

Arrhenius Parameters for the Reactions of Methyl Radicals with Alkenes

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Abstract. The hydrogen abstraction reactions of methyl radicals, generated by thermolysis of di-*t*-butyl peroxide, with a number of alkenes have been investigated in the temperature range 399-434 K. Arrhenius parameters for overall hydrogen abstraction based on the value of the rate constant for recombination of methyl radicals have been obtained for the following compounds: propene, 2-methylpropene, *cis*-2-butene, 2-methyl-2-butene and 2,3-dimethyl-2-butene. They are $\log (A_0/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ of 8.32 ± 0.23 , 8.46 ± 0.10 , 8.49 ± 0.20 , 8.84 ± 0.10 and 8.80 ± 0.10 , and $E_0/\text{kJ mol}^{-1}$ of 38.55 ± 2.80 , 37.00 ± 0.98 , 34.94 ± 2.33 , 35.75 ± 0.83 and 33.40 ± 1.80 , respectively. The results obtained in this study are compared with those available in the literature. The present experimental activation energies are compared with those calculated by a semiempirical method. The computed values are lower than the experimental ones. These discrepancies are due to two defects in the method which are discussed.

Introduction

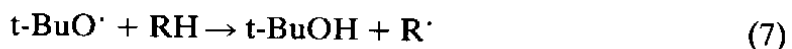
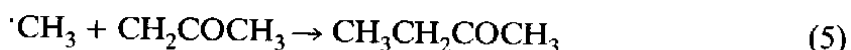
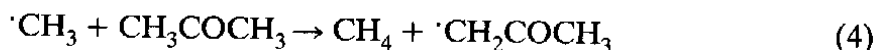
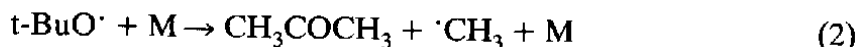
In a previous paper [1], we reported rate data for the reactions of methyl radicals with a number of alkanes. In this paper, we report rate data for the reactions of methyl radicals with alkenes. Our choice of these alkenes for study was dictated by a desire to ascertain the influence of a double bond on the reactivity of the hydrogens on carbon atoms involved in the double bond or adjacent thereto.

Materials and Methods

Mixtures of di-*t*-butyl peroxide and alkene were admitted to the required pressure in a cylindrical pyrex reaction cell (surface to volume ratio 0.80 cm^{-1}). Pressures were measured using a calibrated pressure transducer. After the required time of thermolysis, products were identified by GC-MS system. Di-*t*-butyl peroxide and alkenes were obtained commercially. Details of the apparatus and procedure have been reported previously [1].

Results and Discussion

Thermal decomposition of di-*t*-butyl peroxide (DTBP) in the presence of each studied alkene (RH) at temperatures between 339 and 434 K shows that the reactions taking place are:



In a previous paper [2], we reported Arrhenius parameters for reaction (7). This paper is devoted to reaction (6).

We have shown previously [1], that kinetic analysis of the above scheme led to a linear relationship (8)

$$R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2} = k_6/k_3^{1/2} [\text{RH}] \quad (8)$$

where R_{CH_4} and $R_{\text{C}_2\text{H}_6}$ are the rates of formation of methane and ethane, respectively. In order to verify relationship (8), a series of experiments were performed in which the initial concentration of alkene was varied at constant temperature (Fig. 1). The results show a linear dependence of $R_{\text{CH}_4}/R_{\text{C}_2\text{H}_6}^{1/2}$ on initial [RH] as predicted by relationship (8).

Another series of experiments were carried out in which the thermolysis time was varied at several temperatures for each alkene. Treating the results using relationship (8) and the value³ $\log(k_3) = (10.42 \pm 0.04) \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ independent of temperature over the range used in this work, the values of k_6 at several temperatures were obtained (Table 1). Results for all the alkenes studied are plotted in Fig. 2, and the derived Arrhenius parameters are given in Table 2. The table also gives Arrhenius parameters per reactive C-H bond. The error limits quoted for the Arrhenius parameters are the 95% confidence limits.

