# Kinetics of Abstraction Reactions of *tert*-Butoxyl Radicals with Cyclohexane and Methyl-substituted Cyclohexanes in the Gas Phase

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The reactions of tert-butoxyl radicals, generated by the pyrolysis of di-tert-butyl peroxide with cyclohexane and a number of methyl-substituted cyclohexanes have been studied. The Arrhenius parameters corresponding to overall hydrogen abstraction have been determined in the temperature range 399–434 K based on the values of the Arrhenius parameters for pressure-dependent decomposition of *tert*-butoxyl radicals obtained by Batt and Robinson (L. Batt and G. N. Robinson, *Int. J. Chem. Kinet.*, 1982, **14**, 1053). The compounds studied were cyclohexane, methylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, 1,1-dimethylcyclohexane, 1,1,3-trimethylcyclohexane and 1,2,4-trimethylcyclohexane. Arrhenius parameters for the abstraction of secondary and tertiary hydrogen atoms by *tert*-butoxyl radicals have been determined to be  $log(A/dm^3 mol^{-1} s^{-1}) = 9.23 \pm 0.07$ ,  $E/kJ mol^{-1} = 25.4 \pm 0.9$  and  $log(A/dm^3 mol^{-1} s^{-1}) = 9.90 \pm 0.11$ ,  $E/kJ mol^{-1} = 22.2 \pm 1.1$ , respectively.

In a previous paper<sup>1</sup> rate data have been reported for the gas-phase reactions of *tert*-butoxyl radicals with alkanes, reactions that are among the principal propagating steps in the low-temperature combustion regime. *tert*-Butoxyl radicals were generated by the pyrolysis of di-*tert*-butyl peroxide. The rate of the abstraction reaction with *tert*-butoxyl radicals is determined by comparing it with the rate of decomposition of the radical. This paper is devoted to a study of the abstraction reactions of *tert*-butoxyl radicals with cyclohexane and methyl-substituted cyclohexanes. No previous work has been reported for the hydrogen-abstraction reactions and alkyl-substituted cyclic hydrocarbons and alkyl-substituted cyclic hydrocarbons in the gas phase.<sup>2</sup>

#### Experimental

Di-tert-butyl peroxide (Koch-Light) was dried over anhydrous  $MgSO_4$  and purified by bulb-to-bulb distillation on a vacuum line until no impurities could be detected by GC. Other reactants were commercial samples and were used after degassing and distillation. The apparatus used have been described previously.<sup>1</sup>

Mixtures of di-*tert*-butyl peroxide (5 Torr), cyclohexane or the methyl-substituted cyclohexane (30–120 Torr) and nitrogen were admitted to the required pressure in a cylindrical Pyrex cell (length 15 cm; diameter 3.5 cm). Each reaction mixture was made up to 500 Torr with nitrogen. Pressures were measured using a calibrated pressure transducer and after the required time of pyrolysis, products were analysed by on-line GC.

#### **Results and Discussion**

The decomposition of di-*tert*-butyl peroxide (DTBP) under the conditions of the experiment has been reported.<sup>3,4</sup> The main products formed were acetone, methane, ethane and *tert*-butyl alcohol. In the presence of cyclic hydrocarbon (RH) the only relevant reactions occurring are shown in Scheme 1.

$$DTBP \rightarrow 2Bu^{t}O^{*}$$
(1)

$$Bu'O' + M \rightarrow (CH_3)_2CO + CH_3 + M$$
(2)

$$Bu^{t}O^{*} + RH \rightarrow Bu^{t}OH + R^{*}$$

The Arrhenius parameters for the first-order decomposition of di-*tert*-butyl peroxide obtained in the present work, *i.e.*  $\log(A_{obs}/s^{-1}) = 15.31 \pm 0.30$  and  $E_{obs}/kJ \mod^{-1} = 156.5 \pm 1.5$ based on the rate of formation of acetone are in good agreement with those found by earlier workers.<sup>3,5</sup>

Kinetic analysis of Scheme 1 predicts a linear dependence of  $R_{Bu'OH}/R_{(CH_3)_2CO}$  on [RH] as shown by eqn. (4).

