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DETERMINATION OF DIMERIZATION CONSTANTS OF ORGANIC COMPOUNDS BY NMR SPECTROMETRIC METHODS

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Although many studies have been reported on the determination of association constants for donor-acceptor (D-A) complexes employing absorption[1-5] or nuclear magnetic resonance[6-9] spectroscopic techniques, very little has been reported on the determination of dimerization constants of a single species in its ground state. Excited dimer (excimer) formations of aromatic hydrocarbons have been reported in the literature from their fluorescence studies[10]. Mulliken has considered the possibility of charge-transfer (C-T) complex formation between two identical molecules[11] and McGlynn described Mulliken's theory in terms of group theory[12]. Shuler treated the benzene dimer using free electron theory, and reported the observation of the benzene self complex in solution at high pressure[13].

In this communication, we derive an equation for the determination of dimer aggregates using an NMR spectroscopic technique, and the results obtained employing this equation for several organic compounds are reported.

For the reaction of dimerization,

$$B + B \rightleftarrows B_2 \tag{1}$$

an equation for the equilibrium constant can be written as follows in terms of concentration.

$$K_d = \frac{[B_2]}{[B]\cdot[B]} = \frac{[B_2]}{([B]_0 - [B_2])^2} \tag{2}$$

where $[B]_0$ is the added concentration of B, while [B] is the equilibrium concentration. Solving for the unknown $[B_2]$ in equation 2, followed by square root expansion approximation, one has

$$[B_2] = \frac{K_d\cdot[B]_0^2}{1 + 4K_d[B]_0} \tag{3}$$

Assuming that the proton undergoes a rapid exchange between monomeric and dimeric species, we can write an equation[6],

$$\delta = P_{B_2}\cdot\delta_{B_2} + P_B\cdot\delta_B \tag{4}$$

where δ = the chemical shift of the proton undergoing a rapid exchange between the monomeric and the dimeric species, and P_{B_2} and P_B are defined as:

$$P_{B_2} = \frac{[B_2]}{[B]_0} \quad \text{and} \quad P_B = \frac{[B]}{[B]_0} = \frac{[B]_0 - 2[B_2]}{[B]_0} \tag{5}$$

Substitution of equation 5 into 4 and rearrangement gives

$$(\delta-\delta_B)\cdot[B]_0 = (\delta_{B_2} - 2\delta_B)\cdot[B_2] \tag{6}$$

Combining equations 3 and 6, one obtains

$$\frac{\Delta}{[B]_0} = -4K_d\cdot\Delta + \Delta_0^{B2}\cdot K_d \tag{7}$$

where $\Delta = \delta - \delta_B$ is the measured chemical shift of the dimerized solution, and $\Delta_0^{B2} = \delta_{B_2} - 2\delta_B$ is the chemical shift for the complexed dimer relative to the shift for the uncomplexed B. A plot of $\Delta/[B]_0$ vs. Δ should be linear, whence we calculate K_d and Δ_0^{B2}. The same equation can be derived for the uv-vis absorption spectroscopic technique.

In order to test the validity of equation 7, we performed chemical shift measurements on several aromatic and carbonyl systems at various concentrations (See Table I).

Carbon tetrachloride (Baker Analyzed) was used as a solvent after two fractional distillations unless otherwise mentioned. Benzene (Mallinkrodt Analytical) and acetone (Fischer Certified) were used as received, while acetophenone (Columbia Organic) was used after two distillations under vacuum. Naphthalene (Columbia), azulene (Columbia) and benzophenone (Eastman Organic) were purified by repeated sublimations or recrystallizations from appropriate solvents. Cyclohexane (Fischer Certified) was used as an internal NMR reference throughout the experiment. NMR spectra were taken from the equilibrated solutions at the NMR probe temperature (37-38°C). Before taking an NMR spectrum, each sample was maintained at 37-38°C in a temperature controlled water bath for at least 30 minutes. NMR spectra were taken at the narrowest possible sweep width for the particular dimerized proton to secure the most accurate measurements. Sweep time was always controlled at 1 Hz per sec. Chemical shifts of the sharpest NMR signal were used for the measurements.

The results are listed in Table I and a typical example of a plot of equation 7 for acetophenone system is shown in Fig. 1. The fact that plots of $\Delta/[B]_0$ vs. Δ are straight lines with very good correlations for most systems indicates that equation 7 and the assumptions made in deriving the equation are valid.

Although the nature of the interaction may not be clear at this point, the presence of such forces is obvious from the result. From Table I, one notices that self-complexation constants of carbonyl compounds are considerably higher than those of aromatic hydrocarbons. Mulliken estimated the interaction energy for two benzene molecules to be less than kT at room temperature[11]. Shuler estimated it to be about 200 cal/mole from his spectroscopic measurements at the high pressure[13]. The dispersion energy for the benzene-benzene complex calculated and observed results about the benzene dimer seem to be small enough to support our low self-association constant of benzene. As the molecule becomes bigger, however, forces due to instantaneous electrostatic attractions owing to electron correlation are expected to increase, and the association constant is expected to become higher. The fact that azulene does not show any dimerization in our measurements, however, is very puzzling. Ketones could be expected to have higher association constants, since they have a dipolar group. Acetophenone is expected to be more associated than acetone or benzophenone, since acetophenone is not symmetrical, while the latter two are symmetrical.

Table I. Self-Complexation Constants[a]

Compounds	K_d[b]	$\Delta_0^{B_2}$, Hz	Correlation Coefficients	Concentration Range, mole/ℓ
Benzene	0.0063	82	0.98	0.90 ∿ 11.2
Naphthalene	0.071	54	0.98	2.9 ∿ 4.8
Azulene	0[c,d]	--	--	--
Acetone	0[c]	--	--	--
	0.013[d]	62	0.92	1.4 ∿ 9.5
Benzophenone	0.26	24	0.96	0.1 ∿ 3.2
Acetophenone	0.33	14	0.99	0.10 ∿ 4.3

a. All experiments were done in CCl_4, using cyclohexane as an internal reference, except the acetone system.

b. Equilibrium constant in liter·mole^{-1}.

c. Experiments were done in CCl_4, but there were no detectable changes in chemical shifts.

d. This was done in cyclohexane solvent with the solvent as a reference.

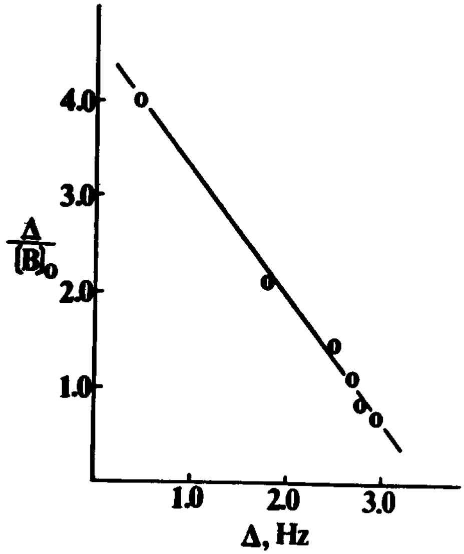

Figure 1. Plot of $\Delta/[B]_0$ vs. Δ for the acetophenone system in CCl_4.

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