

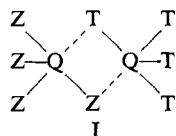
Exchange of Parts between Molecules at Equilibrium. IX. Kinetics and Mechanisms for the Scrambling of Two Substituents on a Central Atom

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Contribution from the Monsanto Company, Central Research Department,
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Abstract: The first steps of several scrambling reactions were examined kinetically. Examples representing different parts of the periodic table and different substituents were selected: (1) $\text{Sb}(\text{CH}_3)_3$ vs. SbCl_3 , (2) $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ vs. $\text{Ti}[\text{OC}(\text{CH}_3)_3]_4$, (3) $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 . Initial rate measurements showed systems 1 and 2 to involve second-order reactions first order in each component, while system 3 is a more complex acid-catalyzed reaction. Enthalpies and entropies of activation are reported and mechanisms are discussed.

A great deal of effort in our laboratory has been directed toward illuminating the equilibrium aspects of scrambling reactions¹ of the type $i\text{QZ}_\nu + (\nu - i)\text{QT}_\nu = \nu\text{QZ}_i\text{T}_{\nu-i}$. The detailed kinetics and mechanisms of these reactions have largely been ignored,² except to assume that the exchanges were probably bimolecular processes occurring through



activated complexes or intermediates such as I. While there is evidence in the literature^{3,4} supporting this hypothesis, it seemed worthwhile to examine experimentally the kinetic detail of several hopefully typical scrambling reactions. The following three examples representing Q atoms from different parts of the periodic table, and a range of substituents were selected: $\text{Sb}(\text{CH}_3)_3$ vs. SbCl_3 , $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ vs. $\text{Ti}[\text{OC}(\text{CH}_3)_3]_4$, and $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 .

Experimental Section

The trimethylantimony was prepared by the method of Hibbert,⁵ the tetrakisdimethylaminotitanium by the method of Bradley,⁶ and the *t*-butyl titanate also according to Bradley.⁷ The tetramethyl silicate and the silicon tetrachloride were obtained from Anderson Chemical Co. and distilled before use. The antimony trichloride (99.8%) was obtained from J. T. Baker Co. and used directly. The above reagents were carefully purified, using proton nuclear magnetic resonance (nmr) spectra as the criterion of purity where possible. The solvents (dimethylformamide, toluene, carbon tetrachloride, and benzonitrile) were purified by standard methods. All subsequent manipulations were carried out in an inert atmosphere.

Kinetic Method. Samples of the two components were weighed into a Varian A-60 nmr tube; then a suitable volume of solvent was added.⁸ The tubes were carefully sealed and zero-time nmr

spectra obtained. The tubes were then immediately placed in constant temperature baths and withdrawn at appropriate time intervals for nmr measurements. The total volume of solution was determined by measuring the height of liquid in the tubes, which were calibrated with distilled water giving a factor of 0.0136 ± 0.0001 ml/mm. The concentration of each component was generally varied between 0.1 and 1.0 *N*.

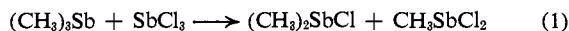
In the $\text{Sb}(\text{CH}_3)_3$ vs. SbCl_3 exchange, the appearance of $\text{Sb}(\text{CH}_3)_2\text{Cl}$ was followed; in the $\text{Ti}[\text{N}(\text{CH}_3)_2]_4$ vs. $\text{Ti}[\text{OC}(\text{CH}_3)_3]_4$ exchange, the appearance of $[(\text{CH}_3)_2\text{N}]_3\text{Ti}[\text{OC}(\text{CH}_3)_3]$ was followed; and in the $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 exchange, the appearance of $\text{Si}(\text{OCH}_3)_3\text{Cl}$ was followed. The form of the rate law was determined by the initial-rate method, and rate constants were obtained until back or subsequent reactions interfered. The $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 and $\text{Sb}(\text{CH}_3)_3$ vs. SbCl_3 systems gave acceptable rate constants out to 30–40% reaction of the starting compounds.

