GAS-PHASE OXIDATION OF ALIPHATIC KETONES

J.A. Barnard

Department of Chemical Engineering, University College London, Torrington Palace, London, W.C. 1, U.K.

M.A. Sheikh

Pakistan Belting Mfg. Co. Ltd., Muridke, Distt. Sheikhupura, Punjab

(Received June 5, 1973)

Abstract. The gas-phase oxidation of aliphatic ketones shows most of the characteristics of hydrocarbon oxidation. The oxidation both in high and low temperature regions proceeds by a free-radical chain reaction. The intermediate responsible for branching is formaldehyde at high temperatures, while at low temperatures branching is brought about by alkyl hydroperoxides. Comparative studies with acetone, butanone and pentan-3-one of the maximum rate and the minimum pressure for cool-flame propagation and the order of reaction were carried out.

The slow combustion of acetone,[1-3] butanone[2,4-6] and pentan-3-one[2,7] has been thoroughly investigated. These ketones exhibit many common features; thus the pressure-time curves are sigmoidal, the maximum rate of reaction as given by $(d\Delta p/dt)_{max}$ shows a region of negative temperature coefficient, and under certain conditions cool-flames appear. In addition the reaction products show many similarities.

Experimental

All these investigations have been carried out in a static system where reaction were followed by pressure change and by detailed chemical analysis. The principal analytical methods used have already been described.[1,3,7,9]

Results and Discussion

The rate of gas-phase oxidation of aliphatic ketones, both in the high and low temperature regions, increases in the order acetone, butanone and pentan-3-one. The results are given in Table 1.

In their behaviour towards oxygen these ketones showed many of the characteristics of low-temperature oxidation. At certain temperatures and pressures cool-flames occurred and the minimum pressure at which cool-flame appeared decreased in the order acetone, butanone and pentan-3-one. The results are presented in Table 2.

At temperatures below 300°C the rate of reaction increased with increasing temperature. Above this point, however, the rate decreased steadily to a minimum at about 380°C before begining to increase again. All the three systems, therefore, exhibited a clearly-defined region of negative temperature coefficient of the rate as shown in Fig. 1.

Assuming a relationship of the form

$$[d(\triangle P)dt)]_{max} = A \exp [(- E/RT)]$$

then in the high and low-temperature zones the following overall activation energies were obtained (Table 3).

It is interesting to note that the reciprocal of the induction period and the acceleration constant show similar variations with temperature (Figs. 2 and 3).

Although the rate of oxidation varied markedly with the structure of the cumbustible substance, there was considerably uniformity in the reaction kinetics.

TABLE 2. MINIMUM PRESSURE FOR COOL-FLAME PROPAGATION.

Fuel	Temperature (°C)	Mixture composition (fuel:oxygen)	P_i (mm) to produce cool flame
Acetone	300	1:1	450
Butanone	300	1:1	200
Pentan-3-one	256	1:1	120

TABLE 1. THE MAXIMUM RATE OF SLOW COMBUSTION OF ACETONE, BUTANONE AND PENTAN-3-ONE.

Fuel	Temperature (°C)	Mixture composition (fuel:oxygen)	Initial pressure (mm)	ρ (mm/min)
Acetone	400	1:1	200	4
	250	1:1	200	1
Butanone	400	1:1	100	9
	250	1:1	100	1·5
Pentan-3-one	400	1:1	80	19·5
	250	1:1	80	4·4

TABLE 3. THE ACTIVATION ENERGY OF THE REACTION IN THE HIGH AND LOW TEMPERATURE ZONES.

