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explains roughly the variation of the diamagnetic susceptibility of water with temperature.

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Hydrogen Isotope Effect in the Oxidation of Benzyldehyde-α-*t* with Aqueous Acid Chromate*

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RECENTLY Wiberg[1] has studied the chromate oxidation of benzaldehyde and of benzaldehyde-α-*d* in 90% acetic acid at 25°; he found the ratio of reaction rate constants, k_H/k_D, to be 4.3±0.2. This difference in rates indicates that the carbonyl hydrogen atom is removed in the rate-determining step of the reaction. In this investigation, the isotope effect in the oxidation of benzaldehyde-α-*t* by aqueous acid chromate at 80° was found to be 7.9±0.3.

Preparation of benzyldehyde-α-t.—Twenty grams (0.5 mole) of chromium trioxide (chromic acid) was added with stirring to a cold solution of 44.4 g (0.6 mole) of *tert*-butyl alcohol in 70 ml of benzene. After this solution was dried with anhydrous sodium sulfate and filtered, it was added to a cooled, stirred solution containing 16.2 g (0.151 mole) of benzyl-α-*t* alcohol (12.2 μC/mmole) and 1 ml of pyridine[2] in 70 ml of benzene. The solution stood at room temperature overnight under a nitrogen atmosphere, and was further treated by the general method of Oppenauer and Oberrauch[3] to obtain benzaldehyde. In order to remove the last traces of benzyl alcohol the benzaldehyde was converted to the crystalline sodium bisulfite addition product and stored in this form until needed. Treatment of this solid with potassium carbonate and subsequent purification gave benzaldehyde (8.54 μC/mmole) with a yield of 41% from the alcohol.

Oxidation of benzaldehyde-α-t.—Controlled reactions were run in cylindrical glass containers each having a volume of 100–200 ml and closed with a cap fitted with a stopcock. An appropriate volume of aqueous solution of 0.0225*M* benzaldehyde-α-*t* was measured into each reaction vessel. This was closed with the cap, evacuated to the vapor pressure of water, refilled with nitrogen through the stopcock, and placed in a thermostat at 80° for one hour. Perchloric acid was added to make the solution 0.4*M* in acid. Potassium dichromate solution was added in such amount as to react with a different fraction of the benzaldehyde in each container.

Table I. Oxidation of benzaldehyde-α-*t* with aqueous chromate.

Benzaldehyde: initial concentration, 0.0225 *M*
initial activity, 8.54 μC/mmole

Perchloric acid: 0.4*M* Temperature: 80°

Final activity of benzaldehyde, μC/mmole	Extent of reaction	k_H/k_T
29.1	0.751	8.3
36.4	0.813	7.5
44.4	0.848	7.9
		Average 7.9±0.3

After five days the chromate color had disappeared from all the tubes, and they were cooled to room temperature. Aliquots were taken for determination of benzaldehyde by precipitation as the 2,4-dinitrophenylhydrazone. The precipitates were recrystallized and assayed for tritium activity; the results are shown in Table I. Other experiments showed that no gain or loss in activity occurred except in the actual oxidation. The isotope effect was found by use of the equation:

$$k_T/k_H = 1 + \log r/\log(1-f). \qquad (1)$$

Here *r* is the ratio of activities of the remaining benzaldehyde and of the original benzaldehyde, and *f* is the fraction of the benzaldehyde reacted.

Discussion.—Wiberg[1] found that benzaldehyde has aldehyde carbon-hydrogen stretching bands at 3.58 and 3.68 μ, and that benzaldehyde-α-*d* has these at 4.76 and 4.83 μ. The deuterium isotope effect at 80° may be calculated from the value found at 25° by the equation,[4]

$$k_1/k_2 = (m_2^*/m_1^*)^{\frac{1}{2}}(\lambda_1/\lambda_2)\ \exp hc(1/\lambda_1 - 1/\lambda_2)/2kT \qquad (2)$$

where m^* is the effective mass of the activated complex in the direction of reaction and λ the wavelength of the stretching band. The value of k_H/k_D at 80° thus calculated is 3.34±0.15.

The ratio of tritium and deuterium isotope effects, $(k_H/k_T)/(k_H/k_D)$, becomes the k_D/k_T ratio. Using the value of 3.34±0.15 for the k_H/k_D ratio and the value of 7.9±0.3 for the k_H/k_T ratio, the k_D/k_T ratio becomes 2.37±0.14.

