Reactions of Oxygenated Radicals in the Gas Phase. Part 13.[1] Reactions of t-Butoxyl Radicals with Alkanes and Alkenes

Mohammed I. Sway and David J. Waddington *
Department of Chemistry, University of York, Heslington, York YO1 5DD

Rate data for the abstraction reactions between t-butoxyl radicals and some hydrocarbons have been determined between 399 and 434 K. The hydrocarbons studied were the alkanes, 2,2-dimethylpropane, butane, and 2-methylpropane; cyclohexane; and the alkenes, propene, 2-methylpropene, *cis*- and *trans*-but-2-ene, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene. The alkoxyl radicals were generated by thermolysis of di-t-butyl peroxide. The experimentally determined activation energies of some of these reactions are compared with those calculated by a semi-empirical method.

The reactions of hydrocarbons with alkoxyl radicals are among the principal propagating steps in the low-temperature combustion regime for alkanes and alkenes. Moreover, alkenes, released into the atmosphere, as products of the partial oxidation of alkanes, play an important role in the chemistry of the atmosphere, for example in the formation of photochemical smog. While alkoxyl radicals can only react with alkanes by abstraction, there are two distinct types of reaction between alkenes and alkoxyl radicals. In one, a radical adds to the double bond of the alkene, leading eventually, in the atmosphere, to a peroxyl radical.[2] In the other, a radical abstracts a hydrogen atom from the alkene, leading to the formation of allyl, alkenylperoxyl, and alkenyloxyl radicals;[3] the last-named, in turn, enters into reactions with other alkenes, forming longer chain unsaturated free radicals which serve as nuclei for organic aerosols in polluted air.[4]

In a previous paper[5] we reported rate data for the reaction of t-butoxyl radicals with some aldehydes and ketones. The radicals were generated by the pyrolysis of di-t-butyl peroxide. The rate of the abstraction reaction with t-butoxyl is determined by comparing it with the rate of decomposition of the radical.

We have now extended the data by examining the abstraction reactions of t-butoxyl radicals with some alkanes and comparing our results with those obtained earlier by Tedder and co-workers[6,7] who obtained rate data for the abstraction reactions between t-butoxyl radicals and butane and 2-methylpropane; they used t-butyl hypochlorite as the radical source. We have also studied the abstraction reaction between t-butoxyl radicals and some alkenes.

Experimental

A static vacuum system was used, with a cylindrical Pyrex reaction vessel (15.0 cm long; 3.5 cm diameter; surface to volume ratio 0.80 cm^{-1}) suspended in an electric furnace, the temperature being controlled to within ±0.1 °C. The line from the reaction vessel led to gas chromatographs (Pye 104 models with flame-ionization and thermal-conductivity detectors) which in turn could be linked to a mass spectrometer (AEI MS 30; 70 eV electron energy; source temperature, 413 K). Pressure measurements were made with a transducer (Consolidated Electrodynamics).

Di-t-butyl peroxide (Koch-Light Laboratories Ltd.) was dried ($\mathrm{MgSO_4}$) and then purified by preparative g.l.c. (10% w/w diethylhexyl sebacate on Gas Chrom Q). Other reactants were obtained commercially and redistilled until no impurities could be detected by g.c.

The columns used for analysis were 20% w/w dinonyl phthalate on Gas Chrom Q (1.5 m length and 4 mm diameter) and two columns filled with 20% w/w diethylhexyl sebacate on Gas Chrom Q (1.5 and 3.0 m length columns with 4 mm diameter).

Results and Discussion

The decomposition of di-t-butyl peroxide (DTBP) under the conditions of the experiment has been studied in detail.[5,8] The formation of the main products, methane, ethane, acetone, and t-butanol, can be rationalised by the simplified mechanism in equations (1)—(5). Calculations[5] based on the rate of

$$\mathrm{DTBP} \longrightarrow 2\mathrm{Bu^tO^\bullet} \tag{1}$$

$$\mathrm{Bu^tO^\bullet} + \mathrm{M} \longrightarrow \mathrm{(CH_3)_2CO} + \dot{\mathrm{C}}\mathrm{H_3} + \mathrm{M} \tag{2}$$

$$\dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{C}}\mathrm{H_3} \longrightarrow \mathrm{C_2H_6} \tag{3}$$

$$\dot{\mathrm{C}}\mathrm{H_3} + \mathrm{(CH_3)_2CO} \longrightarrow \mathrm{CH_4} + \dot{\mathrm{C}}\mathrm{H_2COCH_3} \tag{4}$$

$$\dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{C}}\mathrm{H_2COCH_3} \longrightarrow \mathrm{CH_3CH_2COCH_3} \tag{5}$$

formation of acetone yielded Arrhenius parameters, $\log_{10}(A_{\mathrm{obs.}}/\mathrm{s^{-1}}) = 15.9 \pm 0.3$ and $E_{\mathrm{obs.}}/\mathrm{kJ\ mol^{-1}} = 160.0 \pm 2.9$.

