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NAD(P)$^+$–NAD(P)H Models. 81. Temperature-Dependent Stereospecificity in the Interconversion between Central and Axial Chiralities

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In the oxidation of (4*R*)-Me$_3$MQPH or (4*R*)-Me$_3$PNPH with a series of 1,4-benzoquinone and its derivatives, the *R*/*S* ratio with respect to the axial chirality in the product, i.e., 11*R*-/11*S*- isomer ratio in Me$_3$MQP$^+$ or 7*R*-/7*S*- isomer ratio in Me$_3$PNP$^+$, changes depending on the reaction temperature as well as the reactivity of quinone. It is confirmed that kinetic *R*-preference stems from the entropy-control, whereas kinetic *S*-preference comes out of the enthalpy-control. The relative importance of enthalpy and entropy is discussed in terms of the earliness and lateness of the transition state at the initial electron-transfer step.

It has been reported that the central chirality at the C$_4$-position of 3-[methyl(α-methylbenzyl)carbamoyl]-1,2,4-trimethyl-1,4-dihydroquinoline (Me$_3$MQPH) is converted into the axial chirality with respect to the C$_3$–C$_{\text{carbonyl}}$ bond in 3-[methyl(α-methylbenzyl)carbamoyl]-1,2,4-trimethyl quinolinium ion (Me$_3$MQP$^+$) on oxidation.[1—3] Similar relationship is also observed in the 3-[methyl(α-methylbenzyl)carbamoyl]-1-propyl-2,4-dimethyl-1,4-dihydropyridine (Me$_3$PNPH)/3-[methyl(α-methylbenzyl)carbamoyl]-1-propyl-2,4-dimethylpyridinium ion (Me$_3$PNP$^+$) system (Chart 1).

The oxidation of (4*R*)-Me$_3$MQPH or (4*R*)-Me$_3$PNPH exerts a linear free energy (reactivity-stereospecificity) relationship: The stereospecificity associated with the chirality conversion depends on the oxidation and reduction potentials of the reducing and oxidizing reagents, respectively.[2—4] We proposed previously that the earliness and lateness of the transition state at the initial electron-transfer step results in the difference in Gibbs energy between the *syn*- and *anti*-conformations at the transition state[5,6] exerting the variation in stereospecificity as schematically depicted in Fig. 1.[3,4,7] The *syn*- and *anti*-conformations at the transition state correspond to the *S*- and *R*-products, respectively.

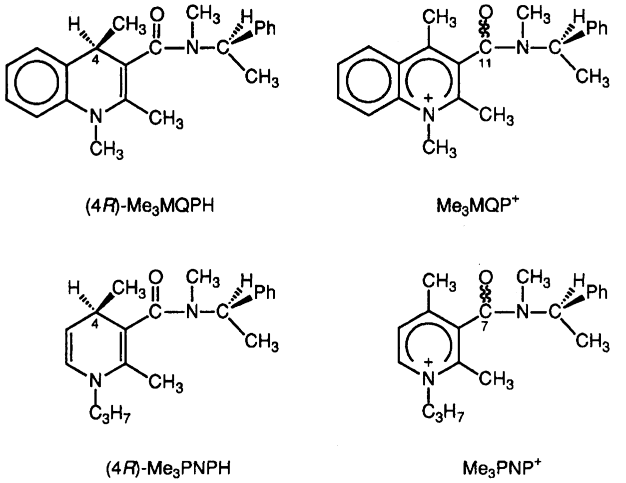

Chart 1.

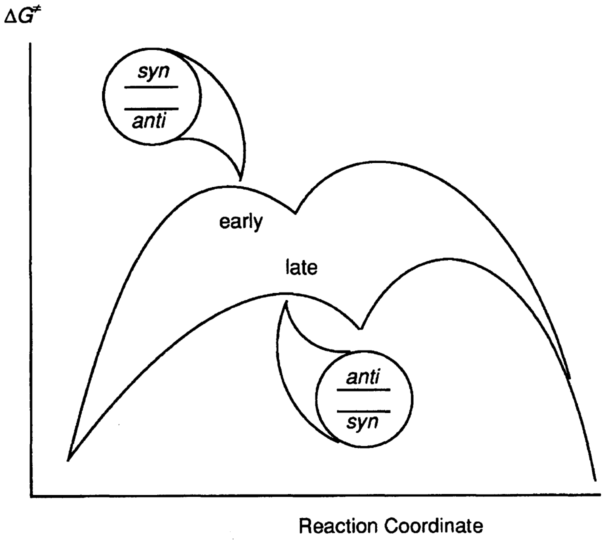

Fig. 1. Schematic illustration of energy surfaces along the reaction coordinate.

