

**Figure 4.** A Plot of percent recovery of CO<sub>2</sub> vs.  $x$ -value for the system of Nd<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> at fixed condition (total pressure of 30 torr and current of 5 mA).

and oxygen vacancies which affect conductivity as well as capability of oxidation. Namely, oxygen vacancies are created with O<sub>2</sub> desorption from the surface of catalysts which have unstable Co<sup>4+</sup> changed into Co<sup>3+</sup> by providing an electron. The amounts of oxygen vacancies proportional to  $x$  values make the diffusion of lattice oxygen easy. Therefore, both of the conductivity and catalytic effects tend to be increased by substitution of Sr<sup>2+</sup>, in general. However, if the substitution of Sr<sup>2+</sup>,  $x$  is larger than 0.6, both of them are decreased slightly<sup>7</sup>. This may be partially due to the reduction of reactivity on the surface by over-produced oxygen vacancy or the

slower reoxidation step in redox cycle of the catalyst.

As shown in the result, the amount of the CO<sub>2</sub> recombination in the catalytic electrode is increased in the order of 0.60 > 0.75 > 0.50 > 0.40 > 0.25 for  $x$  value. In addition, it has a close dependence on the current and the total pressure. When pressure was increased and current was decreased, it was increased. Therefore, Nd<sub>1-x</sub>Sr<sub>x</sub>CoO<sub>3</sub> series can be a good candidate as a catalytic cathode of a sealed-off CO<sub>2</sub> laser.

**Acknowledgement.** This work was supported by the Korea Science and Engineering Foundation.

### References

1. N. Iehisa, K. Fukaya, K. Matsuo, N. Horiuchi, and N. Karube, *J. Appl. Phys.*, **59**(2), 317 (1986).
2. R. J. Carbone, *IEEE J. Quan. Electron.*, **QE-3**(9), 373 (1967).
3. W. C. Dannel and J. C. Jang, "Laser induced chemical processes": Plenum Press, New York (1981).
4. T. Nitadori, T. Ichiki, and M. Misono, *Bull. Chem. Soc. Jpn.*, **61**, 621 (1988).
5. N. Karube, N. Iehisa, K. Fukaya, and Matsuo, *Appl. Phys. Lett.*, **3**(12), 1086 (1983).
6. V. P. Garaschuk, P. A. Vasilets, and V. V. Nakvasnyuk, *Khin. Vys. Energy*, **22**167, 541 (1974).
7. D. S. Rajoria, V. G. Bhide, G. R. Rao, and C. N. R. Rao, *J. C. S. Faraday II*, **70**, 512 (1974).
8. T. Nakamura, M. Misono, and Y. Yoneda, *Chem. Lett.*, 1589 (1981).
9. T. Shimizu, *Chem. Lett.*, 1 (1980).
10. R. R. Hikes, R. C. Miller, and R. Mazelsky, *Physica*, **30**, 1600 (1964).
11. G. H. Jonker, *Philips Res. Rept.*, 24 (1969).

## Temperature Dependence of Carbon-13 Shieldings as a Probe for Conformational Equilibria

Miewon Jung\*

Department of Chemistry, Sungshin Women's University, Seoul 136-742. Received April 26, 1992

The temperature dependence of C-13 chemical shifts are observed for the cyclooctanone arylhydrazones. The temperature-dependent chemical shifts for these derivatives are explained by postulating the existence of two equilibrating structures. In addition, the assignment between the <sup>13</sup>C signals of methylene carbon pairs can be done by application of the  $\gamma$ -substituent effect.

