COMPARISON OF CHARGE SEPARATION IN DIRECT AND REVERSE MICELLES†

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Summary

The photoelectron transfer from zinc porphyrin or chlorophyll to various dialkyl viologens occurs from the triplet state of the sensitizer in oil-in-water cetyltrimethylammonium chloride (CTAC) micelles and in water-in-oil Aerosol OT micelles. The charge separation following the photoelectron transfer is due to the entrance of reduced viologens into the micellar core in oil-in-water CTAC micelles and to bimolecular exchange between water pools in reverse micelles.

1. Introduction

Micellar systems are suitable vehicles for the promotion of photochemical studies to convert light into chemical energy. Many model systems have been suggested which could lead to useful practical systems in the future. Some work in micelles, microemulsions and vesicles [1] suggests that these systems may play an important role as models for photostorage assemblies and photosynthesis.

In the photoredox reactions

$$P + A \longrightarrow P^+ + A^-$$

light acts as an electron pump, promoting charge transfer from the photosensitizer P to the acceptor A. If the chemical potential of A^- and P^+ is to be utilized in subsequent fuel-generating processes, the back reaction must be prevented or retarded [2 - 5].

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We have used oil-in-water cetyltrimethylammonium chloride (CTAC) micelles and water-in-oil Aerosol OT (AOT) reverse micelles as aggregates. AOT can solubilize relatively large amounts of water in hydrophobic solvents. The number of water molecules in a pool can vary considerably and is dependent on the molar ratio of water to AOT in the system [6].

In this paper the forward photoelectron transfer and the back photoelectron transfer from porphyrins to various dialkyl viologens are compared in direct (oil-in-water) and in reverse (water-in-oil) micelles.

2. Experimental section

2.1. Apparatus

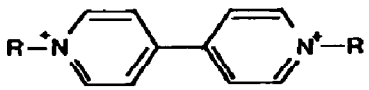
The laser photolysis experiments were performed with a rubis laser. The flash photolysis experiments were carried out with a conventional flash photolysis apparatus [7]. The nuclear magnetic resonance (NMR) experiments were carried out with Brucker WM500 and Varian XL100 spectrometers.

2.2. Materials

The CTAC surfactant, produced by Eastman Kodak, was purified by repeated recrystallization from acetone. The AOT surfactant was purchased from Sigma.

The sensitizers were zinc tetramethylpyridylporphyrin ($ZnTMPyP^{4+}$) or chlorophyll a (Chla). $ZnTMPyP^{4+}$ was synthesized in the laboratory and Chla was produced by Sigma.

The electron acceptors were dialkyl viologens



with $R \equiv C_xH_{2x+1}$. They were synthesized in the department by Dr. Ruaudel and Dr. Baudin.

3. Experimental results

3.1. Photoelectron transfer in oil-in-water micelles

$ZnTMPyP^{4+}$ is a water-soluble porphyrin characterized by an absorption spectrum with maxima at 433, 562 and 606 nm. Its triplet state is formed by flash photolysis and is characterized by an absorption spectrum with a maximum at 470 nm [8] and a lifetime equal to 3 ± 0.5 ms [9].

The $ZnTMPyP^{4+}$ triplet state is quenched by the addition of viologens. The disappearance of the triplet is accompanied by the appearance of new species attributed to the reduced viologen and to the porphyrin cation. The two species are characterized by absorption spectra with maxima at 395 and

and 605 nm for the reduced viologen and 700 nm for the porphyrin cation. The quenching of the porphyrin triplet may be attributed to the following electron transfer (where V represents the dialkyl viologen):

$$^{T}ZnTMPyP^{4+} + V^{2+} \longrightarrow ZnTMPyP^{5+\cdot} + V^{+\cdot}$$

The photoelectron transfer rate constant for several dialkyl viologens ($C_1 \leqslant C_x \leqslant C_{12}$), determined by monitoring the quenching of the triplet at various viologen concentrations, was unchanged in aqueous solution or in CTAC micelles and was found to be approximately the same for all the viologens used. The triplet quenching rate constant is equal to 2.5×10^6 M^{-1} s^{-1} [9]. Hence the forward photoelectron reaction takes place.

