Solvation Effects on Photochemically-Induced Electron Transfer from Tris(bipyridyl)ruthenium to Methylviologen

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Summary

The effects of mixed solvent systems and anions on the rate of reaction of the title compounds were investigated. The results were shown to be best interpreted in terms of ion-pair formation and solvation-desolvation effects, in addition to the factors included in the outer-sphere electron transfer rate theory expounded by Marcus.

Introduction

The photochemical electron transfer from tris-(bipyridyl)-ruthenium(II), $[Ru(bipy)_3]^{2+}$ (and its analogues) to a quencher, *e.g.*, methylviologen, MV^{2+} (and its analogues) has recently attracted enormous attention because of the potential use of the system for water decomposition by solar energy$^{(1, 2)}$. More recent studies on the system include a determination of the electron transfer rate dependency on distance$^{(3)}$, the effects of cations on anionic micellar systems$^{(4)}$, and attempt to decrease the back-reaction by utilizing mercury(II) as the quencher$^{(5)}$. In the hope of obtaining further insight into the factors that influence the photochemically-induced electron transfer reaction rate, we studied the effects of salts and solvents.

A great number of studies has been made on the traditional thermal electron transfer reactions$^{(6)}$. Such anions as halides, CN^- and N_3^- play an important role as bridging groups in the inner-sphere type of electron transfer reactions or as a catalyst in the outer-sphere type of reactions. In addition, a general (primary) salt effect may be expected.

The effect of a mixed solvent such as water-methanol may influence the reaction between the electrically charged species through variation of the dielectric constant of the medium$^{(7-10)}$.

The experimental results reported here, however, do not entirely conform to the classical salt effect nor to the Marcus theory$^{(9, 10)}$ of dependency on the dielectric constant of the medium. They could better be explained in terms of ion-pair formation and solvation-desolvation effects.

Experimental

A solution containing $[Ru(bipy)_3]^{2+}$ was excited with a light of wavelength 470 nm after being deoxygenated, and the emission intensity was recorded at 619 nm on a Perkin-Elmer 650–40 fluorescence spectrophotometer at 25 °C.

A set of seven solutions were prepared for a solvent system. The first solution contained only 1.00 E-5 M of $[Ru(bipy)_3]^{2+}$. This solution was used to determine I_0, the emission intensity for an unquenched system. The second solution contained 5.00 E-3 M of methylviologen in addition to 1.00 E-5 $[Ru(bipy)_3]^{2+}$. The other five solutions contained varied concentrations of an alkali halide in addition to the two compounds already mentioned. Such a set of measurements was repeated two or three times. Series of such measurements with sets of seven solutions were carried out with LiCl, LiI or KI as the alkali halide and with mixed solvents containing differing ratios of H_2O and MeOH or H_2O and Me_2CO.

Methylviologen dichloride was purchased from Sigma Chemical Co., tris(bipyridyl)ruthenium(II) dichloride from Alfa Products, and alkali halides from Mallincrodt or Sigma.

Results

The electron transfer reaction rates were estimated from the fluorescence measurement of $[Ru(bipy)_3]^{2+}$ in the presence of the electron acceptor, methylviologen, and varied concentrations of an alkali halides in a mixed solvent system (water-methanol or water-acetone).

Let I_0 denote the emission intensity of $[Ru(bipy)_3]^{2+}$ in the absence of the quencher (electron acceptor), and I that in the presence of the quencher. If a simple scheme shown below is assumed,

$$\begin{aligned}&R(= [Ru(bipy)_3]^{2+}) + h\nu \rightarrow {}^*R : Ia\\&{}^*R \rightarrow R : k_d\\&{}^*R + M\ (= \text{methylviologen}) \rightarrow R^+ + M^- : k_q\end{aligned} \qquad (1)$$

(where Ia is the intensity of the exciting light and is a constant)

the so-called Stern-Volmer equation is obtained:

$$I_0/I - 1 = (k_q/k_d)[M] \qquad (2)$$

The parameter Y is then defined as:

$$Y = (I_0/I - 1)/[M] \qquad (3)$$

The Y values calculated from the observed I values are given in Table 1 (for water-methanol) and Table 2 (for water-acetone). I_0 values for different solvent systems are listed in Table 3.