### Introduction

The utility of <sup>13</sup>C-NMR spectra for structure studies is well established.<sup>1</sup> The temperature dependence of chemical shifts on the various nuclei have been known for some time, but the use of the effect with <sup>13</sup>C data is relatively recent.<sup>2</sup>

It was once thought that the temperature dependence of chemical shifts could indicate the presence of an equilibrium in which the populations of different structures changed with temperature.<sup>3,4</sup> However, Lambert reported a study in which he could see the temperature dependence of <sup>13</sup>C chemical shifts to confirm the presence of both chair and twist-boat

forms for various neutral cyclohexanes.<sup>5</sup> Lambert found that very good plots of the temperature dependence of chemical shifts could be obtained in most of the cases studied, including situations where there cannot possibly be any conformational equilibrium, *e.g.*, adamantane compounds. The fundamental problem in interpreting temperature dependence of chemical shifts, as pointed out by Lambert<sup>5</sup> and summarized by Sorensen,<sup>6</sup> is to distinguish between "intrinsic" temperature dependent shifts (caused by solution density changes, average bond length changes, changing van der Waals interactions, etc.) and those that are the result of a rapid equilibrium of two or more different structures. Sorensen group have obtained confirmatory evidence for rapidly equilibrating structures in unsymmetrical tertiary 2-adamantyl cations from the temperature dependence of chemical shifts.<sup>7</sup>

The asymmetry is introduced by imine moiety to establish nonidentical environments on the methylene carbon pairs of the cyclooctanone in the present work. <sup>13</sup>C-NMR spectra of cyclooctanone phenylhydrazone and cyclooctanone 2,4-dinitrophenyl hydrazone are obtained at various temperatures in order to find the chemical shifts at which the dynamic process can be "frozen-out" on the NMR time scale and cyclooctanone arylhydrazones can be observed as a stable conformation.

## Experimental

**Synthesis of Cyclooctanone 2,4-Dinitrophenylhydrazone:**<sup>8</sup> **Stock Solution of 2,4-Dinitrophenylhydrazine.** 2,4-dinitrophenylhydrazine (2 g, 0.01 mol) was dissolved in 85% phosphoric acid (50 ml) by heating, then cooled, and 95% ethanol (50 ml) was added. This solution was cooled again and a clarified solution was obtained by suction filtration.

**Cyclooctanone 2,4-Dinitrophenylhydrazone.** Cyclooctanone (6.1 g, 0.048 mol) was dissolved in 95% ethyl alcohol (70 ml), and 2,4-dinitrophenylhydrazine solution (50 ml, 0.1 mol) was added. After collecting the yellow precipitate by suction filtration, the yellow paste was washed with water several times, then recrystallized from ethyl alcohol. Cyclooctanone 2,4-dinitrophenylhydrazone (5 g) was collected as a bright yellow needles (34%) (mp. 178–180°C).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>): 213.21 (s, C<sub>1</sub>), 116.38, 123.66, 132.66, 129.97, 36.79 (s, C<sub>2</sub> or C<sub>8</sub>), 28.50 (s, C<sub>2</sub> or C<sub>8</sub>), 27.37 (s, C<sub>4</sub> or C<sub>6</sub>), 26.20 (s, C<sub>4</sub> or C<sub>6</sub>), 25.42 (s, C<sub>3</sub> or C<sub>7</sub>), 24.56 (s, C<sub>5</sub>), 24.27 ppm (s, C<sub>3</sub> or C<sub>7</sub>).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 11.25 (br s, 1H), 9.15 (s, 1H), 8.00 (m, 1H), 2.60 (m, 4H), 1.62 ppm (m, 6H).

**Synthesis of Cyclooctanone-2,2,8,8-D<sub>4</sub>.**<sup>9</sup> The deuterium labeling at the C-2 and C-8 positions was done by repeating three times treatment of cyclooctanone (12.6 g, 0.1 mol) with D<sub>2</sub>O (54 g, 2.7 mol) using Na<sub>2</sub>CO<sub>3</sub> as a catalyst. The mixture was saturated with NaCl, the organic phase was separated and the aqueous phase was combined, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated. Cyclooctanone was distilled (10.8 g, 80%, bp 70°C, at 3 mmHg) and the product was enriched 90% by <sup>1</sup>H-NMR spectroscopy.

<sup>13</sup>C-NMR (CDCl<sub>3</sub>): 217.71 (s, C<sub>1</sub>), 40.91 (p, *J*<sub>CD</sub> = 19.5 Hz, C<sub>2</sub>, C<sub>8</sub>), 26.82 (s, C<sub>4</sub>, C<sub>6</sub>), 25.19 (s, C<sub>3</sub>, C<sub>7</sub>), 24.44 ppm (s, C<sub>5</sub>).

