (buffer ratio 0.310), benzoic acid (buffer ratio 2.31).

drous magnesium perchlorate. Their melting points were sharp and agreed with literature values.

Solutions of sodium methoxide in methanol were prepared from pure methanol and reagent grade sodium. The latter was freed from surface impurities by rinsing in ether, then by several "rinsings" in pure methanol. The sodium methoxide concentration was determined by titration with standard acid. Constant-boiling hydrochloric acid served as the ultimate acidimetric standard.

Buffered solutions in methanol were prepared by standard quantitative techniques from pure methanol, the carboxylic acid, and standard sodium methoxide. The rate measurements were made only on freshly prepared solutions. At the conclusion of a series of measurements the water content of each solution was checked by Karl Fischer titration and was always less than 0.02 M . The acid-base ratio was verified by potentiometric titration in anhydrous methanol, using glass and calomel microelectrodes, and was usually within 2% of the calculated value.

Unbuffered solutions of hydrochloric acid in methanol were prepared from pure solvent and either the constant-boiling acid or hydrogen chloride gas. The latter was generated from sodium chloride and concentrated sulfuric acid in an all-glass apparatus. At very low concentrations ($< 10^{-6} M$), ion exchange of hydrogen ions from the solution with neutral ions from the glass wall of the container appreciably reduced the hydrogen ion concentration in the solution. This effect could be greatly reduced by the treatment of the glassware: a thorough cleaning with detergent and rinsing was followed by soaking for 24 hours with HCl in methanol of the same nominal concentration as that to be used in the rate measurement. The glassware then was rinsed with pure methanol and dried.

Rate Measurements in Buffered Solutions.—The experiments were performed by preparing series of solutions of constant buffer ratio, and measuring the proton exchange rate, R . For each series, R was plotted against the buffer concentration, and the curve (which was nearly linear at low concentrations) was extrapolated to zero concentration. Representative plots are shown in Fig. 1. The values of R increase with the buffer concentration because the components of the buffer also exchange with methanol. The intercepts R_0 at zero buffer concentration are due to proton exchange involving CH_3OH_2^+ , CH_3OH and CH_3O^- .

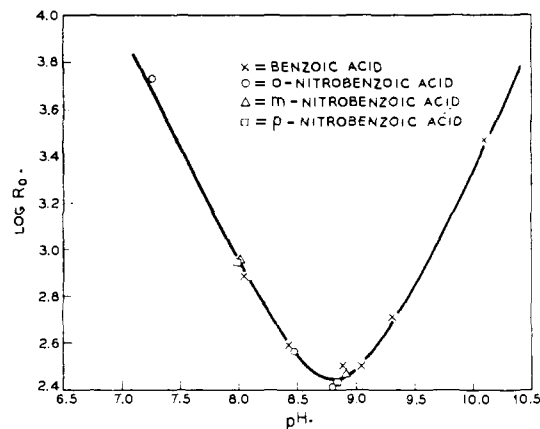


Fig. 2.—Catalytic catenary for proton transfer in methanol, 25°.

This method has the advantage that even very low hydrogen ion concentrations are accurately known, and the method minimizes the effect of traces of water in the solvent.^{17,18}

Buffer Acids.—The method requires that K_A for the buffer acids in methanol be accurately known. This requirement greatly restricts the choice of acids, because the number of acids for which it is satisfied is surprisingly small. We have used a series of substituted benzoic acids for which closely concordant K_A values have been obtained by colorimetric^{17,19} and conductometric²⁰ methods.²¹ Our averages of these values are included in Table IV.

Rate Law.—Extrapolated values for the rate of proton exchange at zero buffer concentration R_0 , are given in Table IV, and their logarithms are plotted versus $\log [\text{MeOH}_2^+]$ in Fig. 2. The plot is a typical catalytic catenary, indicating that the exchange is catalyzed both by methyloxonium ion and methoxide ion. The rate law which fits these data is

$$R_0 = k_{\text{MeOH}_2^+} [\text{MeOH}_2^+] + k_{\text{MeO}^-} K_w / [\text{MeOH}_2^+] \quad (9)$$

At 24.8° these rate constants give "best fit," the standard error of fit being 5.6%

$$k_{\text{MeOH}_2^+} = 8.79 \times 10^{10} \text{ sec.}^{-1}$$

$$k_{\text{MeO}^-} K_w = 2.25 \times 10^{-7} \text{ sec.}^{-1} M^2$$

An accurate recent determination of the autoprotolysis constant of methanol²² leads to $K_w = 1.21 \times 10^{-17} (M^2)$ at 25°. Hence $k_{\text{MeO}^-} = 1.85 \times 10^{10} \text{ sec.}^{-1}$.

