

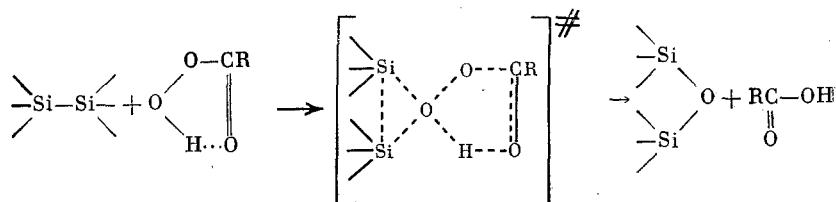
MECHANISM OF OXIDATION OF ORGANOPOLYSILANES

BY PEROXY ACIDS

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Organosilanes are oxidized by peroxy acids to the corresponding siloxanes [1, 2]; it is assumed that the  $\beta$  O atom of the per acid attacks electrophilically the  $\sigma$  Si-Si bond of the polysilane, acting as a nucleophilic center



When electronegative substituents (Cl and OR) are introduced into a polysilane, one should expect significant retardation of the reaction. However, we [3, 4] and Helmer and West [5] obtained the opposite result. It was assumed [4] that the reaction is accelerated by  $n$ ,  $\sigma$  bonding or intramolecular coordination in substituted polysilanes, which can lead to an increase of the energy of the highest occupied molecular orbital (HOMO) of the polysilane [6] and to an increase of its donor ability with respect to electrophilic reagents.

To determine the regularities in the energy change of the HOMO of a polysilane, which, as is known [7-9], is localized on the Si-Si bond, in the present paper we investigated the formation of charge-transfer complexes of tetracyanoethylene (TCE) with some peralkylated and chlorosubstituted polysilanes (Table 1). Charge-transfer complexes of organopolysilanes with TCE were investigated previously in [2], [6], [11], and [13-18], and a linear correlation of the ionization potentials with the frequencies of the charge-transfer band ( $\nu_{ct}$ ) was established [11, 13, 15-18]. We obtained the following data regarding these complexes.

1. Peralkylated polysilanes and organochloropolysilanes form weak contact-type complexes with TCE, as indicated by the low value of the complexation constant  $K_0 \approx 0.2$  liter/mole and lower. The value of  $-\Delta H$  of such complexes does not exceed 3 kcal/mole.
2. The presence of electron-donor  $n$ -Bu and Et substituents in compounds (II)-(IV) leads to a decrease of the charge-transfer frequency by 500-2100  $\text{cm}^{-1}$  in comparison with (I) containing Me substituents.
3. Elongation of the  $\text{Me}(\text{Me}_2\text{Si})_n\text{Me}$  polysilicon chain from  $n = 2$  to  $n = 3$  and 4 [compounds (I), (V), and (VI)] leads to a shift of  $\nu_{ct}$  by 2700 and 4600  $\text{cm}^{-1}$ , respectively, to the low-frequency region, which indicates an increase of the energy of the HOMO of the polysilane in accordance with [11] and [13].
4. Organochlorodisilanes (VII)-(IX) are characterized by a higher frequency of the charge-transfer band,  $\sim 26,500$   $\text{cm}^{-1}$ , and, therefore, by a higher first ionization potential ( $I_1^D$ ) than peralkylated disilanes (I)-(IV), for which the frequency is  $\sim 22,000$ - $24,000$   $\text{cm}^{-1}$ .
5. In the series of organochlorodi- and trisilanes (VII)-(XI) (with one Cl atom in the molecule), there are insignificant decreases of  $\nu_{ct}$  in going from  $\text{Me}_5\text{Si}_2\text{Cl}$  to  $\text{RMe}_2\text{SiSiMe}_2\text{Cl}$  ( $\text{R} = n$ - and  $\text{sec}$ -Bu) and a more significant decrease in going from  $\text{Me}_5\text{Si}_2\text{Cl}$  to chlorotrisilanes (X) and (XI), which indicates an increase of the donor properties of the Si-Si  $\sigma$  bond in this series.

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TABLE 1. Frequency of the Charge-Transfer Band ( $\nu_{CT}$ ), First Ionization Potential ( $I_1^D$ ), Equilibrium Constant of Complexation ( $K_0$ ), Heat of Formation ( $-\Delta H$ ) of Charge-Transfer Complexes of Organopolysilanes with TCE, and Rate Constant of Oxidation of Organopolysilanes by Peroxybenzoic Acid ( $k$ )