It was also suggested that the *syn*-conformation is enthalpically more stable than the *anti*-conformation at least at the transition state.[4,8] Being hinted at by the fact that the *anti*-conformation is preferred by the early transition state, we also proposed that the *anti*-conformation is more favored by the entropy term than the *syn*-conformation.[4]

Kinetic studies on oxidation of *N*-benzyl-1,4-dihydronicotinamide (BNAH) and other NAD(P)H analogs, 3-(α-methylbenzylcarbamoyl)-1,2,4-trimethyl-1,4-dihydroquinoline (Me$_2$MQPH) and 3-(α-methylbenzylcarbamoyl)-1-propyl-2,4-dimethyl-1,4-dihydropyridine (Me$_2$PNPH), with tetrachloro-1,4-benzoquinone (**Q4**: a highly electron-deficient quinone) or 2,6-dichloro-1,4-benzoquinone (**Q2**: a less electron-deficient quinone) have revealed that Gibbs energy of activation is composed of 50—90% of entropy term remaining 50—10% only for enthalpy term.[7] The entropy-control is more significant in the reaction with **Q4** than in the reaction with **Q2**, and the reaction of BNAH or other NAD(P)H analogs with relatively low oxidation potentials is associated with smaller contribution of the entropy term. Thus, all experimental results so far obtained are consistent with our previous proposal on the relation among the late- and early-transition states, the *syn*- and *anti*-conformations, and enthalpy- and entropy-controlled reactions.[3,4,7]

However, we have had no evidence on the most fundamental assumption that both enthalpy and entropy associated with the *anti*-conformation are larger than those associated with the *syn*-conformation at the transition state of the reaction. Therefore, an entropically much less favored reaction assumes the *anti*-conformation at its transition state of initial electron-transfer process in order to compensate the unfavorable entropy of activation, which is a major parameter to control the kinetics, although the *syn*-conformation is always favored by enthalpy.

Since the difference in Gibbs energy of activation to the *syn*- and *anti*-conformational transition states is too small to be detected by independent kinetics with reliable accuracy and since the reaction systems we are going to study are not 100% stereospecific, we studied the temperature dependency of the R/S ratio in the product, which is a direct measure of the *anti*/*syn* ratio at the transition state of the initial electron-transfer step.

We now wish to report the relative importance of the entropy and enthalpy in the *syn*- and *anti*-conformational transition states of the initial electron-transfer step to confirm the validity of our previous proposal.

Experimental

Instruments. ^{1}H NMR spectra were recorded at 200 and 400 MHz on a Varian VXR200 and a JEOL GX400 FT-NMR spectrometers, respectively, in CD_3CN with TMS as an internal standard.

Materials. Acetonitrile was distilled over calcium hydride and used immediately. Magnesium perchlorate was powdered and dried at 160 °C under reduced pressure in the presence of diphosphorus pentaoxide immediately before the use. Me_3MQPH and Me_3PNPH were prepared according to the literature procedures.[1,3] Quinones were obtained from commercial sources (Nacalai Tesque Inc. and Wako Pure Chemicals Industries, Ltd.) and purified by repeated recrystallization.

