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Intermolecular Interaction between $W(CO)_6$ and Alkane Molecules Probed by Ultrafast Vibrational Energy Relaxation: Anomalously Strong Interaction between $W(CO)_6$ and Decane

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The rate of vibrational energy relaxation (VER) is a valuable probe of microscopic intermolecular interaction. In the present article, the VER rate of the T_{1u} CO stretch of $W(CO)_6$ is measured in binary solutions composed of an alkane (hexane, decane, tetradecane) and cyclohexane or CCl_4, with seven mixing volume ratios. The volume ratio dependence indicates that, among the three alkane−cyclohexane solutions, only decane shows an exceptionally strong contribution to the VER process. It is strongly suggested that decane forms a specific solute−solvent complex with $W(CO)_6$. The "V-shaped" dependence of the VER rate on the number of carbons in alkane solvents (Banno, M.; Sato, S.; Iwata, K.; Hamaguchi, H. *Chem. Phys. Lett.* 2005, *412*, 464.) is explained by the solute−solvent complex model. There are no experimental results that suggest the formation of the specific solute−solvent complex in alkane−CCl_4 solutions.

1. Introduction

The mechanism of a chemical reaction is affected significantly by interaction between solute and surrounding solvent molecules. In order to investigate reaction mechanism in solutions, it is essential to acquire the information on the solute−solvent interaction, or the chemical environment for the solute molecules.

The rate of vibrational energy relaxation (VER) is an effective measure of the chemical environment. When a molecule is vibrationally excited, the energy first deposited to the vibration is quickly distributed among the kinetic degrees of freedom in the molecule or in the surrounding solvent molecules.[1] The dynamics of the intermolecular energy transfer is crucially affected by the intermolecular interaction. Observing the VER process of a solute molecule is an effective method to evaluate the molecular environment.

A molecule can be vibrationally excited directly by the irradiation of an infrared (IR) light which is resonant with a vibrational transition of the molecule. In order to observe the vibrational dynamics, time-resolved spectroscopy with ultrashort IR pulses is an ideal method. The VER process in solution has been studied effectively with the time-resolved vibrational spectroscopic methods with ultrashort IR laser pulses, IR pump−probe,[2−25] IR transient grating,[20,26−28] or IR-pump−Raman-probe spectroscopy.[25,29−32] In particular, the solvent dependence of the VER rate has been investigated by several groups. The VER rate of the CN stretch vibration in the cyanide ion[15] or in $Fe(CN)_6^{4-}$[28] was increased by a factor of 3−6 when the solvent was changed from D_2O to H_2O. The VER rate was also changed by several tens of percent for $W(CO)_6$[12,13] and *trans*-stilbene,[33] or by a factor of 7 for 1-methylperylene,[34] when the number of carbon atoms in solvent alkane was changed. However, it is not still fully understood which solute−solvent interactions control the VER rate.

Tungsten hexacarbonyl ($W(CO)_6$) is an octahedral molecule, whose triply degenerate T_{1u} CO stretch vibration exhibits a strong IR absorption. Because of the large cross section of the IR absorption, its VER process has been studied extensively with picosecond IR spectroscopy,[2−9] femtosecond IR spectroscopy,[10−13] and IR-pump−Raman-probe spectroscopy.[29] In our previous results of femtosecond IR pump−probe spectroscopy, the VER time, which is inverse of the VER rate, of the T_{1u} CO stretch exhibited an unexpected solvent dependence in *n*-alkanes (C_nH_{2n+2}, $n = 5−14$).[12,13] The VER time gave its minimum value in decane among the nine alkanes, and the value increased as the number of carbon atoms in the solvent alkane either increased or decreased from that in decane. The "V-shaped" chain-length dependence was not explained by the macroscopic properties of the solvent, such as density, viscosity, or thermal conductivity, none of which exhibited the "V-shaped" dependence on the chain length. The anomalous chain-length dependence of the VER time should indicate presence of a specific intermolecular interaction between $W(CO)_6$ and the solvent alkane molecules which is represented only by the VER rate.

In this study, we observe the VER process of the T_{1u} CO stretch of $W(CO)_6$ in the six series of binary mixtures composed of an alkane (C_nH_{2n+2}, $n = 6, 10, 14$) and cyclohexane or CCl_4 by subpicosecond time-resolved IR pump−probe spectroscopy. We investigate the dependence of the VER rate on the mixing volume ratio of the two solvents to examine the specific interaction between $W(CO)_6$ and the alkane molecules.

