Reactions of Oxygenated Radicals in the Gas Phase. Part 8.[1] Reactions of Alkoxyl Radicals with Aldehydes and Ketones

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Rate data for the abstraction reactions between t-butoxyl radicals and formaldehyde, acetaldehyde, acetone, and [$^2H_6$]acetone were determined between 399 and 434 K. The alkoxyl radicals were generated by thermolysis of di-t-butyl peroxide. Data are obtained for the rate of reactions (6) and (13)—(16) (numbered in the text). The

$$\mathrm{Bu^tO\cdot + HCHO \longrightarrow Bu^tOH + \cdot CHO} \qquad (6)$$

$$\mathrm{Bu^tO\cdot + CH_3CHO \longrightarrow Bu^tOH + \cdot CH_2CHO} \qquad (13)$$

$$\mathrm{Bu^tO\cdot + CH_3CHO \longrightarrow Bu^tOH + CH_3\dot{C}O} \qquad (14)$$

$$\mathrm{Bu^tO\cdot + CH_3COCH_3 \longrightarrow Bu^tOH + \cdot CH_2COCH_3} \qquad (15)$$

$$\mathrm{Bu^tO\cdot + CD_3COCD_3 \longrightarrow Bu^tOD + \cdot CD_2COCD_3} \qquad (16)$$

experimentally determined activation energies of several of these reactions are compared with those that may be calculated by a semi-empirical method.

NOTWITHSTANDING the important role they play in gas-phase oxidation reactions of hydrocarbons and related compounds, experimental rate data for alkoxyl radical reactions are scarce. Often estimated values are used, based on results obtained from complex systems. Up to the present time, the most reliable data have been obtained for the abstraction reactions between t-butoxyl radicals and butane and 2-methylpropane by Tedder *et al.*[2] who used t-butyl hypochlorite as the source of alkoxyl radicals.

The data used for abstraction reactions of alkoxyl radicals on aldehydes, important intermediates in the oxidation of alkanes, are based on competition reactions. However, the systems used were not set up specifically for the purpose; they are complex and open to different interpretations of mechanism. For example, data for reaction (A) have been obtained from the acetaldehyde–

$$\mathrm{CH_3O\cdot + CH_3CHO \longrightarrow CH_3OH + (C_2H_3O)\cdot} \qquad (A)$$

oxygen system at high temperatures.[3] The rate of reaction (A) is compared with that of (B) which is itself

$$\mathrm{CH_3O\cdot + M \longrightarrow CH_2O + H\cdot + M} \qquad (B)$$

not well documented. Further, reaction (A) is a combination of two reactions, one involving abstraction of an α-hydrogen atom and the other abstraction of a β-hydrogen atom. In an earlier study, Hoare and Wellington [4] estimated the rate of reaction (C), from the photolysis of acetone vapour but the results were inter-

$$\mathrm{CH_3O\cdot + HCHO \longrightarrow CH_3OH + \cdot CHO} \qquad (C)$$

preted in terms of a mechanism which has now been modified significantly.[5-10] Indeed, the A factor obtained is two orders of magnitude lower than that found from other studies of alkoxyl radical abstraction reactions.[11]

One of the difficulties facing experimenters is the lack of methods for observing high concentrations of alkoxyl radicals in the gas phase. Thus, one is thrown back to studying abstraction reactions in terms of a competition system. However, it is possible to do this in a relatively 'clean' system where competition to abstraction is with a reaction that has now been studied in detail. In the present work, we have investigated the reactions of t-butoxyl radicals with formaldehyde, acetaldehyde, 2,2,2-trideuterioacetaldehyde, acetone, and [$^2H_6$]acetone. This has enabled us, in turn, to obtain rate data for reactions (6) and (13)—(16) (see later). The reaction chosen to compete is the decomposition of the t-butoxyl radical (2). The rate parameters obtained for this reaction are discussed in some detail in the paper.

EXPERIMENTAL

A static vacuum system similar to that described earlier was used through the study.[11] A cylindrical Pyrex reaction vessel was used (13.5 cm long; 5.9 cm diameter; surface : volume ratio 1 : 1.04 cm^{-1}).

Di-t-butyl peroxide (Koch–Light Laboratories Ltd.) was dried over anhydrous magnesium sulphate and then purified by preparative g.l.c.

