

## ARRHENIUS PARAMETERS FOR THE REACTION OF *tert*-BUTOXYL RADICALS WITH TRIETHYLSILANE

CHRYSSOSTOMOS CHATGILIALOGLU

Istituto dei Composti del Carbonio Contenenti Eteroatomi e loro Applicazioni, C.N.R., via Tolara di Sotto 89, I-40064 Ozzano Emilia (Bologna), Italy

*Summary* — Absolute rate constants for the reaction of *tert*-butoxyl radicals with triethylsilane have been measured in solution by a new indirect method using laser flash photolysis technique. Arrhenius parameters obtained in the temperature range 251–315 K are  $\log(A/M^{-1}s^{-1}) = 8.85 \pm 0.50$  and  $E_a = 2.91 \pm 0.32$  kcal mol<sup>-1</sup>. The discrepancies with the previously obtained gas-phase data are discussed.

We have recently reported the absolute rate constants for the reaction



using laser flash photolysis technique, *viz.*<sup>1</sup>,  $\log(A/M^{-1}s^{-1}) = 8.69 \pm 0.46$  and  $E_a = 2.64 \pm 0.62$  kcal mol<sup>-1</sup>. We have also estimated that about 80% of the attack occurs at the Si-H bond of triethylsilane<sup>1</sup>. The formation of triethylsilyl radicals in this way was considered a sufficiently «instantaneous» process at high silane concentration in order to study their further (secondary) reactions by laser flash photolysis<sup>2-5</sup>. Contemporaneously, Choo and coworkers<sup>6</sup> obtained slightly different Arrhenius parameters for the gas-phase reaction of *tert*-butoxyl radicals with trimethylsilane by using the  $\beta$ -scission of *tert*-butoxyl radicals as competitor, *viz.*<sup>a</sup>,  $\log(A/M^{-1}s^{-1}) = 8.5$  and  $E_a = 3.7$  kcal mol<sup>-1</sup>. However, our rate constant at 298 K is about an order of magnitude larger than the gas-phase value. The fact that the Si-H bond dissociation energy is insensitive to the nature of the alkyl group attached to the silicon atom in  $\text{R}_3\text{SiH}^8$  could mean that some of our kinetic data may be considered unreliable as the formation of silyl radicals may not be an «instantaneous» process<sup>2-5</sup>.

Here we report the Arrhenius parameters for the reaction of *tert*-butoxyl radicals with triethylsilane obtained by a completely new method which makes use of the laser flash photolysis technique and which is somewhat more direct than the one employed previously<sup>1</sup>.

(<sup>a</sup>) In an early study Choo and Gaspar<sup>7</sup>, by using light modulation-EPR technique estimated the absolute rate constant of *tert*-butoxyl radical with trimethylsilane as  $3 \times 10^2 M^{-1}s^{-1}$  at 223 K in solution, but later it was regarded to be too low (see ref. 14 in ref. 6).

## EXPERIMENTAL

### MATERIALS

Di-*tert*-butyl peroxide was passed through activated basic alumina so as to remove traces of *tert*-butyl hydroperoxide. Isooctane (spectroscopic grade) was dried over molecular sieves. Triethylsilane and  $\alpha$ -toluenesulphonyl chloride were obtained commercially and were carefully purified by standard procedures before use.

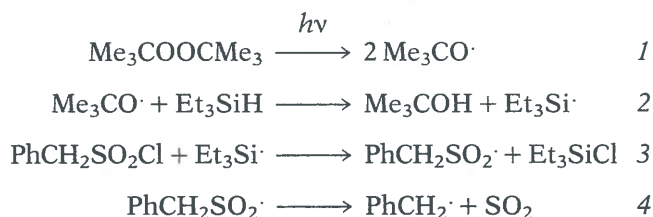
### LASER FLASH PHOTOLYSIS

Samples were contained in 3 mm path length rectangular quartz cells and irradiated with pulses from a Moletron UV-24 nitrogen laser. The experiment was controlled by a PDP 11/03L computer which received and processed the data and provided visual display and hardcopy facilities. Full details of the experimental arrangement have been given elsewhere<sup>9</sup>. All experiments were carried out on deoxygenated samples. The error limits reported correspond to a 95% confidence level and include only random errors.

## RESULTS

All the results reported herein have been obtained by laser flash photolytic techniques employing the pulses (337.1 nm, ~8 ns, up to 10 mJ) from a nitrogen laser for excitation. All experiments were carried out under oxygen-free conditions.