The uncatalyzed exchange of methanol is sufficiently slow so that there is no need to include a kinetic term independent of the hydrogen ion concentration. On the basis of our data, the upper limit of the rate of uncatalyzed exchange is 10 moles liter⁻¹ sec.⁻¹.

Rate Measurements in Unbuffered Solutions.—Inasmuch as the new value for $k_{\text{MeOH}_2^+}$ is forty times greater than that reported previously with unbuffered solutions,³ we decided to do a few experiments in unbuffered solutions to see whether we could reduce the discrepancy. We used the highest acid concentrations at which rate measurements are still practical. By working in the concentration range from 10^{-6} to $10^{-8} M$ we found the line-broadening due to exchange to be 10–50% of the natural line width. Our results

(17) I. M. Kolthoff and L. S. Guss, *J. Am. Chem. Soc.*, **61**, 330 (1939); **62**, 1494 (1940).

(18) (a) H. Goldschmidt and P. Dahll, *Z. physik. Chem.*, **108**, 121 (1924); (b) J. Koskikallio, *Suomen Kemistilehti*, **30B**, 43 (1957).

(19) M. Kilpatrick and C. A. Arenberg, *J. Am. Chem. Soc.*, **75**, 3812 (1953). M. Kilpatrick and W. H. Mears, *ibid.*, **62**, 3047 (1940).

(20) H. Goldschmidt and E. Mathiesen, *Z. physik. Chem.*, **119**, 452 (1926); H. Goldschmidt and F. Aas, *ibid.*, **112**, 423 (1924).

(21) Results obtained for benzoic acid by a potentiometric method using the Pt-H₂ electrode [L. D. Goodhue and R. M. Hixon, *J. Am. Chem. Soc.*, **56**, 1331 (1934)], do not agree well with the colorimetric and conductometric ones, possibly because of catalytic hydrogenation.

(22) J. Koskikallio, *Suomen Kemistilehti*, **30B**, 111, 155 (1957). This value is in good agreement with S. Buckley and H. Hartley, *Phil. Mag.*, **78**, 320 (1929), but differs by a factor of two from the value of N. Bjerrum, A. Unmack and L. Zechmeister, *Kgl. Dansk. Vid. Selsk. Mat. Fys. Medd.*, **5**, 11 (1924).

TABLE IV
VALUES OF THE INTERCEPTS R_0 FOR BUFFERED SOLUTIONS
OF CARBOXYLIC ACIDS IN METHANOL AT 24.8°

[HA]/[NaA]	[MeOH ₂ ⁺] × 10 ⁹ (M × sec. ⁻¹)	R_0 (M × sec. ⁻¹)	R_0 (calcd.) ^a
Benzoic acid, pK_a 9.409			
22.7	8.85	764	803
9.45	3.69	387	385
9.29	3.62	385	380
4.10	1.60	270	281
3.32	1.29	317	287
2.31	0.901	319	328
1.25	0.486	511	505
0.204	0.0798	2930	2820
<i>o</i> -Nitrobenzoic acid, pK_a 7.556			
1.975	54.9	5430	4830
0.122	3.40	368	365
0.0574	1.60	260	281
<i>m</i> -Nitrobenzoic acid, pK_a 8.344			
2.18	9.85	921	889
0.273	1.23	295	291
<i>p</i> -Nitrobenzoic acid, pK_a 8.326			
2.19	10.35	889	932
0.310	1.46	273	282

^aEq. 9; $k_{MeOH_2^+} = 8.79 \times 10^{10} \text{ sec.}^{-1}$, $k_{MeO^-}K_w = 2.25 \times 10^{-7} \text{ sec.}^{-1} M^2$.

are listed in Table V. By pretreating the glassware with methanolic HCl of the same nominal concentration as that used in the experiment, we were able to obtain rate constants which were remarkably consistent, considering the experimental difficulties. Failure to pretreat resulted in appreciable reduction of rate at concentrations below about $5 \times 10^{-4} M$, presumably due to ion exchange with sodium ions in the glass. The apparent rate constant at 24.8° is within a factor of two of the value obtained in buffered solutions. Since the likelihood that the K_A values are in error by a factor of two is very small, we suspect that the discrepancy is due to traces (possibly as little as $10^{-4} M$) of a weakly basic impurity in the methanol solvent. This impurity would have to be a very weak base (the solvent was always found to be nearly neutral by the sensitive method of n.m.r. analysis) and would cause little error in the buffered solutions. In any case, our experiments reduce the discrepancy from a factor of forty to a factor of two.