Measurement of Stereospecificity. Into a 50 ml round-bottomed flask filled with argon and equipped with a magnetic stirrer and sealed with a serum cap, 0.03 mmol of 1,4-benzoquinone or its derivative dissolved in 29 ml of anhydrous acetonitrile was injected through a syringe. The solution was equilibrated in a thermostated bath at 253, 263, 273, 283, 293, 303, 313, or 323 K. The accuracy of the temperature in the thermostat was ±0.1 K. To the solution, 1 ml of thermostated acetonitrile solution containing 0.03 mmol of an NAD(P)H analog and an equivalent amount of anhydrous magnesium perchlorate, if necessary, was injected through a syringe. Then, the reaction mixture was stirred for an appropriate interval (3 h for the reaction with Me_3MQPH and 1 h for the reaction with Me_3PNPH) in the dark. After evaporation of the solvent under reduced pressure, the residue was washed twice with ether. The crude product was dissolved in CD_3CN and subjected to ^{1}H NMR spectroscopy to elucidate the diastereomer ratio in the product as well as the chemical yield. The R/S ratios were measured repeatedly and only those that afforded good reproducibility by more than 3 observations were employed as the final results. The ^{1}H NMR spectra of Me_3MQP^+ and Me_3PNP^+ thus obtained were the same as those reported.[1,3]

Measurement of Water Content in a Solvent. The water content in the solvent was measured on GLC (Porapack Q, 1 m, 453 K) by the similar method reported previously.[10]

Results

The R/S ratios were measured over as wide a temperature range as possible in order to increase the precision and accuracy of the values, and are listed in Table 1. The logarithms of the R/S ratios are plotted in Fig. 2 against the reciprocal of absolute temperatures in order to demonstrate the reliability of the linear relationship. The plots were treated by the least-squares method to obtain linear relationships. The differences in enthalpy and entropy of activation between the *syn*- and *anti*-conformations at the transition state of the initial electron-transfer step were obtained from the slope and intercept of the line, respectively, according to Eq. 1.

$$\begin{aligned} -\ln(R/S) &= \delta\Delta G^{\neq}{}_{R\text{–}S}/RT \\ &= \delta\Delta H^{\neq}{}_{R\text{–}S}/RT - \delta\Delta S^{\neq}{}_{R\text{–}S}/R, \end{aligned} \qquad (1)$$

where the subscript R–S denotes that an activation parameter for the *syn*-conformational transition state (S-product) is subtracted from the corresponding quantity for the *anti*-conformational transition state (R-product). The results are summarized in Table 2.

Discussion

Accuracy of the Observed Results. Since the kinetic parameters listed in Table 2 are rather smaller than those usually appear in literatures to discuss on kinetic properties of a reaction, the associating errors are quite important to convince their physical meaning. Therefore, the validity of the values will be discussed first.

There are some discrepancies in the value of R/S ratios listed in Table 1 from those we have reported previously.[3] The values are perturbed by several reaction conditions such as water content in the solvent or magnesium perchlorate, concentration of substrate, and, of course, reaction temperature. Among those, the water content have been found to exert the largest effect on the stereochemistry of the reaction. Although the R/S ratio changes to certain extent by small change in the amount of contaminating water, it was found, on the other hand, that the difference in enthalpy of activation

Table 1. Temperautre Dependence of the R/S Ratio in the Product

Reducing reagent	Q	Mg^{2+}	T/K 253	263	273	283	293	303	313	323
Me_3MQPH	**Q4**	+	1.31/1	1.34/1	1.32/1	1.46/1	1.41/1	1.48/1	1.46/1	1.45/1
	Q2	+	1/1.06	1/1.06	1/1.05	1/1.04	1/1.03	1/1.04	1/1.08	1/1.08
	Q1	+	1/2.37	1/2.30	1/2.07	1/1.93	1/1.83	1/1.76	1/1.79	1/1.82
	Q0	+	1/8.96	1/9.00	1/8.39	1/7.88	1/7.61	1/6.30	1/5.73	1/5.58
	Q4	−	1.24/1	1.32/1	1.35/1	1.38/1	1.28/1	1.43/1	1.39/1	1.36/1
	Q2	−	1.54/1	1.31/1	1.47/1	1.76/1	1.52/1	1.58/1	1.43/1	1.42/1
	Q1	−					1.24/1			
	Q0	−				No reaction				
Me_3PNPH	**Q4**	−	1.53/1		1.96/1		2.42/1(298 K)			2.28/1
	Q2	−	1/3.55	1/3.20	1/3.05	1/3.20	1/2.54	1/2.48	1/2.21	1/2.05
	Q1	−	1/4.26	—[a]	1/3.77	1/3.38	1/3.72	1/3.01	1/3.13	1/2.94
	Q0	−				No reaction				

a) Because of complexity of the spectrum, the ratio could not be measured.

