April, 1975]   BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 48(4), 1233—1236 (1975)   1233

Kinetics and Steric Course of the Substitution of Various Olefins for the Asymmetric Olefin in *trans*(*N*,olefin)-Chloro-L-prolinato-*trans*-2-buteneplatinum(II)

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(Received December 25, 1974)

Replacement of the coordinated *trans*-2-butene in *trans*(*N*,olefin)[PtCl(L-pro)(*S*,*S*-*trans*-2-butene)] (L-pro= L-prolinate anion) by various olefins in acetone has been studied at −20 to +23 °C. The rate is proportional to concentrations of the complex and the olefin nucleophile. No solvent path is observed. The second order rate constant k_2 (10^{-4} to 10^{-1} M^{-1} s^{-1} at 8.0 °C) can be the measure of each substitution. The $\Delta H^{\neq}$ is around 10 kcal/mol, and $\Delta S^{\neq}$ ranges from −25 to −46 cal/mol K. Substitution of *cis*-2-butene for the asymmetrically coordinated *trans*-2-butene-^{3}H gives equal k_2's on the measurement of CD strength and on that of isotopic exchange. Similar substitution of *trans*-2-butene gives significantly larger k_2 on isotopic exchange than that on CD measurement, indicating sterically selective substitution with retention of configuration. Substitution of ethylene derivatives with various groups on the carbon atoms gives different k_2's depending on the kind of substituents. The steric interaction between the olefin nucleophile and the coordinated ligands seems to be a very important factor in determining the ease of substitution.

In a previous paper we reported the inversion of coordinated olefins in the diastereoisomer *trans*(*N*, olefin) [PtCl(L-pro)(*S*,*S*-*trans*-2-butene)] (L-pro=L-prolinate anion) and its 2-methyl-2-butene analogue, and proposed an S_N2 mechanism involving nucleophilic attack of added olefin molecules.[1] We have attempted to verify the mechanism by use of various olefin nucleophiles including *cis*- and *trans*-substituted ethylene derivatives. On comparing the rates of olefin exchange measured by CD spectroscopy and by isotopic exchange technique with *trans*-2-butene-^{3}H, a novel stereoselectivity was detected in the substitution of *trans*-2-butene for the coordinated *S*,*S*- and *R*,*R*-*trans*-2-butene-^{3}H in the complex in acetone. This paper deals with the verification, and the discussion on mechanism of stereoselectivity with reference to the steric interaction between the incoming olefin molecule and the coordinated ligands.

Experimental

Materials. *trans*(*N*,olefin)[(L-pro)(*S*,*S*-*trans*-2-butene)] was prepared as in Ref. 2. *trans*-(*N*,olefin)[PtCl(L-pro)(*S*,*S*- or *R*,*R*-*trans*-2-butene-^{3}H)]: *trans*-2-Buene-^{3}H was synthesized by the known method,[3] slightly modified to suit for a radiochemical synthesis. Lithium aluminum hydride (1.08 g) containing lithium aluminum tritide (5 mCi, 1.66 mg, New England Nuclear Co.) suspended in diethyleneglycoldiethyl ether was added to a slight excess of *trans*-1,4-dibromo-2-butene in the same solvent in a current of nitrogen. The product, *trans*-2-butene-^{3}H was trapped in dry ice–acetone (Chemical yield 0.8 g, radiochemical yield 16%). The ligand was added to *trans*(*N*,olefin)[PtCl(L-pro)(ethylene)] in acetone. The product was resolved[2] to give *trans*(N,olefin)-[PtCl(L-pro)(*S*,*S*- or *R*,*R*-*trans*-2-butene-^{3}H)]. The purity of the final product (*ca.* 2×10^{-2} μCi/mg) was examined by UV absorption spectrum.

Other Reagents: Extra pure grade *trans*-2-butene and *cis*-2-butene were used without further purification. The purity was checked by gas chromatography. Chemical grade *trans*-1,4-dichloro-2-butene, *cis*-2-butene-1,4-diol, and *cis*- and *trans*-1,2-dichloroethylene were distilled under a reduced pressure. Maleic and fumaric acid were recrystallized from acetone. *cis*-1,4-Dichloro-2-butene[4] and *trans*-1,4-dibromo-2-butene[5] were synthesized by the ordinary method.

