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Light-Induced Electron-Transfer Processes in Anionic Micelles: Specific Electrolyte Effects on the Quenching Process[1,2]

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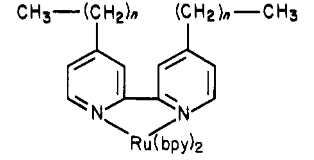
Abstract: The quenching of the surfactant ruthenium bipyridyl complex, **1b**, by methyl viologen in sodium dodecyl sulfate micellar solutions has been investigated in the presence of various electrolytes. By including an exchange equilibrium for methyl viologen and the added electrolyte in the quenching expression, association constants for methyl viologen with the micelles in the presence of added salts are determined. There is a strong dependence of the association constant on the specific electrolyte employed. Further, the quenching rates also vary upon changing the added salt. Relative association constants of the ions added with the micelle, obtained as the inverse of the methyl viologen exchange constant, decrease in the order $Mg^{2+} > (C_2H_5)_4N^+ > Na^+ > Li^+ > NH_4^+$. Such an ordering reflects the importance of both electrostatic and hydrophobic interactions in influencing association of ions with amphiphilic colloids. The dependence of the quenching rate on the specific electrolyte follows an ordering similar to that observed for the binding constants except that Mg^{2+} has a much smaller effect. The results are explained in terms of competition of the added ion with methyl viologen for "trapping sites" on the micelle surface. Thus quenching is influenced by both classical electrostatic and specific ion-pairing contributions.

Bimolecular excited-state processes involving the location of one or both partners in aqueous micelles have been the focus of much recent investigation.[3] In several cases reactions not otherwise observable can be obtained in micellar media due to the solubilization or concentration of reagents to levels unobtainable in homogeneous solution.[4] In other studies it has been found possible to take advantage of the hydrophobic–hydrophilic boundary and Coulombic factors at the micelle–water interface to control both the rates and course of a number of different types of reactions.[5-8] Such reaction control has resulted in proposals that micelles may serve as models for enzymes and biological membranes.[9] Micelles are attractive as models as they appear to be reasonably simple structures and they are readily formed upon solubilization in water. However, although micelles might appear to be relatively simple and well-understood structures, a number of recent investigations have raised important questions.[10] Controversy over several points concerning the structure of micelles, the nature and site of micelle solubilization, and micelle catalysis still exists. Studies using probe molecules to assess micellar properties such as the polarity and viscosity of the microenvironment have frequently produced seemingly contradictory results.[10c] While it is clear that some of the contradictions can be attributed to the residence of probe molecules in different sites, the current understanding of micelle structure, solubilization processes, and control of reactivity remains incomplete and it is clear that much more systematic study will be necessary to obtain an accurate picture.

Previously we reported a study of the quenching of excited states of a micelle-bound surfactant metal complex (**1a**) by the organic



1a, $n = 17$
b, $n = 15$

dication *N,N'*-dimethyl-4,4'-bipyridinium (DMV^{2+}).[11] Although the metal complex is a dication, which should be highly polar, the complex is water insoluble and thus resides exclusively in the micellar pseudophase. The quencher, which has previously been shown to quench the nonsurfactant complex $Ru(bpy)_3^{2+}$ by electron transfer,[12] can reside in either the aqueous phase or highly polar portions of the micellar pseudophase. Studies of the quenching process in aqueous sodium dodecylsulfate (SDS) and cetyltrimethylammonium bromide (CTAB) solutions led to the expected charge effects on the quenching compared to aqueous solution results. Subsequent investigations with similar complexes and a variety of additional quenchers have produced complimentary results.[13] An interesting aspect of our studies with **1a** and DMV^{2+} in aqueous SDS solution was the finding that although DMV^{2+} was strongly bound to the anionic micelles, the quenching of **1a** was a dynamic process involving rapid intermicellar exchange of the DMV^{2+}.[11] An analysis of the intramicellar quenching process enabled an assessment of the intramicellar diffusion rate for the DMV^{2+} which evidently occurs on the polar micellar "surface" as well as a determination of the DMV^{2+}–micellar binding constant and rates of binding and dissociation.