2. Experimental Section

We used a subpicosecond time-resolved IR pump−probe spectrometer to observe the VER process of the T_{1u} CO stretch of $W(CO)_6$. The experimental setup was described in elsewhere.[12] An optical parametric amplifier (OPA) (Spectra Physics, OPA-800CF) was excited by the 800 nm output from a Ti:sapphire regenerative amplifier (Spectra Physics, Spitfire).

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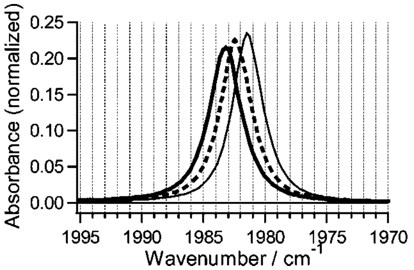

Figure 1. Observed ground-state IR absorption spectra of $W(CO)_6$ in hexane−cyclohexane binary solvents. The mixing volume ratio of cyclohexane is 0 (thick solid line), 0.5 (dotted line), and 1 (thin solid line).

Mid-IR light was generated in an $AgGaS_2$ crystal by difference frequency mixing of the signal and idler outputs in the near-IR region from the OPA. The mid-IR output was separated into two and was used for the pump and probe radiations. The angle between the polarization directions of the pump and probe beams was set to the magic angle, 54.7°, to remove the contribution from the rotation of the transition dipole moment. The sample solution was circulated through a 0.5 mm thick flow cell with two CaF_2 windows. The probe beam was analyzed by a monochromator (Oriel, MS257) and was detected by a MCT detector (Kolmar Technologies, KMPCP11-2.0-J1). The wavenumber resolution of the monochromator was set to 4 cm^{-1}. The center wavenumber of the IR light was set to 1980 cm^{-1}, which corresponded to the peak position of the ground-state absorption band due to the T_{1u} CO stretch of $W(CO)_6$. The spectral width of the IR light was 130 cm^{-1}. The time resolution of the spectrometer, estimated from the cross-correlation trace between the pump and probe pulses, was 200 fs.

The VER process of the T_{1u} CO stretch of $W(CO)_6$ was observed in six sets of binary solutions. One of the three alkanes (C_nH_{2n+2}, $n = 6, 10, 14$) was mixed with cyclohexane or CCl_4 with volume ratios of 0, 0.1, 0.25, 0.50, 0.75, 0.90, and 1. The ratio "0" indicates a pure alkane, whereas "1" indicates pure cyclohexane or CCl_4. $W(CO)_6$, hexane (>96%), decane (>99%), and CCl_4 (>99%) were purchased from Wako Pure Chemicals Industries, Ltd. Tetradecane (>99%) and cyclohexane (>99%) were purchased from Nacalai Tesque, Inc. The concentration of $W(CO)_6$ was 1.3×10^{-3} mol dm^{-3} in all the solutions.

3. Results

3.1. Ground-State IR Absorption. We measured the ground-state IR absorption spectra of $W(CO)_6$ in three sets of binary solutions composed of an alkane (C_nH_{2n+2}, $n = 6, 10, 14$) and cyclohexane. The obtained IR absorption bands due to the T_{1u} CO stretch vibration in the hexane−cyclohexane solutions are shown in Figure 1. The absorption bands are normalized by the area intensity. As shown in Figure 1, the peak position moves to the lower wavenumber direction and the bandwidth decreases as the cyclohexane content increases. The peak position and the bandwidth in the three sets of alkane−cyclohexane solutions are plotted against the mixing volume ratio of cyclohexane in Figure 2a−c. Both the peak position and the bandwidth change linearly as the mixing volume ratio changes for all the three sets of solutions.

We also measured the ground-state IR absorption spectra of $W(CO)_6$ in another three sets of binary solutions with one of the three alkanes and CCl_4. The relationship between the peak position or bandwidth of the T_{1u} CO stretch band and the mixing volume ratio of CCl_4 is shown in Figure 2d−f. The peak position moves to the lower wavenumber direction and the bandwidth increases as the mixing volume ratio of CCl_4 increases in all the three binary solutions. The peak position and the bandwidth change linearly in all the alkane−CCl_4 solutions, as observed for the alkane−cyclohexane solutions.