TABLE V
RATES OF EXCHANGE OF OH-PROTONS AS A FUNCTION OF
NOMINAL HCl CONCENTRATION IN METHANOL CONTAINING
~0.005 M WATER

Nominal HCl concn., M	R (M sec. ⁻¹)	k_{apparent} (sec. ⁻¹)
Measurements at 24.8° (by spin-echo)		
4.6×10^{-5}	2.0×10^{10a}	4.3×10^{10}
2.3×10^{-5}	1.1×10^{10a}	4.9×10^{10}
0.82×10^{-5}	3.6×10^{10d}	4.4×10^{10}
0.41×10^{-5}	$1.4_1 \times 10^{10d}$	3.5×10^{10}
Measurements at -81.6° (by slow passage n.m.r.) ^e		
1.68×10^{-5}	3.4×10^{10e}	2.0×10^9
0.85×10^{-5}	2.2×10^{10e}	2.6×10^9
0.28×10^{-4}	5.4×10^{10b}	1.9×10^9
0.28×10^{-5}	$(2.0 \times 10^9)^a$...

^a Sample tubes thoroughly cleaned with methanol but not pretreated with HCl. ^b Sample tubes pretreated for 24 hrs. with HCl of the same nominal concentration. ^c Results obtained by method a and b did not differ significantly. An average is reported. ^d Sample tubes rinsed with HCl of the same nominal concentration. ^e Average values of R, based on separate measurements for the CH₃ and OH proton resonances.

In Table V the results of measurements at -81.6° are also given. In view of the difficulties mentioned above, the reliability of these results is doubtful. However, they do indicate the order of magnitude of the temperature coefficient of the exchange rate, the enthalpy of activation being estimated as 2.3 kcal.²³ Unfortunately, the total absence of accurate K_A values in methanol far from room temperature prevents us from obtaining a more accurate value by means of buffered solutions.

The rate constant k_{MeO^-} obtained in the buffered solutions at 25° also exceeds the value reported previously,⁸ by a factor of 80. We therefore tried some rate measurements in buffered solutions of sodium methoxide, but consistent results could not be obtained.

Discussion

Proton Exchange and Abnormal Conductance of Hydrogen Ion.—In discussing the acid-catalyzed proton transfer process, we shall use the rate constant obtained in the buffered solutions, that is $k_{MeOH_2^+} = 8.79 \times 10^{10} \text{ sec.}^{-1}$. The limit of error of this value is about ±10%, not counting possible error in K_A . If the error in K_A is measured by the agreement between the colorimetric and conductometric values, that error amounts to about ±10%, and hence the error in $k_{MeOH_2^+}$ to ±15%.

In order to relate the proton exchange rate with the abnormal conductance, we begin with

$$\rho^2 = 6tD_{H^+,abn} = 5.355 \times 10^{-9} t\Lambda_{H^+,abn}^0 \quad (10)$$

In this equation t is the time required for the protonic charge to move a root-mean-square distance ρ by the abnormal mechanism and $D_{H^+,abn}$ is the abnormal contribution to the diffusion coefficient of the formal hydrogen ion species. $D_{H^+,abn}$ can be expressed in terms of the $\Lambda_{H^+,abn}^0$, the abnormal part of the equivalent conductance of the hydrogen ion, as in the second part of eq. 10. We shall estimate the latter from

$$\Lambda_{H^+,abn}^0 = \Lambda_{HCl}^0 - \Lambda_{KCl}^0 \quad (11)$$

The choice of KCl as the model substance for estimating the normal conductance of HCl is rather arbitrary but is not very critical, because the total, or formal value, of $\Lambda_{H^+}^0$ is about three times that for "normal" cations such as the potassium ion.²⁴ Experimental values for Λ^0 are given in Table VI.

The next step is to calculate ρ^2 from a microscopic model of the diffusion process. We shall consider a number of models for the diffusion mechanism.

