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The Mechanism of Ethylene Oxide Formation from 2-Chloroethanol[1,2]

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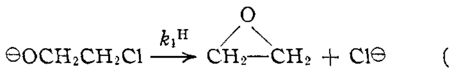
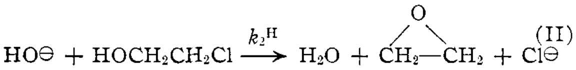
The isotope effect for the reaction of sodium hydroxide with 2-chloroethanol to give ethylene oxide in light and heavy water is found to be $k_{H_2O}/k_{D_2O} = 0.65$ at 25°. A spectroscopic examination of 2-chloroethanol and 2-chloroethanol-*d* makes possible the calculation of the isotope effect consistent with a stepwise mechanism, and an estimate can be made for the concerted mechanism. The magnitude of the observed effect is explicable only if the mechanism for the reaction is stepwise, involving 2-chloroethoxide ion as a true intermediate.

The purpose of the work described in this paper is to determine whether 2-chloroethoxide ion is a true intermediate in the formation of ethylene oxide from sodium hydroxide and 2-chloroethanol, or only a reversibly formed by-product. Thus the problem is to distinguish between mechanisms having the rate-determining steps


(I)


(II)

Mechanisms I and II represent two extremes in relative timing of the displacements on H and on C. Both lead to the same products and give the same kinetics because, regardless of the mechanism, 2-chloroethoxide ion is always present in rapid equilibrium with hydroxide ion and 2-chloroethanol according to

$$[\ominus OCH_2CH_2Cl] = K_H[HO\ominus][HOCH_2CH_2Cl]/[H_2O]$$

The observed second-order rate constant k_H is either $K_H k_1^H$ or k_2^H. One cannot distinguish between them by stereochemical studies or classical kinetic measurements including competition experiments or direct analysis for 2-chloroethoxide ion. However, an alcoholic hydroxyl bond is broken in each mechanism. The isotope effect (k_H/k_D) can therefore be used to determine the timing of the proton transfer, whether it occurs in a prior equilibrium step as in the stepwise mechanism I or during the rate-determining step as in the concerted mechanism II, by comparison of the isotope effects calculated for each of these mechanisms with the observed isotope effect.

Previous Work on Ethylene Oxide Formation from 2-Chloroalkanols.—An excellent review[3] summarizes previous studies. Ethylene oxide formation is first order in hydroxide ion and first order in 2-chloroalkanol (chlorohydrin), second order overall. Other bases are not effective. The hydroxyl group must be *trans* to the chlorine for ring closure to occur. The reverse reaction is first order in ethylene oxide, first order in chloride ion, and also involves a Walden inversion.

The unique effectiveness of hydroxide ion in this reaction does not exclude II because, as Hammett has pointed out,[4] this might be due merely to a large spread in relative reactivities of different bases, *i.e.*, to a high β in the Brønsted catalysis law.

Use of Isotope Effects to Distinguish between Mechanisms I and II.—The isotope effect for mechanism I is $K_H k_1^H/K_D k_1^D$, whereas for mechanism II it is k_2^H/k_2^D. The ratio k_1^H/k_1^D will be a solvent isotope effect only, since the intermediate $ClCH_2CH_2O^-$ is not isotopically substituted and is therefore common to the reaction in both waters. This ratio is small in comparison with isotope effects due to direct isotopic substitution of the reactants and of the transition state. A discussion of its approximate magnitude will be given in a later section of the paper. The isotope effect for mechanism I, aside from this small solvent effect, is determined by a ratio of thermodynamic equilibrium constants, while the isotope effect for mechanism II is determined by a ratio of rate constants.

The isotope effect for mechanism I in light and heavy water, ignoring for the moment the solvent isotope effects, should be given by the ratio of the equilibrium constants $K_H/K_D = K$, which is the equilibrium constant of the exchange reaction

$$HO\ominus + HOCH_2CH_2Cl + D_2O \overset{K}{\rightleftarrows} DO\ominus + DOCH_2CH_2Cl + H_2O$$

$$\frac{k_H}{k_D} = \frac{K_H}{K_D} = K = \frac{Q_{DO^-}Q_{DOR}Q_{H_2O}}{Q_{HO^-}Q_{HOR}Q_{D_2O}} \qquad (1)$$

The isotope effect for mechanism II should be given by

$$\frac{k_H}{k_D} = \frac{k_2^H}{k_2^D} = K^*\left(\frac{\nu_i^H}{\nu_i^D}\right) = K^*\left(\frac{m_D^*}{m_H^*}\right)^{1/2} \qquad (2)$$

where K^* is the equilibrium constant of the exchange reaction

$$HO\ominus + HOCH_2CH_2Cl + (\text{trans. state})_D = DO\ominus + DOCH_2CH_2Cl + (\text{trans. state})_H$$

$$K^* = \frac{Q_{DO^-}Q_{DOR}Q_H^*}{Q_{HO^-}Q_{HOR}Q_D^*}$$

The ratio Q_D^*/Q_H^* is the ratio of complete partition functions for $3N$-7 degrees of vibrational freedom for the transition states, divided by the ratio (ν_i^D/ν_i^H) of the two critical frequencies which become imaginary in the transition states. The

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[1] Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905 and by the National Institutes of Health under Research Grant RG-3711(C and C4).

[2] For further details, *cf.* R. F. W. Bader, Ph.D. Thesis in Organic Chemistry, M. I. T., December, 1957.

[3] A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 243–257.

