# Reactions of Oxygenated Radicals in the Gas Phase. Part 13.1 **Reactions of t-Butoxyl Radicals with Alkanes and Alkenes**

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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.<sup>2</sup> In the other, a radical abstracts a hydrogen atom from the alkene, leading to the formation of allyl, alkenylperoxyl, and alkenyloxyl radicals; <sup>3</sup> 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 <sup>5</sup> 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 <sup>6,7</sup> who obtained rate data for the abstraction reactions between t-butoxyl radicals and butane and 2methylpropane; 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<sup>-1</sup>) suspended in an electric furnace, the temperature being controlled to within  $\pm 0.1$  °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 (MgSO<sub>4</sub>) 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.<sup>5,8</sup> The formation of the main products, methane, ethane, acetone, and t-butanol, can be rationalised by the simplified mechanism in equations (1)-(5). Calculations<sup>5</sup> based on the rate of

$$DTBP \longrightarrow 2Bu'O'$$
(1)

$$Bu^{t}O^{\bullet} + M \longrightarrow (CH_{3})_{2}CO + \dot{C}H_{3} + M$$
 (2)

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

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

$$\dot{C}H_3 + \dot{C}H_2COCH_3 \longrightarrow CH_3CH_2COCH_3$$
(5)

formation of acetone yielded Arrhenius parameters, log<sub>10</sub>-

 $(A_{obs}/s^{-1}) = 15.9 \pm 0.3$  and  $E_{obs}/kJ \text{ mol}^{-1} = 160.0 \pm 2.9$ . 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).

$$d[Bu'OH]/d[(CH_3)_2CO] = k_6[RH]/k_2$$
 (i)

$$Bu'O' + RH \longrightarrow Bu'OH + R'$$
 (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 R' were detectable.

Di-t-butyl peroxide was decomposed in the presence of 2,2dimethylpropane, 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<sup>9</sup> and tetrafluorohydrazine.<sup>10</sup> More recently, Batt and co-workers studied the reaction in detail, using tetrafluoromethane,<sup>11,12</sup> sulphur hexafluoride,<sup>12</sup> and nitrogen <sup>12</sup> as the inert gases and nitric oxide as the radical trap.

