

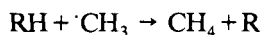
Kinetics of abstraction reactions of methyl radicals with alkanes in gas phase

Mohammad I Sway*

Department of Natural Sciences, Mu'tah University, Mu'tah, Al-Karak P.O. Box 7, Jordan

Received 10 March 1989; revised 7 August 1989; accepted 15 November 1989

Rate data for the abstraction reactions between methyl radicals and some alkanes viz. 2,2-dimethylpropane, 2,2,3,3-tetramethylbutane, cyclohexane, butane and 2-methylpropane (containing primary, secondary and tertiary C-H bonds) have been determined between 399 and 434 K. The methyl radicals are generated by thermolysis of di-*t*-butyl peroxide. From the yields of methane and ethane, Arrhenius parameters for the reaction:



have been obtained. They are $\log (A_g) = 7.93 \pm 0.13$, 7.95 ± 0.14 , 8.07 ± 0.10 , 7.96 ± 0.10 and 8.13 ± 0.20 , and $E_g/kJ \text{ mol}^{-1} = 47.59 \pm 1.56$, 46.17 ± 1.54 , 40.14 ± 1.20 , 38.94 ± 1.20 and 33.60 ± 2.30 , respectively. The data obtained in this work are compared with those obtained by other workers. The experimentally determined activation energies for 2,2-dimethylpropane, cyclohexane, butane and 2-methylpropane are compared favourably with those calculated by a semiempirical method.

One of the most useful methods of obtaining rate data for abstraction reactions by methyl radicals in the gas phase is by comparing the rate of formation of methane with that of ethane as a reference reaction which involves recombination of methyl radicals. In this paper, we report rate data of abstraction reaction of methyl radicals with a group of alkanes containing primary, secondary and tertiary C-H bonds. The Arrhenius parameters determined in the present work are compared with those obtained by other workers using different techniques¹⁻⁵.

Materials and Methods

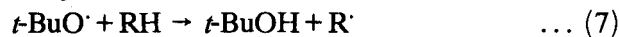
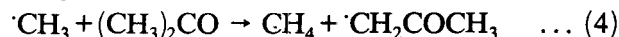
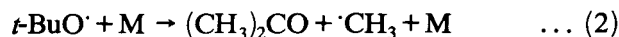
A static vacuum system fitted with a cylindrical pyrex reaction vessel (length = 15 cm; diam = 3.5 cm; surface to volume ratio 0.80 cm^{-1}) suspended in an electric furnace (accuracy $\pm 0.1^\circ\text{C}$) was used. The outlets from the reaction vessel, led to GC-MS system. Pressure measurements were made with a transducer (Consolidated Electrodynamics).

Di-*t*-butyl peroxide (Koch-Light) was dried over anhydrous MgSO_4 and purified by preparative GLC (10% w/w diethylhexyl sebacate on Gas Chrom Q). Other reactants were obtained commercially. The column used for analysis was Porapak Q (length = 3 m; diam = 4 mm). Nitrogen was used as the carrier gas. The retention times of the components of a mixture and the calibrations of products were compared with those of authentic samples chromatographed under identical conditions.

Results and Discussion

The thermal decomposition of di-*t*-butyl peroxide

(DTBP) under the conditions of the experiments has been studied in detail^{6,7}. The main products formed were methane, ethane, acetone and *t*-butanol. The formation of these can be rationalised by the steps (1-7) in Scheme 1.



Scheme 1

Rate constants calculated for the first order decomposition of the peroxide based on the rate of formation of acetone yielded Arrhenius parameters: $\log (A_{\text{obs}}) = (15.3 \pm 0.2)$ and $E = (155.70 \pm 1.37) \text{ kJ mol}^{-1}$.

In a previous paper⁸, we reported rate data for reaction (7). In this paper, we are concerned only with reaction (6).

In a series of experiments, di-*t*-butyl peroxide was allowed to decompose in the presence of the alkanes, at several temperatures between 399 and 434 K. Nitrogen was added to give a constant total initial pressure of 500 torr. The results are shown in Table 1.