**Cyclooctanone-2,2,8,8-D<sub>4</sub> 2,4-Dinitrophenylhydrazone.** <sup>13</sup>C-NMR (CDCl<sub>3</sub>): 164.42, 144.62, 129.42, 123.90, 123.

80, 116.31, 36.32 (p, C<sub>2</sub> or C<sub>8</sub>, *J*<sub>CD</sub> = 19.53 Hz), 27.30 (C<sub>4</sub> or C<sub>6</sub>), 26.15 (C<sub>4</sub> or C<sub>6</sub>), 25.42 (C<sub>3</sub> or C<sub>7</sub>), 24.40 (C<sub>5</sub>), 24.18 ppm (C<sub>3</sub> or C<sub>7</sub>).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 11.22 (m, 1H), 9.2 (m, 1H), 8.45 (m, 1H), 7.95 (m, 1H), 2.53 (m, 1H), 1.85 (m, 4H), 1.51 ppm (m, 6H).

<sup>2</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): 2.55 ppm (br s, 4D).

### Synthesis of Cyclooctanone phenylhydrazone

**Stock Solution of Phenylhydrazine.** Phenylhydrazine (5 ml) was measured with a calibrated pipette and mixed with glacial acetic acid (15 ml), diluted with water (25 ml), and made up the volume to 50 ml with water.

**Cyclooctanone Phenylhydrazone.** Cyclooctanone (6.1 g, 0.05 mol) was dissolved in methyl alcohol (50 ml) and stock solution of phenylhydrazine (50 ml, 1 M) was added. This yellow solution was extracted with pentane and the extract was washed with sat. sodium bicarbonate solution and water, then dried with anhydrous sodium sulfate, filtered, and evaporated. After distillation (bp 157–163°C, at 1 mmHg) 4.32 g of the cyclooctanone phenylhydrazone was obtained (40%).

<sup>13</sup>C-NMR (CDCl<sub>3</sub>): 203.89, 151.47, 145.71, 128.67, 118.91, 112.60, 35.728 (s, C<sub>2</sub> or C<sub>8</sub>), 26.99 (s, C<sub>4</sub> or C<sub>6</sub>), 26.71 (s, C<sub>2</sub> or C<sub>8</sub>), 26.649 (s, C<sub>3</sub> or C<sub>7</sub>), 25.31 (s, C<sub>5</sub>), 25.16 (s, C<sub>2</sub> or C<sub>8</sub>), 23.46 ppm (s, C<sub>3</sub> or C<sub>7</sub>).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>): 7.15 (m, 2H), 7.00 (m, 2H), 6.90 (br s, 1H), 6.75 (m, 1H), 2.45 (m, 2H), 2.15 (m, 2H), 1.68 (m, 4H), 1.48 ppm (m, 6H).

**Cyclooctanone-2,2,8,8-D<sub>4</sub> Phenylhydrazone.** <sup>13</sup>C-NMR (CD<sub>2</sub>Cl<sub>2</sub>): 202.38, 152.64, 146.55, 130.78, 129.65, 119.51, 113.10, 27.68 (s, C<sub>4</sub> or C<sub>6</sub>), 27.60 (s, C<sub>3</sub> or C<sub>7</sub>), 25.97 (s, C<sub>5</sub>), 25.88 (s, C<sub>4</sub> or C<sub>6</sub>), 24.25 ppm (s, C<sub>3</sub> or C<sub>7</sub>).

<sup>1</sup>H-NMR (CD<sub>2</sub>Cl<sub>2</sub>): 7.27 (m, 2H), 7.15 (br s, 1H), 7.10 (m, 2H), 6.85 (m, 2H), 1.82 (m, 4H), 1.58 ppm (m, 6H).

### <sup>13</sup>C-NMR Measurements of Cyclooctanone Derivatives Cyclooctanone 2,4-Dinitrophenylhydrazone

<sup>13</sup>C-NMR spectra were recorded on a Varian XL-300 NMR spectrometer equipped with a broadband probe at 75.4 MHz. Both proton coupled and decoupled <sup>13</sup>C-NMR spectra were obtained to determine multiplicities and aid signal assignment.