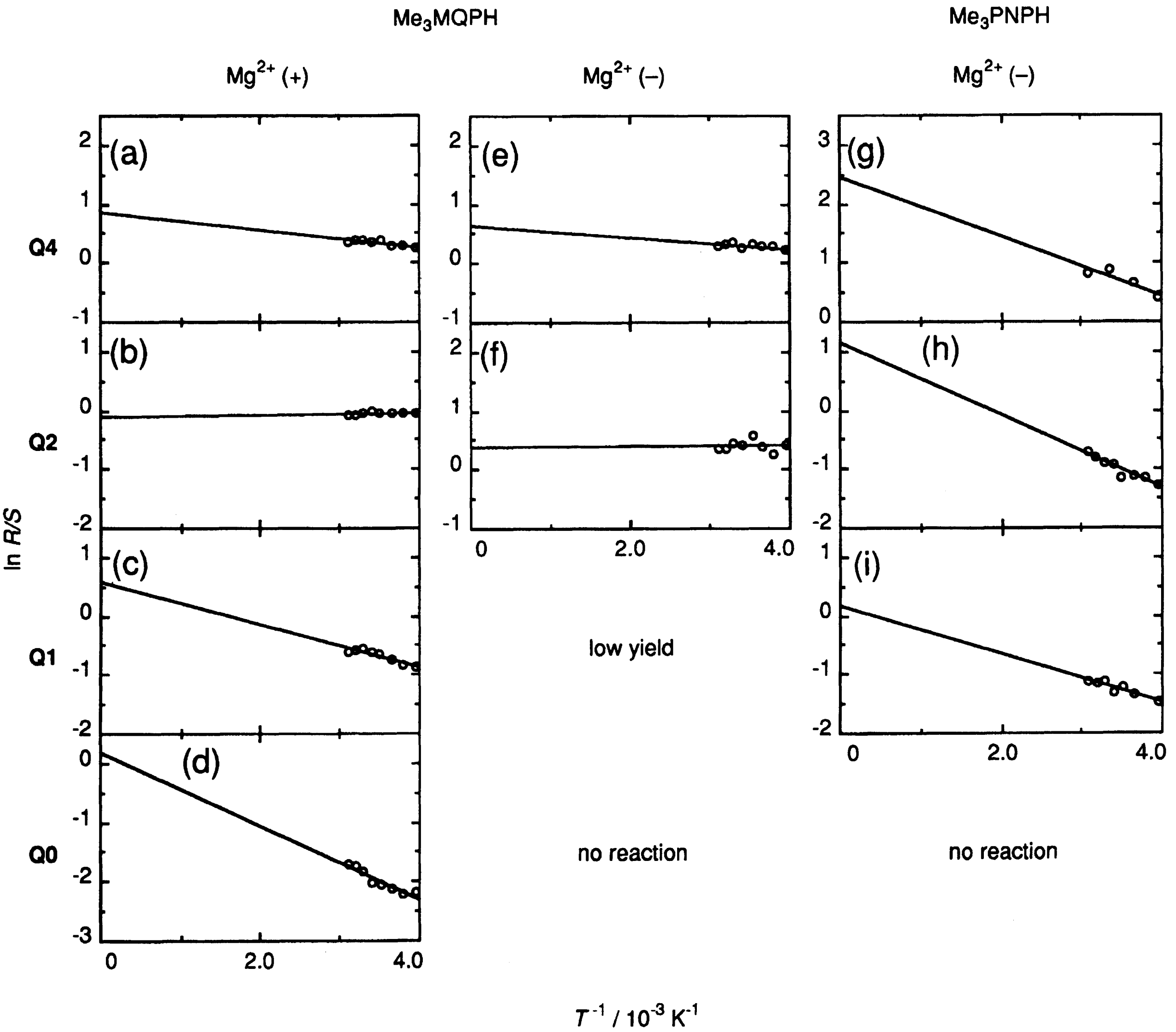

Fig. 2. Plots of ln (R/S) against $1/T$: Me_3MQPH+**Q4**+Mg^{2+}, (a); Me_3MQPH+**Q2**+Mg^{2+}, (b); Me_3MQPH+**Q1**+Mg^{2+}, (c); Me_3MQPH+**Q0**+Mg^{2+}, (d); Me_3MQPH+**Q4**, (e); Me_3MQPH+**Q2**, (f); Me_3PNPH+**Q4**, (g); Me_3PNPH+**Q2**, (h); Me_3PNPH+**Q1**, (i).

Table 2. Difference in Thermodynamic Parameters at 298 K between the *syn*- and *anti*-Conformations at the Transition State

Reducing reagent	Quinone	$E°$/V (vs. SCE)[a)]	Mg^{2+}	$\delta\Delta G^{\neq}{}_{R-S}$ kcal mol^{-1}	$\delta\Delta H^{\neq}{}_{R-S}$ kcal mol^{-1}	$\delta\Delta S^{\neq}{}_{R-S}$ cal mol^{-1} deg^{-1}
Me$_3$MQPH	**Q4**	+0.01	+	−0.19	+0.33±0.06	+1.76±0.19
	Q2	−0.18	+	+0.02	−0.05±0.09	−0.24±0.11
	Q1	−0.34	+	+0.38	+0.65±0.10	+0.89±0.35
	Q0	−0.50	+	+1.13	+1.15±0.15	+0.04±0.50
	Q4	+0.01	−	−0.19	+0.20±0.10	+1.30±0.33
	Q2	−0.18	−	−0.22	+0.04±0.04	+0.86±0.07
	Q1	−0.34	−		Low yield[b)]	
	Q0	−0.50	−		No reaction	
Me$_3$PNPH	**Q4**	+0.01	−	−0.46	+1.09±0.52	+5.32±1.83
	Q2	−0.18	−	+0.37	+1.18±0.34	+2.72±1.32
	Q1	−0.34	−	+0.67	+0.92±0.09	+0.84±0.56
	Q0	−0.50	−		No reaction	

a) Ref. 9. b) The yields of products were so low that the R/S values to be calculated were unreliable.

($\delta\Delta H^{\neq}{}_{R-S}$, the slope of a line shown in Fig. 2) is rarely altered by the amount of contaminating water. However, there is no doubt that the reaction conditions have to be regulated as precisely as possible to obtain the linear relationship: thus, a solution of an NAD(P)H analog containing anhydrous magnesium perchlorate was prepared in a flask and aliquots were pipetted out to obtain solutions for each run in order to keep the water content of the reaction solution in each run constant as well as to keep the temperature constant. Solutions of a quinone and an NAD(P)H