Headline Articles

Thermodynamics and Kinetics of Formation of Intramolecular Naphthalene Dimer Radical Cation Studied by Near-IR Transient Absorption Spectroscopy

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Thermodynamics and kinetics for formation of an intramolecular dimer radical cation of a series of α,ω-di(2-naphthyl)alkanes in solutions were quantitatively investigated by near-IR transient absorption spectroscopy, which allows one to observe dimer radical cations directly. The standard enthalpy ($-\Delta H^\circ$) for the formation of the intramolecular dimer radical cation increased as the chain length between the two naphthyl moieties increased, and was smaller than that of the intermolecular dimer radical cation of 2-ethylnaphthalene. This shows that $-\Delta H^\circ$ depends on the strain required for the chain to form the ring-closure configuration. Destabilization due to repulsion between the two naphthyl moieties in the intramolecular dimer radical cation was evaluated to be ca. 20 kJ mol^{-1}. This value is smaller than that of the naphthalene excimer, indicating that the separation distance and/or the overlap between the two naphthyl moieties are not as restricted as those of the excimer. The activation energy for the formation of the intramolecular dimer radical cation was comparable to the energy for local motions of a few methylene units linking the two naphthalene moieties.

Bichromophoric molecules are useful model compounds for investigating intramolecular interactions between two aromatic groups such as excimers, exciplexes, and dimer radical cations.[1–19] Among them, formation of intramolecular excimers has been most extensively studied since the first report of intramolecular excimers in diphenyl and triphenyl alkanes by Hirayama.[4] This is because the fluorescent properties of excimers and exciplexes enable one to discuss the kinetics[4–7,9–13] and thermodynamics[7,10,11,13] for the geometrical arrangement quantitatively by fluorescence spectroscopy with high sensitivity and time resolution. Many studies have been done so far using bichromophoric molecules in which two chromophores are connected by a chain with various lengths,[7–11] compositions,[11–13] and diastereoisomeric forms.[13] For example, we found that α,ω-di(2-naphtyl)alkanes (DNp*n*, the length of the methylene chain between the two naphtyl groups $n = 3$–12) formed an intramolecular excimer only at $n = 3$, and that the standard enthalpy and the activation energy for the formation of the excimer are 18 and 14 kJ mol^{-1}, respectively.[7] On the other hand, Zachariasse et al. found that dipyrenyl compounds formed intramolecular excimers in a wide range of chain lengths. They discussed the standard enthalpy, the activation energy for the formation of the intramolecular excimers, and dependence of formation yield on the chain length.[8,11] These results show that the formation of excimers strongly depends on the length of the chain.

On the contrary, there is no quantitative study on intramolecular dimer radical cations formed in a series of bichromophoric compounds with various chain lengths. There are only qualitative studies on the formation of intramolecular dimer radical cations formed in bichromophoric compounds linked by short alkane chains.[14–18] The lack of a quantitative study is probably due to difficulties in the evaluation of the numbers of monomer and dimer radical cations. In general, monomer radical cations show absorption overlapping that of dimer radical cations in the UV–visible region, which is covered by conventional transient absorption spectroscopy. Near-IR transient absorption spectroscopy is a powerful tool for observing characteristic absorption bands originating from inter- and intramolecular interactions between aromatic molecules, which correspond to the photon energy in the near-IR region. Dimer radical cations have a characteristic absorption band in the near-IR region, which is called the charge resonance (CR) band. It originates from charge delocalization between two aromatic molecules.[16–21] On the other hand, most radical cations of aromatic molecules have absorption bands in the UV–visible region. Thus, the numbers of monomer and dimer radical cations can be quantitatively evaluated by absorption spectroscopy from the UV–visible to the near-IR wavelength regions, even if the ratio of dimer radical cations to monomer radical cations is low. In addition, observation of CR bands allows one to evaluate the stabilization energy due to the charge delocalization (CR stabilization).[16–21]

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Here, we investigated an intramolecular dimer radical cation in a series of DNp*n* in solutions by near-IR transient absorption spectroscopy. We discuss quantitatively for the first time the kinetics and thermodynamics for the formation of the intramolecular dimer radical cation in DNp*n* and its dependence on the length of the chain between the naphthyl (Np) moieties.