2,2,2-Trideuterioacetaldehyde was prepared by refluxing, in a nitrogen atmosphere, acetaldehyde with deuterium oxide in the presence of pyridine.[12] The product, b.p. 24 °C, was shown by n.m.r. analysis to have 99%, and by mass spectral analysis, 97% deuterium present in the methyl group.

Formaldehyde was prepared by very gentle heating of paraformaldehyde. Other reactants were obtained commercially and redistilled until no impurities could be detected by g.l.c.

Analysis was by g.l.c. (Pye 104 gas chromatographs, fitted with flame ionization and thermal conductivity detectors and temperature programming). The column used for separation of the oxygenated products was 20% (w/w) diethylhexyl sebacate on Gas Chrom Q (2.4 m length; 4 mm diameter).

The identity of the products was confirmed by mass spectrometry (AEI MS 12; 70 eV electron energy; 100 μA trap current; 8 kV accelerating potential; source temperature 378 K).

RESULTS AND DISCUSSION

(a) *Thermal Decomposition of Di-t-butyl Peroxide.*—The thermal decomposition of di-t-butyl peroxide (DTBP) was studied in the temperature range 399—434 K. Analyses were made at up to *ca.* 10% conversion of peroxide. The main products were found to be acetone and ethane; trace amounts of methane were formed.

These products correspond to the simple reaction scheme (1)—(5).[9] Calculations of first-order rate constants were based on the rate of formation of acetone, R_A (Table 1), assuming steady state conditions for t-butoxyl radicals.

$$\mathrm{DTBP} \longrightarrow 2\,\mathrm{Bu^tO\cdot} \quad (1)$$

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

$$\dot{\mathrm{C}}\mathrm{H_3} + \dot{\mathrm{C}}\mathrm{H_3} \longrightarrow \mathrm{C_2H_6} \quad (3)$$

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

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

$$k_{\mathrm{obs}}/\mathrm{s^{-1}} = 0.5\,R_A/[\mathrm{DTBP}] \quad \text{(i)}$$

From the results, Arrhenius parameters, $\log_{10}(A/_{\mathrm{obs}}\mathrm{s^{-1}})$ 15.9 ± 0.3 and E_{obs} 160.0 ± 2.9 kJ mol^{-1}, were calculated for the decomposition of the peroxide. These compare with values of 15.6 and 157.1 ± 2.1 kJ mol^{-1} obtained in a multisurface vessel.[13]

(b) *Reactions of t-Butoxyl Radicals with Formaldehyde.*—Di-t-butyl peroxide was allowed to decompose in the presence of formaldehyde at temperatures between 399 and 434 K and at overall pressures of 20—200 Torr (Table 2). The ratio of rate constants k_6/k_2 were calculated using relationship (ii).

$$\mathrm{Bu^tO\cdot} + \mathrm{HCHO} \longrightarrow \mathrm{Bu^tOH} + \mathrm{\cdot CHO} \quad (6)$$

$$d[\mathrm{Bu^tOH}]/d[\mathrm{(CH_3)_2CO}] = k_6[\mathrm{HCHO}]/k_2 \quad \text{(ii)}$$

In order to obtain values of k_6, values of k_2 must be known. However, values of k_2 are, from the results obtained throughout this work, dependent on the total pressure. They may be estimated in terms of RRK theory.[14,15] The rate constant for a unimolecular reaction occurring *via* reactions (7) and (8) may be

TABLE 1

Decomposition of di-t-butyl peroxide. DTBP, 5 Torr; nitrogen, 495 Torr

T/K	t/s	Acetone (Torr)	$10^6\,k_{\mathrm{obs}}/\mathrm{s^{-1}}$
399	900	0.07	8.8
	1 800	0.15	8.3
	2 700	0.24	8.9
	3 600	0.33	9.1
410	600	0.17	28.3
	1 200	0.37	30.8
	1 800	0.54	30.0
	2 400	0.66	27.5
	3 000	0.80	26.6
	3 600	0.90	25.0
421	600	0.58	96.6
	1 200	1.14	95.0
	1 800	1.93	107
	2 400	2.27	95.0
427	300	0.60	200
	600	1.18	197
	900	1.64	182
	1 200	2.54	212
	1 500	2.83	189
434	180	0.80	444
	300	1.32	440
	420	1.78	423
	540	2.17	402
	600	2.53	421