For a summary of experimental results see Table I.

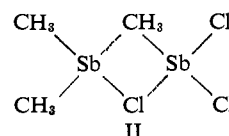
Nuclear Magnetic Resonance. Proton nmr spectra were obtained from a Varian Model A-60 spectrometer, at a frequency of 60,000 Mc, generally using a sweep width of 25 cycles. Quantitative determinations of individual nmr peaks were made with an Ott compensating planimeter. The nmr chemical shifts as measured from tetramethylsilane dissolved in the samples (not extrapolated to infinite dilution) are reported in terms of τ values as follows: 9.26, 8.73, 8.37 for $i = 3, 2, 1$, respectively, in $\text{Sb}(\text{CH}_3)_i\text{Cl}_{3-i}$ (dimethylformamide solvent); 6.92, 6.86, 6.83, 6.80 for $i = 4, 3, 2, 1$, respectively, for the $[\text{N}(\text{CH}_3)_2]$ resonance in $\text{Ti}[\text{N}(\text{CH}_3)_2]_i[(\text{CH}_3)_3\text{CO}]_{4-i}$ (toluene solvent); 6.50 (6.40), 6.43 (6.41), 6.34 (6.38), 6.25 (6.32) for $i = 4, 3, 2, 1$, respectively, in $\text{Si}(\text{OCH}_3)_i\text{Cl}_{4-i}$ (in carbon tetrachloride solvent with values in benzonitrile in parentheses).

Results and Discussion

Trimethylantimony vs. Antimony Trichloride. Initial-rate measurements in dimethylformamide indicate the following first-step reaction to be first order in each component



Second-order rate constants were obtained at 72° ($6.7 \pm 0.5 \times 10^{-5}$ l./mole sec) and 100° ($5.3 \pm 0.5 \times 10^{-4}$ l./mole sec) from which an activation enthalpy of 18 kcal and entropy of -25 eu were calculated. These values are consistent with a mechanism involving the formation of the four-center transition state II. The



(8) In the $\text{Sb}(\text{CH}_3)_3$ vs. SbCl_3 exchange it was necessary to dissolve the solid SbCl_3 in the dimethylformamide before adding the $\text{Sb}(\text{CH}_3)_3$.

(1) E.g., see J. R. Van Wazer and L. Maier, *J. Am. Chem. Soc.*, **86**, 811 (1964); K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 139, 268 (1964); and J. R. Van Wazer and K. Moedritzer, *J. Inorg. Nucl. Chem.*, **26**, 737 (1964); also see D. Grant and J. R. Van Wazer, *J. Organometal. Chem.*, **4**, 229 (1965).

(2) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

(3) S. Winstein, T. G. Traylor, and C. S. Garner, *J. Am. Chem. Soc.*, **77**, 3741 (1955).

(4) A. F. Reid and C. J. Wilkins, *J. Chem. Soc.*, 4029 (1955).

(5) H. Hibbert, *Ber.*, **39**, 160 (1906).

(6) D. C. Bradley and T. M. Thomas, *J. Chem. Soc.*, 3857 (1960).

(7) D. C. Bradley, R. C. Mehrotand, and W. Wardlaw, *ibid.*, 4202 (1952).