TABLE VI
ABNORMAL CONDUCTANCE FOR THE HYDROGEN ION IN
METHANOL

Temp., °C.	Λ_{HCl}^0 (ohm ⁻¹ cm. ²)	Λ_{KCl}^0 (ohm ⁻¹ cm. ²)	$\Lambda_{H^+,abn}^0$ (ohm ⁻¹ cm. ²)
25°	193.2	104.9	88.3
15°	173.0	90.7	82.3
4°	150.4	76.5	73.9
-78.8° ^b	29	9	20

^a A. G. Ogston, *Trans. Faraday Soc.*, 32, 1679 (1936).

^b Our measurements.

1. The simplest model is that of an isotropic random walk. In this model it is assumed that the directions of successive proton transfers are uncor-

(23) In computing this value, the averages of k_{apparent} were corrected for the decrease in the methyloxonium ion concentration due to the 0.005 M water in the solvent: K_A of $H_3O^+ = 0.23$ (M) at 25°^{11,18} and 0.011 at -78.8° (own measurements).

(24) For a summary, see B. E. Conway, "Electrochemical Data," Elsevier Publishing Co., New York, N. Y., 1952, pp. 155, 162, 145.

related. This applies if the lifetime of the methyloxonium ion is long enough to permit its complete reorientation. Because of the assumed rapid reorientation of the molecules, the distance l over which the formal charge is transferred, has to be taken in this case as the average diameter of the methanol molecule. A reasonable estimate of this distance is obtained from the molar volume, assuming random packing of spheres. The result is $l = 4.2 \text{ \AA}$. For a random walk of n steps we have the well-known equation

$$\bar{r}^2 = nl^2 \quad (12)$$

Substituting this into (10) and defining the average time interval between steps as $\theta = t/n$, we have

$$l^2 = 6D_{H^+,abn}\theta \quad (13)$$

The average time interval θ is related to the measured rate of proton exchange by

$$1/\theta = 2k_{MeOH_2^+} \quad (14)$$

The factor two in (14) appears because the transfer process consists of the addition of a proton to a methanol molecule followed by the removal of a proton. There is a chance of 0.5 that the outgoing proton is the same as the one that was added, and thus that no exchange results.

Using the measured value of $k_{MeOH_2^+}$ and the value $l = 4.2 \text{ \AA}$, applicable to the random walk model under discussion, we can obtain a calculated value for $\Lambda_{H^+,abn}^0$ from eqs. 10, 13 and 14. The result is $190 \text{ ohm}^{-1} \text{ cm}^2$ at 25° . This is more than twice the experimental value of about 88, indicating that the assumption of rapid reorientation, on which the model is based, is incorrect.

2. In the case of water there exists evidence that proton transfer takes place by a mechanism of structural diffusion.²⁵ It seems reasonable to try a similar model for methanol. Figure 3 shows a possible scheme for such a process. For the purpose of the calculation, we shall assume that the rotation of the hydrogen-bonded complex as a whole is slow compared to the proton transfer, but that the molecules in the solvation shell can rotate freely about the hydrogen bonds, while otherwise retaining their position in the complex. It is shown in the Appendix (eq. 22) that for this model the mean square diffusion distance \bar{r}^2 after n steps is given by

$$\bar{r}^2 = nl^2 \frac{1 - \cos \varphi}{3 + \cos \varphi} \quad (15)$$

where l is the distance between two hydrogen-bonded oxygen atoms and φ the O—O—O angle in the complex (see Fig. 3).

Substituting eq. 15 into (10) we obtain

$$l^2 = 6D_{H^+,abn}\theta \frac{3 + \cos \varphi}{1 - \cos \varphi} \quad (16)$$

where

$$\theta = t/n$$

For the above process the probability that a proton transfer results in a proton exchange is again 0.5, and eq. 14 applies.²⁶ From eqs. 10, 14 and 16 we

(25) M. Eigen and L. DeMaeyer, in "The Structure of Electrolytic Solutions," John Wiley and Sons, New York, N. Y., 1959, Chapter 5; *Proc. Roy. Soc. (London)*, **A247**, 505 (1958).

