CHEMISTRY LETTERS, pp. 1439-1440, 1982. © The Chemical Society of Japan 1982

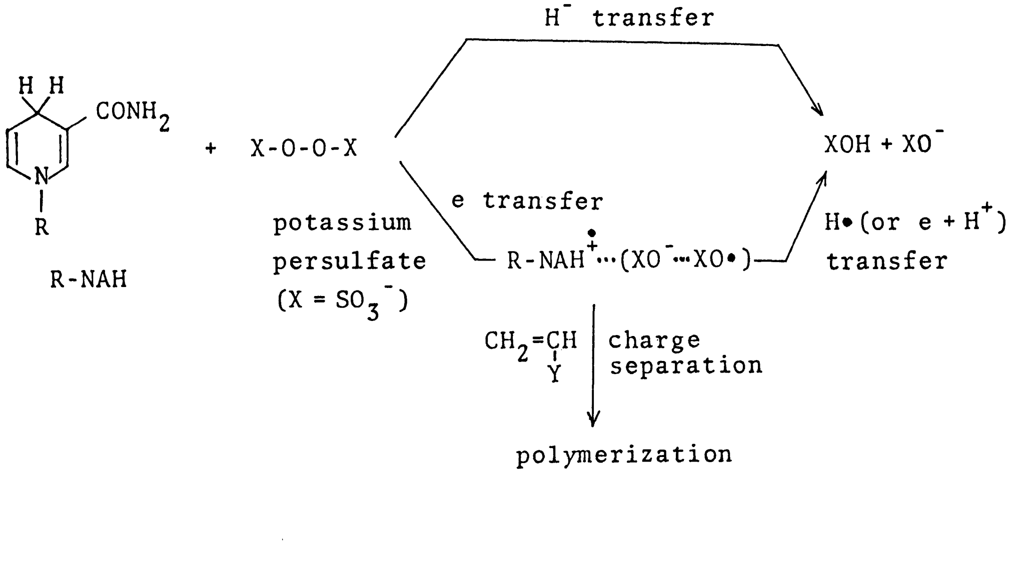
CHARGE SEPARATION ON MICELLE SURFACE WHICH INITIATES RADICAL POLYMERIZATION. EVIDENCE FOR THE MULTI-STEP HYDROGEN TRANSFER FROM NADH MODELS TO PEROXIDES

Seiji SHINKAI,* Takaharu TSUNO, Yukiko ASATANI, and Osamu MANABE
Department of Industrial Chemistry, Faculty of
Engineering, Nagasaki University, Nagasaki 852

Radical polymerization of acrylamide was initiated in the presence of sodium dodecylsulfate, 1-hexadecyl-1,4-dihydronicotinamide, and potassium persulfate. The result supports that the hydrogen transfer from a NADH model compound to peroxides proceeds through the multi-step mechanism.

Since Abeles et al.1) proposed in 1957 that the hydrogen transfer from NADH model compounds to substrates occurs through one-step hydride transfer, the mechanism has been supported by many NADH model studies.2,3) In opposition to their proposal, however, increasing number of reports which argue for multi-step e + H·(or e + H$^+$ + e) transfer have been published.4-6) It seems to us, therefore, that one has to exploit more direct methods to distinguish between these two mechanisms.

In 1971, Wang et al.7) considered that no radical species would be produced if the reduction proceeds through the one-step hydride transfer mechanism, whereas the radical polymerization would be initiated if the reduction really proceeds through the multi-step mechanism. In other words, the redical polymerization may be a candidate to distinguish the reaction mechanisms. However, their attempt was unsuccessful probably because the radical intermediate(s) afforded from NADH model compounds would also act as radical scavengers. Recently, it has been established in the model studies of photosynthesis that the aqueous micelle surface is capable of separating a radical ion pair.8,9) It occurred to us that if one can separate the scavenger species from the growing polymer chain with the aid of micelles, the radical polymerization would take place. Thus, we found for the first time that the polymerization of acrylamide does take place in the presence of sodium dodecylsulfate(SDS), 1-hexadecyl-1,4-dihydronicotinamide(Hxd-NAH) as a NADH model, and potassium persulfate as an electron-acceptor.



