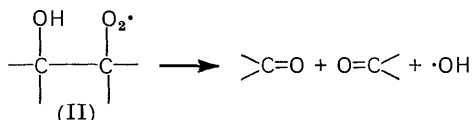


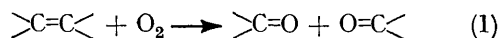
Gas-phase Oxidation of Alkenes: Decomposition of Hydroxy-substituted Peroxyl Radicals

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Carbonyl compounds are the main products of the low-temperature gas-phase oxidation of alkenes. It is suggested that they are formed by consecutive addition of a hydroxyl radical and an oxygen molecule to the alkene, the hydroxy-substituted peroxy radical subsequently decomposing to yield two molecules of carbonyl compounds and the chain carrier. A model system has been investigated, the fuel chosen being 2,3-dimethylbutan-2-ol which gives acetone as the major product at 578 K. In reactions with [^{18}O]-2,3-dimethylbutan-2-ol and oxygen, the ketone is enriched by *ca.* 50%, and this result is consistent with the decomposition of the radical (II).

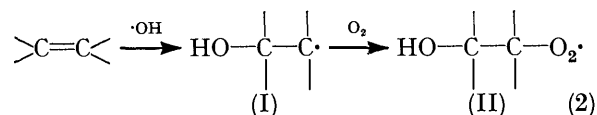


CARBONYL compounds are the principal products of the low-temperature oxidation of aliphatic alkenes in the gas phase.¹⁻⁵ For example, acetaldehyde, acetone and acetaldehyde, acetone, 2-methylpropanal and formaldehyde, and acetone and formaldehyde are the main products from the oxidation of *trans*-but-2-ene,¹ 2-methylbut-2-ene,^{2,3} 3-methylbut-1-ene,⁴ and 2-methylpropene,⁵ respectively. Where different carbonyl compounds are formed from the alkene, it is apparent that one molecule of alkene decomposes to yield two molecules of carbonyl product,²⁻⁴ and the overall reaction may be expressed as (1).



The formation of the carbonyl compounds *via* a dioxetan² is ruled out as the reaction is highly endothermic ($\Delta H^0 = 290 \text{ kJ mol}^{-1}$),⁶ involving a spin-forbidden transition, as oxygen is in its ground state. Knox, on the other hand, suggested that the alkene first undergoes consecutive addition reactions with a hydroxyl or a hydroperoxyl radical and oxygen.⁷ We have suggested that it is the hydroxyl radical that is the

more important species in the low temperature oxidation [reaction (2)].⁸ Both these steps are exothermic (we



calculate, using group additivity data,⁹ by *ca.* -140 kJ mol^{-1} and -110 kJ mol^{-1}). Although Knox suggests that radical (II) then reacts with a hydroperoxyl radical to form a hydroperoxide which in turn decomposes to yield carbonyl compounds and a chain carrier, two further fates of radical (II) may, however, be postulated.

Radical (II) may abstract a hydrogen atom from the parent fuel, forming a hydroperoxide which subsequently yields carbonyl compounds, or it may decompose to form carbonyl compounds and the chain carrier directly. In order to distinguish between the two schemes, we have studied a system which will give radical (II) in high yield, and have chosen 2,3-dimethylbutan-2-ol as the model fuel [reaction (3)]. By using [^{18}O]-2,3-

¹ D. J. M. Ray and D. J. Waddington, *J. Amer. Chem. Soc.*, 1968, **90**, 7176; Fourteenth Symposium (International) on Combustion, The Combustion Institute, in the press.

² C. F. Cullis, A. Fish, and D. W. Turner, *Proc. Roy. Soc.*, 1961, *A*, **262**, 318; 1962, *A*, **267**, 433.

³ D. J. M. Ray, Thesis, University of York, 1970.

⁴ A. Redfearn, unpublished results.

⁵ A. P. Zeelenberg and A. F. Bickel, *J. Chem. Soc.*, 1961, 4014.

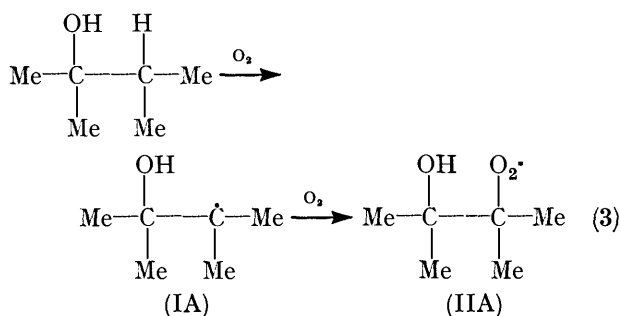
⁶ D. R. Kearns, *J. Amer. Chem. Soc.*, 1969, **91**, 6554.