Table I. Summary of Experimental Results

Concentration, N		k_2 , l./mole sec
Sb(CH ₃) ₃ vs. SbCl ₃ in Dimethylformamide		
72°		
Sb(CH ₃) ₃	SbCl ₃	
0.413	0.300	0.65×10^{-4}
0.688	0.341	0.63
0.362	0.150	0.65
0.396	0.487	0.70
0.276	0.664	0.72
100°		
0.481	0.231	5.3×10^{-4}
0.788	0.202	5.3
0.411	0.373	5.4
Ti[N(CH ₃) ₂] ₄ vs. Ti[O(CH ₃) ₂] ₄ in Toluene		
37°		
Ti[N(CH ₃) ₂] ₄	Ti[O(CH ₃) ₂] ₄	
0.321	0.374	0.43×10^{-4}
0.760	0.456	0.45
0.477	0.110	0.38
0.365	0.526	0.47
1.12	0.578	0.38
72°		
0.426	0.128	2.1×10^{-4}
0.162	0.0584	2.5
0.531	0.314	2.3
Si(OCH ₃) ₄ vs. SiCl ₄ in Carbon Tetrachloride ^{a,b}		
72°, [R-OH] ^c = 0.034 N		
Si(OCH ₃) ₄		
0.496		8.0×10^{-5}
0.246		8.7
0.537		7.8
100°, [R-OH] ^c = 0.034 N		
Si(OCH ₃) ₄		
0.296N		7.3×10^{-7}
0.623		6.7
Si(OCH ₃) ₃ Cl vs. SiCl ₄		
100°, [R-OH] ^c = 0.034 N		
Si(OCH ₃) ₃ Cl		
0.391		6.2×10^{-7}
0.333		6.3
0.922		5.8
Si(OCH ₃) ₄ vs. SiCl ₄ in Benzonitrile at 38°		
Si(OCH ₃) ₄	k_1 , sec ⁻¹ × 10 ⁵	
0.541		5.7
0.613		5.0
0.294		5.7
0.592		5.3

^a Values at 38° summarized in Figure 1. ^b At 72°, the average of nine runs, where [R-OH] is $0.002 \pm 0.001 N$ (by Karl Fischer analysis), gives $k_2 = 6.0 \pm 0.8 \times 10^{-6}$ l./mole sec. ^c [R-OH] refers to total available hydroxyl groups.

relatively large negative activation entropy is in agreement with values observed for other bimolecular reactions believed to involve two sites of attachment in the transition state.^{4,9}

Tetrakisdimethylaminotitanium vs. *t*-Butyl Titanate. The results obtained in toluene solvent for the first exchange in the scrambling of dimethylamino vs. *t*-butoxyl ligands around titanium are similar to those obtained in the antimony example above. Initial rate measurements revealed a rate law of the same form, that is, first order in each component. Second-order rate constants were obtained at 37° ($4.2 \pm 0.4 \times 10^{-5}$ l./mole sec) and 72° ($2.3 \pm 0.2 \times 10^{-4}$ l./mole sec) from which an activation enthalpy of 9.7 kcal and

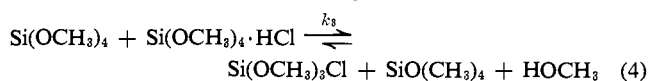
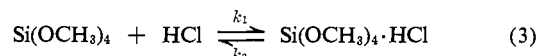
(9) A. Wasserman, *Monatsh.*, **83**, 543 (1952).

entropy of -47 eu were calculated. These values are again consistent with a mechanism involving the formation of a rigid four-center transition state similar to I. The particularly large negative entropy value probably arises from the additional geometrical requirements placed on the already restrained four-membered-ring transition state by the bulkiness of both ligands. In contrast, if the less bulky isopropoxyl ligand is used in place of the *t*-butoxyl, the reaction rate increases more than five orders of magnitude.¹⁰ This rate difference can be accounted for almost entirely on the basis of an entropy change. If we assume a constant ΔH^* for both the isopropoxyl and *t*-butoxyl reactions, then the ΔS^* of the isopropoxyl reaction would be about -24 eu in close agreement with the value obtained above for the antimony exchange.