The cyclooctanone 2,4-dinitrophenylhydrazone was dissolved in CD<sub>2</sub>Cl<sub>2</sub> solvent to obtain <sup>13</sup>C-NMR spectra which were obtained at temperatures from 20°C to –100°C at 20° intervals. Spectra were not obtainable below –100°C due to freezing of the solvent. Other solvents (CFCl<sub>3</sub> and CF<sub>2</sub>Cl<sub>2</sub>) which have lower freezing points were not suitable for use because of low solubility of cyclooctanone 2,4-dinitrophenylhydrazone. In order to aid assigning the carbon signals in the <sup>13</sup>C-NMR spectra, cyclooctanone-2,2,8,8-D<sub>4</sub> 2,4-dinitrophenylhydrazone and cyclooctanone 2,4-dinitrophenylhydrazone were mixed with a 1:2 ratio.

### Cyclooctanone Phenylhydrazone

<sup>13</sup>C-NMR spectra were obtained for unlabeled and labeled cyclooctanone phenylhydrazone in CD<sub>2</sub>Cl<sub>2</sub> as solvent with varying temperature. <sup>13</sup>C-NMR data could not be obtained below –100°C since the compounds started to freeze out below this temperature. In order to compare with <sup>13</sup>C-NMR data of cyclooctanone 2,4-dinitrophenylhydrazone, spectra of cyclooctanone phenylhydrazone and cyclooctanone-2,2,8,8-D<sub>4</sub> phenylhydrazone were obtained in the same CD<sub>2</sub>Cl<sub>2</sub> solvent

**Table 1.** Chemical Shifts of Cyclooctanone 2,4-Dinitrophenylhydrazones

Chemical Shifts (ppm) <sup>a</sup>	Temperature (°C)					
	22.3	2.3	-18.3	-58.4	-78.2	-98.4
C-2	30.76	30.74	30.60	30.39	30.24	30.24
C-3	26.62	26.71	26.75	26.86	26.89	27.24
C-4	28.60	28.48	28.21	27.70	27.40	27.24
C-5	27.80	27.68	27.47	27.13	26.89	26.80
C-6	29.73	29.84	29.85	29.89	29.90	30.18
C-7	26.70	26.68	26.20	25.33	24.77	24.46
C-8	39.08	39.14	39.15	39.16	39.18	39.32

<sup>a</sup>Chemical shifts of methylene carbons are listed and CD<sub>2</sub>Cl<sub>2</sub> was used as internal reference (53.80 ppm).

**Table 2.** Chemical Shifts of Cyclooctanone Phenylhydrazones

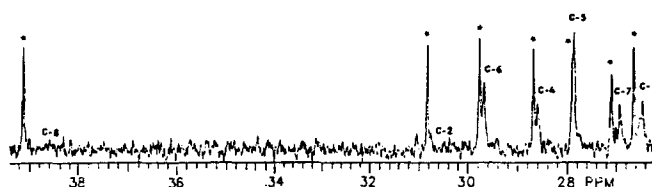
Chemical Shifts (ppm) <sup>a</sup>	Temperature (°C)					
	18.3	1.3	-17.4	-57.6	-78.3	-98.0
C-2	27.56	27.40	27.36	27.21	27.09	26.74
C-3	24.22	24.11	24.15	24.23	23.08	24.04
C-4	25.96	25.73	25.46	24.32	24.31	24.39
C-5	26.09	25.90	25.11	25.33	25.16	24.68
C-6	27.72	27.65	27.70	27.87	27.96	27.87
C-7	27.40	27.17	27.05	26.65	26.34	25.91
C-8	36.48	36.37	36.39	36.49	36.56	36.58

<sup>a</sup>Chemical shifts of methylene carbons are listed and CD<sub>2</sub>Cl<sub>2</sub> was used as internal reference (53.80 ppm).

from 20°C to -120°C with same temperature interval. The spectrum of cyclooctanone phenylhydrazone and the mixture of the deuterated and undeuterated (1 : 2 ratio) phenylhydrazones were compared for purpose of signal assignment, as in the cyclooctanone 2,4-dinitrophenylhydrazone system.