In the present paper we report results of a study of the effect of added cations on the quenching of a similar complex, **1b**, by DMV^{2+} in SDS micelles. The results indicate that both the intramicellar quenching constant and the DMV^{2+}–micelle binding

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(1) Photochemical Reactivity in Organized Assemblies 18, Paper 17: Russell, J. C.; Costa, S. B.; Seiders, R. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 5678–9.

(2) Data taken from the Ph.D. Thesis of Russell H. Schmehl, University of North Carolina, Chapel Hill.

(3) For recent reviews see: (a) Thomas, J. K. *Acc. Chem. Res.* **1977**, *10*, 133. (b) Kalyanasundaram, K. *Chem. Soc. Rev.* **1978**, *4*, 453–72. (c) Yekta, A.; Aikawa, M.; Turro, N. J. *Chem. Phys. Lett.* **1979**, *63*, 543–8.

(4) (a) Burrows, H. D.; Formosinho, S. J.; Pawa, F. J. R. *J. Photochem.* **1980**, *12*, 285–92; (b) Russell, J. C.; Braun, A. M.; Whitten, D. G., unpublished results.

(5) (a) Moroi, Y.; Infelta, P. P.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 573–7. (b) Moroi, Y.; Braun, A. M.; Grätzel, M. *J. Am. Chem. Soc.* **1979**, *101*, 567–73.

(6) Meisel, D.; Matheson, M. S.; Rabani, J. *J. Am. Chem. Soc.* **1978**, *100*, 117–22.

(7) (a) Rodgers, M. A. J.; Wheeler, M. F. da Silva, E. *Chem. Phys. Lett.* **1978**, *53*, 165–9. (b) Rodgers, M. A. J.; Wheeler, M. F. da Silva, E. *Chem. Phys. Lett.* **1976**, *43*, 587–91.

(8) Dederen, J. C.; Auweraer, M. van der; de Schryver, F. C. *Chem. Phys. Lett.* **1979**, *68*, 451–4.

(9) (a) Moss, R. A.; Lee, Y.-S.; Alwis, K. W. *J. Am. Chem. Soc.* **1980**, *102*, 6646–8. (b) Cordes, E. H., Ed. "Reaction Kinetics in Micelles"; Plenum Press: New York, 1973.

(10) (a) Romsted, L. S. In "Micellization, Solubilization and Microemulsions"; Mittal, K. L., Ed.; Plenum Press: New York, 1977; pp 509–30. (b) Bunton, C. A.; Frankson, J.; Romsted, L. S. *J. Phys. Chem.* **1980**, *84*, 2607–11. (c) See: Menger, F. *Acc. Chem. Res.* **1979**, *12*, 111.

(11) Schmehl, R. H.; Whitten, D. G. *J. Am. Chem. Soc.* **1980**, *102*, 1938–41.

(12) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1974**, *96*, 4710–2.

(13) (a) Foreman, T. K., unpublished results. (b) Gaines, G. L., Jr. *Inorg. Chem.* **1980**, *19*, 1710–4.

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constant are strongly affected by added cations. Previous observations of effects produced by added ions on reactions of molecules ion-paired to micelles have focused largely on screening effects produced by the ions.[14-18] Our results suggest that both screening effects and ion-pairing interactions play important roles in the present process; the particular effect of various ions appears closely related to the lyotropic series previously developed in other studies.[19,20]