In yet another series of experiments, initial [alkane] was varied, while [peroxide] was kept fixed at constant temperature (Fig. 1). The results show that

Table 1—Decomposition of di-*t*-butyl peroxide in the presence of alkanes [DTBP, 5 Torr; pressure made up with nitrogen to 500 Torr]

Alkane	T/K	$10^3 [\text{RH}]$ (mol dm ⁻³)	No. of expts.	$10^5 R_{\text{CH}_3}/R_{\text{C}_2\text{H}_5}^{1/2}$ (mol ^{1/2} dm ^{-3/2} s ^{-1/2})	$10^3 k_6/k_3^{1/2}$ (total) (dm ^{3/2} mol ^{-1/2} s ^{-1/2})	$10^4 k_6/k_3^{1/2}$ (per C-H) (dm ^{3/2} mol ^{-1/2} s ^{-1/2})
2,2-dimethyl- propane	399	8.04	3	3.00 ± 0.04	3.72 ± 0.05	3.14 ± 0.02
	410	7.82	3	4.38 ± 0.03	5.60 ± 0.03	4.66 ± 0.03
	418	4.41	1	3.06	6.45	5.79
		6.13	1	4.53	7.39	6.16
		7.66	2	5.34 ± 0.09	6.92 ± 0.06	5.80 ± 0.10
		13.41	1	9.33	6.96	5.80
	423	5.69	1	4.56	8.05	6.71
		7.58	3	6.40 ± 0.18	8.47 ± 0.23	7.06 ± 0.19
		8.91	1	6.94	7.81	6.51
	428	7.48	3	7.08 ± 0.05	9.49 ± 0.07	7.89 ± 0.06
	434	7.39	3	8.91 ± 0.47	11.83 ± 0.29	9.85 ± 0.24
2,2,3,3-tetra- methylbutane	399	0.68	1	0.74	10.83	6.02
		0.76	1	0.79	10.37	5.76
		0.80	1	0.83	10.34	5.74
	410	0.55	1	0.82	15.03	8.35
		0.59	1	0.92	15.63	8.68
		0.78	1	1.20	15.35	8.53
		0.82	2	1.28 ± 0.04	15.53 ± 0.43	8.63 ± 0.23
		1.02	1	1.51	14.85	8.25
	419	0.76	2	1.63 ± 0.0	21.39 ± 0.0	11.88 ± 0.0
		0.75	1	1.65	21.90	12.17
	424	0.76	1	1.90	25.00	13.89
		0.72	1	1.75	24.40	13.56
		0.87	1	2.20	25.30	14.06
	429	0.86	1	2.43	28.32	15.73
		0.78	1	2.16	27.57	15.32
	434	0.70	2	2.22 ± 0.04	31.63 ± 0.61	17.57 ± 0.34
		0.74	1	2.36	31.94	17.74
Cyclohexane	400	2.09	1	11.00	53.00	44.17
		1.81	1	9.42	52.10	43.42
		2.41	1	12.65	52.60	43.80
	411	1.56	1	11.20	12.00	60.00
		2.15	1	14.70	69.00	57.50
		3.12	1	21.00	71.00	59.17
		1.83	1	13.00	71.00	59.17
		2.34	1	18.00	71.00	59.17
	419	2.29	1	19.90	86.90	72.42
	424	1.89	1	19.55	103.50	86.25
	429	2.05	1	24.60	120.00	100.00
		1.87	1	22.60	121.20	101.00
	434	1.55	1	21.50	132.57	110.50
		1.48	1	21.00	130.60	108.80
Butane	399	8.04	1	16.05	19.92	45.20
		4.02	1	8.2	20.38	46.30
	410	7.82	4	20.60 ± 0.05	26.31 ± 0.04	58.80 ± 0.04
	418	7.66	1	26.70	34.90	78.50
		3.83	1	13.10	34.33	77.22
		11.49	1	40.30	35.10	78.90
	423	7.58	3	29.40 ± 0.03	38.92 ± 0.04	86.60 ± 0.05
	428	3.74	2	16.9 ± 0.01	45.20 ± 0.02	101.14 ± 0.2
	434	7.48	3	38.20 ± 0.02	51.72 ± 0.03	114.53 ± 0.25

(contd.)

Table 1—Decomposition of di-*t*-butyl peroxide in the presence of alkanes [DTBP, 5 Torr; pressure made up with nitrogen to 500 Torr]—*Contd.*

Alkane	T/K	$10^3 [\text{RH}]$ (mol dm ⁻³)	No. of expts.	$10^5 R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ (mol ^{1/2} dm ^{-3/2} s ^{-1/2})	$10^3 k_6/k_3^{1/2}$ (total) (dm ^{3/2} mol ^{-1/2} s ^{-1/2})	$10^4 k_6/k_3^{1/2}$ (per C-H) (dm ^{3/2} mol ^{-1/2} s ^{-1/2})
2-Methyl- propane	399	6.83	1	26.40	38.70	358.6
		8.04	2	31.10 ± 0.01	38.64 ± 0.02	358.5 ± 0.2
	410	7.82	2	37.90 ± 0.02	48.53 ± 0.02	443.3 ± 0.4
		8.21	1	40.90	49.8	456.0
	418	4.02	1	22.90	59.86	545.4
		11.49	1	65.30	56.82	515.0
		15.32	1	88.50	57.80	524.8
		7.66	3	44.5 ± 0.03	58.2 ± 0.04	528.9 ± 0.5
	423	3.79	3	27.3 ± 0.02	72.4 ± 0.03	661.9 ± 0.4
	428	7.48	2	56.1 ± 0.03	74.98 ± 0.04	678.9 ± 0.4
		7.25	1	61.2	77.9	708.1
	434	4.25	1	37.0	87.1	778.8
		3.70	2	33.2 ± 0.02	88.8 ± 0.03	796.2 ± 0.5