analog without magnesium perchlorate were prepared and handled similarly. The same concentrations of a substrate and water made it possible to elucidate $\delta\Delta H^{\neq}{}_{R-S}$ accurately. Thus, the value of $\delta\Delta S^{\neq}{}_{R-S}$ (the intercept of a line shown in Fig. 2) is the subject of perturbation by the amount of contaminating water. We, therefore, regulated the water content as well as all the other experimental conditions strictly so as to establish the reliability in relative $\delta\Delta S^{\neq}{}_{R-S}$ value among all reactions. The water content was measured to be 0.07—0.08% (v/v) by GLC analyses throughout the experiments.

The values shown in Table 2 are the average of 2—5 runs and the errors indicated therein were evaluated as the average of standard deviations for each single run. However, at the same time, they represent the mean errors among different runs studied to evaluate the average value.

Reaction in the Presence of Magnesium Ion. In the presence of magnesium ion, (11*S*)-Me$_3$MQP$^+$ was obtained predominantly in the oxidation of (4*R*)-Me$_3$MQPH with a weak oxidizing reagent (e.g., 2-chloro-1,4-benzoquinone: **Q1** or 1,4-benzoquinone: **Q0**), or the reaction prefers the *syn*-conformation at the transition state. As a general trend, the stereospecificity decreases at higher reaction temperatures. In contrast, the favorable conformation at the transition state of the reaction with a relatively strong oxidizing reagent (e.g., **Q4**) in the presence of magnesium ion is anti and the stereospecificity increases with an increase in the reaction temperature. That is, in both cases, the elevated temperatures tend to form the *R*-product. The trend is mathematically indicated by negative slopes for most of the straight lines shown in Fig. 2.