Experimental Section

The sodium dodecyl sulfate used (Aldrich) was purified by soxhlet extraction with hexane for 25 h to remove dodecanol followed by crystallization from ethanol/water (96/4). The sodium chloride, magnesium chloride, lithium chloride, and ammonium chloride (all Fischer Certified) were all vacuum dried before use. Tetraethylammonium chloride (MCB) was recrystallized three times from acetone and dried in a vacuum desiccator before use. Methyl viologen (Aldrich) was used as received. The ruthenium complexes **1a** and **1b** were generously provided by Dr. W. H. F. Sasse and were used without further purification. Water was triply distilled as described previously.[21]

Micellar solutions were prepared by sonication as described in a previous paper.[11]

The quenching of complex **1b** by methyl viologen in various salt solutions was examined primarily by steady-state luminescence methods. Transient decay analysis of quenching was shown to yield quenching constants similar to those observed with the use of steady-state methods. A Perkin-Elmer MPF-2a spectrofluorimeter equipped with a Hamamatsu R-446 red sensitive photomultiplier was used to measure the luminescence. Quenching of **1b** at fixed surfactant and salt concentration in solutions of varying methyl viologen concentration and quenching at constant surfactant and viologen concentration with varying salt concentration were examined. All experiments were performed with aerated solutions and the results were compensated for oxygen quenching. Results obtained in this manner have been demonstrated to be within experimental error of values obtained by examination of freeze–pump–thaw degassed samples.[11]

Results and Discussion

As was previously reported for the system **1a**–DMV^{2+} in SDS micelles,[11] it was found that quenching of the excited state of **1b** in the anionic micellar solution by DMV^{2+} is largely a dynamic process with the Stern–Volmer plots for intensity quenching of the luminescence nearly identical with those for quenching of the excited state lifetime. The luminescence lifetime of the complex, monitored by laser flash spectroscopy, shows only a single exponential decay in each case.[11] The results are best interpreted by a mechanism wherein exchange of quencher molecules between the micelles is rapid relative to the decay rate of the excited chromophore. Thus each molecule of **1b** excited will experience the average number of quenchers per micelle. At any given electrolyte concentration the degree of quenching is a linear function of the number of quenchers per micelle and produces the same slope regardless of the overall surfactant concentration.

This information suggests that quenching results only from micelle-associated viologen. We have previously suggested that the results can be explained by the scheme given in eq 1–4 where

$$2\mathrm{S_m}^+ + \mathrm{DMV_w}^{2+} \underset{k_d}{\overset{k_f}{\rightleftharpoons}} \mathrm{DMV_m}^{2+} + 2\mathrm{S_w}^+ \qquad (1)$$

$$[\mathrm{Ru}^{2+}, \bar{n}\mathrm{DMV}^{2+}]_\mathrm{m} \xrightarrow{h\nu} [\mathrm{Ru}^{2+*}, \bar{n}\mathrm{DMV}^{2+}]_\mathrm{m} \qquad (2)$$

$$[\mathrm{Ru}^{2+*}, \bar{n}\mathrm{DMV}^{2+}]_\mathrm{m} \xrightarrow{k_r + k_n} [\mathrm{Ru}^{2+}, \bar{n}\mathrm{DMV}^{2+}]_\mathrm{m} + \Delta + h\nu \qquad (3)$$

$$[\mathrm{Ru}^{2+*}, \bar{n}\mathrm{DMV}^{2+}]_\mathrm{m} \xrightarrow{k_q} [\mathrm{Ru}^{3+}, \mathrm{DMV}^{+}, (\bar{n} - 1)\mathrm{DMV}^{2+}] \qquad (4)$$

Ru^{2+} = **1b** and $\mathrm{S_m}^+$ and $\mathrm{S_w}^+$ represent the univalent salt concentration in the presence and absence of micelles, respectively. The key here is that $k_d > (k_r + k_n)$ and $k_d > k_q$. The above requirements insure that each molecule of **1b** experiences the average number of quencher molecules resulting in a decay which is a single exponential. In this scheme, diffusion across the micelle surface occurs to establish the collision complex required for electron transfer to occur. Since the volume of the surface shell of the Stern layer is small compared to the solution volume, the local concentration of quencher is much higher than in homogeneous solution. As a result a certain percentage of the methyl viologen will be associated with the complex, **1b**, at the time of excitation and thus some static quenching is to be expected.

