the adsorbed polyelectrolyte, the counterions will be able to penetrate into the space between the phase boundary and the region containing the charged groups of the polyelectrolyte as a result of which penetration double layer will be formed. ψ in eq 11 in fact occurs due to the inclusion within the double layer, negatively charged chloride ions which are expected to exist at a distance outside the penetration region of the interface. The potential in this region containing Cl⁻ ions will be similar to that for the Gouy double layer. With some theoretical reservation about the slipping plane, ψ in eq 11 may be identified with the ζ potential which for the adsorbed polyelectrolyte is a measurable quantity. It has already been shown[1] that for ψ greater than 25 to 30 mv, eq 11 will be independent of ψ ($e^{-2\epsilon\psi/KT} \ll 1$) and hence independent of the model of the double layer.

In eq 7 and 11, z represents the average number of the charge obtained from the ionization of the salt-forming groups of a polyelectrolyte molecule. Its value for a protein solution at a particular pH and ionic strength, usually obtained from the electrometric titration, is fixed and independent of the protein concentration.[5,7] For the flexible polyelectrolyte, it has been experimentally shown[8,9] that the considerable portion of the ionizable groups of the polymer will not dissociate because of the specific binding of the counterions. If the net charge which in this case will be less than that obtained for the complete polyion dissociation is experimentally determinable, we can use it in eq 7 and 11 provided its value is independent of the polymer concentration. More advantageous will be the use of the titration charge for the z value and ψ_d or ζ for the diffuse double-layer potential in eq 11 with the assumption that the specifically bound counterions remain within the Stern layer.

In eq 2, we have neglected the term $n_{Cl^-}\,\mathrm{d}\mu_{Cl^-}$ which will be justified even for the slight variation of C_{Cl^-} or C due to the variation of C_R in the system since

$$n_{Na^+}\,\mathrm{d}\mu_{Na^+} + n_{Cl^-}\,\mathrm{d}\mu_{Cl^-} =$$

$$n_{Na^+}\,\mathrm{d}\mu_{Na^+}\left[1 + \frac{n_{Cl^-}/C_{Cl^-}}{n_{Na^+}/C_{Na^+}}\frac{\mathrm{d}C_{Cl^-}}{\mathrm{d}C_{Na^+}}\right] =$$

$$n_{Na^+}\,\mathrm{d}\mu_{Na^+}\left[1 + e^{-2\epsilon\psi/KT}\frac{1}{z\dfrac{\mathrm{d}C_R}{\mathrm{d}C} + 1}\right] \quad (20)$$

$e^{-2\epsilon\psi/KT}$ equal to $(n_{Cl^-}/C_{Cl^-})/(n_{Na^+}/C_{Na^+})$ by the Boltzmann distribution principle (see eq 10) is less than unity. The value of $z(\mathrm{d}C_R/\mathrm{d}C)$ will be considerably high and the last term within the bracket of eq 20 can safely be neglected with respect to unity.

In eq 3, we have used the concentration term in place of the activity of the polyelectrolyte. The highest concentration of the serum albumin used in the boundary tension measurement[4] is of the order of 10^{-5} mole/l. so that the concentration effect on the activity coefficient is expected to be trivial. However, the activity coefficient γ_h for the rigid spherical polyelectrolyte in the neutral salt solution will be given by the expression[10]

$$\gamma_h = e^{z^2\epsilon^2/2DKT}\left(\frac{1}{b} - \frac{\kappa}{1 + \kappa a}\right) \quad (21)$$

where D is the dielectric constant of the medium, $1/\kappa$ is the Debye–Hückel thickness, b is the radius of the spherical polyion, and a is the closest distance of approach of the center of the sphere to the center of the neighboring small ion. γ_h at a particular pH and ionic strength will be independent of the polyion concentration and eq 3 will also be valid under this condition. The expression for the activity coefficient of the flexible polyelectrolyte, given by Katchalsky, et al., indicates, however, the variation of the coefficient with the variation of C/C_R ratio.[11] Their experimental results[11] indicate that at moderately high salt concentration the activity coefficient is nearly unity and is insensitive to the polyion concentration. It is therefore safe to use eq 7 and 11 for the flexible polyelectrolyte at moderately high salt concentration.

(7) C. Tanford, "Physical Chemistry of Macromolecules," John Wiley and Sons, Inc., New York, N. Y., 1961.

(8) J. R. Huizenga, P. F. Grieger, and F. T. Wall, J. Am. Chem. Soc., 72, 2636, 4228 (1950).