⁷ J. H. Knox, *Combustion and Flame*, 1965, **9**, 297.

⁸ D. J. M. Ray and D. J. Waddington, *Combustion and Flame*, in the press.

⁹ S. W. Benson, 'Thermochemical Kinetics,' Wiley, New York, 1968, p. 150.

dimethylbutan-2-ol, the reactions of radical (IIA) may be elucidated.



EXPERIMENTAL

(a) *Apparatus*.—A static vacuum apparatus (Pyrex) was used, with a cylindrical reaction vessel (14.5 cm long; 5.1

TABLE 1

Mass spectrum of [¹⁸O]-2,3-dimethylbutan-2-ol

The sample was introduced *via* the cold inlet system (70 eV electron energy; 100 μA trap current; 8 kV accelerating potential; source temperature 378 K)

<i>m/e</i>	15	27	29	31	39	41
Relative intensity (%)	7.9	18.5	6.6	20.3	19.6	39.2
<i>m/e</i>	43	45	59	69	87	
Relative intensity (%)	33.0	16.1	100.0	21.8	28.6	

cm i.d.; surface: volume ratio, 1:1.1 cm⁻¹) suspended in an electrical furnace. A Wilson seal allowed a tap in the

using Porapak Q (100—120 mesh; column 1.5 m long, 4 mm i.d.; 473 K; nitrogen as carrier gas). Formaldehyde was determined spectrophotometrically (Unicam SP 500) using chromatropic acid.¹⁰

(c) *Reagents*.—2,3-Dimethylbutan-2-ol (Koch-Light) was 98.1% pure, as determined by g.l.c. [¹⁸O]-2,3-Dimethylbutan-2-ol was prepared by first brominating 2-methylbutan-2-ol to 2,3-dibromo-2-methylbutane,¹¹ which was subsequently hydrolysed with [¹⁸O]water to [¹⁸O]-3-methylbutan-2-one. The ketone on reaction with methyl magnesium iodide,¹² followed by hydrolysis, gave [¹⁸O]-2,3-dimethylbutan-2-ol. The principal impurities were 2-methylbut-2-ene, 2,3-dimethylbut-1-ene, and 2,3-dimethylbut-2-ene, the total hydrocarbon impurities being <2%. Mass spectral analysis (Table 1) of the alcohol is in good agreement with published data.¹³

[¹⁸O]Acetone was prepared by shaking acetone with [¹⁸O]water and a trace of 0.1M-hydrochloric acid. The organic layer separated on addition of potassium carbonate and was dried over the anhydrous salt.

RESULTS AND DISCUSSION

The main products from a fuel-rich mixture of 2,3-dimethylbutan-2-ol and oxygen at 578 K are given in Table 2; they are acetone, carbon monoxide, carbon dioxide, and formaldehyde. These and small amounts of hydrocarbons were the only products that appear to be formed. A carbon balance was not attempted.

The mass spectral analysis of the ¹⁸O-enriched alcohol and ketone involved the repeated scanning of the *m/e*

TABLE 2

Oxidation of 2,3-dimethylbutan-2-ol: analysis of reactants and products at 578 K

Alcohol, 6.7 kN m⁻²; oxygen, 6.7 kN m⁻²

Reaction time (s)	Pressure change (kN m ⁻²)	Acetone (kN m ⁻²)	Carbon dioxide (kN m ⁻²)	Carbon monoxide (kN m ⁻²)	2,3-Dimethylbut-1-ene (kN m ⁻²)	Formaldehyde (kN m ⁻²)	Methane (kN m ⁻²)	Oxygen (kN m ⁻²)	Propene (kN m ⁻²)
60	3.3	3.2	0.1	0.4	0.2	0.1	<0.01	4.4	0.2
120	4.6	4.1	0.5	1.2	0.2	0.3	0.04	0.3	0.3
300	4.9	4.0	0.4	1.1	0.3	0.3	0.07	0.5	0.3
480	4.9	<i>a</i>	0.9	2.3	<i>a</i>	0.1	0.1	<i>a</i>	<i>a</i>
600	4.9	3.7	<i>a</i>	3.3	0.3	0.1	0.2	0.5	0.2
720	4.7	<i>a</i>	1.4	3.4	<i>a</i>	<i>a</i>	0.2	0.2	<i>a</i>
900	4.0	3.4	<i>a</i>	<i>a</i>	0.4	<i>a</i>	<i>a</i>	<i>a</i>	0.3

Small quantities (<0.1 kN m⁻²) of 2-methylbut-2-ene and 2,3-dimethylbut-2-ene were also observed.

