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Viscosity of Liquids under High Pressures

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By using Pak's theory of liquid, a phenomenological theory of viscosity proposed by the authors is applied to liquids under high pressures. The calculated viscosities for various simple substances are in good agreements with those of the observed values over wide pressure ranges.

Introduction

Research on transport properties at high pressures has developed vigorously in recent 30 years. The general behavior of these properties in the gaseous phase is well understood, and it has become possible, to some extent, to interpret theoretically and to predict empirically the effect of high pressure. On the other hand, the transport properties of liquids under pressure have not always been interpreted both empirically and theoretically[1].

For the viscosity of liquids, some theories[2-4] accurately describe the temperature dependence, but these theories fail to account for the variation of the viscosities with pressure. Only one idea assumed by these theories is that the solid volume V_s decreases with increasing pressure. The purpose of this paper is to show that our viscosity equation[5] adequately describes the effect of pressure on the viscosities of liquids.

Theory

Our equation for the viscosity of fluids has the simple form

$$\eta = \tau P_a \tag{1}$$

where τ and P_a are the collision time and absolute pressure (kinetic pressure + internal pressure), respectively. The collision time and the absolute pressure of the fluid are related to the thermodynamic properties of the system as follows

$$\tau = (\pi d^2 n_{ph})^{-1} (\gamma/\rho\beta_T)^{-\frac{1}{2}} \tag{2}$$

$$P_a = 2T\frac{\alpha_P}{\beta_T} - P \tag{3}$$

where d is the collision diameter, n_{ph} is the phonon number density, γ is the heat capacity ratio, and ρ is the fluid density. β_T is he isothermal compressibility, α_P is the isobaric thermal expansion coefficient and P is the pressure. For the calculation of the viscosity at high pressure, we have to know the thermodynamic properties such as ρ, p, α_P, β_T and γ. But unfortunately the experimental value of such properties of liquids have not been known widely at high pressures. Therefore, we can calculate this thermodynamic properties at high pressure using the state equation of the liquid.

According to Pak's theory[6], the partition function of the liquid Q is given as follows

$$Q = \frac{N_t!}{N_s!(N_t - N_s)!}\left[\frac{e^{E_s/RT}}{(1-e^{-\theta/T})^3}\right]^{N_s} \left[\frac{(2\pi mkT)^{3/2}(V-V_s)}{h^3}\right]^{N_g}\frac{1}{N_g!} \tag{4}$$

where E_s, V_s and E_g are the ground state energy and the molar volume of the solid like molecule and the potential energy of the gas like molecule, respectively. θ is the Einstein characteristic temperature and N_t, N_s and N_g are $N(\frac{V}{V_s})$, $N(\frac{V_s}{V})$ and $N(\frac{V-V_s}{V})$ respectively; here N is the Avogdro number. The parametric values E_s, θ , E_g and V_s can be found by the use the following equations

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,N} \tag{5}$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,N} \tag{6}$$

$$A + pV = A_g + pV_g \tag{7}$$

where A_g and V_g are the Helmholtz free energy and the

Direct Synthesis of η^6-1-Functionally Substituted 2,3,4,5-Tetraphenyl-1-Silacyclopentadiene Complexes of Chromium

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We synthesized the novel complexes of (1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene-2,5-yldibenzene)bis(tricarbonylchromium) and tricarbonyl (R,R'-3,4,5-triphenyl-1-silacyclopenta-2,4-diene-2-ylbenzene)chromium(R,R' = Me, R = Me/R' = Cl, R = Ph/R' = Cl) from the reaction of the corresponding R,R'-2,3,4,5-Tetraphenyl-1-silacyclopenta-2,4-diene (abr. R,R'-TPSCp) with chromiumhexacarbonyl. These results reveal that chromium prefer to coordinate to the phenyl substituents of 1-silacyclopentadiene rather than the butadiene moiety of the ring.

