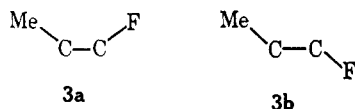terminal Me group together with the fluorine atom favored the *gauche* configuration (3a) over the *trans* (3b)

with $\Delta H_{g \to t}$ = 0.47 kcal/mole. The implication here is that real interaction, lowering the net free energy, must be taking place between one or more hydrogens on the Me group and the fluorine atom, when in the *gauche* form, in order to overcome those energy differences which result in many molecules with structures similar to **3** preferring the *trans* configuration in the gas phase.[11] We suggest that the interaction leading to **3a** being preferred is a hydrogen bond, albeit a weak one, such as we have postulated, between a hydrogen atom on the Me group and one or more lone pairs on the fluorine atom.

The complexities indicated by the $(R - 1)/[L]$ *vs.* [L] plots in the cases of the cations with Ph_3P as ligand are not unlike those noted[2] in the case of Ph_3PO with PipH+. Further study of these systems is warranted. Additional complexes of the type $PipH^+(PPh_3)_2$ and $PipH^+Pi^-(PPh_3)$ might be forming in these systems. In any case, uncertainties involved in the extrapolation (Figure 2) to obtain K_L values for Ph_3P are not great

(11) See, for instance, (a) S. Mizushima, *Pure Appl. Chem.*, 7, 1 (1963); (b) E. B. Wilson, Jr., *Advan. Chem. Phys.*, 2, 367 (1959).

enough to affect the relative order of cation–ligand affinity, just its magnitude. It is curious, however, that the large differences found with other ligands between the PipH+, MePipH+, and EtPipH+ cation–ligand association are so small in the case of Ph_3P with these same cations. Other ligands similar to Ph_3P need to be studied in an effort to understand this contrasting behavior.

Our arguments for the existence of a weak hydrogen bond between a terminal hydrogen atom on the N-ethyl group in N-ethylpiperidinium cation and the oxygen atom in Ph_3PO ligand (or THF) would, of course, be strengthened by a demonstration of appropriate shifts in the pmr spectra or in the infrared spectra of these systems. The concentrations of the cation–ligand complex species in our solutions are typically of the order of 10^{-6} M, less than $^1/_{100}$ of the total salt concentration. We are unaware of either proton magnetic resonance techniques or infrared spectroscopic techniques which are sufficiently sensitive to detect species at such low concentrations. Increasing the concentrations of salt and ligand would serve no useful purpose in this connection. At concentrations higher than the 10^{-4} M range, salt solutions in low dielectric solvents such as PhCl become extremely complex, consisting of charged and uncharged clusters of ions of increasing molecular weight. Interpretation of the spectra (pmr or infrared) of such systems would be extremely difficult, if not impossible. We, at any rate, would be very skeptical of any such interpretation.

Translational Diffusion of Common Monocyclic Hydrocarbons in Carbon Tetrachloride

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Abstract: Measurements have been made of the translational diffusion coefficients of cyclopentane, cyclohexane, and cycloheptane in carbon tetrachloride. The results have been examined in terms of the theories proposed by Kirkwood and Tchen, respectively. Although both theories take into account the hydrodynamic interaction between the solute and solvent, the experimental results do not agree closely with the theoretical values.

One of the best known theoretical studies of the diffusion of polymer chains is that of Kirkwood.[1] The formula (eq 2) for the frictional coefficient derived from this theory is somewhat in error, as has been pointed out by many authors including Zwanzig[2] and Erpenbeck and Kirkwood.[3] For weak hydrodynamic interactions, however, this error may be negligible and, hence, it may be hoped that the formula retains a practical usefulness.

Indeed, the applicability of the Kirkwood formula to short-chain (5 to 28 carbon atoms) *n*-alkanes has al-

ready been demonstrated by Dewan and Van Holde,[4] who obtained good agreement between the calculated and observed values of the frictional coefficient. Further applications of this equation to multi-subunit macromolecules, and a generalization to different size subunits have been presented.[5,6] However, uncertainties as to the range of validity of the theory require that data for more substances of known molecular structure be made available.

(1) J. G. Kirkwood, *J. Polymer Sci.*, 12, 1 (1954).
(2) R. Zwanzig, *J. Chem. Phys.*, 45, 1858 (1966).
(3) J. J. Erpenbeck and J. G. Kirkwood, *ibid.*, 38, 1023 (1963).

(4) R. K. Dewan and K. E. Van Holde, *ibid.*, 39, 1820 (1963).
(5) V. Bloomfield, W. O. Dalton, and K. E. Van Holde, *Biopolymers*, 5, 135 (1967).
(6) V. Bloomfield, K. E. Van Holde, and W. O. Dalton, *ibid.*, 5, 149 (1967).