1/K         mol and         (m)n)         mol and         (m) and <th(m) and<="" th=""> <th(m) and<="" th=""> <th(m) and<="" th=""><th>III.decoration</th><th><b>1</b>7/17</th><th><math>10^{2}P/</math></th><th>Time</th><th>10<sup>6</sup>- [Bu<sup>4</sup>OH]/</th><th>10<sup>6</sup>- [Acetone]/</th><th>[Bu<sup>t</sup>OH] [Acetone]- [RH]/</th><th></th><th><math>\frac{k_2(p)}{k_2(p)}</math></th><th>10<sup>-6</sup>k<sub>6</sub>/ dm<sup>3</sup> mol<sup>-1</sup></th></th(m)></th(m)></th(m)>	III.decoration	<b>1</b> 7/17	$10^{2}P/$	Time	10 <sup>6</sup> - [Bu <sup>4</sup> OH]/	10 <sup>6</sup> - [Acetone]/	[Bu <sup>t</sup> OH] [Acetone]- [RH]/		$\frac{k_2(p)}{k_2(p)}$	10 <sup>-6</sup> k <sub>6</sub> / dm <sup>3</sup> mol <sup>-1</sup>
2,2-Dimethylpropane         399         0.82         30         0.155         4.67         4.14         5.13         0.43         1.26           1.61         30         0.143         4.95         3.60         4.99         0.48         1.16           1.81         30         0.176         5.75         3.81         4.78         0.51         1.16           2.00         30         0.176         5.75         3.81         4.78         0.54         1.46           2.41         30         0.138         5.96         2.89         4.64         0.59         1.21           2.81         30         0.138         5.96         2.89         4.64         0.59         1.21           1.66         20         0.273         10.98         3.19         5.14         0.39         1.63           1.66         20         0.226         12.60         2.24         4.88         0.47         1.53           1.66         20         0.226         12.65         2.32         4.71         0.53         1.60           2.35         20         0.226         12.65         3.32         4.97         0.43         3.16         1.15 <td< th=""><td>Hydrocarbon</td><td>1/K</td><td>moi am <sup>3</sup></td><td>(min)</td><td>mol dm <sup>3</sup></td><td>mol dm <sup>3</sup></td><td>dm<sup>3</sup> mol<sup>-1</sup></td><td>D</td><td><math>k_2(\infty)</math></td><td><b>S</b><sup>-1</sup></td></td<>	Hydrocarbon	1/K	moi am <sup>3</sup>	(min)	mol dm <sup>3</sup>	mol dm <sup>3</sup>	dm <sup>3</sup> mol <sup>-1</sup>	D	$k_2(\infty)$	<b>S</b> <sup>-1</sup>
Butane         1.20         30         0.143         4.95         3.60         4.99         0.48         1.23           1.81         30         0.150         5.70         3.28         4.82         0.53         1.12           2.41         30         0.129         5.82         2.76         4.70         0.57         1.12           2.81         30         0.135         5.96         2.99         4.64         0.59         1.61           1.76         20         0.278         11.96         2.91         4.99         0.43         1.63           1.56         20         0.226         12.80         2.84         4.88         0.49         1.52           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           1.61         30         0.442         5.91         9.90         4.77         3.31         1.60           2.74         20         0.234         13.23         2.27         4.65         0.55         1.62           Butane <td>2,2-Dimethylpropane</td> <td>399</td> <td>0.82</td> <td>30</td> <td>0.155</td> <td>4.67</td> <td>4.14</td> <td>5.13</td> <td>0.43</td> <td>1.26</td>	2,2-Dimethylpropane	399	0.82	30	0.155	4.67	4.14	5.13	0.43	1.26
Butane         1.61         30         0.137         5.34         3.20         4.87         0.51         1.16           2.00         30         0.176         5.75         3.81         4.78         0.54         1.46           2.41         30         0.129         5.82         2.86         4.70         0.57         1.12           2.81         30         0.123         5.96         2.89         4.64         0.59         1.21           1.56         20         0.273         10.98         2.91         4.99         0.43         1.63           1.76         20         0.225         12.60         2.24         4.88         0.47         1.74           2.35         20         0.229         12.65         2.32         4.71         0.53         1.60           2.35         20         0.224         15.23         2.27         4.65         0.55         1.62           Butane         399         0.82         30         0.445         5.91         9.39         4.99         0.47         3.13           1.20         30         0.445         5.91         9.39         4.99         0.47         3.17           2.41			1.20	30	0.143	4.95	3.60	4.99	0.48	1.23
Butane         1.81         30         0.130         5.70         3.28         4.82         0.33         1.23           2.41         30         0.129         5.82         2.76         4.70         0.57         1.12           2.41         30         0.129         5.82         2.76         4.70         0.57         1.12           2.41         30         0.138         5.96         4.29         4.44         0.39         1.61           1.56         20         0.278         11.36         2.91         4.39         0.43         1.63           1.56         20         0.226         12.60         2.84         4.88         0.49         1.52           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         0.425         6.67         7.94         4.78         0.53         3.17           2.00			1.61	30	0.137	5.34	3.20	4.87	0.51	1.16
2.40         30         0.176         5.73         5.73         5.74         4.70         0.57         1.12           2.81         30         0.138         5.96         2.89         4.64         0.59         1.21           1.0         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           1.65         20         0.279         12.60         2.84         4.88         0.49         1.74           1.76         20         0.238         12.82         2.38         4.83         0.49         1.52           2.35         20         0.229         12.65         2.32         4.71         0.53         1.60           2.74         20         0.234         13.23         2.02         4.65         0.55         1.62           Butane         39         0.82         30         0.446         5.39         8.73         4.87         0.51         3.17           1.81         30         0.424         6.39         8.77         4.82         0.53         3.17			1.81	30	0.150	5.70	3.28	4.82	0.53	1.23
Butane         30         0.123         1.30         0.123         1.32         2.82         2.80         4.64         0.59         1.21           410         0.80         20         0.273         10.98         3.19         5.14         0.39         1.61           1.77         20         0.258         11.36         2.91         4.99         0.43         1.63           1.76         20         0.238         12.80         2.38         4.88         0.47         1.52           1.96         20         0.235         12.50         2.62         4.79         0.50         1.70           2.35         20         0.229         12.66         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           2.00         30         0.4425         6.67         7.39         7.19         4.64         0.59         3.01           1.61         30         0.425         6.67         7.39         7.1			2.00	30	0.176	5.75	3.81	4.78	0.54	1.46
410         0.80         20         0.273         10.98         3.19         5.14         0.39         1.61           1.17         20         0.228         11.36         2.91         4.99         0.43         1.63           1.66         20         0.279         12.60         2.84         4.88         0.49         1.74           1.76         20         0.238         12.82         2.33         4.83         0.49         1.52           2.35         20         0.229         12.65         2.32         4.71         0.53         1.60           2.374         20         0.234         13.32         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           2.00         30         0.442         6.39         8.75         4.87         0.51         3.17           1.81         30         0.424         6.39         8.75         4.82         0.53         3.17           2.41         30         0.426         7.39         7.14         4.70         0.57         2.99           2.41			2.41	30	0.129	5.82 5.96	2.76	4.70 4.64	0.57	1.12
<ul> <li>Pautane</li> <li>1.17</li> <li>20</li> <li>0.228</li> <li>11.36</li> <li>2.91</li> <li>4.99</li> <li>0.43</li> <li>1.74</li> <li>1.76</li> <li>20</li> <li>0.238</li> <li>12.82</li> <li>2.38</li> <li>4.83</li> <li>0.49</li> <li>1.52</li> <li>1.96</li> <li>20</li> <li>0.256</li> <li>12.50</li> <li>2.32</li> <li>4.71</li> <li>0.53</li> <li>1.60</li> <li>2.74</li> <li>20</li> <li>0.224</li> <li>12.50</li> <li>2.32</li> <li>4.71</li> <li>0.53</li> <li>1.60</li> <li>2.74</li> <li>20</li> <li>0.224</li> <li>13.23</li> <li>2.27</li> <li>4.65</li> <li>0.55</li> <li>1.62</li> <li>1.61</li> <li>30</li> <li>0.445</li> <li>5.91</li> <li>9.39</li> <li>4.99</li> <li>0.47</li> <li>3.16</li> <li>1.61</li> <li>30</li> <li>0.445</li> <li>5.91</li> <li>9.39</li> <li>4.99</li> <li>0.47</li> <li>3.16</li> <li>1.61</li> <li>30</li> <li>0.445</li> <li>6.67</li> <li>7.94</li> <li>4.78</li> <li>0.51</li> <li>3.17</li> <li>1.81</li> <li>30</li> <li>0.426</li> <li>7.39</li> <li>7.41</li> <li>4.78</li> <li>0.51</li> <li>3.71</li> <li>3.60</li> <li>0.426</li> <li>7.39</li> <li>7.19</li> <li>4.64</li> <li>0.59</li> <li>3.01</li> <li>1.17</li> <li>2.00</li> <li>0.730</li> <li>17.60</li> <li>5.32</li> <li>4.71</li> <li>0.53</li> <li>3.66</li> <li>4.99</li> <li>0.43</li> <li>3.67</li> <li>2.74</li> <li>2.00</li> <li>3.01</li> <li>1.62</li> <li>2.00</li> <li>1.55</li> <li>2.00</li> <li>1.54</li> <li>5.91</li> <li>3.57</li> <li>4.83</li> <li>0.49</li> <li>3.64</li> <li>3.69</li> <li>3.67</li> <li>3.68</li> <li>3.54</li> <li>4.54</li> <li>4.54</li> <li>4.53</li> <li>4.74</li> <li>4.53</li>     &lt;</ul>		410	0.80	20	0.273	10.98	3.19	5.14	0.39	1.61