$$\frac{R_{\text{ButOH}}}{R_{(\text{CH}_3)_2\text{CO}}} = \frac{k_3 \text{ [RH]}}{k_2} \tag{4}$$

where  $R_{Bu_1OH}$  and  $R_{(CH_3)_2CO}$  are the rates of formation of tertbutyl alcohol and acetone, respectively. In a series of experiments di-tert-butyl peroxide (5 Torr) was pyrolysed in the presence of cyclohexane, methylcyclohexane, 1,2-dimethylcyclohexane, 1,3-dimethylcyclohexane, 1,1-dimethylcyclohexane, 1,1,3-trimethylcyclohexane and 1,2,4-trimethylcyclohexane at several temperatures in the range 399-434 K, varying the pyrolysis time (Table 1). In another series of experiments, di-tert-butyl peroxide was allowed to decompose with cyclohexane and methyl-substituted cyclohexanes at 410 K, varying the initial [RH] (Fig. 1). The ratio of rate constants,  $k_3/k_2$ , was calculated using eqn. (4). The rate of formation of tert-butyl alcohol by hydrogen abstraction from the peroxide itself by tert-butoxyl radical was considered to be negligible since only low conversions of peroxide (ca. 10%) were used. Previously<sup>1</sup> we have shown that the decomposition of the tert-butoxyl radical was pressure dependent. In the present work all experiments were performed at a constant total pressure of 500 Torr using nitrogen as a diluent gas.

#### Calculation of $k_2(p)$

(3)

The rate constant for the decomposition of the *tert*-butoxyl radical at pressure, p, using RRK<sup>6</sup> theory has been reported.<sup>1,3</sup> In the present work, the values for  $k_2(\infty)$  were calculated from the Arrhenius parameters reported by Batt and Robinson,<sup>7</sup>  $\log[A_2(\infty)/s^{-1}] = 14.6$  and  $E_2(\infty)/kJ$  mol<sup>-1</sup> = 66.5.<sup>8-10</sup> Using eqn. (4) the ratio  $k_3/k_2(p)$ , and thus  $k_3/k_2(\infty)$  and the value of  $k_3$  itself, were determined (Table 1). The corresponding Arrhenius parameters for all the compounds studied derived from their Arrhenius plots are given in Table 2. The error limits quoted in this table are 95% confidence limits.

	[Bu'OH]				
	[RH]	no. of	[CH <sub>3</sub> COCH <sub>3</sub> ][RH]	$k_{3}/10^{7}$	
$T/\mathbf{K}$	$/10^{-3}$ mol dm <sup>-3</sup>	expts.	$/\mathrm{dm^3\ mol^{-1}}$	$dm^3 mol^{-1} s^{-1}$	
<u> </u>		cyclohexar	ne		
300	2.81	5	$23.1 \pm 1.1$	$0.97 \pm 0.05$	
399 410	2.01	4	$183 \pm 13$	$1.24 \pm 0.08$	
410	2.74	3	$13.3 \pm 0.8$	$1.40 \pm 0.11$	
434	2.59	3	$9.6 \pm 0.7$	$1.86 \pm 0.13$	
		methylcyclohe	exane		
309	2.81	5	42.9 + 2.57	$1.80 \pm 0.09$	
410	2.74	3	33.3 + 1.50	2.18 + 0.11	
420	2.67	3	26.2 + 1.57	$2.75 \pm 0.17$	
434	2.59	3	$17.0 \pm 1.02$	$3.30 \pm 0.23$	
		1,2-dimethylcycl	ohexane		
300	2.81	4	64.4 + 3.86	$2.70 \pm 0.14$	
410	2.74	3	$48.3 \pm 2.42$	$3.16 \pm 0.16$	
420	2.67	3	36.2 + 2.53	$3.80 \pm 0.27$	
434	2.59	3	$25.2 \pm 1.60$	$4.90 \pm 0.34$	
		1,3-dimethylcycl	ohexane		
399	2.81	4	65.6 + 3.50	$2.75 \pm 0.19$	
410	2.74	3	$51.8 \pm 2.72$	$3.39 \pm 0.15$	
420	2.67	3	$39.7 \pm 2.38$	$4.17 \pm 0.25$	
434	2.59	3	$27.6 \pm 1.85$	$5.37 \pm 0.31$	
		1,1-dimethylcycl	ohexane		
399	2.81	3	19.8 + 1.20	0.83 + 0.06	
410	2.74	3	$15.3 \pm 0.61$	$1.00 \pm 0.04$	
420	2.67	4	$11.4 \pm 0.75$	1.20 + 0.08	
434	2.59	3	$8.0 \pm 0.6$	$1.55 \pm 0.12$	
		1,1,3-trimethylcyd	clohexane		
399	2.81	3	40.6 ± 2.64	$1.70 \pm 0.10$	
410	2.74	3	$31.2 \pm 1.56$	$2.04 \pm 0.08$	
420	2.67	3	$23.3 \pm 1.35$	$2.45 \pm 0.13$	
434	2.59	3	$15.6 \pm 1.09$	$3.02 \pm 0.21$	
		1,2,4-trimethylcyd	clohexane		
399	2.01	4	84.0 ± 5.53	3.52 + 0.18	
410	1.98	3	$66.7 \pm 3.82$	$4.36 \pm 0.26$	
420	1.90	4	$47.7 \pm 2.86$	$5.01 \pm 0.30$	
434	1.48	3	$34.0 \pm 2.04$	$6.61 \pm 0.41$	

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Table 1 Decomposition of di-tert-butyl peroxide in the presence of cyclohexane and methyl-substituted cyclohexanes

DTBP, 5 Torr; pressure made up with nitrogen to 500 Torr.