Introduction

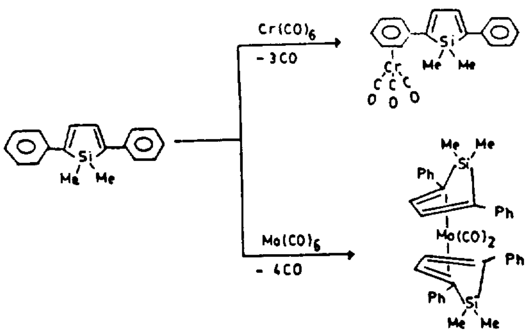
A great number of investigations has focused on the synthesis of 1-silacyclopentadiene η^4-complexes of transition metals because it has been of interest whether η^4-1-silacyclopentadiene complexes will be converted to η^5-1-silacyclopenyadienyl complexes. Still unreported, however, is the generation or detection of such η^4-complexes except mass spectrometric studies[1,2].

Metalcarbonyl complexes of 1,1-diorgano-1-silacylopentadiene[3,4], 1,1-diorgano-3,4-dimethyl-1-silacyclopentadiene[5-8], and 1,1-diorgano-2,5-diphenyl-1-silacylopentadiene[9-13] have been studied extensively. These metal complexes have been restricted to those of iron, cobalt, nickel, molybdenum, and tungsten. All of them are η^4-complexes formed through the butadiene moiety of 1-silacyclopentadiene with carbonyls of iron, cobalt, nickel, molybdenum, tungsten. However, the chromium complexes of 1-silacyclopentadiene are scarcely known. On the other hand, studies for the metal carbonyl complexes of 1-functionally substituted 2,3,4,5-tetraphenyl-1-silacyclopenta-2,4-diene(R, R'-TPSCp) are also scarce in literature[14-16]. Previously, *we reorted* that 1-functionally substituted 2,3,4,5-tetraphenyl-1-silacylopenta-2,4-diene are so reactive to form new η^4-complexes of ironpentacarbonyl directly under mild reaction conditions.[14]

In this respect, we have studied the complexation of chromium with 1-functionally substituted R,R'-TPSCp (R = R' = Me, R = Me/R' = Cl, R = Ph/R' = Cl) and synthesized several new η^6-complexes of chromium.

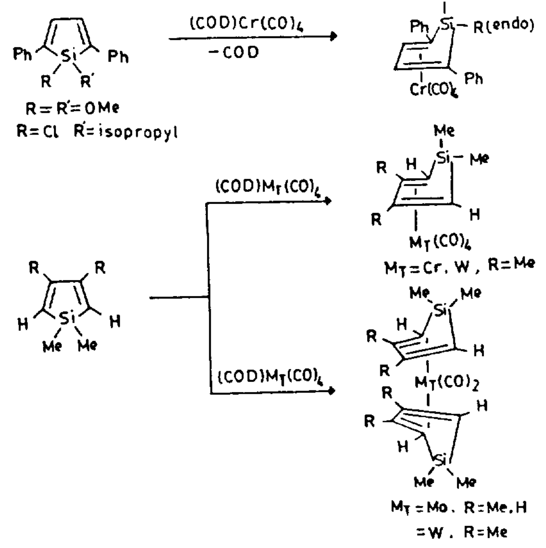
Results and Discussion

It was reported that the reaction of 1,1-dimethyl-2,5-diphenyl-1-silcyclopentadene with chromiumhexacarbonyl led to η^6-complexes of tricarbonyl (1,1-dimethyl-5-phenyl-1-silacyclopentadiene-2-ylbenzene) chromium. Whereas, with molybdenumhexacarbonyl, η^4-complexes of dicarbonyl bis(1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene) molybdenum was formed. From these results, chromium may prefer to form rather η^6-complex with arene than η^4-complex with diene moiety, whereas the molybdenum behaves in the reverse ways[10].