The Arrhenius parameters obtained in this work are compared with those determined by other workers using different techniques [4-6] (Table 2). The Arrhenius

parameters obtained in this study are in good agreement with those recalculated by Kerr and Parsonage [7]. The activation energies determined by Trotman-Dickenson *et al* [4] are constant (Table 2). It has been pointed out several times by the authors [4,8] and by Szwarc and Binks [9, p. 262] that the results of Trotman-Dickenson are suspect because the variations in rate constant appear to be caused by variations of pre-exponential factor rather than activation energy with structure. The activation energies determined by Cvetanovic and Irwin [6] do not show a simple gradation. For example, the activation energy of 2,3-dimethyl-2-butene is much higher than that of propene (Table 2).

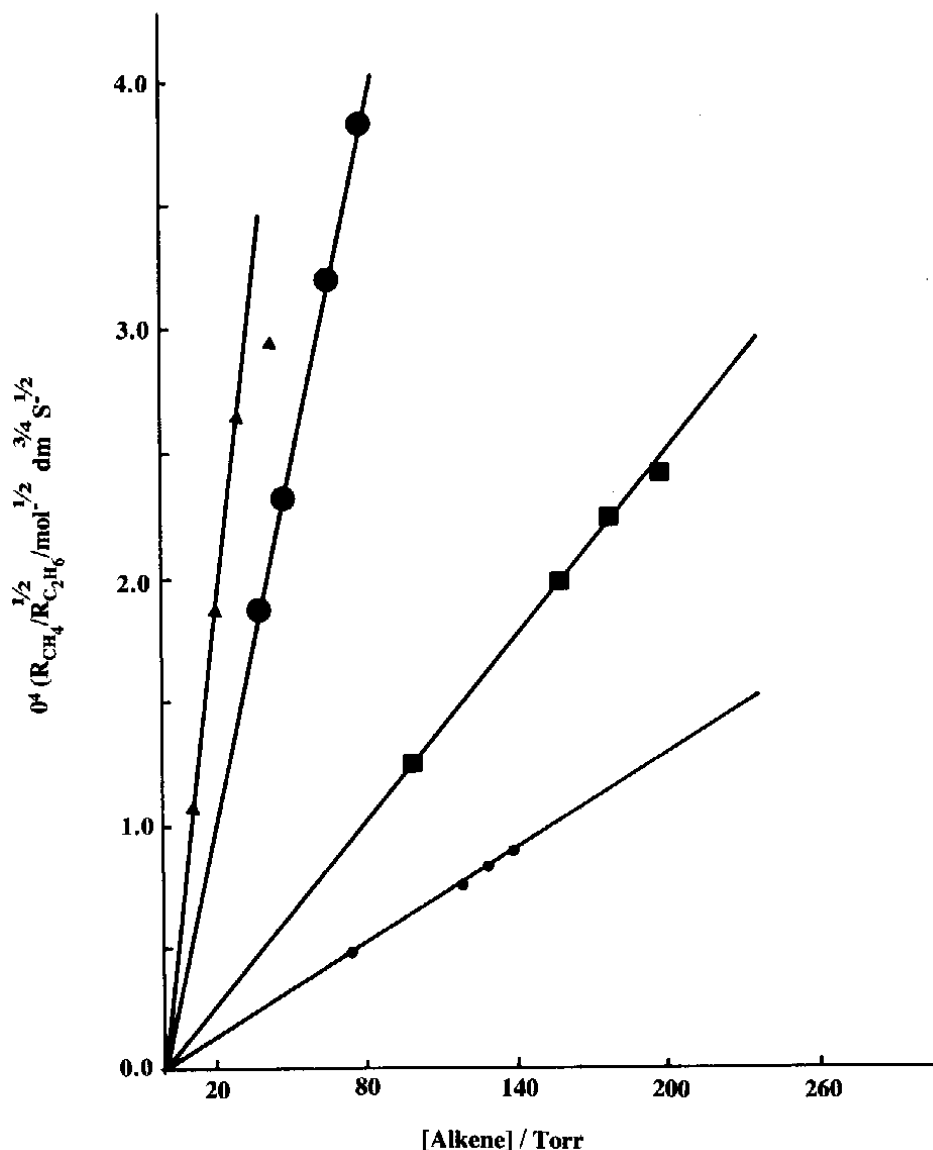


Fig. 1. Reactions of methyl radicals with alkenes at 410 K. Plots of $R_{\text{CH}_4} / R_{\text{C}_2\text{H}_6}$ against alkene concentration. ▲ 2,3-Dimethyl-2-butene; ● 2-Methyl-2-butene; ■ 2-Methylpropene; • Propene

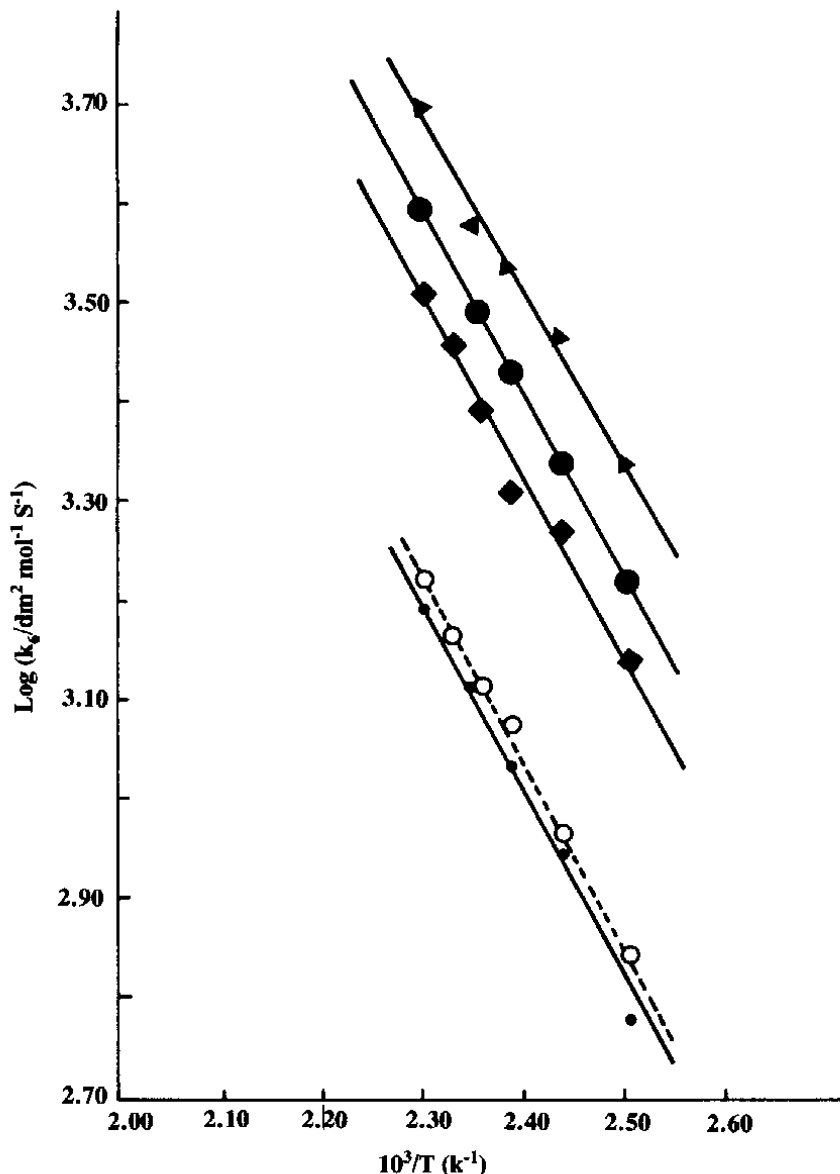


Fig. 2. Arrhenius plots for methyl radical abstraction reaction with alkenes per C-H bond. ▲ 2,3-Dimethyl-2-butene; ● 2-Methyl-2-butene; ■ cis-2-Butene; ○ 2-Methylpropene; • Propene.