Butane         1.56         20         0.279         12.60         2.84         4.88         0.47         1.76           2.35         20         0.256         12.50         2.62         4.79         0.50         1.60           2.35         20         0.229         12.63         2.32         4.71         0.33         1.60           2.37         20         0.229         12.63         2.32         4.71         0.33         1.60           399         0.82         30         0.446         5.38         10.34         5.14         0.43         3.16           1.20         30         0.445         6.59         9.39         4.99         0.47         3.13           1.61         30         0.425         6.67         7.94         4.78         0.51         3.17           2.00         30         0.426         7.39         7.19         4.78         0.54         2.99           2.41         30         0.426         7.39         7.19         4.64         0.59         3.01           1.55         2.00         0.751         13.15         7.32         5.15         0.39         3.71           1.176         20			1.17	20	0.258	11.36	2.91	4.99	0.43	1.63
Butane         176         20         0.236         12.82         2.38         4.83         0.49         1.52           Butane         399         0.82         0.235         12.65         2.23         2.74         0.50         1.70           1.61         30         0.234         13.23         2.27         4.65         0.55         1.62           1.20         30         0.446         5.38         10.34         5.14         0.43         3.16           1.61         30         0.437         6.23         8.75         4.87         0.51         3.17           2.00         30         0.424         6.39         8.27         4.82         0.53         3.17           2.41         30         0.426         7.39         7.19         4.64         0.59         3.01           1.17         200         0.751         13.15         7.32         5.15         0.39         3.71           1.66         20         0.704         15.13         5.72         4.83         0.49         3.64           2.35         20         0.730         18.20         5.14         4.64         0.55         3.66           2.74         20 <td></td> <td></td> <td>1.56</td> <td>20</td> <td>0.279</td> <td>12.60</td> <td>2.84</td> <td>4.88</td> <td>0.47</td> <td>1.74</td>			1.56	20	0.279	12.60	2.84	4.88	0.47	1.74
Butane         1.96         20         0.256         12.50         2.62         4.79         0.50         1.70           Butane         399         0.82         30         0.446         5.38         10.34         5.14         0.43         3.16           Butane         399         0.82         30         0.445         5.91         9.39         4.99         0.47         3.13           1.61         30         0.445         5.91         9.39         4.99         0.47         3.13           2.00         30         0.442         6.39         8.75         4.87         0.51         3.17           2.00         30         0.424         6.39         8.27         4.82         0.53         3.17           2.00         30         0.425         7.39         7.19         4.64         0.59         3.01           2.81         30         0.426         7.39         7.19         4.64         0.59         3.01           1.17         2.00         0.704         15.13         5.97         4.88         0.47         3.65           1.17         2.0         0.704         15.13         5.97         4.88         0.47         3.6			1.76	20	0.238	12.82	2.38	4.83	0.49	1.52
2.35         20         0.234         12.65         2.32         4.71         0.53         1.60           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         0.445         5.91         9.39         4.99         0.47         3.13           2.00         30         0.442         6.39         8.27         4.82         0.53         3.17           1.81         30         0.425         6.67         7.94         4.78         0.54         2.99           2.41         30         0.425         7.39         7.19         4.64         0.59         3.01           1.17         20         0.751         13.15         7.32         5.15         0.39         3.71           1.40         0.80         20         0.750         16.85         5.71         4.79         0.50         3.71           1.76         20         0.730         18.20         5.14         4.64         0.55         3.68           2.744			1.96	20	0.256	12.50	2.62	4.79	0.50	1.70
Butane         399         0.82         30         0.446         5.38         10.34         5.14         0.43         3.16           Butane         399         0.82         30         0.445         5.91         9.39         4.99         0.47         3.13           1.61         30         0.443         5.91         9.39         4.87         0.51         3.17           2.00         30         0.425         6.67         7.94         4.78         0.53         3.17           2.00         30         0.425         6.67         7.94         4.78         0.54         2.99           2.41         30         0.426         7.39         7.19         4.64         0.59         3.01           1.17         2.00         0.751         13.15         7.32         5.15         0.39         3.71           1.17         2.00         0.764         15.13         5.97         4.88         0.47         3.65           1.56         20         0.750         16.85         5.14         0.43         10.8           1.61         30         1.45         5.91         30.59         4.99         0.47         10.5           1.53 <td></td> <td></td> <td>2.35</td> <td>20</td> <td>0.229</td> <td>12.65</td> <td>2.32</td> <td>4.71</td> <td>0.53</td> <td>1.60</td>			2.35	20	0.229	12.65	2.32	4.71	0.53	1.60
Butane         399         0.82         30         0.446         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           2.81         30         0.425         6.67         7.94         4.78         0.53         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         0.730         17.60         5.32         4.71         0.53         3.67           2.74         20         0.730         17.60         5.32         4.71         0.53         3.68           1.96         20         0.730         15.36         35.46         5.14         0.43         10.8           2.01	_		2.74	20	0.234	13.23	2.27	4.65	0.55	1.62
<ul> <li>2-Methylpropane</li> <li>390</li> <li>0.431</li> <li>0.435</li> <li>0.435</li> <li>0.435</li> <li>0.436</li> <li>0.437</li> <li>0.23</li> <li>8.75</li> <li>4.87</li> <li>0.51</li> <li>3.17</li> <li>1.81</li> <li>30</li> <li>0.424</li> <li>6.39</li> <li>8.27</li> <li>4.82</li> <li>0.53</li> <li>3.17</li> <li>2.00</li> <li>30</li> <li>0.425</li> <li>6.67</li> <li>7.94</li> <li>4.78</li> <li>0.54</li> <li>2.99</li> <li>2.41</li> <li>30</li> <li>0.426</li> <li>7.39</li> <li>7.19</li> <li>4.64</li> <li>0.59</li> <li>3.01</li> <li>1.17</li> <li>20</li> <li>0.751</li> <li>13.15</li> <li>7.32</li> <li>5.15</li> <li>0.39</li> <li>3.71</li> <li>1.56</li> <li>20</li> <li>0.704</li> <li>15.13</li> <li>5.72</li> <li>4.88</li> <li>0.47</li> <li>3.64</li> <li>1.96</li> <li>20</li> <li>0.750</li> <li>16.85</li> <li>5.71</li> <li>4.79</li> <li>0.50</li> <li>3.71</li> <li>2.35</li> <li>20</li> <li>0.730</li> <li>16.85</li> <li>5.71</li> <li>4.79</li> <li>0.53</li> <li>3.67</li> <li>2.35</li> <li>20</li> <li>0.730</li> <li>16.85</li> <li>5.71</li> <li>4.79</li> <li>0.53</li> <li>3.67</li> <li>2.35</li> <li>20</li> <li>0.730</li> <li>1.62</li> <li>2.14</li> <li>4.64</li> <li>0.55</li> <li>3.68</li> <li>3.46</li> <li>4.14</li> <li>6.49</li> <li>4.464</li> <li>0.53</li> <li>3.67</li> <li>3.67</li> <li>3.67</li> <li>3.67</li> <li>3.67</li> <li>3.67</li> <li>3.67</li> <li>3.64</li> <li>3.61</li></ul>	Butane	399	0.82	30	0.446	5.38	10.34	5.14	0.43	3.16
2-Methylpropane 399 0.82 30 1.437 6.73 8.75 4.87 0.51 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 1.17 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 0.750 16.85 5.71 4.79 0.50 3.71 2.35 20 0.750 16.85 5.71 4.79 0.50 3.71 2.35 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 2.902 4.87 0.51 10.5 1.61 30 1.45 6.23 2.902 4.87 0.51 10.5 1.81 30 1.41 7.55 2.32.9 4.48 0.53 10.4 2.71 30 1.41 7.55 2.32.9 4.64 0.59 9.48 410 0.80 20 2.58 13.29 24.89 5.15 0.39 12.6 1.76 20 2.50 14.08 22.76 4.99 0.43 12.7 1.81 30 1.41 7.55 2.32.9 4.64 0.55 3.68 2.74 20 0.730 18.20 5.14 4.64 0.55 3.68 1.20 30 1.45 6.23 2.902 4.87 0.51 10.5 1.81 30 1.41 7.55 2.32.9 4.48 0.53 10.4 2.00 30 1.37 6.67 2.5.61 4.78 0.54 9.80 2.71 30 1.41 7.55 2.32.9 4.64 0.59 9.88 410 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 2.39 15.33 19.99 4.83 0.49 12.7 1.56 20 1.36 12.51 13.94 4.88 0.47 12.5 1.88 0.47 12.5 2.74 20 2.42 18.77 16.53 4.64 0.55 11.8 1.96 20 2.42 18.67 4.79 0.50 12.1 2.74 20 2.42 18.77 16.53 4.64 0.55 11.8 1.96 20 2.39 15.33 19.99 4.83 0.49 12.7 1.56 20 1.36 12.51 13.94 4.88 0.47 8.50 1.96 20 2.42 18.77 16.53 4.64 0.55 11.8 1.96 20 1.23 12.24 18.47 16.53 4.64 0.55 11.8 1.96 20 1.23 12.32 12.80 4.79 0.49 8.20 2.74 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 2.57 11.84 4.71 0.52 8.01 2.74 20 1.20 13.22 11.64 4.65 0.54 8.24			1.20	30	0.445	5.91	9.39	4.99	0.47	3.13