The effect of magnesium and other metal ions on the reaction of NAD(P)H analogs was studied extensively,[11—19)] and it has been proposed that magnesium ion forms a ternary complex with the other two reagents to bring them into closer contact to activate both molecules (Fig. 3).[11—14)] At the same time, the association constant, K_{ass}, which was measured by the reported method, predicts that there remains certain amount of uncomplexed Me$_3$MQPH molecules under the reaction conditions employed presently.[20)]

Total vision of the reaction in the presence of magnesium ion, therefore, comes out as follows: The reaction with a less reactive quinone requires the assistance of a magnesium ion. The magnesium ion contributes to fix most of Me$_3$MQPH molecules in the *syn*-conformation at the ground state.[21)] Since the complex achieves the transition state under the molded conditions, the transition state structure has the same con-

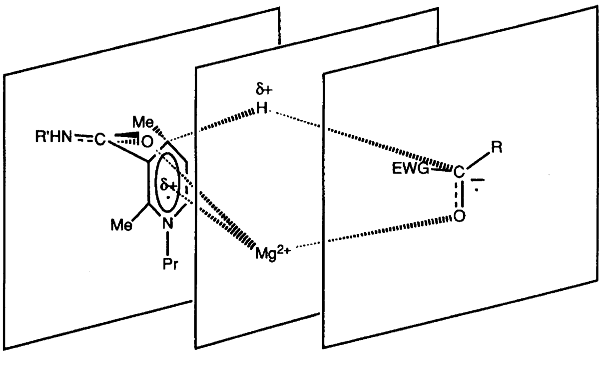

Fig. 3. Schematic illustration of the transition state for the initial electron transfer process.

figuration as depicted in Fig. 3. Here, Gibbs energy of activation from the complex plays an important role to determine the stereochemistry of the transition state, then, that of the product. It is understood from Table 2 that the reaction to the *S*-product is energetically preferred because of favorable enthalpy of activation ($\delta\Delta H^{\neq}{}_{R-S} > T\delta\Delta S^{\neq}{}_{R-S} \geq 0$). To the contrary, the route to the *R*-product is favored by the entropy of activation ($T\delta\Delta S^{\neq}{}_{R-S} > \delta\Delta H^{\neq}{}_{R-S} \geq 0$). The *syn*-specificity at the transition state in these reactions, thus, comes from favorable enthalpy term which exceeds the *anti*-specific entropy term.

On the other hand, a quinone with a high reactivity can oxidize Me_3MQPH without the assistance of magnesium ion. It will be demonstrated in the succeeding paper that the ternary complex in the oxidation of Me_3MQPH with chloranil does not exist even in the presence of excess magnesium ion in contrast to the reaction with 1,4-benzoquinone.22) Kinetic parameters listed in Table 2 indicates also that the parameters for the reactions with a reactive quinone in the presence and absence of magnesium ion are the same within experimental error revealing that the reacting species in both reactions are the same. The *R*/*S* ratios in the product also appear similarly in both reactions (cf. Figs. 2a and 2e).

It is noteworthy that, although relative importance of the enthalpy and entropy terms depends on the reactivity of the quinone, the enthalpy term always asserts the *syn*-preference: At least the *anti*-conformation is not preferred by the enthalpy term ($\delta\Delta H^{\neq}{}_{R-S} \geq 0$) within experimentally acceptable value. Thus, only when the entropy term chooses the preference, the *R*-product is allowed to be formed predominantly.4) Namely, **Q4**, which is a highly electron-deficient quinone, exerts the entropy-controlled *anti*-preference.