(1)

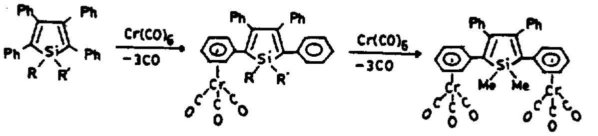
In contrast, the reaction of (COD)Cr(CO)$_4$ with 1,1,3,4-tetramethyl-1-silacyclopentadiene[7], and 1,1-diorgano-2,5-diphenyl-1-silacyclopentadiene[18] were reported to give η^4-complexes of tetracarbonyl (1-silacyclopentadiene) chromium. Whereas, in the reaction of (COD)Mo(CO)$_4$ with 1,1-dimethyl-1-silacyclopentadiene, and 1,1,3,4-tetramethyl-1-silacyclopentadiene, all complexation led to dicarbonylbis (1-silacyclopentadiene) molybdenum like distorted sandwich compound, and the reaction of (COD)W(CO)$_4$ with 1,1,3,4-tetramethyl-1-silacyclopentadiene led to both tetracarbonyl(1,1,3,4-tetramethyl-1-silacyclopentadiene) tungsten and dicarbonylbis(1,1,3,4-tetramethyl-1-silacyclpentadiene) tungsten[7].



(2)

From these results, it was indicated that chromium would not only be able to form η^4-complex from ligand exchange reaction but also be able to form η^6-complex from direct complexation reaction. However, it is somewhat unexpected result that only one phenyl substituent of two does coordinate to chromium, although the ligand of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene has a vertical mirror plane.

In our work, the novel complexes of (1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene-2,5-yldibenzene)-bis(tricarbonylchromium) (III) and tricarbonyl(1,1-dimethyl-3,4,5-triphenyl-1-silacyclopenta-2,4-diene-2-ylbenzene) chromium (II-a) were obtained from the reaction of $Cr(CO)_6$ with R,R′-TPSCp(R = R′=Me). The complex of III was also obtained from the reaction of II-a with chromiumhexacarbonyl. On the other hand, from the reaction of 1-functionally substituted R,R′-TPSCp(R = Me/R′ = Cl, R = Rh/R′ = Cl) with chromiumhexacarbonyl, we isolated η^6-complexes of II-b, II-c, respectively.



(3)

I-a(R=R′=Me) II-a(R=R′=Me)

I-b(R=Me/R′=Cl) II-b(R=Me/R′=Cl) III(R=R′=Me)

I-c(R=Ph/R′=Cl) II-c(R=Ph/R′=Cl)

These novel complexes might have geometric isomers of two, because phenyl substituents of ligand R,R′-TPSCp could not rotate due to the crowding of four bulky phenyl substituents. In fact, by the analysis of the structure of Fe[R,R′-TPSCp](CO)$_3$ (R = Ph/R′ = Cl) the rotation of phenyl is not possible[17]. The chemal shifts of II-a, III and II-b in ^{1}H-NMR were observed at 0.67, 0.86 and 1.12 ppm for methyl group as singlet, respectively. These chemical shift values were more deshielded than 0.47 ppm of ligand (I-a) and 0.86 ppm of ligand(I-b), each chemical shift differences of complex and its ligand were 0.20(II-a), 0.39(III) and 0.26(II-b) ppm. Therefore, it was supposed that the plane of η^6-Phenyl ring was located vertical to the plane of butadiene moiety of ligand (Figure 1.), this made the chemical surroundings of methyl groups equal and such lower field shifts were due to the reduced electron density of Si-Me by the electron withdrawing of chromiumtricarbonyl through the arene ring.

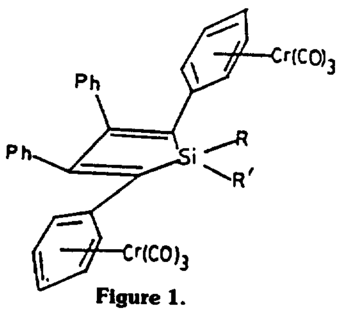


Figure 1.

From these results, we conclude that chromium preper to coordinate to the phenyl substituents of these R,R TPSCp(R = R′ = Me, R = Me/R′ = Cl. R = Ph/R″ = Cl) rather than the butadiene moiety of the ring, the complexation of III may probably proceed *via* II-a followed by the additional complexation with chromiumhexacarbonyl.

Experiments

All reactions were routinely carried out under an atmosphere of nitrogen using anhydrous solvents. Elemental analyses were performed by Yanaco, MT-2 Elemental analyzer at the Chemical analytic Center of the college of Engineering, Seoul National University. ^{1}H-NMR Spectra were obtained on Bruker WP 80 SY, 80 MHz FT-NMR, Mass spectra on Jeon Gas-Chromatography and Mass Spectrometer DMX 300, IR as KBr-pellet on Shimazu IR-440 and Melting point on Wagner & Münz, Co., Capillary type.