The back reaction, monitored at 395 nm, is

$$ZnTMPyP^{5+\cdot} + V^{+\cdot} \longrightarrow ZnTMPyP^{4+} + V^{2+}$$

3.1.1. Dialkyl viologens with less than eight carbon atoms per side-chain

The observed rate constants for the back reaction in micellar solution with dialkyl viologens with less than eight carbon atoms per side-chain were of the same order of magnitude as those observed in aqueous solution. The half-lives $\tau_{1/2}$ of the back reaction for all the reduced viologens used were about 2.5 ms (Fig. 1). These results indicate that, with these viologens, the micellar solution does not perturb the back reaction.

3.1.2. Dialkyl viologens with more than eight carbon atoms per side-chain

The presence or absence of CTAC micelles has a marked effect on the back reaction when dialkyl viologens with more than eight carbon atoms per side-chain are used. In aqueous solution the half-lives of the back reaction are

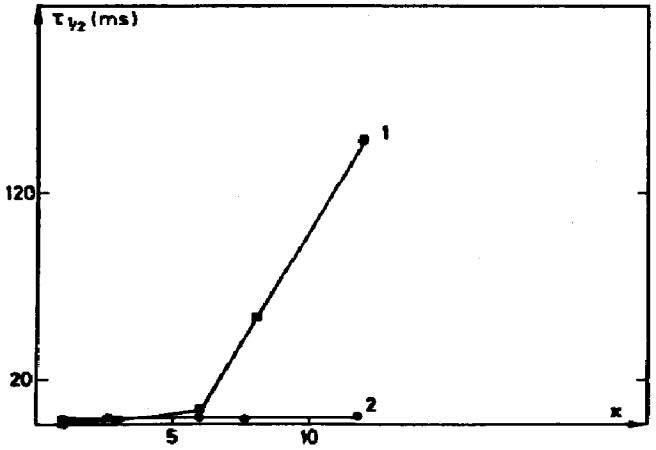


Fig. 1. Half-lives of the back reaction observed at 390 nm with various viologens (x represents the number of carbon atoms of the alkyl chain; [ZnTMPyP] = 5×10^{-6} M; [viologen] = 2×10^{-4} M; [CTAC] = 0.02 M): curve 1, dialkyl viologen in CTAC micelles; curve 2, dialkyl viologen in aqueous solution.

similar to those observed previously with short-chain viologens (approximately 2.5 ms) (Fig. 1). In micellar systems, the back reactions are considerably retarded. The decrease in rate depends on the chain length of the viologen. Figure 1 shows the change in the half-lives $\tau_{1/2}$ of the back reaction in the presence of 0.02 M CTAC together with the number of carbon atoms of the side-chains. τ jumps from 2.5 ms (in aqueous solution for all the viologens used or in CTAC micelles for short-chain dialkyl viologens) to 120 ms (in CTAC solution for long-chain dialkyl viologens) with increasing chain length. The half-lives of the back reaction were determined at various CTAC concentrations from 0 to 0.02 M. Figure 2 shows the reaction half-lives with dioctyl viologen as a function of CTAC concentration from zero to 2×10^{-1} M CTAC; the back reaction half-lives increase from 2 to 50 ms.

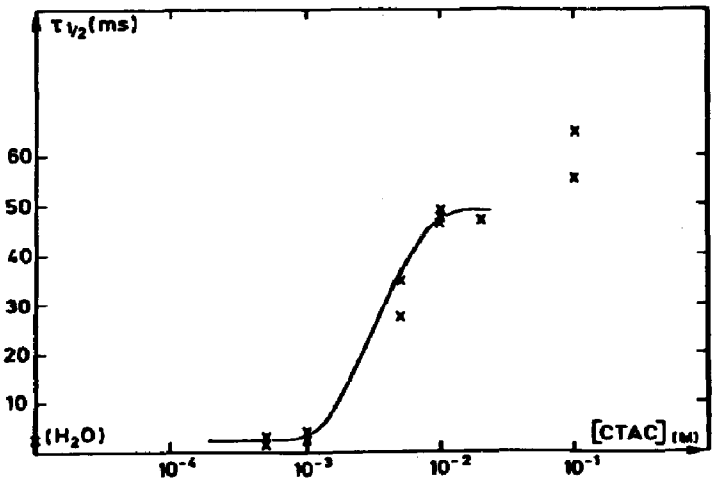


Fig. 2. Variation in the half-life of the back reaction with CTAC concentration ([ZnTMPyP] = 5×10^{-6} M; [dioctyl viologen] = 2×10^{-4} M).