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 242.

quantities m_H^* and m_D^* are the "effective masses," *i.e.*, the reduced masses which govern these imaginary frequencies.(5)

We have made a spectroscopic examination of 2-chloroethanol and 2-chloroethanol-*d* and can therefore calculate the ratio of their partition functions. The partition function ratios for light and heavy water and for hydroxide and deuteroxide ions have been determined previously.(6) The calculation of the partition function ratio for the 2-chloroethanol molecules is deferred until a later section to preserve the continuity of the argument at this point.

The value of K, the isotope effect for mechanism I, is

$$K = (21.36)(47.14)(1/1436) = 0.701$$

The values in parentheses are written in the same order as the appearance of the partition function ratios in equation 1. This value of K, less than unity, is a direct expression of the greater basicity of the deuteroxide ion in heavy water than that of the hydroxide ion in light water. In a previous paper in which the important exchange equilibria for the hydroxide ion were considered, the exchange constant for the equilibrium

$$2HO^{\ominus} + D_2O \rightleftarrows 2DO^{\ominus} + H_2O$$

was calculated to be 0.312.(6) This value also clearly illustrates the enhanced basicity of the deuteroxide ion in heavy water over that of the hydroxide ion in light water. The concentration of the intermediate will therefore be greater in heavy water than in light water, and the reaction will proceed more rapidly in the heavy solvent.

The small secondary solvent isotope effect on the second step of mechanism I has thus far been ignored. This rate-determining step involves the dispersal of charge initially concentrated on the alkoxide ion. Such reactions should proceed faster in heavy water than in light water.(6) This factor would make the predicted isotope effect for mechanism I even lower than 0.701. However, the reduction is not expected to be more than about 10% because solvent isotope effects are generally small, and in this reaction the changes in structure of the surrounding solvent sheath should be especially small because the charge is merely being distributed, not generated nor destroyed.

The ratio of the rate constants for mechanism II can never be less than unity. This can be seen from a consideration of equation 2. If the alcoholic hydrogen atom is transferred to any great extent by the time the transition state is reached, and the bonding to it is relatively tight, then the reduced mass factor in equation 2 will be of the order of 1.39 and assigning maximum values to all the frequencies involving the motion of the hydrogen atom (*i.e.*, those corresponding to the final product, water) results(2) in a value of 450 for the ratio Q_D^*/Q_H^*. This gives a final value for the isotope effect of 2.2. If the transition state is a very long range affair, *i.e.*, close to the reactants in structure, then the reduced mass factor will approach unity and, since the bonding to the hydrogen will be slightly weakened, the product of the remaining ratios in equation 2 will be slightly greater than unity. Thus, both of these extremes of bonding to the alcoholic hydrogen lead to isotope effects which are greater than unity.

The deuteronium ion is a stronger acid than is the hydronium ion,(6) and thus, as in the present case with the differing basicities of the hydroxide and deuteroxide ions, the same criterion of disparity of isotopic rates has been employed previously to determine the mechanism of acid-catalyzed reactions. For example, from the fact that a large number of reactions catalyzed by hydrogen ion proceed only 0.37 – 0.75 times as fast in light water as in heavy water, it was concluded that they all involve protonation by acid in a prior equilibrium step.(7,8) Examples include the enolization of acetone, the hydrolyses of esters and orthoesters, the hydrolyses of sucrose and other acetals, and the reaction of ethyl diazoacetate with water or ethanol, although the enolization and ester reactions exhibit general acid catalysis while the acetals and diazo compound show specific hydrogen-ion catalysis. On the other hand, from the fact that several other reactions catalyzed by hydrogen ion proceed 1.4 to 3.6 times faster in light water than in heavy water, it was concluded that they involve protonation by acid in the rate-determining step.(7,9) Examples supported also by other than isotope effect experiments are the reactions of diphenyldiazomethane with water(10) or ethanol.(11) However, another example, the mutarotation of glucose,(7,9) which was not supported by calculation of isotope effects from spectral data or by other than isotope effect experiments, has more recently been considered to involve protonation by acid in a prior equilibrium.(12)

Comparison of Calculated and Observed Isotope Effects.—The observed rate constants are $1.00 \times 10^{-2}\ M^{-1}$ and $1.54 \times 10^{-2}\ M^{-1}$ sec.$^{-1}$ at 25° in light water and in heavy water, respectively. Each result is an average of nine or more separate kinetic runs. The observed isotope effect is $k_H/k_D = 1.00/1.54 = 0.65$.

The rate in heavy water is 54% greater than the rate in light water. This result is consistent only with mechanism I. The reaction must involve a prior equilibrium step and the intermediate so formed must exist, free from the separated water molecule, for a finite length of time. The calculated value of the isotope effect for mechanism I based solely on the value of K and devoid of all solvent effects is larger than the experimental value by a factor of 1.08. The difference between

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(5) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); J. Bigeleisen, *ibid.*, **17**, 675 (1949); J. Bigeleisen and M. Wolfsberg, *ibid.*, **21**, 1972 (1953); **22**, 1264 (1954); H. S. Johnston, W. A. Bonner and D. J. Wilson, *ibid.*, **26**, 1002 (1957).

(6) C. G. Swain and R. F. W. Bader, paper submitted for publication.

(7) K. F. Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938).

(8) R. P. Bell, "Acid–Base Catalysis," Oxford University Press, London, 1941, p. 145; K. B. Wiberg, *Chem. Revs.*, **55**, 718 (1955).

(9) E. A. Moelwyn-Hughes, *Z. physik. Chem.*, **B26**, 272 (1934); R. P. Bell, ref. 8, p. 151; K. B. Wiberg, ref. 8, p. 720.

(10) P. Gross, H. Steiner and G. Krauss, *Trans. Faraday Soc.*, **32**, 877 (1936).