Procedure. *Kinetic Runs for Loss of Optical Activity:* The complex solution in acetone was cooled, and a certain amount of cooled olefin solution in acetone added with a pipet. The solution was transferred into the cell box of the spectrometer which had been thermostated at the reaction temperatures (8.0, 17.0 and 23.6±0.3 °C). The $\Delta\varepsilon$ value at 370 nm was continuously recorded. The concentrations of the complex and the olefins at the measured temperature were calculated by taking the density of acetone at the given temperatures into consideration.

Kinetic Runs for Isotopic Exchange and Accompanied Loss of Optical Activity: The reaction mixture was similarly prepared and dispensed into 5—9 small glass-stoppered test tubes. They were kept in a thermostat at 8.0 or −20.0 (±0.3) °C, and taken out one by one at appropriate time intervals. The reaction was quenched by immersing the tubes in liquid nitrogen. Free olefin and acetone were evaporated off *in*

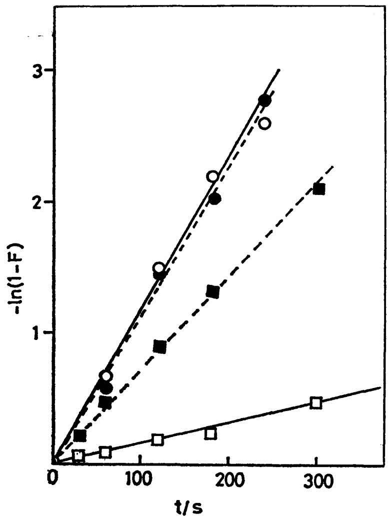

Fig. 1. Decrease in CD strength and in specific counting rate of the complex *trans*(*N*,olefin)[PtCl(L-pro)-(*S*,*S*-*trans*-2-butene-^{3}H)] in acetone with reaction time. Open marks with solid lines by CD measurement and full marks with broken lines by isotopic exchange.
Circles, with *cis*-2-butene (0.17 M) at −20 °C; squares, with *trans*-2-butene (0.19 M) at 8.0 °C.

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vacuo at dry ice–acetone temperature and room temperature, respectively. The residue was dissolved in ethanol and its absorption spectrum, CD strength and β-activity were measured. The decrease in CD strength with time obeyed first order rate law as shown in Fig. 1.

Calculation of the Exchange Constant: In our experiments the complex concentration was very small as compared with the olefin solution. Hence McKay formula can be simplified, and the isotopic exchange constant was approximated by the first order kinetic formula Eq. (1) (Fig. 1)

$$k_{0(\mathrm{iso})} = -\ln(1-F)/t \qquad (1)$$

where F is the fraction of reaction expressed by $(x_t - x_\infty)/(x_0 - x_\infty)$, x's being the specific counting rate of the recovered complex.

Apparatus. Circular dichroism was measured with a JASCO Model ORD/UV-5 Spectrometer with CD attachment. Absorption spectra were recorded with a Hitachi 323 Spectrometer. β-Activity of ^{3}H was recorded with a Nuclear-Chicago Unilux II–A liquid scintillation counter. A Komatsu-Yamato Coolnics and Haake KT 33 thermostat were used.

Results

Isotopic Exchange. The reaction mixtures gave equal absorption spectra throughout given kinetic runs, and the recovered complexes gave almost identical absorption spectrum with the original complex in ethanol. The CD strength at 370 nm in ethanol and the β-activity of the recovered complexes decreased as the reaction vessels were kept longer in the thermostat. All the data of isotopic exchange obeyed the kinetic law of Eq. (1). Hence the $k_{0(\mathrm{iso})}$ is the first order rate constant with respect to the complex concentration. The k_0 values are proportional to the concentration of added olefins (Fig. 2) and Eq. (2) is given in the range 0.05 to 0.3 M.

$$k_{0(\mathrm{iso})} = k_{2(\mathrm{iso})}[\mathrm{olefin}] \qquad (2)$$

The CD strength of the recovered complex also obeyed first order rate law with respect to the complex concentration and the rate constant $k_{0(\mathrm{cd})}$ is the first order rate constant. When the olefin concentration of the reaction mixture was changed, Eq. (3) was substantiated.

$$k_{0(\mathrm{cd})} = k_{2(\mathrm{cd})}[\mathrm{olefin}] \qquad (3)$$

The k_2's are second order rate constants, and tabulated in Table 1.