2-Methylpropane 399 0.82 30 1.43 6.23 6.67 7.94 4.78 0.53 3.19 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 3.71 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 1.61 30 1.45 6.23 29.02 4.87 0.51 10.5 1.61 30 1.45 6.23 29.02 4.87 0.51 10.5 1.81 30 1.41 7.55 23.29 4.64 0.59 9.80 2.71 30 1.41 7.55 23.29 4.64 0.57 10.1 2.81 30 1.41 7.55 23.29 4.64 0.59 9.80 2.71 30 1.41 7.55 23.29 4.64 0.59 9.80 2.71 30 1.41 7.55 23.29 4.64 0.59 9.80 2.71 30 1.41 7.55 23.29 4.64 0.55 10.3 1.56 20 2.42 15.13 20.51 4.88 0.47 12.5 1.56 20 2.42 15.13 20.51 4.88 0.47 12.5 1.56 20 2.42 15.13 20.51 4.88 0.47 12.5 1.66 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 18.77 16.53 4.64 0.55 11.8 1.96 20 1.32 11.34 15.25 5.00 0.43 8.54 1.96 20 1.36 11.34 15.25 5.00 0.43 8.54 1.96 20 1.36 12.51 13.94 4.88 0.47 8.50 1.96 20 1.			1.61	30	0.437	6.23	8.75	4.87	0.51	3.17
2-Methylpropane 399 0.82 30 1.45 5.91 30.59 4.99 0.43 1.73 2.41 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 0.744 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 0.730 17.60 5.32 4.71 0.53 3.67 2.74 20 0.730 17.60 5.32 4.71 0.53 3.67 2.74 20 0.730 17.60 5.32 4.71 0.53 3.67 1.20 30 1.45 5.91 30.59 4.99 0.47 10.2 1.61 30 1.45 5.91 30.59 4.99 0.47 10.2 1.61 30 1.45 5.91 30.59 4.99 0.47 10.2 1.61 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 7.55 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 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 <i>trans</i> -But-2-ene 410 0.80 20 1.48 10.95 17.33 5.15 0.39 8.82 1.96 20 1.23 11.34 4.88 0.47 8.50 1.96 20 1.23 11.34 4.88 0.47 8.50 1.96 20 1.23 11.34 4.88 0.47 8.50 1.96 20 1.24 18.77 16.53 4.64 0.55 11.8 1.96 20 1.24 18.77 16.53 4.64 0.55 11.8 1.96 20 1.24 18.77 16.53 4.64 0.55 11.8 1.96 20 1.23 11.34 4.88 0.47 8.50 1.96 20 1.23 11.34 4.88 0.47 8.50 1.96 20 1.20 13.22 11.64 4.65 0.54 8.24			1.81	30	0.424	6.39	8.27	4.82	0.53	3.17
2-Methylpropane 399 0.82 30 1.53 5.18 35.46 5.14 0.43 10.8 1.20 0.730 17.60 5.32 4.71 0.53 3.67 2-Methylpropane 399 0.82 30 1.53 5.38 35.46 5.14 0.43 10.8 1.20 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 7.55 23.29 4.64 0.59 9.80 410 0.80 20 2.58 13.29 24.89 5.15 0.39 12.6 1.71 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 1.76 20 2.42 15.13 20.51 4.88 0.47 12.5 1.76 20 2.42 15.62 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 1.77 1.56 20 1.23 11.34 4.88 0.47 8.50 1.96 20 1.20 13.22 11.64 4.65 0.54 8.24			2.00	30	0.425	0.07	7.94	4.78	0.54	2.99
2-Methylpropane       309       0.820       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       6.53       2.90       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 <td></td> <td></td> <td>2.41</td> <td>30</td> <td>0.410</td> <td>7.03</td> <td>7.41</td> <td>4.70</td> <td>0.57</td> <td>2.99</td>			2.41	30	0.410	7.03	7.41	4.70	0.57	2.99
<ul> <li>410</li> <li>10, 17</li> <li>10, 17</li> <li>10, 17</li> <li>11, 18</li> <li>11, 14</li> <li>11, 19</li> <li>11, 19</li></ul>		410	2.01	20	0.420	12.15	7.19	5 1 5	0.33	3.01
2-Methylpropane         399         0.43         1.17         20         0.744         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         3.68           2-Methylpropane         399         0.82         30         1.53         5.38         35.46         5.14         0.43         10.8           1.20         30         1.45         6.23         29.02         4.87         0.51         10.53           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         7.55         32.29         4.64         0.59         9.80           2.71         30         1.41         7.55         32.29         4.64         0.59		410	0.80	20	0.751	13.13	1.32	5.15	0.39	3./1
1.30       20       0.70       15.13       5.77       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       7.01       25.88       4.64       0.59       9.80         410<			1.17	20	0.741	14.22	5.00	4.99	0.43	3.73
2-Methylpropane       399       0.82       30       1.53       5.14       4.64       0.55       3.67         2-Methylpropane       399       0.82       30       1.53       5.38       35.46       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       25.06       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         1.56       20       2.42       16.62 <td></td> <td></td> <td>1.50</td> <td>20</td> <td>0.684</td> <td>15 33</td> <td>5 72</td> <td>4.83</td> <td>0.49</td> <td>3.64</td>			1.50	20	0.684	15 33	5 72	4.83	0.49	3.64
I = 1, 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, 1.20, 30, 1.45, 5.91, 30.59, 4.99, 0.47, 10.2, 1.61, 30, 1.45, 5.91, 30.59, 4.99, 0.47, 10.2, 1.61, 30, 1.45, 5.91, 30.59, 4.99, 0.47, 10.2, 1.61, 30, 1.45, 5.91, 30.59, 4.99, 0.47, 10.2, 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, 7.55, 23.29, 4.64, 0.59, 9.80, 2.71, 30, 1.41, 7.55, 23.29, 4.64, 0.59, 9.80, 2.71, 30, 1.41, 7.55, 23.29, 4.64, 0.59, 9.80, 2.71, 30, 1.41, 7.55, 23.29, 4.64, 0.59, 9.80, 2.71, 30, 1.41, 7.55, 23.29, 4.64, 0.59, 9.80, 2.71, 1.56, 20, 2.42, 15.13, 20.51, 4.88, 0.47, 12.5, 1.56, 20, 2.42, 15.13, 20.51, 4.88, 0.47, 12.5, 1.76, 20, 2.39, 17.60, 17.41, 4.71, 0.53, 12.0, 1.76, 20, 2.39, 17.60, 17.41, 4.71, 0.53, 12.0, 1.76, 2.74, 20, 2.42, 18.77, 16.53, 4.64, 0.55, 11.8, 1.76, 20, 2.39, 17.60, 17.41, 4.71, 0.53, 12.0, 1.76, 2.74, 20, 1.35, 11.34, 15.25, 5.00, 0.43, 8.54, 1.56, 20, 1.35, 11.34, 15.25, 5.00, 0.43, 8.54, 1.56, 20, 1.23, 12.35, 11.34, 15.25, 5.00, 0.43, 8.54, 1.56, 20, 1.23, 12.30, 12.51, 13.94, 4.88, 0.47, 8.50, 1.96, 20, 1.23, 12.30, 12.51, 13.94, 4.88, 0.47, 8.50, 1.96, 20, 1.23, 12.32, 11.64, 4.65, 0.54, 8.24			1.96	20	0.750	16.85	5.71	4.79	0.50	3 71
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           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 </th <td></td> <td></td> <td>2.35</td> <td>20</td> <td>0.730</td> <td>17.60</td> <td>5.32</td> <td>4.71</td> <td>0.53</td> <td>3.67</td>			2.35	20	0.730	17.60	5.32	4.71	0.53	3.67
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<			2.74	20	0.730	18.20	5.14	4.64	0.55	3.68
$trans-But-2-ene \qquad \begin{array}{ccccccccccccccccccccccccccccccccccc$	2-Methylpropane	399	0.82	30	1.53	5.38	35.46	5.14	0.43	10.8
$trans-But-2-ene = \begin{array}{ccccccccccccccccccccccccccccccccccc$			1.20	30	1.45	5.91	30.59	4.99	0.47	10.2
$trans-But-2-ene \qquad \begin{array}{ccccccccccccccccccccccccccccccccccc$			1.61	30	1.45	6.23	29.02	4.87	0.51	10.5
$trans-But-2-ene \qquad \begin{array}{ccccccccccccccccccccccccccccccccccc$			1.81	30	1.41	6.39	27.51	4.82	0.53	10.4
$trans-But-2-ene = \begin{array}{ccccccccccccccccccccccccccccccccccc$			2.00	30	1.37	6.67	25.61	4.78	0.54	9.80
#10       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       2.42       18.67       4.79       0.50       12.1         2.35       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       1.23       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 <t< th=""><td></td><td></td><td>2.71</td><td>30</td><td>1.41</td><td>7.01</td><td>25.08</td><td>4.70</td><td>0.57</td><td>10.1</td></t<>			2.71	30	1.41	7.01	25.08	4.70	0.57	10.1
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 <i>trans</i> -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       1.23       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		410	2.81	30	1.41	7.55	23.29	4.04	0.59	9.80
$trans-But-2-ene = \begin{array}{ccccccccccccccccccccccccccccccccccc$		410	0.80	20	2.58	13.29	24.89	5.15	0.39	12.6
1.36 $20$ $2.42$ $13.13$ $20.31$ $4.88$ $0.47$ $12.3$ $1.76$ $20$ $2.39$ $15.33$ $19.99$ $4.83$ $0.49$ $12.7$ $1.96$ $20$ $2.42$ $16.62$ $18.67$ $4.79$ $0.50$ $12.1$ $2.35$ $20$ $2.39$ $17.60$ $17.41$ $4.71$ $0.53$ $12.0$ $2.74$ $20$ $2.42$ $18.77$ $16.53$ $4.64$ $0.55$ $11.8$ <i>trans</i> -But-2-ene $410$ $0.80$ $20$ $1.48$ $10.95$ $17.33$ $5.15$ $0.39$ $8.82$ $1.17$ $20$ $1.35$ $11.34$ $15.25$ $5.00$ $0.43$ $8.54$ $1.56$ $20$ $1.36$ $12.51$ $13.94$ $4.88$ $0.47$ $8.50$ $1.96$ $20$ $1.23$ $12.32$ $12.80$ $4.79$ $0.49$ $8.20$ $2.35$ $20$ $1.17$ $12.67$ $11.84$ $4.71$ $0.52$ $8.01$ $2.74$ $20$ $1.20$ $13.22$ $11.64$ $4.65$ $0.54$ $8.24$			1.17	20	2.50	14.08	22.70	4.99	0.43	12.7
1.10 $20$ $2.37$ $10.33$ $10.37$ $1.83$ $10.43$ $10.43$ $12.7$ $1.96$ $20$ $2.42$ $16.62$ $18.67$ $4.79$ $0.50$ $12.1$ $2.35$ $20$ $2.39$ $17.60$ $17.41$ $4.71$ $0.53$ $12.0$ $2.74$ $20$ $2.42$ $18.77$ $16.53$ $4.64$ $0.55$ $11.8$ <i>trans</i> -But-2-ene $410$ $0.80$ $20$ $1.48$ $10.95$ $17.33$ $5.15$ $0.39$ $8.82$ $1.17$ $20$ $1.35$ $11.34$ $15.25$ $5.00$ $0.43$ $8.54$ $1.56$ $20$ $1.36$ $12.51$ $13.94$ $4.88$ $0.47$ $8.50$ $1.96$ $20$ $1.23$ $12.32$ $12.80$ $4.79$ $0.49$ $8.20$ $2.35$ $20$ $1.17$ $12.67$ $11.84$ $4.71$ $0.52$ $8.01$ $2.74$ $20$ $1.20$ $13.22$ $11.64$ $4.65$ $0.54$ $8.24$			1.30	20	2.42	15.15	10 00	4.00	0.47	12.5
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			1.70	20	2.39	16.62	18.67	4.05	0.49	12.7
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$			2 35	20	2 39	17.60	17 41	4 71	0.50	12.1
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			2.74	20	2.42	18.77	16.53	4.64	0.55	11.8
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	trans-But-2-ene	410	0.80	20	1.48	10.95	17.33	5.15	0.39	8.82
$\begin{array}{cccccccccccccccccccccccccccccccccccc$			1.17	20	1.35	11.34	15.25	5.00	0.43	8.54
1.96201.2312.3212.804.790.498.202.35201.1712.6711.844.710.528.012.74201.2013.2211.644.650.548.24			1.56	20	1.36	12.51	13.94	4.88	0.47	8.50
2.35201.1712.6711.844.710.528.012.74201.2013.2211.644.650.548.24			1.96	20	1.23	12.32	12.80	4.79	0.49	8.20
2.74 20 1.20 13.22 11.64 4.65 0.54 8.24			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