(11) J. D. Roberts and W. Watanabe, This Journal, **72**, 4869 (1950); J. D. Roberts, C. M. Regan and I. Allen, *ibid.*, **74**, 3679 (1952); J. D. Roberts and C. M. Regan, *ibid.*, **74**, 3695 (1952).

(12) Reference 3, p. 205; C. G. Swain, A. J. Di Milo and J. P. Cordner, *ibid.*, **80**, 5983 (1958).

the two results is close to that predicted for the solvent isotope effect.

The agreement of the observed and calculated results for mechanism I and disagreement for any form of mechanism II establishes that the mechanism of reaction of hydroxide ion with 2-chloroethanol involves 2-chloroethoxide ion as a true intermediate along the main reaction path with very high certainty.

It is hard to see any other mechanistic tool that could even have been brought to bear on this question, since the point at issue was not the existence of 2-chloroethoxide ion in the solution nor the rapidity of its equilibrium with 2-chloroethanol (these were already taken for granted) but only the direction of the reaction path.

Calculation of the Partition Function Ratio for 2-Chloroethanol.—The ratio (Q_t'/Q_t) for the translational degrees of freedom is $(m'/m)^{3/2} = 1.019$ as determined by the molecular weights.

The 2-chloroethanol molecule possesses a total of five rotational degrees of freedom, three of which correspond to the rotations of the molecule as a whole about its three principal axes, and the remaining two to internal rotations, one a motion of the CH_2Cl group about the CC bond and the other a motion of the HO group about the OC bond. The internal as well as the external degrees of rotational freedom must be taken into account in the evaluation of the rotational partition function.

Dennison and co-workers[13] showed that the hydroxyl group in gaseous methanol executes a librational motion about the OC axis, rather than a free rotation. Stuart and Sutherland[14] found spectroscopic evidence for a librational motion of the alcoholic hydrogen in liquid methanol and also in a large number of other alcohols. Their investigation revealed a broad band with a maximum at 670 cm.$^{-1}$, extending from 800 to 500 cm.$^{-1}$. Deuteration shifted the band maximum to 475 cm.$^{-1}$. That this frequency must arise from a true deformational motion of the hydrogen at right angles to the HOC plane is evident from the value of the frequency ratio, 1.40, a value very close to the theoretical limit of $\sqrt{2}$. Stuart and Sutherland also noted that dilution of the alcohol with an inert solvent such as carbon tetrachloride greatly decreased the intensity of the 670 cm.$^{-1}$ band. This behavior is to be expected, because at high dilutions of the alcohol the extent of hydrogen bonding will be very slight.

The Pitzer–Gwinn approximation[15] for the partition function of a hindered internal rotor will be employed to describe the hindered internal rotational motions. Pitzer has shown that the total rotational kinetic energy matrix may be diagonalized in such a way that the external rotational degrees of freedom about the three principal moments of inertia (I_a, I_b and I_c) of the molecule may be separated from the internal rotations. Thus the total partition function may be factored into two terms, one for the external rotations of the molecule, and the other as given by the Pitzer–Gwinn approximation for the hindered internal rotation. As previously mentioned,[6] the isotopic ratio for the Pitzer–Gwinn approximation reduces to the ratio of the quantum harmonic oscillator partition functions. Thus the ratio of the complete rotational partition functions for 2-chloroethanol is

$$\frac{Q_r'}{Q_r} = \left(\frac{I_a'I_b'I_c'}{I_aI_bI_c}\right)^{1/2} \frac{Q_q'}{Q_q} \qquad (6)$$

Pitzer has shown that these should be calculated for the equilibrium conformation of the molecule. The *trans* conformation is most probably the more stable form of the 2-chloroethanol molecule in solution and it is also the conformation which the molecule must assume for epoxide formation to occur. The factor involving the moments of inertia in equation 6 was calculated for this conformation and found to be 1.053. This factor changed by only 1% when determined for three other conformations.

The librational frequency for 2-chloroethanol, as reported in the Experimental section, is 670 cm.$^{-1}$. This is the value employed in the calculation of the internal contribution to the rotational partition function. The contribution from the other top within the 2-chloroethanol molecule, the CH_2Cl group, must be equal for the two isotopic molecules for the following reason. The frequency ratio for the hydroxyl and deuteroxyl librational motions is so close to the square root of two that the motion of the two tops cannot be coupled to any great extent. If a coupling of the motions were present, the ratio of the librational frequencies for the hydroxyl group would be greatly reduced, as masses other than and much heavier than the hydrogen and deuterium atoms would be involved in the librational motions of the latter two atoms. Thus, whether the motion of the CH_2Cl group is hindered or not is of no interest in the calculation of the partition function ratio. Therefore, there is but one motion contributing to the ratio of the partition functions for the internal rotations. The complete rotational partition function ratio Q_r'/Q_r is $(1.053)(1.711) = 1.801$.

The observation of the Raman and infrared spectra of 2-chloroethanol and 2-chlorethanol-*d* revealed the presence of two complementary sets of frequencies for the internal vibrations. Methods of the spectroscopic investigation and a detailed assignment of frequencies are given in the Experimental section.

The ratio of the vibrational partition functions must contain contributions from all those vibrations whose frequencies are altered on deuteration of the alcohol, *i.e.*, the vibrations associated with the HOC group. The vibrational modes of this group of atoms may be considered as arising from the following motions: the stretching motion of the HO bond, ν_{HO}; the stretching motion of the OC bond, ν_{OC}; the in-plane bending motion of the HOC group, δ_{HO}; and the torsional or out-of-plane bending motion of the HOC group, τ_{HO}. The latter vibration, τ_{HO}, has been included as a hindered rotation in the rotational partition function

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[13] J. S. Koehler and D. M. Dennison, *Phys. Rev.*, **57**, 1006 (1940); D. C. Burkhard and D. M. Dennison, *ibid.*, **84**, 408 (1951).

