

SPARK-IGNITED EXPLOSIONS IN CHILLED VESSELS

PART 1.—HYDROGEN + OXYGEN MIXTURES

BY A. J. EVERETT * AND G. J. MINKOFF

Chemical Engineering Dept., Imperial College of Science and Technology,
London S.W.7

Received 8th December, 1955

The formation of hydrogen peroxide in low pressure, spark-ignited explosions of hydrogen and oxygen has been re-examined, particularly in view of recent developments in the "water discharge" and $H + O_2$ system. Many factors affect the peroxide yield including the extent of reaction, the length of the electrodes, the presence of inert gases and of carbon monoxide. The nature of the surface affects not only the amount of peroxide, but its dependence on the mixture composition. On ice coatings, the peroxide yield rises continuously from lean to rich mixtures, while a boric-acid-surface introduces an additional reaction forming hydrogen peroxide in explosions of the stoichiometric mixture. The mechanism of Egerton and Minkoff is discussed in the light of recent developments, with particular reference to the stabilization of HO_2 .

The mechanism of the formation of up to 30 % (weight/volume) H_2O_2 on the chilled walls of the vessel in which a low-pressure, spark-ignited explosion of hydrogen and oxygen has taken place is still not understood.^{1, 2} The u.-v. absorption experiments of Egerton and Minkoff,² for example, which indicated the gas-phase formation of H_2O_2 , were based on the assumption that the speed of the flame was similar to that in open tubes.

However, it is now known both from high-speed flame photography^{3, 4} and from high-speed u.-v. absorption spectroscopy of the explosions,^{5, 6} that much of the observed absorption was probably due to "hot" oxygen, and that no decision about the seat of formation of hydrogen peroxide can be made from such experiments.

A number of anomalies have recently become apparent, as pointed out by Oldenberg⁷ and by Minkoff.⁸ In addition, Townes⁹ has shown, using microwave absorption, that the amount of peroxide formed on cold walls is independent of the OH concentration, and that some other unidentified molecule is present in the gases resulting from electrical discharges through water vapour.

New experimental results on the formation of hydrogen peroxide in hydrogen + oxygen explosions are described here; the effect of different surfaces on peroxide formation and on flame quenching are presented in part 2, and results from methane explosions are considered in part 3, together with the general mechanisms of peroxide formation.

EXPERIMENTAL

The apparatus is similar to that described earlier.²

Cylinder gases, dried in liquid oxygen, were stored in 2-l. flasks and mixtures made up in a third flask by pressure measurement. The reaction vessel consisted of a Pyrex tube usually 1.9 cm diam. and 20 cm long, sealed at one end and provided with a B19 socket at the other. The electrode system, which was inserted into the socket, consisted of a B19 extended cone to the base of which were sealed 2 mm diam. Pyrex tubes 1 cm long.

* present address: Wellcome Research Labs., Beckenham, Kent.

A carbon filament was sealed into each of the tubes so that no carbon protruded from the Pyrex sleeve. A capillary side-arm provided with a tap and a B10 socket was attached at a point about 18 cm from the bottom of the vessel. Another system which was designated as the "Multistatic" was also used. This was an automatic arrangement, electrically controlled, which enabled single explosions to succeed each other at a selected rate, usually three per minute, the vessel remaining cooled for the desired number of explosions. As the rate of explosion was less than in the Egerton and Minkoff system (about 100/min), the effects of temperature gradients across the ice film formed were reduced considerably.

For flow experiments, a modified tube was used (fig. 1), in which the gases, after mixing, entered at the lower end. They were ignited by a flame produced by a continuous spark across shielded electrodes in a compartment at the side of the tube. This prevented the products from being contaminated by electrode materials.

Single explosions were carried out by admitting the explosive mixture to the reaction vessel immersed in the refrigerant. The tap on the side-arm of the reaction vessel was closed and the mixture ignited with a spark from a 50 c/s step-up transformer, the spark energy being 0.1 J. The extent of reaction was determined by measuring the initial and final pressures, and a correction applied to compensate for the space which was not at the constant low temperature. Since at -80° or at -183° the vapour pressure of water is negligible, the quantity of hydrogen consumed in the reaction was calculated from the contraction ratio, no allowance being made for the hydrogen peroxide.* The latter was estimated by the iodometric and titanous chloride procedures described elsewhere,¹⁰ and the yield presented as mole $\text{H}_2\text{O}_2/\text{g}$ atom H burned = y . The products of explosions in coated vessels were always estimated with titanous chloride, which is insensitive to ozone.

One of the main results of this work has been to show that the number of factors which control the yield is even larger than had been suggested in earlier communications. In particular, the state of the surface, the shape and length of the electrodes and of the vessel, and the extent of reaction all affect the results. The trends which are described in the following sections are therefore based on a very large number of experiments.

The reproducibility of experiments in uncoated vessels was fairly good (to within $\pm 6\%$). In general, variation within a group was considerably less than between groups carried out on different days, which could be as much as $\pm 10\%$.

THE STATE OF THE SURFACE

The results are considerably affected by the nature of the surface; higher yields can be obtained by coating the walls either with an ice film or with boric acid. In one set of experiments, without coating, it was shown that 50% of the peroxide decomposed in a warming-up time of 30 sec, but the concentration at room temperature then remained constant. Another experiment showed that when the freshly-formed peroxide was allowed to remain in contact with the boric acid coating at room temperature for 14 h, only 27% decomposition occurred.