## Results and Discussion

The chemical shifts of cyclooctanone 2,4-dinitrophenyl hydrazone (1) and phenylhydrazone (2) at various temperatures are summarized in Tables 1 and 2. All seven methylene carbon peaks of these compounds, unlike cyclooctanone,<sup>10</sup> are seen separately at room temperature because of the asymmetry introduced by the nonlinear C=N-N bond angle. Complete deuteration on  $\alpha$  and  $\alpha'$  positions was achieved to aid signal assignments for these methylene carbons. A spectrum of a 2 : 1 mixture of cyclooctanone 2,4-dinitrophenylhydrazone and cyclooctanone 2,2,8,8-D<sub>4</sub> 2,4-dinitrophenylhydrazone is shown in Figure 1. The labeling allows assignment of the pairs C-2 and C-8, C-3 and C-7, and C-4 and C-6 based on distance from the label. The signals of carbons in labeled and unlabeled compounds are not coincident due to intrinsic isotope shift.<sup>10</sup> Deuterium substitution causes a small change in chemical shift, arising from changes in the vibrationally averaged nuclear shielding. A slight change in bond length and bond angle is a primary cause of the upfield intrinsic isotope shifts. The assignment can be explained by the following: (1) The most deshielded pair at 39.08 ppm

**Figure 1.** <sup>13</sup>C-NMR spectrum of 2 : 1 mixture of cyclooctanone 2,4-dinitrophenylhydrazone (\*) and cyclooctanone-2,2,8,8-D<sub>4</sub> 2,4-dinitrophenylhydrazone at 22.3°C.

and 30.82 ppm in Figure 1 can be assigned to the undeuterated C-2 and C-8 carbons characterized by a sharp singlet. This can be assigned because these carbons, among the methylene carbons, get the greatest deshielding effect due to the imine moiety. The signals around 38.6 ppm and 30.4 ppm are weak, broad and complex due to low signal-noise ratio, reduced signal intensity, signal multiplicity and absence of the nuclear overhauser enhancement and therefore are hard to distinguish (Deuteration of a carbon results in a dramatic diminution of its carbon signal in a proton decoupled spectrum<sup>11</sup>). However, it is certain that these signals are of the deuterated C-2 and C-8 carbons because of the one-bond isotope effect.<sup>10</sup> This one-bond isotope shift provides a slight upfield shift of the directly deuterated <sup>13</sup>C signal about 0.3 ppm per deuterium. C-2 is easily assigned as upfield from C-8 because it is syn to the anilino substituent on the imine nitrogen and will be shielded by the  $\gamma$ -substituent effect.<sup>11</sup> This effect arises from locally polarized electron distributions by steric polarization of C-C bond within a molecule. A steric perturbation of a C-H bond leads to a drift of charge along the bonds towards carbon, causing orbital expansion of carbon. Hence, increased shielding causes an upfield shift for C-2 carbon within a sterically crowded position in the NMR spectrum. (2) C-3 and C-7, C-4 and C-6 carbons are assigned according to the different intrinsic isotope shifts.<sup>10</sup> The two-bond effect of deuterium substitution on <sup>13</sup>C chemical shifts are smaller than the one-bond effect (directly deuterated carbons), but inherently more valuable. Two-bond isotope effect is typically one-third to one-quarter the magnitude of the one-bond effect, i.e., roughly 0.1 ppm per deuterium. Thus, signals at 26.70 ppm and 26.62 ppm with upfield isotope shift about 0.2 ppm in Figure 1 are assigned to C-3 and C-7 carbons which are separated by two-bond from the deuterium. The three-bond isotope effect are clearly smaller by a typical factor of about one-third to one-quarter of the two-bond effect.<sup>10</sup> The 28.60 ppm and 29.73 ppm are assigned to C-4 and C-6 carbons (upfield isotope shift 0.07 ppm). The remaining signal at 27.80 ppm is for the C-5 carbon which shows no resolved isotope effect.