Some of the general features of the results shown in Tables 1, 2 and 3 are:

(A) I_0 depends on the composition of the mixed solvent. Since I_0 is proportional to Ia/k_d, this means that k_d is dependent on the composition of the solvent. Since the absorption and emission spectra of $[Ru(bipy)_3]^{2+}$ have been found to be independent of the solvent composition, k_d can be assumed to be c/I_0, where c is a constant. The lifetime of $^*[R(bipy)_3]^{2+}$ has been estimated to be 0.6 microsec in water$^{(11)}$, *i.e.*, $k_d = 1.67\,E\,6\,s^{-1}$ in water. Using this figure, k_d values in the mixed solvent system may be estimated (see Table 3).

(B) Dependency on alkali halides: When corrected for the difference in concentration, Y values for KI and LiI are identical within experimental errors, but those for I^- and Cl^- are not. This indicates (i) that the salt effect in terms of the ionic strength is not a dominant factor, and (ii) that the electron transfer reaction depends on the anion but not on alkali cations.

(C) Y values appear to be linear with respect to the molar concentration of the halide anion [X]. However, at closer

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Table 1. Y values in MeOH-H_2O mixture. $[Ru(bipy)_3^{2+}]$ = 1.00 E–5 M for LiCl and LiI series = 8.56 E–6 M for KI series; $[MV^{2+}]$ = 5.00 E–3 M.

MeOH vol.%	$[X^-]$ added (M)	0	1.25 E–2	2.50 E–2	3.75 E–2	5.00 E–2	6.25 E–2
0	LiCl	176	284	341	391	435	468
	LiI	190	406	576	701	815	924
	KI	186	401	551	689	814	920
10	LiCl	185	277	327	374	414	452
	LiI	186	404	546	711	839	944
	KI	159	368	520	643	760	853
20	LiCl	147	219	270	311	344	377
	LiI	157	356	524	666	772	893
30	LiCl	111	174	218	252	286	310
	LiI	115	286	425	551	656	753
40	LiCl	98	154	198	230	257	281
	LiI	99	264	414	527	620	707
	KI	78	221	336	435	516	597
50	LiCl	80	132	167	204	229	249
	LiI	83	250	390	511	598	692
60	LiCl	84	132	168	207	243	265
	LiI	79	259	429	550	662	781
	KI	82	216	352	460	544	635
70	LiCl	79	137	184	218	248	269
	LiI	85	308	511	681	831	948
	KI	63	279	460	580	719	820
80	LiCl	95	166	228	266	302	337
	LiI	92	433	724	970	1195	1392
90	LiCl	112	208	271	335	375	408

Table 2. Y values in Me_2CO-H_2O mixture. $[Ru(bipy)_3^{2+}]$ = 1.00 E–5 M, $[MV^{2+}]$ = 5.00 E–3 M.

Me_2CO vol.%	$[X^-]$ added (M)	0	1.25 E–2	2.50 E–2	3.75 E–2	5.00 E–2	6.25 E–2
10	LiCl	256	336	399	440	462	503
	LiI	254	489	643	841	1000	1150
20	LiCl	153	219	270	321	349	383
	LiI	155	308	435	581	783	913
30	LiCl	110	159	195	232	261	284
	LiI	107	263	398	549	704	830
40	LiCl	89	146	189	221	248	268
	LiI	96	206	309	404	510	568
50	LiCl	107	168	226	262	302	330
	LiI	109	251	415	510	610	746
60	LiCl	135	247	309	361	410	452
	LiI	137	347	515	682	782	879
70	LiCl	246	427	578	672	724	776
	LiI	258	627	919	1236	1505	1755

Table 3. k_d values in mixed solvent systems.

MeOH-H_2O Vol.% (org.)	I_0	k_d(1/s)	Me_2Co-H_2O Vol.% (org.)	I_0	k_d(1/s)
0	202 ± 7	1.67 E6	0	207 ± 7	1.67 E6
10	247 ± 6	1.37 E6	10	281 ± 5	1.19 E6
20	272 ± 6	1.25 E6	20	324 ± 5	1.05 E6
30	291 ± 2	1.17 E6	30	341 ± 4	0.99 E6
40	307 ± 2	1.12 E6	40	345 ± 5	0.94 E6
50	296 ± 4	1.10 E6	50	365 ± 7	0.90 E6
60	337 ± 7	1.07 E6	60	379 ± 2	0.89 E6
70	317 ± 8	1.05 E6	70	381 ± 6	0.89 E6
80	303 ± 12	1.05 E6			
90	299	1.04 E6			

