THE EFFECT OF VARIOUS SURFACES ON THE SLOW COMBUSTION OF SOME KETONES

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Abstract. The slow combustion of acetone, methyl ethyl ketone and diethyl ketone has been studied in reaction vessels which had been pretreated in various ways. The results are consistent with the idea that on a KCl-coated surface peroxy radicals and peroxides are destroyed, whereas in an acid-washed or boric acid-coated vessel these species are relatively stable.

The effect of reaction vessel surface on combustion reactions is extremely complex and not at all well-understood. In respect of their effect on the kinetics of combustion reactions, Walsh et al.[1] consider that surface can be divided into three classes, viz. (a) acid surfaces such as silica and boric acid, (b) metallic oxides and salts, and (c) metals.

This paper is concerned primarily with surfaces in classes (a) and (b). On class (a) surfaces, HO_2 radicals are preserved, or converted into H_2O_2 which is also preserved, while on class (b) surface HO_2 radicals and H_2O_2 are speedily converted to H_2O and O_2. The effect of surfaces on the products of hydrocarbon combustion below about 350°C has been examined by Knox et al.[2,3] The nature of the surface apparently affected the yields of many of the oxygenated products and it was concluded that reactions of alkylperoxy radicals on the wall were important. Atherton et al.[4] have also produced some evidence for the importance of wall reactions of alkylperoxy radicals in hydrocarbon combustion, this effect being important at low temperatures and becoming far less significant at 370°C and above.

In contrast to these findings, experiments in a rapid compression machine[5] and in a single-pulse shock-tube[6] have suggested that surface reactions play only a very small part in product formation.

This paper describes the results of some experiments on the slow combustion of three ketones in reaction vessels which were pretreated in various ways; only pressure-time curves were recorded and no systematic work on product formation in different vessels was carried out. Extensive analytical work in nitric acid-washed Pyrex vessels has been reported elsewhere.[7,8]

Experimental

The experiments were carried out in a static system at temperatures between about 250–500°C. The reaction was followed by pressure change using either a mercury manometer or a glass spiral-gauge, previous work[7,8] having shown that this was a valid method of measuring reactant consumption. Both Pyrex and silica reactors were used; these were cylindrical, 8 cm long and 7 cm in dia. During all this work the reactors were evacuated to better than 10^{-4} torr between each run.

The fuels used (acetone, methyl ethyl ketone and diethyl ketone) were the best commercially available grades and were purified further by methods described elsewhere.[7,8] Oxygen from a cylinder was passed slowly through soda lime, silica gel and a trap cooled to —80°C before use.

The normal pretreatment of the reaction vessel involved repeated washing in concentrated nitric acid, followed by rinsing with twenty changes of deionised water. Vessels coated with a soluble material (such as boric acid, potassium chloride or potassium hydroxide) were prepared by rinsing an acid-washed vessel with a concentrated solution of the appropriate compound and then slowly and carefully evacuating the vessel while it was warmed and rotated to ensure the formation of a uniform deposit. Some experiments were carried out using a vessel washed twice with HF (10%) and then rinsed many times with water.

Results and Discussion

The combustion of all three ketones normally takes place by two different mechanisms, one operating below about 280, the other above about 320°C. This is discussed in detail elsewhere.[7-10]

The first few runs performed in a new vessel normally resulted in a very low rate of reaction and a long induction period. On performing further runs, the rate of reaction gradually increased and the induction period shortened. A typical set of runs is shown in Fig. 1. Table 1 shows that with the exception of methyl ethyl ketone in its low-temperature combustion regime, the ease of attaining the reproducible aged surface condition is in the order acetone < methyl ethyl ketone < diethyl ketone. For the last compound, the aged state was reached almost immediately.