TABLE 2

Decomposition of di-t-butyl peroxide in the presence of formaldehyde. DTBP, 5 Torr

T/K	HCHO (Torr)	t/s	10^2(Bu^{t}OH) (Torr)	10^2(Me$_2$CO) (Torr)	$\frac{[\mathrm{Bu^tOH}]}{[\mathrm{HCHO}][\mathrm{Me_2CO}]}$ (dm^3 mol^{-1})
399	15	2 700	2.7	11.8	380
	25	900	1.9	7.1	270
	25	1 200	2.5	8.6	290
	25	1 800	3.5	13.5	260
	25	2 400	4.8	15.8	300
	25	3 000	6.4	22.8	280
	50	2 700	8.2	13.5	300
	75	2 700	10.6	12.5	280
410	15	1 200	4.3	31.0	240
	20	1 200	4.9	32.7	190
	25	600	3.9	17.8	230
	25	1 200	6.9	31.9	220
	25	1 800	9.1	40.9	230
	25	2 400	13.0	60.2	220
	25	3 000	15.4	73.6	210
	35	1 200	8.0	31.0	180
	40	1 200	9.7	30.0	210
434	10	300	5.2	134.0	110
	15	300	7.0	139.0	91
	25	120	5.6	65.0	94
	25	240	11.1	145.0	83
	25	300	12.4	149.0	89
	25	360	10.4	148.0	76
	25	420	15.1	171.0	95
	35	300	14.5	127.7	88
	45	300	19.8	124.8	96

$$\mathrm{X + M \rightleftharpoons X^* + M} \qquad (7)$$

$$\mathrm{X^* \longrightarrow Products} \qquad (8)$$

described by equation (iii). The Kassel integral

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

$I(S,B,D)$ is given by equation (iv) where $B = E/RT$, $D =$

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

$\log(A/Z[\mathrm{M}])$, Z is the collision frequency, and S is the number of effective oscillators in the energized molecule.

S may be set equal to C_{vib}/R for the species X.[16] Provided $S > B/3$,[17] good agreement between computed fall-off curves for the rate constant, k *versus* pressure based on RRK theory with that computed by Rice–Ramsburger–Kassel–Marcus (RRKM) theory for a number of unimolecular reactions is obtained, including the decomposition of the t-butoxyl radical.[16] Table 3 lists the vibrational frequencies for t-butyl alcohol which were used to calculate values of C_{vib}/R for the radical.[16,18] Parameters S, B, and D were estimated from available data (Table 4) and I evaluated from tables computed by Emanuel.[19]

TABLE 3

Vibrational frequencies assigned to the t-butoxyl radical [16,18]

Frequency (cm^{-1})	Degeneracy
2 980	6
2 900	3
1 465	6
1 350	4
1 200	2
1 106	2
1 013	3
919	1
748	1
450	3
350	2
250	3

TABLE 4

Numerical values for parameters S and B in the Kassel integral

T/K	S	B
399	11.8	21.4
410	12.1	20.9
434	12.9	19.7

The collision diameters were estimated by the method reported by Bondi.[20] Thus the variation of log $[k_2(\mathrm{p})/k_2(\infty)]$ with D and hence the values of this ratio of rate constants at different pressures and temperatures were calculated.

In order to obtain values of k_6, values of $k_2(\infty)$ must be known. However, they, in turn, depend on competition experiments. Arrhenius parameters for reaction (2) have been determined by one of three types of competition reaction. In some, the rate of reaction (2) is compared with radical association reactions (*e.g.* the reaction of alkoxyl radicals with nitric oxide [21,22] and with difluoroamino-radicals [23]).

In others, the rate of reaction (2) is compared with the rates of hydrogen-abstraction reactions by the alkoxyl radical (*e.g.* with phenol,[24] ethylenediamine [25]). A third method is to compare the rate of reaction (2) with the addition reaction of the alkoxyl radical with alkenes.[26] There is a considerable discrepancy between the values of A_2 and E_2 found by such experiments. For example, values of A are 10^3—10^4 lower than that expected from analogy with other unimolecular reactions and from theoretical estimates from transition-state theory.[22] More recently, experimental results have been analysed in terms of Lindemann–Hinshelwood theory [22] and higher A factors obtained.