Experimental

Materials. 1,3-Di(2-naphthyl)propane (DNp3) was synthesized from Wolff–Kishner reduction of 1,3-di(2-naphthyl)propan-1-one, which was prepared by the hydrogenation of the product obtained from the condensation of 2-naphthaldehyde and 2-acetonaphthone in an alkaline ethanol solution.[5] 1,5-Di(2-naphthyl)pentane (DNp5) was synthesized from the reduction of 1,5-di(2-naphthyl)pentan-3-one, which was prepared by the hydrogenation of the product obtained from the condensation of 2-naphthaldehyde and acetone. 1,7-Di(2-naphthyl)heptane (DNp7) and 1,12-di(2-naphthyl)dodecane (DNp12) were synthesized from the reduction of the corresponding α,ω-di(2-naphthoyl)alkanes, which were prepared by the Grignard reactions of 2-naphthonitrile and the corresponding α,ω-dibromoalkanes. The detailed synthesis of this DNp*n* series has been described elsewhere.[7] The monomeric compound of 2-ethylnaphthalene (EtNp) was purchased from Tokyo Kasei Kogyo Co. and was used without further purification. *o*-Dicyanobenzene (*o*-DCNB) used as an electron acceptor was purchased from Tokyo Kasei Kogyo Co. and was used after several recrystallizations. Acetonitrile (spectroscopic grade) was purchased from Nacalai Tesque and was used without further purification. The sample solutions in 1-cm quartz cells were degassed by the freeze–pump–thaw method. The concentration of the naphthalene compounds was adjusted to 0.3 mM where intermolecular formation of a Np dimer radical cation is negligible. The concentration of *o*-DCNB was 0.1 M.

Measurements. A nanosecond laser pulse (308 nm, ~0.5 mJ cm^{-2}, fwhm 17 ns) from a XeCl excimer laser (Lambda Physik EMG101MSC) was used as an excitation light source. For measurement of transient absorption decay, a pulsed 500-W xenon flash lamp was used as a monitor light source. The monitor light in the direction normal to the excitation light was passed through a monochromator (Ritsu, MC-10N) before detection. A photomultiplier tube (Hamamatsu Photonics, R5188) was used as a detector. The temperature of a sample cell set in a quartz Dewar vessel was controlled by precooled nitrogen gas. For measurement of transient absorption spectra, a steady-state 150-W xenon lamp was used as a monitor light source. A photomultiplier tube (Hamamatsu Photonics, R1477) and an InAs photovoltaic detector (Hamamatsu Photonics, P838) were used for the detection in the visible region from 400 to 850 nm and in the near-IR region from 780 to 2000 nm, respectively.

Results and Discussion

Figures 1a and 1b show the transient absorption spectra for radical cations of EtNp at 295 and 233 K, respectively, formed in an acetonitrile solution with 6 mM EtNp and 0.1 M *o*-DCNB 1, 2, 3, and 5 µs after laser excitation. At 295 K, three characteristic absorption bands were observed, as shown in Fig. 1a. The sharp absorption band at 675 nm is ascribed to the monomer radical cation of EtNp.[16,17] The broad absorption bands around 590 and 1100 nm are ascribed to the local excitation (LE) and charge resonance bands of the intermolecular dimer radical cation of EtNp.[16,17] At 233 K, the sharp absorption band at 675 nm disappeared completely, while the two broad absorption bands due to the dimer radical cation remained, as shown in Fig. 1b. The molar absorption coefficients are reported to be 4500 M^{-1} cm^{-1} at 675 nm for the absorption of the monomer radical cation and 4400 M^{-1} cm^{-1} at 1100 nm for the CR band of the dimer radical cation.[19] Thus, we can evaluate the concentrations of the dimer radical cation [D$^+$] as well as the monomer radical cation [M$^+$] from these characteristic absorption bands.