Table I. Quenching of Complex **1b** by Methyl Viologen in SDS (0.02 M)

salt	[salt], M	k_{obsd}, M^{-1} s^{-1}	$\mathcal{N}^2$ [a,b]	$1/k_{\mathrm{obsd}} \times 10^4$, M^{-1} s^{-1}
NH_4Cl	0.2	1555	181	6.43
	0.4	1385	709	7.22
	0.6	1245	1583	8.03
	0.8[c]	962	2803	10.39
$MgCl_2$	0.1[c]	2123	13.47	4.71
	0.2	1760	26.6	5.68
	0.3	1621	39.8	6.17
	0.4	1490	52.9	6.71
	0.5	1349	66.1	7.41
NaCl	0.05	3064	23	3.26
	0.10	2918	75	3.43
	0.20	2403	272	4.16
TEAC	0.02	8547	2.66	1.12
	0.04	7246	8.69	1.38
	0.06	6369	18.17	1.57
	0.08	4878	32.12	2.05
LiCl	0.08	2170	31	4.75
	0.4	1705	709	5.87
	0.6	1395	1583	7.17
	1.0	930	4370	10.75

[a] For $MgCl_2$,[b] NH_4Cl, and TEAC, values of 0.2 for α and 0.001 M for the cmc were used in the calculation of $\mathcal{N}^2$. For NaCl an α of 0.2 and a cmc of 0.008 M were assumed. [b] $\mathcal{N}$ instead of $\mathcal{N}^2$ must be used for Mg^{2+}. [c] Not included in regression analysis.

Added cations can, of course, affect the process outlined above in several ways. The equilibrium, eq 1, as shown above explicitly involves any or all cations present in the solution. Moreover the intramicellar quenching process, eq 4, should be modified and it is possible that excited state decay in the absence of quencher, eq 3, could also be somewhat influenced. The bulk of this paper thus deals with the specific effects produced by the commonly used ions Li$^+$, Na$^+$, Mg^{2+}, NH$_4^+$, and $(C_2H_5)_4N^+$.

If a few assumptions are made, a quantitative analysis of the above scheme may be made which provides values for the exchange constant of DMV^{2+} with the counterions of the micelle as well as the quenching rate in the volume of the Stern layer of the micelle. The assumptions that must be made are: (a) the degree of dissociation of the micelle remains constant with varying surfactant and supporting electrolyte concentration, (b) the aggregation number of the micelles also remains constant under the varying conditions, (c) no cooperative interactions between counterions or counterions and head groups occur, (d) the activities of the ions in solution are proportional to their concentration, and (e) the ion–ion exchange rates are rapid relative to the excited state decay. It was shown earlier that both the cmc and the aggregation number depend upon the electrolyte concentration;[22,23] no attempt to compensate for these variations shall be made here. A description of the ion-exchange equilibrium employing these approximations has been presented by Quina and Chaimovich.[24] The kinetic analysis given here extends this to luminescence

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(14) Bruhn, H.; Holzwarth, J. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1006–11.

(15) Pelizzetti, E.; Paramuro, E. *Inorg. Chem.* **1979**, *18*, 882–3.

(16) Grätzel, M.; Thomas, J. K. *J. Phys. Chem.* **1979**, *78*, 2248–54.

(17) Romsted, L. S.; Cordes, E. H. *J. Am. Chem. Soc.* **1968**, *90*, 4404–9.

(18) Cordes, E. H.; Dunlap, R. B. *Acc. Chem. Res.* **1969**, *2*, 329–37.

(19) See: Weiser, H. B., "Colloid Chemistry"; Wiley: New York, 1949; p 295.

(20) Larsen, J. W.; Magid, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 5774–81.