Batt and Milne [27] have considered the problem of finding a more accurate value of A_2 in the following way. A_9 can be found by experiment. However, equation (v)

$$\mathrm{Bu^tONO \longrightarrow Bu^tO\cdot + NO} \qquad (9)$$

applies where $\Delta S^\circ_{-9} = S^\circ_{\mathrm{Bu^tO}} + S^\circ_{\mathrm{NO}} - S^\circ_{\mathrm{Bu^tONO}}$ (these values can be obtained by group additivity data [28-30]) and Δn = (number of product species — number of reactant species). E_{-9} is assumed to be zero. Batt and

$$\ln(A_{-9}/A_9) = \Delta S^\circ - {}_9/R - \Delta n(1 + \ln RT) \qquad \text{(v)}$$

Milne show that $\log_{10}(A_{-9}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 10.4$, which compares with an earlier estimated value of 7.0.[31] Using reaction (—9) as the competitive reaction, $\log_{10}(A_2/\mathrm{s^{-1}}) = 15·5$. A similar value is obtained on recalculating data obtained by Yee Quee and Thynne [22] (allowing for DTBP and nitric oxide to have similar efficiencies as energy-transfer agents [31,32]).

However, as Batt and Milne [27] have pointed out, the value of 10^{15} s^{-1} for A_2 may be too high. Using, for example, a value of ΔS°_{-2}, calculated from group additivity data, and this value for A_2, a value of $\log_{10}(A_{-2}/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 8.3$ is obtained which is similar to that found for the addition of methyl radicals to the isoelectronic molecule, 2-methylpropene.[33] In a later paper by Batt *et al.*,[34] a referee points out that A factors for radical addition to $\mathrm{C_\pi – O_\pi}$, in carbonyl compounds, are lower than the rate of addition of radicals to $\mathrm{C_\pi – C_\pi}$ bonds by a factor of 10. Bearing these arguments in mind, rate data for t-butoxyl radical attack on aldehydes and ketones have been calculated using the revised data of $k_2(\infty)/\mathrm{s^{-1}} = 10^{14.5}\exp(-71\,600\ \mathrm{J\ mol^{-1}}/RT)$. However, in order that our data may be compared directly with that obtained in other studies,[35] our results have also been calculated, and will be given when appropriate, using the higher value of $k_2(\infty)/\mathrm{s^{-1}} = 10^{15.5}\exp(-71\,600\ \mathrm{J\ mol^{-1}}/RT)$.

From data in Table 2, values of k_6 are obtained (Table 5) leading to values of $\log_{10}(A_6/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 9.85 \pm 0.24$ and $E_6 = 19.3 \pm 2.3$ kJ mol^{-1}. [If the higher value of $k_2(\infty)$ is used, values of $\log_{10}(A_6/\mathrm{dm^3\ mol^{-1}\ s^{-1}}) = 10.15 \pm 0.20$ and $E_6 = 16.5 \pm 2.2$ kJ mol^{-1} are found.]

(c) *Reactions of t-Butoxyl Radicals with* 2,2,2-*Tri-*

TABLE 5

Rate constants for the reactions of t-butoxyl radicals with aldehydes and ketones †

Substrate	Reaction number	k/dm^3 mol^{-1} s^{-1} 399 K	410 K	421 K	427 K	434 K
HCHO	(6)	2.0×10^7	2.4×10^6			3.3×10^7
$CH_3C\mathit{H}O$	(14)	1.0×10^7				1.5×10^7
$C\mathit{H}_3CHO$	(13)	4.9×10^5				7.2×10^5
$C\mathit{D}_3CHO$	(10)	1.1×10^5				
CH_3COCH_3	(15)	5.9×10^6	6.8×10^6	8.7×10^6	9.6×10^6	1.1×10^7
CD_3COCD_3	(16)	1.1×10^6	1.4×10^6	1.9×10^6	2.0×10^6	2.5×10^6

† $k_2/s^{-1} = 10^{14.5} \exp(-71{,}500/\text{J mol}^{-1})/RT$.

deuterioacetaldehyde and with Acetaldehyde.—Experiments were performed in which DTBP was decomposed in the presence of 2,2,2-trideuterioacetaldehyde to investigate relative rates of attack at α-C–H and β-C–D bonds in this aldehyde by t-butoxyl radicals. The mass spectrum of the mixture of t-butyl alcohol and [^{2}H]-alcohol, eluted from the gas chromatograph column, was recorded. The peak height of m/e 59, the most abundant peak, and peak height of m/e 60 were measured (Table 6). A correction was made for (M + 1) carbon-13 to the m/e 60[36] peak to obtain the ratio of rate constants k_{10}/k_{11}. The average value of k_{10}/k_{11} is $(1.0 \pm 0.2) \times 10^{-2}$.

