Direct Measurement of Intramolecular Electron Transfer in a Series of Artificial Photosynthesis Processes

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Abstract. We have directly determined the intramolecular electron transfer rate and revealed its mechanism in supramolecular complexes during CO_2 photoreduction by time-resolved infrared spectroscopic measurements over a wide temporal range.

1 Introduction

Artificial photosynthesis is a chemical process for creating high-energy molecules from CO_2 as a carbon source and H_2O as an electron source using sunlight. However, no examples of practical artificial photosynthesis have been realized yet, though many attempts have been made as part of the effort to address the global energy problem. One difficulty is that a photosynthesis system is composed of multi-step chemical processes involving many chemical species. The best method to understand these processes is the direct measurement of intermediate species using ultrafast spectroscopy. However, few studies have been made compared to biological photosynthesis. We have studied artificial photosynthesis using time-resolved infrared vibrational (TR-IR) spectroscopy in a wide temporal range from femtoseconds to microseconds, which makes it possible to identify chemical species step by step even in mixed solutions [1-7].

Electron transfer from a photosensitizer to a reaction center is one of the most important processes in artificial photosynthesis. However, it has never been directly observed and its mechanism is unknown because the process occurs during the course of multi-step chemical reactions. In the CO_2 reduction photocatalytic reaction, electron transfer occurs after electron injection from a reductant triggered by photoexcitation of the photosensitizer. Further processes are involved before CO_2 is reduced to CO, and the temporal range of the overall processes is from femtoseconds to microseconds [1,8]. We studied this series of chemical reactions using TR-IR spectroscopy and evaluated the electron transfer rates in various supramolecular complexes having different bridging ligands. From these rate constants, we determined the mechanism for intramolecular electron transfer in the supramolecular complexes.

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2 Experimental

TR-IR spectra over a wide temporal range were measured by a pump-probe method using a femtosecond Ti:sapphire amplifier and a sub-nanosecond Nd:YVO$_4$ laser. A mid-infrared probe pulse (pulse duration = 120 fs, tuneable range = 1000–4000 cm^{-1}) was generated by optical parametric amplification (OPA) and difference-frequency generation from part of the output of the amplifier. The probe pulse passed through an infrared flow cell and was detected by a mid-infrared detector array equipped with a polychromator. The 532-nm pump pulse was generated by OPA and sum-frequency generation from the other part of the output of the amplifier. The temporal delay between the pump and probe pulses was from 100 fs to 1.2 ns and was created by an optical delay line. For measurements more than 1 ns, another 532-nm pump pulse was generated by second harmonic generation of the output of the sub-nanosecond laser (wavelength = 1064 nm, pulse duration = 600 ps), which was electronically synchronized with the amplifier with a timing jitter of <200 ps.

3 Results and Discussion

The supramolecular complexes under study were Ru-Re complexes, consisting of a Ru unit as a photosensitizer, a Re unit as a reaction center, and a bridging ligand. Figure 1 shows the reaction scheme for the early stage of CO$_2$ photoreduction for this type of supramolecular complex. Briefly, electron transfer occurs from the one-electron reduced Ru unit (Ru$^{\cdot-}$) to the Re unit, followed by electron injection from the strong reductant (BIH) to the photo-excited Ru unit (^{3}Ru*). Typical concentrations of Ru-Re and BIH were 0.2 mM and 0.3 M, respectively, in a mixed solvent DMF-TEOA (5:1 v/v).

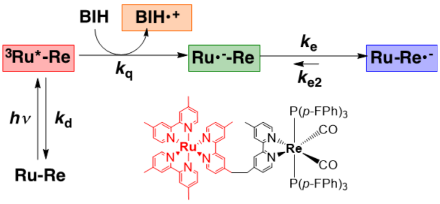

Fig. 1. Reaction scheme for the early stage of CO$_2$ photoreduction using Ru-Re supramolecular complex. k_d, k_q, k_e, and k_{e2} are the rate constants for each process.

