Electron Spin Resonance Measurements of Propagation and Termination Rate Constants during the Liquid-phase Oxidation of Hydrocarbons

By **John E. Bennett,* John A. Eyre,** and **Raymond Summers,** Shell Research Ltd., Thornton Research Centre, P.O. Box 1, Chester CH1 3SH

The application of e.s.r. spectroscopy has enabled alkylperoxyl radicals (the chain carriers) to be detected in several liquid hydrocarbons undergoing autoxidation at high temperatures. Quantitative measurements have been made for two hydrocarbons, decalin and 2,6,10,14-tetramethylpentadecane, and from the data obtained the propagation rate constants, k_p, have been calculated. The termination rate constants, $2k_t$, have also been measured by e.s.r., the results being used to calculate the rate constants for initiation by the decomposition of hydroperoxide in decalin over a limited temperature range.

THE autoxidation of liquid hydrocarbons at relatively low temperatures (<373 K) has been extensively studied and methods are available for the determination of the rate constants of the propagation and termination reactions. Because of the chain character of the oxidation most of the methods rely on the creation of a non-steady-state either by photolysis [1,2] or by the addition of inhibitors.[3] Another method, which has been applied at higher temperatures, involves the determination of the steady-state concentration of peroxyl radicals by adding an excess of a very reactive inhibitor, which in effect ' titrates ' the radicals; the excess of inhibitor is determined from the length of the resulting induction period.[4]

In this paper we describe the application of e.s.r. spectroscopy to the observation of the peroxyl radicals and the measurement of their concentration during the oxidation of several hydrocarbons at elevated temperatures (350—420 K). Both steady-state and non-steady-state methods have been used and the measurements have permitted the propagation and termination rate constants to be determined directly.

EXPERIMENTAL

E.s.r. Measurements.—The experimental measurements involved the autoxidation or initiated oxidation of a hydrocarbon *in situ* in the sample cavity of the e.s.r. spectrometer.

A major experimental problem was to maintain the concentration of oxygen in the hydrocarbon whilst it was oxidized. When a standard e.s.r. sample tube (3 mm i.d.)

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[1] J. A. Howard and K. U. Ingold, *Canad. J. Chem.*, 1965, **43**, 2729.

[2] D. G. F. Hendry, *J. Amer. Chem. Soc.*, 1967, **89**, 5433.

[3] H. Berger, A. M. W. Blaauw, M. M. Al, and P. Smael, *Adv. Chem. Series*, 1968, **75**, 346.

[4] H. Berger, Chem. Soc. Annual Meeting, Manchester, 1972, Abstract 2.4a.

was used a sufficient gas flow could not be obtained without lifting the whole column of liquid up the tube, thus making the spectrometer inoperable. To overcome this problem a Varian wide-access cavity was used as it could accept sample tubes up to 25 mm external diameter. For the present experiments, however, this diameter was reduced, initially to 10 mm, so that the sample tube could be surrounded by a second, concentric tube through which hot air was blown to heat the sample. Further, to keep the cavity cool, a stream of cold nitrogen was blown in through a third, co-axial tube. The sample was oxygenated by blowing oxygen or air through a sinter in the central tube.

A further experimental problem was that the Q factor of the sample cavity decreased rapidly as the polar oxidation products (mainly hydroperoxide) accumulated in the sample during oxidation. Consequently, after a short time, the spectrometer became inoperable. To minimize this effect, the diameter of the sample tube was reduced to 5 mm, a compromise being made between the two conflicting requirements, *viz.* the ease of oxygenation of the sample and the degradation of the Q factor. The diameter of the sample tube was increased immediately above the active part of the cavity to act as a bubble breaker.