inspection, a double reciprocal plotting of 1/Y *vs.* 1/[X] was shown to give a much better linearity; *i.e.*, Y can be expressed as:

$$1/Y = a + b/[X] \quad \text{or} \quad Y = [X]/(b + a[X]) \tag{3}$$

Results (B) and (C) indicate the following reaction scheme:

$$\begin{aligned} &R + X \rightleftharpoons RX : K \\ &R \rightarrow {}^*R : I_a \\ &RX \rightarrow {}^*RX : I_a \\ &{}^*R \rightarrow R : k_d \\ &{}^*RX \rightarrow RX : k_d' \\ &{}^*RX + M \rightarrow R^+ + M^- + X : k_2 \end{aligned} \tag{4}$$

Assuming a steady state condition with respect to [*R] and [*RX], $k_d = k_d'$ and that the rate of the direct reaction between *R and M is negligible compared to the one above, and using the mass balance $[R]_0 = [R] + [RX]$ ([*RX] is negligible), one obtains:

$$I = (k_d I_0/(1 + K[X]))((1/k_d) + K[X]/(k_d + k_2[M])) \qquad (5)$$

The assumption that $k_d = k_d'$ can be rationalized, because the quenching effect of I^- (as well as Cl^-) on the *R species was observed to be negligible(12). Since $I_0 = I_a/k_d$ and $I = \{[{}^*R] + [{}^*RX]\}$, Equation (5) can be written as:

$$Y = (I_0/I - 1)/[M] = K(k_2/k_d)[X]/(1 + (k_2/k_d)[M] + K[X]) \qquad (6)$$

This can be rearranged to:

$$(1/Y) = (k_d/k_2) + (((k_d/k_2) + [M])/K)(1/[X]) \qquad (7)$$

This is in agreement with the observed results [Equation (3)]. Since k_d values have been estimated as mentioned earlier, k_2 and K values can be estimated from the intercept and the slope of the plot of (1/Y) against (1/[X]). The data with LiI require some qualification, because chloride salts of $[Ru(bipy)_3]^{2+}$ and MV^{2+} were used. That is, at lower [LiI] values, the system contained considerable proportions of both Cl^- and I^-, and hence it is rather complicated to analyze the data at lower [LiI] values. Therefore, only the data at higher I^- concentrations were used for the estimation of slopes and intercepts. Obviously, no such complication occurs in the case of LiCl; thus all the points were used. Naturally the estimated values of slope and intercept would contain larger uncertainties in the case of I^- than in the case of Cl^-. The estimated values of K and k_2 are tabulated in Tables 4 and 5.

Table 4. Association constant K as estimated from intercept and slope of (1/Y) *vs.* (1/[X]).

MeOH-H$_2$O Vol.% (org.)	for Cl	for I	Me$_2$CO-H$_2$O Vol.% (org.)	for Cl	for I
0	167.7	124.4	0	162.7	124.4
10	189.5	100.9	10	313.3	138.8
20	151.3	102.1	20	160.1	72.7
30	112.6	77.1	30	125.2	58.5
40	100.3	80.8	40	87.5	50.7
50	80.0	71.7	50	98.8	61.0
60	84.1	75.1	60	107.3	91.8
70	71.2	83.9	70	177.7	151.1
80	78.0	130.3			
90	84.7				

Table 5. k_2 values as estimated from k_d/intercept.

MeOH-H$_2$O Vol.% (org.)	for Cl	for I	Me$_2$CO-H$_2$O vol.% (org.)	for Cl	for I
0	1.00E8	3.43E9	0	1.00E9	3.43E9
10	7.30E8	4.28E9	10	6.52E8	3.21E9
20	5.67E8	3.13E9	20	4.72E8	6.41E9
30	4.64E8	3.20E9	30	3.31E8	4.97E9
40	4.11E8	2.33E9	40	3.51E8	3.49E9
50	3.81E8	2.73E9	50	4.00E8	5.50E9
60	3.72E8	3.34E9	60	6.14E8	2.90E9
70	4.37E8	5.61E9	70	1.08E9	8.36E9
80	5.58E8	1.17E9			
90	7.27E8				

Discussion

The results in Tables 4 and 5 indicate:

(a) k_2 values are greater with I^- than with Cl^-;
(b) k_2 values depend on the organic content of the mixed solvent in a unique way (Figure 1);
(c) The association constants K between the ruthenium complex and halogen anion are greater for Cl^- than for I^-;
(d) The association constants K vary with the solvent composition in a unique way, just like the case of k_2 (Figure 3).