3.2. Time-Resolved IR Spectroscopy. We observed the VER process of the T_{1u} CO stretch of $W(CO)_6$ in the six sets of binary solutions by subpicosecond time-resolved IR spectroscopy. In this method, after the vibrational excitation by the IR pump pulse, the bleach and recovery of the ground-state IR absorption band are observed by the IR probe light. The recovery of the depleted absorption corresponds to the VER process $v = 0 \leftarrow 1$. Obtained recovery curves in the hexane−cyclohexane solutions are shown in Figure 3 for the cyclohexane volume ratio of 0, 0.5, and 1. Because the perturbed free induction decay (PFID) may interfere with the depletion signal for the negative time delays as well as for the positive time delays where the pump and probe pulses are temporally overlapped with each other, we discuss the time dependence recorded only after 2 ps.[36] All the observed recovery curves are well fitted by a single-exponential function. The decay rates represent the VER rate.

We measured the mixing volume ratio dependence of the VER rate in the six sets of binary solutions. The VER rate in the alkane−cyclohexane binary solutions, hexane−cyclohexane, decane−cyclohexane, and tetradecane−cyclohexane, is plotted against the mixing volume ratio of cyclohexane in Figure 4a−c, respectively. As shown in Figure 4, parts a and c, the VER rate changes linearly with the mixing volume ratio for the hexane−cyclohexane and tetradecane−cyclohexane solutions. The VER rate dependence corresponds well to the linear dependence of the peak position and the bandwidth observed in the ground-state IR absorption, as mentioned in section 3.1.

However, the linear relation between the VER rate and the mixing volume ratio is not observed in the decane−cyclohexane solutions. The VER rate deviates downward from the linear function as shown in Figure 4b. Because the VER rate in decane, 7.9 ns^{-1}, is smaller than the rate in cyclohexane, 12.5 ns^{-1}, by almost 40%, the downward deviation indicates that decane contributes to the VER process more than cyclohexane does.

The VER rate shows a linear dependence in all of the alkane−CCl_4 binary solutions. The VER rates in hexane−CCl_4, decane−CCl_4, and tetradecane−CCl_4 are plotted against the mixing volume ratio of CCl_4 in Figure 5a−c, respectively. Unlike the alkane−cyclohexane solutions mentioned above, no obvious deviation from the linear relation is found. The dependence of the VER rate on the mixing volume ratio corresponds well to that of the peak position or width of the ground-state IR absorption band. The specificity of decane is observed only in the alkane−cyclohexane solutions.

4. Discussion

As described in section 3.2., in the decane−cyclohexane binary solutions, decane contributes to the VER rate of $W(CO)_6$ more than cyclohexane does. The exceptionally strong contribution from decane to the VER process indicates the presence of a specific interaction between decane and $W(CO)_6$. The specific interaction is, however, not observed for the hexane−cyclohexane and tetradecane−cyclohexane solvents. From these results, it is possible to conclude that the length of decane is most suitable to exhibit the specific interaction with $W(CO)_6$ among the three alkane solvents.

In order to evaluate the "chain-length-dependent" interaction between $W(CO)_6$ and alkanes, we compare the shapes of the solute and the solvent molecules. $W(CO)_6$ is an octahedral, or quasi-spherical, molecule with a diameter of 0.64 nm. The half-