(26) In the previous model the statistical factor of 0.5 was the result of the two protons in the ion being equivalent as a result of rapid

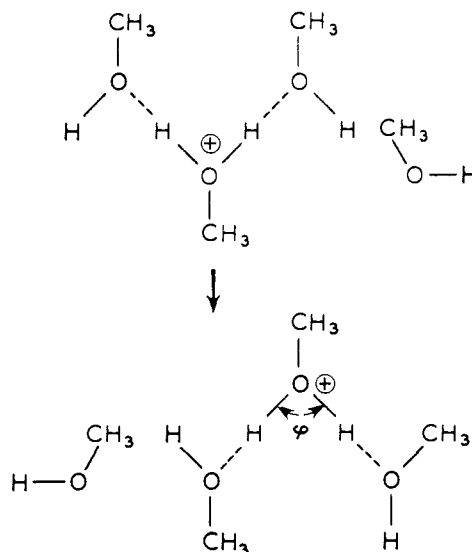


Fig. 3.—Model of a possible mechanism for proton movement by structural diffusion.

can again obtain a calculated value of $\Lambda_{H^+,abn}^0$ if the O—O distance l and the O—O—O angle φ in the hydrogen-bonded structure are known. In liquid²⁷ and crystalline²⁸ methanol l is known to be about 2.7 \AA , and we shall adopt this value. It seems reasonable that φ lies between the tetrahedral angle ($109^\circ 28'$) and the value found in crystalline methanol²⁸ (119°). For this range we obtain $\Lambda_{H^+,abn}^0 = 40$ to $48 \text{ ohm}^{-1} \text{ cm}^2$. This is significantly different from the experimental value of $88 \text{ ohm}^{-1} \text{ cm}^2$.

It will be noted that the discrepancy for model 1 is in the opposite sense to that for model 2. As a structural diffusion model with much larger O—O distances is unreasonable, it seems that some kind of model has to be adopted in which the O—O distance of 2.7 \AA is retained but in which the possible jump directions are more nearly isotropic. Two possibilities come to mind.

3. A model in which each step consists of the transfer of a number of protons, for example in a termolecular process or in a Grotthus chain. This is shown schematically in Fig. 4. Equations 25 and 26 of the Appendix apply for a termolecular structural diffusion process. Using the same values of l and φ as in the previous model, we calculate the abnormal conductance as $\Lambda_{H^+,abn}^0 = 64$ to $79 \text{ ohm}^{-1} \text{ cm}^2$.

The limiting case in which each charge transfer involves many molecules (*i.e.*, a long Grotthus chain, m in Fig. 4 is large) is also treated in the Appendix. The result is given in eqs. 28 and 29. The calculated abnormal conductance for the long chain model is $\Lambda_{H^+,abn}^0 = 80$ to $117 \text{ ohm}^{-1} \text{ cm}^2$. A structural diffusion model with three or more molecules involved in the exchange seems therefore consistent with the observations.

4. The other possibility is a model in which the pyramidal structure of the methyloxonium ion in reorientation. In the present model, however, the protons retain their individuality, and the factor of 0.5 is rather due to the 0.5 chance for forward propagation of the proton (resulting in exchange) and 0.5 chance of return of the proton (not resulting in exchange).

(27) G. G. Harvey, *J. Chem. Phys.*, **6**, 111 (1938).

(28) K. J. Tower and W. N. Lipscomb, *Acta. Cryst.*, **5**, 606 (1952).

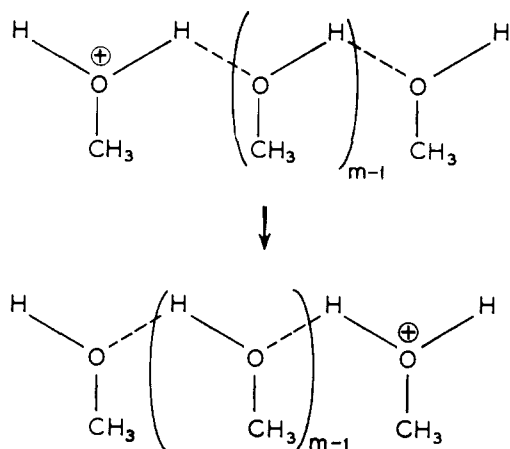


Fig. 4.—Model of polymolecular structural diffusion.

verts rapidly. A reasonable model is shown in Fig. 5. It is suggested by this figure that there are three methanol molecules in the tight solvation shell, two being held by hydrogen bonds and the third by charge-dipole attraction. The protons are assumed to exchange rapidly between the three positions in which they can form hydrogen bonds. Obviously this exchange of the proton positions makes the charge jump directions more nearly isotropic, and the diffusion distance will be more nearly that calculated for a random walk. The relevant equations are (30) and (31). The calculated conductance becomes $\Lambda_{\text{H}^+, \text{abn}}^0 = 64$ to $79 \text{ ohm}^{-1} \text{ cm}^2$.