(21) See: Kuhn, H.; Mobius, D.; Bucher, H. In "Physical Methods of Chemistry"; Weissberger, A., Rossiter, B., Eds.; Wiley: New York, 1972; Vol. 1, Part 3b, p 577.

(22) Mukerjee, P. *Adv. Colloid Interfac. Sci.* **1967**, *1*, 241–75.

(23) Mysels, K.; Princen, L. H. *J. Phys. Chem.* **1959**, *63*, 1696–1700.

(24) (a) Quina, F. H.; Chaimovich, H. *J. Phys. Chem.* **1979**, *83*, 1844–50. (b) Chaimovich, H.; Bonilha, J. B. S.; Politi, M. J.; Quina, F. H. *J. Phys. Chem.* **1979**, *83*, 1851–4.

Table II. Exchange Equilibrium Constants and Stern–Volmer Constants Obtained from Table I

salt	slope	intercept	corr coeff	K	k_{SV}, M^{-1} s^{-1}	$k_{SV}C_d\bar{V}$, M^{-1} s^{-1}
NH_4Cl	1.12×10^{-7}	6.30×10^{-4}	0.991	5625	1587	7.5
$MgCl_2$	4.36×10^{-6}	4.47×10^{-4}	0.996	102	2237	10.6
NaCl	3.65×10^{-7}	3.17×10^{-4}	0.999	868	3155	15
TEAC	3.01×10^{-6}	1.08×10^{-4}	0.993	279	9259	44
LiCl	1.36×10^{-7}	4.85×10^{-4}	0.999	3566	2061	9.9

quenching. The initial equilibrium, eq 1, describes the association of MV^{2+} with a micelle of constant size having a cmc and degree of dissociation, α, independent of the added electrolyte concentration. The equilibrium constant, K, is simply:

$$K = \frac{[DMV]_m[S]_w^2}{[DMV]_w[S]_m^2} \qquad (5)$$

Since quenching of the excited complex **1b** results from interaction exclusively with micelle-bound methyl viologen the Stern–Volmer expression may be written:

$$I^0/I = 1 + k_{sv}[DMV]_m \qquad (6)$$

where k_{sv} is the product of the lifetime of **1b** and the quenching rate constant observed in the volume of micelles present, reflecting both intramicellar diffusion and quenching events. Thus, in order to analyze the above expression adequately, a practical expression for the concentration of DMV^{2+} within the micelle must be derived. One means of accomplishing this analysis is to make the following assumptions and apply them to the equilibrium of eq 1.

$$\text{(a)} \qquad [DMV]_T = [DMV]_w + [DMV]_m \qquad (7)$$

$$\text{(b)} \qquad [S]_w = \alpha c_D + \text{cmc} + [S]_T + 2[DMV]_m \approx \alpha c_D + \text{cmc} + [S]_T \qquad (8)$$

$$\text{(c)} \qquad [S]_m = (1 - \alpha)c_D - 2[DMV]_m \approx (1 - \alpha)c_D \qquad (9)$$

In the above equations, α represents the degree of dissociation of the micelles, cmc is the critical micelle concentration, c_D is the concentration of micellized surfactant (c_T – cmc), and $[S]_T$ is the concentration of added electrolyte. Equation 5 may be analyzed for the bound methyl viologen concentration by employing the above approximations.

$$[DWV]_m = [K/(N^2 + K)][DMV]_T \qquad (10)$$

The term N^2 of eq 10 is:

$$N^2 = ([S]_w/[S]_m)^2 = (\alpha c_D + \text{cmc} + [S]_T/(1 - \alpha)c_D)^2 \qquad (11)$$