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

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.<sup>5</sup> Essentially, RRK theory was used.<sup>13</sup> 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

$$Bu'O' + M \Longrightarrow Bu'O'' + M$$
(7)

$$Bu^{t}O^{*} \longrightarrow (CH_{3})_{2}CO + \dot{C}H_{3}$$
 (8)

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

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

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

frequency and S is the number of effective oscillators in the energised molecule. Parameters S,B,D were estimated from available data.<sup>5,14</sup> 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;<sup>15</sup> those for the hydrocarbons were checked against values already used in the literature.<sup>16</sup> 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

				[Bu <sup>t</sup> OH]			
		10 <sup>2</sup> [RH]/	Number	[CH <sub>3</sub> COCH <sub>3</sub> ][RH]/		$k_2(p)$	10 <sup>-6</sup> k <sub>6</sub> /
Hydrocarbon	<i>T</i> /K	mol dm <sup>-3</sup>	of expts.	dm <sup>3</sup> mol <sup>-1</sup>	D	$k_2(\infty)$	dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
2,2-Dimethylpropane	399	1.81	3	$\textbf{3.04} \pm \textbf{0.04}$	4.75	0.55	$\textbf{1.19} \pm \textbf{0.01}$
	410	1.76	4	$\textbf{2.47} \pm \textbf{0.03}$	4.76	0.50	$1.61\pm0.02$
		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	$1.18\pm0.02$	4.77	0.50	$\textbf{2.66} \pm \textbf{0.05}$
Cyclohexane	399	0.32	4	$26.1\pm3.2$	4.79	0.53	$9.8\pm1.2$
	410	0.31	3	$19.1 \pm 1.3$	4.80	0.49	$12.1 \pm 0.9$
		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	$\textbf{8.57} \pm \textbf{0.63}$	4.81	0.49	$18.9 \pm 1.4$
Butane	399	1.81	7	$\textbf{7.88} \pm \textbf{0.14}$	4.76	0.55	$3.08\pm0.05$
	410	1.76	5	$5.69\pm0.03$	4.77	0.50	$3.70\pm0.02$
		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	$\textbf{2.83} \pm \textbf{0.13}$	4.78	0.49	$6.23\pm0.31$
2-Methylpropane	399	1.81	7	$\textbf{26.18} \pm \textbf{0.59}$	4.76	0.55	$10.2\pm0.2$
	410	1.76	5	18.65 + 0.15	4.77	0.50	$12.1 \pm 0.1$
		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	$\textbf{8.27} \pm \textbf{0.26}$	4.78	0.49	$18.2\pm0.5$





**Figure 2.** Decomposition of di-t-butyl peroxide in the presence of alkenes at 410 K, 5 Torr. Analyses at 20 min.  $\diamond$ , 2,3-Dimethylbut-2-ene;  $\Box$ , 2-methylbut-2-ene;  $\bigcirc$ , *cis*-but-2-ene;  $\triangle$ , *trans*-but-2-ene;  $\bigtriangledown$ , 2-methylpropene; and  $\bullet$ , propene

Figure 1. Decomposition of di-t-butyl peroxide in the presence of saturated hydrocarbons at 410 K, 5 Torr.  $\bigcirc$ , 2,2-Dimethylpropane (analyses at 30 min);  $\Box$ , butane (analyses at 20 min);  $\diamondsuit$ , cyclohexane (analyses at 25 min);  $\diamondsuit$ , 2-methylpropane (analyses at 20 min)

Emanuel.<sup>17</sup> 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,<sup>12</sup> log $[A_2(\infty)/s^{-1}] = 14.6$  and  $E_2(\infty) = 66.5$  kJ mol<sup>-1</sup>, which have been obtained by

			Number	[Bu <sup>t</sup> OH]			
		10 <sup>3</sup> [RH]/	of	[CH <sub>3</sub> COCH <sub>3</sub> ][RH]/		$\frac{k_2(p)}{p}$	10 <sup>-6</sup> k <sub>6</sub> /
Alkene	T/K	mol dm <sup>-3</sup>	expts.	dm <sup>3</sup> mol <sup>-1</sup>	D	k₂(∞)	dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
Propene	399	8.04	4	$5.18 \pm 0.28$	4.78	0.54	1.99 ± 0.11
	410	7.82	5	$3.82\pm0.25$	4.79	0.49	$2.43\pm0.16$
		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
	42.4	17.60	1	3.40	4.76	0.50	2.21
<b></b>	434	7.39	4	$1.76 \pm 0.07$	4.80	0.49	$3.85\pm0.12$
2-Methylpropene	399	8.04	4	$13.59 \pm 0.25$	4.78	0.54	5.21 ± 0.10
	410	7.82	4	$9.96 \pm 0.43$	4.79	0.49	$6.35 \pm 0.28$
		4.30	1	9.71	4.80	0.49	6.19
		11./3	1	10.34	4.78	0.50	6.72
		15.09	1	10.01	4.78	0.50	6.51
	121	7 30	1	9.39	4.//	0.30	6.23
air Dut 2 and	434	7.39	4	4.47	4.80	0.49	9.86 ± 0.50
cis-But-2-ene	399	8.04	4	$16.93 \pm 0.16$	4.78	0.54	$6.49 \pm 0.06$
	410	7.82	5	$11.96 \pm 0.42$	4.79	0.49	$7.62 \pm 0.27$
		1.96	1	11.07	4.80	0.49	7.01
		3.91	1	11.87	4.80	0.49	7.56
		9.70	1	11.70	4.78	0.50	7.01
		19.55	1	11.45	4.77	0.50	7.44 7.54
	434	7 39	1	$5.34 \pm 0.11$	4.70	0.51	$11.78 \pm 0.25$
trans-But-2-ene	399	8.04	5	$17.47 \pm 0.50$	4.00	0.42	$6.70 \pm 0.19$
num but 2 one	410	7 82	1	$17.47 \pm 0.50$	4.70	0.34	$8.15 \pm 0.00$
	410	2 74	1	$12.00 \pm 0.14$	4.79	0.49	$8.13 \pm 0.09$
		9.78	1	11.70	4.80	0.49	7 45
		11.73	î	11.63	4.78	0.50	7.56
		17.60	ī	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 $\pm$ 0.07	4.80	0.49	$12.67\pm0.15$
2-Methylbut-2-ene	399	4.02	4	$\textbf{36.60} \pm \textbf{0.31}$	4.79	0.53	$14.13\pm0.17$
	410	3.91	4	$27.61 \pm 1.66$	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	$11.07 \pm 0.58$	4.81	0.49	$24.40 \pm 1.27$
2,3-Dimethylbut-2-ene	399	1.60	4	$88.55 \pm 4.15$	4.79	0.53	$\textbf{33.95} \pm \textbf{1.48}$
	410	1.56	4	$60.11 \pm 0.31$	4.80	0.49	$38.29 \pm 0.20$
		1.96	1	59.72	4.80	0.49	38.04
		2.35	1	58.06	4.80	0.49	36.98
	40.4	1.14	I	38.48	4.80	0.49	37.25
	434	1.48	4	25.90 ± 0.80	4.81	0.49	57.15 ± 1.90

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

very careful experimental observation.<sup>11,18,19</sup> The values suggested by Choo and Benson <sup>20</sup> 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)