The pre-exponential factors per allylic C-H bond determined in this work (Table 2) are similar, indicating that the abstraction reactions of methyl radicals with alkenes are isoentropic. This suggests that these reactions have a similar transition state structure. The present activation energies decrease on passing from propene to 2,3-dimethyl-2-butene. The difference in activation energies is approximately in agreement with the difference observed in the standard enthalpy change for the abstraction of allylic hydrogen atoms from alkenes by methyl radicals (Table 3). This difference in the activation energies may be explained in terms of the relative stabilities of the radicals resulted from reaction (6).

Table 1. Determination of rate constants for the abstraction reactions of methyl radicals with alkenes

Alkene	T/K	$10^{-3} k_p / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Total)	$10^{-3} k_p / \text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (per C-H bond)
Propene	399	1.81 ± 0.12	0.60 ± 0.07
	410	2.77 ± 0.05	0.93 ± 0.03
	419	3.28 ± 0.04	1.09 ± 0.02
	425	3.99 ± 0.03	1.33 ± 0.01
	434	4.72 ± 0.04	1.58 ± 0.02
2-Methylpropene	399	4.19 ± 0.09	0.70 ± 0.05
	410	5.30 ± 0.23	0.89 ± 0.11
	419	7.26 ± 0.47	1.21 ± 0.23
	424	7.91	1.32
	429	8.93 ± 0.07	1.49 ± 0.01
	434	10.19 ± 0.11	1.70 ± 0.02
cis-2-Butene	399	8.24 ± 0.12	1.38 ± 0.03
	410	11.33 ± 0.21	1.89 ± 0.04
	418	12.24 ± 1.03	2.04 ± 0.08
	423	14.80 ± 0.16	2.47 ± 0.04
	428	17.40 ± 0.95	2.90 ± 0.16
	434	18.23 ± 0.57	3.04 ± 0.10
2-Methyl-2-butene	399	15.00 ± 1.92	1.66 ± 0.18
	410	19.66 ± 0.56	2.19 ± 0.10
	419	24.00 ± 0.36	2.67 ± 0.04
	424	27.70 ± 0.44	3.08 ± 0.05
	434	35.40 ± 0.51	3.94 ± 0.06
2,3-Dimethyl-2-butene	399	26.10 ± 0.46	2.18 ± 0.04
	410	35.20 ± 1.22	2.92 ± 0.10
	419	41.50 ± 1.10	3.46 ± 0.09
	424	46.01 ± 1.06	3.84 ± 0.09
	434	60.30 ± 0.65	5.03 ± 0.06

Generally, the abstraction reactions of methyl radicals with alkenes are faster than those of alkanes [1]. This mirrors the enthalpy differences for the reactions of methyl radicals with the two classes of hydrocarbons (Table 3), the abstraction reactions of methyl radicals with alkenes being more exothermic than those of alkanes.

The present experimental activation energies for alkenes are compared with those calculated using the semi-empirical method due to Zavitsas *et al.* [10,11]. The

Table 2. Arrhenius parameters for the abstraction reactions between methyl radicals and alkenes