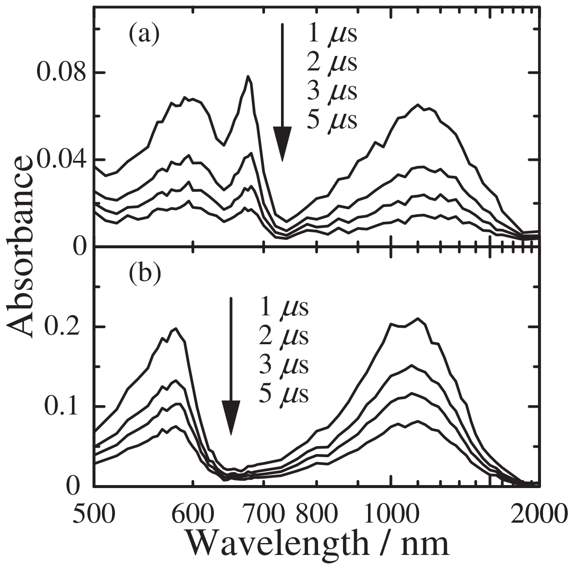


Fig. 1. Transient absorption spectra for radical cations of 6 mM EtNp in acetonitrile solutions with 0.1 M *o*-DCNB 1, 2, 3, and 5 µs after laser excitation at (a) 295 K and (b) 233 K.

The dimer radical cation of Np formed not only intermolecularly, but also intramolecularly. A sharp absorption band at 675 nm and a broad absorption band around 1250 nm were observed in the transient absorption spectrum of DNp5 at 295 K in an acetonitrile solution with 0.3 mM DNp5 and 0.1 M *o*-DCNB.[19] The sharp and the broad absorption bands were ascribed to the monomer radical cation and the intramolecular dimer radical cation of DNp5, respectively. Figure 2 shows the time evolution of the ratio of dimer radical cations [D$^+$] to monomer radical cations [M$^+$] formed in DNp5 at various temperatures. The ratio was evaluated from the absorbance at 675 and 1050 nm. There are two characteristic time domains in the time evolution of the ratio. The ratio increased in the earlier time domain and saturated in the later time domain. The rise in the ratio in the earlier time domain shows dynamic formation of the intramolecular dimer radical cation. From the data obtained in the earlier time domain, we will discuss the kinetics and the activation energy E_D for the formation of the intramolecular dimer radical cation in the latter half of this paper. From the data obtained in the later time domain, we will discuss the standard enthalpy $-\Delta H^\circ$ for the formation in the next section.

Thermodynamics of the Formation of the Dimer Radical Cation of DNp*n*. Figure 3 shows the van't Hoff plots for the formation of the dimer radical cation in DNp5, 7, 12, and EtNp. Each $-\Delta H^\circ$ evaluated from the slopes is listed in Table 1, with the experimental error, which was less than 4 kJ mol^{-1} for all compounds. The standard enthalpy $-\Delta H^\circ$ for the dimer radical

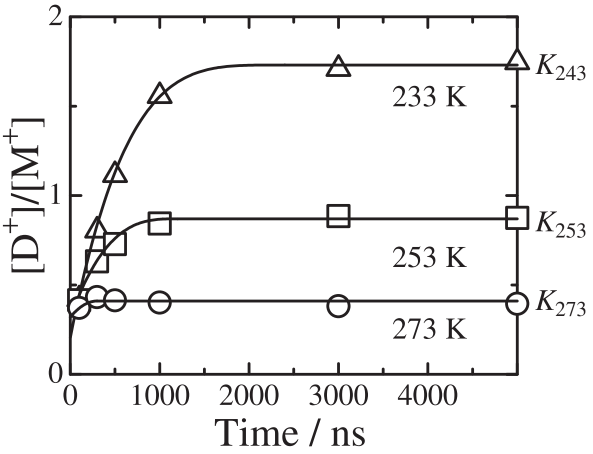


Fig. 2. Time evolution of $[D^+]/[M^+]$ for DNp5 after laser excitation at several temperatures. The circle, rectangle, and triangle indicate the value of $[D^+]/[M^+]$ at 273, 253, and 233 K, respectively.