TABLE 6

Reaction of t-butoxyl radicals with 2,2,2-trideuterioacetaldehyde at 399 K. Mass spectra of t-butyl alcohol and [^{2}H]alcohol

Run number	Peak height (m/e 59) (mm)	Peak height (m/e 60) (mm)	$\dfrac{\text{Peak ht. } (m/e\ 60) - 3.3\%\ \text{Peak ht. } (m/e\ 59)}{\text{Peak ht. } (m/e\ 59)}$
1	34	1.4	8.2×10^{-3}
2	29	1.3	1.2×10^{-2}
3	42	1.8	9.5×10^{-3}
4	22	1.0	1.2×10^{-2}
5	30	1.3	1.0×10^{-2}
			Mean value $(1.0 \pm 0.2) \times 10^{-2}$

TABLE 7

Decomposition of di-t-butyl peroxide in the presence of acetaldehyde

T/K	DTBP (Torr)	MeCHO (Torr)	t/s	Bu^{t}OH (Torr)	Me$_2$CO(Torr)	$\dfrac{[\text{Bu}^t\text{OH}]}{[\text{MeCHO}][\text{Me}_2\text{CO}]}$ (dm^3 mol^{-1})
399	20	10	3 600	0.22	1.96	310
	20	10	3 600	0.26	2.06	320
	30	10	3 600	0.34	2.87	290
	50	30	2 010	0.66	2.25	240
	50	50	840	0.47	0.89	260
	50	100	900	0.66	0.85	190
	50	100	3 600	2.37	2.83	210
434	20	10	132	0.12	2.78	120
	20	10	132	0.12	2.74	120
	30	10	126	0.14	4.02	94
	50	17	126	0.33	6.39	82
	50	50	132	0.69	6.24	60
	50	100	120	1.06	5.34	54

$$\text{Bu}^t\text{O}\cdot + CD_3CHO \longrightarrow \text{Bu}^t\text{OD} + \cdot CD_2CHO \qquad (10)$$

$$\text{Bu}^t\text{O}\cdot + CD_3CHO \longrightarrow \text{Bu}^t\text{OH} + CD_3\dot{C}O \qquad (11)$$

$$\frac{k_{10}}{k_{11}} = \frac{\text{Peak height } (m/e\ 60) - 3.3\%\ \text{Peak height } (m/e\ 59)}{\text{Peak height } (m/e\ 59)}$$

Table 7 gives results for the decomposition of DTBP in the presence of acetaldehyde. Similar calculations to those described in section (b) yield values for reaction (12) of k_{12} $(1.1 \pm 0.1) \times 10^7$ and $(1.6 \pm 0.1) \times 10^7$ dm^3 mol^{-1} s^{-1} at 399 and 434 K.

$$\text{Bu}^t\text{O}\cdot + CH_3CHO \longrightarrow \text{Bu}^t\text{OH} + \cdot CH_2CHO \text{ or } CH_3CO\cdot \qquad (12)$$

One can find approximate values for the rate constants for reactions (13) and (14). The α-C–H frequency in

$$\text{Bu}^t\text{O}\cdot + CH_3CHO \longrightarrow \text{Bu}^t\text{OH} + \cdot CH_2CHO \qquad (13)$$

$$\text{Bu}^t\text{O}\cdot + CH_3CHO \longrightarrow \text{Bu}^t\text{OH} + CH_3\dot{C}O \qquad (14)$$