[14] A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.*, **20**, 1977 (1952); **24**, 559 (1956).

[15] J. E. Kilpatrick and K. S. Pitzer, *ibid.*, **17**, 1064 (1949).

and need not be considered further. In the hydrogen alcohol, the bending vibration of the HOC group, δ_{HO}, is apparently coupled with a deformation mode of the CH_2 group, $\nu_{\mathrm{CH_2}}$, giving rise to two new mixed vibrations. These are designated as $[\delta_{\mathrm{HO}} + \nu_{\mathrm{CH_2}}]$. On deuteration of the alcohol the coupling between these two modes is broken down and two new bands appear, one due to the bending motion of the DOC group, δ_{DO}, and the uncoupled value of the $\nu_{\mathrm{CH_2}}$ deformation frequency. The OC stretching vibration, ν_{OC}, appears as a close doublet with a separation of approximately 20 cm.$^{-1}$ in both the hydrogen and the deuterated alcohols. Furthermore, as mentioned earlier, two sets of ν_{OC} and δ_{HO} bands are present. The ν_{HO} and τ_{HO} bands are so broad that only one distinct maximum could be discerned in these cases. The two sets of bands fall into two complementary sets, a high frequency group and a low frequency group, with the ν_{HO} and τ_{HO} frequencies common to each. Thus all told ten bands are displaced on deuteration of the alcohol. The frequencies of these bands and their vibrational assignments are given in Table I of the Experimental section. The letters H or L following each pair of frequencies designate to which set, either high or low, the bands belong. Mean values of the two pairs of ν_{OC} frequencies were used in the calculation of the vibrational partition function ratios, which were separately calculated for the high and low bands. These ratios were found to be $Q_v'/Q_v = 26.27$ and 25.12, respectively. The two values differ by 4%. Since it is not known which set of bands corresponds to which conformation of the alcohol in solution (if this is indeed the cause of the doubling) and since the difference between the two sets is small, the value of the vibrational partition function ratio was obtained by taking the average of the two values, 25.70. The uncertainty in the vibrational partition function ratio is then 2%.

The complete partition function ratio for 2-chloroethanol is

$$Q_{\mathrm{DOR}}/Q_{\mathrm{HOR}} = (1.019)(1.801)(25.70) = 47.14$$

Experimental

Materials.—Heavy water was 99.5% D_2O from the Stuart Oxygen Co.

2-Chloroethanol was Eastman Kodak Co. white label, redistilled through a two-foot fractionating column packed with glass helices, b.p. 47.0–47.1° at 25 mm.

2-Chloroethanol-*d* was prepared through the reaction of the borate ester of the alcohol with heavy water.

$$3ClCH_2CH_2OH + B(OH)_3 \longrightarrow B(OCH_2CH_2Cl)_3 + 3H_2O$$

$$B(OCH_2CH_2Cl)_3 + 3D_2O \longrightarrow 3ClCH_2CH_2OD + B(OD)_3$$

The procedure employed in the preparation of the borate ester paralleled one for the preparation of butyl borate.[16] 2-Chloroethanol, 1.506 moles, b.p. 127–128°, was mixed with 0.3766 mole of boric acid in a 200-ml. round-bottom flask, fitted with a glass-helices fractionating column 40 cm. long and heated in an oil-bath at about 140°. A total of 22.5 g. of water distilled from the reaction mixture over a period of eight hours. The theoretical quantity of water was 27 g. The borate ester was recovered from the reaction mixture by a fractional distillation, collecting 45 g., b.p. 126 ± 0.1° at 5 mm. No attempt was made to obtain the theoretical yield by a continued distillation since only a small quantity of the final product was required for spectroscopic examination. The borate ester (14.5 g.) was only partially decomposed with heavy water (3.5 ml.) in the second step of the synthesis in order to avoid a forerun of water in the distillation of the alcohol and because the heavy water is treated as the limiting substance in a synthesis. The addition of the water caused a heavy precipitate of boric acid to form. This was filtered in a closed system to prevent contamination by water vapor. The filtrate was distilled through a vacuum-jacketed Holzmann column.[17] The alcohol was collected at a constant temperature of 127 ± 0.1° at atmospheric pressure.

The infrared spectrum of this compound which is reproduced in Fig. 1 indicates that all contamination by light water was successfully avoided in the synthesis of the heavy alcohol, since the 3 μ region of the spectrum is devoid of any absorption. The HO group exhibits a very intense absorption in this region.

Spectral Data.—Infrared and Raman spectra were obtained for the pure alcohols 2-chloroethanol and 2-chloroethanol-*d*. The infrared spectra were obtained for the sodium chloride region, 5000 to 640 cm.$^{-1}$, and for the potassium bromide region, 830 to 460 cm.$^{-1}$. In both of these regions the spectra were obtained by pressing a drop of the alcohol between two 1-mm. thick silver chloride plates. The sample thickness was from 5 to 10 μ. The sodium chloride region was calibrated with the 6.238 μ line of polystyrene and the potassium bromide region with ammonia gas. The instrument employed was a Baird model AB-2 double beam spectrophotometer.

The Raman spectra were obtained with the instrument of the Massachusetts Institute of Technology Spectroscopy Laboratory.[18] Filters (1 cm.) of saturated sodium nitrite and 0.01% du Pont Rhodamine 5GDN were employed. The instrument was calibrated with the electronic excitation spectrum of neon gas. The original readings were in ångström units and are the values in air. These readings were converted to corresponding values in cm.$^{-1}$ in vacuum by use of the tables of Kayser.[19] The error in the reading of a sharp well defined peak in the infrared spectra is of the order of 2 cm.$^{-1}$ in the region below 2000 cm.$^{-1}$. The corresponding error in the case of the Raman spectra is less than 1.0 cm.$^{-1}$. Fig. 1 gives the infrared spectra of both alcohols.