Proton NMR experiments were performed with 0.02 M CTAC micelles in the absence and presence of dimethyl or dioctyl viologen. The viologens were in their oxidized form or chemically reduced. The CTAC NMR spectrum remained unchanged on addition of any alkyl viologens in their oxidized form. The entrance of viologen into the micelles should induce a shift of the surfactant proton lines as a result of the influence of the ring current of the bipyridyl unit [10]. This absence of a perturbation of the spectrum even with 5×10^{-3} M dimethyl and dioctyl viologen in their oxidized forms and with reduced dimethyl viologen confirms that they are located in the bulk aqueous phase. In the presence of 2×10^{-4} M of reduced dioctyl viologen the NMR lines are broader than those obtained with pure CTAC. Figure 3 shows the change in width of the CTAC NMR lines on increasing the reduced dioctyl viologen concentration. The transverse relaxation rates of the CTAC protons are thus enhanced by the paramagnetic viologen, which indicates the presence of the viologen in the CTAC micelles. Figure 4 shows

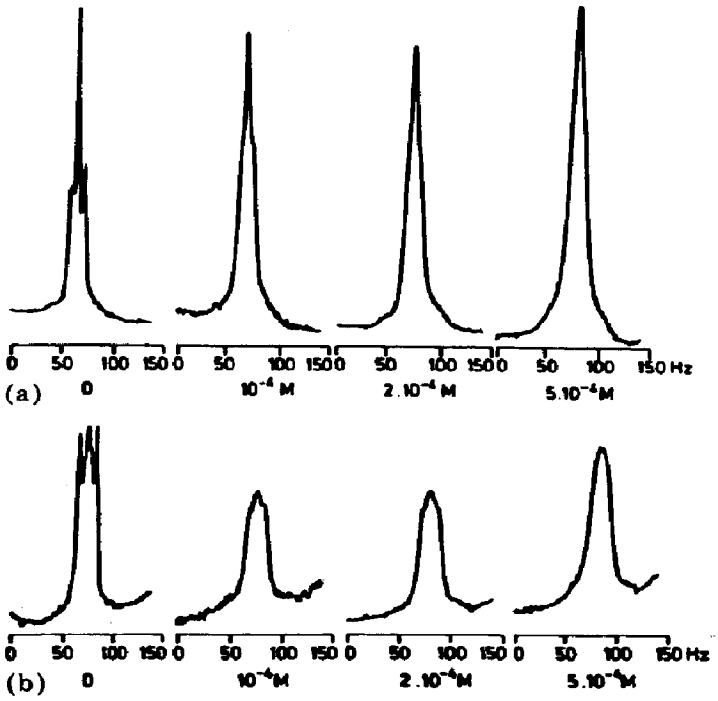


Fig. 3. Change in the proton NMR line of CTAC with various chemically reduced dioctyl viologen concentrations: (a) H_{16}; (b) H_1.

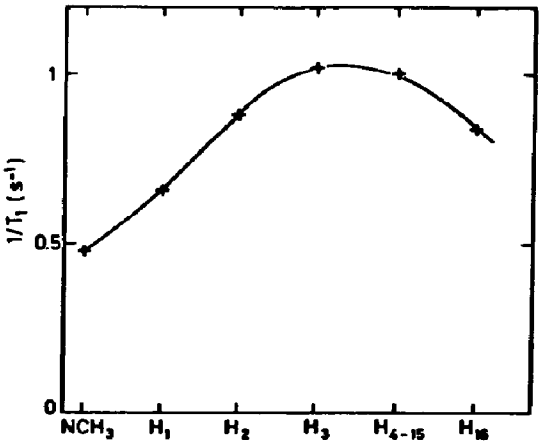


Fig. 4. Longitudinal relaxation rates induced by the reduced dioctyl viologen (without consideration of the contribution of the relaxation rate of the CTAC proton) for different protons of the CTAC molecules ([CTAC] = 0.02 M; $[(C_8)_2V^+] = 1 \times 10^{-4}$ M).

the longitudinal relaxation rates induced by the reduced dioctyl viologen for different protons of the CTAC molecule (where NCH_3 represents the methyl group of the polar head, H_1, H_2 and H_3 are attributed to the methylene located immediately after the polar head group and H_{16} is the terminal methyl group). The influence of the paramagnetic viologen is stronger for H_3, for H_{16} and for the unresolved line corresponding to the H_4 - H_{15} protons

than for the methyl group of the polar head. This suggests that the location of the reduced dioctyl viologen is in the hydrocarbon core.