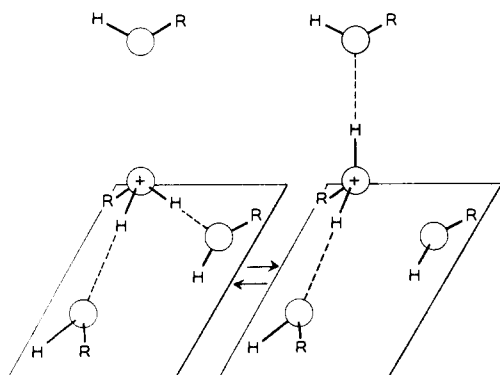


Fig. 5.—Schematic representation of the inversion of the methyloxonium ion postulated in one model.

The above results suggest that in methanol the charge transfer takes place by some process of structural diffusion. Our results do not define the details of the mechanism. Any of the models discussed in 3 and 4 are consistent with the experimental facts.

If we make the reasonable assumption that the diffusion mechanism is independent of the temperature, we may use the abnormal conductance data to obtain an expression for $1/\tau$ as a function of temperature. The result, based on the data of Table VI, is given in eq. (17), where the pre-exponential factor is proportional to T as required by the simple form of the transition-state theory.

$$1/\tau = 0.91 \times 10^{10} T \exp(1620/RT) \quad (17)$$

The enthalpy of activation is thus found to be 1.62 kcal. This value is comparable in magnitude to the

activation enthalpy for viscous flow of the solvent (1.7 kcal. at 25°) and for self-diffusion of the solvent (2.2 kcal. at 25°).²⁹

Proton Exchange and Abnormal Conductance of Methoxide Ion.—The abnormal part of the mobility of the methoxide ion is too small to be evaluated from conductance data. For example, in methanol at 25° , Λ^0 is 53.0 for methoxide ion, 51.3 for chloride ion, and 44.7 for $\text{CH}_3\text{OCO}_2^-$ ion. An analysis like the one above for the methyloxonium ion is therefore impossible for the methoxide ion. The most we can do is to estimate the abnormal conductance from the rate constant for exchange and show that it is not inconsistent with the observed conductance data. We assume a random walk model [eq. 12] with a jump distance $l = 2.7 \text{ \AA}$. and $\theta = 1/k_{\text{MeO}^-}$ obtaining

$$\Lambda_{\text{MeO}^-, \text{abn}}^0 = 8.4 \text{ ohm}^{-1} \text{ cm}^2$$

The normal equivalent conductance of the methoxide ion is therefore estimated as

$$\Lambda_{\text{MeO}^-, \text{normal}}^0 = 45 \text{ ohm}^{-1} \text{ cm}^2$$

It is striking that the exchange rate, and accordingly the abnormal conductance, of the methoxide ion are an order of magnitude lower than those for the methyloxonium ion. At present we can only speculate why this is so. It seems probable that the structural diffusion model applies. The rate determining step in this model could be either the proton transfer itself, or the rate of addition of favorably oriented solvent molecules to the solvated ion. If the latter process were rate determining, it would follow that the alignment of the methanol molecules with their oxygen atom toward the complex is accomplished more rapidly than alignment with the hydrogen atom toward the complex. This could be because the methanol molecule has two unshared electron pairs on the oxygen, but only one hydrogen atom. Thus the number of available acceptor sites is twice the number of donor sites for hydrogen bond formation.³⁰ On the other hand the proton transfer might be rate determining, at least for the methoxide ion. Eigen and DeMaeyer²⁵ have suggested that the same may be true for the hydroxide ion in water. A reduction in proton transfer rate is to be expected from the larger O—O distance in the negative ions.