Spectral Interpretations.—The alcohols 2-chloroethanol and 2-chloroethanol-*d* both exhibit sharp bands at 661 and 475 cm.$^{-1}$ in the infrared which tend to obscure the torsional bands. The 661 cm.$^{-1}$ band is probably due to CCl stretching and the 475 cm.$^{-1}$ could be a skeletal vibration. However, due to the broad nature of the torsional bands their presence is still very evident. In the spectrum for the deuterated compound in the potassium bromide region (Fig. 1), a base line is maintained between peaks in the 15 μ (667 cm.$^{-1}$) region. This is not the case for the hydrogen alcohol. For the hydrogen alcohol a band is evident beginning at 12.5 μ (800 cm.$^{-1}$) and extending to approximately 19 μ (526 cm.$^{-1}$). The two films used in obtaining the spectra for the two alcohols were of approximately equal thickness. Since this is the case, one may plot the excess % transmittance of the hydrogen alcohol over that of the deuterated form in this region of the spectrum. This procedure results in a broad band with maximum absorption at approximately 670 cm.$^{-1}$. Similarly, there is evidence of a broad band beginning at 17 μ (588 cm.$^{-1}$) in the deuterated alcohol, while there is no absorption aside from the tail of the τ_{HO} band in this region of the spectrum for the hydrogen alcohol. Both spectra show a decrease in % transmittance past 21.4 μ (468 cm.$^{-1}$) due to the opacity of the silver chloride plates in this region. A plot of the difference in the % transmittance of the deuterated alcohols as compared to the hydrogen alcohol gives a band with a center at approximately 475 cm.$^{-1}$. The Raman spectra for the two alcohols yield similar results. The torsional bands for 2-chloroethanol and 2-chloroethanol-*d* therefore occur at 670 and 475 cm.$^{-1}$ as found in a large number of other alcohols.

The bands due to the stretching motions of the HO and DO groups occur at 3353 and 2486 cm.$^{-1}$, respectively, in the infrared.

In addition the OC stretch ν_{OC} and the bending motion of the HOC group δ_{HO} should exhibit frequency shifts on deu-

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(16) J. R. Johnson and S. W. Tompkins, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 106.

(17) C. W. Gould, G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

(18) R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951).

(19) H. G. J. Kayser, "Tabelle der Schwingungszahlen," S. Hirzel, Leipzig, 1925.

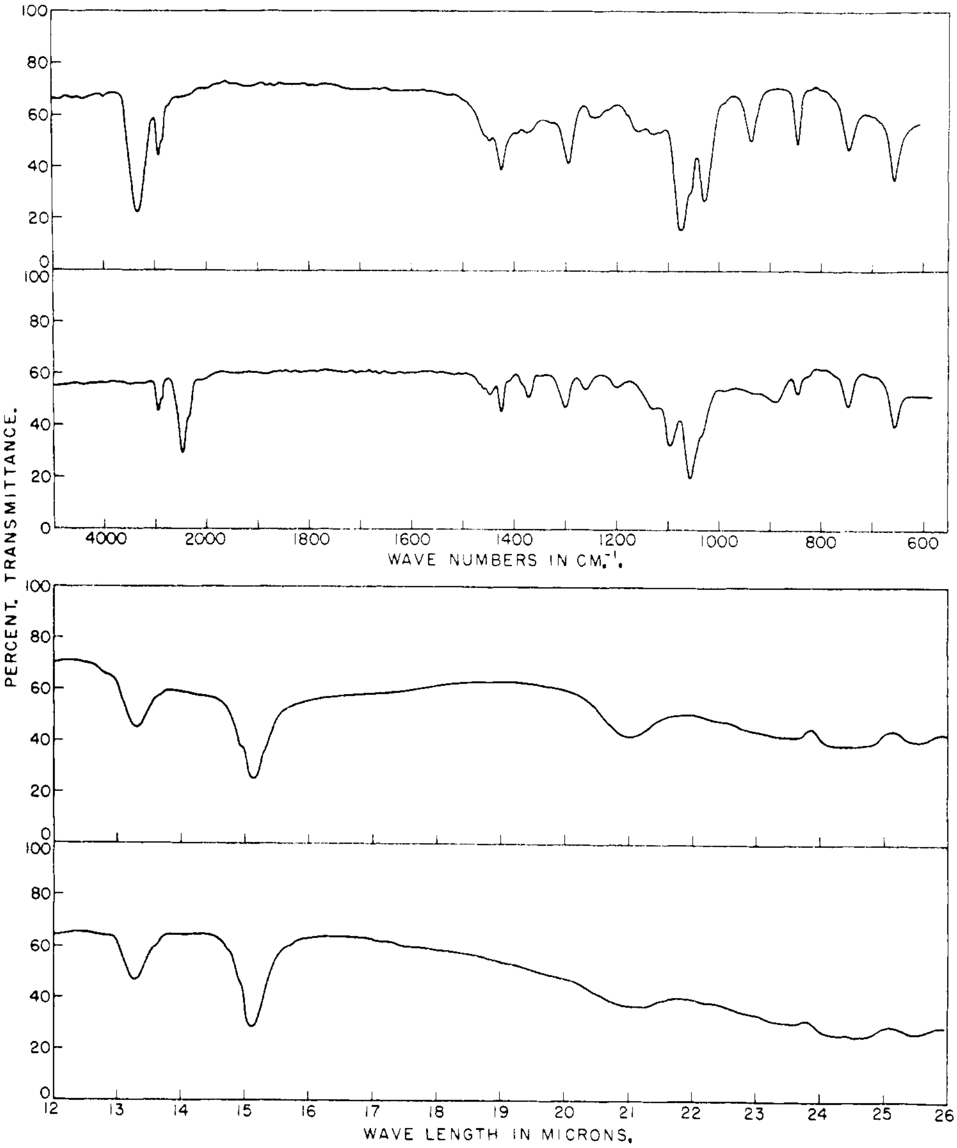

Fig. 1.—Infared spectra of 2-chloroethanol and 2-chloroethanol-*d* in the NaCl region (top) and KBr region (bottom).