Radical concentrations were measured by calibration with a standard solution of α,α'-diphenyl-β-picrylhydrazyl (DPPH) in the sample tube at the end of the experiment. Nitrogen was bubbled through the solution at a flow rate similar to that used in the oxidation so that the error owing to the gas bubbles occupying part of the sample volume was minimized. The first derivative e.s.r. spectra were integrated electronically and the areas of the resulting absorption spectra were compared to obtain the absolute concentration of peroxyl radicals, due correction being made for the difference in temperature. A carbon marker was included in the sample tube so that the change in sensitivity of the spectrometer owing to the decrease in the Q factor could be monitored and the necessary correction made to the calibration throughout the oxidation.

Propagation Rate Constants.—The propagation rate constant, k_p, was determined by measuring the concentration of peroxyl radicals and the overall rate of reaction during the autoxidation of the hydrocarbon.

Oxygen was initially removed from the hydrocarbon in the sample tube by bubbling nitrogen through the sinter. The sample was heated to the required temperature and the oxidation was started by replacing the nitrogen flow with oxygen. The temperature of the sample was monitored throughout the experiment by means of a thermocouple positioned in the liquid just above the active region of the sample cavity. The temperatures were held constant to ±1 K for the duration of the experiment.

The overall rate of reaction was determined by measuring the hydroperoxide concentration during the oxidation. Samples of the hydrocarbon were withdrawn from the cell at intervals during the experiment and the hydroperoxide was determined iodometrically. The iodine, which was liberated after treatment with a solution of potassium iodide in propan-2-ol–acetic acid solution at 353 K was titrated with sodium thiosulphate.

Termination Rate Constants.—Two methods were used for the determination of the termination rate constant, $2k_t$.

Thermal initiation. In this method, the hydrocarbon was heated to the required temperature and oxygen was bubbled through the sample. Then, a high concentration (10^{-1}M) of a free-radical initiator, azobisisobutyronitrile (AIBN) or dibenzoyl peroxide (DBP), was injected into the sample and the steady-state concentration of peroxyl radicals was measured. Although the rates of decomposition of AIBN and DBP are accurately known, the actual efficiency of chain initiation in a given system by either initiator may be less than unity because of the cage effect.

Photolytic initiation. This technique has been described previously [5,6] for tertiary and secondary alkylperoxyl radicals. In the present work, the temperature range over which the technique was applied was extended to 390 K. In most of these experiments di-t-butyl peroxide (DTBP) was used as the photolytic initiator but at the higher temperatures (>370 K) dicumyl peroxide (DCP) was used. The rate of initiation by DCP was *ca.* 50% higher than that for DTBP. The rate constants for the decay of $RO_2\cdot$ radicals were the same (within experimental error) at a given temperature with either initiator.

Materials.—The pure hydrocarbons (decalin, 2,6,10,14-tetramethylpentadecane, 2-methylhexadecane, and hexadecane) were obtained from commercial sources and were percolated through an activated silica gel column prior to use. This treatment removed any trace polar materials, particularly any products formed by oxidation during storage (*e.g.* hydroperoxides, alcohols, or ketones). DTBP was distilled and percolated through a silica gel column prior to use; AIBN, DCP and DBP were used without purification.

RESULTS AND DISCUSSION

The generally accepted mechanism for the liquid-phase oxidation of hydrocarbons comprises reactions (1)—(5). Reaction (1) is slow, so that at elevated temperatures reaction (4) rapidly becomes the major source of chain initiation. Under these conditions equations (6) and (7) obtain. The overall rate of oxidation is given by (8). Relationship (8) is valid provided

$$RH + O_2 \longrightarrow \text{Radicals} \longrightarrow R\cdot \qquad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (2)$$

$$RO_2\cdot + RH \xrightarrow{k_p} RO_2H + R\cdot \qquad (3)$$

$$RO_2H \xrightarrow{2k_i} RO\cdot + OH\cdot \longrightarrow 2R\cdot \qquad (4)$$

$$RO_2\cdot + RO_2\cdot \xrightarrow{2k_t} \text{Products} \qquad (5)$$

$$2k_i[RO_2H] = 2k_t[RO_2\cdot]^2 \qquad (6)$$

$$\therefore [RO_2\cdot] = (k_i/k_t)^{\frac{1}{2}}[RO_2H]^{\frac{1}{2}} \qquad (7)$$