Table 1. Second order rate constants of the substitution of 2-butene for the coordinated *trans*-2-butene in [PtCl(L-pro)(*S,S*- or *R,R*-*trans*-2-butene)] in acetone

Added olefin[a]	*cis*-2-butene		*trans*-2-butene[c]	
T/°C	8.0	−20.0	8.0	−20.0
$k_{2(\mathrm{cd})SS}/10^{-3}\mathrm{M^{-1}s^{-1}}$ [b]	347	70.9±7.6	6.2	0.9
$k_{2(\mathrm{iso})SS}/10^{-3}\mathrm{M^{-1}s^{-1}}$	—	70.2±4.1	32.3	5.6
$k_{2(\mathrm{cd})RR}/10^{-3}\mathrm{M^{-1}s^{-1}}$ [b]	—	—	5.5	(0.9)[d]
$k_{2(\mathrm{iso})RR}/10^{-3}\mathrm{M^{-1}s^{-1}}$	—	—	16.6	(2.1)[d]

a) Concn range: [2-butene], 0.05—0.3 M; [complex], 0.0015 M. b) *SS* and *RR* in the suffices denote the configuration of coordinated *trans*-2-butene in the original complex. cd and iso in parentheses denote that the k_2's were obtained by the measurement of CD strength and isotopic exchange, respectively. c) See the legend of Fig. 2. d) Calcd from only one run.

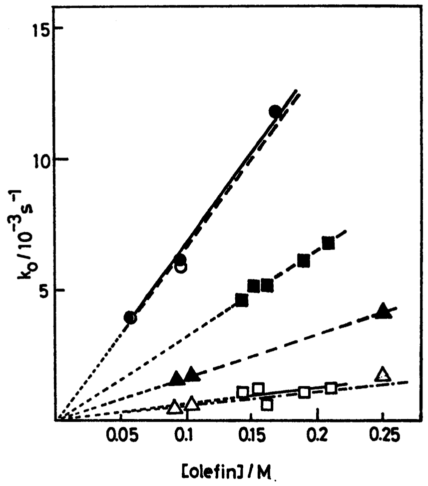

Fig. 2. Dependence of the rate constant k_0 upon the olefin concentration in acetone.
Open marks by CD measurement ($k_{0(\mathrm{cd})}$) and full marks by isotopic exchange ($k_{0(\mathrm{iso})}$). —○— and --●-- substitution of *cis*-2-butene for *S,S*-*trans*-2-butene at −20 °C; —□— and --■-- substitution of *trans*-2-butene for *S,S*-*trans*-2-butene at 8.0 °C; —△— and —▲— substitution for *R,R*-*trans*-2-butene at 8.0 °C. (The free *trans*-2-butene contained 1.0% *cis*-2-butene, and the individual plots were corrected for the contribution of the *cis*-isomer.)

Substitution. When those olefins in Table 3 were added to the *trans*(N,olefin)[PtCl(L-pro)(*S,S*-*trans*-2-butene)] in acetone, the UV absorption changed little, whereas the CD strength at 370 nm decreased. The final CD pattern was almost equal to that of *trans*(N,olefin)[PtCl(L-pro)(ethylene)], which gives only the vicinal effect of coordinated L-prolinate. The rate of decrease in CD strength obeyed first order rate law with respect to the complex concentration, and the rate constant $k_{0(\mathrm{cd})}$ was proportional to the olefin concentration. Second order rate constants $k_{2(\mathrm{cd})}$ can be calculated as in Eq. (3). They are listed in Table 3 together with the activation parameters obtained by the measurements at 8.0, 17.0 and 23.6 (±0.3 °C).

Discussion

Replacement of olefins in *trans*(N,olefin)[PtCl(L-pro)(olefin)] complexes by other olefins gave little change in the visible and UV absorption spectrum. Throughout the present isotopic exchange and CD measurements, the absorption spectra of the reaction mixtures and the recovered species gave little change. The geometrical isomers *trans*(O,olefin) [PtCl(L-pro)(olefin)] give different absorption patterns in UV region. Hence we can conclude that the essential structure of the complex remained unchanged throughout the present experiments, and only substitution of olefins for the coordinated olefin has taken place.