Di-t-butyl peroxide was allowed to decompose with alkanes (Figure 1) (butane, cyclohexane, 2-methylbutane, and 2,2-dimethylpropane) and with alkenes (Figure 2) (propene, 2-methylpropene, *cis*-but-2-ene, *trans*-but-2-ene, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene). The ratio of rate constants k_6/k_2 was calculated using relationship (i) where RH is the added alkane or alkene in reaction (6).

$$\mathrm{d[Bu^tOH]/d[(CH_3)_2CO]} = k_6[\mathrm{RH}]/k_2 \tag{i}$$

$$\mathrm{Bu^tO^\bullet} + \mathrm{RH} \longrightarrow \mathrm{Bu^tOH} + \mathrm{R^\bullet} \tag{6}$$

The extent of reaction was small enough to ensure that the concentration of t-butanol formed from the peroxide itself was minute compared with that formed by reaction (6). Further, no products from $\mathrm{R^\bullet}$ were detectable.

Di-t-butyl peroxide was decomposed in the presence of 2,2-dimethylpropane, butane, and 2-methylpropane at 399 and 410 K, and *trans*-but-2-ene at 410 K, varying the total pressure (Table 1). The variation in the ratio of [t-butanol] to [acetone][hydrocarbon] clearly shows that the decomposition of the t-butoxyl radical is pressure dependent. This has been observed several times, for example in the reactions with phenol[9] and tetrafluorohydrazine.[10] More recently, Batt and co-workers studied the reaction in detail, using tetrafluoromethane,[11,12] sulphur hexafluoride,[12] and nitrogen[12] as the inert gases and nitric oxide as the radical trap.

Table 1. Decomposition of di-t-butyl peroxide in the presence of hydrocarbons. Effect of varying the total pressure: DTBP, 5 Torr; hydrocarbon, 200 Torr; nitrogen pressure varied

Hydrocarbon	T/K	10^2P/ mol dm^{-3}	Time (min)	10^6-[Bu^{t}OH]/ mol dm^{-3}	10^6-[Acetone]/ mol dm^{-3}	$\frac{[\mathrm{Bu^tOH}]}{[\mathrm{Acetone}]\text{-}[\mathrm{RH}]}$/ dm^3 mol^{-1}	D	$\frac{k_2(p)}{k_2(\infty)}$	$10^{-6}k_6$/ dm^3 mol^{-1} s^{-1}
2,2-Dimethylpropane	399	0.82	30	0.155	4.67	4.14	5.13	0.43	1.26
		1.20	30	0.143	4.95	3.60	4.99	0.48	1.23
		1.61	30	0.137	5.34	3.20	4.87	0.51	1.16
		1.81	30	0.150	5.70	3.28	4.82	0.53	1.23
		2.00	30	0.176	5.75	3.81	4.78	0.54	1.46
		2.41	30	0.129	5.82	2.76	4.70	0.57	1.12
		2.81	30	0.138	5.96	2.89	4.64	0.59	1.21
	410	0.80	20	0.273	10.98	3.19	5.14	0.39	1.61
		1.17	20	0.258	11.36	2.91	4.99	0.43	1.63
		1.56	20	0.279	12.60	2.84	4.88	0.47	1.74
		1.76	20	0.238	12.82	2.38	4.83	0.49	1.52
		1.96	20	0.256	12.50	2.62	4.79	0.50	1.70
		2.35	20	0.229	12.65	2.32	4.71	0.53	1.60
		2.74	20	0.234	13.23	2.27	4.65	0.55	1.62
Butane	399	0.82	30	0.446	5.38	10.34	5.14	0.43	3.16
		1.20	30	0.445	5.91	9.39	4.99	0.47	3.13
		1.61	30	0.437	6.23	8.75	4.87	0.51	3.17
		1.81	30	0.424	6.39	8.27	4.82	0.53	3.17
		2.00	30	0.425	6.67	7.94	4.78	0.54	2.99
		2.41	30	0.418	7.03	7.41	4.70	0.57	2.99
		2.81	30	0.426	7.39	7.19	4.64	0.59	3.01
	410	0.80	20	0.751	13.15	7.32	5.15	0.39	3.71
		1.17	20	0.741	14.22	6.68	4.99	0.43	3.73
		1.56	20	0.704	15.13	5.97	4.88	0.47	3.65
		1.76	20	0.684	15.33	5.72	4.83	0.49	3.64
		1.96	20	0.750	16.85	5.71	4.79	0.50	3.71
		2.35	20	0.730	17.60	5.32	4.71	0.53	3.67
		2.74	20	0.730	18.20	5.14	4.64	0.55	3.68
2-Methylpropane	399	0.82	30	1.53	5.38	35.46	5.14	0.43	10.8
		1.20	30	1.45	5.91	30.59	4.99	0.47	10.2
		1.61	30	1.45	6.23	29.02	4.87	0.51	10.5
		1.81	30	1.41	6.39	27.51	4.82	0.53	10.4
		2.00	30	1.37	6.67	25.61	4.78	0.54	9.80
		2.71	30	1.41	7.01	25.08	4.70	0.57	10.1
		2.81	30	1.41	7.55	23.29	4.64	0.59	9.80
	410	0.80	20	2.58	13.29	24.89	5.15	0.39	12.6
		1.17	20	2.50	14.08	22.76	4.99	0.43	12.7
		1.56	20	2.42	15.13	20.51	4.88	0.47	12.5
		1.76	20	2.39	15.33	19.99	4.83	0.49	12.7
		1.96	20	2.42	16.62	18.67	4.79	0.50	12.1
		2.35	20	2.39	17.60	17.41	4.71	0.53	12.0
		2.74	20	2.42	18.77	16.53	4.64	0.55	11.8
trans-But-2-ene	410	0.80	20	1.48	10.95	17.33	5.15	0.39	8.82
		1.17	20	1.35	11.34	15.25	5.00	0.43	8.54
		1.56	20	1.36	12.51	13.94	4.88	0.47	8.50
		1.96	20	1.23	12.32	12.80	4.79	0.49	8.20
		2.35	20	1.17	12.67	11.84	4.71	0.52	8.01
		2.74	20	1.20	13.22	11.64	4.65	0.54	8.24

