# Arrhenius Parameters for the *tert*-Butoxy Radical Reactions with Trimethylsilane in the Gas Phase

Chan Ryang Park, Se Ahn Song, Yong Eun Lee, and Kwang Yul Choo*

Contribution from the Department of Chemistry, Seoul National University, Seoul 151, Korea. Received April 5, 1982

Abstract: Arrhenius parameters for the hydrogen abstraction reaction of *tert*-butoxy radicals with trimethylsilane were measured in the temperature range 43–65 °C. The absolute rate constants were determined by studying the competitive reactions between *tert*-butoxy radical decomposition [t-BuO $\xrightarrow{\text{decomp}}$ CH$_3$COCH$_3$ + CH$_3$ (4)] and hydrogen abstraction reaction from trimethylsilane [t-BuO $\xrightarrow{+ \text{HSi(CH}_3)_3}$ t-BuOH + Si(CH$_3$)$_3$ (5)]. Arrhenius parameters for reaction 5 are found to be log A (L/mol·s) = 8.5 and E_a (kcal/mol) = 3.7. For comparison purposes the *tert*-butoxy radical reaction with the carbon analogue isobutane was also studied. For this reaction log A (L/mol·s) = 8.4 and E_a = 4.3 kcal/mol were obtained. The activation energy and the properties of the activated complex for the trimethylsilane reaction were estimated by using the recently modified BEBO method. The calculated activation energy was in good agreement with the experimental result. The Arrhenius parameters for *tert*-butoxy radical reactions with various hydrogen donors can be reasonably expressed by the following simple rules: log A (for reactions with polyatomic hydrogen donors) = 8.4 ± 0.5 L/mol·s per hydrogen, and E_a (kcal/mol) = 0.42ΔH + 8.7 (± 0.7).

Alkoxy radicals are known to be one of the most important intermediates in combustion,[1] atmospheric reactions,[2] and biological systems.[3] In the presence of hydrogen donors (R–H) the alkoxy radical reactions may have two competitive pathways: the hydrogen abstraction reaction (reaction 1) and the self-decomposition (reaction 2). Consequently the distribution of final

$$\text{RO·} \xrightarrow{+ \text{R'H}} \text{ROH} + \text{R'} \qquad (1)$$

$$\text{RO·} \xrightarrow{\text{decomp}} \text{products} \qquad (2)$$
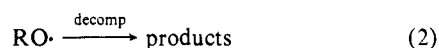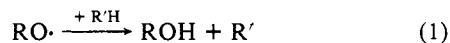
products for the chemical reactions that have alkoxy radical intermediates in their reaction paths sensitively depends on the relative rate constants for reactions 1 and 2 at a given temperature.

Among alkoxy radicals *tert*-butoxy radical reactions have been the most extensively studied. In the liquid phase the relative rate constants for reactions 1 and 2 with different alkoxy radicals and hydrocarbon donors were studied by the research groups of Walling,[4] Ingold,[5] and Zavitsas.[6] They also found that the activation energies for reactions 1 and 2 were sensitively dependent on the solvent polarities. *tert*-Butoxy radicals have also been widely used for the generation of silicon and germanium centered free radicals for EPR study.[7] Very recently a spectroscopic technique was used for the absolute measurement of the rate constants for reaction 1 with various hydrocarbons in the liquid phase at low temperatures (−60–22 °C).[8,9]

Among the many research groups that reported gas phase alkoxy radical reactions, the most extensive study of the relative rate constants for the alkoxy radical reactions had been done by Batt and co-workers.[10] Baldwin et al.[11] (as well as Batt's group[12])

evaluated the reported Arrhenius parameters for reaction 2 in the gas phase and gave a simple Evans–Polanyi type equation for the activation energies of various alkoxy radical decomposition reactions. However, recently one of the present authors and Benson[13] reevaluated the reported values and reported the most reliable Arrhenius parameters for all alkoxy radical decomposition reactions in the gas phase.

No report has been published on the alkoxy radical reactions with Si–H bonded compounds in the gas phase.[14] The reactivity of the Si–H bond on hydrogen abstraction reactions has long been controversial.[15] Strausz and co-workers[16] reported hydrogen abstraction reactions of CH$_3$ and CF$_3$ radicals with Si–H bonded compounds. The A factors for silicon compounds were found to be identical with those for hydrocarbon analogues, while activation energies were quite different for those two classes of compounds. They also calculated activation energies by the classical BEBO method[17] and found a reasonable agreement with experiment. Walsh recently[18] critically evaluated the bond dissociation energy for the Si–H bond in H–Si(CH$_3$)$_3$ and reported it to be 90.3 kcal/mol, which is about 3–4 kcal/mol lower than the t-C–H bond dissociation energy in isobutane, a carbon analogue of trimethylsilane.