Assignments within the C-3 and C-7, and C-4 and C-6 pairs can be achieved by application on the temperature dependence of the chemical shifts. The temperature dependence of the chemical shifts of (1) and (2) is illustrated in Figures 2 and 3. The interesting feature of these plots is that for each pair of carbon atoms, defined by being the same numbers of bonds removed from C-1, one of the carbon atoms moves upfield and the other downfield as the temperature decreases. For example, the pair of carbons where assignment can be made unequivocally, C-2 moves upfield (toward smaller  $\delta$  values) as the temperature drops, while

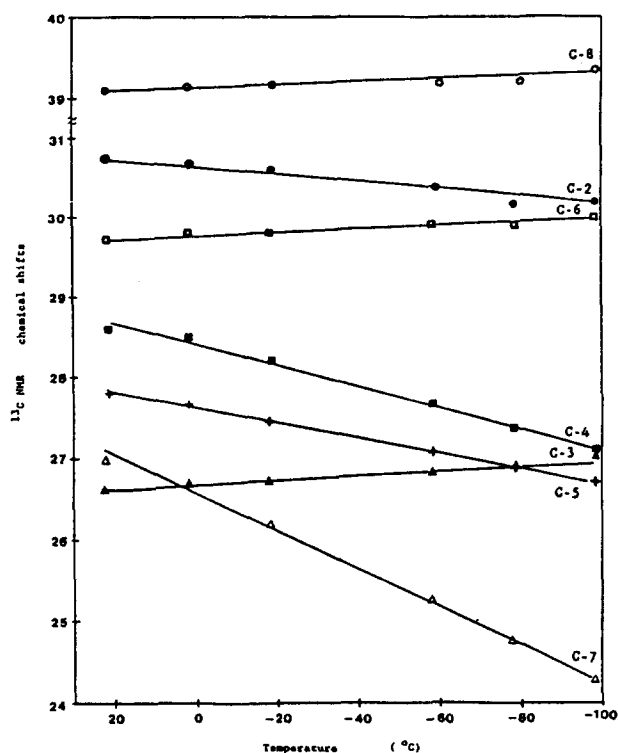


Figure 2. Relationship of chemical shifts versus temperatures in derivative (1).

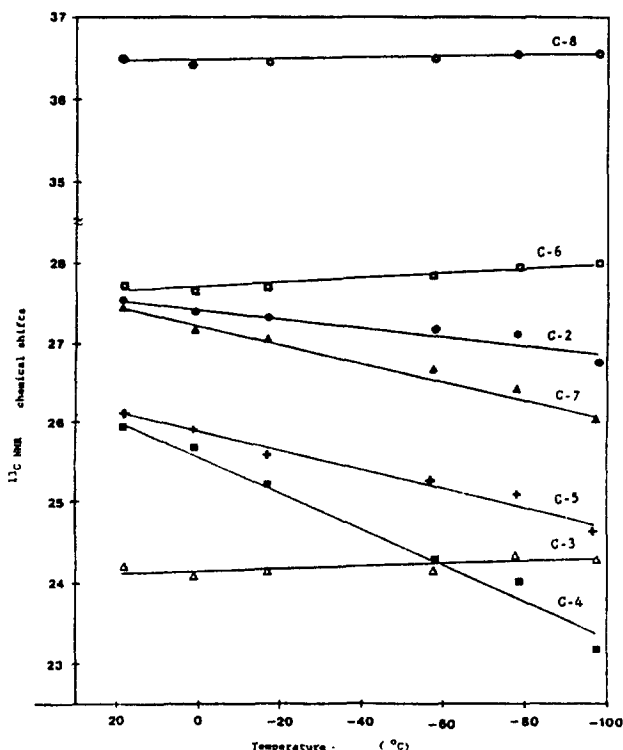


Figure 3. Relationship of chemical shifts versus temperatures in derivative (2).