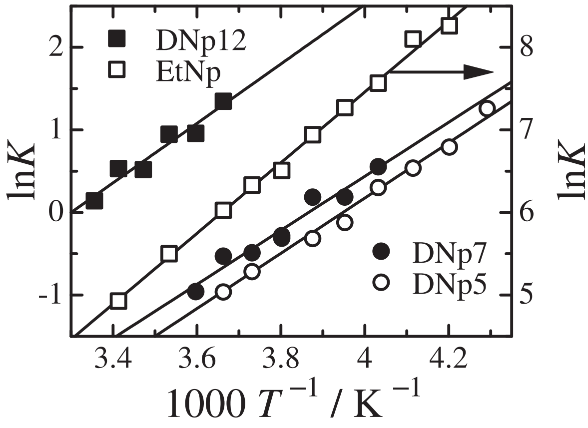
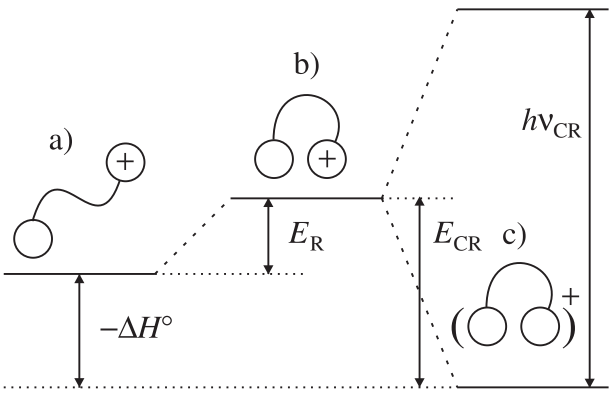


Fig. 3. van't Hoff plots for the formation of the dimer radical cation of DNp*n* ($n = 5$, 7, and 12) and EtNp. The open circle, closed circle, closed rectangle, and open rectangle indicate the value of $\ln K$ for DNp5, 7, 12, and EtNp at various temperatures, respectively.

Table 1. Values of $-\Delta H^\circ$, E_{CR}, E_R, k_D, and E_a for the Dimer Radical Cation of DNp*n* ($n = 5$, 7, and 12) and EtNp

	$-\Delta H^\circ$ /kJ mol^{-1}	E_{CR} /kJ mol^{-1}	E_R /kJ mol^{-1}	k_D /10^6 s$^{-1\,a)}$	E_a /kJ mol^{-1}
DNp5	27 ± 2	47 ± 2	20 ± 4	3.7 ± 0.4	15 ± 2
DNp7	27 ± 3	49 ± 2	22 ± 5	2.0 ± 0.2	15 ± 2
DNp12	30 ± 4	53 ± 2	23 ± 6	19 ± 2	13 ± 2
EtNp	36 ± 1	54 ± 2	19 ± 3	—	—

a) At 248 K.



Scheme 1. Schematic energy diagrams for $-\Delta H^\circ$, E_{CR}, and E_R. a) The two Np moieties are far from each other and the charge is localized on either of the Np moieties. b) The mutual configuration of the two Np moieties is the same as that of the dimer radical cation, but the charge is localized. c) The mutual configuration is the same as that of b), and the charge is delocalized between the Np moieties.

cation of Np was larger than that of the excimer of Np and comparable to that of the excimer of pyrene.[7] This is one of the reasons why the intramolecular dimer radical cation of Np can be formed for all of DNp*n*, while the intramolecular excimer of Np cannot be formed apart from DNp3. The standard enthalpy $-\Delta H^\circ$ increased in the following order: the intramolecular dimer radical cation with a shorter methylene chain (DNp5, DNp7) < the intramolecular dimer radical cation with a longer methylene chain (DNp12) < the intermolecular dimer radical cation (EtNp). These results indicate that the strain in shorter methylene chains prevents formation of a stable dimer radical cation. The chain length is too short for DNp5 and DNp7 to form a dimer radical cation that is as stable as the intermolecular Np dimer radical cation of EtNp, but is long enough for DNp12 to do so. This tendency corresponds to that of the CR stabilization energy E_{CR}, which has been discussed elsewhere.[19]