We, therefore, decided to obtain the absolute rate constants for *tert*-butoxy radical reactions with trimethylsilane to shed some light on the reactivity of the Si–H bond toward alkoxy radicals. The Arrhenius parameters themselves are important since most of the silicon and germanium centered radicals have been generated and reactions studied by the initial *tert*-butoxy radical reaction with Si–H or Ge–H bonds.[7] For comparison purposes Arrhenius parameters for *tert*-butoxy radical reactions with isobutane were also obtained to check the generality of the report by Strausz and co-workers on the similarities of A factors between the two types of reactions.

The activation energy and the properties of the *tert*-butoxy-trimethylsilane activated complex were calculated and compared

(1) D. L. Allara. T. Mill, G. D. Hendry, and F. R. Mayo, *Adv. Chem. Ser.*, No. 76, 40 (1968); C. Walling, *Pure Appl. Chem.*, **15**, 69 (1968).

(2) J. N. Pitts and B. J. Finlayson, *Angew. Chem., Int. Ed. Engl.*, **14**, 1 (1975).

(3) W. A. Pryor in "Free Radicals in Biology", Vol. 3, Academic Press, NY, 1976.

(4) C. Walling and J. A. Mcguiness, *J. Am. Chem. Soc.*, **91**, 2053 (1969), and references therein.

(5) D. J. Carlson and K. U. Ingold, *J. Am. Chem. Soc.*, **89**, 4855 (1967); K. U. Ingold and D. J. Carlson, *ibid.*, **89**, 4891 (1967).

(6) A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.*, **94**, 7390 (1972).

(7) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **90**, 7155 (1968); **91**, 3938 (1969).

(8) H. Paul, R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, **100**, 4520 (1978); P. K. Das, M. V. Encinas, S. Steenken, and J. C. Scaiano, *ibid.*, **103**, 4162 (1981).

(9) S. K. Wong, *J. Am. Chem. Soc.*, **101**, 1235 (1979).

(10) L. Batt and R. D. McCulloch, *Int. J. Chem. Kinet.*, **8**, 911 (1976).

(11) A. C. Baldwin, J. R. Barker, D. M. Golden, and G. D. Hendry, *J. Phys. Chem.*, **81**, 2483 (1977).

(12) L. Batt, *Int. J. Chem. Kinet.*, **11**, 977 (1979), and references therein.

(13) K. Y. Choo and S. W. Benson, *Int. J. Chem. Kinet.*, **13**, 833 (1981).

(14) In liquid phase at −50 °C t-BuO· reactions with trimethylsilane were studied indirectly: K. Y. Choo and P. P. Gaspar, *J. Korean Chem. Soc.*, **21**, 270 (1977). The estimated value, 3 × 10^2 M^{-1} s^{-1}, was regarded to be too low.

(15) H. J. Emeleus and D. B. Sowerby, Eds., "MTP International Review of Science. Inorganic Chemistry", Butterworths, London, Series 1, Vol. 1, 1972; Series 2, Vol. 2, 1975.

(16) O. P. Strausz, E. Jakubowski, H. S. Sandhu, and H. E. Gunning, *J. Chem. Phys.*, **51**, 552 (1969); E. Jakubowski, H. S. Sandhu, H. E. Gunning, and O. P. Strausz, *J. Chem. Phys.*, **52**, 4242 (1970).

(17) H. S. Johnston and C. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).