An aged vessel became deaged if a large amount of air was admitted or if the temperature was changed by more than about 20°C. After deaging, the aged reproducible condition was usually reestablished after only one or two runs. It was noted that a completely mercury-free system apparently required less ageing than one in which mercury vapour from manometers was present.
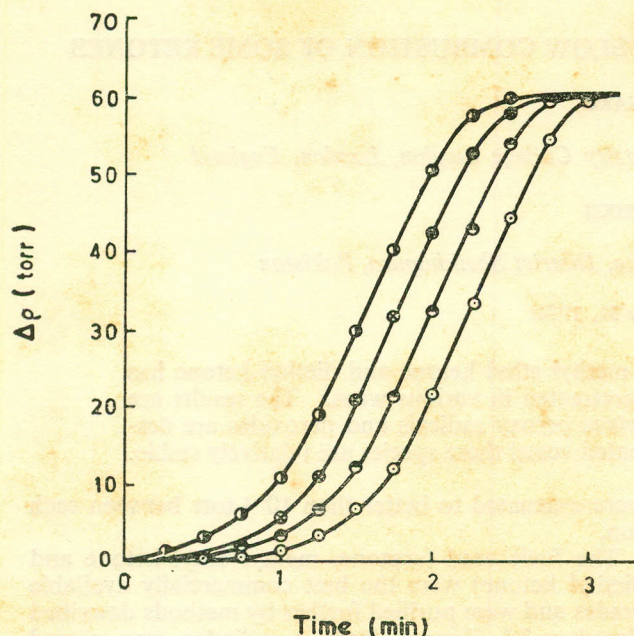
Fig. 1. The ageing of a nitric acid-washed Pyrex reaction vessel. Reactants 50 torr methyl ethyl ketone and 50 torr oxygen. Temperature 450°C.

(⊙ 1st run, ◐ 2nd run, ⊗ 3rd run, ◖ 4th run and subsequent runs)

TABLE 1. AGEING OF NITRIC-ACID-WASHED PYREX REACTORS.

Fuel	Temp. (°C)	Initial pressure of reactants		Number of runs to reach reproducible surface state
		Fuel	Oxygen	
Acetone	498	100	100	<20
	250	100	100	About 10
Methyl ethyl ketone	400	50	50	3–4
	250	50	50	Variable
Diethyl ketone	400	40	40	2–3
	250	40	40	2–3

The behaviour of otherwise-similar vessels could also be very irreproducible. Thus, in the case of four Pyrex vessels of identical dimensions, Kirschner[11] noticed that two made from one batch of Pyrex gave very similar results, while in the two made from another batch, it was impossible to obtain consistent results.

This strange irreproducibility from batch to batch of Pyrex is also illustrated by the work of Luckett and Pollard[12] on the one hand, and of Brench[13] on the other, on the slow combustion, cool flames and two-stage ignition of isobutane in a static system using acid-washed Pyrex reaction vessels of similar dimensions. Luckett and Pollard report that reproducible results were only obtained after a fine layer of carbon had been deposited on the surface of the reaction vessel as a result of two-stage ignitions, and that this required about 200 runs. Even so, the reproducibility was lost when the vessel was exposed to the atmosphere. The experience of Brench was markedly different: in his work, highly reproducible results were obtained after about 20 runs and thereafter this reproducible state was readily reestablished after any change in conditions. No deposit of carbon was visible on the surface of Brench's fully-aged reactor.

In the present work it was noticed that Pyrex vessels pretreated in the same way could give very different results. This is shown in Table 2 which summarises the behaviour of a number of different reaction vessels towards the slow combustion of methyl ethyl ketone.

Some of the irreproducibility in coated vessels could be traced to variations in the thickness and impurity of coating.

With acetone also it has been found that the surface coating may have a profound effect on the reaction rate.[14] In the low temperature regime, nitric acid-washed, HF-washed and boric acid-coated vessels gave pressure-time curves in which the rates of reaction were very similar and the induction periods only slightly different. However, a KCl-coating reduced the rate of pressure change to a very low value, and indeed over a period of some hours a small pressure decrease was observed. With a KOH-coating this effect was even more marked. At high temperatures,

TABLE 2. EFFECT OF VARIOUS PRETREATMENTS ON THE SLOW COMBUSTION OF 50 TORR OF METHYL ETHYL KETONE and 50 TORR OF OXYGEN.

| Reactor No.	Symbol in Fig. 2	Material	Pretreatment	Rate of reaction (torr/min)		Induction period (min)	
				450°C	250°C	450°C	250°C
1	⊙	Pyrex	Nitric acid-washed	36	2.4[a]	2.0	453[a]
2	◐	"	"	35.5	—	1.25	>500
3	◖	"	"	62	1.5	1.25	30
4	●	"	HF-washed	100	17.0[b]	0.5	246[b]
5	◓	Silica	Nitric acid-washed	60	1.8	1.0	210
6	×	Pyrex	Boric acid-coated	87	—	1.25	—
7	△	"	"	88	7.0[c]	1.0	70[c]
8	▲	"	"	84	1.4	1.25	202
9	▽	"	"	86	13.5[a]	1.0	348[a]
10	▼	"	"	20	—	4.3	—
11	⊡	"	"	67	1.8	1.9	264

[a]270–275°C, [b]300°C, [c]330°C

boric acid increased the reactions rate, while a KCl-coating again the rate and also changed the auto-catalytic nature of the reaction so that the pressure-time curve was no longer sygmoidal. The marked effect of KCl-coating on the slow combustion of acetone was also noted by Hoare and Lill[15] in particular a KCl-coating not only drastically reduced the amount of methyl hydroperoxide present, but also inhibited cool-flame formation. This is consistent with the ideas advanced earlier[1] which place a KCl-surface in class (b) on which peroxides (which are responsible for chain-branching) are destroyed.