3.2. Photoelectron transfer in water-in-oil micelles

Chla in AOT reverse micelles is characterized by an absorption spectrum centred at 668 and 430 nm. On laser photolysis, the triplet–triplet absorption spectrum is characterized by a band centred at 720 nm [10]. The triplet kinetics decay is first order and its lifetime is 250 μs.

The photoelectron transfer from Chla to dialkyl viologens was studied in AOT reverse micelles. On laser photolysis of the Chla–dialkyl viologen system in reverse micelles, the Chla triplet–triplet absorption spectrum was observed at the end of the laser pulse. A few microseconds after the laser pulse, the triplet–triplet absorption decayed and a new absorption was observed at 850 and 750 nm which is attributed to the Chla cation. Hence the photoelectron transfer reaction occurring from the triplet state is the following:

$$^{T}\text{Chla} + V^{2+} \longrightarrow \text{Chla}^{+\cdot} + V^{+\cdot}$$

In the presence of dialkyl viologen, the decay of the Chla triplet state follows a complex rate law (Fig. 5). To determine the triplet quenching rate constant k_q it is assumed that the reactants are distributed amongst the water pools according to a Poisson distribution law [3, 4, 11]. The kinetics treatment produces the following time dependence for the triplet of Chla [3, 4, 11]:

$$\ln\left(\frac{[^{T}\text{Chla}]}{[^{T}\text{Chla}]_0}\right) = -(k_0 + k_e[V])t - \bar{n}\{1 - \exp(-k_q)\,t\} \qquad (1)$$

where $[^{T}\text{Chla}]$ and $[^{T}\text{Chla}]_0$ are the Chla triplet concentrations at time t and time zero respectively, k_0 is the first-order rate constant governing the triplet

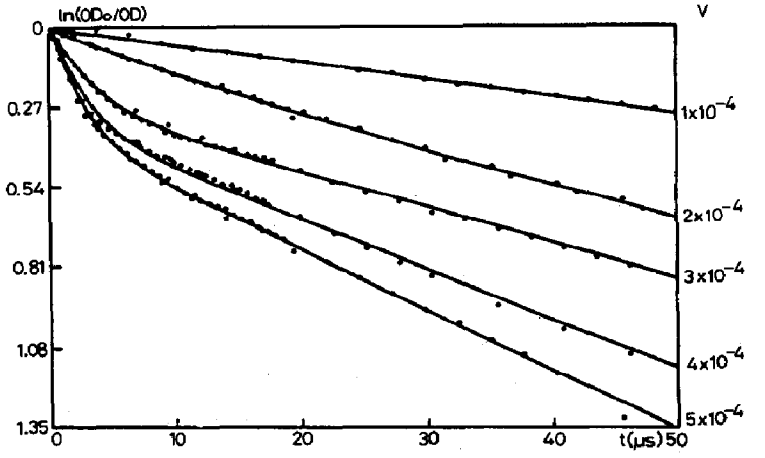


Fig. 5. Kinetics treatment for a Poisson distribution: ●, experimental data; ——, simulated curve.

Chla decay in the absence of viologen, k_q is the intramicellar quenching rate constant, k_e is the bimolecular rate exchange constant involving collisions between the water pools, and $\bar{n}$ = [V]/[WP] where [V] and [WP] are respectively the viologen and the water pool concentrations. Equation (1) is identical with

$$\ln\left(\frac{OD}{OD_0}\right) = -C_1 t - C_2\{1 - \exp(-C_3)\, t\} \qquad (2)$$

where OD and OD_0 are the optical densities of the Chla triplet state at time t and time zero respectively. Figure 5 shows the experimental and simulated curves. The photoelectron rate constant k_q from the Chla triplet state is equal to $5 \times 10^5\ s^{-1}$ for all the dialkyl viologens used.