The CR stabilization energy E_{CR} of the dimer radical cation formed in DNp*n* can be evaluated from the CR bands, whose peak wavelength corresponds to about half of the energy required for the CR transition.[16–21] The E_{CR} due to the charge delocalization was larger than the thermodynamical stabilization energy $-\Delta H^\circ$ for all the DNp*n*. The difference between E_{CR} and $-\Delta H^\circ$ is equal to the repulsion energy E_R, which is due to the electronic repulsion between a neutral Np moiety and a Np radical cation in a configuration where a dimer radical cation could be formed. Scheme 1 shows the relationship among $-\Delta H^\circ$, E_{CR}, and E_R; i.e., $E_R = E_{CR} - (-\Delta H^\circ)$. The dimer formation would be conveniently divided into two steps: 1) cyclization to a conformation where the two Np moieties have the same mutual configuration as the dimer radical cation, but the charge is localized in one of the two Np moieties; 2) charge delocalization without any conformational changes. These values are summarized in Table 1. The experimental error in E_{CR} originating from the evaluation of the peak wavelength of the CR bands was less than 2 kJ mol^{-1}, which corresponds to a deviation of ca. 50 nm in the peak wavelength. The values of E_R are about 20 kJ mol^{-1} for the intramolecular dimer radical cation of all the DNp*n* as well as for the intermolecular dimer radical cation of EtNp. This is smaller than that of E_R for the Np excimer, which is reported to be about 30 kJ mol^{-1}.[22] This difference suggests that the separation distance and/or the overlap of the two Np moieties in the dimer radical cation is not as restricted as those of the Np excimer. This is probably because the CR interaction is less dependent on the separation distance and/or the overlap between two aromatic moieties than the exciton interaction. For example, an intramolecular dimer radical cation is formed in *trans*-1,2-di(*N*-carbazolyl)cyclobutane,[16] where no intramolecular excimer is formed.[14] Consequently, the overlapping structure for the Np dimer radical cation is slightly distorted from the symmetrical sandwich structure to avoid the π-electron repulsion between the two aromatic moieties. Yamamoto et al. reported that the Np dimer radical cation with a sandwich structure is less stable than that with a partially overlapping structure.[17] Badger and Brocklehurst obtained a similar result from their calculations.[21] These reports support our interpretation.

Kinetic Study for the Formation of the Dimer Radical Cation of DNp*n*. In this section, we discuss the kinetics for the formation of the intramolecular dimer radical cation of DNp*n* in the time domain before the equilibrium is established. In this paragraph, we explain a model for analyzing the kinetics and demonstrate the validity of the model. We assume a kinetic scheme for the formation of the intramolecular dimer radical cation, as shown in Scheme 2. The monomer radical cation of DNp*n* and the counter anion are generated by photoinduced electron transfer from one Np moiety in the excited state to a dopant electron acceptor. The intramolecular dimer radical cation of DNp*n* is formed by the charge delocalization between the monomer radical cation and the neutral Np moiety in a DNp*n* molecule. Both monomer and dimer radical cations return to the neutral state through charge recombination with an acceptor anion. The kinetic parameters, k_D, $k_D{}^{-1}$, k_R, and $k_R{}'$ for each DNp*n* represent the rate constants for the formation of the dimer radical cation, the dissociation of the dimer radical cation, the recombination of the monomer radical cation with an acceptor radical anion, and the recombination of the dimer radical cation with an acceptor radical anion, respectively. $[M^+]$, $[D^+]$, and $[A^-]$ represent the concentrations of the monomer radical cation, the dimer radical cation, and an acceptor radical anion, respectively. The following differential equations are derived from Scheme 2.