acetaldehyde and the C–D frequency in its deuteriated analogue are 2 963 and 2 130 cm^{-1}, respectively,[37] from which it can be calculated that $k_H/k_D \leqslant 4.5$ at 399 K. This gives a value for k_{13}/k_{14} of $(4.7 \pm 0.8) \times 10^{-2}$. Thus, using values of k_{12} above and the ratio k_{13}/k_{14}, $k_{13} = (4.9 \pm 1.5) \times 10^5$ and $k_{14} = (1.0 \pm 0.7) \times 10^7$ dm^3 mol^{-1} s^{-1} at 399 K; corresponding values at 434 K are $(7.2 \pm 0.2) \times 10^5$ and $(1.5 \pm 0.6) \times 10^7$ dm^3 mol^{-1} s^{-1}. Assuming that $A_6 = A_{13} = A_{14}$, the value for $(E_{13} - E_{14})$ is 10.7 ± 0.5 kJ mol^{-1}, giving values of $E_{14} = 15.2 \pm 0.8$ and $E_{13} = 25.9 \pm 0.4$ kJ mol^{-1}.

Furthermore, k_{10} can now be found. The ratio of

k_{10}/k_{11} has been determined as above and is $(1.0 \pm 0.2) \times 10^{-2}$. Given $k_{11} = k_{14}$, a value of k_{10} of $(1.1 \pm 0.3) \times 10^5$ dm^3 mol^{-1} s^{-1} at 399 K is found. If $A_{11} = A_{14}$, a value of E_{10} of 30.4 ± 0.6 kJ mol^{-1} is obtained.

(d) *Reactions of t-Butoxyl Radicals with Acetone and* [$^2H_6$]*Acetone.*—Experiments were performed in which DTBP was decomposed in presence of acetone and [$^2H_6$] acetone (Tables 8 and 9). Values of Arrhenius parameters for reactions (15) and (16) were calculated (Table 10).

TABLE 8

Decomposition of di-t-butyl peroxide in the presence of acetone. DTBP, 5 Torr

T/K	Me_2CO (Torr)	t/s	10^2Bu^tOH (Torr)	$\frac{[Bu^tOH]}{[Me_2CO^*][Me_2CO]}$ (dm^3 mol^{-1})
399	45	900	1.0	82
	45	1 800	2.2	84
	45	2 700	3.2	80
	45	3 600	4.4	82
410	30	2 400	5.0	64
	45	600	1.8	60
	45	1 200	3.5	54
	45	1 800	5.0	52
	45	2 400	7.1	60
	45	3 000	8.7	61
	70	2 400	10.0	55
	75	2 400	12.7	52
421	45	600	4.4	44
	45	1 200	9.0	46
	45	1 800	13.7	42
	45	2 400	17.5	45
427	45	300	4.2	41
	45	600	7.5	37
	45	900	10.0	37
	45	1 200	14.7	34
	45	1 500	17.1	35
434	45	180	4.3	33
	45	300	6.2	29
	45	420	8.5	29
	45	540	10.0	24
	45	600	11.0	27

[Me_2CO^*] = acetone formed from DTBP, calculated from Table 1.

$$Bu^tO\cdot + CH_3COCH_3 \longrightarrow Bu^tOH + \cdot CH_2COCH_3 \quad (15)$$

$$Bu^tO\cdot + CD_3COCD_3 \longrightarrow Bu^tOD + \cdot CD_2COCD_3 \quad (16)$$

(e) *Calculation of Activation Energies for Hydrogen Abstraction Reactions by t-Butoxyl Radicals.*—Zavitsas [38-40] has shown that activation energies for hydrogen-abstraction reactions (17) can be estimated. It is

$$AH + B\cdot \longrightarrow BH + A\cdot \quad (17)$$

assumed that the transition state is linear and partial bonding in A–H and B–H is equal. The transition state is described in terms of a resonance hybrid in which forms (II) and (III) have equal energy.

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

The total bonding energy in the transition state is made up of three terms. One term is the average bonding energy of structures (II) and (III) which can be described as $^1E_{AH}{}^{\ddagger}$. This can be estimated from the semi-empirical Morse equation (vi) where D_e is the Morse

$$^1E_{AH} = D_e[(1 - e^{-\beta(r-r_e)})^2 - 1] \quad \text{(vi)}$$

curve dissociation energy, r_e is the equilibrium internuclear distance of the bond (in Å), and r is the distance at which the bond is being evaluated.