Surface effects appear to be less important with diethyl ketone, although the experiments with various coating were far less extensive. However, in a normal nitric acid-washed vessel, a reproducible aged surface condition was very quickly established in either a new vessel or one which had been deaged in some way. In diethyl ketone combustion Hoare and Lill[15] again found that the cool-flame limits were shifted towards higher pressures in a KCl-coated vessel. This is consistent with the observations on acetone.

Comparison of this work with that of others,[11],[14],[16],[17] shows that, on the whole, the rate of low-temperature combustion of acetone and methyl ethyl ketone is less sensitive to random surface effects than that of the high-temperature reaction. Thus, when the measurements on the slow combustion of methyl ethyl ketone made by Bardell and Hinshelwood[17] and by ourselves in several different reaction vessels are plotted on the same graph (Fig. 2) the low-temperature results are in satisfactory agreement, whereas the high-temperature results show more scatter.

The induction periods showed a much larger variation from vessel to vessel. In particular, the induction periods for methyl ethyl ketone combustion below 280°C were far longer than for the other two compounds studied, showing that there are still some features of the combustion of this compound which are not understood.

The increased rate of combustion of acetone and methyl ethyl ketone observed in a boric acid-coated vessels at 450°C suggests that HO_2 radicals or hydrogen peroxide are important in the reaction mechanisms. The amounts of hydrogen peroxide detected in the reaction products were extremely small[8] and it seems more probable that the species conserved is the HO_2 radical which can then play an important part in the reaction via radical/radical processes,[18] such as:

$$RO_2 + HO_2 \longrightarrow RO + OH + O_2$$
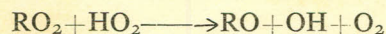
The low-temperature reaction is less sensitive to surface effects, except when the surface (KCl) is particularly destructive towards peroxy radicals and peroxides. It appears, therefore, that HO_2 radicals are probably not important in the reaction mechanism at low temperatures. Molecular hydroperoxides are, however, involved in the chain-branching steps[7],[8],[15] but these compounds react very rapidly in the gas phase and consequently surface effects are minor.

All the observations in the present work are, therefore, consistent with the ideas originally put forward by Walsh *et al.*[1]
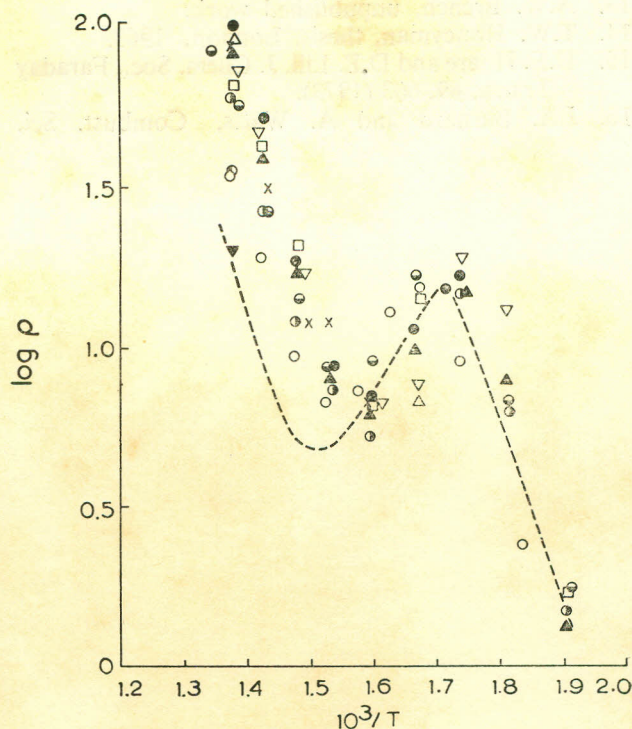

Fig. 2. The variation of the maximum rate of pressure change, ρ torr/min, with temperature, T ○ Dotted line, Bardwell and Hinshelwood's results[17] in a silica reactor. Other symbols listed in Table 2.

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