Typical reaction conditions are as follows: [SDS] = 3.0×10^{-2} M, [R-NAH] = 1.0×10^{-3} M, [potassium persulfate] = 1.0×10^{-3} M, [monomer] = 0.10 M, 40°C, 24 h, pH 9.05 with 0.02 M borate, and anaerobic (N_2). The yield of poly(acrylamide) afforded in the presence of SDS, Hxd-NAH, and potassium persulfate was 81%.[10] On the other hand, the polymerization of acrylamide did not take place under the following reaction conditions[10]: (i) potassium persulfate, (ii) potassium persulfate + SDS, (iii) potassium persulfate + 1-propyl-1,4-dihydronicotinamide(Pr-NAH), and (iv) potassium persulfate + Pr-NAH + SDS. Thus, the polymerization cannot be explained by the thermal decomposition of potassium persulfate in the absence or the presence of the SDS micelle. These findings suggest that the radical polymerization is due to the charge separation of Hxd-NAH$^{\overset{\bullet}{+}}$•$SO_4^{\overset{\bullet}{-}}$ at the anionic micelle surface followed by the radical initiation by $SO_4^{\overset{\bullet}{-}}$ in the bulk phase. In the absence of the micelle, the initial electron transfer from Pr-NAH to potassium persulfate is immediately followed by the H•(or H^+ + e) transfer as an intra-complex step, so that $SO_4^{\overset{\bullet}{-}}$ cannot attack the vinyl monomer. This is the first crucial role of the micelle.

Acrylonitrile was not polymerized in the presence of potassium persulfate, Hxd-NAH, and SDS. This polymer is essentially insoluble in water. One may thus consider that even though $SO_4^{\overset{\bullet}{-}}$ initiates the radical polymerization, the growing chain bound to the micelle phase receives H•(or H^+ + e) from Hxd-NAH$^+$ therein. Meanwhile, poly(acrylamide) is soluble only in water. Thus, the growing chain would be kept separated from Hxd-NAH$^+$ in the micelle phase. This is the second role of the micelle.

In conclusion, the radical polymerization initiated by an NADH model plus potassium persulfate supports that the hydrogen transfer proceeds through the multi-step mechanism involving the initial electron transfer followed by the H•(or H^+ + e) transfer. Further investigation is now continued in this laboratory.

REFERENCES

1) R. H. Abeles, R. F. Hutton, and F. H. Westheimer, J. Am. Chem. Soc., 79, 712 (1957).
2) D. J. Creighton and D. S. Sigman, J. Am. Chem. Soc., 93, 6314 (1971) and references cited therein.
3) L. C. Kurz and C. Frienden, J. Am. Chem. Soc., 97, 677 (1975).
4) A. Ohno, H. Yamamoto, and S. Oka, J. Am. Chem. Soc., 103, 2041 (1981) and references cited therein.
5) S. Yasui, K. Nakamura, A. Ohno, and S. Oka, Bull. Chem. Soc. Jpn., 55, 196 (1982).
6) D. M. Chipman, R. Yaniv, and P. van Eikeren, J. Am. Chem. Soc., 102, 3244 (1980).
7) C. Wang, S. M. Linnell, and N. Wang, J. Org. Chem., 36, 525 (1971).
8) K. Kano, K. Takuma, K. Ikeda, D. Nakajima, Y. Tsutsui, and T. Matsuo, Photochem. Photobiol., 27, 695 (1978).
9) P.-A. Brugger, P. P. Infelta, A. M. Braun, and M. Grätzel, J. Am. Chem. Soc., 103, 320 (1981).
10) The polymer was recovered by pouring the aqueous reaction mixture into methanol. The product was identified by comparing with the authentic poly(acrylamide).

(Received July 1, 1982)