The decays of the Chla cation and the reduced viologen are unchanged with the various dioctyl viologens, and a complex kinetics decay of the Chla cation monitored at 850 nm is observed (Fig. 6). The short-time part of the

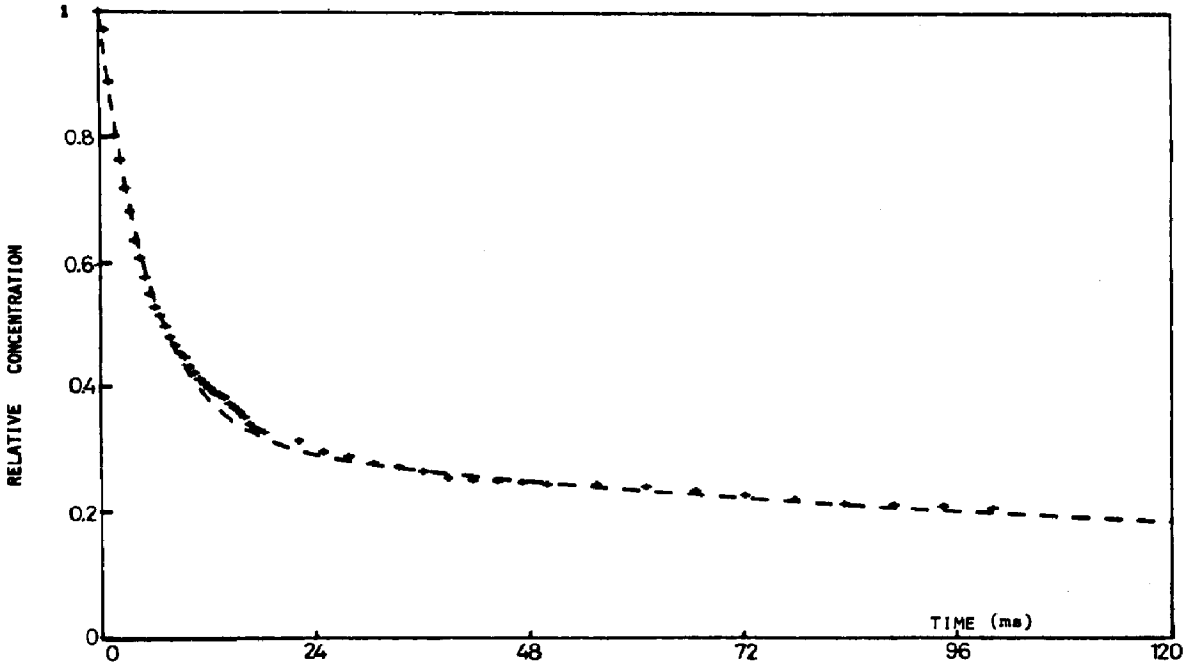
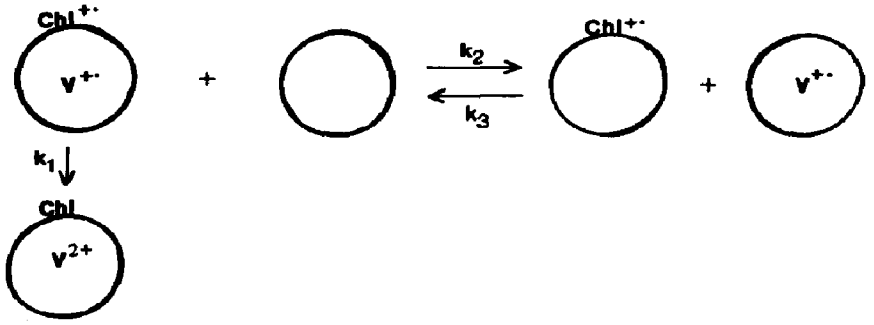


Fig. 6. Variation in the relative $Chla^{+\cdot}$ concentration with time.

decay curves is attributed to the intramicellar back reaction, whereas the long-time kinetics decay is attributed to the exchange of photolytic products (the Chla cation and the reduced viologen) from one droplet to another, which produces a delay in the back electron transfer. These processes can be represented by the following:



where the circles represent the micelles.