teration. The identification of these two frequencies in the spectra of alcohols constitutes a problem of current interest in spectroscopy. There is at present no general agreement as to which frequencies correspond to these motions. However, some results recently published by Tarte and Deponthière[20] greatly clarify the situation. They obtained the infrared spectra of a number of alcohols in the gas phase. All previous attempts to assign the δ_{HO} bending mode had favored either the 1250 cm.$^{-1}$ region or the 1000–1100 cm.$^{-1}$ region, with possible overlapping by the strong ν_{OC} band in the latter case. Tarte and Deponthière noted that on deuteration of ethyl alcohol two bands were strongly shifted. The first of these was the 1243 cm.$^{-1}$ band assigned by Stuart and Sutherland[14,21] to the δ_{HO} mode, which is shifted to 890 cm.$^{-1}$ on deuteration. The point of interest, however, is that the second band exhibited identical spectroscopic behavior on deuteration of the alcohol. It occurred at 1030 cm.$^{-1}$ in the spectrum obtained by Stuart and Sutherland and it is strongly overlapped by the ν_{OC} band. On deuteration of the alcohol, this band, which Stuart and Sutherland did not detect, is shifted to 790 cm.$^{-1}$. They conclude that for primary alcohols the presence of two δ_{HO} bands is more the rule than the exception. They state that rotational isomerism could explain this doubling of the δ_{HO} mode but that additional results would be needed to verify this.

The results reported here for 2-chloroethanol and its deuterated form parallel those of Tarte and Deponthière, *i.e.*, deuteration of the alcohol is accompanied by the disappearance of two bands and the appearance of two new low-lying bands. One of the bands displaced on deuteration of 2-chloroethanol, the 1033 cm.$^{-1}$ band, is in the same region of the spectrum as the corresponding one for ethanol. The infrared spectrum of 2-chloroethanol-*d* gives no clear indication of a band at 790 cm.$^{-1}$. In the Raman spectrum, however, a sharp band of medium intensity appears at 773 cm.$^{-1}$.

To aid in the interpretation of the spectra for 2-chloroethanol and 2-chloroethanol-*d*, a frequency correlation diagram for the region below 1500 cm.$^{-1}$ has been constructed in Fig. 2. The listings of the frequencies are composites of both the infrared and Raman spectra. A number of the bands in the infrared spectra, *e.g.*, in the 1420 cm.$^{-1}$ region, were badly merged, but an examination of the Raman spectra frequently made it possible to separate them. In agreement with the observations of Tarte and Deponthière for ethanol, two new low lying bands, at 773 cm.$^{-1}$ and at approximately 900 cm.$^{-1}$, were found in the spectrum of the deuterated alcohol. These bands are both assigned to DOC bending vibrations, δ_{DO}. The corresponding vibrations for the bending of the HOC group are apparently

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[20] P. Tarte and R. Deponthiere, *J. Chem. Phys.*, **26**, 962 (1957).

[21] S. Krimm, C. Liang and G. B. B. M. Sutherland, *ibid.*, **25**, 778 (1956).

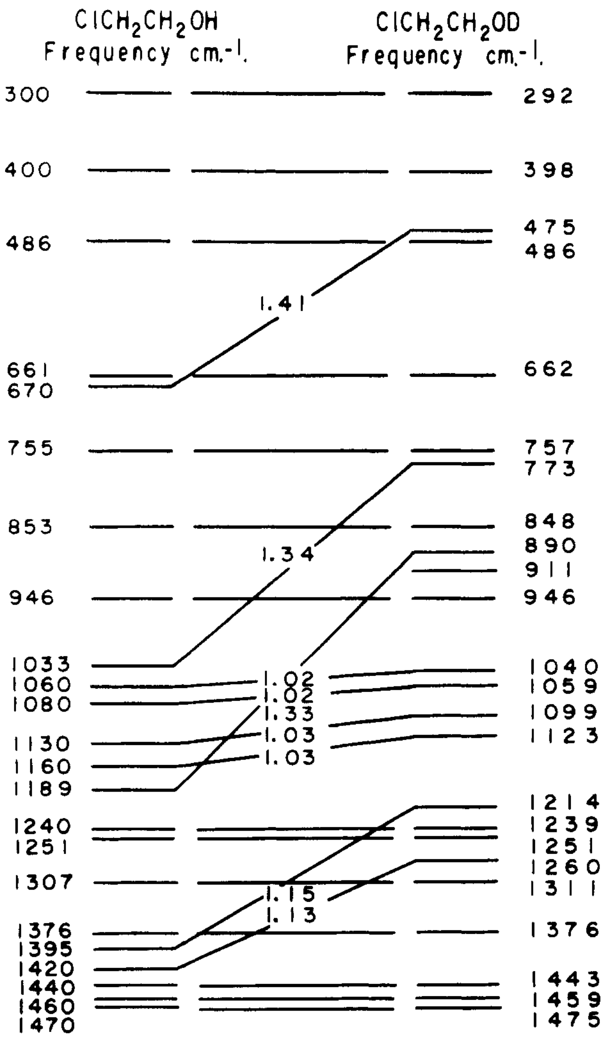


Fig. 2.—Frequency correlation diagram for 2-chloroethanol and 2-chloroethanol-*d*.