Tetramethyl Silicate vs. Silicon Tetrachloride. Initial-rate measurements in carbon tetrachloride solvent on the first exchange in the Si(OCH₃)₄ vs. SiCl₄ system revealed a rate law of an entirely different form from those described above. A second-order rate constant was obtained at 72°, but the reaction was found not to be first order in each component but zero order in SiCl₄ and second order in Si(OCH₃)₄. Further experiments showed the reaction to be acid catalyzed, the acid arising *via* the reaction of traces of moisture in the solvent with SiCl₄ to give HCl. A standard solvent was then prepared by adding a measured amount of methanol to the carbon tetrachloride, bringing the total R-OH (and therefore [HCl]) concentration to 0.034 N .¹¹ The reaction was found to be first order in acid concentration. Initial rate measurements at 100° showed a rate law of the same form but that the third-order rate constant had a slightly lower value than obtained at 72° ($2.4 \pm 0.1 \times 10^{-3}$ l.²/mole² sec at 72°; $2.0 \pm 0.1 \times 10^{-3}$ l.²/mole² sec at 100°), confirming the complex nature of the reaction.¹² Experiments at 38° were more informative, showing a mixed-order dependence on [Si(OCH₃)₄] for an order lying between 1 and 2. The mathematical model best representing the data is

$$\text{rate} = \frac{k_1 k_3 [\text{HCl}] [\text{Si}(\text{OCH}_3)_4]^2}{k_2 + k_3 [\text{Si}(\text{OCH}_3)_4]} \quad (2)$$

and the most likely mechanism is thought to be



In this sequence, the concentration of Si(OCH₃)₄·HCl is assumed to be small and constant. The negative temperature coefficient can be accounted for by postulating a greater change in k_2 than in k_3 with temperature.

A plot of $(a - x)/(dx/dt)$ vs. $1/(a - x)$, where a is the original silicate concentration and x is the reaction variable, yields a straight line of slope $k_2/k_3 k_1 [\text{HCl}]$ (see Figure 1), which is the reciprocal form of the rate

(10) H. Weingarten and J. R. Van Wazer, *J. Am. Chem. Soc.*, **87**, 724 (1965).

(11) The original H₂O concentration in the CCl₄ was known only approximately from Karl Fischer analysis, 20 ± 10 ppm. Corrections in the [HCl] were made for each run since the amount of solvent varied.

(12) O. K. Rice, *J. Chem. Phys.*, **4**, 53 (1936).

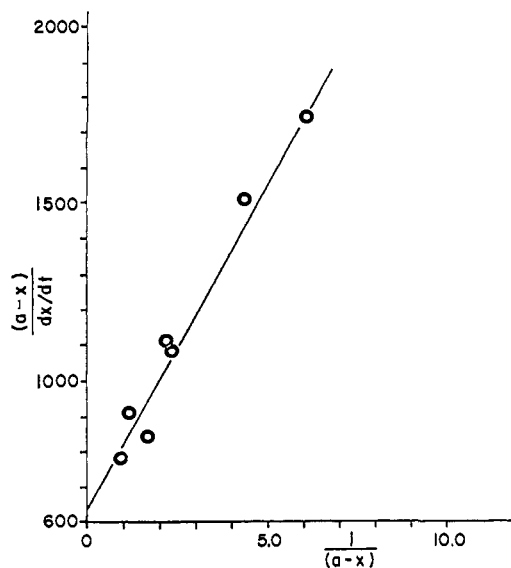


Figure 1. Plot of $(a-x)/(dx/dt)$ vs. $1/(a-x)$ for $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 exchange at 38° .

constants reported at 72 and 100° times $1/[\text{HCl}]$. The value of the third-order rate constant at 38° , calculated from the plot in Figure 1, is $2.6 \pm 0.3 \times 10^{-3} \text{ l.}^2/\text{mole}^2 \text{ sec}$.

A possible role for the second molecule of methyl silicate is that of solvating agent for any charge separation occurring in the k_3 transition state. This hypothesis suggested an experiment in which a more polar solvent than carbon tetrachloride would be used. A sufficiently polar solvent would compete with the $\text{Si}(\text{OCH}_3)_4$ as solvating agent, causing the reaction to become first order in methyl silicate. The exchange was carried out in benzonitrile at 38° and found to be

first order in methyl silicate while still zero order in silicon tetrachloride. A pseudo-first-order rate constant of $5.3 \pm 0.4 \times 10^{-5} \text{ sec}^{-1}$ was obtained. A second-order rate constant could not be calculated since the $[\text{HCl}]$ was not determined.

