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The Ring Opening Reaction of Cyclopolysilanes, $(R_2Si)_n$ $(n=3—6)$, with Iodine. A Kinetic Study

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Synopsis. Reactions of a series of peralkylcyclopolysilanes with iodine were found to proceed via second-order kinetics. Rate constants show that, in general, the smaller rings react faster than larger rings. Values of the activation parameters, E_a and $\Delta G^{\neq}$, decreased with the decreasing ring size and are parallel with those of the oxidation potentials and of the lowest transition energies.

It is well-known that the Si-Si bond in cyclopolysilanes undergoes electrophilic cleavage reaction by halogens to give the corresponding ring-opening adducts, α,ω-dihalopolysilanes. Although several studies on the halogen-cleavage reactions of cyclopolysilanes have appeared so far,1) there are no reports on their kinetic behaviors. In our continuing work of polysilanes,1e,2) we now report a kinetic study on the ring-opening reactions of a series of peralkylcyclopolysilanes with iodine (Eq. 1).

$$[R_2Si]_n + I_2 \rightarrow I(R_2Si)_nI \quad (n = 3 - 6) \qquad (1)$$

Rates were determined by spectroscopic method and the reaction was found to obey typical second-order kinetics within 20% completion. Unfortunately, the reactions of the smallest ring, $[(Bu^tCH_2)_2Si]_3$, was so fast that the rate constant could not be betermined by the present method at any convenient temperatures.

Table 1 shows the absolute rate constants at three different temperatures together with the relative rates of the cyclopolysilanes at 20 °C, that of $Me_3SiSiMe_3$ being taken as standard. The relative rates of the cyclopolysilanes (20 °C) were thus found to fall in the order:

$$[(Bu^tCH_2)_2Si]_3 \gg [Bu^tMeSi]_4(241) \approx [Pr^i{}_2Si]_4(237) >$$
$$[Bu^s{}_2Si]_4(58) > [Bu^n{}_2Si]_5(11) \approx [Pr^n{}_2Si]_5(8) >$$
$$[Me_2Si]_6(1) \approx Me_6Si_2(1)$$

As might be expected from the intrinsic internal strain, the smaller rings generally react faster than

Table 1. The Rate Constants in the Reactions of Cyclopolysilanes with Iodine in Dichloromethane3)

Compound	$k_2\times10^2/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$ a)			$k_x/k_{Me_6Si_2}$ b) (293 °K)
	303 °K	293 °K	283 °K	
$[(Bu^tCH_2)_2Si]_3$	— c)	— c)	— c)	5500 d)
$[Bu^tMeSi]_4$	730	563	393	241
$[Pr^i{}_2Si]_4$	817	553	383	237
$[Bu^s{}_2Si]_4$	185	136	92.5	58
$[Bu^n{}_2Si]_5$	42.5	30.9	17.9	11
$[Pr^n{}_2Si]_5$	35.6	23.5	14.7	8
$[Me_2Si]_6$	5.24	3.08	1.64	1
$Me_3SiSiMe_3$	1.00	0.583	0.314	1

a) Average value from three runs. b) Number of the Si-Si bonds in cyclopolysilane was taken into account for the calculations. c) Reaction rate was too fast to be determined. d) Value estimated from the regression line (correlation coefficient, $\gamma=0.94$) obtained on the basis of the relative rates in the larger rings, $n=4—6$.

Table 2. Activation Parameters for the Ring Opening Reactions and Values of Oxidation Potential (E_{pa}) and Longest Absorption Wavelength (λ_{max}) for the Cyclopolysilanes3,4)

Compound	E_a	$\Delta S^{\neq}_{293}$	$\Delta G^{\neq}_{293}$	E_{pa} a)	λ_{max} b)
	kcal mol⁻¹	cal mol⁻¹ K⁻¹	kcal mol⁻¹	V vs. SCE	nm
$[(Bu^tCH_2)_2Si]_3$	— c)	— c)	— c)	+0.44	310sh
$[Bu^tMeSi]_4$	5.29	−34.6	16.1	+0.94	300
$[Pr^i{}_2Si]_4$	6.56	−38.9	16.1	+1.00	290sh
$[Bu^s{}_2Si]_4$	6.00	−39.3	16.9	+1.10	290sh
$[Bu^n{}_2Si]_5$	7.49	−37.4	17.9	+1.40	262
$[Pr^n{}_2Si]_5$	7.69	−37.2	18.0	+1.42	260
$[Me_2Si]_6$	10.0	−33.2	19.1	+1.45	258sh
$Me_3SiSiMe_3$	9.94	−36.8	20.1	— c)	193.5

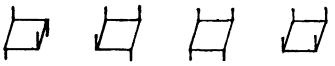
a) The first anodic peak potential in MeCN; see Ref. 4. b) The longest-wavelength absorption band in cyclohexane; see Ref. 2b and 2d. c) Not determined.

larger rings. This trend shows that the principal factor in determining the reaction rates is ring strain, although the rates for the cyclotetrasilanes vary in a range of 1—4 times as the steric bulk of the substituents varies.

Table 2 lists the activation parameters, electrochemical oxidation potentials, and the longest-wavelength UV absorptions. Values of activation energy decrease with the decreasing ring size and are parallel with those of the oxidation potentials as well as the lowest transition energies. Thus, the promotion of the HOMO level in smaller rings due to the increasing ring strain can be seen in these energy terms.[3—5] The large negative values of $\Delta S^{\neq}$ indicate considerable loss of freedom in the transition states, which are common in bimolecular reactions. In short, the rates and activation parameters for the reactions of the cyclopolysilanes are primarily related to the ring size, although other factors such as steric congestion at the reaction site and the geometrical structures of the ring system[6] have to be also taken into account. Further investigation for such ring opening reactions will be described elsewhere.[7]

Experimental

Materials. All the samples used for the rate study were the cyclopolysilanes reported previously.[2d] The sample of $[\mathrm{Bu}^t\mathrm{MeSi}]_4$ was a mixture comprising four stereoisomers (a—d), the distribution of which was determined by a high-resolution NMR spectrum (400 MHz) (see Ref. 2d):


(a) (b) (c) (d)

(a)/(b)/(c)/(d)=13/73/12/2
|: *t*-Butyl group

Measurements of the reaction rates. The CH_2Cl_2-solution of approximately equimolar concentrations of two substrates (a slightly excess in cyclosilanes) ($1—6\times10^{-3}$ mol dm^{-3}) were prepared and kept in a constant temperature bath. Two 2-ml solutions of the substrates were mixed and allowed to react in a spectrometer. The rates were determined by recording concentrations of iodine as a function of time which were monitored by the UV absorption of iodine at λ 555 nm. The rate constant of $[\mathrm{Bu}^t\mathrm{MeSi}]_4$ sample was determined as a total average of the isomer mixture (see above).

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