Nature of the decrease in CD strength. The substitution reaction of Eq. (4) with *cis*-2-butene

$$[\mathrm{PtCl(L\text{-}pro)}(S,S\text{-}trans\text{-}2\text{-butene})] + cis\text{-}2\text{-butene} \rightleftharpoons [\mathrm{PtCl(L\text{-}pro)}(cis\text{-}2\text{-butene})] + trans\text{-}2\text{-butene} \qquad (4)$$

gave equal $k_{2(\mathrm{iso})}$ and $k_{2(\mathrm{cd})}$ (Table 1). Hence the

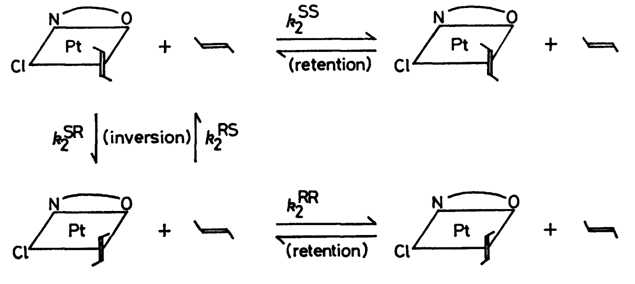

Fig. 3. Individual routes of the substitution of *trans*-2-butene for *S*,*S*- and *R*,*R*-*trans*-2-butene in the complex. Arcs represent L-prolinate. (*cf.* the note for Fig. 4).

decrease in CD strength at 370 nm should be exclusively due to the intermolecular substitution. Our proposal in Ref. 1 is thus verified. It is also made clear that there is no local proton exchange between free and coordinated olefin molecules.

Stereoselectivity. In the reaction between *trans*-2-butene and *trans*(*N*,olefin)[PtCl(L-pro)(*S*,*S*-*trans*-2-butene)], $k_{2(\mathrm{iso})}$ is significantly bigger than $k_{2(\mathrm{cd})}$. The former includes substitutions both with retention and with inversion of configuration of coordinated olefin, and the latter does only substitution with inversion of configuration. The same is true for the replacement of coordinated *R*,*R*-*trans*-2-butene. Hence the reactions are summerized as shown in Fig. 3. When the second order rate constants of individual routes of substitution between free *trans*-2-butene and coordinated *S*,*S*- and *R*,*R*-*trans*-2-butene are named as in Fig. 3, the following relationships are given between the individual k_2's and the observed k_2's. (The subscripts *SS* and *RR* denote the configuration of *trans*-2-butene in the original complexes.)

$$k_{2(\mathrm{iso})SS} = k_2^{SS} + k_2^{SR} \tag{5}$$

$$k_{2(\mathrm{iso})RR} = k_2^{RR} + k_2^{RS} \tag{6}$$

$$k_{2(\mathrm{cd})SS} = k_2^{SR} + k_2^{RS} \tag{7}$$

$$k_{2(\mathrm{cd})RR} = k_2^{RS} + k_2^{SR} \tag{8}$$

When the ratio of k_2^{SR} and k_2^{RS} is defined as Eq. (9),

$$K_{(SR)} = k_2^{SR}/k_2^{RS} \tag{9}$$

the $K_{(SR)}$ should be related to the CD strength due to the coordinated olefin in the equilibrated solution. The CD pattern of the reaction mixtures at infinite time is practically identical with that of non-prochiral olefin complexes such as *trans*(*N*,olefin)[PtCl(L-pro)(ethylene)], and $K_{(SR)}$ can be approximated to be unity. Hence Eq. (10) is substantiated.

$$k_{2(\mathrm{cd})SS} = 2k_2^{SR} = 2k_2^{RS} = k_{2(\mathrm{cd})RR} \tag{10}$$

Table 2 gives the rate constants calculated in accordance with Eqs. (5) to (8). The k_2^{SR} and k_2^{RS} values obtained by use of diastereoisomers of *trans*(*N*,olefin)[PtCl(L-pro)(*S*,*S*- or *R*,*R*-*trans*-2-butene)] as substrate coincide with each other, indicating equal probability of inversion. The ease of substitution reaction with retention of configuration seems to differ from each other so that k_2^{SS} is *ca.* twice as big as k_2^{RR}. The ratio of second order rate constants with retention and with inversion of configuration are *ca.* 10 and 5, respectively for the complexes with *S*,*S*- and *R*,*R*- *trans*-2-butene ligand.