HydrocarbonTable $T/K$ dm³ mol <sup>-1</sup> s <sup>-1</sup> 2,2-Dimethylpropane2399 $1.19 \pm 0.01$ 1399 $1.23 \pm 0.23$ 2410 $1.64 \pm 0.06$ 1410 $1.64 \pm 0.05$ Cyclohexane2399 $9.80 \pm 1.20$ 2410 $12.0 \pm 1.0$ 2434 $18.9 \pm 1.4$ Butane2399 $3.08 \pm 0.05$ 1399 $3.09 \pm 0.05$ 2410 $3.67 \pm 0.06$ 1410 $3.68 \pm 0.04$ 2434 $6.23 \pm 0.31$ 2-Methylpropane23991399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1 $399$ $10.2 \pm 0.2$ 1 $10.2 \pm 0.2$ 1 $10.2 \pm 0.5$ 2434 $18.2 \pm 0.5$ Propene33993 $410$ $2.37 \pm 0.17$ 3 $434$ $3.85 \pm 0.12$ 2-Methylpropene3 $399$ 3 $410$ $7.53 \pm 0.52$ $3$ $3410$ $7.53 \pm 0.52$ $3$ $434$ $11.8 \pm 0.30$ $trans$ -But-2-ene $3$ $399$ $4.11 \pm 10.2$ $3$ $3$ $410$ $7.91 \pm 0.20$ 2-Methylbut-2-ene $3$ $399$ $4.14 \pm 1.3$ $2.3$ -Dimethylbut-2-ene $3$ $3$ $434$ $2.7 \pm 1.9$		Data from		10 <sup>-6</sup> k <sub>6</sub> /
2,2-Dimethylpropane2399 $1.19 \pm 0.01$ 1399 $1.23 \pm 0.23$ 2410 $1.64 \pm 0.06$ 1410 $1.63 \pm 0.11$ 2434 $2.66 \pm 0.05$ Cyclohexane2399 $9.80 \pm 1.20$ 2410 $12.0 \pm 1.0$ 2434 $18.9 \pm 1.4$ Butane2399 $3.08 \pm 0.05$ 1399 $3.09 \pm 0.10$ 2410 $3.67 \pm 0.06$ 1410 $3.68 \pm 0.04$ 2434 $6.23 \pm 0.31$ 2-Methylpropane23991 $2.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.5$ 2434 $12.3 \pm 0.5$ 2434 $12.3 \pm 0.5$ 2434 $18.2 \pm 0.5$ Propene33993410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene33993410 $7.53 \pm 0.52$ 3410 $7.53 \pm 0.52$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene339934342,3-Dimethylbut-2-ene33434434 $2.5 = 3$ 434 $2.5 = 3$ 434 $2.7 \pm 1.9$	Hydrocarbon	Table	T/K	dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup>
1399 $1.23 \pm 0.23$ 2410 $1.64 \pm 0.06$ 1410 $1.63 \pm 0.11$ 2434 $2.66 \pm 0.05$ Cyclohexane2399 $9.80 \pm 1.20$ 2410 $12.0 \pm 1.0$ 2434 $18.9 \pm 1.4$ Butane2399 $3.08 \pm 0.05$ 1399 $3.09 \pm 0.10$ 2410 $3.67 \pm 0.06$ 1410 $3.67 \pm 0.06$ 1410 $3.68 \pm 0.04$ 2434 $6.23 \pm 0.31$ 2-Methylpropane239912.2 \pm 0.5Propene33993410 $2.37 \pm 0.5$ 2434 $3.85 \pm 0.12$ 2-Methylpropene33993410 $6.38 \pm 0.34$ 3434 $3.86 \pm 0.50$ cis-But-2-ene33993410 $7.53 \pm 0.52$ 3410 $7.91 \pm 0.33$ 434 $11.8 \pm 0.30$ trans-But-2-ene33434410 $7.91 \pm 0.33$ 34342-Methylbut-2-ene334342,3-Dimethylbut-2-ene33399434 $2.7 \pm 1.9$	2,2-Dimethylpropane	2	399	$1.19\pm0.01$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	399	$1.23\pm0.23$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2	410	$1.64 \pm 0.06$
$\begin{array}{c ccccc} 2 & 434 & 2.66 \pm 0.03 \\ \hline Cyclohexane & 2 & 399 & 9.80 \pm 1.20 \\ 2 & 410 & 12.0 \pm 1.0 \\ 2 & 434 & 18.9 \pm 1.4 \\ \hline Butane & 2 & 399 & 3.08 \pm 0.05 \\ 1 & 399 & 3.09 \pm 0.10 \\ 2 & 410 & 3.67 \pm 0.06 \\ 1 & 410 & 3.68 \pm 0.04 \\ 2 & 434 & 6.23 \pm 0.31 \\ \hline 2 & 434 & 6.23 \pm 0.31 \\ \hline 2 & 434 & 6.23 \pm 0.31 \\ \hline 2 & 410 & 12.2 \pm 0.2 \\ 1 & 399 & 10.2 \pm 0.2 \\ 1 & 399 & 10.2 \pm 0.2 \\ 1 & 399 & 10.2 \pm 0.6 \\ \hline 2 & 410 & 12.2 \pm 1.1 \\ 1 & 410 & 12.3 \pm 0.5 \\ \hline 2 & 434 & 18.2 \pm 0.5 \\ \hline 2 & 434 & 18.2 \pm 0.5 \\ \hline Propene & 3 & 399 & 1.99 \pm 0.11 \\ \hline 3 & 410 & 2.37 \pm 0.17 \\ \hline 3 & 434 & 3.85 \pm 0.12 \\ \hline 2 -Methylpropene & 3 & 399 & 5.21 \pm 0.10 \\ \hline 3 & 410 & 6.38 \pm 0.34 \\ \hline 3 & 434 & 9.86 \pm 0.50 \\ \hline cis-But-2-ene & 3 & 399 & 6.49 \pm 0.06 \\ \hline 3 & 410 & 7.53 \pm 0.52 \\ \hline 3 & 434 & 11.8 \pm 0.30 \\ trans-But-2-ene & 3 & 399 & 6.70 \pm 0.19 \\ \hline 3 & 410 & 7.91 \pm 0.35 \\ 1 & 410 & 8.30 \pm 0.30 \\ \hline 3 & 434 & 12.7 \pm 0.20 \\ \hline 2 -Methylbut-2-ene & 3 & 399 & 14.1 \pm 0.2 \\ \hline 3 & 434 & 24.4 \pm 1.3 \\ \hline 2,3-Dimethylbut-2-ene & 3 & 399 & 34.0 \pm 1.5 \\ \hline 3 & 410 & 7.9 \pm 0.9 \\ \hline 3 & 410 & 7.9 \pm 0.9 \\ \hline 3 & 410 & 7.9 \pm 0.9 \\ \hline 3 & 434 & 7.2 \pm 1.9 \\ \hline \end{array}$		1	410	$1.63 \pm 0.11$
Cyclohexane2399 $9.80 \pm 1.20$ 2410 $12.0 \pm 1.0$ 2434 $18.9 \pm 1.4$ Butane2399 $3.08 \pm 0.05$ 1399 $3.09 \pm 0.10$ 2410 $3.67 \pm 0.06$ 1410 $3.68 \pm 0.04$ 2434 $6.23 \pm 0.31$ 2-Methylpropane23991399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.6$ 2410 $12.2 \pm 1.1$ 1410 $12.3 \pm 0.5$ 2434 $18.2 \pm 0.5$ Propene33993410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene33995.21 \pm 0.1033410 $6.38 \pm 0.34$ 3434 $9.86 \pm 0.50$ cis-But-2-ene33993410 $7.53 \pm 0.52$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 33434 $12.7 \pm 0.20$ 2-Methylbut-2-ene33993434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene33993434 $7.2 \pm 1.9$		2	434	$2.66 \pm 0.05$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Cyclohexane	2	399	$9.80 \pm 1.20$
2 $434$ $18.9 \pm 1.4$ Butane2 $399$ $3.08 \pm 0.05$ 1 $399$ $3.09 \pm 0.10$ 2 $410$ $3.67 \pm 0.04$ 2 $410$ $3.68 \pm 0.04$ 2 $434$ $6.23 \pm 0.31$ 2-Methylpropane2 $399$ $10.2 \pm 0.2$ 1 $399$ $10.2 \pm 0.2$ 1 $399$ $10.2 \pm 0.6$ 2 $410$ $12.2 \pm 1.1$ 1 $410$ $12.3 \pm 0.5$ 2 $434$ $18.2 \pm 0.5$ Propene3 $399$ $1.99 \pm 0.11$ 3 $410$ $2.37 \pm 0.17$ 3 $434$ $3.85 \pm 0.12$ 2-Methylpropene3 $399$ 5.21 \pm 0.10 $3$ 3 $410$ $6.38 \pm 0.34$ 3 $434$ $9.86 \pm 0.50$ cis-But-2-ene $3$ $399$ $6.70 \pm 0.19$ $3$ $3$ $410$ $7.91 \pm 0.35$ 1 $410$ $8.30 \pm 0.30$ $3$ $434$ $12.7 \pm 0.20$ 2-Methylbut-2-ene $3$ $399$ $4.11 \pm 0.2$ $3$ $410$ $7.9 \pm 0.9$ $3$ $410$ $7.9 \pm 0.9$ $3$ $410$ $7.9 \pm 0.9$ $3$ $434$ $7.2 \pm 1.9$		2	410	$12.0 \pm 1.0$
Butane2399 $3.08 \pm 0.05$ 1399 $3.09 \pm 0.10$ 2410 $3.67 \pm 0.06$ 1410 $3.68 \pm 0.04$ 2434 $6.23 \pm 0.31$ 2-Methylpropane2399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.6$ 2410 $12.2 \pm 1.1$ 1410 $12.3 \pm 0.5$ 2434 $18.2 \pm 0.5$ Propene33993410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene33995.21 \pm 0.1034103434 $9.86 \pm 0.50$ cis-But-2-ene33996.70 \pm 0.1933410 $7.53 \pm 0.52$ 1410 $8.30 \pm 0.30$ 3434 $11.8 \pm 0.30$ trans-But-2-ene33996.70 \pm 0.1933410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene333994.11 \pm 0.234107.9 \pm 0.934347.9 \pm 0.934347.9 \pm 0.93434		2	434	$18.9 \pm 1.4$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Butane	2	399	$3.08\pm0.05$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	399	$3.09 \pm 0.10$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		2	410	$3.67 \pm 0.06$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	410	$3.08 \pm 0.04$
2-Methylpropane2399 $10.2 \pm 0.2$ 1399 $10.2 \pm 0.2$ 2410 $12.2 \pm 1.1$ 1410 $12.3 \pm 0.5$ 2434 $18.2 \pm 0.5$ 2434 $18.2 \pm 0.5$ Propene3399 $1.99 \pm 0.11$ 3410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene3399 $5.21 \pm 0.10$ 3410 $6.38 \pm 0.34$ 3434 $9.86 \pm 0.50$ cis-But-2-ene3399 $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene33993410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene339934342,3-Dimethylbut-2-ene33434343437.9 \pm 0.9343437.9 \pm 0.93434		2	434	$0.23 \pm 0.31$
