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NOTE

RATE CONSTANTS FOR TRIMETHYLSILYL RADICAL REACTIONS

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No data have been reported regarding the rate of combination of silyl radicals, but recent work on the thermal decomposition of hexamethyldisilane[1] enables values to be deduced for the auto-combination rate constant for trimethylsilyl radicals and also for the cross-combination of methyl and trimethylsilyl radicals.

RESULTS

Auto-combination of trimethylsilyl radicals

Indirect values for velocity constants for dimerisation can be obtained[2,3] from the reverse reaction (*e.g.* hexamethyldisilane pyrolysis) using the relation $A_{\text{forward}}/A_{\text{back}} = \exp(\Delta S/R)$. For a dimerisation such as:

$$2\,(CH_3)_3Si^{\cdot} \underset{k_f}{\overset{k_b}{\leftrightarrows}} (CH_3)_3SiSi(CH_3)_3$$

assuming the activation energy for the forward reaction to be zero, the thermodynamic expression becomes:

$$\log k_f = \log A_b + \Delta S/2.3R + 4.8$$

where k_f is in mole$^{-1}\cdot$cm$^3\cdot$sec^{-1}, A_b in sec^{-1}, ΔS is the entropy change in cal$\cdot$deg$^{-1}\cdot$mole^{-1} at 25° and 1 atmosphere and the term 4.8 is a correction for the change in the number of molecules when the radicals combine.

There are few entropy values[4] for silyl radicals and compounds, however the relevant values for hexamethyldisilane and trimethylsilyl may be deduced as follows. $S^\circ[(CH_3)_3Si^{\cdot}]$ may be regarded as equal to $S^\circ[(CH_3)_3SiH]$ plus a correction of $R\cdot\ln 2$ for the electronic contribution, hence $S^\circ[(CH_3)_3Si^{\cdot}] = 80.4$ cal$\cdot$deg$^{-1}\cdot$mole^{-1}. The entropy of hexamethyldisilane (HMDS) may be estimated using the Benson and Buss Atomic Additivity Rules[5] and, making a correction of 18.8 cal$\cdot$deg$^{-1}\cdot$mole^{-1} for the symmetry of the molecule, we obtain $S^\circ(\text{HMDS}) = 105.0$ cal$\cdot$deg$^{-1}\cdot$mole^{-1}. It has been found that, for many heavily substituted molecules, these atomic additivity rules yield values which are slightly high ($\sim 5\%$), *e.g.* S°(hexamethylethane) is calculated to be 98.4 whereas the experimental value is 93.1 cal$\cdot$deg$^{-1}\cdot$mole^{-1}. This arises because of the inability of the Additivity Rules to correct for steric strain; it is likely that there will be rather less steric strain in hexamethyldisilane, so we shall (arbitrarily) assume that a further correction of only 2.5 entropy units is required to account for this and hence S°(HMDS) = 102.5.

ΔS is therefore -58.3 cal·deg^{-1}·mole^{-1} and $\log(k_f/A_b) = -8.0$. Davidson[1] has reported that $\log A_b = 13.5$ (sec^{-1}) so that $\log k_f = 5.5$, *i.e.*, trimethylsilyl radicals combine with a velocity constant of $10^{5.5}$ mole^{-1}·cm^3·sec^{-1}. This is appreciably lower than for the auto-combination of many other radicals, *e.g.* CH_3 $10^{13.34}$ (ref. 6), CF_3 $10^{13.36}$ (ref. 7), CH_3O $10^{12.2}$ (ref. 8), CCl_3 $10^{13.5}$ (ref. 9).

Cross-combination of methyl and trimethylsilyl radicals

$$2\,(CH_3)_3Si^\cdot \xrightarrow{(1)} (CH_3)_3SiSi(CH_3)_3$$

$$2\,CH_3^\cdot \xrightarrow{(2)} C_2H_6$$

$$CH_3^\cdot + (CH_3)_3Si^\cdot \xrightarrow{(3)} (CH_3)_4Si$$

Simple collision theory suggests that the rate of cross-combination of two radicals should equal twice the geometric mean of the rates of the two dimerisations, *i.e.* $k_3/(k_1 \cdot k_2)^{0.5} = 2$. For a large number of radicals this correlation has been confirmed.

Since $k_1 = 10^{5.5}$ and $k_2 = 10^{13.34}$, then $k_3 = 10^{9.4}$ mole^{-1}·cm^3·sec^{-1}. Other values which have been reported for radical combination with methyl radicals have been: CH_3O $10^{13.1}$ (ref. 8), NO_2 $10^{12.8}$ (ref. 8), CH_3SO_2 $10^{10.5}$ (ref. 10).