From the carbon-hydrogen and the carbon-deuterium stretching wavelengths found for benzaldehyde,[1] the carbon-tritium wavelengths can be calculated by the equation,

$$\lambda_2 = \lambda_1(m_2^*/m_1^*)^{\frac{1}{2}}, \qquad (3)$$

where m^* is the reduced mass of the atoms involved. The carbon-tritium wavelengths thus calculated are 5.77, 5.93, 5.63, and 5.71 μ. Using an average value of 5.76 μ for the carbon-tritium wavelength and 4.80 μ for the carbon-deuterium wavelength in Eq. (2), k_D/k_T at 80° is found to be 2.00.

The agreement between the "experimental" k_D/k_T ratio of 2.37 ± 0.14 and the "theoretical" one of 2.00 is good considering the difference in reaction conditions and the approximations in the equations used.

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Nuclear Magnetic Resonance of Water Sorbed on Fibrous Materials*

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SEVERAL authors have recently measured the motion of water molecules in the sorbed state, using a nuclear magnetic resonance (NMR) method.[1–3] It is interesting to compare the results, such as correlation times, of the NMR measurements on sorbed water with similar quantities obtained from dielectric measurements,[4–6] and to find the relationship between these observations.

Employing a Varian high resolution type NMR spectrometer, we have measured the line widths of the water sorbed on the native cellulose, "mulberry paper," in the range of the moisture contents from 10 to 180% at 20°C. Half-width of the NMR absorption line for the sorbed water in cps *vs* the moisture content is shown in Fig. 1, in which the data obtained by other researchers[1,2] are also shown. There is a fairly good agreement between the gradients of each curve in the same range of concentration.

According to the dielectric measurements on sorbed water,[7] the sorbed water is classified into two classes, that is, localized sorbed water and mobile sorbed water, the latter having two states. In other words, there are three states, corresponding with three moisture content ranges: 0–5%, 5–20% (or 5–30%), and over 20% (or 30%), respectively.[4] In the NMR measurement of the sorbed water, the observation of the line width due to the localized water is beyond the range of the observation of our apparatus. Therefore, the observed variation of the line widths, which are plotted in Fig. 1, reasonably expected to come from the mobile water. It is quite apparent that the mobile water is not unique but divided into two states having different dependency on the moisture content, that is, the state with a sharp gradient and that with a gradual gradient, as shown in Fig. 1. The boundary of these states may be at moisture content of about 20%. The above classification, which is deduced from dielectric measurement, seems to be qualitatively applicable to the explanation of the existence of the two states of the mobile water in the NMR observation.

On the other hand, there is the theoretical expected relation between dielectric constant time τ_D and NMR correlation time τ_N,[8] that is

$$\tau_D = 3\tau_N \tag{1}$$

τ_N is calculated from the observed line width through Kubo-Tomita[9] and Solomon[10] equation.

$$T_2^{-1} = (\langle\sigma_0^2\rangle/3)\{3\tau_N + [5\tau_N/(1+\omega^2\tau_N^2)] + [2\tau_N/(1+4\omega^2\tau_N^2)]\} \tag{2}$$

where ω is NMR resonance frequency and $\langle\sigma_0^2\rangle$ is the second moment in the case of a rigid lattice. Remembering $T_2^{-1} = (\langle\sigma_0^2\rangle)^{\frac{1}{2}}$ in the rigid case we take T_2 to be 5×10^{-6} sec for ice at -40°C, and then obtain τ_N for the sorbed water from Eq. (2). These values are tabulated in Table I.

It is worth noting that τ_N is not the same order of magnitude but much larger than τ_D for the same moisture contents. This suggests to us that the water molecules in the sorbed state do not rotate with spherical symmetry even in the mobile sorbed water which is assumed in the derivation of Eq. (2). Two different

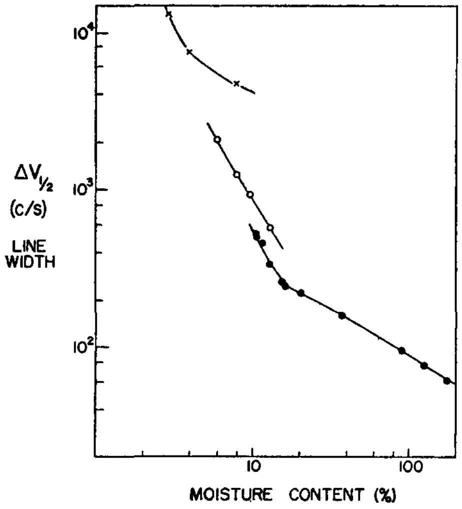

Fig. 1. NMR line width *vs* the moisture content. ×, Tanaka-Yamagata's data; ○, Shaw's data; ●, our data.