In principle, this technique allows  $k_2$  to be measured directly by monitoring either the decay of the reagent or the growth of the product radicals of the reaction. However, the transient absorptions due to *tert*-butoxyl and triethylsilyl radicals are too weak to be convenient for kinetic studies<sup>2,10</sup>. We therefore concentrated our efforts to find a substrate that: (i) reacts with silyl radicals in an extremely rapid way so that  $\text{Et}_3\text{Si}\cdot$  generation is at least 5 times slower than their decay, and (ii) provides at the same time a radical product suitable for measurements. The following system was found to be very convenient:



Triethylsilyl radical reacts with  $\alpha$ -toluenesulphonyl chloride (see eq. 3) with a rate constant of  $5.7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$  at 300 K to give the corresponding sulphonyl radical which decomposes unimolecularly according to eq. 4 with a rate constant larger than  $2 \times 10^8 \text{ s}^{-1}$  at room temperature<sup>11</sup>. Consequently, the kinetics of formation of  $\text{PhCH}_2\cdot$  radicals will be the same as that of the slowest elementary step in the system, i.e. reaction 2.

Measurements of  $k_2$  were carried out by monitoring the transient absorption produced when samples containing 0.01 M of  $\text{PhCH}_2\text{SO}_2\text{Cl}$  in  $\text{Me}_3\text{COOCMe}_3$  (400  $\mu\text{l}$ ) and  $\text{Et}_3\text{SiH}$  in isooctane (1600  $\mu\text{l}$  total, with  $\text{Et}_3\text{SiH}$  equal to 400, 600, 800, 1000, and 1200  $\mu\text{l}$ ) were excited by the laser pulse. This pulse is absorbed by the peroxide which undergoes a fast and efficient decomposition (reaction 1). The sequence of reactions 2, 3, and 4 yields the detectable species  $\text{PhCH}_2\cdot$ . The buildup of the signal due to  $\text{PhCH}_2\cdot$  follows pseudo-first-order kinetics (see figure 1), and an experimental rate constant,  $k_{\text{exp}}$ , can be derived according to eq. 5,

$$\ln \frac{A_\infty}{A_\infty - A_t} = k_{\text{exp}} t \quad 5$$

where  $k_{\text{exp}}$  is a first-order experimental rate constant,  $t$  is the time,  $A_\infty$  is the transient optical density in the plateau region, and  $A_t$  is the optical density at time  $t$ . The values of  $k_{\text{exp}}$  are related to the rate constant of interest according to eq. 6,

$$k_{\text{exp}} = k_0 + k_2[\text{Et}_3\text{SiH}] \quad 6$$

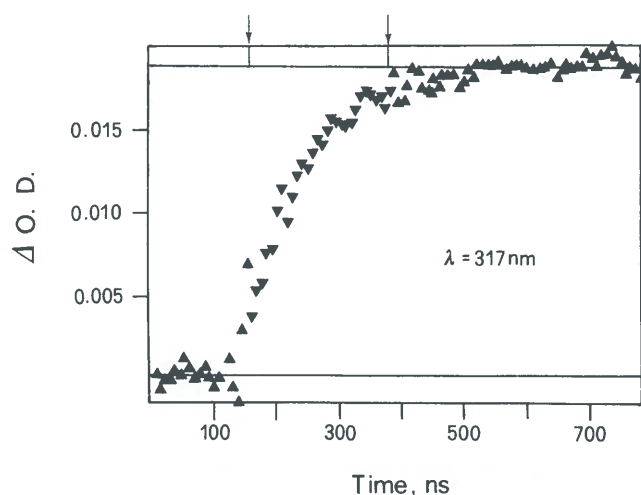


Fig. 1 - Representative buildup trace monitored at 317 nm for  $[\text{Et}_3\text{SiH}] = 3.14 \text{ M}$  and  $[\text{PhCH}_2\text{SO}_2\text{Cl}] = 0.01 \text{ M}$  at 266 K. The section between the arrows corresponds to the points used for kinetic calculations.

where  $k_0$  is the rate of *tert*-butoxyl in the solvent and includes all pseudo-first-order modes of decay other than reaction with  $\text{Et}_3\text{SiH}$ ;  $k_2$  is the bimolecular rate constant for reaction of *tert*-butoxyl radicals with triethylsilane.