In many systems of thermal electron transfer studied(6) including Fe^{III}–$Fe^{II}(phen)_3$, the catalytic effectiveness has been found to be $Cl^- < I^-(< N_3^- < CN^-)$(13). Result (a) is consistent with this general trend.

One of the most interesting results is the dependence of k_2 values on the composition of the mixed medium. A trend similar to Figure 1 for rate constant *vs* water-ethyleneglycol composition has been observed for an uranium(IV)/uranium(VI) electron exchange reaction(14). The phenomena of this kind have not received an adequate explanation.

Marcus theory(9, 10) on the electron transfer rate of outer-sphere type indicates:

$$k_2 = \exp(-\Delta G^*/RT) \qquad (8)$$

$$\Delta G^* = (\lambda/4)(1 + (\Delta G^0/\lambda)^2 + W_r + \Delta G^*_{in} + \Delta G^*_0 \qquad (9)$$

The first term of Equation (9) is the so-called driving force dependent on the reduction potential difference ΔG^0 between the oxidant and the reductant. Since the absorption and emission spectra of $[Ru(bipy)_3]^{2+}$ and MV^{2+} are independent of the solvent composition and the presence of halide ion, this term can be assumed to be constant. The second term W_r is the work required to bring the two reactants to the reaction distance, d, and can be written as:

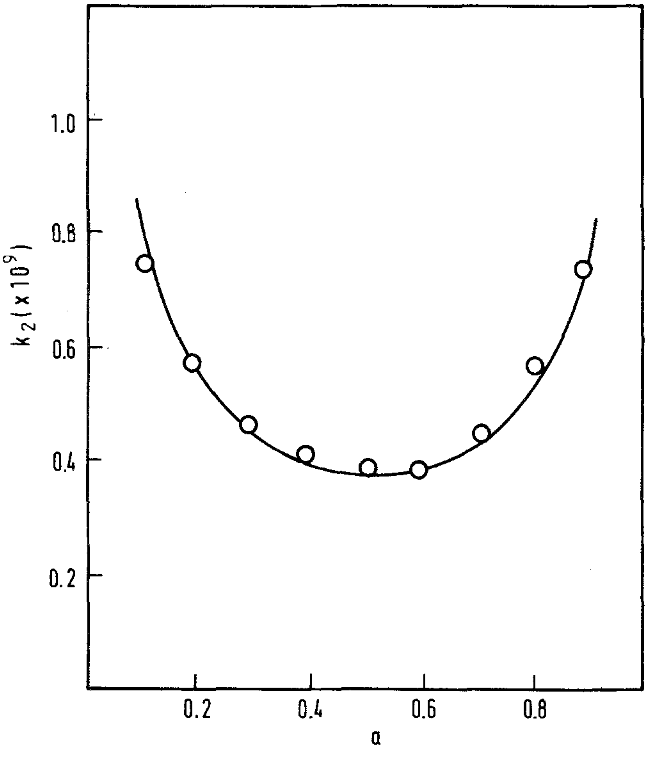

Figure 1. The dependence of the rate constant k_2 on the solvent composition a (a = volume percentage of the organic component) for LiCl/MeOH-H$_2$O system. The circles represent the experimental data and the solid curve is the theoretical value (see the text).

$$w_r = q_1q_2/Dd(1 + \beta d\sqrt{\mu}) \qquad (10)$$

where q_1 and q_2 are the electric charges of the reactants, D the static dielectric constant of the solvent, μ the ionic strength and $\beta = (8\pi N^2e^2/1000\,DRT)^{1/2}$. The $\beta d\sqrt{\mu}$ is the Debye Hückel correction term and may be neglected to a first approximation. The third term ΔG^*_{in} is the energy required to reorganize the inner-sphere coordination structure and is independent of the solvent composition. The fourth term G^*_0 is the energy required to reorganize the outer-sphere coordination shells and is given by the following formula in Marcus theory.