The stereospecificity of the reaction with Me_3PNPH in the presence of magnesium ion is far more shifted toward the *S*-preference.3) Since the error in measuring such a largely shifted value is large, and moreover, the experimentally obtained *R*/*S* ratio is rather labile depending on the reaction conditions, we concluded that it is meaningless to discuss on the kinetic parameters in this system. So the *R*/*S* ratios in the products, Arrhenius plots, and kinetic parameters are all neglected from the Tables and Figs.

Reaction in the Absence of Magnesium Ion. The reaction in the absence of magnesium ion was also studied to obtain detailed insight into the role of magnesium ion. Since the yields of products from the reactions of Me_3MQPH with less reactive reagents, however, are very low (5—10% in the reaction with **Q1** and 0% with **Q0**), the data from these reactions are excluded from the discussion. Nevertheless, in the reaction of Me_3MQPH with **Q2**, it will be safe to conclude that the stereospecificity does not change appreciably throughout the temperatures studied, which, in turn, indicates that the enthalpy term plays small role to determine the *R*/*S*-preference. Therefore, the *R*/*S*-preference in this reaction is controlled by entropy and since the entropy of activation is larger for the *anti*-conformational transition state than for the other ($\delta\Delta S^{\neq}{}_{R-S} \geq 0$), Gibbs energy of activation favors in affording the *R*-predominant product in contrast to the reaction in the presence of magnesium ion.

It should be noted that the preferences in the reactions with **Q2** and **Q1** change from *S* to *R* when magnesium ion is subtracted from the reaction system. The shift in preferency suggests that entropy term becomes the predominant factor in the absence of magnesium ion.

The term "entropy" can be substituted by "probability of the reaction to occur". The above-mentioned result suggests, therefore, that the effective encounter between the reducing and oxidizing reagents occurs quite hardly without magnesium ion in the reaction with less reactive quinones.7) The productive encounter complex which promotes an electron to transfer from the reducing reagent to the oxidizing one can proceed further reaction to migrate the proton. Those which could not undergo the electron transfer returns to the initial state. This encounter process, but not the proton-migration process, determines the stereochemistry of the reaction. Once an electron starts to transfer within the encounter complex, the system enters into an irreversible process. The possibility of the reaction to occur (i.e., entropy) governs the stereochemistry of the reaction.

Since Me_3PNPH is more reactive than Me_3MQPH, the reliability of the values obtained here is much better than that for Me_3MQPH. In the sense that the stereochemical preference changes depending on the reactivity of the oxidizing reagent, this reaction system is similar to that of Me_3MQPH with magnesium ion. Here again, the enthalpy of activation favors the *syn*-conformation, whereas the entropy term prefers the *anti*-conformation.

The reaction with **Q4** again proves the idea that the *anti*-conformation becomes to be preferred when the entropy term associated with the *syn*-conformation becomes extraordinary unfavorable. It should be noted that the difference in enthalpy between the *syn*- and *anti*-conformations in this reaction is the largest among the systems studied in favor of the former conformation. Nevertheless, the largest entropy difference shifts the preference toward the *anti*-side.

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5) The *syn*-conformational transition state is the one, in which the carbonyl oxygen of the side-chain carbamoyl group and the dissociating hydrogen on the C_4-position point the same face and vice versa.

6) We believe that the encounter complex with a correct conformation only can enter into the irreversible electron-transfer process. Therefore, the stereochemistry of the reaction has already been defined at the stage of the transition state for the initial electron-transfer step.$^{7)}$ Also see latter discussions.

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20) The association constant between Me_3MQPH and a magnesium ion in acetonitrile have been estimated based on UV spectroscopy: cf. D. J. Creighton, Ph. D. Thesis, University of California, Los Angeles, 1972, pp. 174—175. The calculated K_{ass} is 1.2×10^3. Therefore, uncomplexed Me_3MQPH which remains in the reaction mixture under the reaction conditions employed (each 1 mM of Me_3MQPH and magnesium ion) is calculated to be ca. 60%.

21) From ^{1}H NMR study, it has been elucidated that the *syn*/*anti* ratio, which is ca. 25/75 at the ground state without magnesium ion, changes dramatically in the presence of magnesium ion toward the *syn*-side so as to make *syn*/*anti*= ca. 70/30.$^{22)}$

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