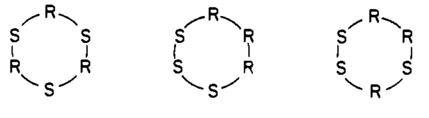
$$2R_6Li_6 \rightleftharpoons 3R_4Li_4 \qquad K_{258\ K} = 2.3\ M$$

to be 7 kcal and 28 eu, qualitatively consistent for dissocation.[13] Below 200 K the tetramer/hexamer ratio increases, accompanied by some precipitation, presumably hexamer.

Comparison of peak areas establishes the other shifts for tetramer and hexamer (Table I). The $C_1$, $C_3$, and $C_4$ resonances of hexamer show fine structure, e.g., *four* peaks for $C_3$ (Figure 1). We believe this arises from diasteromeric aggregates that invert slowly at $C_2$, relative to the NMR time scale. The latter effect was also observed for 2-lithiooctane and 4-*tert*-butylcyclohexyl)lithium.

Assuming that the *sec*-butyllithium hexamer exists as the octahedral structure[5] with the six alkyl groups arranged around the equatorial plane, there are 13 ways of arranging $R_nS_{6-n}$ ($n$ = 0–6), 10 being enantiomeric pairs, and three are $R_3S_3$ (**1**). But we observe only four resonances for $C_3$, which is just the number of molecular formulas of the diastereomers $R_nS_{6-n}$ ($R_6 = S_6$, $R_5S = RS_5$, $R_2S_4 = R_4S_2$, $R_3S_3$). Then it appears that intraaggregate C, Li exchange must average the shifts among diastereomeric hexamers that have the same content but different structures, e.g., the three forms of $R_3S_3$, **1**, even at 173 K. This conclusion is supported by the $^6$Li NMR, which consists, at 183 K, of five sharp lines $\Delta\nu \sim 0.3$ Hz, the large one correlating with tetramer and the others with hexamer (Figure 2).[14]



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Above 232 K the fine structure of $C_2Li$ of tetramer, due to $J(^{13}C, ^6Li)$ of 6.1 Hz, broadens out, fleetingly resolves into lines 4.6 Hz apart ($^3/_4$ of 6.1 Hz) aound 272 K and broadens again on further warming. We propose that a combination of *intra*- and *inter*aggregate carbon–lithium bond exchange, respectively, is responsible for these effects. By 272 K intraaggregate C, Li bond exchange becomes fast enough to give the spectrum of the fluxional tetramer. Above 272 K interaggregate exchange averages all $^{13}C$, $^6Li$ couplings. By 300 K this effect averages the resonances of the diastereomeric hexamers with that for tetramer[15] to a single spectrum. Thus the order of decreasing rates of these dynamic processes is, for C, Li bond exchange, intraaggregate > interaggregate, both much faster than inversion at $C_2Li$. The intraaggregate exchange in the hexamers is so much faster than that for tetramer that the former is still fluxional (relative to the NMR time scale) at 173 K.

Finally at high concentrations, 6.7 M, the $^{13}C$ NMR of *sec*-butyllithium shows a weak six-line resonance, 1:3:5:5:3:1, at 10.52 ppm, separation 4.9 Hz. We propose that this comes from two overlaid 1:2:3:2:1 multiplets for diastereomeric dimers, whose centers are separated by 2.5 Hz.

In sum this work establishes *sec*-butyllithium to exist in hydrocarbon media as a mixture of dimer (minor), hexamer, and tetramer that undergoes at equilibrium fast intra- and interaggregate C, Li bond exchange and much slower inversion at $C_2Li$.

**Acknowledgment.** This research was supported by the National Science Foundation Grant 8007439. The NMR equipment at Ohio State University was financed in part by a grant from the National Science Foundation. We thank Dr. Charles Cottrell, Chemical Instrumentation Center, Ohio State University, for his help.

**Registry No.** *sec*-Butyllithium, 598-30-1.

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[13] Using IR, a Russian group obtained $\Delta H$ of 4.9 kcal: Serutun, V. M.; Antonov, N. G.; Zgonnik, V. N.; Kalninsh, K. K. *J. Organomet. Chem.*, **1978**, *145*, 265–267.

[14] 38.73-MHz, 15-$\mu$s pulse, repeated every 16.38 s, 500-Hz spectral width.

[15] The tetramer shows no shifts among diastereomers, since the alkyl groups are less crowded than in hexamers.