Details on how $k_2(p)$, the value of the rate constant for the decomposition of the radical at pressure, p, has been calculated are discussed in an earlier paper.[5] Essentially, RRK theory was used.[13] The rate constant for the unimolecular decomposition of the radical was assumed to occur by two processes, equations (7) and (8) and the rate constants can be described by

$$\mathrm{Bu^tO^{\bullet}} + \mathrm{M} \rightleftharpoons \mathrm{Bu^tO^{\bullet *}} + \mathrm{M} \qquad (7)$$

$$\mathrm{Bu^tO^{\bullet *}} \longrightarrow (\mathrm{CH_3})_2\mathrm{CO} + \dot{\mathrm{C}}\mathrm{H_3} \qquad (8)$$

relation (ii). The Kassel integral $I(S,B,D)$ is given by relation (iii), where $B = E/RT$, $D = \log(A/Z[\mathrm{M}])$. Z is the collisional

$$k(p) = k_{\infty}I(S,B,D) \qquad \text{(ii)}$$

$$I(S,B,D) = \frac{1}{(S-1)!}\int_0^{\infty} \frac{x^{S-1}e^{-x}\mathrm{d}x}{1 + 10^{\mathrm{D}}[x/(B+x)]^{S-1}} \qquad \text{(iii)}$$

frequency and S is the number of effective oscillators in the energised molecule. Parameters S,B,D were estimated from available data.[5,14] For values of Z, one needs values of the collisional diameters of the t-butoxyl radicals, nitrogen, and hydrocarbons. The collision diameters were calculated by a method due to Bondi;[15] those for the hydrocarbons were checked against values already used in the literature.[16] $I(S,B,D)$ was then evaluated from tables computed by

Table 2. Decomposition of di-t-butyl peroxide in the presence of some hydrocarbons. DTBP, 5 Torr; pressure made up with nitrogen to 500 Torr

Hydrocarbon	T/K	10^2[RH]/ mol dm^{-3}	Number of expts.	$\frac{[\text{Bu}^t\text{OH}]}{[\text{CH}_3\text{COCH}_3][\text{RH}]}$/ dm^3 mol^{-1}	D	$\frac{k_2(p)}{k_2(\infty)}$	$10^{-6}k_6$/ dm^3 mol^{-1} s^{-1}
2,2-Dimethylpropane	399	1.81	3	3.04 ± 0.04	4.75	0.55	1.19 ± 0.01
	410	1.76	4	2.47 ± 0.03	4.76	0.50	1.61 ± 0.02
		1.56	1	2.59	4.77	0.50	1.68
		1.17	1	2.62	4.78	0.50	1.67
		0.78	1	2.67	4.79	0.49	1.70
	434	1.66	4	1.18 ± 0.02	4.77	0.50	2.66 ± 0.05
Cyclohexane	399	0.32	4	26.1 ± 3.2	4.79	0.53	9.8 ± 1.2
	410	0.31	3	19.1 ± 1.3	4.80	0.49	12.1 ± 0.9
		0.27	1	19.3	4.80	0.49	12.3
		0.33	1	18.2	4.80	0.49	11.6
		0.45	1	17.8	4.80	0.49	11.3
	434	0.30	3	8.57 ± 0.63	4.81	0.49	18.9 ± 1.4
Butane	399	1.81	7	7.88 ± 0.14	4.76	0.55	3.08 ± 0.05
	410	1.76	5	5.69 ± 0.03	4.77	0.50	3.70 ± 0.02
		0.78	1	5.66	4.79	0.49	3.61
		0.98	1	5.54	4.78	0.50	3.60
		1.17	1	5.63	4.78	0.50	3.66
		1.49	1	5.57	4.77	0.50	3.62
		1.56	1	5.68	4.77	0.50	3.69
	434	1.66	4	2.83 ± 0.13	4.78	0.49	6.23 ± 0.31
2-Methylpropane	399	1.81	7	26.18 ± 0.59	4.76	0.55	10.2 ± 0.2
	410	1.76	5	18.65 ± 0.15	4.77	0.50	12.1 ± 0.1
		0.78	1	17.38	4.78	0.49	11.1
		1.17	1	19.41	4.78	0.50	12.6
		1.56	1	20.05	4.77	0.50	13.0
	434	1.66	4	8.27 ± 0.26	4.78	0.49	18.2 ± 0.5