$$\Delta G^*_0 = \left(\frac{q_1 - q_2}{2}\right)^2 \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{d}\right] \left(\frac{1}{n^2} - \frac{1}{D}\right) \qquad (11)$$

where a_1 and a_2 are the radii of the reactants and n is the refractive index of the solvent. The variation of n values in the solvent systems used is much smaller than that in D value, $1/n^2$ term may be regarded to be constant in comparison with 1/D term. Therefore ΔG^* can be written as:

$$\Delta G^* = \text{constant} + B(1/D) \qquad (12)$$

In terms of the rate constant,

$$\ln(k_2/k_2') = -(B/RT)(1/D) \qquad (13)$$

where

$$B = (q_1q_2/d) - \left(\frac{q_1 - q_2}{2}\right)^2 \left[\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{D}\right] \qquad (14)$$

If it is assumed to a first approximation that $a_1 = a_2$ and $d = a_1 + a_2$, then $B = 1.75/d$ (assuming that $q_1 = +1$ and $q_2 = +2$). Thus a plot of log k_2 *vs* (1/D) should give rise to a straight line of a negative slope. The graph of log k_2 *vs* (1/D) is shown for a LiCl/water-methanol system in Figure 2. The first part can be fitted to a straight line of negative slope, but log k_2 values increase again after a minimum with the increase of 1/D, in contrast to expectation. Therefore, it is clear that the Marcus theory alone does not adequately explain the trend observed in the present study.

The rate of the sixth reaction in the scheme above [(Equation (4)] is expressed as:

$$\text{Rate} = k_2[{}^*RX][M] \qquad (15)$$

Since M species would be coordinated completely by solvent molecules (water = W and/or organic solvent = S), it might be assumed, as before, that M species should dissociate one of the solvent molecules in order to bind *RX species. The outer-sphere electron transfer theory by Marcus[9, 10] does not take this factor into consideration. Let us denote such a species as an effective M species. Therefore, the rate should be expressed as follows:

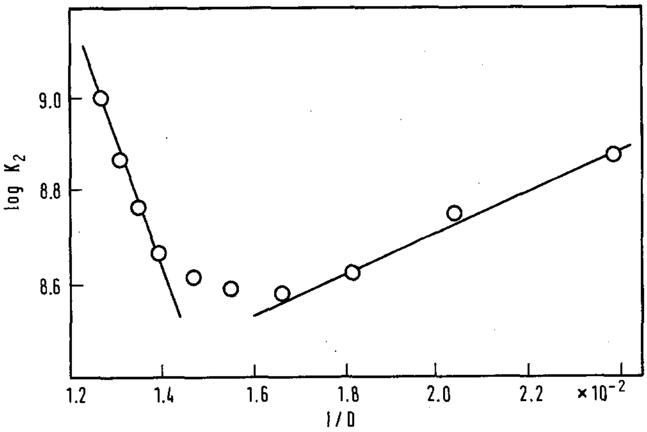

Figure 2. The dependence of log k_2 on 1/D (D = dielectric constant of the solvent) for LiCl/MeOH-H_2O.

$$\text{Rate} = k_2^0[{}^*RX][\text{effective M}] = k_2^0[{}^*RX][M]F \qquad (16)$$

where [effective M] = [M]F. That is, k_2 can be expressed as:

$$k_2 = k_2^0F \qquad (17)$$

where k_2^0 is the true rate constant and F is a factor relating the effective M concentration to the nominal M concentration. F can be estimated as follows. M species is actually MS_mW_n, and dissociates either S or W. This can be described by:

$$\begin{aligned} &MS_{m-1}W_n + S \rightleftharpoons MS_mW_n : K_{MS} \\ &MS_mW_{n-1} + W \rightleftharpoons MS_mW_n : K_{MW} \end{aligned} \qquad (18)$$

Therefore, the effective M concentration is given by:

$$\begin{aligned} [\text{effective M}] &= [MS_{m-1}W_n] + [MS_mW_{n-1}] \\ &= [MS_mW_n]((1/K_{MS}[S] + (1/K_{MW}[W])) \end{aligned} \qquad (19)$$