C-8 becomes slightly more deshielded. The same is true even at the more remote C-3 and C-7, and C-4 and C-6 pairs. This behavior is exactly what would be expected if

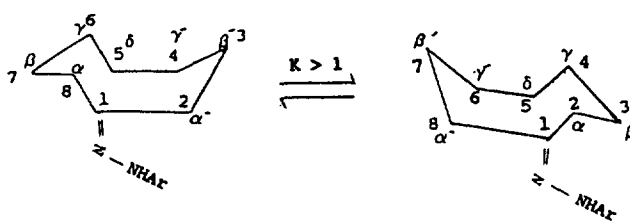


Figure 4. Equilibrium structures of boat-chair conformers for cyclooctanone derivative.

a rapid equilibrium among boat-chair conformers were being shifted to favor one particular boat-chair, which would contribute progressively more to each time-averaged spectrum as the temperature is lowered. Movement of C-2 upfield with lower temperature is consistent with more weighting of shifts from a boat-chair conformer with C-2 in the  $\alpha$  position while the downfield movement of C-8 would suggest more  $\alpha'$  character in the weighted average. Thus, in the equilibrium shown in Figure 4, the second structure could be concluded to be more stable, increasing in population as the temperature decreases. Following this reasoning, if C-2 moves upfield, then C-3 should move downfield and C-4 upfield because the  $\alpha$ ,  $\beta'$ , and  $\gamma$  carbons are more shielded than the corresponding  $\alpha'$ ,  $\beta$ , and  $\gamma'$  carbons in the boat-chair conformation of cyclooctanone derivatives. The chemical shifts of sterically perturbed carbon atoms are found at upfield than for similar carbons which are not spatially crowded. The magnitude of these shifts, however, exhibits a strong dependence upon the conformational geometry existing between the C-H bonds in the two interacting groups.

Each carbon within a  $\gamma$ -gauche relationship tends to show a higher shielding effect relative to those not in the  $\gamma$ -gauche arrangement. The upfield shifts associated with the  $\gamma$ -gauche effect is one of the most useful diagnostic effects in C-13 NMR spectroscopy.<sup>12</sup> Stothers *et al.* used the  $\gamma$ -gauche relationship to assign the C-13 NMR shifts for *cis*-decalin derivatives upon the examination of the expected geometrical and conformational effects on the C-13 shieldings.<sup>13</sup> Wehrli also used this  $\gamma$ -gauche relationship to assign chemical shifts of cyclodecanone.<sup>14</sup> The occurrence of the  $\gamma$ -gauche effect was correlated with conformational properties of cyclooctanone derivatives in the C-13 NMR spectral data. The upfield chemical shifts will be contributed to the carbon in a pair which has more  $\gamma$ -gauche relationships to other carbons in a more stable structure as lowering the temperature. The chemical shifts of arylhydrazone derivatives of cyclooctanone show an opposite temperature dependence for the methylene carbon in a pair. Such behavior is uniquely consistent with a populated equilibrium argument.

Although direct NMR evidence can't be seen for an equilibrium, such as "frozen-out" spectrum or even any indication of line broadening as the temperature drops, the temperature-dependent NMR chemical shifts show unequivocal evidence for a populated equilibrium involving two different "structures" of cyclooctanone arylhydrazones.

## References

- (a) J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y. (1972); (b) G. C. Levy and

- G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley Interscience, New York, N.Y. (1972).
2. J. B. Lambert and J. D. Roberts, *J. Am. Chem. Soc.*, **87**, 3884 (1965).
3. H. J. Scheider, W. Freitag, V. Hopper, *Org. Magn. Reson.*, **13**, 266 (1980).
4. H. N. Cheng and F. A. Bovey, *Org. Magn. Reson.*, **11**, 457 (1978).
5. J. B. Lambert, A. R. Vagenas, and S. J. Somani, *J. Am. Chem. Soc.*, **103**, 6398 (1981).
6. T. S. Sorensen, R. P. Kirchen, and K. Ranganayakulu, *J. Am. Chem. Soc.*, **109**, 7811 (1987).
7. T. S. Sorensen, *J. Am. Chem. Soc.*, **109** (1987).
8. L. F. Fieser and K. L. Williamson, In "Organic experiments" 5th Ed., Heath, D. C. and Company, Lexington, M. A. (1983).
9. A. C. Cope, D. M. Gals, *J. Am. Chem. Soc.*, **83**, 3747 (1963).
10. (a) M. W. Jung, *Bull. Korean Chem. Soc.*, **12**, 224 (1991); (b) D. A. Forsyth, *Isot. Org. Chem.*, **6**, 1 (1984).
11. M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963).
12. B. W. Cheney and D. M. Grant, *J. Am. Chem. Soc.*, **89**, 5315 (1967).
13. J. B. Stothers and R. E. Klinck, *Org. Mag. Res.*, **12**, 561 (1979).
14. F. W. Wehrli, D. Jeremic, M. C. Mihailovic, and S. J. Milosavijevic, *J. Chem. Soc. Chem. Commun.*, 302 (1978).