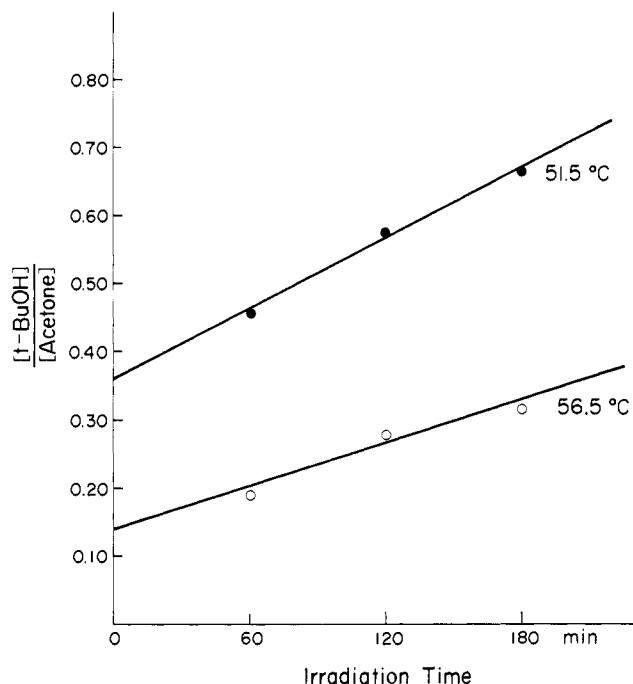(18) R. Walsh, *Acc. Chem. Res.*, **14**, 246 (1981).

Figure 1. $[t\text{-BuOH}]/[\text{acetone}]$ ratios extrapolated to zero reaction times.
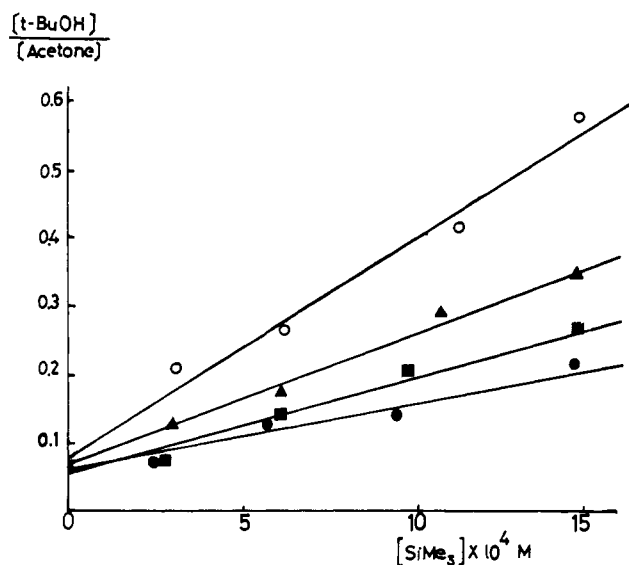

Figure 2. $[t\text{-BuOH}]/[\text{acetone}]$ ratios (extrapolated to zero reaction times) vs. $\text{HSi(CH}_3)_3$ at different reaction temperatures: (O) 43.0 °C, (▲) 51.3 °C, (■) 56.5 °C, (●) 64.5 °C.
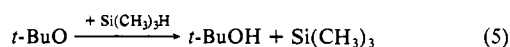
with experimental results by using the recently modified BEBO method.[19]

Experimental Section

tert-Butoxy radicals were generated by ultraviolet photolysis of di-*tert*-butyl peroxide (DTBP)

$$t\text{-BuO-O-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO·} \qquad (3)$$

In the presence of proper amounts of trimethylsilane, $\text{HSi(CH}_3)_3$, *tert*-butoxy radicals react through the following two major routes:

$$t\text{-BuO} \xrightarrow{\text{unimolecular decomp}} \text{CH}_3\text{COCH}_3 + \text{CH}_3 \qquad (4)$$

$$t\text{-BuO} \xrightarrow{+\ \text{Si(CH}_3)_3\text{H}} t\text{-BuOH} + \text{Si(CH}_3)_3 \qquad (5)$$

Methyl C–H bonds in $\text{HSi(CH}_3)_3$ and DTBP are known to be much less

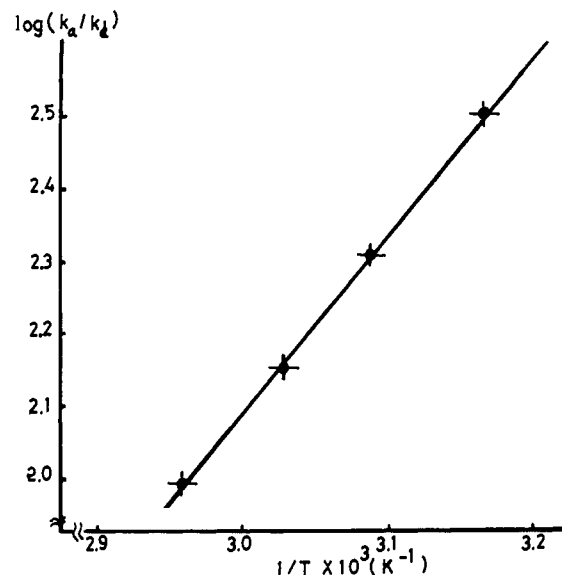(19) C. M. Marschoff and A. Jatem, *Chem. Phys. Lett.*, **56**, 35 (1978).