Alkene	$\text{Log}(A_0/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$	$E_0/\text{kJ mol}^{-1}$	(Ref.)	$\text{Log}(A_0/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})^*$	$E_0^*/\text{kJ mol}^{-1}$	No. of active C-H bonds
Propene	8.32 ± 0.23	38.55 ± 2.80	(this work)	7.82 ± 0.20	38.55 ± 2.80	3
	7.60	32.22	(4)			
	8.14	36.80	(7)			
	8.08	34.30	(5)			
	7.83	30.10	(6)			
	7.95	35.60	(7)			
2-Methylpropene	8.46 ± 0.10	37.00 ± 0.98	(this work)	7.68 ± 0.10	37.00 ± 0.98	6
	7.77	30.54	(4)			
	8.04	33.05	(6)			
	8.68	38.60	(7)			
cis-2-Butene	8.49 ± 0.20	34.94 ± 2.33	(this work)	7.71 ± 0.20	34.94 ± 2.33	6
	8.18	32.21	(4)			
	8.11	31.80	(6)			
	7.26	30.54	(9)			
	8.58	37.20	(7)			
	8.75	37.20	(7)			
2-Methyl-2-butene	8.84 ± 0.10	35.75 ± 0.83	(this work)	7.89 ± 0.10	35.75 ± 0.83	9
	7.80	28.03	(6)			
	8.42	33.50	(7)			
	8.69 ± 0.40	35.60 ± 4.18	(7)			
2,3-Dimethyl-2-butene	8.80 ± 0.10	33.40 ± 1.80	(this work)	7.72 ± 0.10	33.40 ± 1.70	12
	8.40	32.64	(4)			
	9.06	38.10	(7)			
	9.05	37.24	(6)			
	8.89 ± 0.40	36.40 ± 4.20	(7)			

* Per C-H bond

Table 3. Calculations of enthalpy difference for the abstraction reactions of methyl radicals with alkenes and alkanes

Alkene ^(a)	$\Delta H^\circ/\text{kJ mol}^{-1}$	Alkane ^(b)	$\Delta H^\circ/\text{kJ mol}^{-1}$
Propene	- 78.2	2,2-Dimethylpropane	- 21.3
2-Methylpropene	- 76.1	2,2,3,3-Tetramethylbutane	- 28.0
cis-2-Butene	- 83.3	Cyclohexane	- 42.0
2-Methyl-2-butene	- 82.4	Butane	- 38.1
2,3-Dimethyl-2-butene	- 85.8	2-Methylpropane	- 54.8

(a) ΔH° for allylic C-H bond(b) ΔH° for primary, secondary and tertiary C-H bond

details of this method has been reported elsewhere [2]. The spectroscopic data required for the calculation of activation energies are shown in Table 4. The calculated activation energies are listed in Table 5. The calculated values are much lower than the experimental ones. This method was successful when applied to the reactions of t-butoxy radicals with alkanes and alkenes [2] as well as reactions of methyl radicals with alkanes [1]. The less success of this method in the present work may be explained as follows. If the C-C frequency in all complexes is set at 790 cm^{-1} instead of 850 cm^{-1} and the other spectroscopic data are kept constant as in Table 5, a good fit can be obtained between the calculated and experimental activation energies (Table 5, Column 4). This discussion point to two defects in the method. The first is that more accurate spectroscopic data are required for complex molecules, particularly for their vibrational frequencies. The second is that with reactions which are more exothermic or endothermic than *ca.* $\pm 63\text{ kJ mol}^{-1}$, Zavitsas himself has shown [10] that considerable errors occur for the calculated activation energies and this has been confirmed in this study. However, in the present work we consider the rate data for the experimental activation energies are well enough documented to allow for the method to be checked fairly.

Table 4. Spectroscopic data used in calculation of activation energies for hydrogen atom abstraction from alkenes by methyl radicals