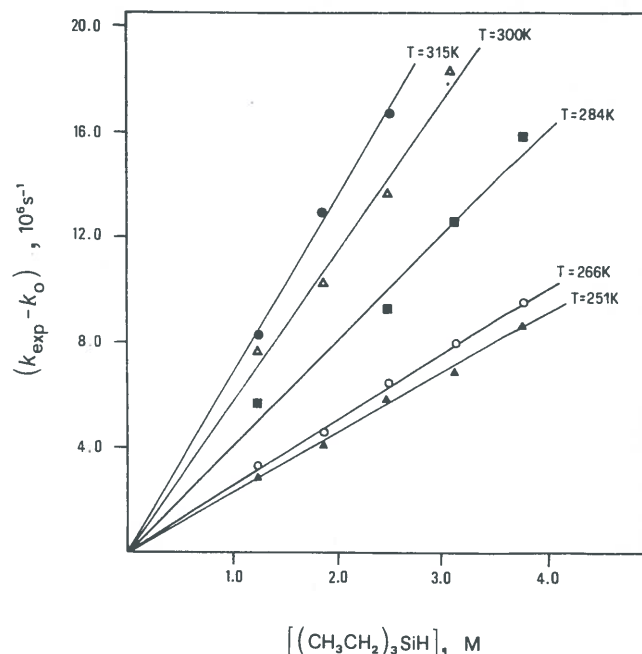


Fig. 2 - Plot of the experimental pseudo-first-order rate constants (corrected for  $k_0$ ) for the reaction of *tert*-butoxyl radicals with triethylsilane at different temperatures.

The rate constant,  $k_2$ , can be determined by measuring  $k_{\text{exp}}$  for different concentrations of  $\text{Et}_3\text{SiH}$  and plotting according to eq. 6. Figure 2 shows the plot of  $k_{\text{exp}}$  (corrected for  $k_0$ , since these values are dependent upon experimental conditions) versus  $[\text{Et}_3\text{SiH}]$  at different temperatures. The values obtained from the slopes give  $k_2$ . For this system the temperature dependence was measured between 251 and 315 K and could be represented by

$$\log(k_2/\text{M}^{-1}\text{s}^{-1}) = (8.85 \pm 0.50) - (2.91 \pm 0.32)/\Theta \quad 7$$

where  $\Theta = 2.303RT \text{ kcal mol}^{-1}$ ;  $k_2 = (5.3 \pm 0.5) \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  at 298 K. The errors correspond to 95% confidence limits.

## DISCUSSION

The present kinetic data, although obtained on a quite complex system, are in gratifying agreement with our previous data obtained by using diphenylmethanol as a probe<sup>1</sup>. Figure 3 shows an Arrhenius plot including all rate constants measured by the two methods. Thus, the temperature dependence between 251 and 345 K could be represented by:

$$\log(k_2/\text{M}^{-1}\text{s}^{-1}) = (8.78 \pm 0.32) - (2.80 \pm 0.44)/\Theta \quad 8$$

where  $\Theta = 2.303RT \text{ kcal mol}^{-1}$ ;  $k_2 = 5.3 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  at 298 K.

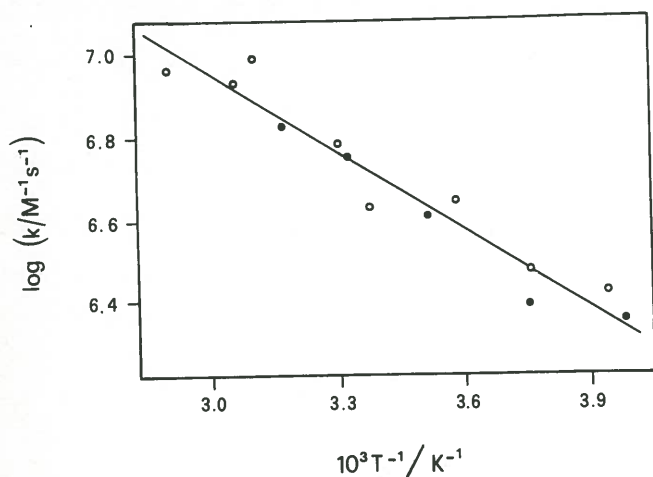


Fig. 3 - Arrhenius plot for the reaction of *tert*-butoxyl radical with triethylsilane using diphenylmethanol (○) and  $\alpha$ -toluenesulphonyl chloride (●) as probes.

However, our rate constants are considerably higher than the gas-phase values of Choo and coworkers<sup>6</sup> (see above). Although a phase and/or a specific solvent effect cannot be ruled out as an explanation for these differences, it does seem rather unlikely for rate constants to be an order of magnitude lower in gas phase than in non-polar hydrocarbon solvents. We therefore attribute these discrepancies to the approximations employed in the kinetic analysis of the data obtained in the gas phase, in particular, either to a very small temperature range or inaccuracies in the rate constants of the reference reaction<sup>b</sup>. It is also worth mentioning that

<sup>(b)</sup> It should be noticed that very different Arrhenius parameters for the decomposition of *tert*-butoxyl radicals have appeared in the literature. The Arrhenius parameters for the decomposition of *tert*-butoxyl radicals used by Choo and coworkers are values that have been estimated and, consequently, may be subject to relatively large errors<sup>12</sup>.

the BEBO calculations carried out by Choo and coworkers<sup>6</sup> for the reaction



give an activation energy of 2.3 kcal mol<sup>-1</sup> which is in close agreement with our experimental values.

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