TABLE 9

Decomposition of di-t-butyl peroxide in the presence of [$^2H_6$]acetone. DTBP, 5 torr

T/K	$(CD_3)_2CO$ (Torr)	t/s	10^2Bu^tOD (Torr)	$\frac{[Bu^tOD]}{[Me_2CO^*][(CD_3)_2CO]}$ (dm^3 mol^{-1})
399	15	2 700	0.2	18
	45	900	0.2	19
	45	1 800	0.4	15
	45	2 700	0.6	14
	45	3 600	0.8	15
	65	2 700	0.9	17
	95	2 700	1.1	13
410	30	2 400	0.9	12
	45	600	0.4	14
	45	1 200	0.7	11
	45	1 800	1.1	11
	45	2 400	1.4	12
	45	3 000	1.7	12
	70	2 400	2.1	12
	95	2 400	3.2	12
421	45	600	0.9	10
	45	1 200	1.8	9
	45	1 800	2.9	9
	45	2 400	3.6	9
427	45	300	0.8	8
	45	600	1.6	8
	45	900	2.1	8
	45	1 200	2.7	6
	45	1 500	3.4	7
434	45	180	1.1	8
	45	300	1.5	7
	45	420	1.8	6
	45	540	2.3	7
	45	600	2.7	6

[Me_2CO^*] = acetone formed from DTBP, calculated from Table 1.

D_e is calculated from D° by adding the zero-point energy [equation (vii)], and β from relation (viii).

$$D_e = D^\circ + 0.001\,43\omega_o \quad \text{(vii)}$$

$$\beta = 0.1218\omega_o\,(\mu/350\,D^\circ)^{\frac{1}{2}} \quad \text{(viii)}$$

TABLE 10

Arrhenius parameters for the reactions between t-butoxyl radicals with aldehydes and ketones

		Using $\log_{10}(A_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 14.5$		Using $\log_{10}(A_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}) = 15.5$	
Substrate	Reaction number	$\log_{10}(A/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	E/kJ mol^{-1}	$\log_{10}(A/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$	E/kJ mol^{-1}
HCHO	(6)	9.9 ± 0.2	19.3 ± 2.3	10.2 ± 0.2	16.5 ± 2.2
CH_3COCH_3	(15)	10.1 ± 0.1	25.7 ± 1.3	10.5 ± 0.3	23.9 ± 3.3
CD_3COCD_3	(16)	10.2 ± 0.2	31.6 ± 3.0	10.3 ± 0.3	27.2 ± 2.8

Values for the reactions with acetaldehyde [(13) and (14)] are given in the text.

ω_0 is the equilibrium vibrational stretching frequency of the bond (in cm^{-1}) and μ is the reduced mass in atomic mass units of two bonded atoms.

The second term needed in order to find the total bonding energy is the delocalisation energy of one odd electron over three atoms, $E_R^‡$. Zavitsas suggested that the value of $E_R^‡$ can be assumed to be similar to the delocalisation energy of the allyl radical. The third energy term is concerned with the repulsion (antibonding) energy between A and B, ${}^3E_{AB}^‡$. This must be considered because the simultaneous bonding of H to both A and B [structure (I)] requires the electron spins in structure (IV) to be either $\uparrow \downarrow \uparrow$ or $\downarrow \uparrow \downarrow$. ${}^3E_{AB}^‡$ can be calculated from the modification (ix) to the Morse equation. The experimental energy of activation

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

$$ E_{\text{total}}^‡ = {}^1E_{AB}^‡ + E_R^‡ + {}^3E_{AB}^‡ \qquad \text{(x)} $$

will be the difference between $E_{\text{total}}^‡$ and $D_e(A - H)$. A small correction is applied for zero-point energy (ZPE) effects in the transition state [equation (xi)].

$$ \text{ZPE}^‡ = 0.5\, (\text{ZPE}_{AH} + \text{ZPE}_{BH}) \qquad \text{(xi)} $$

TABLE 11

Data used for calculations of the activation energy for hydrogen-atom abstraction from formaldehyde, from β-C–H bonds in acetaldehyde, and from acetone by t-butoxyl radicals

