

Electron-Transfer Reactions between the Semiquinone Anion Radical and Metallo-tetraphenylporphyrins

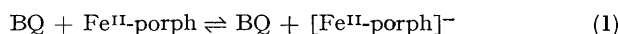
By AKIHIKO YAMAGISHI,* FUMIYUKI WATANABE, and TAKESHI MASUI

(Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo, 060, Japan)

Summary The rates of electron-transfer from 2,5-di-*t*-butylbenzoquinone anion radical to Co^{II}, Fe^{II}, and Mg^{II}-tetraphenylporphyrins in tetrahydrofuran have been determined with a stopped-flow apparatus, and the second-order rate constants obtained were: $k(\text{Co}^{\text{II}}) = (5 \pm 2) \times 10^5$, $k(\text{Fe}^{\text{II}}) = (9 \pm 4) \times 10^6$, and $k(\text{Mg}^{\text{II}}) > 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ at 25 °C; a mechanism for the reaction of the Fe^{II}-porphyrin involving initial electron transfer to the metal atom, followed by relocation on the porphyrin ring is suggested.

We report here a study of electron-transfer reactions between 2,5-di-*t*-butylbenzoquinone (BQ) anion radical and Co^{II}, Fe^{II}, and Mg^{II}-tetraphenylporphyrins (M^{II}-porph) in tetrahydrofuran. These reactions were chosen in order to investigate which particular property of a metalloporphyrin plays a decisive role in determining the rate of the electron-accepting process; more specifically, we hoped to settle the question of whether electron-transfer occurs by way of the central metal ion or the periphery of the porphyrin ring, and also if the route is dependent on the type of central metal ion.

When a solution of BQ ($3 \times 10^{-4} \text{ M}$) was added to a mixture of Fe^{II}-porph ($1 \times 10^{-5} \text{ M}$) and its one-electron reduced form, [Fe^{II}-porph]⁻ ($1 \times 10^{-5} \text{ M}$), which was prepared by reduction with sodium mirror, the electronic absorption peak at 328 nm due to BQ⁻, the anion radical of BQ, appeared with a simultaneous decrease in the absorption at 515 nm due to [Fe^{II}-porph]⁻. As the temperature of the solution was lowered, the absorption due to [Fe^{II}-porph]⁻ increased reversibly. These results confirmed the occurrence of the reversible one-electron transfer reaction (1) between BQ and Fe^{II}-porph⁻. The equilibrium constant of this reaction was estimated from the magnitude



of the absorption decrease at 515 nm on addition of various amounts of BQ ($1\text{--}4 \times 10^{-4} \text{ M}$): $K_{\text{Fe}} = (2 \pm 1) \times 10^2$ at 5 °C. The presence of similar equilibria was confirmed in the case of Co^{II}- and Mg^{II}-porph, the equilibrium constants being $K_{\text{Co}} = (5 \pm 2) \times 10^2$ and $K_{\text{Mg}} = (3 \pm 2) \times 10^{-2}$ at 25 °C; the absorption peaks at 660 and 570 nm were used for determining the concentrations of [Co^{II}-porph]⁻ and [Mg^{II}-porph]⁻, respectively. The observed order $K_{\text{Co}} > K_{\text{Fe}} > K_{\text{Mg}}$ agrees with reported data on the reduction potentials of these metallo-porphyrins.¹

The rates of these electron-transfer reactions were measured with a stopped-flow apparatus under helium.² A solution of Na⁺BQ⁻ ($5 \times 10^{-6} \text{ M}$) was mixed with a solution of Fe^{II}-porph ($5 \times 10^{-5} \text{ M}$) after the apparatus had

been rinsed thoroughly with the same solutions. A transient increase in [Fe^{II}-porph]⁻ concentration was observed after ca. 10 ms with a simultaneous decrease in Na⁺BQ⁻ concentration. Under these conditions, the starting Na⁺BQ⁻ was oxidized almost completely to neutral BQ. The pseudo-first-order rate constant, which represents roughly the forward rate of the reaction, increased approximately linearly with the increase in the initial concentration of Fe^{II}-porph ($3\text{--}8 \times 10^{-5} \text{ M}$). From these results, the second-order rate constant of the forward reaction was determined to be $k_{\text{Fe}} = (9 \pm 4) \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$. k_{Fe} decreased from 9×10^6 to $5 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ on addition of Na⁺BPh₄⁻ ($0\text{--}3.3 \times 10^{-2} \text{ M}$). This may be attributed to the formation of the ion-pair Na⁺BQ⁻, which is less reactive than free BQ⁻. The rate for Co^{II}-porph was obtained similarly; $k_{\text{Co}} = (5 \pm 2) \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ in the absence of Na⁺BPh₄⁻. For Mg^{II}-porph, a solution of Mg^{II}-porph ($1 \times 10^{-5} \text{ M}$) and Na⁺[Mg^{II}-porph]⁻ ($2 \times 10^{-5} \text{ M}$) was mixed with a solution of BQ ($2 \times 10^{-5} \text{ M}$). Although all the [Mg^{II}-porph]⁻ was oxidized to neutral species under these conditions, a transient change in absorption was not observed. Thus, the lower limit of the backward rate constant of this reaction was estimated to be $5 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$, leading to $k_{\text{Mg}} > 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$.

For Fe^{II}- and Co^{II}-porph, the k_{M} values are obviously below an encounter-controlled value, implying the existence of an activating process in the reaction. Since it has been established that neither solvation nor ion-pairing of the semiquinone ion radical would provide such a high energy barrier as observed here,^{3,4} the low values for k_{Co} and k_{Fe} must arise from a particular property of the metalloporphyrins. Since one-electron-reduction of Co^{II}-porph is known to take place at the central Co^{II} ion (Co^{II} → Co^I),¹ a large structural change in co-ordination structure around the cobalt ion may take place during the course of electron transfer.⁵ This may cause an energy barrier, leading to the observed low value of k_{Co} , as widely acknowledged in redox reactions involving metal complexes in aqueous solution.⁶ If this is the case, it is notable that k_{Fe} is also well below an encounter-controlled value, although reduction of Fe^{II}-porph occurs in the porphyrin ring.¹ A possible interpretation is that in the case of Fe^{II}-porphyrin also, electron-transfer proceeds by way of the central Fe^{II} ion, accompanied by a large change in the structure of the Fe^{II} co-ordination sphere. In other words, the central metal provides a point of entry for the incoming electron, irrespective of the final location of the electron. However, the high value of k_{Mg} is considered to reflect a small change in co-ordination structure during the reduction.

(Received, 15th December 1977; Com. 1272.)

¹ J. H. Fuhrhop, K. M. Kadish, and D. G. Davis, *J. Amer. Chem. Soc.*, 1973, **95**, 5140.

² A. Yamagishi, *Bull. Chem. Soc. Japan*, 1976, **49**, 1417.

³ A. Yamagishi, *J. Phys. Chem.*, 1976, **80**, 1271.

⁴ A. Yamagishi, *Bull. Chem. Soc. Japan*, 1976, **49**, 1754.

⁵ R. A. Truxillo and D. G. Davis, *Analyt. Chem.*, 1975, **47**, 2260.

⁶ F. Basolo and R. G. Pearson, 'Mechanism of Inorganic Reactions,' Wiley, New York, 1967.