R,R′-TPSCp(R = R′ = Me, R = Me/R′ = Cl, R = Ph/R′ = Cl). These compound were prepared according to the procedure imporved by us[17]. 105 mmol of R_nSiCl_{4-n} was added at the temperature of liquid nitrogen to 120 m*l* of diethylether suspenison of 1,4-dilithio-tetraphenylbutadiene obtained from 10.7g(60 mmol) of diphenylacetylene and 0.5g (71mg atom) of lithium. The reaction mixture was allowed to warm to room temperature with stirring vigorously for three hours. The greenish-yellow solution was separated from the precipitate by decantation. The residue was extracted by adding 100 m*l* of diethylether two or three times. After the solution thus obtained was concentrated to an half of its volume, and was kept at-20 °C for one day. Greenish-yellow crystals of R,R′-TPSCp(R = R′ = Me, R = Me/R′ = Cl, R = Ph/R′ = Cl) were obtained.

R,R′-TPSCp(R = R′ = Me) (I-a); mp. 181 °C(lit,[19] 181-182 °C), Anal. Calcd. (found) for $C_{30}H_{26}Si$, C, 86.91 (85.70). H, 6.32(6.24), mass *m/e* 414(M$^+$), 399(M$^+$-Me), ^{1}H-NMR(CDCl$_3$, ppm), 0.47(s, 6H, SiMe), 6.7-7.2 (brd.m, 2OH, Ph), ^{13}C-NMR(CDCl$_3$, ppm), -3.92 (SiMe), 154.01(C-2.5), 141.89(C-3,4), 139.91, 138.87, 130.01, 128.83, 127.92, 127.38, 126.18, 125,52(Ph), IR(cm^{-1}), δ_{Si-Me} = 1240.

R,R′-TPSCp(R = Me/R′ = Cl)(I-b); mp. 190-191 °C(lit.[20] 194-195 °C), Anal. Calcd. (found) for $C_{29}H_{23}ClSi$, C, 80.07 (79.83, H, 5.33(5.41), mass *m/e* 434(M$^+$), 419(M$^+$-Me), ^{1}H-NMR(CDCl$_3$ ppm), 0.86(s, 3H, SiMe), 6.7-7.2(brd. m, 2OH, Ph), ^{13}C-NMR(CDCl$_3$, ppm), 0.34(SiMe), 155.30(C-2.5), 137.98 (C-3,4), 137,83, 136,62, 130.02, 129,35, 128,43, 127.93, 127.15, 126.71(Ph), IR(cm^{-1}), δ_{Si-Me} = 1245.

R,R′-TPSCp(R = Ph/R′ = Cl)(I-c); mp. 169 °C(lit.[20] 181-183 °C), Anal. Calcd. (found) for $C_{34}H_{25}ClSi$, C, 82.26(81.97), H, 5.04(4.97), mass *m/e* 497(M$^+$), 462(M$^+$-Cl), ^{1}H-NMR(CDCl$_3$, ppm), 6.7-7.2(brd. m, Ph), 7.2-7.8(brd. m, Ph), ^{13}C-NMR(CDCl$_3$, ppm), 156.30(C-2,5), 137.82(C-3,4), 134.39, 131.16, 130.31, 128.50(SiPh), 137.22, 135.77, 129.71, 129.21, 127.97, 127.70, 126.94, 126.40(Ph).