It has been suggested by Zwanzig that, for the case of ring molecules, a deviation of about 10% is to be expected between the experimental and calculated results. This error estimate is based on the hydrodynamically exact calculation by Tchen[7] of the frictional coefficient for a rigid ring. Tchen's results differ by about 10% from those obtained by applying the Kirkwood equation to the rigid-ring model.

With the intention of providing data on simple ring molecules to aid further theoretical development, as well as of experimentally checking the validity of the Kirkwood equation for these molecules, we have undertaken the present study of cyclopentane, cyclohexane, and cycloheptane in carbon tetrachloride.

Experimental Section

A. **Materials.** The cyclopentane and cyclohexane used in this work were Spectroquality reagents obtained from the Matheson Coleman and Bell Co. The cycloheptane was obtained from K and K Laboratories, Inc. The carbon tetrachloride was a Fisher Certified reagent. All the hydrocarbons were freshly distilled before use.

B. **Apparatus and Procedure.** The apparatus and experimental techniques were identical with those used by Dewan and Van Holde[4] in their work on the n-alkanes. Briefly they consisted of an adaptation of the Rayleigh interferometric method to a modified Pearson electrophoresis apparatus. Diffusion occurred in a special Tiselius cell with a twin channel in the center section; the boundaries were initially sharpened by siphoning. The temperature was maintained at $25.00 \pm 0.01°$. A Bausch and Lomb bench comparator was used to measure the fringes on the photographic plates which recorded the Rayleigh patterns.

The diffusion coefficient, D, was computed from the experimental data by a method discussed by Schachman.[8] The apparent diffusion coefficients were plotted vs. the reciprocal time and linearly extrapolated by a least-squares technique to obtain the diffusion coefficients at zero reciprocal time. This procedure corrects for initial boundary imperfections.[4]

Calculations

The experimentally observed frictional coefficient is defined by

$$f_0 = kT/D \tag{1}$$

where k is Boltzmann's constant and T is the temperature in degrees Kelvin.

One set of calculated values of the frictional coefficient reported in this work is obtained from the Kirkwood equation[1]

$$f_{c,K} = n\zeta[1 + (\zeta/6\pi n\eta)\sum_{\substack{i,j=1 \\ i \neq j}}^{n}\langle 1/R_{ij}\rangle_{av}]^{-1} \tag{2}$$

where n is the number of $-CH_2-$ monomer units in the molecule and η is the coefficient of viscosity of the solvent (9.027×10^{-3} g/cm sec for CCl_4 at 25.00°).[9] The quantity ζ is the frictional coefficient of each individual monomer unit. To the first approximation, the monomer units may be considered as spheres of radius $b/2$, where b is the C–C bond distance (1.533 A); hence, by Stokes' law

$$\zeta = 6\pi\eta b/2 \tag{3}$$

The value of $n\zeta$ is a first approximation (sometimes called the "free draining" approximation) to the fric-

(7) C. M. Tchen, *J. Appl. Phys.*, **25**, 463 (1954).
(8) H. K. Schachman in "Methods in Enzymology," Vol. 4, S. P. Colowick, and N. O. Kaplan, Ed., Academic Press Inc., New York, N. Y., 1957, pp 78–95.
(9) This value was obtained by a linear interpolation of log η vs. $1/T$ from data in the "International Critical Tables."

tional coefficient of the molecule, and in general, is not very accurate. The quantity $\langle 1/R_{ij}\rangle_{av}$ is the time average of the reciprocal distance between monomer units i and j. To obtain this average, we have made use of the configurational analyses of the three cycloalkanes done by Hendrickson.[10]

Straight-chain molecules can exist in a number of quite different configurations, all having energies nearly equal to the lowest configurational energy. In contrast ring molecules composed of a small number of monomer units possess a distinct lowest energy configuration. We make the assumption that the ring molecule spends most of its time in this configuration,[11] and that it is unnecessary to consider other configurations in calculating $\langle 1/R_{ij}\rangle_{av}$.[12]

The geometries of the ring molecules are given by Hendrickson in terms of the C–C–C bond angles assuming that the bond lengths remain constant. It is, thus, fairly easy to calculate R_{ij} from these data.

For cyclopentane, R_{ij} falls into two classes. When the i and j units are adjacent, R_{ij} is equal to b, and, when the i and j units are separated by an intermediate unit

$$R_{ij} = b[2(1 - \cos\theta)]^{1/2} \tag{4}$$

where θ is the C_i–C–C_j bond angle.

For cyclohexane and cycloheptane, there is a third class of R_{ij} occurring when the i and j units are separated by two intermediate units labeled α and β.
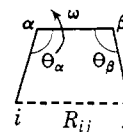
For this case

$$R_{ij} = b[3 - 2(\cos\theta_\alpha + \cos\theta_\beta - \cos\theta_\alpha\cos\theta_\beta + \sin\theta_\alpha\sin\theta_\beta\cos\omega)]^{1/2} \tag{5}$$

where ω is the angle between the plane containing units i, α, and β and that containing units α, β, and j.