Table 2—Determination of rate constants for reaction (6)

Temp (K)	k_6 (dm ³ mol ⁻¹ s ⁻¹) (total)	Temp (K)	k_6 (dm ³ mol ⁻¹ s ⁻¹) (total)
<i>2,2-Dimethylpropane</i>		<i>Butane</i>	
399	$(6.03 \pm 0.05) \times 10^2$	399	$(3.27 \pm 0.02) \times 10^3$
410	$(9.07 \pm 0.03) \times 10^2$	410	$(4.26 \pm 0.04) \times 10^3$
418	$(11.22 \pm 0.05) \times 10^2$	418	$(5.64 \pm 0.03) \times 10^3$
423	$(13.28 \pm 0.20) \times 10^2$	423	$(6.31 \pm 0.04) \times 10^3$
428	$(15.33 \pm 0.07) \times 10^2$	428	$(7.33 \pm 0.02) \times 10^3$
434	$(19.16 \pm 0.29) \times 10^2$	434	$(8.39 \pm 0.03) \times 10^3$
<i>2,2,3,3-Tetramethylbutane</i>		<i>2-Methylpropane</i>	
399	$(17.03 \pm 0.22) \times 10^2$	399	$(6.28 \pm 0.02) \times 10^3$
410	$(24.91 \pm 0.36) \times 10^2$	410	$(8.00 \pm 0.03) \times 10^3$
419	$(35.10 \pm 0.25) \times 10^2$	418	$(9.43 \pm 0.04) \times 10^3$
424	$(40.34 \pm 0.37) \times 10^2$	423	$(11.74 \pm 0.05) \times 10^3$
429	$(45.28 \pm 0.38) \times 10^2$	428	$(12.40 \pm 0.04) \times 10^3$
434	$(51.50 \pm 0.50) \times 10^2$	434	$(14.26 \pm 0.03) \times 10^3$
<i>Cyclohexane</i>			
400	$(8.52 \pm 0.03) \times 10^3$		
411	$(11.45 \pm 0.05) \times 10^3$		
419	14.1×10^3		
424	16.8×10^3		
429	19.6×10^3		
434	$(21.34 \pm 0.10) \times 10^3$		

increase in [alkane] increases the yield of methane while that of ethane is decreased. However, the ratio $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ remained unaffected.

In the presence of an alkane (RH), methane is formed by reaction (6). From the proposed reactions of methyl radicals, it can be seen that the rate of formation of methane, R_{CH_4} is given by relationship (8).

$$R_{\text{CH}_4} = k_4 [\cdot\text{CH}_3] [(\text{CH}_3)_2\text{CO}] + k_6 [\cdot\text{CH}_3] [\text{RH}] \quad \dots (8)$$

the rate of formation of ethane, $R_{\text{C}_2\text{H}_6}$ is given by relationship (9).

$$R_{\text{C}_2\text{H}_6} = k_3 [\cdot\text{CH}_3]^2 \quad \dots (9)$$

However, under our experimental conditions, [methane] in reaction (4) is expected to be negligible compared with that formed in reaction (6). Thus, from relationships (8) and (9) we get relationship (10).

$$k_6/k_3^{1/2} = R_{\text{CH}_4}/(R_{\text{C}_2\text{H}_6}^{1/2} [\text{RH}]) \quad \dots (10)$$

Table 3—Arrhenius parameters for abstraction reactions between methyl radicals and alkanes