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# Solvation of the Methyl Radical and Its Implications

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In the absence of any specific chemistry, it is not immediately obvious how an alkyl radical in solution should be affected by a solvent—a dilemma that, among other consequences, seriously hinders attempts to determine radical conformation through ESR measurements.[1] As a first step in rectifying this situation, we wish to propose what we believe is the first quantitative treatment of a novel kind of solvation: solvation by *vibrational polarizability*.[2] This solvation mechanism should presumably be responsible for the vast majority of the solvent effects on radicals such as the methyl radical, but the mechanism may also have implications for a variety of other species.

Physically, the polarizability of a solute can lead to an interaction with the solvent because polarizability implies a fluctuating charge distribution and thus the creation of instantaneous dipoles. Accordingly, if the solvent is polar (or even merely polarizable) one gets dipole–induced dipole forces (or induced dipole–induced dipole—dispersion—forces).[3] This picture is, of course, rather schematic, but it is, nonetheless, the basis for the extremely useful Drude oscillator formulation of polarizability[3,4] in which the instantaneous dipole moment of a molecule, **m**, oscillates harmonically with a force constant equal to the reciprocal of the polarizability, $\alpha$,

$$\mathcal{H} = {}^1\!/_2\alpha\omega^2\pi^2 + (2\alpha)^{-1}\mathbf{m}^2 \tag{1}$$

Here the Hamiltonian, $\mathcal{H}$, is expressed in terms of the frequency of oscillation, $\omega$, and the momentum, $\pi$, conjugate to **m**.

While the usual presumption in writing this equation is that the charge fluctuation is due to electrons continually redistributing themselves around fixed nuclei, there is no reason why one could not have a situation in which the oscillating dipole results from a vibration of a molecule which itself causes significant charge displacement. For example, a molecule that is symmetric (e.g., planar) in its equilibrium configuration and consequently does not have a permament dipole moment can instantaneously acquire one by vibrating into a less symmetric (e.g., bent) configuration.

The magnitude of the solvation free energy accruing from this *vibrational polarizability* is easily calculated from existing theory. If, as will often be the case, the dipole moment is proportional to the normal coordinate,[5] $z$,

$$m = \epsilon z \tag{2}$$

where $\epsilon$ is a constant with units of charge, and if the vibration is harmonic, then eq 1 is still applicable with the (now) vibrational polarizability given in terms of the force constant $k$ as

$$\alpha_v \equiv \epsilon^2/k \tag{3}$$

By then applying the approach of Pratt and Hoye and Stell,[4] one can show that the classical molar solvation free energy of such

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[1] Some examples of discrepancies between experimental and simple (gas phase) theories are given by: Fessenden, R. W. *J. Chim. Phys. Phys.-Chim. Biol.* **1964**, *61*, 1570–1575. Krusic, P. J.; Meakin, P.; Jesson, J. P. *J. Phys. Chem.* **1971**, *75*, 3438–3453. Krusic, P. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 846–860. Chen, K. S.; Edge, D. J.; Kochi, J. K. *Ibid.* **1973**, *95*, 7036–7043. For some reviews, see: Kochi, J. K. *Adv. Free Radical Chem.* **1975**, *5*, 189–317. Sullivan, P. D.; Menger, E. M. *Adv. Magn. Reson.* **1977**, *9*, 1–48.

[2] A qualitative version of this idea (which emphasized the difference in the "static" solvation between extreme planar and nonplanar forms instead of considering the "dynamic" solvation caused by the vibrational motion) was first proposed by: Griller, D. S.; Ingold, K. U.; Krusic, P. J.; Fischer, H. *J. Am. Chem. Soc.* **1978**, *100*, 6750–6752.

[3] Hirschfelder, J. O.; Curtiss, F. C.; Bird, R. B. "Molecular Theory of Gases and Liquids"; Wiley: New York, 1954; Chapter 13.

[4] Pratt, L. R. *Mol. Phys.* **1980**, *40*, 347–360. Hoye, J. S.; Stell, G. *J. Chem. Phys.* **1980**, *73*, 461–468.

[5] We are assuming small vibrational amplitude throughout the paper.