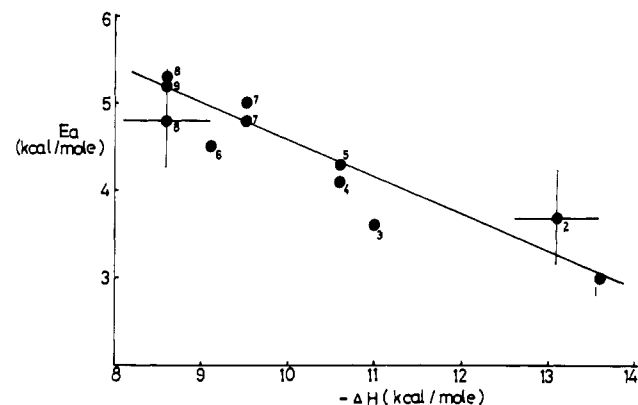Figure 3. Arrhenius plot for the relative rate constant ratios.

Figure 4. E_a vs. ΔH for *tert*-butoxy radical reactions with various hydrogen donors. The error bars in the plot are the probable error limits on the reported E_a and ΔH values: (1) isopropyl alcohol, (2) trimethylsilane, (3) ethanol, (4, 5) isobutane, (6) cyclohexane, (7) cyclopentane, (8) methanol, (9) methyl *tert*-butyl ether.

reactive than Si–H bonds for hydrogen abstraction reactions.[20] Quantitative analyses of the major reaction products were carried out with a gas chromatograph that was directly connected to the photolysis cell via a six-way gas sampling valve. Absolute concentrations were measured from the calibration curves obtained with known concentrations of standard samples.[21]

A temperature-controlled, conventional static photolysis reactor (volume 46.5 mL) was directly connected to the gas sampling valve via a capillary glass tube. The dead volume of the reactor is estimated to be less than 0.5 mL. The temperature of the reactor was controlled and read within 0.5 °C by a precalibrated temperature controller and readout unit (Omega Co. No. 4001KC). All pressure measurements were done with electronic pressure transducers (MKS Baratron) to maintain a mercury-free vacuum system. As an ultraviolet light source a 200 W super pressure mercury lamp (Bausch and Lomb) was used.[22]

Di-*tert*-butyl peroxide (MCB Chemicals) was purified by the known

(20) P. P. Gaspar, A. D. Haizlip, and K. Y. Choo, *J. Am. Chem. Soc.*, **94**, 9032 (1972).

(21) The lower boiling components of the products (*t*-BuOH, acetone, $\text{HSi(CH}_3)_3$, Me_4Si, and ethane) were separated with (Silicon DC-200 (2 m) + Porapak Q (20 cm)) a mixed column at 110 °C. With the He flow rate of 50 mL/min, retention times are *t*-BuOH 8.6 min and acetone 4.4 min, respectively. The higher boiling components (hexamethyldisilane, DTBP, and a trace amount of $\text{Si(CH}_3)_3\text{O-}t\text{-Bu}$) were separated with a SiliconOV-1 column (2 m) at 50 °C.

(22) Controlled experiments with different monochromatic light wavelengths from 2500 to 2800 Å (±10 Å) obtained on a monochromator did not show any significant change in the product distributions. The radiation output of the lamp showed negligible intensity below ca. 2500 Å.

Arrhenius Parameters for Hydrogen Abstraction

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Table I. [*t*-BuOH]/[Acetone] Ratios (Extrapolated to Zero Reaction Times) vs. [HSi(CH$_3$)$_3$] at Different Reaction Temperatures[a]

43.0 °C	[HSi(CH$_3$)$_3$] × 10^4 M	3.12	6.30	11.35	15.30
	[*t*-BuOH]/[acetone]	0.201	0.269	0.425	0.573
51.5 °C	[HSi(CH$_3$)$_3$]	2.88	6.05	10.44	15.18
	[*t*-BuOH]/[acetone]	0.127	0.170	0.277	0.358
56.5 °C	[HSi(CH$_3$)$_3$]	2.59	5.86	9.72	15.00
	[*t*-BuOH]/[acetone]	0.075	0.139	0.202	0.268
64.5 °C	[HSi(CH$_3$)$_3$]	2.45	5.54	9.18	15.03
	[*t*-BuOH]/[acetone]	0.075	0.127	0.145	0.216

[a] Probable errors in the [*t*-BuOH]/[acetone] ratios are ±0.005.