Fuel	Initial pressure (mm)		E (kcals/mole)	
	P_F	P_O	High-temp zone	Low-temp zone
Acetone	133	67	35	26
Butanone	50	50	26–27	25
Pentan-3-one	40	40	33	24
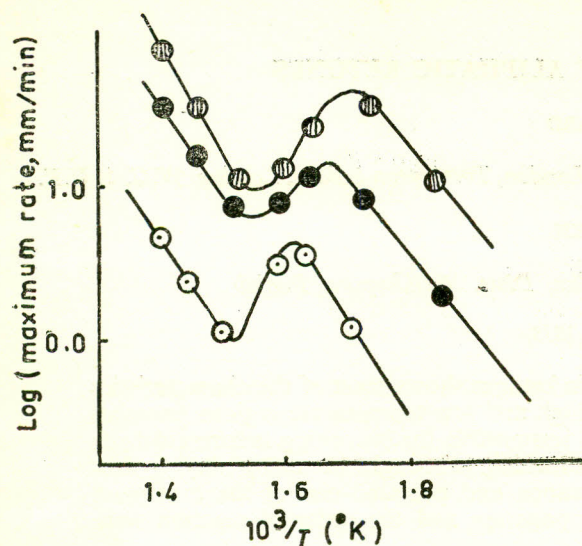
Fig. 1. Variation of maximum rate of reaction with temperature ($\odot P_a$, 100 mm; P_o, 100 mm; $\bullet P_{bu}$, 50mm; P_o, 50 mm; ⦻ P_p, 40 mm; P_o, 40 mm).
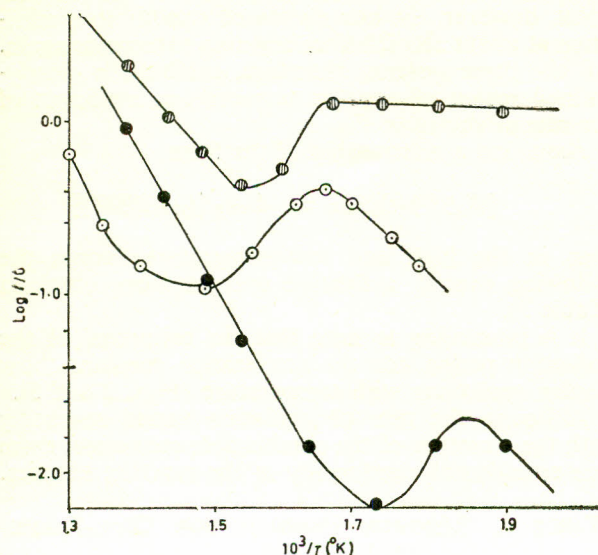
Fig. 2. Variation of the induction period with temperature ($\odot P_a$, 133 mm; $\bullet P_{bu}$, 50 mm; P_o, 50 mm; ⦻ P_p, 40 mm; P_o, 40 mm).

Fig. 3. Effect of temperature on the net branching factor. ($\odot P_a$, 133 mm; P_o, 67 mm; $\bullet P_{bu}$, 50 mm; P_o, 50 mm; ⦻ P_p, 40 mm; P_o, 40 mm).

TABLE 4. THE ORDER OF REACTION WITH RESPECT TO TOTAL PRESSURE, FUEL PARTIAL PRESSURE AND OXYGEN-PARTIAL PRESSURE.

Fuel	Temperature regime	Order with respect to		
		Total pressure*	Fuel	Oxygen
Acetone	High	2·3	1·3	1·3
	Low	1·1	1·6	0·2
Butanone	High	2·0	1·5	1·0
	Low	2·6	†	†
Pentan-3-one	High	2·3	1·4	1·0
	Low	2·3	1·4	1·0

*Total pressure refers to a 1:1 mixture; † no results were available due to extremely long incubation period.

498°C $CH_3COCH_3 + O_2 \longrightarrow 1.4\ CO + 1.1\ H_2O + 0.8\ CH_4 + 0.4\ HCHO + $ minor products

450°C $CH_3CH_2COCH_3 + 1.3\ O_2 \longrightarrow 1.5\ CO + 0.5\ H_2O + 0.3\ HCHO + 1.1\ CH_3OH + 0.3\ C_2H_4 + 0.15\ CH_4 + $ minor products.

450°C $CH_3CH_2COCH_2CH_3 + 1.6O_2 \longrightarrow 1.43CO + 0.65\ H_2O + 0.25\ HCHO + 0.17\ CH_3OH + 0.75\ C_2H_4 + 0.41\ H_2O_2 + 0.25\ CO_2 + 0.15\ CH_4 + $ minor products.

whereas in the low-temperature regime the following stoichiometry was observed.

284°C $CH_3COCH_3 + 2.5\ O_2 \longrightarrow 0.65\ CO_2 + 1.25\ CO + 0.5\ HCHO + 1.75\ H_2O + 0.6\ CH_3OH.$

250°C $CH_3CH_2COCH_3 + 2.5\ O_2 \longrightarrow 1.3\ CO_2 + 0.6\ CO + 0.65\ HCHO + 0.75\ H_2O + 1.0\ CH_3OH + 0.04\ CH_3COOH + 0.04\ CH_3OH + 0.03\ H_2O_2 + 0.07\ CH_4 + $ minor products.

Thus, the order of reaction with respect to total initial pressure in both high and low-temperature regions was generally in the neighbourhood of two. In the high temperature region, the maximum rate was dependent on both oxygen and fuel pressure to approximately the same extent, but tended to be somewhat more sensitive to fuel. This was also true in low-temperature regime for pentan-3-one oxidation, but with acetone, the maximum rate was almost independent of oxygen, whereas with butanone a quite definite inhibition by excess oxygen was observed. The results are given in Table 4.