If additivity is assumed, as a first approximation, regarding [S] and [W], they can be related to the volume composition of the solvent, a = volume fraction of the organic component in the mixed solvent. That is:

$$[S] = 1000\,ad_s/M_s, \quad [W] = 1000(1 - a)d_w/18 \qquad (20)$$

where d_w and d_s are the density of water and that of the organic liquid, respectively, and M_s is the molecular weight of the organic compound. Putting Equation (20) into Equation (19) gives rise to:

$$\begin{aligned} F &= (1/1000\,K_{MW})\,((18/(1\text{–}a) + (M_s/(K_{MS}/K_{MW})ad_s)) \\ &= F'(1/1000\,K_{MW}) \end{aligned} \qquad (21)$$

Therefore,

$$k_2 = k_2^0F = k_2^0F'/1000\,K_{MW} \qquad (22)$$

F′ can easily be calculated as a function of a, if (K_{MS}/K_{MW}) is known. Assuming that k_2^0 is dependent on 1/D in the manner of Equation (13), the following expression can be obtained:

$$\log k_2 = C + \log(k_2'/K_{MW}) + \log(F'/1000) - (B/2.3\,RT)(1/D) \qquad (23)$$

$(\log k_2 - \log(F'/1000))$ then should be linear with respect to (1/D). Therefore, from a plot of $[\log k_2 - \log(F'/1000)]$ *versus* (1/D), B and $\log(10^c\,k_2'/K_{MW})$ values may be evaluated. In order to do this, one has to choose an appropriate (K_{MS}/K_{MW}) value. This can be done in such a way that the overall best agreement may be obtained between the experimental and the theoretically calculated [from Equation (23)] values of k_2. The best fit was obtained with $K_{MS}/K_{MW} = 4.0$, $B/2.3\,RT = 27.3$ and $(10^c\,k_2'/K_{MW}) = 10.25$ for the case of LiCl/water-methanol. The calculated k_2 values are represented by the solid curve in Figure 1. The circled points are the experimentally determined values. The agreement is generally good, despite the crude assumptions made; *i.e.*, the simple additivity for [S] and [W] (and molar concentration instead of activity was used), and that m and n values as well as K_{MS} and K_{MW} are independent of the solvent composition.

From the experimentally determined B/2.3 RT value (= 27.3), the reaction distance d of B = 1.75/d [this was obtained from Equations (10), (12) and (15)] can be estimated as follows:

$$B/2.3\,RT = 27.3 = 1.75\,Ne^2/2.3\,(4\pi\varepsilon RT)d \qquad (24)$$

the d value obtained from this calculation is 1.5×10^{-9} m or 15 Å. This is quite reasonable in view of this rough estimate; d value for the same system has been estimated to be 14 Å^2 or 10 − 14 Å from the emission life time in a rigid system$^{(3)}$. The value estimate may be improved if one takes into consideration the Debye-Hückel term and the different values for a_1 and a_2, but this cannot be done with any more confidence. The reasonableness of the d-value estimate, however, indicates that Equation (23) is basically correct, and henceforth that the unique dependence of k_2 on the solvent composition is essentially due to the solvation-desolvation effects of the reactants. A recent study$^{(15)}$ on the effect of water-methanol mixed solvent on a bimolecular reaction also suggests the importance of desolvation of the reactants.

Such comparisons between the experimental k_2 values and the calculated values have been tried for the other cases: LiI/water-methanol and LiCl/water-acetone. Although the agreement between the observed and the calculated values of k_2 for these latter systems is not as good as that for LiCl/water-methanol, the general trend seems to be in agreement with the postulate made above; *i.e.*, the reaction takes place between *RX and the effective M species.

These results suggest that Marcus theory$^{(9, 10)}$ is not sufficient, and that ΔG* [of Equation (9)] should contain a term due to the dissociation of a solvent molecule from the coordination sphere. This effect is incorporated in terms of F factor in the present framework, but could be incorporated as an energy of dissociation of the solvent molecule. That is:

$$\Delta G^{\ddagger}_{d}\,(\text{dissociation of solvent}) = -RT\ln F \qquad (25)$$

In a pure solvent this factor is constant and would not appear explicitly in the expression of ΔG*. However, as the present study indicates, this factor may need to be considered in order to obtain a proper rate constant value; *i.e.*:

$$\Delta G^{*} = (\text{driving force}) + w_r + \Delta G^{\ddagger}_{in} + \Delta G^{\ddagger}_{0} + \Delta G^{\ddagger}_{d} \qquad (26)$$

It might be argued, alternatively, that one solvent molecule may need to dissociate from each of the reactants. This assumption leads to a situation in which k_2 depends not on the first order, but on the second of K_{MS} and K_{MW}. This cannot in any way be fit to the experimental results. This implies that the dissociation of the solvent molecule from the *RX species is not required for the reaction, or that it requires so little energy which is independent of the solvent composition, and hence its effect would not manifest itself.