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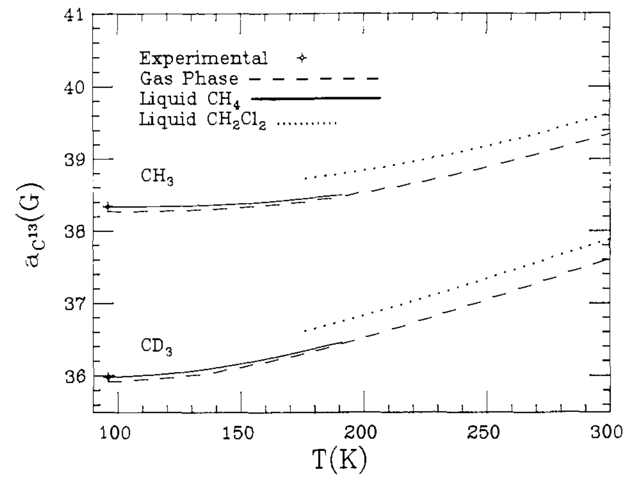

**Figure 1.** The predicted $^{13}$C hyperfine-splitting constants (in gauss) of $CH_3\cdot$ and $CD_3\cdot$ as a function of temperature in the gas phase (dashed line), in liquid methane under its own vapor pressure (solid line), and in liquid dichloromethane under its own vapor pressure (dotted line). The experimental points are from liquid methane at 96 K (ref 12). Note the predicted splitting difference of 0.28 G between the two liquids at 180 K.

a dilute solute in either a polar or a polarizable solvent can be written

$$G_{\text{solvation}} = \tfrac{1}{2}k_BT \ln [1 - 2\alpha_v E(\mu)] \qquad (4)$$

where $k_BT$ is the thermal energy and $-\mu^2 E(\mu)$ is the molar internal energy of a liquid of hard spheres with an effective permanent dipole moment $\mu$.[6]

For this effect to be important, the solute must (1) not be strongly solvated by another mechanism and (2) have a vibration with the correct symmetry and a large $\alpha_v$ (which means, in practice, a small force constant). On both these counts, the methyl radical ($CH_3\cdot$) and its associated pyramidal inversion ($\nu_2 = 606$ cm$^{-1}$)[7] are appropriate. We should note, however, that this $\nu_2$ mode is neither harmonic nor classical.[7] Nonetheless, a straightforward generalization of the recently proposed quantal version of the Pratt–Hoye and Stell theory[8] enabled us to demonstrate that we can treat the vibration approximately by quantizing an *effective potential*, $V_{\text{eff}}(z)$, consisting of the sum of the gas-phase potential, $V_0(z)$, and the classical solvent contribution, $W(z)$,

$$V_0(z) = az^2 + bz^4 + \ldots \qquad (5a)$$

$$W(z) = -cz^2 \qquad (5b)$$

$$V_{\text{eff}}(z) = (a - c)z^2 + bz^4 + \ldots \qquad (5c)$$

where $a$ and $b$ are both positive for the special case of the methyl radical[7] and

$$c = \epsilon^2 E(\mu) \qquad (6)$$

is always positive, since solvation lowers the energy.

With the aid of gas-phase data,[7] an accurate, though approximate, form for $E(\mu)$,[9] and the estimate[10] of the constant $\epsilon = 0.566e$, we obtain solvation free energies for $CH_3\cdot$ at 180 K of 4.0 and 33.0 cal in liquid $CH_4$ and $CH_2Cl_2$, respectively.[11] While not particularly large, the latter amount of solvation should be readily accessible to an ESR experiment through the $^{13}$C hyperfine-splitting constant, $a(^{13}\text{C})$, since to a good approximation[12]

$$a(^{13}\text{C}) = a_0 + a_2\langle\theta^2\rangle \qquad \theta \equiv R_0 z \qquad (7)$$

with the brackets representing the ensemble average (subject to $V_{\text{eff}}$) of the bending angle,[13] $\theta$, squared. We thus present the splitting constants predicted[14] from eq 7 (Figure 1) mainly in hopes that they will stimulate some more experimental work in the area.

We also note, in closing, that the existence of vibrational polarizability has some noteworthy consequences. To begin with, it is likely that the hindered internal rotation of radicals of the form $R_2HCCR_2\cdot$ should be correlated with the pyramidal bend at the radical site.[15] Hence there should be an indirect solvent effect on conformation—enough, perhaps, to account for some of the current discrepancies between experimental and theoretical results for the $\beta$ hydrogen hyperfine splitting as a function of temperature.[1]

Much more interesting though, is the possibility that the vibrational solvation could be strong enough to cause $c$ to be greater than $a$ in eq 5c. In that case, the effective potential in the liquid phase would have a double well, causing the solvated molecule to have a *nonplanar* equlibrium configuration—even though the molecule is planar in the gas phase. This kind of fundamental structural change[16] between the gas and liquid phases (what might be called an *intramolecular phase transition*) would be sufficiently unprecedented to merit further investigation, if only because it would encourage a more cautious appraisal of the significance of a bent molecular geometry in solution (and, for that matter, of a planar geometry in the gas phase). While the methyl radical with $\alpha_v\sigma^{-3} = 0.034$ has too small a vibrational polarizability[17] to see this effect, it is certainly not out of the question that some molecule could have an appropriate vibration with a force constant low enough to allow a solvent to change the molecule's point group.