Alkane	$\log(A^t)$	$E_a/\text{kJ mol}^{-1}$	Ref.	$\log(A_a)$	$E_a/\text{kJ mol}^{-1}$	Ref.	$E_a(\text{calc.})/\text{kJ mol}^{-1}$
2,2-Dimethylpropane	9.01 ± 0.13	47.59 ± 1.56	(This work)	$7.93 \pm 0.13^{(a)}$	$47.59 \pm 1.56^{(a)}$	(This work)	46.30
	8.21	41.8	(1)				
	8.14	43.5	(2)				
	8.96	49.4	(3)				
	8.73	48.1	(4)				
	8.96	48.9	(5)				
	8.96 ± 0.30	49.37 ± 2.93	(10)	7.90 ^(a)	48.12 ^(a)	(10)	
2,2,3,3-tetra-methylbutane	9.28 ± 0.14	46.17 ± 1.55	(This work)	$7.95 \pm 0.14^{(a)}$	46.17 ± 1.55	(This work)	
	8.12	39.24	(1)				
	9.16	48.12	(10)				
Cyclohexane	9.13 ± 0.10	39.94 ± 1.10	(This work)	$8.07 \pm 0.10^{(b)}$	$40.14 \pm 1.20^{(b)}$	(This work)	40.79
	8.21	34.7	(1)				
	8.16	34.7	(2)				
	9.12	41.0	(11)				
Butane	8.74 ± 0.10	39.96 ± 1.15	(This work)	$7.96 \pm 0.10^{(b)}$	$38.94 \pm 1.20^{(b)}$	(This work)	40.38
	7.92	34.8	(1)				
	8.73	41.8	(12)				
	8.27	38.1	(2)				
2-Methylpropane	8.26 ± 0.20	34.21 ± 2.39	(This work)	8.13 ± 0.20	$33.60 \pm 2.30^{(c)}$	(This work)	34.46
	7.60	31.0	(1)				
	7.95	32.3	(13)	8.02	33.0	(14)	
	8.3	36.4	(3)				

(a) Per primary C–H bond. (b) Per secondary C–H bond. (c) Per tertiary C–H bond

Table 4—Spectroscopic data used in calculation of activation energies for H-atom abstraction from alkanes by methyl radicals

	D_{298}^0 (kJ mol ⁻¹)	$r_e^{(i)}$ (Å)	ω (cm ⁻¹)	ZPE (kJ mol ⁻¹)	D_e (kJ mol ⁻¹)	β (Å ⁻¹)
CH ₃ –H	435.0 ^(a)	1.09	2967 ^(j)	17.75	453	1.785
(CH ₃) ₃ CCH ₂ –H	414.2 ^(b)	1.09	2952 ^(k)	17.66	431.9	1.819
CH ₃ –CH ₂ C(CH ₃) ₃	351.5 ^(c)	1.54	955 ^(l)	5.74	357.3	1.658
c–C ₆ H ₁₁ –H	400 ^(d)	1.10	2898 ^(m)	17.34	410.7	1.831
c–C ₆ H ₁₁ –CH ₃	347.3 ^(e)	1.54	930 ⁽ⁿ⁾	5.50	353.8	1.599
$\begin{array}{c} \text{H} \\ \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$	394.4 ^(f)	1.09	2890 ⁽ⁿ⁾	17.30	412.7	1.821
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CH}_2\text{CHCH}_3 \end{array}$	347.3 ^(g)	1.54	930 ^(o)	5.50	352.9	1.616
(CH ₃) ₃ C–H	380.7 ^(h)	1.09	2890 ^(p)	17.29	398.0	1.855
(CH ₃) ₃ C–CH ₃	334.7 ^(h)	1.54	900 ^(e)	5.38	340.1	1.593

(a) Golden D M & Benson S W, *Chem Rev*, **69** (1969) 125. (b) Kerr J A, *Chem Rev*, **66** (1966) 465. (c) By analogy from similar simple compounds. (d) Ferguson K C & Whittle E, *Trans Faraday Soc*, **67** (1971) 2618. (e) Zavitsas A A, *J Am chem Soc*, **94** (1972) 2779. (f) By analogy from isobutane. (g) By analogy from similar simple compounds. (h) Benson S W, *Thermochemical kinetics*, (Wiley, New York) 1968, pp 215. (i) Benson S W, *Thermochemical kinetics*, (Wiley, New York) 1968, pp 208. (j) Bellamy L J, *The Infrared spectra of complex molecules*, (Chapman and Hall, London) 1975, pp 13. (k) By analogy from ethane. (l) By analogy from ethane. (m) Average of symmetric and asymmetric stretching vibrations. (n) By analogy from 2-methylpropane. (o) McMurtry H L & Thornton V, *Analyt Chem*, **24** (1952) 313. (p) Fox & Martin, *Proc roy Soc*, **A175** (1940) 208, 234.