The dependence of K values for the ion-pair formation on the solvent composition resembles that of k_2 values (see Figure 3). This suggests that the major factor here again is the solvation-desolvation of the chemical species involved. This assumption can be described as:

$$R + X\,(\text{effective}) \rightleftharpoons RX : K^0 \qquad (27)$$

where

$$[\text{effective } X] = [XS_{m-1}W_n] + [XS_mW_{n-1}] = [X]P \qquad (28)$$

$$XS_{m-1}W_n + S \rightleftharpoons XS_mW_n : K_{XS}$$

$$XS_mW_{n-1} + W \rightleftharpoons XS_mW_n : K_{XW} \qquad (29)$$

$$P = (1/K_{XW}[W]) + (1/K_{XS}[S]) \qquad (30)$$

Therefore,

$$K_{obs} = K^0P \qquad (31)$$

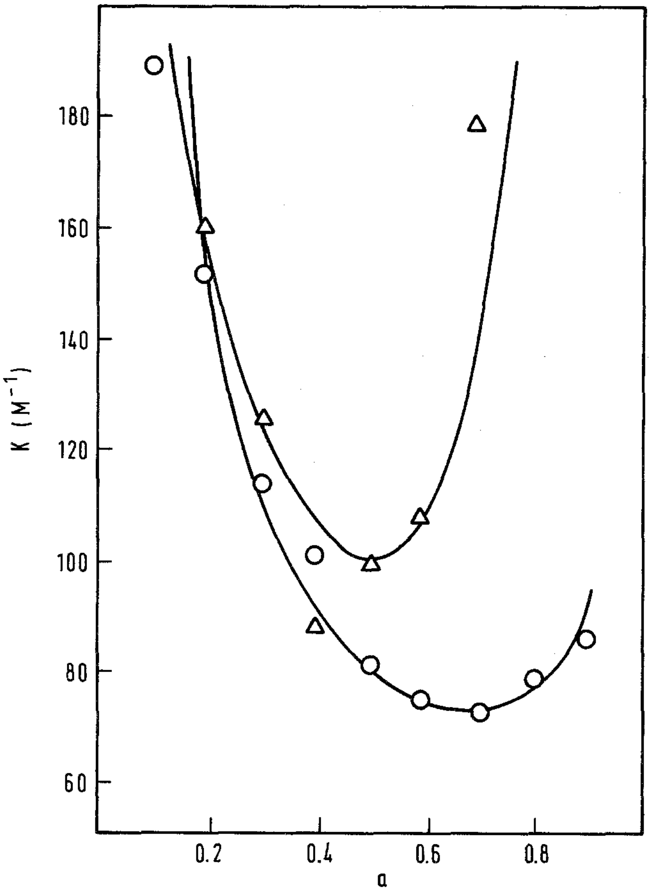

Figure 3. The dependence of the ion-pair formation constant K on the solvent composition a (a = vol.% of the organic component) for LiCl/MeOH-H_2O system (–O–) and for LiCl/Me_2CO-H_2O system (–Δ–). The circles or triangles represent the experimental values and the solid curves represent the theoretically calculated values (see the text).

K^0 is certainly dependent on the solvent composition or D, as follows:

$$-RT\ln K^0 = \text{const.} + (Nq_1q_2e^2/4\pi\varepsilon r)(1/D) \qquad (32)$$

where each symbol has a similar connotation to that of the corresponding one in Equation (10). All combined, one obtains:

$$\log K_{obs} = \text{const.} + \log P - (Np_1q_2e^2/4\pi\varepsilon rRT)(1/D) \qquad (33)$$

P values can be estimated, as above, assuming such a K_{XS}/K_{XW} value that would make the plot of log (K_{obs}/P) linear to (1/D) with the slope $(-Nq_1q_2e^2/4\pi\varepsilon rRT)(1/D)$. The theoretical K values can then be calculated from Equation (33), using the slope value determined from the plot. This has been tried with the systems of LiCl/methanol-water and LiCl/acetone-water. The solid lines in Figure 3 represent the theoretical K values thus evaluated. The agreement between the theoretical and experimental values is generally good, except for both extremes a = 0 and a = 1 where the simple additivity assumption cannot hold.