Reactions of silyl radicals

No directly-obtained kinetic data are available for the abstraction of hydrogen atoms from a substrate by silyl radicals. Kerr's data[11] for the reaction of methyl radicals with trimethylsilane indicate that $A_4 = 10^{11.1}$ and $E_4 = 7.0$ kcal·mole^{-1}.

$$CH_3^\cdot + HSi(CH_3)_3 \underset{(5)}{\overset{(4)}{\rightleftarrows}} CH_4 + (CH_3)_3Si^\cdot$$

Using the reported value[12] of -25.6 kcal·mole^{-1} for $\Delta H_f^\circ[(CH_3)_3Si^\cdot]$, we find $E_5 = 29.5$ kcal·mole^{-1}. Since $\log(A_4/A_5) = \Delta S/2.3R$, and since $\Delta S = 0.2$ cal·deg^{-1}·mole^{-1} then: $\log k_5$ (mole^{-1}·cm^3·sec^{-1}) $= 11.1 - 29500/(2.303\ R \cdot T)$.

It is apparent that trimethylsilyl radicals abstract hydrogen atoms at a very slow rate. Reaction (5) may be compared with the rate at which tert-butyl radicals abstract from methane:

$$(CH_3)_3C^\cdot + CH_4 \underset{(7)}{\overset{(6)}{\rightleftarrows}} (CH_3)_3CH + H_3C^\cdot$$

By a similar method to that described above it is found: $\log k_6$ (mole^{-1}·cm^3·sec^{-1}) $= 10.8 - 21000/(2.303\ R \cdot T)$.

At 162° (where $2.303\ R \cdot T$ is 2000), $k_6/k_5 \sim 10^4$ so that tert-butyl radicals (which themselves do not readily abstract hydrogen atoms) are considerably more reactive than are trimethylsilyl radicals.

Although alkyl radicals isomerise, they are observed to do so only at relatively high temperatures and, because of their ready reactivity in other modes, such reactions do not form a major part of the chemistry of such radicals. In the case of trimethylsilyl radicals because of their lack of reactivity by hydrogen atom removal or by radical–radical reactions, it is to be expected that reaction paths involving isomerisation or radical decomposition will constitute an important part of their chemistry.

Another likely reaction path will be the addition to an olefin, *e.g.*:

$$(CH_3)_3Si^{\bullet}+C_2H_4 \rightarrow (CH_3)_3SiCH_2\dot{C}H_2$$

A value of -74.9 kcal·mole^{-1} can be estimated for $\Delta H_f^\circ[(CH_3)_3SiC_2H_5]$ using the bond additivity rules[5]. Assuming that the bond strength $D[H\text{-}C_2H_4\text{-}Si(CH_3)_3]$ is ~ 98 kcal·mole^{-1}, then we find $\Delta H_f^\circ[(CH_3)_3Si\dot{C}_2H_4]$ to be -29 kcal·mole^{-1} and the heat of the addition reaction to be -16 kcal·mole^{-1}. The corresponding addition reaction of methyl radicals to ethylene is about 25 kcal·mole^{-1} exothermic.

REFERENCES

1 I. M. T. Davidson and I. L. Stephenson, *J. Chem. Soc., A*, (1968) 282.
2 A. F. Trotman-Dickenson, *Gas Kinetics*, Butterworths, London, 1955, pp. 16, 33.
3 A. F. Trotman-Dickenson, *An Introduction to Free Radicals*, Methuen, London, 1959, p. 34.
4 H. E. O'Neal and M. A. Ring, *Inorg. Chem.*, 5 (1966) 435.
5 S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 29 (1958) 546.
6 A. Shepp, *J. Chem. Phys.*, 24 (1956) 939.
7 P. B. Ayscough, *J. Chem. Phys.*, 24 (1956) 944.
8 P. Gray, R. Shaw and J. C. J. Thynne, *Progress in Reaction Kinetics*, Vol. 4, Pergamon, London 1967, p. 63.
9 J. M. Tedder and J. C. Walton, *Chem. Commun.*, (1966) 160.
10 A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 63 (1967) 2708.
11 J. A. Kerr, D. H. Slater and J. C. Young, *J. Chem. Soc., A*, (1967) 134.
12 S. J. Band, I. M. T. Davidson and C. A. Lambert, *J. Chem. Soc., A*, (1968) 2068.