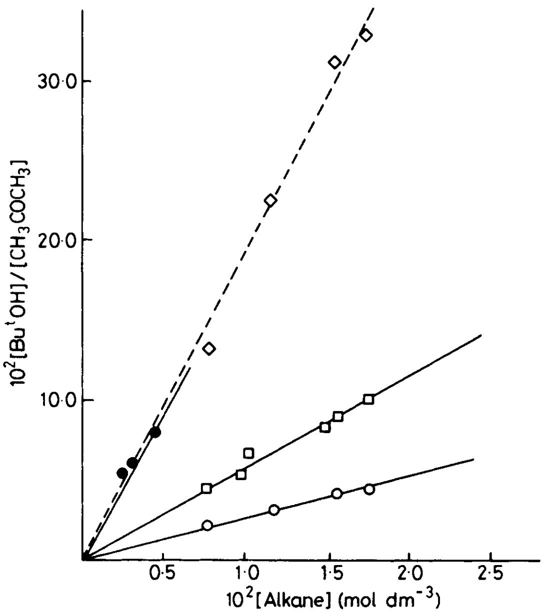


Figure 1. Decomposition of di-t-butyl peroxide in the presence of saturated hydrocarbons at 410 K, 5 Torr. ○, 2,2-Dimethylpropane (analyses at 30 min); □, butane (analyses at 20 min); ●, cyclohexane (analyses at 25 min); ◇, 2-methylpropane (analyses at 20 min)

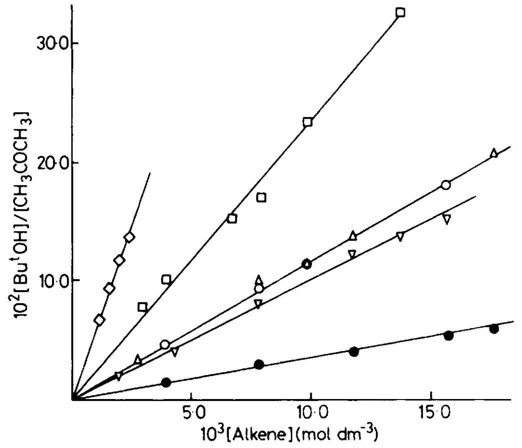


Figure 2. Decomposition of di-t-butyl peroxide in the presence of alkenes at 410 K, 5 Torr. Analyses at 20 min. ◇, 2,3-Dimethylbut-2-ene; □, 2-methylbut-2-ene; ○, *cis*-but-2-ene; △, *trans*-but-2-ene; ▽, 2-methylpropene; and ●, propene

Emanuel.[17] The variation of $[k_2(p)/k_2(\infty)]$ with D and hence at different pressures and temperatures were calculated. In the tables of data given in the paper, the values for $k_2(\infty)$ were calculated frm Arrhenius parameters. There are numerous values of $A_2(\infty)$ and $E_2(\infty)$ in the literature, but we have used the most recent values of Batt and Robinson,[12] $\log[A_2(\infty)/\text{s}^{-1}] = 14.6$ and $E_2(\infty) = 66.5$ kJ mol^{-1}, which have been obtained by

Table 3. Decomposition of di-t-butyl peroxide in the presence of alkenes. DTBP, 5 Torr; pressure made up with nitrogen to 500 Torr

Alkene	T/K	10^3[RH]/ mol dm^{-3}	Number of expts.	$\frac{[\mathrm{Bu^tOH}]}{[\mathrm{CH_3COCH_3}][\mathrm{RH}]}$/ dm^3 mol^{-1}	D	$\frac{k_2(p)}{k_2(\infty)}$	$10^{-6}k_6$/ dm^3 mol^{-1} s^{-1}
Propene	399	8.04	4	5.18 ± 0.28	4.78	0.54	1.99 ± 0.11
	410	7.82	5	3.82 ± 0.25	4.79	0.49	2.43 ± 0.16
		3.91	1	3.80	4.80	0.49	2.42
		11.73	1	3.55	4.78	0.49	2.31
		15.64	1	3.44	4.77	0.50	2.24
		17.60	1	3.40	4.76	0.50	2.21
	434	7.39	4	1.76 ± 0.07	4.80	0.49	3.85 ± 0.12
2-Methylpropene	399	8.04	4	13.59 ± 0.25	4.78	0.54	5.21 ± 0.10
	410	7.82	4	9.96 ± 0.43	4.79	0.49	6.35 ± 0.28
		4.30	1	9.71	4.80	0.49	6.19
		11.73	1	10.34	4.78	0.50	6.72
		13.69	1	10.01	4.78	0.50	6.51
		15.64	1	9.59	4.77	0.50	6.23
	434	7.39	4	4.47	4.80	0.49	9.86 ± 0.50
cis-But-2-ene	399	8.04	4	16.93 ± 0.16	4.78	0.54	6.49 ± 0.06
	410	7.82	5	11.96 ± 0.42	4.79	0.49	7.62 ± 0.27
		1.96	1	11.07	4.80	0.49	7.01
		3.91	1	11.87	4.80	0.49	7.56
		9.78	1	11.70	4.78	0.50	7.61
		15.64	1	11.45	4.77	0.50	7.44
		19.55	1	11.38	4.76	0.51	7.54
	434	7.39	4	5.34 ± 0.11	4.80	0.49	11.78 ± 0.25
trans-But-2-ene	399	8.04	5	17.47 ± 0.50	4.78	0.54	6.70 ± 0.19
	410	7.82	4	12.80 ± 0.14	4.79	0.49	8.15 ± 0.09
		2.74	1	12.59	4.80	0.49	8.02
		9.78	1	11.70	4.80	0.49	7.45
		11.73	1	11.63	4.78	0.50	7.56
		17.60	1	11.77	4.77	0.50	7.65
		19.55	1	11.65	4.76	0.51	7.72
	434	7.39	4	5.75 ± 0.07	4.80	0.49	12.67 ± 0.15
2-Methylbut-2-ene	399	4.02	4	36.60 ± 0.31	4.79	0.53	14.13 ± 0.17
	410	3.91	4	27.61 ± 1.66	4.80	0.49	17.59 ± 1.06
		2.93	1	12.32	4.80	0.49	17.26
		5.87	1	15.29	4.79	0.49	17.17
		6.65	1	12.32	4.79	0.49	14.61
		7.82	1	12.32	4.79	0.49	13.89
		9.78	1	11.73	4.78	0.50	15.21
		13.69	1	11.34	4.77	0.50	15.10
	434	3.69	4	11.07 ± 0.58	4.81	0.49	24.40 ± 1.27
2,3-Dimethylbut-2-ene	399	1.60	4	88.55 ± 4.15	4.79	0.53	33.95 ± 1.48
	410	1.56	4	60.11 ± 0.31	4.80	0.49	38.29 ± 0.20
		1.96	1	59.72	4.80	0.49	38.04
		2.35	1	58.06	4.80	0.49	36.98
		1.14	1	58.48	4.80	0.49	37.25
	434	1.48	4	25.90 ± 0.80	4.81	0.49	57.15 ± 1.90