(9) F. T. Wall, H. Terayama, and S. Techakumpuch, J. Polymer Sci., 20, 477 (1956).

(10) J. T. Edsall and J. Wyman, "Biophysical Chemistry," Vol. 1, Academic Press, New York, N. Y., 1958, p 514.

(11) J. Bockris, Ed., "Modern Aspects of Electrochemistry," Butterworth and Co., Inc., Washington, D. C., 1954, pp 18–20.

Spin–Spin Coupling in Di-*t*-butyl Carbinol

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During a study of hydrogen bonding by di-*t*-butyl carbinol (DTBC) in carbon tetrachloride, we observed OH proton spin–spin coupling both in pure carbon tetrachloride and in solutions containing an excess (over the DTBC concentration) of the 16 hydrogen bonding bases listed in the Experimental Section. Figures 1–3
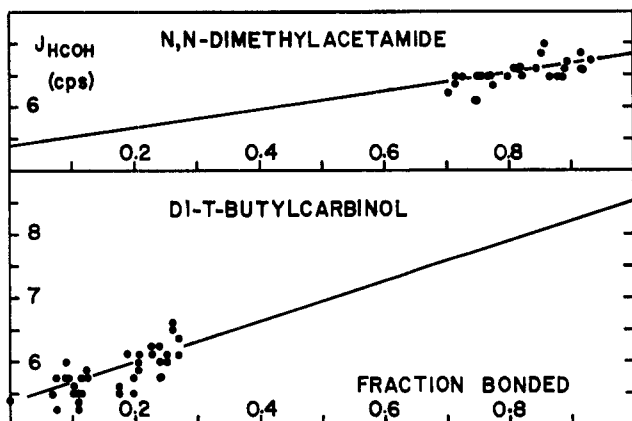
Figure 1. Plots of observed J_{HCOH} (cps) vs. fraction of DTBC which is hydrogen bonded by heteroassociation with N,N-dimethylacetamide and self-association.
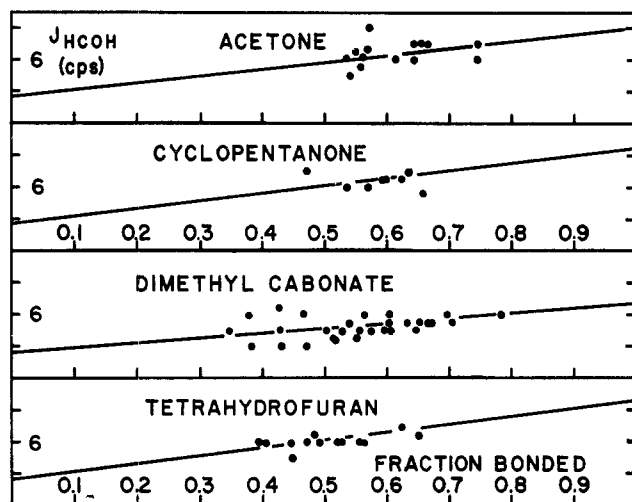

Figure 2. Plots of observed J_{HCOH} (cps) vs. fraction of DTBC which is hydrogen bonded by heteroassociation with acetone, cyclopentanone, dimethyl carbonate, and tetrahydrofuran.
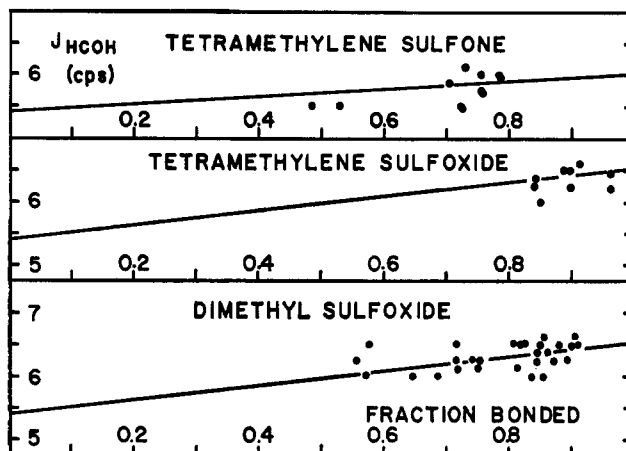

Figure 3. Plots of observed J_{HCOH} (cps) vs. fraction of DTBC which is hydrogen bonded by heteroassociation with tetramethylene sulfone, tetramethylene sulfoxide, and dimethyl sulfoxide.