Table II. Input Data for BEBO Calculations

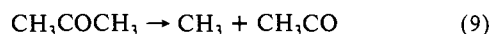|	D_0 (kcal/mol)	R (Å)	ω_e (cm^{-1})	F (N cm^{-1})	p	β (10^8 cm^{-1})
H-Si(CH$_3$)$_3$	90.3	1.48	2125	2.587	1.017	
H-OCH$_3$	103.6	0.96	3682	7.389	1.016	
MeO-Si(CH$_3$)$_3$	103.0	1.63	1050	4.350		2.14

Table III. Calculated Properties of the Activated Complex for the Reaction MeO + SiH(CH$_3$)$_3$ → MeOH + Si(CH$_3$)$_3$ at 500 K

$n_1^{\ddagger}$	$n_2^{\ddagger}$	E_a (kcal/mol)	ν (cm^{-1})	F (× 10^5 dyn/cm)
0.9	0.1	2.30	$\nu_s = 1752$	$F_\rho = -0.0811$
			$\nu_b = 219.1$ (2)	$F_\sigma = 2.349$
			$\nu_1 = 133.2$	$F_{11} = 2.320$
				$F_{22} = -0.0514$
				$F_{12} = 0.2667$
				$F_b = 0.0168$

method[23] and transferred to the reactor after degassing the lower boiling components before each experiment. Trimethylsilane (PCR Inc.) and isobutane (Matheson) were used without further purifications. After several freeze–thaw cycles no detectable impurities were found by gas chromatography.

Results and Discussion

McMillan and co-workers showed that reactions 3,4,6,7,8, and 9 were important in the photolysis of DTBP at low temperatures.[24]

$$t\text{-BuO}\text{—}\text{O-}t\text{-Bu} \xrightarrow{h\nu} 2t\text{-BuO} \quad (3)$$

$$t\text{-BuO} \rightarrow CH_3COCH_3 + CH_3 \quad (4)$$

$$2CH_3 \rightarrow C_2H_6 \quad (6)$$

$$t\text{-BuO} + (CH_3)_3CO\text{—}OC(CH_3)_3 \rightarrow$$
$$CH_2(CH_3)_2COOC(CH_3)_3 + t\text{-BuOH} \quad (7)$$

$$CH_3 + HSi(CH_3)_3 \rightarrow CH_4 + Si(CH_3)_3 \quad (8)$$

$$CH_3COCH_3 \rightarrow CH_3 + CH_3CO \quad (9)$$
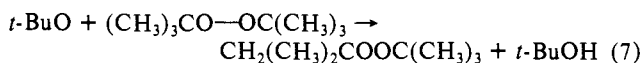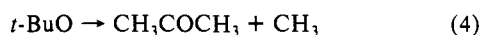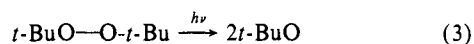
Since we are only interested in the formation of acetone and *tert*-butyl alcohol in our kinetic analyses, reaction 6 can be excluded in our considerations. Reaction 8 is also unimportant since excess amounts of HSi(CH$_3$)$_3$ are present in the reaction system at all times. Reaction 7 is also unimportant; Hendry et al.[25] estimated that reaction 7 should have log A = 9.0 1/mol·s and E_a = 7.93 kcal/mol. The expected rate constant for reaction 7

(23) A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1108 (1956).
(24) G. R. McMillan, *J Am. Chem. Soc.*, **82**, 2422 (1960).
(25) D. G. Hendry, T. Mill, L. Piszkiewics, J. A. Howard, and E. K. Eigenmann, *J. Phys. Chem. Ref. Data*, **3**, 937 (1974); the Arrhenius parameters are for the reactions *t*-BuO + *t*-BuO-*t*-Bu → *t*-BuOH + CH$_2$-(CH$_3$)$_2$CO-*t*-Bu. We expect negligible difference in Arrhenius parameters between this reaction and reaction 7.