1 $399$ $10.2 \pm 0.6$ 2410 $12.2 \pm 1.1$ 1410 $12.3 \pm 0.5$ 2434 $18.2 \pm 0.5$ 2434 $18.2 \pm 0.5$ Propene3 $399$ $1.99 \pm 0.11$ 3410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene3 $399$ $5.21 \pm 0.10$ 3410 $6.38 \pm 0.34$ 3434 $9.86 \pm 0.50$ cis-But-2-ene3 $399$ $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene3 $399$ $6.70 \pm 0.19$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene3 $399$ 3410 $16.4 \pm 2.5$ 3434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene3 $399$ 3434 $7.2 \pm 1.9$	2-Methylpropane	2	399	$10.2 \pm 0.2$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		1	399	$10.2 \pm 0.6$
1410 $12.3 \pm 0.3$ 2434 $18.2 \pm 0.5$ Propene3399 $1.99 \pm 0.11$ 3410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene3399 $5.21 \pm 0.10$ 3410 $6.38 \pm 0.34$ 3434 $9.86 \pm 0.50$ cis-But-2-ene3399 $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene33993410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene33993410 $16.4 \pm 2.5$ 3434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene33993434 $57.2 \pm 1.9$		2	410	$12.2 \pm 1.1$ 12.2 + 0.5
2 $334$ $10.2 \pm 0.3$ Propene3 $399$ $1.99 \pm 0.11$ 3 $410$ $2.37 \pm 0.17$ 3 $434$ $3.85 \pm 0.12$ 2-Methylpropene3 $399$ $5.21 \pm 0.10$ 3 $410$ $6.38 \pm 0.34$ 3 $434$ $9.86 \pm 0.50$ cis-But-2-ene3 $399$ $6.49 \pm 0.06$ 3 $410$ $7.53 \pm 0.52$ 3 $434$ $11.8 \pm 0.30$ trans-But-2-ene3 $399$ $6.70 \pm 0.19$ 3 $410$ $7.91 \pm 0.35$ 1 $410$ $8.30 \pm 0.30$ 3 $434$ $12.7 \pm 0.20$ 2-Methylbut-2-ene3 $399$ 410 $16.4 \pm 2.5$ 3 $434$ 2,3-Dimethylbut-2-ene33 $410$ 3 $410$ 3 $410$ 3 $410$ 3 $410$ 3 $7.9 \pm 0.9$ 3 $434$		2	434	$12.3 \pm 0.3$ 18 2 + 0 5
Propene3399 $1.99 \pm 0.17$ 3410 $2.37 \pm 0.17$ 3434 $3.85 \pm 0.12$ 2-Methylpropene3399 $5.21 \pm 0.10$ 3410 $6.38 \pm 0.34$ 3434 $9.86 \pm 0.50$ cis-But-2-ene3399 $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene3399 $6.70 \pm 0.19$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene33993410 $16.4 \pm 2.5$ 3434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene33993434 $57.2 \pm 1.9$	P	2	200	$10.2 \pm 0.3$
2-Methylpropene 3 410 2-Methylpropene 3 410 3 434 3.85 $\pm$ 0.12 2-Methylpropene 3 410 6.38 $\pm$ 0.34 3 434 9.86 $\pm$ 0.50 <i>cis</i> -But-2-ene 3 434 11.8 $\pm$ 0.30 <i>trans</i> -But-2-ene 3 410 7.53 $\pm$ 0.52 3 410 7.53 $\pm$ 0.52 3 434 11.8 $\pm$ 0.30 <i>trans</i> -But-2-ene 3 410 7.91 $\pm$ 0.35 1 410 8.30 $\pm$ 0.30 3 434 12.7 $\pm$ 0.20 2-Methylbut-2-ene 3 434 2-Methylbut-2-ene 3 434 2-Methylbut-2-ene	Propene	3	399	$1.99 \pm 0.11$
2-Methylpropene $3$ $399$ $5.21 \pm 0.10$ $3$ $410$ $6.38 \pm 0.34$ $3$ $410$ $6.38 \pm 0.34$ $3$ $434$ $9.86 \pm 0.50$ <i>cis</i> -But-2-ene $3$ $399$ $6.49 \pm 0.06$ $3$ $410$ $7.53 \pm 0.52$ $3$ $434$ $11.8 \pm 0.30$ <i>trans</i> -But-2-ene $3$ $399$ $6.70 \pm 0.19$ $3$ $410$ $7.91 \pm 0.35$ $1$ $410$ $8.30 \pm 0.30$ $3$ $434$ $12.7 \pm 0.20$ 2-Methylbut-2-ene $3$ $399$ $14.1 \pm 0.2$ $3$ $434$ $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene $3$ $399$ $34.0 \pm 1.5$ $3$ $434$ $57.2 \pm 1.9$		3	410	$2.37 \pm 0.17$ 3.85 $\pm 0.12$
2-Methylpropene3 $399$ $5.21 \pm 0.10$ 3410 $6.38 \pm 0.34$ 3434 $9.86 \pm 0.50$ cis-But-2-ene3 $399$ $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene3 $399$ $6.70 \pm 0.19$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene3 $399$ 3410 $16.4 \pm 2.5$ 3434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene3 $399$ 3434 $37.9 \pm 0.9$ 3434 $57.2 \pm 1.9$	0.16 / 1	2	200	$5.05 \pm 0.12$
$\begin{array}{c} 3 & 410 & 0.33 \pm 0.34 \\ 3 & 434 & 9.86 \pm 0.50 \\ \hline cis-But-2-ene & 3 & 399 & 6.49 \pm 0.06 \\ 3 & 410 & 7.53 \pm 0.52 \\ 3 & 434 & 11.8 \pm 0.30 \\ \hline trans-But-2-ene & 3 & 399 & 6.70 \pm 0.19 \\ 3 & 410 & 7.91 \pm 0.30 \\ 1 & 410 & 8.30 \pm 0.30 \\ 3 & 434 & 12.7 \pm 0.20 \\ \hline 2-Methylbut-2-ene & 3 & 399 & 14.1 \pm 0.2 \\ 3 & 410 & 16.4 \pm 2.5 \\ 3 & 434 & 24.4 \pm 1.3 \\ \hline 2,3-Dimethylbut-2-ene & 3 & 399 & 34.0 \pm 1.5 \\ 3 & 410 & 37.9 \pm 0.9 \\ 3 & 434 & 57.2 \pm 1.9 \end{array}$	2-Methylpropene	3	399	$5.21 \pm 0.10$
cis-But-2-ene3399 $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene3399 $6.70 \pm 0.19$ 3410 $7.91 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene33993410 $16.4 \pm 2.5$ 3434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene33993434 $37.9 \pm 0.9$ 3434 $57.2 \pm 1.9$		3	410	$0.38 \pm 0.34$ 9.86 $\pm$ 0.50
cts-But-2-ene3399 $6.49 \pm 0.06$ 3410 $7.53 \pm 0.52$ 3434 $11.8 \pm 0.30$ trans-But-2-ene3399 $6.70 \pm 0.19$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene33993434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene33993434 $37.9 \pm 0.9$ 3434 $57.2 \pm 1.9$		5	200	0.00 <u>+</u> 0.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	cis-But-2-ene	3	399	$6.49 \pm 0.06$
$trans$ -But-2-ene3399 $6.70 \pm 0.19$ 3410 $7.91 \pm 0.35$ 1410 $8.30 \pm 0.30$ 3434 $12.7 \pm 0.20$ 2-Methylbut-2-ene33993434 $24.4 \pm 1.3$ 2,3-Dimethylbut-2-ene33993434 $37.9 \pm 0.9$ 3434 $37.9 \pm 0.9$ 3434 $37.2 \pm 1.9$		3	410	$7.33 \pm 0.32$ 11.8 $\pm$ 0.30
trans-But-2-ene3399 $6.70 \pm 0.19$ 34107.91 $\pm 0.35$ 14108.30 $\pm 0.30$ 343412.7 $\pm 0.20$ 2-Methylbut-2-ene3399341016.4 $\pm 2.5$ 343424.4 $\pm 1.3$ 2,3-Dimethylbut-2-ene3399343437.9 $\pm 0.9$ 343457.2 $\pm 1.9$	. D ( 0	3	200	$11.0 \pm 0.30$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	trans-But-2-ene	3	399	$6.70 \pm 0.19$
2-Methylbut-2-ene $\begin{array}{cccccccccccccccccccccccccccccccccccc$		3	410	$7.91 \pm 0.33$ 8 30 $\pm$ 0 30
2-Methylbut-2-ene 3 399 14.1 $\pm$ 0.20 3 410 16.4 $\pm$ 2.5 3 434 24.4 $\pm$ 1.3 2,3-Dimethylbut-2-ene 3 399 34.0 $\pm$ 1.5 3 434 57.2 $\pm$ 1.9		3	434	$12.7 \pm 0.20$
2-Methylbut-2-ene 3 399 14.1 $\pm$ 0.2 3 410 16.4 $\pm$ 2.5 3 434 24.4 $\pm$ 1.3 2,3-Dimethylbut-2-ene 3 399 34.0 $\pm$ 1.5 3 410 37.9 $\pm$ 0.9 3 434 57.2 $\pm$ 1.9	2 Mathulbut 2 and	2	200	$12.7 \pm 0.20$
2,3-Dimethylbut-2-ene $\begin{array}{cccccccccccccccccccccccccccccccccccc$	2-Methylbut-2-ene	3	399 410	$14.1 \pm 0.2$ $16.4 \pm 2.5$
2,3-Dimethylbut-2-ene 3 399 $34.0 \pm 1.5$ 3 410 $37.9 \pm 0.9$ 3 434 $57.2 \pm 1.9$		3	434	$10.4 \pm 2.3$ $24.4 \pm 1.3$
2,3-Dimethylout-2-ene 3 399 $34.0 \pm 1.5$ 3 410 $37.9 \pm 0.9$ 3 434 $57.2 \pm 1.9$	2.2 Dimethollow 2 m	5	200	$24.7 \pm 1.5$
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2,5-Dimethylbut-2-en	2	399 410	$34.0 \pm 1.3$ $37.0 \pm 0.0$
		3	410	$57.7 \pm 0.9$ $57.2 \pm 1.9$
		5	777	J/ 1 1.J