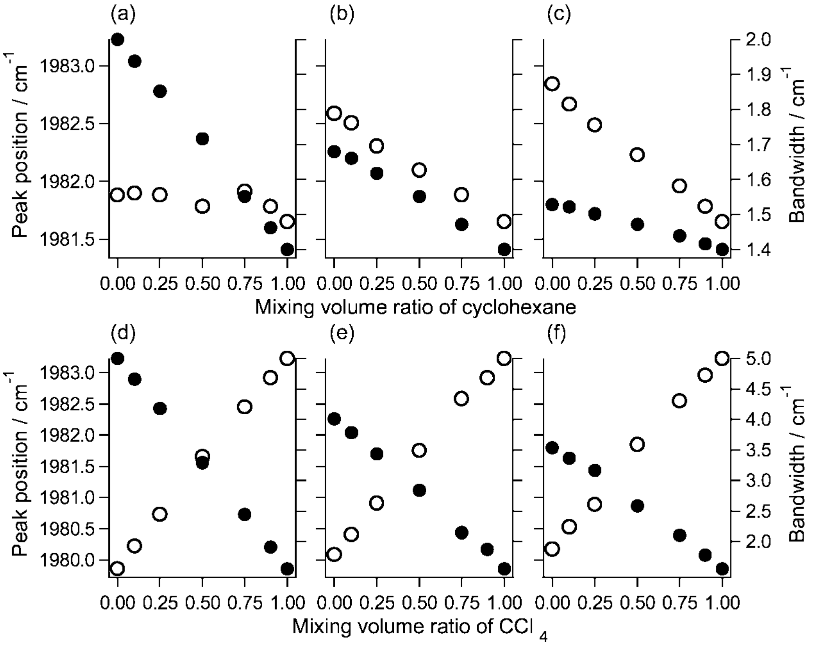

Figure 2. Relation between the peak position (filled circle, left axis) or the bandwidth (open circle, right axis) of the ground-state IR absorption band of the T_{1u} CO stretch of $W(CO)_6$ and the mixing volume ratio of cyclohexane or CCl_4 in hexane−cyclohexane (a), decane−cyclohexane (b), tetradecane−cyclohexane (c), hexane−CCl_4 (d), decane−CCl_4 (e), and tetradecane−CCl_4 (f) solutions.

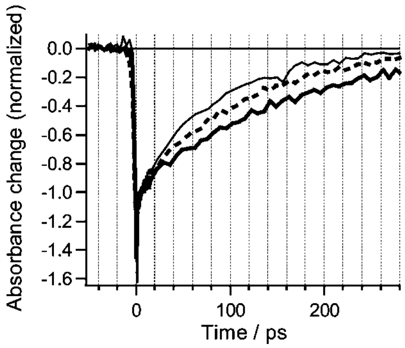

Figure 3. Observed bleach and recovery of the T_{1u} CO stretch of $W(CO)_6$ in hexane−cyclohexane binary solvents. Kinetics for the cyclohexane volume ratio of 0 (thick solid line), 0.5 (dotted line), and 1 (thin solid line) are shown.

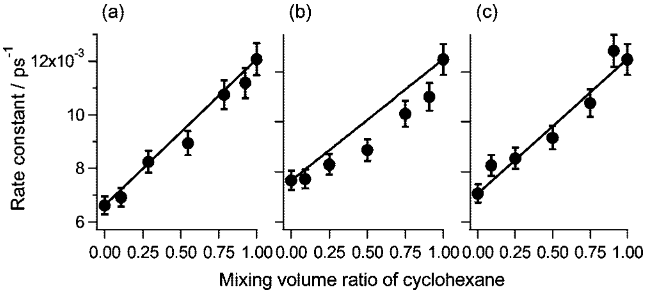

Figure 4. Relation between the VER rate and the mixing volume ratio of cyclohexane in hexane−cyclohexane (a), decane−cyclohexane (b), and tetradecane−cyclohexane (c) solutions. The solid lines represent the linear dependence.

length of its circumference is 1.01 nm. Decane is a quasi-linear molecule with its length of 1.14 nm, corresponding well with the half-length of the circumference of $W(CO)_6$. In thermal equilibrium, for alkane molecules, there are two conformations around each single bond between two methylene (CH_2) groups, trans and gauche.[37] A typical enthalpy difference between the trans and gauche conformations is 143 J mol^{-1}, which results in the relative population of 0.65 for the gauche conformer and 0.35 for the trans at 300 K. When the conformation at a CH_2−CH_2 single bond changes from trans to gauche, the wirelike alkane molecule bends by 104°. By introducing three gauche conformations to the 1.14 nm all-trans chain, the decane molecule takes a shape that surrounds a spherical $W(CO)_6$ molecule as the two peripheral CH_3 groups interacts simultaneously with the two CO groups on the opposite sides of $W(CO)_6$. In the T_{1u} CO stretch mode of $W(CO)_6$, the two opposite CO groups vibrate with the phase difference of π. The interactions between the CH_3 groups and the CO groups in a solvation complex may result in the strong contribution of decane to the VER process.

The length of all-trans hexane, 0.64 nm, is smaller than the half-length of the circumference of $W(CO)_6$, 1.01 nm. Therefore, hexane cannot form the solvation complex with $W(CO)_6$ in the same way as decane does. The length of all-trans tetradecane is 1.65 nm. For the formation of a similar solvation complex with $W(CO)_6$, some of the CH_2−CH_2 single bonds in tetradecane need to take the gauche conformation to reduce the distance between the two peripheral CH_3 groups to 1.01 nm. Unlike decane, however, it will be difficult to reduce the CH_3−CH_3 distance by 40% and, at the same time, keep contacting with $W(CO)_6$ along its spherical surface.