TABLE I

FREQUENCIES DISPLACED BY ISOTOPIC SUBSTITUTION IN $ClCH_2CH_2OH$ AND $ClCH_2CH_2OD$

$ClCH_2CH_2OH$		$ClCH_2CH_2OD$		
Frequency, cm.$^{-1}$	Assignment	Frequency, cm.$^{-1}$	Assignment	Group
670	τ_{HO}	475	τ_{DO}	L and H
1033	$[\delta_{HO} + \nu_{CH_2}]$	773	δ_{DO}	L
1060	ν_{OC}	1040	ν_{OC}	L
1080	ν_{OC}	1059	ν_{OC}	L
1130	ν_{OC}	1099	ν_{OC}	H
1160	ν_{OC}	1123	ν_{OC}	H
1189	$[\delta_{HO} + \nu_{CH_2}]$	900	δ_{DO}	H
1395	$[\delta_{HO} + \nu_{CH_2}]$	1214	ν_{CH_2}	L
1420	$[\delta_{HO} + \nu_{CH_2}]$	1260	ν_{CH_2}	H
3353	ν_{HO}	2486	ν_{DO}	H and L

TABLE II

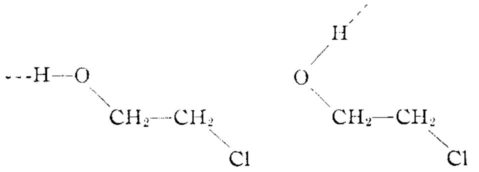
KINETIC DATA ON REACTION OF SODIUM HYDROXIDE WITH 2-CHLOROETHANOL IN WATER SOLUTION AT 25°

NaOH, *M*	$HOCH_2CH_2Cl$, *M*	Solvent	$k \times 10^2$, M^{-1} sec.$^{-1}$
0.327	0.328	H_2O	0.972[a]
.0327	.0820	H_2O	1.00[a]
.0327	.0820	H_2O	0.99[a]
.0327	.0820	H_2O	1.02[a]
.0327	.0820	H_2O	1.02[a]
.0330	.125	H_2O	1.04[a]
.0330	.125	H_2O	1.02[a]
.0270	.0790	H_2O	0.973
.0270	.0790	H_2O	0.996
.0270	.0790	H_2O	1.01
.0270	.0820	H_2O	0.977
.0270	.0820	H_2O	0.972
.0340	.0850	D_2O	1.51[a]
.0340	.0850	D_2O	1.54[a]
.0340	.0850	D_2O	1.51[a]
.0340	.0850	D_2O	1.54[a]
.0281	.0788	D_2O	1.57
.0281	.0820	D_2O	1.60
.0339	.0781	D_2O	1.54
.0339	.0781	D_2O	1.55
.0339	.0781	D_2O	1.53

[a] Runs by A. D. Ketley at 25.2°. All others by R. F. W. Bader at 25.0°.

coupled with some vibration of the CH_2 group, *i.e.*, a total of four bands are greatly displaced on deuteration. The present results indicate that there are two sets of mixed vibrations present, of the type previously described for primary alcohols by Sutherland[21] and by Mizushima,[22] a set at 1420 and 1189 cm.$^{-1}$ and another at 1395 and 1033 cm.$^{-1}$. On deuteration of the alcohol the coupling of the masses which give rise to these mixed vibrations is broken down and four new frequencies appear, two of them at 1260 and 1214 cm.$^{-1}$ and the other two at 773 and 900 cm.$^{-1}$. The former two are probably due to some now uncoupled deformation vibration of the CH_2 group, and the latter two are the frequencies of the pure DOC bending motions. The frequency shifts are comparable for each set of doublets, being 1.34 and 1.33 for the low frequencies and 1.15 and 1.13 for the high frequencies. This would indicate that a similar type of coupling is operative in each case. Corresponding to the two sets of δ_{HO} and δ_{DO} vibrations, there are two sets of bands which shift only slightly, by 1.02 and 1.03, and both of which are doublets. The two sets of doublets occur in regions of the spectrum associated with the ν_{OC} stretching vibration, at 1070 and 1145 cm.$^{-1}$, and they are so assigned. The mass displacement of the frequency would be expected to be small for a CO stretching vibration since the motion of the hydrogen is slight for this mode. Since Tarte and Deponthière investigated the spectra of gaseous samples, no mixing of the δ_{HO} and ν_{CH_2} vibrations occurred, and hence they observed no shifts in frequency in the region of 1400 cm.$^{-1}$. The coupling is apparently possible only with the δ_{HO} vibrations for the associated forms of the alcohol.

Table I lists the frequencies which are shifted by isotopic substitution of the hydroxylic hydrogen atom, together with their vibrational assignments. The symbol $[\delta_{HO} + \nu_{CH_2}]$ stands for a mixed vibration arising from some coupled motion of the CH_2 group and the HOC group. The doubling of the vibrations associated with the HOC group is most likely due to the presence of two different stable hydrogen-bonded configurations of the HOC group in the liquid state. Both of the configurations are most likely to be of the *trans* form with respect to the relative position of the chlorine and oxygen atoms, but they may differ in the position of the hydrogen atom.