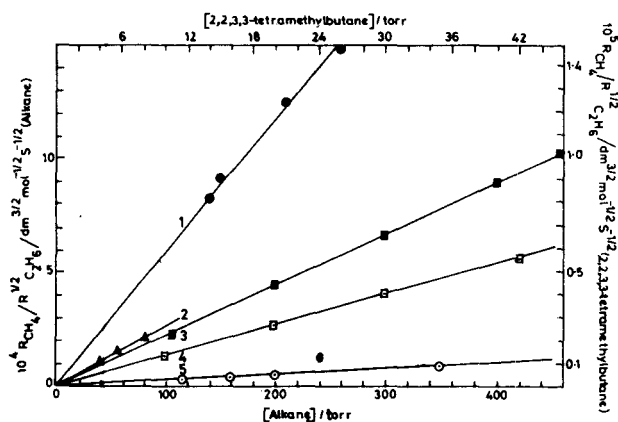


Fig. 1—Decomposition of di-*t*-butyl peroxide (pressure 5 torr) in the presence of alkanes. Reactions of methyl radicals with alkanes. [● 2,2,3,3-tetramethylbutane: reaction time, 25 min., 410 K; ▲ cyclohexane; reaction time, 10 min., 410 K; ■ 2-methylpropane: reaction time, 15 min., 418 K; ◇ butane: reaction time, 20 min., 418 K; and ○ 2,2-dimethylpropane: reaction time, 20 min., 418 K]

The ratio of rate constants $k_6/k_3^{1/2}$ was calculated using relationship (9) where, RH, is the added alkane in reaction (6). The results are shown in Table 1. Since the Arrhenius parameters of reaction (3) are well documented, the recommended value by Walker⁹ being $\log(k_3) = (10.42 \pm 0.04)$, the same was used in the present work. Using the ratio $k_6/k_3^{1/2}$ and thus $k_3^{1/2}$, values for k_6 were obtained (Table 2). Arrhenius parameters for reaction (6) are given in Table 3. The error limits were computed using a conventional least-mean square program.

Rate constants for reaction (6) per primary, secondary and tertiary C–H bonds were calculated from the data obtained assuming the additivity principle. A comparison of the present rate data with that available in literature (Table 3) shows that the Arrhenius parameters obtained presently are in good agreement with those reported by other workers^{1–5,10–14}. This observation leads to the following conclusion: (i) The source of methyl radicals and the temperature range are independent of rate of reaction, since the data reported in the literature were

obtained using different sources of methyl radicals and different temperature ranges. (ii) The slight discrepancies in the reported data and the present data are due to experimental errors.

The experimental activation energies determined in this work for alkanes have been compared with those calculated using the semiempirical method due to Zavitsas *et al.*^{15,16}. This method has been discussed in detail⁸. Application of this method requires known spectroscopic data of reactant and product molecules, i.e. infrared stretching modes. These parameters were found to affect the activation energy significantly. The spectroscopic data required for the calculation of activation energies are given in Table 4. Using these data, activation energies have been calculated for methyl radical abstraction reactions with alkanes (Table 3). The agreement between the calculated activation energies and the experimental ones is very good.

References

- 1 Trotman-Dickenson A F, Birchard J B & Steacie E W, *J chem Phys*, 19 (1951) 163.
- 2 Rebert R E & Steacie E W, *Canad J Chem*, 32 (1954) 40.
- 3 Kerr J A & Timlin D, *J chem Soc A*, (1959) 1241.
- 4 Furmisky E & Laidler K J, *Canad J Chem*, 50 (1972) 1123.
- 5 Berkley R E, Safarik I, Gunning H E & Strausz O P, *J phys Chem*, 77 (1973) 1734.
- 6 Selby K & Waddington D J, *J chem Soc, Perkin Trans II* (1979) 1251.
- 7 Al-Akeel N Y, Selby K & Waddington D J, *J chem Soc, Perkin Trans II* (1981) 1036.
- 8 Sway M I & Waddington D J, *J chem Soc, Perkin Trans II* (1984) 63.
- 9 Walker R W, *Reaction kinetics, Specialist Periodical Report*, (Chem Soc, London) Vol. 2 (1977) Chap 3.
- 10 Kerr J A & Parsonage M J, *Evaluated kinetic data on gas phase hydrogen transfer reactions of methyl radicals* (Butterworths, London and Boston) 1976.
- 11 Gordon A S & Smith S R, *J phys Chem*, 66 (1962) 521.
- 12 Dorfman L M & Gomer R, *Chem Rev*, 46 (1950) 499.
- 13 Blake A R & Kutschke K O, *Canad J Chem*, 37 (1957) 1462.
- 14 Jackson W M, McNesby J R & de Darwent B, *J phys Chem*, 37 (1962) 1610.
- 15 Zavitsas A A, *J Am chem Soc*, 94 (1972) 2779.
- 16 Zavitsas A A & Melikian A A, *J Am chem Soc*, 97 (1975) 2757.