	D_{298}°	(ed) r_e	ω	ZPE	D_e	β
CH ₃ -H	435.0 ^(a)	1.09	2967 ^(e)	17.75	453.0	1.785
CH ₂ CHCH ₂ -H	369.9 ^(a)	1.09	2895 ^(f)	17.32	387.2	1.926
CH ₃ -CH ₂ CHCH ₂	311.7 ^(b)	1.55	850 ^(g)	5.09	316.8	0.8029
H-CH ₂ C(CH ₃):CH ₂	364.5 ^(c)	1.09	3085 ^(h)	17.59	377.3	1.983
CH ₃ -CH ₂ C(CH ₃):CH ₂	311.7 ^(b)	1.55	850 ^(g)	5.09	316.8	0.8029
H-CH ₂ CH:CHCH ₃	360.0 ^(c)	1.09	3010 ^(h)	17.59	377.4	1.9080
CH ₃ -CH ₂ CH:CHCH ₃	311.7 ^(b)	1.55	850 ^(g)	5.09	316.8	1.5590
H-CH ₂ C(H):C(CH ₃) ₂	355.5 ^(c)	1.09	3020 ^(h)	17.86	373.4	2.0260
CH ₃ -CH ₂ C(H):C(CH ₃) ₂	311.7 ^(b)	1.55	850 ^(g)	5.09	316.8	0.8029
H-CH ₂ C(CH ₃):C(CH ₃) ₂	349.5 ^(c)	1.09	3030 ^(h)	18.13	367.6	2.0737
CH ₃ -CH ₂ C(CH ₃):C(CH ₃) ₂	311.7 ^(b)	1.55	850 ^(g)	5.09	316.8	0.8029

Units: D_{298}° , D_e , and ZPE in kJ mol⁻¹; ω in cm⁻¹, β in Å⁻¹; r_e in Å

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Table 5. Calculated and experimental activation energies for hydrogen atom abstraction by methyl radicals from alkenes

Alkene	Exptl. E_a /kJ mol ⁻¹	Calcd. E_a^* /kJ mol ⁻¹ ($\omega = 850$ cm ⁻¹)	Calcd. E_a^* /kJ mol ⁻¹ ($\omega = 780$ cm ⁻¹)
Propene	38.50 ± 2.80	30.01	38.36
2-Methylpropene	37.00 ± 0.98	28.20	36.71
cis-2-Butene	34.94 ± 2.33	27.18	35.37
2-Methyl-2-butene	35.75 ± 0.88	25.96	34.05
2,3-Dimethyl-2-butene	33.40 ± 1.79	24.33	32.33

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ثوابت أرهينيوس لتفاعلات جذور الميثيل مع الألكينات

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ملخص البحث. لقد تم دراسة تفاعلات استخلاص جذور الميثيل، التي تم الحصول عليها بالتفكك الحراري لمركب ثنائي -٢- بيوتيل بيروكسيد، مع عدد من الألكينات بين درجات الحرارة ٣٩٩ - ٤٣٤ (كالوري). وقد تم تعيين قيم أرهينيوس الإجمالية لاستخلاص الهيدروجين بالنسبة لقيمة ثابت سرعة تفاعل تجميع جذور الميثيل (تفاعل مرجع) لكل من الألكينات الآتية: برويين، ٢- ميثيل برويين، سز-٢- بيوتين، ٢- ميثل -٢- بيوتين و٢، ٣- ثنائي ميثل -٢- بيوتين. وقيم أرهينيوس على التسوالي: $0,10 \pm 8,84$ ، $0,20 \pm 8,49$ ، $0,10 \pm 8,46$ ، $0,23 \pm 8,32$ $\text{Log}(A_0/\text{dm}^3 \text{mol}^{-1} \text{S}^{-1})$ و $0,10 \pm 8,80$ وطاقة التنشيط ($2,80 \pm 38,55 \text{ E}_0/\text{KJ mol}^{-1}$)، $0,98 \pm 37,00$ ، $34,94$ ، $2,33 \pm 35,75$ ، $0,83 \pm 33,40$ و $1,80 \pm 33,40$. قد تم مقارنة النتائج التي تم الحصول عليها في هذه الدراسة بالنتائج المتوفرة في المجالات العلمية. كما تم مقارنة طاقة التنشيط التي تم الحصول عليها في هذه الدراسة بالقيم المحسوبة نظريا باستخدام طريقة (Semi-empirical) وقد بنيت هذه الدراسة أن قيم طاقة التنشيط المحسوبة أقل من القيم العلمية وأن هذا الاختلاف ما بين القيم النظرية والتجريبية يعود إلى عيبين في الطريقة وقد تم مناقشتها.