Compound	Polysilane	$\nu_{CT} \cdot 10^{-3}$ , cm <sup>-1</sup>	$I_1^D$ , eV		$K_0$ † liter/mole	$\epsilon$ , liters/(mole · cm)	$-\Delta H$ , kcal/mole	$k \cdot 10^3$ ‡ liters/(mole · min)
			calcu- lated*	lit. re- ference				
(I)	Me <sub>3</sub> SiSiMe <sub>3</sub>	23,8	8,68	8,69 [10]	—	—	—	8 (25)
(II)	<i>n</i> -BuMe <sub>2</sub> SiSiMe <sub>3</sub>	23,3	8,57	—	0,15±0,05	100	2	6
(III)	<i>n</i> -BuMe <sub>2</sub> SiSiMe <sub>2</sub> Bu- <i>n</i>	22,6	8,45	—	0,20±0,15	80	3	5
(IV)	Et <sub>3</sub> SiSiEt <sub>3</sub>	21,7	8,31	—	0,03±0,03	600	2	—
(V)	Me <sub>3</sub> SiSiMe <sub>2</sub> SiMe <sub>3</sub>	21,1	8,19	8,19 [10]	—	—	—	— (54)
(VI)	Me <sub>3</sub> Si(SiMe <sub>2</sub> ) <sub>2</sub> SiMe <sub>3</sub>	19,2	7,90	7,98 [10]	—	—	—	— (75)
(VII)	Me <sub>3</sub> SiSiMe <sub>2</sub> Cl	26,5	9,08	—	—	—	—	280 (330)
(VIII)	<i>n</i> -BuMe <sub>2</sub> SiSiMe <sub>2</sub> Cl	26,3	9,05	—	0,10±0,10	200	2	150
(IX)	<i>n</i> rop.BuMe <sub>2</sub> SiSiMe <sub>2</sub> Cl	26,3	9,05	—	—	—	—	180
(X)	Me <sub>3</sub> SiSiMe <sub>2</sub> SiMe <sub>2</sub> Cl	23,8	8,65	—	—	—	—	420
(XI)	(Me <sub>2</sub> Si) <sub>2</sub> SiMeCl	22,1	8,37	8,42 [8]	—	—	—	740
(XII)	ClMe <sub>2</sub> SiSiMe <sub>2</sub> Cl	29,0	9,48	—	—	—	—	150
(XIII)	Me <sub>2</sub> SiSiMeCl <sub>2</sub>	28,8	9,48	—	—	—	—	40

\*The first ionization potential was calculated from the linear relation between  $I_1^D$  and  $\nu_{CT}$  given in [11].

†For the remaining compounds of this series,  $K_0$  is close to zero and could not be determined because of the negative values of  $1/\epsilon$  in the Benesi-Hildebrandt equation [12].

‡Rate constant for second-order oxidation of organopolysilanes by peroxybenzoic acid is hexane at 20°C [3, 4]; the data for benzene at 35°C are given in parentheses. The rate constant of the first oxidation step is given for tri- and tetrasilanes (V), (VI), (X), and (XI) [3].

6. There is a significant increase of  $\nu_{CT}$  when a second Cl atom is introduced in the disilane [compound (XII) and (XIII)] in the 2 or 1 position, which indicates a significant decrease of the donor ability of the Si-Si  $\sigma$  bond.

7. As is evident from the values of  $\nu_{CT}$ , symmetrical and unsymmetrical arrangements of the two Cl atoms have no effects on the values of the first ionization potentials [compounds (XII) and (XIII)], but  $I_1^D$  of 2-chloroheptamethyltrisilane (XI) is significantly lower (by 0.28 eV) than the first ionization potential of unsymmetrical isomer (X) (the uniqueness of the 2 position in trisilanes was noted in [19]).

From a comparison of the frequencies of the charge-transfer band (or the values of  $I_1^D$ ) with the rate constants of oxidation of polysilanes by peroxybenzoic acid, we find the following. Despite the significant increase of  $I_1^D$  when a Cl atom is introduced into a peralkylpolysilane, the rate constant of oxidation increases. However, if we consider separately two series of compounds, one of which is permethylated polysilanes Me(Me<sub>2</sub>Si)<sub>*n*</sub>Me (1) and the second of which is organochloropolysilanes (2), we observe in these series a tendency to retardation of the reaction with increasing values of  $I_1^D$  (Fig. 1). There is a linear relation of the logarithm of the rate constant to the frequency of the charge-transfer band for the considered series (there is a tendency to such a relation in the second case):

$$\ln k = -(0.24 \pm 0.03) \cdot 10^{-3} \nu_{CT} + (2.11 \pm 0.66) \quad (1)$$

$N = 3, r = 0.992$

$$\ln k = -(0.32 \pm 0.08) \cdot 10^{-3} \nu_{CT} + (6.85 \pm 2.02) \quad (2)$$

$N = 7, r = 0.883$

where  $N$  is the number of points, and  $r$  is a correlation coefficient (confidence interval of 0.95).