This fact indicates that both diastereoisomers are subject to olefin exchange more easily with retention of configuration than with inversion of configuration. Such a stereoselectivity is of a novel kind, and the present result is the first example. The reason why such a stereoselectivity is observed cannot be made clear at the present stage. The kinetic formulae have no term for the solvent path, and solvent molecules do not seem to give significant contribution. Difference in affinities between *trans*-2-butene nucleophile and the diastereoisomers is quite unlikely, and some kind of steric effect between the nucleophile and the coordinated ligands should be responsible. The $\Delta H^{\ddagger}$ values for k_2^{SS} and k_2^{SR} are 8.2 and 9.1 kcal mol^{-1} and the $\Delta S^{\ddagger}$ values are -38 and -40 cal mol^{-1} K^{-1}, respectively. These figures are only approximate, because measurements were made at two temperatures.

TABLE 2. CALCULATED RATE CONSTANTS FOR INDIVIDUAL ROUTES OF SUBSTITUTION AND THEIR RATIOS (*cf.* Fig. 3)

T/°C	+8.0	−20.0
$k_2/10^{-3}\mathrm{M}^{-1}\,\mathrm{s}^{-1}$		
k_2^{SS}	29	5.1
k_2^{RR}	14	(1.7)$^{c)}$
k_2^{SR} $^{a)}$	3.1	0.45
k_2^{SR} $^{b)}$	2.8	(0.46)$^{c)}$
k_2^{SS}/k_2^{RR}	2.1	(3)$^{c)}$
k_2^{SS}/k_2^{SR} $^{a)}$	9.4	11
k_2^{RR}/k_2^{SR} $^{b)}$	5.0	(3.7)$^{c)}$

a) The original complex contained *S*,*S*-*trans*-2-butene (Eqs. (7) and (9)). b) The original complex contained *R*,*R*-*trans*-2-butene (Eqs. (8) and (9)). c) Calcd from only one run.

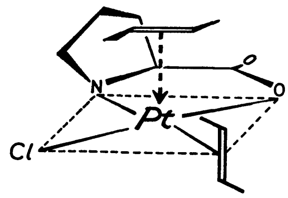

Fig. 4. Probable nucleophilic attack of *trans*-2-butene towards the complex.
The coordinated *trans*-2-butene was claimed to be rotating around the bond axis between Pt(II) and C=C[6]; the ligand is so illustrated as to make the configuration clear.

Figure 4 shows the possible mode of approach of the olefin nucleophile to the complex. (It was claimed that the coordinated olefin is rotating at a high rate around the metal–(C=C) axis[6]; the figure was so drawn as to make the configuration of the ligand clearer.)

Substitution. Whenever a large excess of olefin is added to the *trans*(*N*,olefin)[PtCl(L-pro)(*S*,*S*-*trans*-2-butene)] solution in acetone, the coordinated olefin is replaced by the added olefin and only a negligible amount of the original complex remains after a certain lapse of time. The CD pattern of the reaction mixture at infinite time is almost identical with that of [PtCl(L-pro)(ethylene)], and no other reaction than substitution of the olefin is feasible. The substitution

TABLE 3. SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE SUBSTITUTION OF VARIOUS OLEFINS FOR THE *S*,*S*-*trans*-2-BUTENE IN [PtCl(L-pro)(*S*,*S*-*trans*-2-BUTENE)] IN ACETONE MEASURED BY CD STRENGTH