From a kinetics treatment the rate constant k_1 of the intramicellar back reaction does not depend on the water content w and is found to be equal to 108 s^{-1}. The exchange rate constant k_2 of the photolytic products is equal to 1.6×10^5 M^{-1} s^{-1} whereas the back reaction rate constant k_3 is 3×10^7 M^{-1} s^{-1}.

4. Discussion

4.1. Photoelectron transfer in oil-in-water micelles

The similar values for the forward photoelectron transfer rate constant determined with the various viologens in aqueous and in CTAC micellar solutions and the unchanged CTAC NMR spectrum in the presence of viologens in their oxidized form indicate that the forward photoelectron transfer occurring from the $ZnTMPyP^{4+}$ triplet state takes place in the bulk aqueous phase.

The data obtained, in CTAC micelles, on the back reaction processes with the various viologens can be split into two parts.

(a) For dialkyl viologens with less than eight carbon atoms per side-chain, the half-lives of the back reaction observed with the various viologens are of the same order of magnitude as those obtained in aqueous solution. With these viologens it has been shown that the CTAC NMR spectrum is not changed by the presence of reduced viologens. These results strongly support the suggestion that the back reaction of the reduced viologen and the porphyrin cation occurs in the bulk aqueous phase.

(b) For dialkyl viologens with eight or more carbon atoms per side-chain, the half-lives of the back reaction are strongly increased in comparison with those obtained in aqueous solution. This change in the half-lives of the back reaction with CTAC concentration (Fig. 3) strongly suggests a micellar effect: the increase in the half-life of the back electron transfer corresponds to the CTAC critical micellar concentration [3, 4, 11]. NMR experiments have shown that the CTAC spectrum is strongly perturbed by the presence

of reduced dioctyl viologen but not by its oxidized form. Such perturbations indicate the entrance of reduced viologen into the micelles. These results can be related to the increase in hydrophobic character accompanying viologen reduction [12] and are in agreement with those already published for oil-in-water micelles [5] using monohexadecyl viologen. However, our results show a stronger retardation than do those previously obtained.

4.2. Photoelectron transfer in water-in-oil reverse micelles

The photoelectron transfer in reverse micelles from Chla to various viologens occurs from the triplet state of the sensitizer. A Poisson distribution was used to draw up a kinetics model from which the rate constants were deduced: the rate constant of the forward photoelectron transfer determined at various water contents was found to be equal to $5 \times 10^5\ s^{-1}$.

The forward photoelectron transfer and the back photoelectron transfer are intramicellar processes. The marked difference between the rate constants of the forward reaction ($5 \times 10^5\ s^{-1}$) and the back reaction ($108\ s^{-1}$) can only be explained by a different mechanism between the two processes.

(1) The intramicellar forward photoelectron transfer could occur by a long-distance mechanism increasing the probability of formation of two radical cations.

(2) The intramicellar back reaction implies a close proximity of the two radicals which is unlikely because the reactants are located on either side of the interface. The exchange rate constant of the Chla cation and the reduced viologen from one droplet to another ($k_2 = 1.6 \times 10^5\ s^{-1}$) is small in comparison with the exchange rate constant of the dialkyl viologen determined from the kinetics treatment of the Chla triplet state decay ($k_e = 3 \times 10^7\ M^{-1}\ s^{-1}$). To explain such a difference we assume that each collision is not efficient. However, the unchanged kinetics decay of the back reaction with the various dialkyl viologens indicates that the interactions between the head polar groups of oil-in-water micelles are stronger than the hydrophobic character of the reduced dioctyl viologen. Hence the delay in the back reaction is attributed to a change in the mechanism between the forward and the back reaction and not to the hydrophobic character of the reduced dioctyl viologen as was deduced by Willner [13].

5. Conclusion

In this paper we have described the favourable intervention of amphiphilic electron relays in the photoelectron transfer reaction from $ZnTMPyP^{4+}$ to dialkyl viologens in oil-in-water micelles. In the presence or absence of CTAC micelles, the forward photoelectron transfer occurs in the bulk aqueous phase. The back photoelectron transfer can be considerably retarded by the entrance of reduced dialkyl viologen into the micellar core.

In reverse (water-in-oil) micelles the forward electron transfer and the back electron transfer are unchanged with the various dialkyl viologens used

but a delay in the back reaction is observed probably due to the change in the chemical mechanism between the forward and the back reaction, implying bimolecular collisions in the back reaction.

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