Substitution of eq 10 into eq 6 gives the modified Stern–Volmer equation, eq 12, applicable to the quenching of the complex **1b** by methyl viologen in SDS:

$$I^0/I = 1 + k_{sv}[K/(N^2 + K)][DMV]_T \qquad (12)$$

$$k_{obsd} = k_{sv}[K/(N^2 + K)] \qquad (13)$$

The term $K/(N^2 + K)$ reflects the fraction of the $[DMV]_T$ that is bound to the micelle. Furthermore, N^2 predicts the dependence of the rate on the surfactant concentration and also an effect of ionic strength opposite to that expected for quenching of a dicationic sensitizer by a dicationic quencher in homogeneous solution.[25] By varying either the surfactant concentration or the salt concentration the observed rate constant changes. If the above expression is valid then the observed quenching constant should be related to the concentration of salt and surfactant by

$$\frac{1}{k_{obsd}} = \frac{1}{k_{sv}} + \frac{1}{k_{sv}K}N^2 \qquad (14)$$

Table III. Intramicellar Quenching Constants for 1b by Methyl Viologen in the Presence of Cations[a]

added cation	$k_q \times 10^{-7}$, M^{-1} s^{-1}	added cation	$k_q \times 10^{-7}$, M^{-1} s^{-1}
TEA^+	5.67	Li^+	1.28
Na^+	1.93	NH_4^+	0.97
Mg^{2+}	1.36		

[a] k_q is obtained from the intercept of the $1/k_{obsd}$ vs. N^2 plots and is analogous to homogeneous solution quenching rates in the limit of zero ionic streneth. Thus the k_q value for Na^+ represents a standard for SDS micelles.

Thus plots of $1/k_{obsd}$ vs. N^2 should be linear. From this the exchange constant for DMV^{2+} with the cation may be obtained. However, our previous study revealed that nearly all of the methyl viologen is attached to the micelles for the varying surfactant concentrations examined. In such situations, the differences in rates correspond merely to dilution of the bound viologen within the Stern region. At a much lower surfactant concentration, 0.012 M SDS, the degree of quenching does not correlate with the average number of quenchers per micelle as do higher surfactant concentrations since not all the DMV^{2+} is bound. In order to make use of eq 14 one must insure that changes in the rate of quenching are the result of the ion-exchange process. Because of this limitation, only experiments in which the ionic strength was varied were applied to eq 14. In Table I quenching data for a variety of a salts are shown; the results for the analysis of the data according to eq 14 providing exchange constants are presented in Table II. The results indicate that DMV^{2+} binding to SDS is strongly dependent upon the specific electrolyte employed with K for methyl viologen association decreasing in the order $NH_4^+ > Li^+ > Na^+ > TEA^+ > Mg^{2+}$.

Moreover, the Stern–Volmer quenching constant, k_{sv}, increases in the order $NH_4^+ < Li^+ < Mg^{2+} < Na^+ < TEA^+$. The values of k_{sv} in Table II represent the quenching rate in the entire solution volume as eq 12 does not present DMV_T in the micelle volume exclusively. This can be compensated for by multiplying the constant obtained by $c_D\bar{V}$, the volume of micelles per unit volume of water, where $\bar{V}$ represents the volume of micelles per mole of surfactant (Table II.)[26] The measured Stern–Volmer constants in the micelle volume range from 7.5 to 44 M^{-1} s^{-1}; the average value is 18.8 M^{-1} s^{-1}. The quenching constants k_q (Table III) range from 9.7×10^6 to 5.67×10^7 M^{-1} s^{-1}. The above values of k_q represent both diffusional processes on the micelle surface as well as the quenching event itself (eq 15). The term γ reflects the fraction of collisions that results in quenching (vide infra).

$$k_q = k_{diff}\gamma \qquad (15)$$

In evaluating the overall effects of the added cations on the DMV^{2+} quenching process, it is perhaps best to examine first the effect on the binding equilibrium. The inverse of K should reflect

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(25) See: Pethybridge, A. D.; Pure, J. E. "Progress in Inorganic Chemistry", Edwards, J. O., Ed.; Wiley-Interscience: New York, 1973; Vol. 17, pp 327–90.