Because of the complexity of first exchange in the $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 reaction, it was of interest to determine if the same type of mechanism would be operative in the subsequent, much slower, steps of the equilibration. To this end a sample¹³ of $(\text{CH}_3\text{O})_3\text{SiCl}$ was prepared by equilibrating¹⁴ the appropriate mixture of methyl silicate and silicon tetrachloride at 120° for 200 hr. Initial rate measurements for the exchange between $\text{Si}(\text{OCH}_3)_3\text{Cl}$ and SiCl_4 at 100° in carbon tetrachloride to give $\text{Si}(\text{OCH}_3)_2\text{Cl}_2$ and $\text{Si}(\text{OCH}_3)\text{Cl}_3$ showed the reaction to be of the same form as the $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 exchange, that is, zero order in SiCl_4 and second order in $\text{Si}(\text{OCH}_3)_3\text{Cl}$. A third-order rate constant of $1.8 \pm 0.2 \times 10^{-5} \text{ l.}^2/\text{mole}^2 \text{ sec}$ was calculated.

Conclusion

While it appears likely that mechanisms involving four-center transition states will be common in scrambling chemistry it is not yet possible to predict the mechanism, or more precisely the form of the rate law, on an *a priori* basis.

Acknowledgment. The authors wish to thank William A. White for his valuable assistance.

(13) This sample obtained by equilibration contained 84% $\text{Si}(\text{OCH}_3)_3\text{Cl}$, 9.7% $\text{Si}(\text{OCH}_3)_4$, and 6.3% $(\text{CH}_3\text{O})_2\text{SiCl}_2$; therefore, it was necessary to make a correction for the $\text{Si}(\text{OCH}_3)_4$ vs. SiCl_4 reaction. An attempt to enrich the mixture in $\text{Si}(\text{OCH}_3)_3\text{Cl}$ by distillation through a Vigreux column of one or two theoretical plates failed to show any noticeable change in concentration.

(14) K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, **3**, 268 (1964)

Carbon Monoxide Exchange with Some Metal–Metal Bonded Metal Carbonyls

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Abstract: Investigations on the kinetics of ^{14}CO exchange with $\text{Hg}[\text{Co}(\text{CO})_4]_2$ in solution are reported. The results show that all CO's exchange at the same rate, that the rate of exchange is first order, and that it is only slightly affected by the nature of the solvent. It is suggested that the mechanism for exchange perhaps involves an insertion (or ligand migration) reaction. The replacement of CO by phosphines gave complicated results that are not understood. Studied in less detail was the exchange of ^{14}CO with the compounds $\text{Cd}[\text{Co}(\text{CO})_4]_2$, $(\text{CH}_3)_3\text{SnCo}(\text{CO})_4$, $(\text{C}_6\text{H}_5)_3\text{SnCo}(\text{CO})_4$, $\text{CH}_3\text{COCO}(\text{CO})_4$, $(\text{C}_6\text{H}_5)_3\text{PAuCo}(\text{CO})_4$, and $(\text{C}_6\text{H}_5)_3\text{PAuMn}(\text{CO})_5$.

Investigations of the exchange of carbon monoxide with simple metal carbonyls containing metal–metal bonds are limited to the compounds $\text{Co}_2(\text{CO})_8$ ¹ and $\text{Mn}_2(\text{CO})_{10}$.² The cobalt compound undergoes rapid

exchange with ^{14}CO , whereas at room temperature in benzene solution the manganese compound exchanges with an estimated half-life greater than 10 years. A kinetic study shows that for $\text{Co}_2(\text{CO})_8$ the rate of exchange is first order and all eight CO's exchange at the same rate. On this basis it was suggested¹ that the rapid rate of exchange was due to the bridged structure

(1) F. Basolo and A. Wojcicki, *J. Am. Chem. Soc.*, **83**, 520 (1961).

(2) D. F. Keeley and R. E. Johnson, *J. Inorg. Nucl. Chem.*, **11**, 33 (1959).