Table IV. Arrhenius Parameters for Alkoxy Radical Reactions in the Gas Phase[g]

radical	substrate	log A[a]	E_a[a]	$-\Delta H$	ref
CH$_3$O	HC(CH$_3$)$_3$	8.3	4.1	10.6[b]	c
t-BuO	cyclohexane	9.3	4.5	9.1[d]	e
	HSi(CH$_3$)$_3$	8.5	3.7	13.1[f]	this work
	HC(CH$_3$)$_3$	8.4	4.3	10.6[b]	this work

[a] Log A in L/mol·s and E_a in kcal/mol unit. [b] K. Y. Choo et al., *Int. J. Chem. Kinet.*, **8**, 45 (1976). [c] See P. S. Nangia and S. W. Benson, *ibid.*, **12**, 169 (1980). [d] S. H. Jones and E. Whittle, *ibid.*, **2**, 479 (1970). [e] C. Walling and P. Wagner, *J. Am. Chem. Soc.*, **85**, 2333 (1963). [f] R. Walsh, *Acc. Chem. Res.*, **14**, 246 (1981); K. Y. Choo and M. Choe obtained D(H–Si(CH$_3$)$_3$) = 90.1 kcal/mol: *Chem. Phys. Lett.*, **89**, 115 (1982). [g] The probable errors in the values are log A = ±0.5 L/mol·s and E_a = ±0.5 kcal/mol.

Table V. Arrhenius Parameters for *t*-BuO Radical Reactions in Solution[a]

radical	substrate	log A[b]	E_a[b]	$-\Delta H$	ref
t-BuO	CH$_3$OH	8.6	5.3	8.6[c]	d
		8.9	4.8		e
	CH$_3$CH$_2$OH	8.7	3.6	11.0[f]	e
	(CH$_3$)$_2$CHOH	8.4	3.0	13.6[g]	e
	cyclopentane	9.1	5.0	9.6[h]	d
		9.4	4.8		e
	CH$_3$OC(CH$_3$)$_3$	8.8	5.2	8.6[c]	d

[a] We only included the reported values from recent direct kinetic studies. See footnotes d and e. [b] Log A in L/mol·s and E_a in kcal/mol unit. [c] F. R. Cruikshank and S. W. Benson, *J. Phys. Chem.*, **73**, 733 (1969). [d] S. K. Wong, *J. Am. Chem. Soc.*, **101**, 1235 (1979). [e] H. Paul, R. D. Small, Jr., and J. C. Scaiano, *ibid.*, **100**, 4520 (1978). The Arrhenius parameters were calculated from their reported rate constants and assumed A factor, log A = 8.4 (per hydrogen). See the text for details. [f] Z. B. Alfassi and S. W. Benson, *J. Phys. Chem.*, **76**, 3314 (1972). [g] R. Walsh and S. W. Benson, *J. Am. Chem. Soc.*, **88**, 3480 (1966). [h] S. Furuyama, D. M. Golden, and S. W. Benson, *Int. J. Chem. Kin et.*, **2**, 83 (1970).

at 320 K is ca. 10$^{3.6}$ L/mol·s. With the usual concentration of DTBP about 10^{-4}–10^{-5} mol/L, k_7 (DTBP) becomes <10^{-4} s^{-1}. With the accepted Arrhenius parameters[13] for k_4 (log A = 14.1, E_a = 15.3), k_4 at 320 K is 10$^{3.6}$ s^{-1}, which is at least three orders of magnitude faster than k_7. Reaction 9 is very difficult to eliminate totally in our experimental system. A blank experiment with acetone indicates a small amount of acetone decomposition at a prolonged irradiation with a UV lamp. However, the efficiency of acetone decomposition was found to be much lower than that of DTBP decomposition at early reaction times due to the large concentration and higher quantum yield of DTBP decomposition. The product ratios was extrapolated to zero reaction time from the plot of the product ratios vs. irradiation times to correct the effect due to the secondary reactions, especially due to the acetone decomposition. Such a plot is shown in Figure 1.

Under the conditions that [HSi(CH$_3$)$_3$] ≫ [DTBP] and at early reaction times we thus may only consider reactions 4 and 5 as the major reactions for *tert*-butoxy radicals. From eq 4 and 5 we obtain

$$\frac{[t\text{-BuOH}]_{t\to 0}}{[\text{acetone}]_{t\to 0}} = \frac{R(t\text{-BuOH})}{R(\text{acetone})} = (k_a/k_d)[\text{HSi(CH}_3)_3] + C \quad (10)$$

where c is the small and nearly constant term that is related to the fact that some *t*-BuOH was formed even when no HSi(CH$_3$)$_3$ was present in the system.[26]

Under our experimental pressures (i.e., total pressure of 10 torr or more) *t*-BuO radical decomposition, reaction 4, was found to be in the high-pressure limit. A total pressure change from 10 torr to 1 atm with addition of Ar or He as an inert third body did not change the [*t*-BuOH]/[acetone] ratios. Under the total

(26) See ref 29.

pressure of less than 5 torr, changes in the ratios were noticed, indicating the fall-off behavior of t-BuO radical decomposition reactions.