show plots of J_{HCOH} vs. the fraction of DTBC which is hydrogen bonded. Reasonable lines through the scatter of experimental points yield the following approximate J_{HCOH} values (in cps) for nine hydrogen-bonded complexes of DTBC: dimer, 8.5; N,N-dimethylacetamide, 6.8; tetrahydrofuran, 6.6; cyclopentanone, 6.6; dimethyl carbonate, 6.2; acetone, 6.5; tetramethylene sulfone, 6.0; tetramethylene sulfoxide, 6.5; and dimethyl sulfoxide, 6.5. Measurement of J_{HCOH} (cps) for DTBC at three concentrations (0.015, 0.023, and 0.032 m) where there is no hydrogen-bond formation, as evidenced by the concentration independence of the OH chemical shift, gave the results 5.4 ± 0.2, 5.4 ± 0.4, 5.4 ± 0.1, and 5.4 ± 0.1 at 25, 17, 8, and −5°, respectively. Consequently, the intercept in Figures 1–3 for hydrogen-bonded fraction of zero is 5.4 cps as

this value was assumed in visually obtaining the lines shown. The temperature independence for J_{HCOH} implies that the two conformers of monomeric DTBC shown in Figure 4 have equal energy since J_g and J_t are expected to be unequal. Then the observed J_{HCOH} of 5.4 cps equals $(^1/_3)$ $(J_t + 2J_g)$. The different values of the fraction of DTBC that is hydrogen bonded in the heteroassociation studies correspond to different concentrations of base (all in the 0.2 to 4.0 m range) and different temperatures (all in the −15 to +65° range) for a low (all in the 0.04 to 0.3 m range) and constant concentration of DTBC with each base. For the self-association case, the different values of the fraction of bonded DTBC correspond to different DTBC concentrations (all in the 0.04 to 3.00 m range) and temperatures (all in the −10 to +26° range). The fraction of DTBC that is hydrogen bonded was calculated from measured OH chemical shifts at known DTBC and base concentrations and temperatures using the free and bonded OH chemical shifts of DTBC. The heteroassociation and self-association data were treated by the methods of Li[1] and Patterson and Hammaker,[2,3] respectively, to obtain the difference between the free and bonded OH chemical shift. The free OH chemical shifts were measured directly in dilute solutions (0.01 to 0.03 m) of DTBC in carbon tetrachloride. More details of these hydrogen-bonding studies will be given elsewhere.[2,3]

The interpretation of the increase in J_{HCOH} upon hy-

(1) R. Mathur, E. D. Becker, R. B. Bradley, and N. C. Li, J. Phys. Chem., 67, 2190 (1963).

(2) L. K. Patterson, Ph.D. Thesis, Kansas State University, 1966.
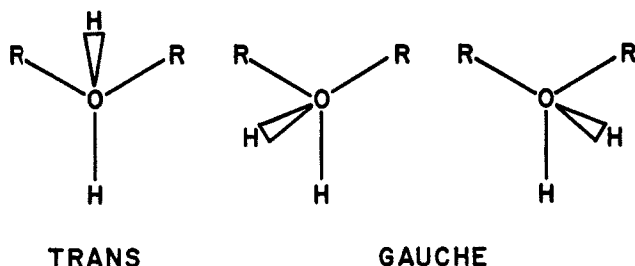
(3) L. K. Patterson and R. M. Hammaker, to be published.

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Figure 4. Conformational isomers (about the C–O bond) for an R_2CHOH secondary alcohol.