	$Bu^tO–H$	H–CHO	$Bu^tO–CHO$	$H–CH_2CHO$	$Bu^tO–CH_2CHO$ and $Bu^tO–CH_2COCH_3$	$H–CH_2COCH_3$
D°_{298}/kJ mol^{-1}	438 [a]	364 [a]	405 [b,c]	412 [a]	339 [c,d]	401 [h]
R_e/kJ mol^{-1}	0.96 [e]	1.09 [e]	1.37 [e,f]	1.09 [e]	1.43 [e]	1.09 [e]
$R^‡$/kJ mol^{-1}	1.12	1.16	2.38	1.17	2.29	1.17
ω/cm^{-1}	3 617 [g]	2 822 [g]	1 190 [g]	2 963 [g]	1 100 [c]	2 981 [g]
ZPE/kJ mol^{-1}	22	17	7	18	7	18
D_e/kJ mol^{-1}	460	381	412	430	346	419
β	2.211 64	1.850 06	2.0599	1.8198	2.0520	1.9380

[a] Ref. 41. [b] Assumed equal to $D^\circ(CH_3O–COCH_3)$. [c] Ref. 29. [d] Assumed equal to $D^\circ(C_2H_5O–CH_3)$. [e] Ref. 42. [f] Assumed equal to C–O bond length in methyl formate. [g] Ref. 37. [h] Ref. 39.

Thus the data needed for the calculations are those for the Morse functions, namely values for bond dissociation energies, i.r. stretching frequencies, bond lengths for A–B, A–H, and B–H, and their masses. The energy of the transition state is evaluated at a distance r_{BH} by first calculating ${}^1E_{BH}$ from equation (vi) and then by solving for the distance r_{AH} corresponding to an energy ${}^1E_{BH}$, also using equation (vi). Solution of this equation gives two values for r_{AH}: the value required is that where $r_{AH} > r_{AH(e)}$. The antibonding energy ${}^3E_{AB}^‡$ is then evaluated, where $r_{AB} = r_{AH} + r_{BH}$. The sum of the terms in equation (x) gives the energy of one possible transition state. The procedure is repeated at 0.01 Å increments of r_{BH} until the minimum energy of $E_{\text{total}}^‡$ is found.

TABLE 12

Observed and calculated activation energies (kJ mol^{-1}) for the reactions of t-butoxyl radicals with aldehydes and ketones

Substrate	Reaction number	E_{obs} [a]	E_{obs} [b]	E_{calc}
HCHO	(6)	19.3	16.5	14.3
CH_3CHO	(13)	25.9	24.1	26.8
CH_3COCH_3	(15)	25.7	23.9	20.5

[a] $\log_{10}(A_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$ taken as 14.5. [b] $\log_{10}(A_2/\text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1})$ taken as 15.5.

Zavitsas has demonstrated that this method yields results (of which over 100 have been published) for activation energies of abstraction reactions that are in close agreement with experimental results.

However he was unable to test his theory convincingly using reactions between alkoxyl radicals and carbonyl compounds: it is now possible to do so.

Data used in our calculations for the energy of activation of hydrogen atom abstraction from formaldehyde, acetaldehyde, and acetone by t-butoxyl radicals are given in Table 11, and the results given in Table 12. There is reasonable agreement; this method of calculation will be reviewed in a subsequent paper devoted to other abstraction reactions of alkyl and alkoxyl radicals.[43]

(f) *Comparison of Rate Data for the Reactions of t-Butoxyl Radicals with Aldehydes and Ketones.*—The results in this study show that, for the reactions of t-butoxyl radicals with aldehydes and ketones, the rates of reaction are broadly parallel with the dissociation energies for the bond RCO–H. The accepted literature values for D°(HCO–H) and $D^\circ(CH_3CO–H)$ are 364 ± and 359 ± kJ mol^{-1}, respectively.[44]

Zavitsas [38] discusses the value of $D^\circ(CH_3COCH_2–H)$ in some detail. He reviews the literature values which range from 385 (ref. 45) to 410 kJ mol^{-1} (ref. 46). His results, however, indicate an intermediate value of 401 kJ mol^{-1} which he suggests is not incompatible with the higher value. He points out the value of 410 kJ mol^{-1} was obtained from the reaction of acetone with bromine atoms which is complex below 534 K. Ignoring values of rate constants just above this region, he recalculates the value to be 407 ± 8 kJ mol^{-1}. Our results suggest that $D^\circ(H–CH_2CHO)$ is similar to that attributed to $D^\circ(CH_3COCH_2–H)$.

One of us (K. S.) thanks the Science Research Council for a studentship.

[0/1984 *Received, 30th December, 1980*]

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