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REDOX BEHAVIOR OF METHYLVIOLOGEN CATION RADICAL INCORPORATED INTO A HYDROPHOBIC ORGANIC PHASE BY LIPOPHILIC STABLE ANIONS

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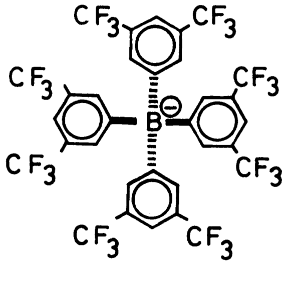
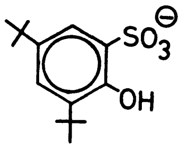
Tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (TFPB$^-$) could incorporate methylviologen radical cation (MV$^{+\cdot}$) and dication (MV^{2+}) into hydrophobic organic solvent, while 2-hydroxy-3,5-di-tert-butylbenzenesulfonate (HBBS$^-$) could hold only the radical cation in the organic solvent. MV$^{+\cdot}$ incorporated with TFPB$^-$ could easily transfer the electron to an acceptor at the interface between the organic and aqueous phases, and played the role of an efficient catalytic electron mediator across an organic liquid membrane.

The redox reactions of methylviologen (MV^{2+}) and its higher alkyl derivatives have been extensively investigated, since the viologens have been proved to be effective electron mediators in photoinduced redox reactions[1] and powerful reductants useful in organic syntheses.[2] Recently much attention has been paid to the behaviors of viologen radical cations incorporated into a hydrophobic organic solvents in respects to the role as an electron carrier across an organic liquid membrane[3] and reducing agents working in nonpolar organic media. Although the viologen radical cation is soluble in hydrophobic organic solvents to some extents, its dication form is hardly soluble in such solvents, even if the N-alkyl substituent is replaced with longer ones,[4] mostly partitioned into an aqueous phase.

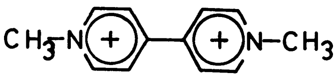
We attempted to incorporate such hydrophilic viologens into hydrophobic organic solvents in the form of ion pair with highly lipophilic organic anions. Such ion pairs, if successfully retained in the organic liquid phase, would work as an electron carrier which could transfer electron from a donor in an aqueous phase to an acceptor in a separate aqueous phase across an organic liquid mem-



TFPB$^-$



HBBS$^-$



MV^{2+}

brane separating the two aqueous phases.

In our previous works on the anion-catalyzed phase transfer catalysis, $TFPB^-$ was found to be a highly lipophilic anion, to catalyze diazo-coupling,[5)] Friedel-Crafts alkylation,[6)] and nitrosation[7)] in a dichloromethane-water two-phase system, and to be sufficiently stable under strong acidic and oxidative conditions.[8)] Na^+TFPB^- is practically insoluble in water, but soluble in such organic solvents as dichloromethane (solubility is ca. 5×10^{-3} mol dm^{-3}) and toluene. $HBBS^-$, whose sulfonate group is stabilized by the o-hydroxyl group, is also highly lipophilic.[9)]

In this communication, we describe the redox behaviors of $MV^{+\cdot}$ incorporated with $TFPB^-$ and $HBBS^-$ into hydrophobic organic solvents.

Extractions of $MV^{+\cdot}$[10)] and MV^{2+} from an aqueous solution (0.01 dm^3) of $MV^{2+}Cl^-_2$ or $MV^{+\cdot}Cl^-$ (both 1×10^{-4} mol dm^{-3}) containing sodium chloride (0.1 mol dm^{-3}) into dichloromethane (0.01 dm^3) containing Na^+TFPB^- were carried out by shaking the two-phase mixtures under a nitrogen atmosphere. The fractions extracted into the organic phase are plotted against $TFPB^-$ concentration in Fig. 1. The extracted fraction of $MV^{+\cdot}$ increased linearly with the slope of 2/3 up to 6.5×10^{-5} mol dm^{-3} of $TFPB^-$, suggesting that $MV^{+\cdot}$ was extracted in the form of $(MV^{+\cdot})_3(TFPB^-)_2Cl^-$ in this region. MV^{2+} incorporated into the organic phase with $TFPB^-$ could be easily exchanged with $MV^{+\cdot}$ in the aqueous phase. $HBBS^-$ also effective to extract $MV^{+\cdot}$ to a similar extent to $TFPB^-$, as shown in Fig. 1 (Curve c), while almost ineffective for MV^{2+} (Fig. 1 (Curve d)). Ordinary tetraphenylborate anion was extremely labile to decompose in the presence of MV^{2+}.[11)]

$MV^{+\cdot}$ has been known to be immediately oxidized by oxygen under an aerobic condition. $MV^{+\cdot}$ incorporated with $TFPB^-$ into dichloromethane was, however, fairly stable under the same condition, the half-life time ($t_{1/2}$) of $MV^{+\cdot}$ was about 3.5 h, as shown in Fig. 2 (Curve a). Addition of a small amount of methanol into the solution caused the immediate oxidation of $MV^{+\cdot}$ to MV^{2+} (Fig. 2 (Curve b)), whereas $MV^{+\cdot}$ in methanol was stable under an anaerobic condition. Organic oxidants such as benzoquinone (BQ) and 9,10-anthraquinone (AQ), also oxidized $MV^{+\cdot}$ at slower rates, as shown in Fig. 2 (Curves c and d). The important question why the $MV^{+\cdot}$ resisted to the oxidation by the above oxidants is still remained to be solved.