$$-d[RH]/dt = -d[O_2]/dt = d[RO_2H]/dt = k_p[RO_2\cdot][RH] \qquad (8)$$

that the kinetic chain length is high (this assumption is discussed later and is shown to hold for the present experiments). Hence, from equations (7) and (8), (9) is

$$d[RO_2H]/dt = k_p[RH](k_i/k_t)^{\frac{1}{2}}[RO_2H]^{\frac{1}{2}} \qquad (9)$$

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[5] J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, 1970, **66**, 386.

[6] J. A. Howard and J. E. Bennett, *Canad. J. Chem.*, 1972, **50**, 2374.

derived which, on integration yields (10) and this, on

$$2[RO_2H]^{\frac{1}{2}} = k_p[RH](k_i/k_t)^{\frac{1}{2}}t \qquad (10)$$

substituting for $(k_i/k_t)^{\frac{1}{2}}$ from equation (7), gives (11).

$$2[RO_2H] = k_p[RH][RO_2\cdot]t \qquad (11)$$

The propagation rate constant, k_p, can be determined directly from this relationship if $[RO_2\cdot]$ and $[RO_2H]$ at a given time are known.

E.s.r. Measurements.—Our initial experiments showed that the e.s.r. spectrum of a free-radical species could be detected during the autoxidation of a hydrocarbon which contained a tertiary C–H bond (2-methylhexadecane, 2,6,10,14-tetramethylpentadecane, or decalin). A weak signal was also observed in hexadecane which possesses only primary and secondary C–H bonds. All the spectra were similar, that for decalin being shown in Figure 1.

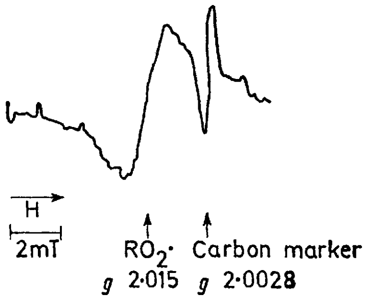

FIGURE 1 First derivative e.s.r. spectrum observed during the autoxidation of decalin at 424 K

The isotropic g factor (2·015) of the spectrum was typical of that generally attributed to peroxyl radicals. The signal disappeared when the oxygen flow was interrupted, showing that oxygen was involved in the formation of the free radicals.

Propagation Rate Constants.—Quantitative measurements of the concentration of $RO_2\cdot$ radicals were made during the autoxidation of decalin at 416 and 424 K, and of 2,6,10,14-tetramethylpentadecane (TMP) at 413 K. During the early stages of the autoxidation, the concentration of $RO_2\cdot$ radicals increased with time, but then reached a steady value, indicating that the oxidation was proceeding at a constant rate (probably determined by the rate of diffusion of oxygen into the hydrocarbon). As the concentration of radicals increased the line width of the signal decreased (from a maximum of *ca.* 2·2 to a minimum of 1·2 mT). This decrease is typical of the line narrowing which is observed for peroxyl radicals when the concentration of oxygen in solution is reduced.[6] Thus, this observation supports the above suggestion that the rate of diffusion of oxygen into the solution became the rate-limiting process in the later stages of the autoxidation.

The concentrations of hydroperoxide and $RO_2\cdot$ radicals were measured at intervals during the early part of the autoxidation before the rate was limited by the rate of diffusion of oxygen into solution. The results for decalin and TMP are plotted according to equation (11) in Figure 2 and the values of k_p derived from the plots are given in Table 1.

TABLE 1

Propagation rate constants, k_p

Hydrocarbon	T/K	[RH]/ mol l^{-1}	k_p[RH]/ s^{-1}	k_p/ l mol^{-1} s^{-1}	Ref.
Decalin	424	5·81 *	150	26	This work
Decalin	416	5·85 *	126	22	This work
Decalin	403	5·70	80	14	4
TMP	413	2·60 *	100	38	This work

* Determined experimentally during the course of this work.