very careful experimental observation.[11,18,19] The values suggested by Choo and Benson [20] lead to values of k_6 within our experimental errors. However, to enable data for reaction (6) to be recalculated if further data for reaction (2) become available, values for the ratio $[k_2(p)/k_2(\infty)]$ are given in the Tables. Values of S and B are independent of the value of A_2; data for the parameter D depend on A_2 and this would have to be recalculated.

A further series of experiments were carried out with some alkanes (2,2-dimethylpropane, cyclohexane, butane, and 2-methylpropane) and alkenes (propene, 2-methylpropene, *cis*-but-2-ene, *trans*-but-2-ene, 2-methylbut-2-ene, and 2,3-dimethylbut-2-ene) at a constant overall pressure using nitrogen as the inert gas.

The rates of formation of t-butanol and acetone were measured up to *ca.* 10—20% conversion of the peroxide and with very low conversion of the hydrocarbon (Tables 2, 3, 4). Using relation (i) the ratio $k_6/k_2(p)$, and thus $k_6/k_2(\infty)$ and the value of k_6 itself, were obtained. Arrhenius parameters for reaction (6) are given in Table 5. The error limits were computed using a conventional least-means square program.

Rate constants for abstraction by t-butoxyl radicals per primary and secondary C–H bond were calculated from the data obtained for 2,2-dimethylpropane and cyclohexane, respectively (Table 5). These were then checked against the data obtained from the results in which butane was the added alkane. A satisfactory correlation was obtained assuming the additivity principle. From results with 2-methylpropane, data

Table 4. Reaction of t-butoxyl radicals with hydrocarbons. Determination of rate constants for reaction (6)

Hydrocarbon	Data from Table	T/K	$10^{-6}k_6$/ dm^3 mol^{-1} s^{-1}
2,2-Dimethylpropane	2	399	1.19 ± 0.01
	1	399	1.23 ± 0.23
	2	410	1.64 ± 0.06
	1	410	1.63 ± 0.11
	2	434	2.66 ± 0.05
Cyclohexane	2	399	9.80 ± 1.20
	2	410	12.0 ± 1.0
	2	434	18.9 ± 1.4
Butane	2	399	3.08 ± 0.05
	1	399	3.09 ± 0.10
	2	410	3.67 ± 0.06
	1	410	3.68 ± 0.04
	2	434	6.23 ± 0.31
2-Methylpropane	2	399	10.2 ± 0.2
	1	399	10.2 ± 0.6
	2	410	12.2 ± 1.1
	1	410	12.3 ± 0.5
	2	434	18.2 ± 0.5
Propene	3	399	1.99 ± 0.11
	3	410	2.37 ± 0.17
	3	434	3.85 ± 0.12
2-Methylpropene	3	399	5.21 ± 0.10
	3	410	6.38 ± 0.34
	3	434	9.86 ± 0.50
cis-But-2-ene	3	399	6.49 ± 0.06
	3	410	7.53 ± 0.52
	3	434	11.8 ± 0.30
trans-But-2-ene	3	399	6.70 ± 0.19
	3	410	7.91 ± 0.35
	1	410	8.30 ± 0.30
	3	434	12.7 ± 0.20
2-Methylbut-2-ene	3	399	14.1 ± 0.2
	3	410	16.4 ± 2.5
	3	434	24.4 ± 1.3
2,3-Dimethylbut-2-ene	3	399	34.0 ± 1.5
	3	410	37.9 ± 0.9
	3	434	57.2 ± 1.9

for abstraction reactions from a tertiary C–H bond were obtained.