**Acknowledgment.** We are indebted to Ronald Lawler and Tony DeSimone for illuminating discussions. This work was largely supported by the National Science Foundation under Grant CHE-8121474, but acknowledgement is also due the donors of the Petroleum Research Fund, administered by the American Chemical Society.

**Registry No.** Methyl, 2229-07-4.

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(6) In this form, the theory assumes a dilute solution of a hard-sphere solute in a hard-sphere solvent (both of diameter $\sigma$) with dipole–dipole interactions between the species. Thus, associated (hydrogen bonded) liquids, matrices, and glasses are all specifically excluded as "solvents". The effective dipole moment, $\mu$, is the experimental solvent dipole moment, $\mu_0$, if the solvent is polar but not polarizable. Otherwise $\mu$ is obtained by solving

$$\mu^2 = \mu_0{}^2[1 - 2\alpha_0 E(\mu)]^{-2} + 3k_BT\alpha_0[1 - 2\alpha_0 E(\mu)]^{-1}$$

self-consistently (where $\alpha_0$ is the solvent polarizability).

(7) Yamada, C.; Hirota, E.; Kawaguchi, K. *J. Chem. Phys.* **1981**, *75*, 5256–5264.

(8) Thompson, M. J.; Schweizer, K. S.; Chandler, D. *J. Chem. Phys.* **1982**, *76*, 1128–1135. Hoye, J. S.; Stell, G. *Ibid.* **1981**, *75*, 5133–5142.

(9) The Padé approximant cited in ref 4 is used. This Padé is based on one given by: Rushbrooke, G. S.; Stell, G.; Hoye, J. S. *Mol. Phys.* **1973**, *26*, 1199–1215.

(10) This estimate is calculated from the ab initio dipole moments given in: Chipman, D. M. *J. Chem. Phys.* **1983**, *78*, 3112–3132.

(11) These free energies were calculated from the quantal version of eq **4** given in ref 8.

(12) Fessenden, R. W. *J. Phys. Chem.* **1967**, *71*, 74–83. See also: Chipman, D. M., ref 10.

(13) The angle $\theta$ is defined to be the angle between a C–H bond and the plane of the hydrogens. $R_0 = 1.079$ Å is the C–H bond length and $z$ is the coordinate defined in ref 7.

(14) The constants $a_0 = 26.92$ G and $a_2 = 1140$ G/rad$^2$ were determined by requiring that experimental results for $CH_3\cdot$ and $CD_3\cdot$ in $CH_4$(l) at 96 K (ref 11) match our calculations *including* solvation. Our results should therefore be taken as predictions only for the gas phase, for other solvents, and for higher temperatures than 96 K in $CH_4$(l).

(15) The most direct evidence of this correlation is provided by electronic structure calculations. See, for example: Pacansky, J.; Dupuis, M. *J. Chem. Phys.* **1978**, *68*, 4276–4278. Pacansky, J.; Coufal, M. *Ibid.* **1980**, *72*, 5285–5286. Paddon-Row, M. N.; Houk, K. N. *J. Am. Chem. Soc.* **1981**, *103*, 5046–5049. However, this idea can also be justified qualitatively by the expectation that the torsional potential ought to depend on hyperconjugation between the radical site and the $\beta$ hydrogen. This interaction, in turn, should change significantly as the radical site rehybridizes during a vibration.

(16) By a "fundamental structural change" we mean to exclude (somewhat arbitrarily) not only chemical changes, such as those in which the solvent acts as a ligand or a reactant, but also internal rotations.

(17) The transition should occur when $2\alpha_v E(\mu) = 1$. Since the maximum value of $E(\mu)\sigma^3$ at dichloromethane's highest density is 2.25 at 1 atm., the transition cannot occur in liquid dichloromethane unless $\alpha_v\sigma^{-3}$ is greater than 0.22. This observation is in accord with the comments made by Griller et al.[2] regarding the possibility of the *t*-Bu radical having undergone a solvent-induced structural change via this same mechanism. The estimated solvation energy of 20–80 cal/mol in alkane solution (also is accord with out calculation) was judged to be too small to account for the apparent barrier to inversion.