Tricarbonyl(1,1-dimethyl-3,4,5,-triphenyl-1-silacyclopenta-2,4-diene-2-ylbenzene)chromium(II-a) and (1,1-dimethyl-3,4-diphenyl-1-silacyclopenta-2,4-diene-2,5-yldibenzene)bis(tricarbonylchromium) (III). A mixture of 1.24g (3.0 mmol) of I-a and 1.54g(7.0 mmol) of chromiumhexacarbonyl in 80 m*l* of toluene was refluxed with stirring for 60 hrs. The greenish yellow solution of toluene was changed to orange, scarlet and finally dark-red. After the solvent was distilled off in vacuum, with sublimating of the residual chromiumhexacarbonyl followed by washing with 20 m*l* of *n*-pentane, 70 m*l* of *n*-hexane was given to the residue. The extraction of the residue with *n*-hexane was repeated 5-6 times and collected. The *n*-hexane solution of orange was standed for 20 hrs at room temperature, the orange solution with black precipitate was obtained. After seperatin of the precipitate by decantation, the solution was condensed to a σ half and kept at room temperature for 72 hrs, then scarlet crystals were obtained. Recrysatlization from *n* -hexane two or three times gave 0.42g of scarlet crystals (II-a). And, after extraction of the residue insoluble to *n* - hexane with 70 m*l* of ether, the ether solution of red was standed for 20 hrs at room temperature. Then, the ether solution was decantated, crystalization for one week at room temperature gave 0.93g of red crystals (III).

II-a: Scarlet crystal (Yield, 25%), mp, 172 °C(decomp.), Anal. Calcd.(found) for $C_{33}H_{26}O_3SiCr$, C;71.97(71.04), H;4.75(4.61), Mass, 550(M^+) 522(M^+-CO), 466(M^+-3CO), 414(ligand), ^{1}H-NMR($CDCl_3$, ppm), 0.67(s, 6H, Si-CH_3), 4.87-5.45(brd.m, 5H, Cr-Ph), 6.64-7.23(brd. m, 15H, Ph), IR(cm-1), ν_{co} = 1965, 1905, 1880.

III: Red crystal(Yield, 45%), mp, 184 °C (decomp.), Anal. Calcd. (found) for $C_{33}H_{26}ClO_6SiCr_2$, C; 62.79(63.01), H; 4.75 (3.92), Mass, 686(M^+), 550(M^+-Cr-6CO), 518(M^+-6CO), 466(M^+-Cr-6CO), 414(ligand), ^{1}H-NMR ($CDCl_3$, ppm), 0.86 (s, 6H, Si-CH_3), 4.74-5.44(brd. m, 10H, Cr-Ph), 6.64-7.23(brd.m, 10H, Ph), IR(cm^{-1}), ν_{Co} = 1950, 1865.

Reaction of II-a with Chromiumhexacarbonyl. A mixture of 0.55g(1 mmol) of II-a and 0.44g(2 mmol) of chromiumhexacarbonyl in 60 m*l* of toluene was refluxed with stirring for 40 hrs. The scarlet solution was changed to dark-red. The remaining treatment was same above procedure, Yield (40%).

II-b and II-c were prepared with 1.0 mmol of the corresponding R,R′-TPSCp(R = Me/R′ = Cl, R = Ph/R′ = Cl) with 3.0 mmol of chromiumhexacarbonyl principally in identical manner as described in the preparation of II-a, III, II-b and II-c were crystalized from ether-pentane, ether, respectively.

II-b. Red crystal (Yield, 0.26g, 60%), mp. 162 °C, Anal. Calcd. (found) for $C_{32}H_{23}ClO_3SiCr$, C; 67.31(68.27), H; 4.06(4.06), Mass, 570(M^+), 486(M^+-3CO), 434(ligand), ^{1}H-NMR($CDCl_3$, ppm), 1.12(s, 3H, Si-CH_3), 4.81-5.82(brd. m, 5H, Cr-Ph), 6.70-7.23(brd.m, 15H, Ph), IR(cm^{-1}), ν_{Co} = 1950, 1880.

II-c: Red crystal(0.38g, 60%), mp. 178 °C, Anal. Calcd. (found) for $C_{37}H_{25}ClO_3SiCr$, C;70.19(68:35), H;3.98(4.08), Mass, 632(M^+), 604(M^+CO), 548(M^+-3CO), 496(ligand), ^{1}H-NMR($CDCl_3$, ppm), 7.23-7.95(brd.m.5H, Ph), 4.82-5.26 (brd.-m, 5H, Cr-Ph), 6.82-7.23(brd.m, 15H, Ph), IR(cm^{-1}), ν_{Co} = 1960, 1915, 1895, 1875.

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