## Mechanistic Change-Over in Nucleophilic Solvent Assisted Reactions

Dae Dong Sung\*, Yang Hee Kim, Yoo-Mee Park, Zoon Ha Ryu<sup>†</sup>, and Ickchoon Lee<sup>‡</sup>

Department of Chemistry, Dong-A University, Pusan 604-714

<sup>†</sup>Department of Chemistry, Dong-Eui University, Pusan 614-010

<sup>‡</sup>Department of Chemistry, Inha University, Incheon 402-751. Received March 20, 1992

Rate constants of methanolyses of *para*-Z-substituted benzenesulfonyl chlorides have been determined in various isodielectric solvent mixtures. A third-order kinetic behavior has been observed in the methanolysis of *p*-nitrobenzenesulfonyl chloride in methanol-nitromethane mixture from the correlation figure of logarithms of rate constants were plotted against *Y*-values based on solvolyses of 1-adamantyl tosylate.  $S_N1$ - $S_N2$  mixing mechanisms are favored by neutral or weak electron-donating and weak electron-withdrawing substituents of *p*-Z-substituted benzenesulfonyl chlorides in methanol-nitrobenzene mixture. While the methanolyses of *para*-Z-substituted benzenesulfonyl chlorides in methanol-ethylene glycol solvent mixture are appropriate for  $S_N2$  mechanism from the mechanistic criterion by means of *m*-values.

### Introduction

Factors influencing nucleophilicity of anions and transition state involved in the nucleophilic substitution reactions have long held the interest of mechanistic chemists. The solvolytic reactions in which a solvent molecule attacks to the electrophilic center as a nucleophile have been investigated widely. The solvolytic reaction mechanism, were studied for various organic reactions based on the model substrates such as *tert*-butyl chloride and 2-adamantyl tosylate.<sup>1</sup> The conclusions derived from the detailed solvent effects on the rates of nucleophilic substitution reactions were applied to a large number of solvent-assisted reactions.<sup>2</sup> While a correlation of these kinetic results with thermodynamic properties of nucleophile has generally been unsatisfactory.

A different mechanistic view is raised a question in argument for the sulfonyl transfer reaction<sup>3</sup> involved solvent assistance when the kinetic results have been applied to the mechanistic criterion based on the correlation of kinetic results and thermodynamic properties.

A much discussed question<sup>3</sup> arising in the direct displace-

ment process for sulfonyl transfer concerns the timing of bond formation and cleavage, that is, whether the structure of seven-coordinate including sulfur atom corresponds to a transition state or penta-coordinate intermediate.

A good case of a two-step process proceeding *via* a pentacoordinate intermediate has been suggested by Kice<sup>3b</sup> and supported by the isolation of hypervalent analogues by Perkins and Martin.<sup>4</sup> Even though those proposals are well recognized in that case of sulfonyl transfer reaction such as alkyl sulfonyl halide solvolyses, while a very different mechanistic aspect is shown in the particular case of nucleophilic substitution reaction of arenesulfonic ester with hydroxide as shown their evidence is in better agreement with a one-step mechanism.<sup>5</sup>

On the other hand, the solvolytic reactions of arenesulfonyl chlorides were proposed to occur through very different mechanisms extend from dissociative  $S_N2$  to  $S_A N$ .<sup>6</sup> In sulfonyl transfer reactions, each mechanism could show variable transition state structures, *e.g.*, from dissociative  $S_N2$  to  $S_A N$  with increasing nucleophilic assistance by influence of solvent. Recently isodielectric binary solvent mixtures such as aceto-