$$\frac{d[M^+]}{dt} = -k_D[M^+] - k_R[A^-][M^+] + k_D^{-1}[D^+] \qquad (1)$$

$$\frac{d[D^+]}{dt} = k_D[M^+] - k_D^{-1}[D^+] - k_R'[A^-][D^+]. \qquad (2)$$

A boundary condition holds over the entire time range.

$$[A^-] = [M^+] + [D^+]. \qquad (3)$$

The initial conditions are as follows:

$$[M^+] = [M^+]_0 \quad \text{at } t = 0 \qquad (4)$$

$$[D^+] = 0 \quad \text{at } t = 0. \qquad (5)$$

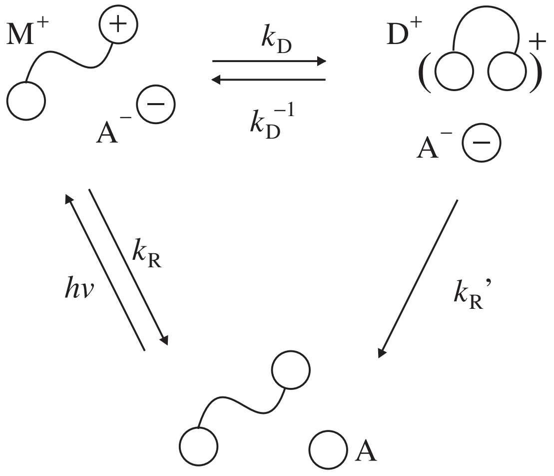
We assumed that the charge recombination reactions are diffusion-controlled. Thus, we can set $k_R = k_R{}'$. Under such initial and boundary conditions and the assumption, the system of the differential equations can be solved.

$$[M^+] = \frac{[M^+]_0[k_D^{-1} + k_D \exp\{-(k_D + k_D^{-1})t\}]}{(k_D + k_D^{-1})(1 + [M^+]_0 k_R t)} \qquad (6)$$

$$[D^+] = \frac{[M^+]_0[k_D - k_D \exp\{-(k_D + k_D^{-1})t\}]}{(k_D + k_D^{-1})(1 + [M^+]_0 k_R t)} \qquad (7)$$

$$[A^-] = \frac{[M^+]_0}{1 + [M^+]_0 k_R t}. \qquad (8)$$

The time evolution of the absorbance at 675 and 1050 nm were fitted with Eqs. 6 and 7, respectively. The values of $[M^+]_0$, k_D, and k_R were evaluated from the fitting. For example, Fig. 4 shows the time evolution of the absorbance at 675 and 1050 nm for DNp7 at 248 K with the fitting curves drawn by solid lines. The values of $[M^+]_0$, k_D, and k_R were evaluated from the fitting to be 2.5×10^{-5} M^{-1}, 2.0×10^6 s^{-1}, and 6.5×10^9 $M^{-1}s^{-1}$, respectively. The fitting curves agreed well with the experimental data. This agreement demonstrates that our model can explain the kinetics of the formation. The value of



Scheme 2. Kinetic scheme for the intramolecular dimer radical cation. The parameters, k_D, $k_D{}^{-1}$, k_R, and $k_R{}'$ represent the rate constants for the formation of the dimer radical cation, the dissociation of the dimer radical cation, the recombination of the monomer radical cation with an acceptor radical anion, and the recombination of the dimer radical cation with an acceptor radical anion, respectively.