Added olefin	R[b]	$k_{2(cd)}/10^{-3}M^{-1}s^{-1}$			$\varDelta H^{\neq}$	$\varDelta S^{\neq}$
		8.0 °C	17.0 °C	23.6 °C	kcal·mol^{-1}	cal K^{-1} mol^{-1}
cis- 2-Butene	CH_3	347	480	621	9.6	−26
trans-		4.1	6.3	9.7	8.4	−39
cis- 1,2-Dichloroethylene	Cl	0.63		1.08	(8)	(−44)
trans-		0.081		0.22	(10)	(−40)
Maleic acid	COOH	18.5		47	(10)	(−32)
Fumaric acid	COOH	1				
cis- 1,4-Dichloro-2-butene	CH_2Cl	150		310	(7)	(−36)
trans-		8.8		19.2	(8)	(−40)
cis-2-Butene-1,4-diol	CH_2OH	335		775	(9)	(−29)
trans-1,4-Dibromo-2-butene	CH_2Br	8.05		22	(10)	(−31)
2-Methyl-2-butene[a]	CH_3	3.41	5.35	7.29	8.0	−41
2,3-Dimethyl-2-butene[a,c]	CH_3			0.22	8.0	−46
Styrene[a]	C_6H_5	303	480	621	7.6	−34

a) Data from Ref. 1. b) Substituents on ethylene. c) Activation papmeters from data at 23.6, 31.5 and 39.5 °C.

of the olefins listed in Table 3 obeyed Eq. (3) and the $k_{2(cd)}$ and the activation parameters are given there.

Electronic Effect: When the k_2 values are compared with one another for either the *cis* or the *trans* olefins with one substituent on each of ethylenic carbon, an overall decrease in rate is seen in the following squence.

$-CH_3 \simeq -CH_2Cl \simeq -CH_2OH \simeq -CH_2Br > -COOH > -Cl$

Introduction of electro-nagative substituents on ethylenic carbon decreases the rate significantly. More electro-negative chlorine (3.25) decreases the rate to a greater extent than less electro-negative carboxyl[7] (2.60)(*cf.* methyl 2.50) does. Increase in electronegativity of the substituent should bring about decrease of electron density in the bonding orbital of the ethylene moiety, and thus decrease of the σ-bond strength between platinum(II) and olefin. Our previous proposal that strength of the σ-metal–ligand bond would be responsible in determining the substitution rate of olefins[1], has thus found further experimental support.

Substitution of chlorine, bromine and hydroxyl for the methyl protons of 2-butene does not give big change in k_2's. The order of k_2 change is different for the *cis*-olefins and the *trans*-olefins. The significance of k_2 can be different for the two kinds of geometrically isomeric olefin nucleophiles (see below), and no further discussion will be made at the present stage.

Steric Effect: An overall trend is seen in Table 3 that the *cis*-isomers give larger k_2 values than the *trans*-isomers do. It is also seen that increase in number of methyl groups on ethylenic carbons decreases the k_2 quite remarkably. These factors should be ascribed to some kind of steric effect at the rate-determining step.

Since the *trans*-isomers and 2-methyl-2-butene are prochiral and can bring forward stereo-selectivity as mentioned above, the $k_{2(cd)}$ value of their substitution reckons the rate of substitution with inversion of configuration. On the other hand, the *cis*-isomers, styrene and 2,3-dimethyl-2-butene are not prochiral and their k_2 values represent the real rate of substitution. Hence the k_2 values for these two series of olefins should not be directly compared. However, the ratio of k_2's for substitution with retention and those with inversion of configuration is not extremely big; *i.e.* it is *ca.* 10 for *trans*-2-butene (Table 2). Hence such comparisons should not be very unfair so far as the discussion remains qualitative.

The olefin nucleophiles in Table 3 (except those with very electro-negative groups on ethylenic carbons) could be classified into three groups according to the k_2 values. The *cis*-isomers and styrene give the biggest k_2's, 2,3-dimethyl-2-butene gives the smallest k_2, and others, *i.e.* the *trans*-isomers and 2-methyl-2-butene, give intermediate values. Members of each group seem to have common feature in their structures. The first group has substituent only on one side of the C=C bond axis and has two protons on the other side. The third group has at least one proton on one side of the axis, and 2,3-dimethyl-2-butene has no proton on either side. If the nucleophilic attack of the olefin molecule were visualized as shown in Fig. 4, the assemblage around the C=C bond axis would be responsible in determining the ease of approach to the substrate. It seems as if the number of vacant site (*i.e.* with proton) on one side of the C=C bond axis were an important factor in determining the ease of approach.

The $\varDelta H^{\neq}$ values in Table 3 do not give useful information, because they are more or less similar to one other, when experimental errors are taken into consideration. The $\varDelta S^{\neq}$ values do not differ very significantly from one another but could be reckoned to reflect the steric factor to some extent.

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