^a Analyses were not performed.

furnace to connect the vessel directly to the vacuum line, thus eliminating 'dead space'. The line led to gas chromatographs (Pye 104 models, equipped with flame ionization and thermal conductivity detectors) linked, *via* a stainless steel capillary tube at 378 K, to a mass spectrometer (AEI MS 12; 70 eV electron energy; 100 μA trap current; 8 kV accelerating potential; source temperature 378 K). Pressure measurements were made with a transducer.

(b) *Analysis*.—Reactants and most products were determined by g.l.c., their identity being confirmed from their mass spectra. Oxygen, carbon monoxide, and carbon dioxide were determined on silica gel (60—85 mesh; column 3 m long, 4 mm i.d.; 323 K; argon as carrier gas). 2,3-Dimethylbutan-2-ol and the other products were determined

¹⁰ C. E. Bricker and H. R. Johnson, *Analyt. Chem.*, 1945, **17**, 400.

¹¹ F. C. Whitmore, W. L. Evers, and H. S. Rothrock, *Org. Synth.*, 1943, **2**, 408.

regions of interest.¹⁴ The alcohol did not dehydrate if the stainless steel capillary tube between the gas chromatograph and the mass spectrometer was below 390 K, and, for the experiments, the tube was kept at 378 K. The alcohol has a weak parent peak at *m/e* 102 and scanning at a lower electron voltage did not improve its size significantly. The base peak, *m/e* 59, and a large peak at *m/e* 87, both of which contain the oxygen atom, were used and the *m/e* regions 58—61 and 86—89 were scanned. The *m/e* region 57—60 was used for acetone, for although the base peak is at *m/e* 43, readings at *m/e* 45 are ambiguous.

¹² V. J. Shiner, *J. Amer. Chem. Soc.*, 1954, **76**, 1603.

¹³ R. A. Friedel, J. L. Schultz, and A. G. Sharkey, *Analyt. Chem.*, 1956, **28**, 926.

¹⁴ C. G. Swain, G.-I. Tsuchihashi, and L. J. Taylor, *Analyt. Chem.*, 1963, **35**, 1415.

Intensity ratios for prepared samples of [^{18}O]-2,3-dimethylbutan-2-ol were measured using three separate series of experiments conducted over a period of several weeks. There appears to be a negligible amount of exchange between the [^{18}O]alcohol and either the gas chromatographic packing material, Porapak Q, (I_{89}/I_{87} ;

and I_{58}/I_{59} for the alcohol were 1.6 and 3.6% respectively and I_{57}/I_{58} for acetone was 2.8%, which were found to be of negligible importance in the calculations.

While the formaldehyde is no doubt produced, at least in part, following attack on the methyl groups of the alcohol, it is most likely that acetone is formed from

TABLE 3
Intensity ratios (%) obtained from the mass spectra of 2,3-dimethylbutan-2-ol

Reaction series	Alcohol	I_{60}/I_{59}	I_{61}/I_{59}	I_{88}/I_{87}	I_{89}/I_{87}	Method of insertion
A	^{16}O	3.16 ± 0.02	0.21 ± 0.01	5.47 ± 0.03	0.32 ± 0.01	Cold inlet
B	^{18}O			7.75 ± 0.06	1.04 ± 0.01	Cold inlet
C	^{18}O	4.70 ± 0.03	0.78 ± 0.01	7.60 ± 0.09	1.00 ± 0.02	From liquid injections <i>via</i> g.l.c. and steel capillary
D	^{18}O	4.38 ± 0.09	0.77 ± 0.02	7.45 ± 0.06	1.00 ± 0.02	From reaction vessel, <i>via</i> g.l.c. and steel capillary
Ref. 15	^{16}O	3.39	0.24	5.62	0.33	

series B and C; Table 3), or between the alcohol and the walls of the reaction vessel (I_{89}/I_{87} and I_{61}/I_{59} ; series B and D; Table 3). Similar results were obtained for [^{18}O]acetone (Table 4). Separation of the unenriched

TABLE 4

Intensity ratios (%) obtained from the mass spectra of acetone

(a) Samples of acetone and [^{18}O]acetone prepared by exchange with [^{18}O]water

Reaction series	Acetone	I_{59}/I_{58}	I_{60}/I_{58}	Method of insertion
A	^{16}O	3.83 ± 0.04	0.27 ± 0.01	Cold inlet
B	^{18}O	3.92 ± 0.04	0.74 ± 0.01	Cold inlet
C	^{18}O	3.47 ± 0.11	0.71 ± 0.02	From liquid injection <i>via</i> g.l.c. and steel capillary
D	^{18}O	3.60 ± 0.09	0.67 ± 0.03	From reaction vessel, <i>via</i> g.l.c. and steel capillary