To our knowledge, there has been only one other determination of k_p at a comparable temperature. Berger *et al.*[4] using the peroxyl radical ' titration ' technique determined k_p for decalin at 403 K (Table 1). The agreement between the two methods is good.

Termination Rate Constants.—Thermal initiation. From the measurement of concentration of $RO_2\cdot$ it is possible to calculate $2k_t$ from equation (12) provided that the rate of chain initiation, R_i, is also known.

$$2k_t = R_i/[RO_2\cdot]^2 \qquad (12)$$

At the high temperature of our autoxidation experiments, the rate of initiation increased throughout the oxidation as the concentration of hydroperoxide increased. Thus, in order to measure $2k_t$, it was necessary to reduce the temperature to a level at which the decomposition of the hydroperoxide was negligible. This technique has been applied previously to measure $2k_t$ for cumene [7] and 1,1-diphenylethane.[8]

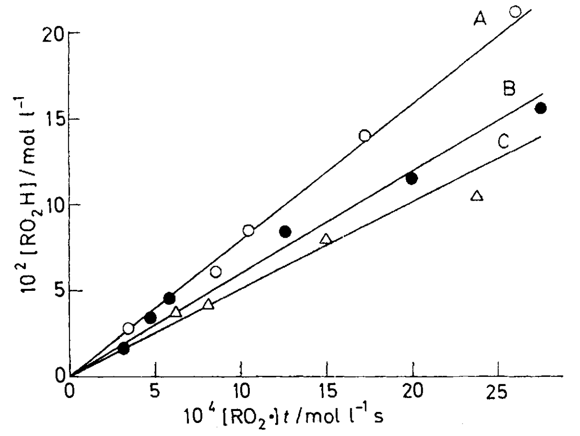

FIGURE 2 Plots of $[RO_2H]$ and $[RO_2\cdot]t$ for autoxidation of A, decalin at 424 K; B, decalin at 416 K; and C, TMP at 413 K

The concentration of $RO_2\cdot$ radicals was measured in TMP and hexadecane at 361 K in the presence of 10^{-1}M-AIBN. DBP was also used as the initiator but although

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[7] Ya. S. Lebedev, V. F. Tsepalov, and V. Ya. Shlyapintokh, *Doklady Akad. Nauk. S.S.S.R.*, 1961, **139**, 1409.

[8] A. F. Guk, V. F. Tsepalov, V. F. Shuvalov, and V. Ya. Shlyapintokh, *Izvest. Akad. Nauk. S.S.S.R.*, 1968, **10**, 2250.

giving a higher yield of radicals than did AIBN at the start of the experiment, the signal decayed rapidly (probably owing to induced decomposition of the initiator). The values of $2k_t$ obtained by this method are given in Table 2.

TABLE 2

Termination rate constants, $2k$, at 361 K

Hydrocarbon	$2k_t$/l mol^{-1} s^{-1}	Method
TMP	$3{\cdot}0 \times 10^6$	Thermal initiation
Hexadecane	$4{\cdot}8 \times 10^7$	Thermal initiation
Hexadecane	$2{\cdot}2 \times 10^7$	Photolytic initiation
Decalin	$1{\cdot}6 \times 10^6$	Photolytic initiation

The rate of the chain initiation, R_i, by AIBN was calculated using the value for AIBN decomposition measured by a DPPH scavenging technique.[9] This value is *ca.* 25% lower than that measured by nitrogen evolution[10] because some of the radicals recombine in the solvent cage, and thus do not initiate oxidation. The main source of error lies in the uncertainty about the efficiency of chain initiation by the initiator.