(26) In order to make comparisons with literature values for micellar parametrs, the total micellar volume was employed rather than the volume of the Stern region alone. Martinek has estimated the micellar volume of SDS to be 0.25 M^{-1}.[27]

(27) Martinek, J.; Berezin, I. V. *Russ. Chem. Rev.* (*Engl. Transl.*) **1978**, *42*, 787–802.

(28) See: Balzani, V.; Moggi, L.; Manifrin, M. F.; Bolletta, F.; Laurence, G. S. *Coord. Chem. Rev.* **1975**, *15*, 321–431.

(29) By way of comparison, k_{diff} in water, calculated by the Debye–Smoluchowski equation,[30] is 1.28×10^9 M^{-1} s^{-1}; this reflects, of course, both the polarity (dielectric constant) and viscosity of the medium.

(30) See: Petrucci, S. "Ionic Interactions"; Petrucci, S., Ed.; Academic Press: New York, 1971; Vol. 2, chapter 7.

the relative binding constants for the various cations with SDS. The order thus obtained for $1/K$ is $Mg^{2+} > TEA^+ > Na^+ > Li^+ > NH_4^+$. This order seems reasonable and appears to follow a decreasing charge/size ratio except for the organic cation, TEA^+. It is probable that the latter ion has additional bonding capabilities for the micelle and it would not be unreasonable to propose that much of the binding of TEA^+ to the micelle occurs as the result of both electrostatic attraction to the head groups and hydrophobic interactions with the micelle interior. In the series studied it seems clear that, due to its relative hydrophobicity, this ion is the only one which would be effective in reducing the high surface potentials associated with these interfaces. Looking at the overall series from a slightly different perspective the order obtained correlates well, except for NH_4^+, with the lyotropic series developed for SDS by Larsen and Magid[20] for quite different phenomena. Thus the effect of electrolytes on the binding equilibria appears to be relatively well-defined.

The source of the variation of the intramicellar quenching constants (Table III) with change in electrolyte appears to be less clear. Certainly the deviations observed are well outside of experimental error, but the overall differences are much smaller than those observed for the binding constants. It is reasonable that the term γ from eq 15 is unlikely to be affected by changes in the electrolyte, thus it appears that the variations in k_q must be due to changes in the rate of diffusion in the micellar pseudophase. In attempting to evaluate these values a difficulty is that it is impossible to measure k_{diff} in the micelles in the absence of added electrolyte.

Generally, adding electrolyte increases the diffusional collision rate between two ions of like charge. Making this assumption, the predicted rate of diffusion in the absence of electrolyte should be lower than the slowest rate observed, $4.8 \times 10^7\ M^{-1}\ s^{-1}$. Thus, the greatest effect here is produced by TEA^+. The results could be interpreted as indicating that this ion affects the intramicellar diffusion of DMV^{2+} the most, while all the other ions studied have much smaller effects, paralleling the differences in the relative association of the added electrolytes with the micelles. An alternative explanation would be that TEA^+ produces an effective acceleration of k_{diff} by reducing trapping sites at the hydrocarbon–water interface such that the DMV^{2+} is much more mobile in the surface region. In any event, it is clear that the effect of the other cations, though clearly real, is relatively small and not easily interpretable in terms of previously observed phenomena. These results emphasize the caution that must be used in extrapolating reactions in homogeneous solutions to micelles or micelle–water interfaces for evaluation of physical properties of the micelle such as the micropolarity or microviscosity.