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 ( $D^{\circ} = 452 \text{ kJ mol}^{-1}$ ),<sup>21</sup> 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  $\log(A_6/dm^3mol^{-1}s^{-1})$  of 8.3  $\pm$  0.7, 8.2  $\pm$  0.1, and 8.1  $\pm$  0.2 for primary, secondary, and tertiary C-H bonds and corresponding values of  $E_6$  of 34.7  $\pm$  4.3, 29.0  $\pm$  0.7, and 23.8  $\pm$  1.3 kJ mol<sup>-1</sup>. We are unable to compare their results directly for they used values of  $log(A_2/s^{-1}) = 13.4$  and  $E_2 = 70.2$  kJ mol<sup>-1</sup> as recommended by Benson and O'Neal,<sup>22</sup> 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 semiempirical 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

$$AH + B' \longrightarrow BH + A'$$
 (iv)

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

$$A \cdots H \cdots B (I)$$

$$A : H \quad B \cdot (II)$$

$$AH + B \cdot \longrightarrow \qquad A \cdot + BH$$

$$AH + B \cdot \bigoplus (III)$$

$$\dot{A} \quad \dot{H} \quad \dot{B} (III)$$

$$\dot{A} \quad \dot{H} \quad \dot{B} (IV)$$

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  ${}^{1}E_{AH}^{\ddagger}$ , estimated from equation (v).  $D_{e}$  is calculated from  $D^{0}$  by adding the zero-point energy

$${}^{1}E_{AH}^{\ddagger} = D_{e}[(1 - e^{-\beta(r-r_{e})})^{2} - 1]$$
 (v)

[equation (vi)], and  $\beta$  from relation (vii).

$$D_{\rm e} = D^0 + 0.001 \ 43\omega_0$$
 (vi)

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

The second term  $E_R^{\ddagger}$  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  ${}^{3}E_{AB}^{\ddagger}$ , the repulsion (anti-bonding) energy between A and B, is calculated using a modified Morse equation, (viii).

$${}^{3}E_{AB}^{\ddagger} = 0.45 D_{e}[(1 + e^{-\beta(r-r_{e})})^{2} - 1]$$
 (viii)

The experimental energy of activation is the difference between  $E_{total}^{\dagger}$  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  ${}^{1}E_{BH}$  and then solving for the distance  $r_{AH}$  corresponding to an energy  ${}^{1}E_{BH}$ . The antibonding energy  ${}^{3}E_{AB}{}^{\ddagger}$  is evaluated where  $r_{AB} = r_{AH} + r_{BH}$ . 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<sup>-1</sup> for 2,2-dimethylpropane, chosen because it is the vibrational frequency of several simple ethers,<sup>26</sup> this leads to  $E_{calc.} = 28.3$  kJ mol<sup>-1</sup>. Zavitsas and Melikian <sup>25</sup> used a value

Hydrocarbo	on	$\log(A_6/dm^3 mol^{-1} s^{-1})$	$E_6/\text{kJ} \text{ mol}^{-1}$	$\log(A_6^a/dm^3 \text{ mol}^{-1} \text{ s}^{-1})$	$E_6$ $^{a}/\text{kJ}$ mol <sup>-1</sup>	E <sub>6</sub> (calc.)/ kJ mol <sup>-1</sup>
2,2-Dimethylpro	opane	$10.33\pm0.18$	$\textbf{32.4} \pm \textbf{1.4}$	$9.25\pm0.18$	32.4 ± 1.4	28.3
Cyclohexane		$10.54 \pm 0.09$	$27.0\pm0.3$	9.44 + 0.03	27.0 + 0.3	23.1
Butane		$10.27 \pm 0.27$	$28.9 \pm 2.1$	9.56 + 0.45 <sup>b</sup>	$28.9 + 3.6^{\circ}$	22.6 "
2-Methylpropan	e	$10.14 \pm 0.05$	$23.9 \pm 0.4$	9.97 + 0.10 <sup>c</sup>	$23.0 \pm 0.4$ °	18.8 °
Propene		$9.90\pm0.29$	$27.6 \pm 2.3$	9.42 + 0.29	$27.6 \pm 2.3$	ca. 34
2-Methylpropen	e	$10.16 \pm 0.17$	$26.3 \pm 1.4$	$9.38 \pm 0.17$	26.3 + 1.4	
cis-But-2-ene		$10.07 \pm 0.32$	$25.0\pm2.6$	9.59 + 0.32	25.0 + 2.6	
trans-But-2-ene		$10.29 \pm 0.23$	$26.5 \pm 1.8$	$9.81 \pm 0.23$	26.5 + 1.8	
2-Methylbut-2-e	ne	$10.13 \pm 0.23$	$22.8 \pm 1.8$	9.18 + 0.23	22.8 + 1.8	
2,3-Dimethylbut	-2-ene	10.40 $\pm$ 0.41	$\textbf{22.0} \pm \textbf{3.2}$	9.32 $\pm$ 0.41	$22.0 \pm 3.2$	

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

<sup>a</sup> Per C-H bond. <sup>b</sup> For CH<sub>2</sub>. <sup>c</sup> For CH.

Differences in experimental activation energies

	This work	Ref. 7
$(E_{\text{prim.}} - E_{\text{sec.}})/\text{kJ mol}^{-1}$	3.4-5.2	5.7
$(E_{\text{sec.}} - E_{\text{tert.}})/\text{kJ mol}^{-1}$	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 <sup>⊕</sup> <sub>298</sub> /kJ mol <sup>-1</sup>	<i>r</i> <sub>e</sub> /Å	$\omega/cm^{-1}$	ZPE/kJ mol <sup>-1</sup>	$D_{e}/\mathrm{kJ}~\mathrm{mol}^{-1}$	β/Å
Me₃CO-H	439.7 ª	0.97 <sup>b</sup>	3 617 °	22.0	461	2.177
Me <sub>3</sub> CCH <sub>2</sub> –H	414.2 <sup>d</sup>	1.09 <sup>b</sup>	2 952 e	17.7	432	1.819
Me <sub>3</sub> COCH <sub>2</sub> CMe <sub>3</sub>	341 <sup>f</sup> ,ø	1.43 *	1 060 '	6.2	347	1.985
cyclo-C <sub>6</sub> H <sub>11</sub> −H	400 <sup>J</sup>	1.10 *	2 898 c.*	17.4	417	1.816
Me <sub>3</sub> CO <sup>-</sup> cyclo-C <sub>6</sub> H <sub>11</sub>	341 <sup><i>i</i></sup>	1.43 *	1 060 '	6.2	347	1.945
MeCH₂CHMe ↓ H	395.4 <sup>m</sup>	1.09 "	2 890 <sup>i</sup>	17.3	413	1.821
Me <sub>3</sub> CO <sup>-</sup> CH(Et)Me	341 °	1.43 *	1 060 '	6.2	347	1.930
Me₃C−H	380.7 <sup>g</sup>	1.09 "	2 890 <sup>p</sup>	17.3	398	1.855
Me <sub>3</sub> CO–CMe <sub>3</sub>	341 <sup>g.q</sup>	1.43 *	1 060 '	6.2	347	1.985
H-CH2CHCH2	369.9 r	1.09 <sup>g</sup>	2 895 °	17.3	387	1.884
Me <sub>3</sub> CO-CH <sub>2</sub> CHCH <sub>2</sub>	284.5 <sup>g</sup>	1.43 <i>ª</i>	1 050 1	6.3	291	2.149

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

of  $\omega = 1.031 \text{ cm}^{-1}$  without giving a specific reason, although the value is out of the range quoted in the literature, and this leads to  $E_{\text{calc.}} = 31.4 \text{ kJ mol}^{-1}$ . Similarly, if a value of  $D^0$ [(CH<sub>3</sub>)<sub>3</sub>CO-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>] is taken as 345.2 kJ mol<sup>-1</sup>, the upper limit given in the literature for the corresponding molecule CH<sub>3</sub>O-CH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub>, the calculated activation energy becomes 29.7 kJ mol<sup>-1</sup>.

Similar calculations for the reactions between alkenes and t-butoxyl radicals show a considerable discrepancy between experimental results, for example, for propene  $E_a = 27.6 \pm 2.3 \text{ kJ mol}^{-1}$  but the calculated value is 0.5 kJ mol}^{-1}. One source of error is in the value given to the stabilisation energy,  $E_{\rm R}^{\ddagger}$ . 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.

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