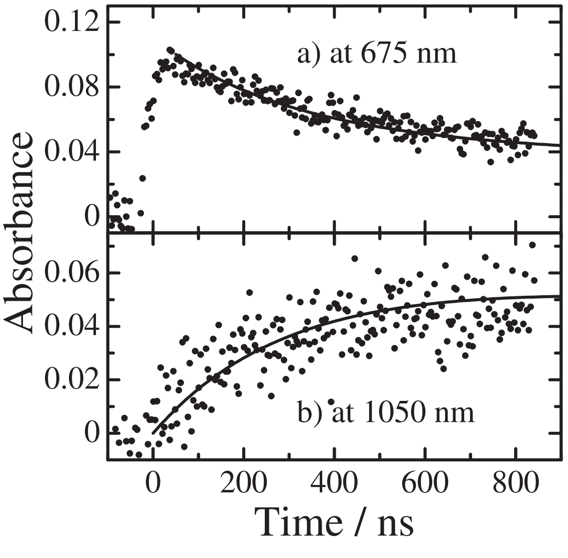


Fig. 4. Time evolution of absorbance at (a) 675 and (b) 1050 nm for DNp7 after laser excitation at 248 K. The dots and solid lines show the experimental data and the fitting curves, respectively.

k_R obtained from the fitting was similar to that evaluated from the viscosity of the solvent under the diffusion-controlled condition.[23] This agreement proves that our assumption is valid: the charge recombination reactions are diffusion-controlled. We obtained these kinetic parameters for the series of DNp*n* at 248 K: $k_D > 10^8$ s^{-1} for DNp3, $k_D = 3.7 \times 10^6$ s^{-1} for DNp5, $k_D = 2.0 \times 10^6$ s^{-1} for DNp7, $k_D = 1.9 \times 10^7$ s^{-1} for DNp12. The experimental error for k_D originating from noise in the time evolution was ca. ±10 percent. We will discuss the dependence of k_D on the length of the methylene chain n in the next paragraph.

The rate constant for the formation of the intramolecular dimer radical cation was largest at $n = 3$. The values of k_D decreased by two orders of magnitude at $n = 5$ and 7, and by one order of magnitude at $n = 12$. The k_D for DNp3 was roughly estimated to be more than 10^8 s^{-1} in the range of temperature measured from 233 to 295 K because the time constant for the rapid rise of the CR band corresponded to the width of the laser pulse (FWHM = 20 ns) even at 233 K, where the value of k_D should be smallest. The rapid formation is because the propane chain is favorable for formation of dimer radical cations in a parallel configuration, which is consistent with the Hirayama rule.[4] The value of k_D is larger than that for the intramolecular excimer at $n = 3$, which is 1.9×10^7 s^{-1} at 233 K and 4.8×10^7 s^{-1} at 253 K.[7] That the formation of the intramolecular dimer radical cation is faster than the intramolecular excimer may be due to the less restricted separation distance and/or the overlap between the two Np moieties required for the formation of the dimer radical cation than those for the excimer. On the contrary, the dimer radical cation of DNp5 and DNp7 were formed slowly, in several microseconds. This is one of the reasons why DNp5 and DNp7 cannot form an intramolecular excimer: the lifetime of Np in the excited state is as short as 55 ns.[7] The dimer radical cation of DNp12 was formed about 10 times faster than those of DNp5 and DNp7. This dependence of k_D can be explained in terms of the ring-closure probability of the DNp*n* molecules. The ring-closure probability of DNp5, DNp7, and DNp12 corresponds to that of alkane chains with 8, 10, and 15 methylene units, respectively, because two aromatic groups forming a dimer radical cation can be considered as three methylene units forming a half part of a cyclohexane ring in the chair conformation.[8,19] The observed dependence is enhanced compared with the ring-closure probability of alkane chains. The probability predicts that alkane chains with 8 to 13 methylene units are virtually unclosed, while those with more than 14 methylene units can take closed conformations.[24] Sisido and his co-worker calculated the distribution of the end-to-end distances r for DNp*n* molecules (n = 3–16).[25] They found that no conformation leads to an end-to-end distance of $r < 0.5$ nm for all the DNp*n* molecules in the ground state. Thus, the enhancement of the dimer formation results from the large stabilization energy of the charge delocalization in the dimer radical cation, which allows the DNp*n* cation to form closed conformations more easily than the corresponding neutral molecules.