The present data shows that the relative rates depend upon the number and type of abstractable hydrogen atoms in the substrates. In particular, the rate constants are largely determined by the number of tertiary hydrogen atoms, and the compounds may be classified into those containing 0, 1, 2 or 3 tertiary hydrogens. Assuming the additivity principle, the overall rate of abstraction can be expressed as the sum of contributions from each primary, secondary and tertiary

 
 Table 2
 Arrhenius parameters for the overall abstraction of hydrogen atoms by tert-butoxyl radicals

compound	$log(A_3/dm^3 mol^{-1} s^{-1})$	$E_3/kJ$ mol <sup>-1</sup>
cyclohexane methylcyclohexane 1,2-dimethylcyclohexane 1,3-dimethylcyclohexane 1,1-dimethylcyclohexane 1,1,3-trimethylcyclohexane 1,2,4-trimethylcyclohexane	$10.43 \pm 0.05 \\ 10.57 \pm 0.04 \\ 10.67 \pm 0.03 \\ 11.06 \pm 0.06 \\ 10.28 \pm 0.06 \\ 10.36 \pm 0.05 \\ 10.84 \pm 0.04$	$26.3 \pm 0.525.2 \pm 0.324.8 \pm 0.427.7 \pm 1.025.7 \pm 0.623.9 \pm 0.925.2 \pm 0.7$

hydrogen atom, then it is possible to derive values for the individual rate constants and their Arrhenius parameters.

Inspection of the data in Table 1 shows that the contribution to the overall rate constants from abstraction of primary hydrogen atoms is very small (ca. 8% at 434 K), consequently the rate constant for abstraction of a primary hydrogen atom,  $k_p$ , cannot be derived from the present data. In order to calculate overall rate constants a value of  $k_p$  is required and it was assumed that abstraction of hydrogen atoms from methyl groups of substituted cyclohexanes was similar to that from the methyl groups in 2,2-dimethylpropane, for which its Arrhenius parameters were reported<sup>1</sup> as  $\log(A_p/dm^3 mol^{-1} s^{-1}) = 9.25 \pm 0.18$  and  $E_p/kJ mol^{-1} = 32.4 \pm 1.4$ . The mean value of rate constant for abstraction of secondary H atom,  $k_{\rm s}$ , was calculated from the overall rate constant for cyclohexane,  $k(cyclohexane) = 12k_s$ , and also from the overall rate for 1,1-dimethylcyclohexane, constant k(1,1-dimethylcyclohexane) =  $6k_p + 10k_s$ , by using the above value of  $k_p$ . A mean value of  $k_t$  was then derived from  $k_p$  and  $k_s$ , and the overall rate constant for each of the compounds methylcyclohexane, 1,2-, and 1,3-dimethylcyclohexane, 1,1,3-, and 1,2,4-trimethylcyclohexane. Using the mean values of  $k_s$  and  $k_{\rm t}$  obtained from the observed overall rate constants at

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Fig. 1 Decomposition of di-tert-butyl peroxide (5 Torr) in the presence of (a) 1,1-dimethylcyclohexane, (b) cyclohexane, (c) 1,1,3-trimethylcyclohexane, (d) methylcyclohexane, (e) 1,2-dimethylcyclohexane, (f) 1,3-dimethylcyclohexane, (g) 1,2,4-trimethylcyclohexane. Reaction time 28 min, 410 K

several temperatures in the range 399–434 K, the derived Arrhenius parameters are given in Table 3.

A comparison of the present data with those reported previously<sup>1</sup> (Table 3) shows that the Arrhenius parameters are in good agreement.

 
 Table 3
 Arrhenius parameters for abstraction of primary, secondary and tertiary H atoms (per atom)

	$\frac{\log(A/dm^3)}{mol^{-1} s^{-1}}$	<i>E</i> /kJ mol <sup>-1</sup>	ref.
primary	$9.25 \pm 0.18$	$32.4 \pm 1.4$	1
secondary	$9.23 \pm 0.12$	$25.4 \pm 1.2$	this work
-	$9.44 \pm 0.03$	$27.0 \pm 0.3$	1
	$9.56 \pm 0.45$	$28.9 \pm 3.6$	1
tertiary	$9.90 \pm 0.15$	$22.2 \pm 0.9$	this work
	$9.97 \pm 0.10$	$23.0 \pm 0.4$	1

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