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Organo Halide Addition to $Pd_2(Ph_2PCH_2PPh_2)_3$. Preparation of Novel Methylene- and Phenylene-Bridged Complexes by Two-Center, Three-Fragment Oxidative Addition

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Abstract: Dihalomethanes react with $Pd_2(dpm)_3$ (dpm = bis(diphenylphosphino)methane) to form $Pd_2(dpm)_2(\mu\text{-}CHR)X_2$ (X = I, Br, Cl; R = H, CH_3). $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ undergoes substitution to form $Pd_2(dpm)_2(\mu\text{-}CH_2)L_2^{2+}$ (L = pyridine, methyl isocyanide). The Pd–C (methylene) bond resists insertion of carbon monoxide, isocyanides, or sulfur dioxide. Reaction of $Pd_2(dpm)_3$ with 1,2-diiodobenzene yields $Pd_2(dpm)_2(\mu\text{-}C_6H_4)I_2$. Addition of phenyl isocyanide dichloride to $Pd_2(dpm)_3$ yields $Pd_2(dpm)_2(\mu\text{-}CNPh)Cl_2$ while a corresponding reaction involving oxalyl chloride produces $Pd_2(dpm)_2(\mu\text{-}CO)Cl_2$. Addition of methyl halide to $Pd_2(dpm)_3$ produces $Pd_2(dpm)_2(CH_3)_2X_2$ (X = Br, I) which exist as the molecular A-frame $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]^+X^-$ in solution. Protonation of $Pd_2(dpm)_2(\mu\text{-}CH_2)I_2$ with fluoroboric acid yields brown, crystalline $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]BF_4$ in which a bridging methylene has been converted into a terminal methyl group. Dynamic aspects of the structure of $[Pd_2(dpm)_2(\mu\text{-}X)(CH_3)_2]^+$ and $[Pd_2(dpm)_2(\mu\text{-}I)(CH_3)I]^+$ are described.

The oxidative addition reaction represents a fundamental transformation of organometallic chemistry.[1] While oxidative addition reactions of mononuclear complexes have received considerable study, comparable studies on binuclear transition-metal complexes have only recently begun to appear. From this limited number of studies, the transannular oxidative addition summarized by eq 1 has emerged as a common type of reaction for ligand-bridged, binuclear complexes.

$$X\text{–}Y + M^nM^n \rightarrow X\text{–}M^{n+1}\text{–}M^{n+1}\text{–}Y \qquad (1)$$

This reaction results in a formal, one-electron oxidation of each metal and in the creation of a metal–metal single bond. Examples of this type of reaction include the addition of halogens to $Rh_2(dpm)_2(CO)_2Cl_2$ (dpm = bis(diphenylphosphino)methane),[2] $Rh_2(dpm)_2(CNR)_4^{2+}$,[2,3] $Rh_2[CN(CH_2)_3NC]_4^{2+}$,[4] $Pd_2(dpm)_3$,[5] and $Au_2[(CH_2)_2P(CH_3)_2]_2$,[6] the addition of methyl halides to $Rh_2[CN(CH_2)_3NC]_4^+$,[4] and $Au_2[(CH_2)_2P(CH_3)_2]_2$,[6] and the addition of dihydrogen to $Ir_2(t\text{-}BuS)_2(CO)_4$.[7]

The study reported here involves the addition of organic halides to the binuclear palladium(0) complex $Pd_2(dpm)_3$.[8] Transannular oxidative additions to give palladium(I) dimers do not occur. Rather, oxidative addition results in the formation of palladium(II) complexes. With organic dihalides this reaction results in the

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[1] Collman, J. P.; Hegedus, L. S. "Principles and Applications of Transition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 176-258.

[2] Balch, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 8049-8054.

[3] Balch, A. L.; Labadie, J. W.; Delker, G. *Inorg. Chem.* **1979**, *18*, 1224-1227.

[4] Lewis, N. S.; Mann, K. R.; Gordon, J. G., II; Gray, H. B. *J. Am. Chem. Soc.* **1976**, *98*, 7461-7463.

[5] Hunt, C. T.; Balch, A. L. *Inorg. Chem.* **1981**, *20*, 0000-0000.

[6] Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85-89.

[7] Thorez, A.; Maisonnat, A.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1977**, 518-519.

0002-7863/81/1503-3764$01.25/0