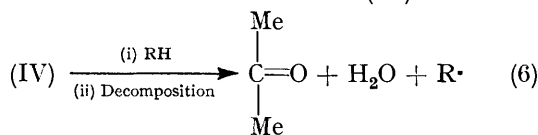
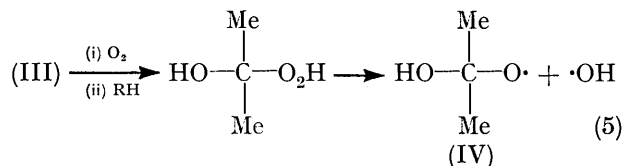
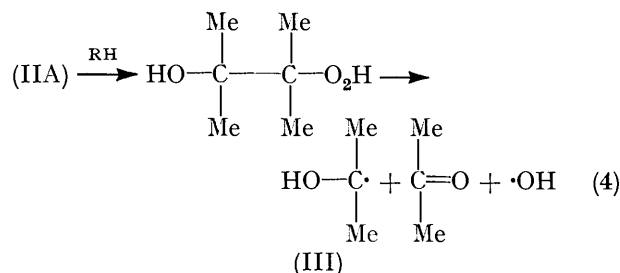
Ref. 15 ^{16}O 3.38 0.24
(b) Acetone formed by the oxidation of [^{18}O]-2,3-dimethylbutan-2-ol at 578 K

Alcohol, 6.7 kN m^{-2} ; oxygen 6.7 kN m^{-2} ;	Sample taken at 600 s
I_{59}/I_{58}	4.00 ± 0.05
I_{60}/I_{58}	0.57 ± 0.01

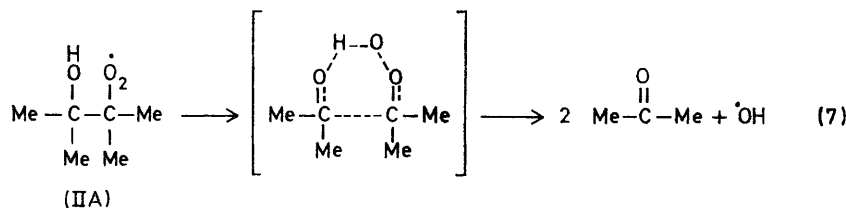
and enriched forms was not apparent during the analysis by g.l.c.

Table 4 also shows the intensity ratios obtained for acetone formed by the oxidation of [^{18}O]-2,3-dimethylbutan-2-ol. Using I_{88}/I_{87} and I_{89}/I_{87} ratios for the

2,3-dimethylbutan-2-ol in either or both of two ways, *via* radical (IIA). First (IIA) may yield a hydroperoxide by hydrogen abstraction and this will form, eventually, two molecules of acetone (for it is important to postulate that the radical, formed from each alkene molecule produces two molecules of carbonyl compounds¹⁻⁵) [reactions (4)–(6)]. By this mechanism, 50% of the



acetone formed from reaction (6) will be enriched. This means that 25% of the total yield of acetone will contain



alcohol, it appears that $50.8 \pm 9.3\%$ of the ketone is enriched, while the value is $55.2 \pm 8.5\%$, using the I_{60}/I_{59} and I_{61}/I_{59} ratios. These calculations account for the occurrence of ^2H , ^{13}C , and ^{17}O . The values of I_{86}/I_{87}

^{18}O , because for each molecule of acetone formed by reaction (6), one molecule is also formed by reaction (4).

¹⁵ J. H. Beynon, 'Mass Spectrometry and its Applications to Organic Chemistry,' Elsevier, New York, 1960, pp. 448, 491.

On the other hand, if radical (IIA) undergoes decomposition, it forms two molecules of acetone in the same reaction, and the enrichment of acetone will be 50%, as is found in this work. The most feasible reaction, therefore appears to be that *via* a 6-membered transition state which is both sterically and energetically possible. We calculated that a concerted reaction is exothermic by *ca.* -66 kJ mol^{-1} . The chain carrier is regenerated and reaction (7) must therefore be considered to be one of the more important propagation reactions in the low-

temperature oxidation of alkenes by molecular oxygen in the gas phase, confirming the mechanism suggested in earlier work.¹⁶

One of us (D. J. M. R.) is grateful to the S.R.C. for a Studentship.

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¹⁶ D. J. M. Ray and D. J. Waddington, Thirteenth Symposium (International) on Combustion, The Combustion Institute, 1971, 261.