Finally, using results from Table 4, values for abstraction from an allylic C–H bond were found (Table 5), using the reasonable assumption that the vinylic C–H bond ($D^{\ominus}$ = 452 kJ mol^{-1}),[21] was too strong for abstraction to take place under these conditions.

The effect of changing the structure of the hydrocarbon on the rate of reaction (6) can now be discussed. Tedder and coworkers studied the reactions between t-butoxyl radicals and alkanes, using hexane and 2,3-dimethylbutane as substrates and the light-induced decomposition of t-butyl hypochlorite as the source of t-butoxyl radicals.[7] They obtained values of $\log(A_6/\mathrm{dm^3 mol^{-1} s^{-1}})$ of 8.3 ± 0.7, 8.2 ± 0.1, and 8.1 ± 0.2 for primary, secondary, and tertiary C–H bonds and corresponding values of E_6 of 34.7 ± 4.3, 29.0 ± 0.7, and 23.8 ± 1.3 kJ mol^{-1}. We are unable to compare their results directly for they used values of $\log(A_2/\mathrm{s^{-1}}) = 13.4$ and $E_2 = 70.2$ kJ mol^{-1} as recommended by Benson and O'Neal,[22] and it is uncertain whether the values of the rate constant, k_2, they used were indeed pressure independent. However, we can compare the *differences* between primary and secondary and between secondary and tertiary attack (Table 5). We favour our technique as the source of radicals is cleaner (there is danger of contamination of chlorine in t-butyl hypochlorite[7]), the reaction mechanism is simpler, and the data were obtained over a wide range of conditions to test the dependence of reaction (2) on pressure.

The values for the activation energies for the reaction (6) show the expected correlation with bond dissociation energies (Table 5). We have used these values to test the semi-empirical technique for calculating activation energies of abstraction reactions. Zavitsas and co-workers[23–25] assumed that, for reaction (iv) the transition state is linear and partial

$$\mathrm{AH} + \mathrm{B}^{\cdot} \longrightarrow \mathrm{BH} + \mathrm{A}^{\cdot} \qquad \text{(iv)}$$

bonding in A–H and B–H is equal. The transition state is described as a resonance hybrid, (I)—(IV).

$$\begin{array}{ccc} & \mathrm{A}\cdots\mathrm{H}\cdots\mathrm{B}\ \text{(I)} & \\ & \mathrm{A} : \mathrm{H} \quad \mathrm{B}^{\cdot}\text{(II)} & \\ \mathrm{AH} + \mathrm{B}^{\cdot} \longrightarrow & & \longrightarrow \mathrm{A}^{\cdot} + \mathrm{BH} \\ & {}^{\cdot}\mathrm{A} \quad \mathrm{H} : \mathrm{B}\ \text{(III)} & \\ & \dot{\mathrm{A}} \quad \dot{\mathrm{H}} \quad \dot{\mathrm{B}}\ \text{(IV)} & \end{array}$$

The total bonding energy in the transition state has three terms. One is the average bonding energy of (II) and (III), which are assumed to equal ${}^1E_{\mathrm{AH}}{}^{\ddagger}$, estimated from equation (v). D_e is calculated from D^0 by adding the zero-point energy

$${}^1E_{\mathrm{AH}}{}^{\ddagger} = D_e[(1 - e^{-\beta(r-r_e)})^2 - 1] \qquad \text{(v)}$$

[equation (vi)], and β from relation (vii).

$$D_e = D^0 + 0.001\,43\omega_0 \qquad \text{(vi)}$$

$$\beta = 0.1218\omega_0(\mu/350\ D^0)^{\frac{1}{2}} \qquad \text{(vii)}$$

The second term $E_{\mathrm{R}}{}^{\ddagger}$ is the delocalisation energy of one odd electron over three atoms and is assumed to be similar to the stabilisation energy of the allyl radical. A third energy term ${}^3E_{\mathrm{AB}}{}^{\ddagger}$, the repulsion (anti-bonding) energy between A and B, is calculated using a modified Morse equation, (viii).

$${}^3E_{\mathrm{AB}}{}^{\ddagger} = 0.45\ D_e[(1 + e^{-\beta(r-r_e)})^2 - 1] \qquad \text{(viii)}$$

The experimental energy of activation is the difference between $E_{\mathrm{total}}{}^{\ddagger}$ and D_e(A–H). A small correction is made for the zero-point energy (ZPE) in the transition state.

The data needed for the calculations are those for Morse functions and the energy of the transition state is evaluated at a distance r_{BH} by first calculating ${}^1E_{\mathrm{BH}}$ and then solving for the distance r_{AH} corresponding to an energy ${}^1E_{\mathrm{BH}}$. The anti-bonding energy ${}^3E_{\mathrm{AB}}{}^{\ddagger}$ is evaluated where $r_{\mathrm{AB}} = r_{\mathrm{AH}} + r_{\mathrm{BH}}$. The procedure is repeated at 0.01 Å increments of r_{BH} until a minimum activation energy is found.

It is now possible to look at this simple theory and compare the data obtained with the experimental results obtained in this study. Table 6 gives the data used in the calculations for the reactions with the alkanes, and Table 5 compares the two sets of data of activation energy obtained.