Table I shows the experimental results of the change of [t-BuOH]/[acetone] ratios (extrapolated to zero reaction times[27]) with different trimethylsilane HSi(CH$_3$)$_3$ concentrations at different reaction temperatures. Under the usual experimental conditions the HSi(CH$_3$)$_3$ concentrations were kept ca. 10 times or larger than those of DTBP in order to have the HSi(CH$_3$)$_3$ concentrations invariant during the experiment.

In Figure 2 [t-BuOH]$_{t\rightarrow0}$/[acetone]$_{t\rightarrow0}$ ratios were plotted against HSi(CH$_3$)$_3$ concentrations. From the slope of the figure the absolute rate constant ratios (reference eq 10) at different temperatures were obtained. The exact positions of the intercepts in the plot seem to be a complicated function of the initial concentrations of DTBP and the reaction temperatures. No attempt was made to accurately analyze the intercepts since the differences in the intercepts at different temperatures and initial DTBP concentrations were found to be negligibly small and therefore did not affect the measurements of absolute rate constant ratios. A more accurate analysis of the dependence of the intercept on temperature and initial DTBP concentration will give some insight about the mechanism of t-BuOH formation even without the presence of HSi(CH$_3$)$_3$ in the system.[29]

The Arrhenius plot for the rate constant ratios is shown in Figure 3. By using the most reasonable Arrhenius parameters for k_d (log $A_d = 14.1$ s^{-1} and $E_{ad} = 15.3$ kcal/mol),[13] we obtained log $A_a = 8.5$ L/mol·s and $E_{aa} = 3.7$ kcal/mol for the hydrogen abstraction reaction of t-BuO radicals with HSi(CH$_3$)$_3$:

$$t\text{-BuO} + \text{HSi(CH}_3)_3 \rightarrow t\text{-BuOH} + \text{Si(CH}_3)_3$$
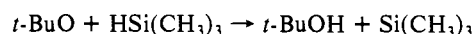
By using the same experimental procedures and kinetic analyses with isobutane in place of HSi(CH$_3$)$_3$, we obtained[30] log $A = 8.4$ L/mol·s and $E_a = 4.3$ kcal/mol for the reaction

$$t\text{-BuO} + \text{HC(CH}_3)_3 \rightarrow t\text{-BuOH} + \text{C(CH}_3)_3$$
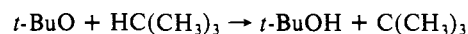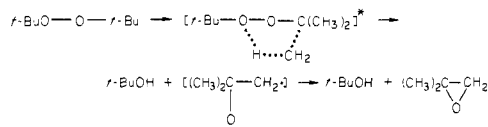
These Arrhenius parameters are almost identical with the reported values (log $A = 8.3$ L/mol·s and $E_a = 4.1$ kcal/mol) for methoxy radical reactions with isobutane.[31]

Therefore, HSi(CH$_3$)$_3$ is found to be more reactive than the hydrocarbon analogue, isobutane, in hydrogen abstraction reactions due mainly to the lower activation energy for the former reaction.

A factors were found to be almost identical for both types of reactions. This finding is in good agreement with the conclusion of Strausz and co-workers,[16] who also obtained almost identical A factors for CH$_3$ and CF$_3$ radical reactions with Si–H and analogous C–H bonds, respectively.

BEBO calculations were carried out with recently determined values[32] of Lennard–Jones rare gas potentials and with the modified C values suggested by Gilliom.[33] A detailed method of calculating transition-state properties and tunneling corrections can be found in the literature.[34] In actual calculations we had to use CH$_3$O instead of t-BuO due to the lack of available input data for the t-BuO system. The calculated activation energy should not be affected by this slight change since we assumed only a triatomic system, [O···H····Si], in actual BEBO calculations.