As expected, the slope of the plot of Equation (33) is positive, because $q_1 = -1$ and $q_2 = +2$, whereas the slope for Equation (23) is negative (for $q_1 = +1$ and $q_2 = +2$). The r values (distance between the reactants) estimated from the slope of Equation (33) fall in the range 6–14 Å, which is reasonable. All these results seem self-consistent and would indicate that the model proposed here is viable, and probably basically correct.

It has been implicity assumed that the desolvation of the Ru complex (or the RX complex as discussed earlier) is inconsequential for the kinetic and the thermodynamic behaviours of the system under study. One indication that the desolvation of the other species such as X^- or MV^{2+}, rather than that of the Ru-containing species, is the important one comes from the relative values K_{MS}/K_{MW} or K_{XS}/K_{XW} as defined above. From the k_2 analysis for Cl^-/methanol-water system K_{MS}/K_{MW} was estimated to be 4; K_{XS}/K_{XW} values for Cl^-/methanol-water and Cl^-/acetone-water were about 0.02 and 0.08, respectively. A number of studies(16, 17) indicates that cations are usually solvated by organic solvent molecules such as methanol or acetone more preferentially than by water molecules in a mixed solvent system, whereas simple anions such as halide bind water more strongly than the organic solvent molecules. Thus, K_{XS}/K_{XW} values are certainly consistent with the assumption that the dissociation of solvent molecules is from X^- species rather than a cation. The K_{MS}/K_{MW} values obtained (4.0) is consistent with the assumption that the outer-sphere dissociation should occur from a cationic species as in Equation (18). However, this argument does not necessarily specify the cation to be MV^{2+} species as postulated here.

One final point that needs to be discussed is whether X^- forms an ion-pair with the Ru species (*i.e.*, the assumption made above) or with MV^{2+} (the alternative assumption). The alternative hypothesis cannot be distinguished from the present one by simply fitting the data to rate equation such as Equation (3), because the alternative mechanism would also lead to the same form of [X] dependence. However, the alternative hypothesis would lead to a solvent-composition dependency of K values that is radically different from that shown in Table 4 and Figure 3. Since the data in Figure 3 has been demonstrated to be reasonably explainable in terms of the present hypothesis, the alternative is inconsistent with the whole scheme and can probably be discarded. This in turn implies either that the desolvation of the Ru species is not required for the ion-pair formation or that it requires so little energy that its effect would be insignificantly dependent of the solvent composition. A similar conclusion has been reached with respect to the RX species, as discussed earlier. This conclusion may be justified in terms of the structure of the complex; *i.e.*, the bulky ligands on the complex would reduce its ionic potential significantly, thus diminishing the solvation energy.

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Synthesis and Structure of New Arylnickel(II) Malonato-complexes

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Summary

Interaction of malonate anions with chloro(aryl)bis(organophosphine)nickel(II) complexes leads to the formation of stable (aryl)(malonato)(organophosphine)nickel(II) species, as shown by i.r. and ^1H n.m.r. data. The crystal and molecular structure of (diethylmalonato-O,O)(α-naphthyl)(triphenylphosphine)nickel(II), determined by x-ray methods (space group $P\bar{1}$, $a = 10.767(9)$, $b = 16.253(16)$, $c = 9.835(13)$ Å, $\alpha = 108.97(10)^0$, $\beta = 106.08(10)^0$, $\gamma = 89.11(7)^0$, $Z = 2$; $R = 0.070$ for 3650 independent observed reflections), shows distorted square-planar O_2PC coordination about the nickel with bond distances: Ni-P, 2.142(2) Å; Ni-O, 1.888(5) and 1.936(5) Å; Ni-C, 1.887(8) Å. The parameters and bonding of the triphenylphosphine-nickel and naphthyl moieties in the complex are normal, whereas considerable electron-delocalisation occurs in the planar ethylmalonate moiety. The σ-naphthyl ligand is oriented almost perpendicularly to the NiO_2CP core-malonate plane.

Introduction

The role of Ni complexes in catalytic coupling reactions has been investigated in recent years(1). It has been established

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