We concluded that the VER rate of the T_{1u} CO stretch mode of $W(CO)_6$ shows a "V-shaped" dependence on the number of carbon atoms in the alkane solvent.[12,13] This unexpected solvent dependence is readily explained by the present solvation complex model. Decane has the most suitable shape to form the solvation complex with $W(CO)_6$ among normal alkanes. In this complex, the peripheral CH_3 groups of decane have a strong interaction with a set of two opposite CO groups of $W(CO)_6$. This interaction may accelerate the vibrational energy migration from $W(CO)_6$ to decane. When the carbon chain length of the alkane solvent either increases or decreases from decane, the efficiency of the formation of the solvation complex decreases. Therefore, the VER time of the T_{1u} CO stretch mode of $W(CO)_6$ shows the "V-shaped" dependence with its minimum at decane.

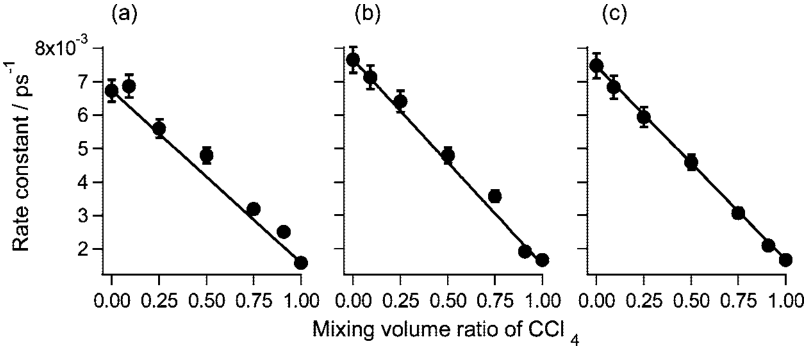

Figure 5. Relation between the VER rate and the mixing volume ratio of CCl_4 in hexane−CCl_4 (a), decane−CCl_4 (b), and tetradecane−CCl_4 (c) solutions. The solid lines represent the linear dependence.

The experimental result suggests that the peripheral CH_3 group of decane accelerates the solute VER process more quickly than the CH_2R group, where R represents an alkyl group, of a longer alkane chain. It is likely that the vibrational energy on the CO stretch mode of $W(CO)_6$, 2000 cm^{-1}, is effectively transferred to the CH_2 or CHR bend modes of alkane solvents at 700 to 1500 cm^{-1}.[38] In tetradecane, for example, two CH_2R groups or one CH_3 and one CH_2R group have a distance similar to that of the CH_3 groups in decane and could have equally accelerated the VER process of the two opposite CO groups in $W(CO)_6$. The difference between the CH_3 group and the CH_2R group is the presence of an alkyl group instead of a hydrogen atom.

There are several possible mechanisms that might account for the faster VER process observed with the CH_3 group than with the CH_2R group. First, the peripheral CH_3 group will approach the CO ligand more freely because the volume of the hydrogen atom is much smaller than that of the alkyl group. Second, the dipole moment change by the CH_2 bend vibrations is larger than that by the CHR bend vibrations. Finally, the energy difference (500−600 cm^{-1}) between the CO stretch and CH_2 bends is smaller than that (600−800 cm^{-1}) between the CO stretch and the CHR bends. If the vibrational energy deposited to the CO ligands is more effectively transferred to the CH_2 bend vibrations than to the CHR bend vibration by either of these reasons, the CH_3 group will accelerate the VER process more than the CH_2R group does.

Several fast phenomena in solution observed with time-resolved spectroscopic techniques were accounted for with specific solvation processes. The geminate recombination of I_2 after photodissociation in CCl_4 occurs within 10−15 ps, which is smaller than the value estimated from the diffusion equation.[39] This result was explained by a cage effect of the solvating molecules. The cage effect was also discussed for metal carbonyl complexes, including $W(CO)_6$, in alkane solutions in an ultraviolet (UV)-pump−IR-probe study.[40] The geminate recombination of photodissociated CO and $W(CO)_5$ proceeds in less than 200 fs after the UV excitation. The result suggests a presence of a certain solvation structure between $W(CO)_6$ and alkane molecules. In a time-resolved Raman study of 1,4-diphenyl-1,3-butadiene (DPB), the vibrational energy deposited to a C=C stretch mode in the S_1 state is dissipated exceptionally fast in pentane, compared with any alkane solvents with longer chain lengths.[41] The specificity of pentane was attributed to the formation of a solvation structure between the olefin moiety of DPB and pentane which have similar structures and sizes.