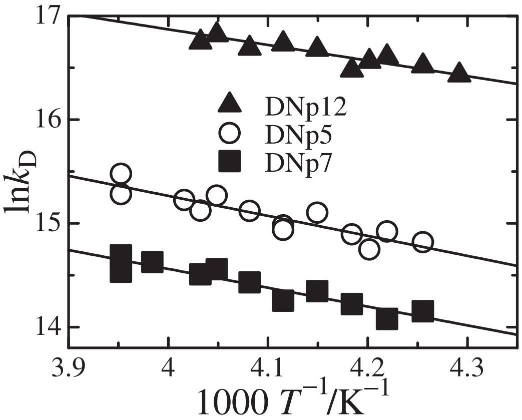


Fig. 5. Arrhenius plots for the formation of the intramolecular dimer radical cation of DNp*n*. The open circle, rectangle, and triangle indicate the value of ln k_D for DNp5, 7, and 12 at various temperatures, respectively.

We measured the formation rate k_D for a series of DNp*n* over a temperature range from 233 to 253 K. Figure 5 shows the Arrhenius plots for the formation of the intramolecular dimer radical cation of DNp*n*. The values of the apparent activation energy E_a obtained from the slopes were 15, 15, and 13 kJ mol^{-1} for DNp5, DNp7, and DNp12, respectively. The experimental error for E_a originating from the evaluation of k_D was less than 2 kJ mol^{-1}. The values of the activation energy E_D for the formation of the dimer radical cation were 8, 8, and 6 kJ mol^{-1} for DNp5, DNp7, and DNp12, respectively, because the activation energy E_η of acetonitrile is reported to be 7 kJ mol^{-1}.[26] These values of E_D are smaller than those of E_R for all the DNp*n* molecules. This difference in energy demonstrates that a transition state of the intramolecular dimer formation is more stable than the state shown in Scheme 1b. In other words, the positive charge is delocalized over the two aromatic moieties at an early stage of the formation process where the two aromatic moieties are not as close as the geometry of the dimer radical cation. Considering the experimental errors, we conclude that these observed values of E_D are independent of the chain length n and are rather comparable to or less than that of the activation energy required for the conformational transition of methylene chains. Thus, we conclude that the formation of the dimer radical cation is controlled by local motions of a few methylene units linking two aromatic moieties as well as by the hydrodynamic force of solvents. The dependence of k_D on the chain length results from a frequency factor for encounter of the two Np moieties, not from the activation energy E_D, because motions required to form the dimer radical cation are probably so local that only a few units from the Np moieties participate in the dimer formation.

Conclusion

The thermodynamics and the kinetics for the formation of the intramolecular dimer radical cation in the series of DNp*n* in acetonitrile solutions were quantitatively investigated by transient absorption measurement in the wavelength region of the UV–visible to the near-IR, where characteristic absorption bands for the monomer radical cation and the dimer radical cation are observed. The standard enthalpy $-\Delta H^\circ$ evaluated from the van't Hoff plots has a good relation with the charge resonance energy E_{CR}, which increased with a decrease in the strain of the methylene chain for the formation of the intramolecular dimer radical cation. The value of the repulsion energy E_R was evaluated to be ca. 20 kJ mol^{-1} for all DNp*n*, which is smaller than that of the Np excimer by ca. 10 kJ mol^{-1}. This difference indicates that the separation distance and/or the overlap between the two Np moieties in the dimer radical cation are not as restricted as those in the Np excimer. The rate constants for the formation of the dimer radical cation k_D was evaluated from the time evolution of the absorption bands for the monomer and the dimer radical cation. Compared with the ring-closure probability of methylene chains, the dependence of k_D on the chain length was enhanced by the stabilization energy of the charge delocalization in the dimer radical cation. The activation energy E_D for the formation of the dimer radical cation of DNp*n* was comparable to the energy for local motions of a few methylene units linking the two Np moieties. These findings provide quantitative understanding of the behavior of intramolecular dimer formation, such as dependence of dimer formation yield on temperature and on the length of a chain linking two chromophores.

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