It is, of course, the data used for determining the parameters in the transition state that are crucial to the success of the calculations. For example, when using a value of $\omega = 1\,060$ cm^{-1} for 2,2-dimethylpropane, chosen because it is the vibrational frequency of several simple ethers,[26] this leads to $E_{\mathrm{calc.}} = 28.3$ kJ mol^{-1}. Zavitsas and Melikian[25] used a value

Table 5. Arrhenius parameters for the abstraction reactions between t-butoxyl radicals and hydrocarbons

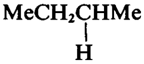
Hydrocarbon	$\log(A_6/dm^3\ mol^{-1}\ s^{-1})$	E_6/kJ mol^{-1}	$\log(A_6{}^a/dm^3\ mol^{-1}\ s^{-1})$	$E_6{}^a$/kJ mol^{-1}	E_6(calc.)/ kJ mol^{-1}
2,2-Dimethylpropane	10.33 ± 0.18	32.4 ± 1.4	9.25 ± 0.18	32.4 ± 1.4	28.3
Cyclohexane	10.54 ± 0.09	27.0 ± 0.3	9.44 ± 0.03	27.0 ± 0.3	23.1
Butane	10.27 ± 0.27	28.9 ± 2.1	9.56 ± 0.45 [b]	28.9 ± 3.6 [b]	22.6 [b]
2-Methylpropane	10.14 ± 0.05	23.9 ± 0.4	9.97 ± 0.10 [c]	23.0 ± 0.4 [c]	18.8 [c]
Propene	9.90 ± 0.29	27.6 ± 2.3	9.42 ± 0.29	27.6 ± 2.3	*ca.* 34
2-Methylpropene	10.16 ± 0.17	26.3 ± 1.4	9.38 ± 0.17	26.3 ± 1.4	
cis-But-2-ene	10.07 ± 0.32	25.0 ± 2.6	9.59 ± 0.32	25.0 ± 2.6	
trans-But-2-ene	10.29 ± 0.23	26.5 ± 1.8	9.81 ± 0.23	26.5 ± 1.8	
2-Methylbut-2-ene	10.13 ± 0.23	22.8 ± 1.8	9.18 ± 0.23	22.8 ± 1.8	
2,3-Dimethylbut-2-ene	10.40 ± 0.41	22.0 ± 3.2	9.32 ± 0.41	22.0 ± 3.2	

[a] Per C–H bond. [b] For CH_2. [c] For CH.

Differences in experimental activation energies

	This work	Ref. 7
$(E_{prim.} - E_{sec.})$/kJ mol^{-1}	3.4—5.2	5.7
$(E_{sec.} - E_{tert.})$/kJ mol^{-1}	9.4	10.9

Table 6. Spectroscopic data used in the calculations of activation energies for abstraction reactions between t-butoxyl radicals and hydrocarbons

	$D^\ominus{}_{298}$/kJ mol^{-1}	r_e/Å	ω/cm^{-1}	ZPE/kJ mol^{-1}	D_e/kJ mol^{-1}	β/Å
Me_3CO–H	439.7 [a]	0.97 [b]	3 617 [c]	22.0	461	2.177
Me_3CCH_2–H	414.2 [d]	1.09 [b]	2 952 [e]	17.7	432	1.819
Me_3CO–CH_2CMe_3	341 [f,g]	1.43 [h]	1 060 [i]	6.2	347	1.985
cyclo-C_6H_{11}–H	400 [j]	1.10 [b]	2 898 [c,k]	17.4	417	1.816
Me_3CO–cyclo-C_6H_{11}	341 [l]	1.43 [h]	1 060 [i]	6.2	347	1.945
 $MeCH_2\underset{\overset{\vert}{H}}{C}HMe$	395.4 [m]	1.09 [n]	2 890 [i]	17.3	413	1.821
Me_3CO–CH(Et)Me	341 [o]	1.43 [h]	1 060 [i]	6.2	347	1.930
Me_3C–H	380.7 [g]	1.09 [n]	2 890 [p]	17.3	398	1.855
Me_3CO–CMe_3	341 [g,q]	1.43 [h]	1 060 [i]	6.2	347	1.985
H–CH_2CHCH_2	369.9 [r]	1.09 [g]	2 895 [c]	17.3	387	1.884
Me_3CO–CH_2CHCH_2	284.5 [g]	1.43 [g]	1 050 [l]	6.3	291	2.149

[a] L. Batt, K. Christie, R. T. Milne, and A. J. Summers, *Int. J. Chem. Kinet.*, 1974, **6**, 877. [b] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, Ithica, N.Y., 1960, 3rd edn. [c] R. Shimanouchi, 'Tables of Molecular Vibrational Frequencies,' NRSDS-NBS-39, Washington D.C., 1972. [d] J. A. Kerr, *Chem. Rev.*, 1966, **66**, 465. [e] By analogy with ethane. [f] Assumed equal to $D^\ominus{}_{298}$ (CH_3O–CH_2CMe_3). [g] S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1976, 2nd edn. [h] By analogy with simple compounds. [i] L. J. Bellamy, 'The Infrared Spectra of Complex Molecules,' Chapman and Hall, London, 1980, 2nd edn. [j] K. C. Ferguson and E. Whittle, *Trans. Faraday Soc.*, 1971, **67**, 2618. [k] Average of symmetric and antisymmetric stretching vibrations. [l] By analogy with simple ethers. [m] By analogy with 2-methylpropane. [n] L. E. Sutton, 'Tables of Interatomic Distances,' Chem. Soc. Spec. Publ., 1965, vol. 18. [o] Assumed equal to $D^\ominus{}_{298}$(MeO–$CHMe_2$). [p] J. J. Fox and A. E. Martin, *Proc. R. Soc. London, Ser. A*, 1940, **175**, 208. [q] Assumed equal to $D^\ominus{}_{298}$(MeO–CMe_3). [r] Ref. 21.