drogen bond formation shown in Figures 1–3 requires consideration of some earlier work. Methanol is a model compound for temperature variation considerations since only one conformational isomer exists, so there can be no change in conformational isomer population with temperature. In addition, methanol appears to be completely associated at room temperature and below since there is no free OH stretching band in methanol's infrared spectrum. Powles and Strange[4] report only a small increase in J_{HCOH} for methanol with temperature from 4.95 cps at $-60°$ to 5.13 cps at 23°. This result implies that J_{HCOH} is independent of temperature for our purpose. Measurements of J_{HCOH} for pure methanol,[4] 0.22 M methanol in carbon tetrachloride,[5] and 0.22 M methanol in dimethyl sulfoxide[5] all at 23° of 5.13, 5.3 ± 0.2, and 5.2 ± 0.1 cps, respectively, imply that J_{HCOH} for a free OH group and a hydrogen-bonded OH group in the same conformational isomer are about equal since the first and last cases correspond to all hydrogen-bonded OH groups and the second case to half free OH groups and half hydrogen bonded OH groups.[6] These considerations support the view of Moniz, Poranski, and Hall[5] and Rader[7] that changes in J_{HCOH} due to hydrogen bond formation are best assigned to changes in conformational isomer population upon hydrogen-bond formation with minimum steric hindrance to the approach of the hydrogen-bonding base to the OH group determining which conformational isomer is favored. Thus, for primary alcohols (RCH_2OH) the conformational isomer with two J_g contributions to J_{HCOH} is favored by hydrogen-bond formation over that with one J_g and one J_t contribution to J_{HCOH}. For R_2CHOH secondary alcohols, the conformational isomer with $J_{HCOH} = J_g$ is favored over that with $J_{HCOH} = J_t$. Then for both primary and secondary alcohols, acceptance of $|J_t| > |J_g|$ predicted[8] and found[9] for J_{HCCH} requires the observed J_{HCOH} to decrease as the fraction of OH groups which are hydrogen bonded increases provided that the R · group is sufficiently bulky to exert a significant steric effect. The results for DTBC, where R = t-Bu

is expected to exert a significant steric effect, shown in Figures 1–3, indicate an increase in J_{HCOH} as the fraction of OH groups which are hydrogen bonded increases. Consequently, acceptance of the conformational isomer population change explanation for the effect of increased extent of hydrogen bonding on J_{HCOH} requires that $|J_g| > |J_t|$, the reverse of the situation for J_{HCCH} and for J_{HCOH} in primary alcohols[5] and cyclohexanols.[7] If the hydrogen-bonded complex exists only in the *gauche* isomer, then the intercept for complete hydrogen-bond formation should be the same for all cases when it is assumed that the only way hydrogen-bond formation affects the J_{HCOH} value is by changes in conformational isomer population. However, if the hydrogen-bonded complex may exist in both the *trans* and *gauche* forms with the *gauche* isomer being more abundant than in monomeric DTBC, then the intercepts in Figures 1–3 would be different with the most sterically hindred bases having the larger intercepts. The observed intercepts are consistent with such a situation since the heteroassociation cases give intercepts between 6.0 and 7.0 cps while the self-association case where the OH group oxygen of DTBC is the most sterically hindered of the basic groups considered gives 8.5 cps as the intercept. For the DTBC dimer, J_{HCOH} is an average of J_{HCOH} for two OH groups. Work in our laboratory[2,3] and experience with hindered alcohols[10] indicates that DTBC will form dimers but not trimers or higher polymers due to steric hinderance and that the DTBC dimer is linear with a free OH group and a bonded OH group. Assuming the oxygen of DTBC to be approximately sp^3 hybridized, both isomers in Figure 4 have at least one of the orbitals occupied by the nonbonding electron pairs in a best possible steric position for bonding to the OH group proton of another DTBC molecule. Then it seems reasonable

(4) J. G. Powles and J. H. Strange, *Mol. Phys.*, **8**, 169 (1964).

(5) W. B. Moniz, C. F. Poranski, Jr., and T. N. Hall, *J. Am. Chem. Soc.*, **88**, 190 (1966).

(6) Our nmr measurements for ethanol in dimethyl sulfoxide show that the OH chemical shift is concentration independent when the ethanol concentration is less than 25–35 mole %. Thus, ethanol and methanol as well exist completely as hydrogen-bonded complexes at 0.22 M in dimethyl sulfoxide. Near-infrared intensity measurements (1.4 μ) show that at 0.22 M in carbon tetrachloride half the methanol OH groups are free and half are hydrogen bonded.

(7) C. P. Rader, *J. Am. Chem. Soc.*, **88**, 1713 (1966).

(8) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Am. Chem. Soc.*, **85**, 2870 (1963).

(9) See, for example, L. E. Erickson, *ibid.*, **87**, 1867 (1965); L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, pp 84–87.

(10) F. A. Smith and E. C. Creitz, *J. Res. Natl. Bur. Std.*, **46**, 145 (1951).

that the free OH group of the DTBC dimer will have $J_{HCOH} = (^1/_3) (2J_g + J_t) = 5.4$ cps as does the monomer. Now $J_{HCOH} = 8.5$ cps $= (^1/_2) (5.4 + J_g)$ for the DTBC dimer having its bonded OH group only in the *gauche* conformational isomer so that $J_g = 11.6$ cps and $J_t = -7.0$ cps if the measured J_{HCOH} is positive. If the bonded group has some *trans* conformational isomer present, $J_g > 11.6$ cps and $J_t < -7.0$ cps for J_{HCOH} positive. These absolute magnitudes of J_g and J_t are not too unreasonable; however, the reversal of relative magnitude between J_g and J_t compared to J_{HCCH} in general and J_{HCOH} for primary alcohols and cyclohexanols remains to be explained.