$MV^{+\cdot}$ incorporated with $HBBS^-$ was very reactive with such oxidants as described above (Fig. 2 (Curves e, f, and g)). The inertness of $MV^{+\cdot}$ incorporated with $TFPB^-$, therefore, seemed not to be the intrinsic nature of $MV^{+\cdot}$ in hydrophobic media, but due to an effect caused by the counter anion, $TFPB^-$.

$MV^{+\cdot}$ incorporated with $TFPB^-$ in dichloromethane was rapidly oxidized to the MV^{2+} when vigorously stirred with aqueous oxidants such as ferricyanide and 9,10-anthraquinone-2,6-disulfonate ($AQDS^{2-}$), as shown in Fig. 3 (A). The rates in the two-phase system were much faster than in the dichloromethane solution system mentioned above. $MV^{+\cdot}$ incorporated with $HBBS^-$ also reacted with the aqueous oxidants at approximately same rate to that of $TFPB^-$ (Fig. 3 (B)). One may say that $MV^{+\cdot}$ incorporated with $TFPB^-$ was reactive enough at the interface between the organic and aqueous phases.

In summary, $MV^{+\cdot}$ could be incorporated into dichloromethane by $TFPB^-$ and

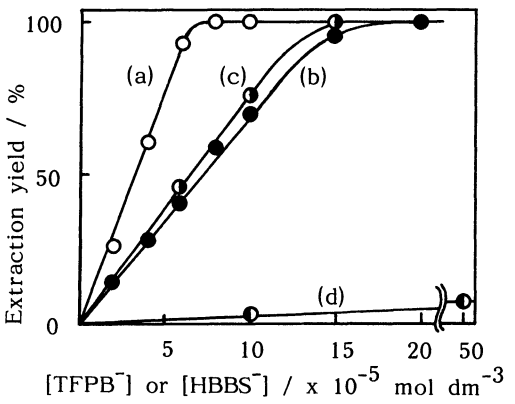


Fig. 1. Ion-pair extraction of $MV^{+\cdot}$ and MV^{2+} from an aqueous phase into a dichloromethane phase.

Extracted fractions of the cations were determined with UV and VIS spectra at 257 for MV^{2+} and 610 nm for $MV^{+\cdot}$. (a); $MV^{+\cdot}$-$TFPB^-$, (b); MV^{2+}-$TFPB^-$, (c); $MV^{+\cdot}$-$HBBS^-$, and (d); MV^{2+}-$HBBS^-$ systems.

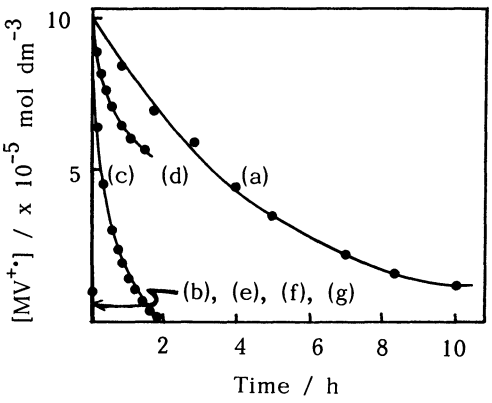


Fig. 2. Oxidation of $MV^{+\cdot}$ in a dichloromethane solution.

Concn. of $MV^{+\cdot}$ (1×10^{-4} mol dm^{-3}) is equal in all systems at the initial stage. (a); $[TFPB^-] = 1 \times 10^{-4}$ mol dm^{-3} under an aerobic condition (bubbled air for 1 min). (b); added MeOH (20% v/v) to the system (a). (c); $[TFPB^-] = 1 \times 10^{-4}$ and $[BQ] = 1 \times 10^{-3}$ mol dm^{-3} under a nitrogen atmosphere. (d); $[AQ] = 1 \times 10^{-3}$ mol dm^{-3} in place of BQ in the system (c). (e), (f), and (g); $[HBBS^-] = 2 \times 10^{-4}$ mol dm^{-3} in place of $TFPB^-$ in the systems (a), (c), and (d), respectively.

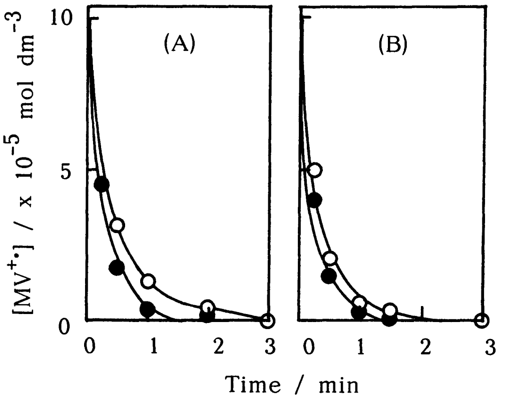


Fig. 3. Oxidation of $MV^{+\cdot}$ in a water-dichloromethane two-phase system under a nitrogen atmosphere.