The nature of relations (1) and (2) suggests that during oxidation of the Si-Si bond by peroxy acids, formation of a charge-transfer complex can occur, similarly to the studied  $\sigma, \pi$ -

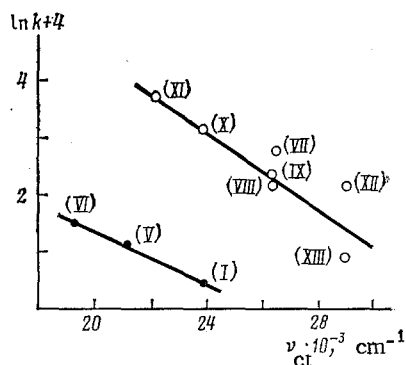


Fig. 1. Relation of the logarithm of the rate constant of oxidation of organosilanes by peroxybenzoic acid to the frequency of the charge-transfer band of the [polysilane-TCE] complex.

type complexation of polysilane with TCE, but the energy characteristics of the donor and complex as a whole ( $I_1^D$  and  $\nu_{ct}$ ) but are not the only factor determining the oxidation rate. The nature of the change of the frequency  $\nu_{ct}$  does not make it possible to explain the increase of the rate constant of oxidation in going from hexamethyldisilane (I) to pentamethylchlorodisilane (VII) or, for example, the difference in the rate constants of oxidation for symmetrical (XII) and unsymmetrical (XIII) dichlorotetramethyldisilanes, having identical values of the energy of the HOMO. Possibly, in this case an important role is played by the structural characteristics of the transition complex complex.

#### EXPERIMENTAL

The electronic spectra of the charge-transfer complexes of the organopolysilanes with TCE were reported on a Perkin-Elmer 402 spectrophotometer in the range of 350-600 nm. The thickness of the absorbing layer was 1 cm, and the solvent was  $\text{CH}_2\text{Cl}_2$ . The donor concentration was 0.1-0.5 mole/liter, and the acceptor concentration was 0.05 mole/liter. The thermodynamic characteristics of the charge-transfer complexes were calculated with the Benesi-Hildebrandt equation (3) at T 295 and 275°K:

$$\frac{C_A l}{D} = \frac{1}{C_D} \frac{1}{K_{0e}} + \frac{1}{\epsilon} \quad (3)$$

where  $C_A$  and  $C_D$  are the concentrations of the acceptor and the donor, respectively;  $D$  is the optical density of the absorption band of the charge-transfer complex;  $l$  is the thickness of the absorbing layer;  $K_0$  is the complexation constant; and  $\epsilon$  is the extinction coefficient of the complex. The value of  $\epsilon$  for a specific donor and the unchanged acceptor was determined from the segment of the ordinate axis cut off by the straight line of (3) in coordinates

$\frac{C_A l}{D}(y) - \frac{1}{C_D}(x)$ . The rate constants of the reaction of organopolysilanes with peroxybenzoic

acid were determined according to the procedure of [3]. The values of the rate constants for compounds (V), (VI), (X), and (XI), containing two or three Si-Si bonds, were found from the initial segment of the straight line in coordinates  $1/C$ -time for an equimolar ratio of the reagents [3].

#### CONCLUSIONS

1. The first ionization potentials ( $I_1^D$ ) of peralkylated and chloro-substituted organopolysilanes were determined by electron spectroscopy.

2. In oxidation of organopolysilanes by peroxybenzoic acid, the reaction is retarded with increasing values of  $I_1^D$  in the range of individually taken series of permethylated or chloro-substituted polysilanes. Replacement of an alkyl group at Si by a Cl atom leads to acceleration of the reaction, despite an increase of  $I_1^D$ .

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KINETICS AND INTERMEDIATE PRODUCTS IN THE  
INTERACTION OF STRAIGHT-CHAIN AND CYCLIC  
HYDROCARBON RADICALS WITH 9,10-ANTHRAQUINONE

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Quinones are used widely as inhibitors of free-radical reactions because of their ability to act as "traps" for free radicals. Interaction of alkyl radicals with quinones results in the formation of aroxyl radicals [1-3].

The kinetic parameters of reactions of radical addition to quinones have been established for a few radicals [4, 5]. No information has been reported on the kinetics of interaction of cycloalkyl radicals with 1,4-benzoquinone.

In the work reported here, we used a pulse radiolysis technique with optical registration of the destruction of hydrocarbon radicals R in determining the rate constants for the interaction of cyclododecyl radicals and n-dodecyl radicals with 9,10-anthraquinone (Q) in the corresponding liquid hydrocarbons, at various temperatures.



## EXPERIMENTAL

The hydrocarbon radicals were generated by a pulse of accelerated electrons (ELU-10 accelerator, pulse duration 1.5  $\mu$ sec) in liquid solutions of 9,10-anthraquinone at various concentrations in high-purity n-dodecane or cyclododecane; the solutions were thoroughly pumped down after purging with He. During the time of preparation of the apparatus for the

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