In the case of cyclohexane, for example

$$\sum_{\substack{i,j=1 \\ i \neq j}}^{n}\langle 1/R_{ij}\rangle_{av} = \frac{2n}{b} + 2\sum_{j=1}^{6}(1/R_{i,i+2}) + 2\sum_{i=1}^{3}(1/R_{i,i+3}) \tag{6}$$

where the $-CH_2-$ units have been numbered as in the following diagram.

The first term is the sum of all the reciprocal distances of the first type; the second term involves distances of the second type, etc.

Following Zwanzig's suggestion made in his note, we have also calculated a set of values of the frictional coefficients using a formula derived by Tchen. For a rigid ring composed of n elements of length b, Tchen's

(10) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).
(11) These most stable configurations are a "puckered" ring for cyclopentane, the chair configuration for cyclohexane, and a twisted chair configuration for cycloheptane.
(12) When the average was calculated using the higher energy configurations mentioned in Hendrickson's work,[10] $f_{c,K}$ differed by less than one unit in the third significant figure from the values in Table I.

Table I. Diffusion and Frictional Coefficients of Cycloalkanes in CCl_4 at $25.00 \pm 0.01°$

Compound	$D \times 10^5$, cm^2/sec	$f_0 \times 10^9$, g/sec	$n\zeta \times 10^9$, g/sec	$\sum_{ij}\langle 1/R_{ij}\rangle_{av} \times$ 10^9, cm^{-1}	$f_{c,K} \times 10^9$, g/sec	$f_{c,T} \times 10^9$, g/sec
Cyclopentane	1.29_5	3.17_7	6.53_0	1.06_6	2.47_9	4.42_0
Cyclohexane	1.21_9	3.37_5	7.83_6	1.46_6	2.72_8	4.76_4
Cycloheptane	1.26_8	3.24_5	9.14_2	1.91_3	2.95_4	5.11_8

equation is given in the form

$$f_{c,T} = \frac{36\pi\eta nb}{11 \ln n} \tag{7}$$

where η is again the viscosity of the solvent, n the number of $-CH_2-$ units, and b the length of the C–C bond.

Results and Discussion

Table I exhibits the results of experimental studies and theoretical calculations.

It is apparent that in all three cases there are discrepancies between observed frictional coefficients and calculated values using the Kirkwood ($f_{c,K}$) and Tchen ($f_{c,T}$) equations. With the Kirkwood equation, there is a discrepancy of 22% in the case of cyclopentane, 19% in cyclohexane, and 9% in cycloheptane. With Tchen's equation, the discrepancies are even larger. Since Tchen's theory is based on a thin torus model, the discrepancy is not surprising.

There are several possible reasons for the discrepancy between the experimental results and those calculated by the Kirkwood theory. First, there is the error inherent in the derivation of the Kirkwood formula from the theory. Zwanzig has pointed out that this error may be as high as 10%, and our results certainly do not contradict him. Secondly, the Kirkwood theory assumes that the solute molecule acts as a string of beads moving through a solvent which acts as a continuous fluid. For a ring structure, this assumption presumes that the solvent can flow freely through the

hole in the ring, but this is certainly not true for the small cycloalkanes in any real solvent. The smaller cycloalkanes must act more as spheres than strings of beads.

This analysis is supported by a comparison of our values of f_0 with the values Dewan and Van Holde obtained for the n-alkanes. In units of g/sec, the above authors obtained 2.624×10^{-9} for the frictional coefficient of n-pentane, $2.73_9 \times 10^{-9}$ for n-hexane, and $3.07_7 \times 10^{-9}$ for n-heptane. All three values are smaller than those of the corresponding cycloalkanes. According to the Kirkwood formula, the frictional coefficient will be larger for a straight chain than a ring because $\sum_{i,j}^{n}\langle 1/R_{ij}\rangle_{av}$ is smaller for a straight chain. That just the opposite is true can be explained by the failure of the Kirkwood theory to adequately take into account the high resistance of the hole in the ring to solvent flow. Zwanzig's conclusion that the rigid ring should diffuse and sediment more slowly than the rigid rod appears to be correct.

Finally, as mentioned previously,[4] the assumption that Stokes' law can be applied to units as small as $-CH_2-$ in CCl_4 is certainly open to question.

Thus, our data indicate that no existing theory can exactly describe the frictional properties of small ring molecules. While Tchen's model is inapplicable, Kirkwood's theory is inaccurate. Although Kirkwood's theory does agree with our results to within 10–20%, this agreement may arise in part from compensating errors.