Appendix

Calculation of Diffusion Distance for Structural Diffusion Models. 1. Charge Transfer to Adjacent Sites.—We consider a methyloxonium ion with two methanol molecules attached to it by strong hydrogen bonds. The elementary steps of the charge transfer are indicated in Fig. 6. First, molecule 4 is added to the hydrogen bonded complex, it being assumed that all directions consistent with the bond angle φ are equally probable. The possible directions are on a cone as indicated in Fig. 6b. Next the charge jumps from atom 2 to atom 3 (Fig. 6c), and finally the loss of molecule 1 from the complex (Fig. 6d) completes the elementary charge transfer process. It will be assumed that the next charge transfer can take place with equal probability to molecule 4 or to molecule 2. In other words, the transfer in the backward direction is just as probable as in the forward direction. Note that, if the charge returns to molecule 2, the latter is still in the same position, but

(29) J. R. Partington, R. F. Hudson and K. W. Bagnall, *J. chim. phys.*, **55**, 77 (1958).

(30) This explanation would predict nearly equal rates in water, while actually the rates differ by a factor of about 2.6.

molecule 1 has been replaced and can now be anywhere on a cone defined by the bond angle φ .

We now wish to calculate the mean square distance \bar{r}^2 over which the charge has moved after n steps as described above. The calculation uses a method analogous to that for the related problem of randomly coiled polymer chains.^{31,32} We closely follow Flory's derivation.³² The vector displacement r , of the charge after n steps is

$$r = \sum_{i=1}^n l_i \quad (18)$$

where l_i is the vector describing the i th step. The mean square value of r is therefore

$$\bar{r}^2 = \sum_{i=1}^n \sum_{j=1}^n \overline{l_i \cdot l_j} \quad (19)$$

Writing the sums explicitly we have

$$\begin{aligned} \bar{r}^2 = & \overline{l_1 \cdot l_1} + \overline{l_1 \cdot l_2} + \overline{l_1 \cdot l_3} + \dots + \overline{l_1 \cdot l_n} + \\ & \overline{l_2 \cdot l_1} + \overline{l_2 \cdot l_2} + \overline{l_2 \cdot l_3} + \dots + \overline{l_2 \cdot l_n} + \\ & \overline{l_3 \cdot l_1} + \overline{l_3 \cdot l_2} + \overline{l_3 \cdot l_3} + \dots + \overline{l_3 \cdot l_n} + \dots \end{aligned} \quad (20)$$

The n terms on the main diagonal each give l^2 . The $2(n-1)$ terms of the type $\overline{l_i \cdot l_{i \pm 1}}$ are each the average value of the projection of a step vector on the one immediately preceding it. There is a chance of 0.5 that the charge moves forward in the second step, in which case $\overline{l_i \cdot l_{i+1}} = -l^2 \cos \varphi$. If the charge moves backward in the second step, $\overline{l_i \cdot l_{i+1}} = -l^2$. Hence the total contribution of the terms adjacent to the main diagonal is $-(n-1)(1 + \cos \varphi)$.

We shall next discuss the $2(n-2)$ terms of the type $\overline{l_i \cdot l_{i \pm 2}}$. There are now four possibilities, each with a probability of 0.25.

- Both the $(i \pm 1)$ th step and the $(i \pm 2)$ th step are forward. ("Backward" and "forward" steps will be relative to the immediately preceding step.) This gives a contribution for each term of $-l^2 \cos^2 \varphi$.
- The $(i \pm 1)$ th step is forward and the $(i \pm 2)$ th step is backward. This gives per term $+l^2 \cos \varphi$.
- The $(i \pm 1)$ th step is backward and the $(i \pm 2)$ th step is forward. This gives again $+l^2 \cos \varphi$.
- The $(i \pm 1)$ th step and the $(i \pm 2)$ th step are backward. This gives l^2 .

Hence the total contribution of the $2(n-2)$ terms is $\frac{1}{2}(n-2)l^2(1 + \cos \varphi)^2$. It can be shown that in general $\overline{l_i \cdot l_{i \pm 1}} = \overline{l_i \cdot l_j}[-\frac{1}{2}(1 + \cos \varphi)]$.

Adding all terms gives

$$\bar{r}^2 = nl^2 \left[1 - \frac{2(n-1)}{n} \frac{(1 + \cos \varphi)}{2} + \frac{2(n-2)}{n} \left(\frac{1 + \cos \varphi}{2} \right)^2 - \dots \right] \quad (21)$$

Only the result for large n is of interest here, and is

$$\bar{r}^2 = nl^2 \frac{1 - \cos \varphi}{3 + \cos \varphi} \quad (22)$$

2. Termolecular Proton Transfer.—Instead of charge transfer to nearest neighbors, we shall now treat a slightly different model in which the elementary process involves three molecules, and results in transfer of the charge to a next-nearest neighbor site. A single elementary step in this model is equivalent to two successive steps of the first model, the second step being always a forward step, (*i.e.*, in the same direction as the preceding one). The derivation of an expression for \bar{r}^2 is similar to that for the bimolecular case, except that in every even-numbered step the charge always moves forward. Odd-numbered steps have again the same probability of going backward as forward.