The position and the width of the ground-state IR absorption band change monotonically when the mixing ratio of binary solutions, including the decane−cyclohexane solutions, changes as shown in Figure 2. The result indicates that the interaction between decane and $W(CO)_6$ contributes not largely to the dephasing and the rotational diffusion but to the VER process. From the ground-state IR absorption bandwidth, the dephasing and the rotational diffusion proceed with a time constant of approximately 5 ps. It is probable that the VER rate for $W(CO)_6$ solvated in decane is different from that for $W(CO)_6$ in ordinary solvents, whereas the dephasing and the rotational diffusion rates are almost identical in all of the solvents.

The intermolecular energy transfer will be faster when the solute−solvent interaction is stronger. Because the VER rate in cyclohexane, 12.5 ns^{-1}, is larger than that in decane, 7.9 ns^{-1}, it may seem likely that cyclohexane interacts stronger with $W(CO)_6$ than decane does. However, in the decane−cyclohexane solutions, the contribution of decane to the VER rate is larger than that of cyclohexane, as discussed on Figure 4b. Decane may isolate $W(CO)_6$ from cyclohexane by the solvation complex, which will hinder the more effective energy transfer from $W(CO)_6$ to cyclohexane.

In alkane−CCl_4 solutions, the specific contribution of decane to the VER rate as in the alkane−cyclohexane solutions is not observed, as shown in Figure 5. The result indicates that CCl_4 interferes with the formation of the solvation complex between $W(CO)_6$ and decane. For the alkane−cyclohexane solutions, all of the solvent molecules are hydrocarbons. The shape and size of the solvent molecule plays a major role when the solute interacts with the solvents in the alkane−cyclohexane solutions. However, CCl_4 might interact with $W(CO)_6$ in a way different from alkanes and cyclohexane do. It is most likely that the interaction between $W(CO)_6$ and CCl_4 interferes with the formation of the solvation complex between $W(CO)_6$ and decane or destroys it.

In a previous study on the dephasing process of the T_{1u} CO stretch mode of $W(CO)_6$, it was suggested that the triple degeneracy was broken by microscopic solute−solvent interaction.[35] The symmetry breaking of the spherical molecule by the solute−solvent interaction is important when discussing the molecular dynamics in solution. However, in all the binary solvents used, the absorption band due to the T_{1u} CO stretch mode exhibits a symmetric shape, as shown in Figure 2. In the present study, we do not have clear experimental results indicating the symmetry breaking process.

The VER process in solution has been investigated theoretically with the low-frequency force−force time correlation function of the solvent.[42−44] These theoretical studies were also applied to the VER process of $W(CO)_6$ in supercritical fluids.[45,46] The VER time for $W(CO)_6$ is expected to depend largely on the force−force correlation function of the binary solvents. It will be difficult, however, to simulate the correlation function of binary solvents and its mixing ratio dependence at the present stage. We expect that the anomalous solvent dependence of the VER rate will be interpreted more quantitatively by theoretical approaches in the near future.

5. Conclusion

To elucidate the relationship between the VER rate and the solute−solvent intermolecular interaction, we have investigated the VER process of the T_{1u} CO stretch of $W(CO)_6$ in the six sets of binary solutions, formed by one of the three alkanes (C_nH_{2n+2}, $n = 6, 10, 14$) and cyclohexane or CCl_4, while changing the mixing volume ratio. In the hexane−cyclohexane and tetradecane−cyclohexane solutions, the VER rate changes linearly with the mixing volume ratio of cyclohexane. In the decane−cyclohexane solutions, however, the VER rate deviates from the linear relation. Decane has the most suitable length to interact with $W(CO)_6$ to form the solvation complex, in which a decane molecule keeps a contact with the $W(CO)_6$ molecule along the spherical surface and, at the same time, the two peripheral CH_3 groups of decane interact with the two opposite CO groups of $W(CO)_6$. This interpretation also accounts for the “V-shaped” solvent dependence of the VER time of $W(CO)_6$ in the *n*-alkane solutions.[12,13]

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