The input parameters for the calculations are shown in Table II. The calculated activation energy and transition-state properties are listed in Table III. The calculated activation energy (2.3 kcal/mol) is in reasonable agreement with the experimental value. Selected Arrhenius parameters for alkoxy radical reactions with various hydrogen donors are listed in Table IV. It seems reasonable to assume that A factors for alkoxy radical reactions with polyatomic hydrogen donors are all in the general range of log $A = 8.4 \pm 0.5$ L/mol·s per hydrogen basis. Since cyclohexane has 12 available hydrogens for the abstraction reaction its A factor per hydrogen becomes $10^{8.2}$ 1/mol·s.

Recently, more direct kinetic studies of *tert*-butoxy radical reactions with various hydrocarbons in the liquid phase have been carried out by time-resolved ESR[9] and laser photolysis–optical detection techniques.[8] Wong[9] obtained almost identical Arrhenius parameters as those for gas-phase results for the *tert*-butoxy radical reactions with hydrocarbons in solution at low temperatures. Scaiano et al.[8] extensively studied *tert*-butoxy radical reactions with various hydrocarbons in the liquid phase and reported rate constants at 22 °C. In Table V we listed their results after calculating activation energies with their reported rate constants and assumed Arrhenius A factors (i.e., log $A = 8.4$ L/mol·s per hydrogen). We omitted any reactions that may go through a transition state that has restricted rotations, such as toluene, that will give smaller A factors due to the delocalization of electrons in the transition state.

In Figure 4 we plotted -ΔH vs. E_a for *tert*-butoxy radical reactions with various hydrogen donors, excluding the reactions that might go through delocalized transition states. The plot can be reasonably represented by the following simple empirical equation

$$E_a \text{ (kcal/mol)} = 0.42\Delta H + 8.7 \ (\pm 0.7)$$

From Tables IV and V and the above relation we can now conclude that for most of the *tert*-butoxy radical reactions with various polyatomic hydrogen donors Arrhenius parameters may be predicted by the following simple empirical equations

$$\log A \text{ (per hydrogen)} = 8.4 \pm 0.5 \text{ L/mol·s}$$

$$E_a \text{ (kcal/mol)} = 0.42\Delta H + 8.7 \ (\pm 0.7)$$

(27) It is important to get the ratios at early reaction times. In addition to the possibility of secondary reactions of alkoxy radicals with acetone and t-BuOH and the photodecomposition of acetone, t-BuOH may react with Si=CH$_2$ to form t-BuOSi(CH$_3$)$_3$. It is now well known that in liquid phase photolysis of HSi(CH$_3$)$_3$ with DTBP considerable amounts of t-BuOSi(CH$_3$)$_3$ can be formed at longer irradiation times.[28] The photolyses were carried out only up to about 10% decomposition of DTBP and the data were again extrapolated to zero reaction times to minimize these undesired reactions.
(28) B. Cornett, K. Y. Choo and P. P. Gaspar, *J. Am. Chem. Soc.*, **102**, 377 (1980); K. Y. Choo, Ph.D. Thesis, Washington University, 1973.
(29) It is quite difficult to assume that most of the t-BuOH was formed only from the hydrogen abstraction reaction of t-BuO with DTBP, reaction 7, since the rate of this reaction is much slower than the decomposition reaction rate. We think at least some of the t-BuOH might originate from the intermolecular decomposition of photoexcited DTBP itself:

t-BuO—O—t-Bu → [t-Bu—O—O—C(CH$_3$)$_2$]* →
                                        H····CH$_2$

t-BuOH + [(CH$_3$)$_2$C—CH$_2$·] → t-BuOH + (CH$_3$)$_2$C—CH$_2$
                    | \O/
                    O

          O
A small amount of (CH$_3$)$_2$C—CH$_2$ was formed in the reaction mixture. A further experiment on this interesting mechanistic possibility is underway in our laboratory.
(30) K. Y. Choo and S. A. Song, unpublished results; M. S. Thesis, S. A. Song, Seoul National University, 1981.
(31) P. S. Nangia and S. W. Benson, *Int. J. Chem. Kinet.*, **12**, 1692 (1980), and references therein.

(32) J. M. Farrar and Y. T. Lee, *J. Chem. Phys.*, **56**, 5801 (1972); C. H. Chem. P. E. Siska, and Y. T. Lee, *ibid.*, **59**, 601 (1973).
(33) R. D. Gilliom, *J. Chem. Phys.*, **65**, 5027 (1976).
(34) N. L. Arther and J. A. McDonell, *ibid.*, **56**, 3100 (1972).