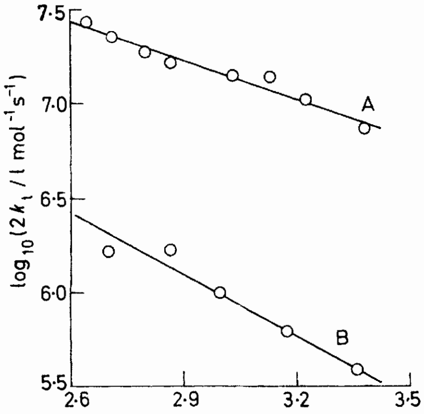

FIGURE 3 Arrhenius plots of $2k_t$ for A, hexadecane and B decalin

Photolytic initiation. A more reliable method of measuring the termination rate constants is the photolytic technique, used previously to measure $2k_t$ for tertiary[5] and secondary[6] alkylperoxyl radicals at low temperatures. It has been possible to extend the temperature range up to 378 K and values of $2k_t$ were measured for decalin and hexadecane in the range 293—378 K. From the Arrhenius plots (Figure 3) the rate constants are given by: $2k_t = 1{\cdot}9 \times 10^9 \exp(-20{\cdot}9 \times 10^3/RT)$ l mol^{-1} s^{-1} for decalin and $2k_t = 3{\cdot}6 \times 10^9 \exp(-12{\cdot}5 \times 10^3/RT)$ l mol^{-1} s^{-1} for hexadecane.

It is of interest that the activation energy of the termination reaction in hexadecane is lower than that in decalin. In the case of hexadecane only secondary peroxyl radicals take part in the termination reaction, whereas in decalin, both secondary and tertiary radicals are involved. The activation energy for decalin, in fact, lies between the values expected for secondary–secondary or tertiary–tertiary radical recombination, the latter value being 33 ± 5 kJ mol^{-1}.

The values of $2k_t$ at 361 K determined by the two methods are in reasonable agreement (Table 2). The results obtained by the photolytic method are the more accurate and the agreement is an indication that the DPPH scavenger method gives a reasonable measure of R_i for the present system. Furthermore, the photolytic method can be applied over a much wider temperature range than that for the thermal method.

Initiation Rate Constants.—Using equation (6) the rate constant, k_i, for the initiation reaction (4) can be calculated from the experimental values of concentrations of $RO_2{\cdot}$ radicals and the termination rate constant, $2k_t$. (The termination rate constants were obtained by a short extrapolation of the Arrhenius plots to the relevant temperatures.) For the present results on decalin the values of k_i are calculated as $1{\cdot}5 \times 10^{-5}$ s^{-1} at 416 K and $3{\cdot}6 \times 10^{-5}$ s^{-1} at 424 K. From these limited data, the rate constant for the decomposition of decalin hydroperoxide is $k_d = 4{\cdot}4 \times 10^{13} \exp(-162 \times 10^3/RT)$ s^{-1}.

This experimental value of the activation energy is close to the O–O bond dissociation energies in alkyl hydroperoxides, which are calculated[11] to lie in the range 170—185 kJ mol^{-1}.

Chain Length.—The measurement of k_p by the method described above is dependent on the assumption that the kinetic chain length (ν) was relatively high during the autoxidation. The value of ν for decalin can be calculated from equation (13) using our experimental values for k_p and $2k_t$. These calculations show that the chain

$$\begin{aligned}\nu &= (\text{Rate of propagation})/(\text{rate of termination}) \\ &= k_p[\text{RH}]/2k_t[\text{RO}_2{\cdot}] \qquad (13)\end{aligned}$$

length drops during the autoxidation from 75 at the beginning to 15 at the end of the period during which measurements were made. The error involved in the calculation of k_p is inversely proportional to ν and is <5% even at the end of the period when $\nu = 15$. The corresponding error in the calculated value of ν is also <5% [equation (13)] and thus the assumption made in deriving equation (8) is fully justified.

[4/016 *Received, 4th January,* 1974]

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[9] C. E. H. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216.

[10] F. M. Lewis and M. S. Matheson, *J. Amer. Chem. Soc.*, 1949, **71**, 747.

[11] S. W. Benson, *J. Chem. Phys.*, 1964, **40**, 1007.