Kinetic Procedure.—The rate of hydrolysis of 2-chloroethanol was measured in light and in heavy water by titrimetric determination of the rate of disappearance of the hydroxide ion. Stock solutions of 2-chloroethanol in light water and in heavy water approximately 0.16 *M* were pre-

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[22] C. Tanaka, K. Kuratani and S. Mizushima, *Spectrochim. Acta*, **9**, 265 (1957).

pared and stored in the refrigerator. All transfers of heavy water were made with syringes, previously dried at 200° for five hours, assembled while hot and stored in a desiccator over Drierite. The solutions of sodium deuteroxide were prepared by allowing approximately 0.03 g. of sodium to react with 27 ml. of heavy water under a stream of dry carbon dioxide-free nitrogen gas. The heavy water was aerated with the nitrogen gas for 0.5 hour before the addition of the sodium to ensure the removal of any carbon dioxide which may have been initially present in the liquid. Five ml. of a standard sodium hydroxide solution (or of a standard deuteroxide solution in heavy water) was introduced into a 10-ml. glass-stoppered volumetric flask by means of a 5-ml. pipet. The flask and its contents were placed in a 25° bath, as was approximately 6 ml. of the 2-chloroethanol stock solution. When temperature equilibrium had been attained, 5 ml. of the 2-chloroethanol solution was added to the 10-ml. volumetric flask containing the sodium hydroxide solution by means of a 5-ml. pipet. The solution was rapidly and thoroughly shaken and a stopwatch started. One-ml. pipets were used to transfer samples of the solution into 25-ml. erlenmeyer flasks containing approximately 10-ml. of ice-cold water, three drops of brom thymol blue indicator and a magnetic stirring bar. The flasks were placed in a shallow ice-bath atop a magnetic stirrer and titrated with 0.01 *M* hydrochloric acid from a 5-ml. microburet.

Kinetic Data.—Table II lists the measured second-order rate constants from 21 kinetic runs.

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Preparation of Some Organosilanediols and Phenylsilanetriol by Direct Hydrolysis Using Aniline as Hydrogen Chloride Acceptor[1]

BY TOSHIO TAKIGUCHI

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An improved preparation of unstable silanols involving the hydrolysis of the corresponding chlorosilanes with the theoretical amount of water in ether in the presence of aniline as hydrogen chloride acceptor has been developed. Dimethylsilanediol, diethylsilanediol, diphenylsilanediol and phenylsilanetriol were obtained in pure form by this procedure. Methyltrichlorosilane was also hydrolyzed by the proposed method, but all attempts to obtain a monomeric product have failed.

A striking feature of many organosilanols is their marked tendency to condense to polymeric products. For this reason, direct hydrolytic procedures have only been applied to the preparation of relatively stable silanols, the preparation of diethylsilanediol[2,3] by means of special techniques having been the utmost achievement.

The previous failure to obtain dimethylsilanediol and phenylsilanetriol by direct hydrolysis has been attributed to the extreme instability or rapidity of condensation of these compounds; these silanols, therefore, have heretofore been prepared from the corresponding alkoxysilanes.[4–6]

The general difficulty in preparing unstable silanols by direct hydrolysis from the corresponding chlorosilanes presumably has resulted both from the substantially heterogeneous character of the reaction and from the catalytic effect of hydrogen chloride produced thereby. Without proper precaution, especially against the polymerizing effect of hydrogen chloride, any successful preparation cannot be expected.

Therefore, the hydrolysis of chlorosilanes under carefully controlled mild conditions has generally been the aim of previous investigators.[2–3,7–9]

In the present paper we wish to report an improved method for the preparation of some unstable silanols including both dimethylsilanediol and phenylsilanetriol directly from the corresponding chlorosilanes. Our finding[10] that aniline is an excellent acceptor of hydogen chloride in dry ether, precipitating aniline hydrochloride almost quantitatively, prompted a successful hydrolysis of some chlorosilanes in ether in presence of the theoretical amounts of water and aniline.

When one mole of di- or trichlorosilane (ether solution) was added to an ether solution containing two moles (three moles for trichlorosilane) each of distilled water and aniline, aniline hydrochloride was precipitated and the corresponding silanols were obtained in pure form from the filtrate after evaporation under diminished pressure, the reaction being expressed by the general equation

$$R_nSiCl_{4-n} + (4-n)C_6H_5NH_2 + (4-n)H_2O \longrightarrow R_nSi(OH)_{4-n} + (4-n)C_6H_5NH_3Cl$$

Dimethylsilanediol, diethylsilanediol, diphenylsilanediol and phenylsilanetriol were prepared in good yield by essentially the same procedure although the degree of care required during the preparation varies with the stability of the product.

Dimethylsilanediol, diethylsilanediol, diphenylsilanediol and phenylsilanetriol are colorless

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(1) A brief outline of this method is being submitted in the *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*) as a Short Communication.

(2) P. A. DiGiorgio, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **68**, 344 (1946).

(3) P. D. George, L. H. Sommer and F. C. Whitmore, *ibid.*, **75**, 1585 (1953).

(4) Dimethylsilanediol from dimethyldimethoxysilane; S. W. Kantor, *ibid.*, **75**, 2712 (1953).

(5) Dimethylsilanediol from dimethyldiethoxysilane; J. F. Hyde, *ibid.*, **75**, 2166 (1953).

(6) Phenylsilanetriol from phenyltrimethoxysilane; L. J. Tyler, *ibid.*, **77**, 770 (1955).

(7) J. F. Hyde and R. C. DeLong, *ibid.*, **63**, 1194 (1941).

(8) C. A. Burkhard, *ibid.*, **67**, 2173 (1945).

(9) S. Fukukawa, *Science & Industry, Japan*, **30**, 71 (1956).

(10) T. Takiguchi, *J. Chem. Soc. Japan* (*Ind. Chem. Sect.*), **61**, 1236 (1958).