of $\omega = 1\ 031$ cm^{-1} without giving a specific reason, although the value is out of the range quoted in the literature, and this leads to $E_{calc.} = 31.4$ kJ mol^{-1}. Similarly, if a value of D^0 [$(CH_3)_3CO$–$CH_2C(CH_3)_2$] is taken as 345.2 kJ mol^{-1}, the upper limit given in the literature for the corresponding molecule CH_3O–$CH_2C(CH_3)_3$, the calculated activation energy becomes 29.7 kJ mol^{-1}.

Similar calculations for the reactions between alkenes and t-butoxyl radicals show a considerable discrepancy between experimental results, for example, for propene $E_a = 27.6 \pm 2.3$ kJ mol^{-1} but the calculated value is 0.5 kJ mol^{-1}. One source of error is in the value given to the stabilisation energy, $E_R{}^{\ddagger}$. It must be larger than the stabilisation energy of the allyl radical. The stabilisation energy of the pentadienyl radical, to which it may be compared is 77 kJ mol^{-1},[27,28] and this leads to a calculated value for the activation energy for the reaction between propene and t-butoxyl radical of *ca.* 34 kJ mol^{-1}. Obviously the simple theory needs some refinement in order to cope with the radical abstraction reactions from unsaturated molecules.

References

1 Part 12, M. I. Sway and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1983, 139.

2 D. J. M. Ray and D. J. Waddington, 14th International Symposium on Combustion, The Combustion Institute, Pittsburgh, 1973, p. 259.

3 D. J. M. Ray and D. J. Waddington, *Combust. Flame*, 1973, **21**, 327.

4 M. J. Prager, E. R. Stephens, and W. E. Scott, *Ind. Eng. Chem.*, 1960, **52**, 521.

5 N. Y. Al Akeel, K. Selby, and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1981, 1036.

6 J. L. Brokenshire, A. Nechvatal, and J. M. Tedder, *Trans. Faraday Soc.*, 1970, **66**, 2029.

7 I. K. Stoddart, A. Nechvatal, and J. M. Tedder, *J. Chem. Soc., Perkin Trans. 2*, 1974, 473.

8 K. Selby and D. J. Waddington, *J. Chem. Soc., Perkin Trans. 2*, 1979, 1259.

9 M. F. R. Mulcahy and D. J. Williams, *Aust. J. Chem.*, 1964, **17**, 1291.

10 P. Cadman, A. F. Trotman-Dickenson, and A. J. White, *J. Chem. Soc. A*, 1971, 2296.

11 L. Batt, *Int. J. Chem. Kinet.*, 1979, **11**, 977.

12 L. Batt and G. N. Robinson, *Int. J. Chem. Kinet.*, 1982, **14**, 1053.

13 P. J. Robinson and K. A. Holbrook, 'Unimolecular Reactions,' Wiley–Interscience, London, 1972.

14 D. M. Golden, R. K. Solly, and S. W. Benson, *J. Phys. Chem.*, 1971, **75**, 1333.

15 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

16 A. F. Trotman-Dickenson, J. R. Birchard, and E. W. R. Steacie, *J. Chem. Phys.*, 1951, **19**, 163.

17 G. Emanuel, *Int. J. Chem. Kinet.*, 1972, **4**, 591.

18 L. Batt and R. J. Milne, *Int. J. Chem. Kinet.*, 1976, **8**, 59.

19 L. Batt, R. D. McCulloch, and R. T. Milne, 'Proceedings of the Symposium on Chemical Kinetics Data for the Upper and Lower Atmosphere,' ed. S. W. Benson, Wiley–Interscience, New York, 1975, *Int. J. Chem. Kinet.*, 1975, symposium 1, 441.

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

21 D. M. Golden and S. W. Benson, *Chem. Rev.*, 1969, **69**, 125.

22 S. W. Benson and H. E. O'Neal, 'Kinetic Data on Gas-phase Unimolecular Reactions,' NSRDS—NBS 21, Washington D.C., 1970, p. 585.

23 A. A. Zavitsas, *J. Am. Chem. Soc.*, 1972, **94**, 2779.

24 A. A. Zavitsas and J. A. Pinto, *J. Am. Chem. Soc.*, 1972, **94**, 7390.

25 A. A. Zavitsas and A. A. Melikian, *J. Am. Chem. Soc.*, 1975, **97**, 2757.

26 R. B. Barnes, R. C. Gore, U. Liddel, and Van Zandt Williams, 'Infra-red Spectroscopy: Industrial Applications and Bibliography,' Reinhold, New York, 1974.

27 A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1980, **76**, 266.

28 A. B. Trenwith, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 3131.

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