On the basis of these assumptions, the various terms in eq. (20) are generated by the formulas

$$\begin{aligned} \overline{l_i \cdot l_i} &= l^2 \\ \overline{l_i \cdot l_{i+1}} &= -l_i \cdot l_j [1 + \cos \varphi]/2 \text{ when } j \text{ is even} \\ \overline{l_i \cdot l_{i+1}} &= -l_i \cdot l_j \cos \varphi \text{ when } j \text{ is odd} \end{aligned} \quad (23)$$

(31) H. Eyring, *Phys. Rev.*, **39**, 746 (1932).

(32) P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, 1953.

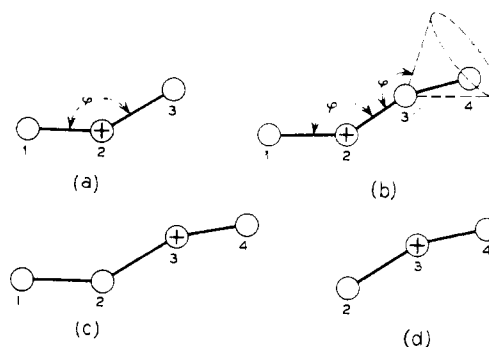


Fig. 6.—Model for structural diffusion serving as basis for the calculation of diffusion distance. Each circle represents an oxygen atom in the hydrogen-bonded structure.

Equations 23 enable us to evaluate the right-hand side of eq. 20. When n is large, the result reduces to

$$\bar{r}^2 = nl^2 \frac{1 - \cos \varphi}{2 + \cos \varphi} \quad (24)$$

where n is the number of transitions between adjacent sites. Since in this model each elementary process moves the charge to a next-nearest neighbor site, the number N of such elementary processes is equal to $n/2$. Hence we obtain the final result

$$\bar{r}^2 = 2Nl^2 \frac{1 - \cos \varphi}{2 + \cos \varphi} \quad (25)$$

In the assumed termolecular mechanism, each elementary step on the average results in the exchange of one proton. This is because in a forward step, two methanol protons are exchanged, while in a backward step, none exchange. Hence

$$\theta = 1/k_{M_eOH_2^+} \quad (26)$$

3. Polymolecular Proton Transfer.—We assume here that in an elementary process $m+1$ molecules are involved, and therefore that the charge moves m molecules away. For m sufficiently large the mean square distance of the charge transfer is³³

$$\bar{L}^2 = ml^2 \frac{1 - \cos \varphi}{1 + \cos \varphi} \quad (27)$$

For sufficiently large m the direction of successive elementary steps is random. After N such steps the charge has moved therefore by

$$\bar{r}^2 = N\bar{L}^2 = Nmml^2 \frac{1 - \cos \varphi}{1 + \cos \varphi} \quad (28)$$

In order to find the average number of protons exchanged per elementary process we assume that the subsequent step involves mostly new methanol molecules, because it is highly improbable that the same hydrogen-bonded path will persist for a time of the order of θ . In order to make this model consistent with the ones discussed before, we shall assume that the methanol molecule adjacent to the methyl-oxonium remains in the path, while all others are replaced. However, this detail is in fact of no consequence to the result of the calculation. On the basis of this model the average number of protons exchanged per elementary step is $m-1$. Hence

$$\theta = (m-1)/k_{M_eOH_2^+} \approx m/k_{M_eOH_2^+} \quad (29)$$

4. Bimolecular Model with Three Methanol Molecules in Tight Solvation Shell.—This is the model shown in Fig. 5. The charge can jump with equal probability in either of the three directions. Hence transfer in a backward direction has a probability of 0.333. Otherwise the calculation is analogous to the one given under 1. The result is

$$\bar{r}^2 = nl^2 \frac{1 - \cos \varphi}{2 + \cos \varphi} \quad (30)$$

The probability of proton exchange per elementary process is 0.5. Hence

$$\theta = 1/(2k_{M_eOH_2^+}) \quad (31)$$

(33) Ref. 32, page 415, eq. 22.