(A); $[TFPB^-] = 1 \times 10^{-4}$ mol dm^{-3}. (B); $[HBBS^-] = 2 \times 10^{-4}$ mol dm^{-3}. (-o-); oxidized with $Fe(CN)_6^{3-}$ (1×10^{-3} mol dm^{-3} in H_2O). (-●-); oxidized with $AQDS^{2-}$ (1×10^{-3} mol dm^{-3} in H_2O). Initial concn. of $MV^{+\cdot}$ was 1×10^{-4} mol dm^{-3} and aqueous phase contained NaCl (0.1 mol dm^{-3}) at pH = 7.

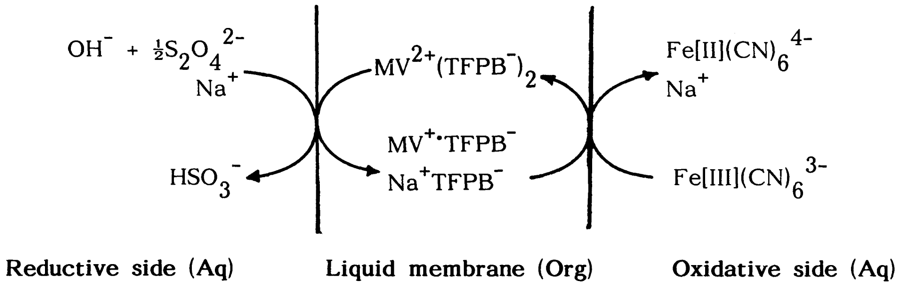


Fig. 4. Schematic representation of the redox reaction in the liquid membrane system.

$HBBS^-$ in the form of associated ion pairs, though the latter was less efficient, and MV^{2+} was incorporated only by $TFPB^-$ into hydrophobic organic solvents. $MV^{+\cdot}$ incorporated with $TFPB^-$ was rather inactive in the organic phase, differing from that with $HBBS^-$, while both ion pairs were equally reactive at the interface, capable to transfer electron to the oxidant dissolved in the aqueous phase. Thus the associated ion pair of methylviologen and $TFPB^-$ would act as an efficient catalytic electron mediator which transfers electron from one aqueous phase to the other across an organic liquid membrane. In a model membrane system,[12] aqueous ferricyanide (1×10^{-3} mol in 0.01 dm^3) was reduced with aqueous sodium dithionite (4.5×10^{-3} mol in 0.03 dm^3 containing potassium carbonate (4.5×10^{-3} mol)) which was separated from the former phase by a dichloromethane phase incorporting the electron mediator, $MV^{+\cdot}TFPB^-$, and Na^+TFPB^- (1×10^{-5} mol of $TFPB^-$ in 0.05 dm^3 of CH_2Cl_2 and 2.5%(v/v) of hexanol), both aqueous phases containing 0.1 mol dm^{-3} of sodium chloride. The cation transport process was also coupled with the electron transfer in the same direction. The amount of 1.5×10^{-4} mol of ferricyanide was reduced in the initial 24 h under an experimental condition. The result indicated that methylviologen, when combined with $TFPB^-$, was retained in a dichloromethane phase and transferred electron 15 cycles on an average during the period of time. The process occurring in the membrane system are presumably represented in Fig. 4. Without $TFPB^-$ no reduction of ferricyanide proceeded at all.

References

1) For example, M. Grätzel, Acc. Chem. Res., 14, 376 (1981).
2) M. Okawara, T. Endo, and Y. Saotome, Polymer Reprints, Japan, 31, 526 (1982), and references therein.
3) I. Tabushi, A. Yazaki, N. Koga, and K. Iwasaki, Tetrahedron Lett., 21, 373 (1980).
4) I. Tabushi, Kokagaku, 7, 39 (1983).
5) H. Iwamoto, M. Yoshimura, T. Sonoda, and H. Kobayashi, Bull. Chem. Soc. Jpn., 56, 796 (1983); H. Kobayashi, T. Sonoda, H, Iwamoto, and M Yoshimura, Chem. Lett., 1981, 579.
6) H. Kobayashi, T. Sonoda, and H. Iwamoto, Chem. Lett., 1982, 1185.
7) H. Iwamoto, T. Sonoda, and H. Kobayashi, Tetrahedron Lett., 24, 4703 (1983).
8) Unpublished data in this laboratory.
9) A. Brändström, "Preparative Ion Pair Extraction," Apotekarsocieteten, Stockholm (1976), p. 89.
10) $MV^{+\cdot}$ was generated by reduction of MV^{2+} with sodium dithionite in a dichloromethane-water two-phase system in the presence of such lipophilic organic anions under a nitrogen atmosphere.
11) MV^{2+} was reduced by tetraphenylborate under the light, where the borate decomposed oxidatively.
12) Lehn and his coworker reported a similar reaction system using a nickel bisdithiolene as an electron mediator: J. J. Grimaldi and J. M. Lehn, J. Am. Chem. Soc., 101, 1333 (1979).

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