Figure 2a shows examples of TR-IR spectra for this reaction in a complex with a C$_2$H$_4$ bridging ligand (C2). The transient absorption bands at 1836 and 1907 cm^{-1} are assigned to a complex with a reduced Re unit (Ru-Re$^{\cdot-}$) [9]. Since the intensities of these bands correspond to the amount of this species, we plot one of them as a function of delay time as black dots in Fig. 2b. To reproduce this temporal profile, we set up the rate equations according to the scheme in Fig. 1 [1]. The rate constants k_d and k_q were determined to be 1.34×10^6 s^{-1} and 1.2×10^9 M^{-1}s^{-1} based on the luminescence lifetimes of the Ru unit and the dependence of the quenching rate on the reductant concentration (Stern–Volmer plot), respectively. In addition, the ratio k_{e2}/k_e was determined to be 9 from the UV/Vis spectra for a photo-steady state. Thus, only one parameter remains undetermined, the electron transfer rate from the Ru unit to the Re unit, k_e. We carried out a least-squares fit by solving the rate equations using these rate constants and determined the electron transfer rate to be $k_e = 1.4 \times 10^9$ s^{-1}. The obtained concentrations of Ru-Re$^{\cdot-}$, the complex with a reduced Ru unit (Ru$^{\cdot-}$-Re), and the complex with a photoexcited Ru unit (^{3}Ru*-Re) are indicated by blue, green, and red lines in Fig. 2b, respectively. We repeated these measurements and calculations for another four supramolecular complexes having different bridging ligands, RC2, C4, COC, and C6, and plotted the logarithm of the rate constants as a function of the bond length between the Ru and Re units along the bridging ligand (r) in Fig. 2c. We found a linear correlation between these values except for the RC2 bridging ligand, which is exceptional because it is a double bridging ligand.

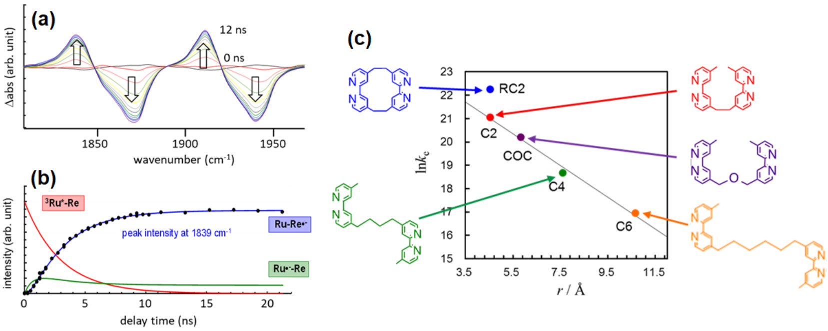

Fig. 2. (a) Selected TR-IR spectra measured while the reaction in Fig. 1 occurs. (b) Temporal profiles of peak intensity at 1839 cm^{-1} and concentrations simulated by solving the rate equations. (c) Logarithmic plot of k_e vs. bond length for five different bridging ligands. The insets show the structures of the bridge ligands.

According to semi-classical theory [10], the electron transfer rate, k_e, is expressed by the equation: $k_e \propto \exp(-\beta(r - r_0))$, where β is a coefficient factor, and r and r_0 are the distance and the close contact distance between the donor and the acceptor, respectively. It is known that the coefficient β strongly depends on the mechanism of the electron transfer, for example, $\beta \sim 3.4$ Å^{-1} for through-space [11], $\beta \sim 0.8$-1.0 Å^{-1} for through-alkyl-bond [10,12]. Our plot of k_e vs. r in Fig. 2c shows good exponential correlation, except for RC2. From this the coefficient factor was determined to be $\beta \sim 0.67$ Å^{-1}. Because this value is close to 0.8–1.0 Å^{-1}, we concluded that the electron transfer occurs by a through-alkyl-bond mechanism. Intriguingly, this result indicates that the flexibility of the bridging ligand does not affect the electron transfer, although it is possible that the two units directly collide with each other when they are connected by a long alkyl chain such as C6.

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