The basic reactions for the three ketones were all very similar, yielding a considerable variety of reaction products. The stoichiometry of these reactions in the early stages at high temperatures corresponded to
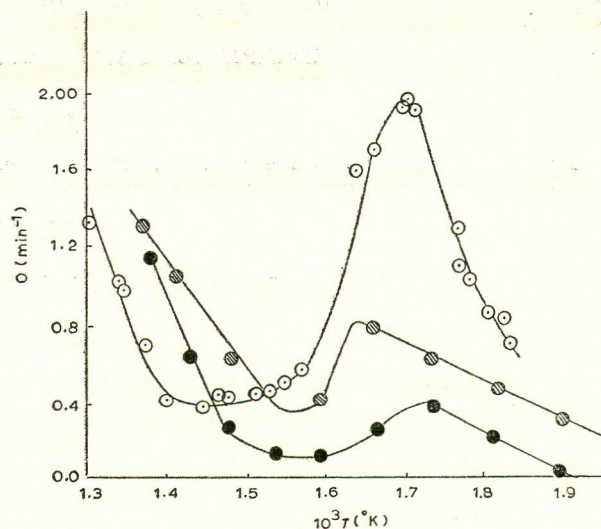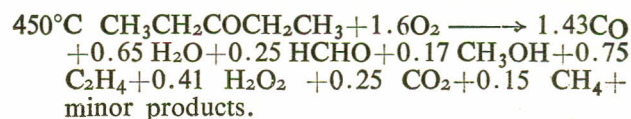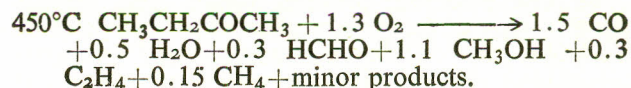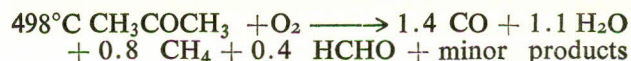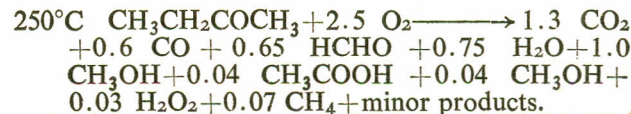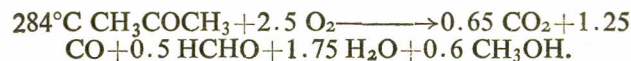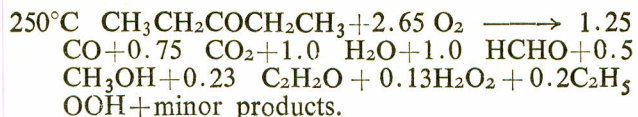
250°C $CH_3CH_2COCH_2CH_3 + 2.65 O_2 \longrightarrow 1.25 CO + 0.75 CO_2 + 1.0 H_2O + 1.0 HCHO + 0.5 CH_3OH + 0.23 C_2H_2O + 0.13 H_2O_2 + 0.2 C_2H_5 OOH + $ minor products.

Most of the major products were the same in both regimes. Some interesting products were found which were present in small quantities. Among the minor products of the high-temperature slow combustion of these three ketones, acetone gave ethylene oxide, butanone gave 1,2-propene oxide and pentan-3-one gave 1,2-butene oxide. These can be formed by RO_2 isomerisation, followed by ejection of CO during ring closure.[1,8]
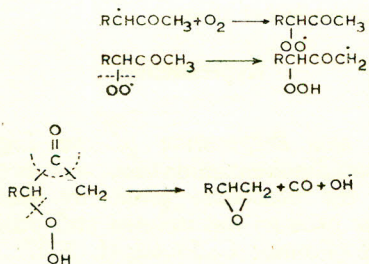
The reaction schemes for all the three ketones involved degenerate chain branching. In the high-temperature regime formaldehyde was the only substance satisfying all the requirements of the branching intermediate.[1-4] In the low-temperature regime branching was brought about by alkyl hydroperoxide.[1-4]

References

1. J.A. Barnard and T.W. Honeyman, Proc. Royal Soc., **236A**, 248, 279 (1964).
2. J.A. Barnard, Adv. Chem. Ser., **76**, 94 (1968).
3. E. Kirschner, Ph.D. thesis, University of London, (1965).
4. M. Akbar and J.A. Barnard, Trans. Faraday Soc., **64**, 3049 (1968).
5. J. Bardwell and C. Hinshelwood, Proc. Royal Soc., **207A**, 461 (1951).
6. J. Bardwell and C. Hinshelwood, Proc. Royal Soc., **201A**, 26(1950).
7. M. Akbar and J.A. Barnard, Trans. Faraday, Soc., **64**, 3035 (1968).
8. A. Fish and D. Swern, *Peroxide Mechanism* (J. Wiley, New York, 1970), p. 141.
9. M. Akbar, Ph.D. thesis, University of London (1966).
10. T.W. Honeyman, Ph.D. thesis, University of London, (1963.)