Experimental Section

Carbon tetrachloride (Fisher Scientific Co., Spectrograde) was dried by storage in an open beaker in a desiccator containing P_2O_5 until the spectrum of carbon tetrachloride in a 1-cm cell *vs.* air had no OH stretching absorption. Di-*t*-butyl carbinol (DTBC) was synthesized from *t*-butyl chloride and methyl pivalate using essentially the procedure of Bartlett and Schneider.[11] The final purification of DTBC was accomplished using either preparative gas chromatography (Wilkins Instrument Co. Autoprep) or distillation through a platinum spinning-band column. The following hydrogen-bonding bases (highest grades available from Fisher Scientific Co. or Aldrich Chemical Co.) were purified and/or dried using standard techniques:[2] acetone, benzonitrile, benzophenone, cyclopentanone, N,N-dimethylacetamide, dimethyl carbonate, dimethyl sulfite, dimethyl sulfoxide, *p*-dioxane, diphenyl carbonate, diphenyl sulfoxide, pyridine, tetrahydrofuran, tetramethylene sulfone, tetramethylene sulfoxide, and triethylamine.

All solution-making and sample tube-filling manipulations were carried out in a drybox under a nitrogen atmosphere which was continuously dried and recirculated using Linde Type 13-X molecular sieve and a 08-000-77 Dia-Pump recirculator (Air Controls, Inc., Narbeth, Pa.). All spectra were run on a Varian A-60 nmr spectrometer. The Varian V-6057 variable temperature system was used to maintain desired temperatures to within $\pm 2°$.

(11) P. D. Bartlett and A. Schneider, *J. Am. Chem. Soc.*, **67**, 141 (1945).

Theoretical Study of Isoelectronic Molecules: Oxygen and Ethylene

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The O_2 molecule is unusual in having a triplet ground state. This peculiarity is attributed to the degeneracy of the antibonding orbitals π_{gx} and π_{gy}, each of which is occupied by one electron. In C_2H_4, which is isoelectronic with O_2, the degeneracy is split by the presence of the H atoms, and C_2H_4 therefore has a singlet ground state.

We have studied the relation between these two molecules by applying to O_2 a perturbation[1] in which the charge of each O nucleus is decreased by $2\Delta Z$, while fractional protons, each with charge ΔZ, appear at the positions[2] corresponding to the H nuclei in C_2H_4. The case $\Delta Z = 1$ corresponds to the transformation of O_2 to C_2H_4. The effect of this perturbation on the energy of O_2 was calculated by first-order perturbation theory, using the SCF wave function of O_2 published by Kotani, *et al.*[3]

The perturbation operator is

$$\Omega = \Delta Z \sum_{i=1}^{16} 2r_{ia}^{-1} + 2r_{ib}^{-1} - r_{ic}^{-1} - r_{id}^{-1} - r_{ie}^{-1} - r_{if}^{-1}$$

where the summation is over the electrons, and r_{ia} represents the distance of electron i from nucleus a. The O (or C) nuclei are labeled a and b; the pseudo-H nuclei are labeled c, d, e, f. Integrals of the form $\int \chi_a(1) r_{1c}^{-1} \chi_b(1) d\tau_1$, involving atomic orbitals centered on a and b and the distance from a third center c, were evaluated by expanding r_{1c}^{-1} in a Neumann series.[4] Each term of this series contains Legendre functions of the prolate spheroidal coordinates of electron 1 and nucleus c in the a–b coordinate system. The integrals were evaluated term by term with the aid of an IBM 1620 digital computer. The one- and two-center integrals are elementary.

(1) B. R. Gilson and J. Arents, *J. Chem. Phys.*, **38**, 1572 (1963).

(2) L. E. Sutton, Ed., "Table of Interatomic Distances and Configurations in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958.

(3) M. Kotani, Y. Mizuno, K. Kayama, and E. Ishiguro, *J. Phys. Soc. Japan*, **12**, 707 (1957).

(4) J. Miller, J. M. Gerhauser, and F. A. Matsen, "Quantum Chemistry Integrals and Tables," University of Texas Press, Austin, Texas, 1959, p 12.