It is very probable (see part 2) that part of the decomposition is caused by surface destruction of the peroxide by a reaction which can be suppressed by ice or boric acid. For greater reproducibility, most of the work reported was therefore done in tubes coated

* With the concentrations of H_2O_2 obtained, the formation of H_2O_2 had only a small effect on the deduced extent of reaction.

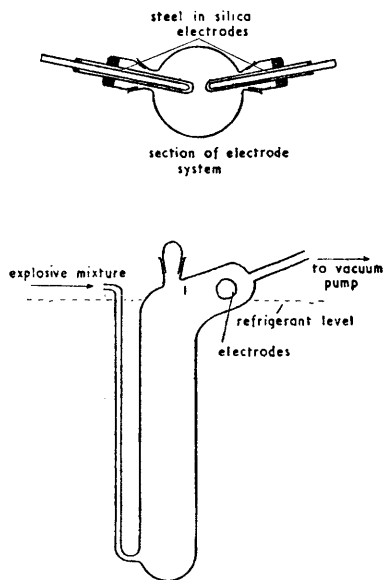


FIG. 1.—Vessel for explosions in flow system.

with boric acid. This was deposited, before each experiment, by shaking an alcoholic solution of C.P. boric acid in the tube, which was connected by rubber tubing to a pump. To complete the evaporation of the alcohol, gentle heat was applied until a translucent coating remained. Occasionally this film became detached from the wall.

THE NUMBER OF EXPLOSIONS

The most relevant results are those obtained with the multistatic apparatus, since complications due to heat transfer through the ice film are reduced as far as possible.

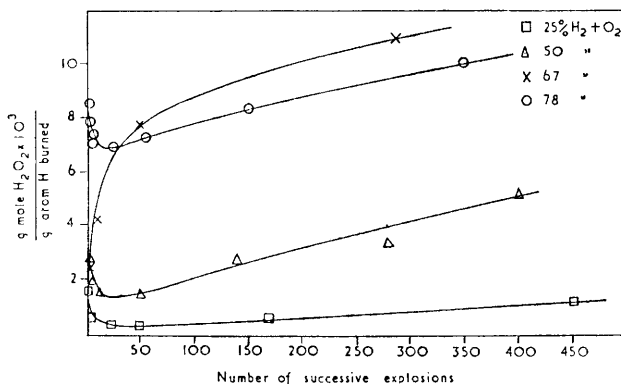


FIG. 2.—Effect of number of explosions on peroxide yield.

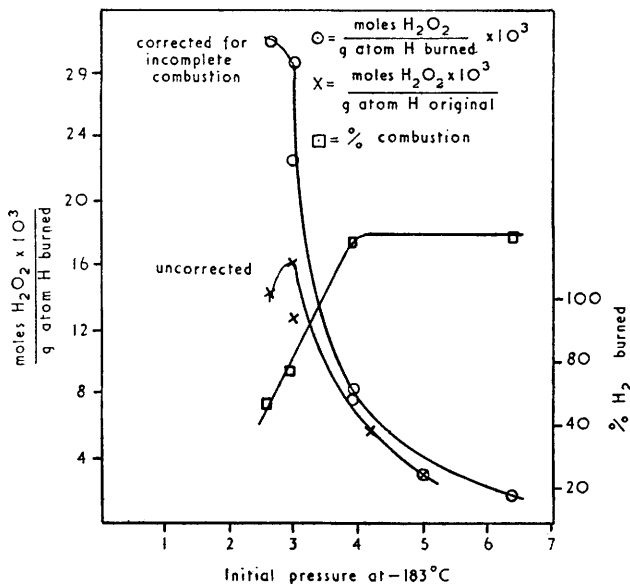


FIG. 3.—Effect of pressure on peroxide yield.

The yield from the stoichiometric mixture is different from the others since it rises immediately and rapidly (fig. 3), and is more susceptible to the presence of ice on the walls. This is illustrated in table 1, which shows, from 50 explosions, the effect on the yield y , of initially coating the walls with an ice film made from liquid water.

Using the 67 % mixture, it was shown that ice at the bottom of the tube, or ice frozen from a stream of wet air, and films of wax, or of frozen carbon dioxide, had no effect on y . However, the length of the electrodes, which, as shown below, can markedly affect y , also affected the percentage increase in y caused by an ice film. The general result was

that any modification of the system which led to an increase in y tended to reduce the effect of ice coating. A possible explanation is that the frozen products of the stoichiometric mixture contain more trapped radicals (since the theoretical flame temperature is the highest), and that the interaction of these with the peroxide is reduced by the ice film. After a large number of explosions, the yields from all the mixtures increased at the same slow rate.

TABLE 1
Electrodes 1.8 cm long; $p = 5$ cm
 $y \times 10^3$ from 50 explosions

% H ₂	no ice isolated previously	with ice coating	% increase
25	0.24	0.24	0
50	1.41	2.07	47
67	7.69	13.22	72
78	7.28	8.11	11

EFFECT OF INITIAL PRESSURE

Both in coated and uncoated vessels, the yield of peroxide increased with decreasing pressure. As reported by Egerton and Minkoff, the yield of peroxide expressed as $[\text{H}_2\text{O}_2]/[\text{H}_2]$ (initial) passed through a maximum. However, this maximum coincided with the pressure at which combustion became incomplete, and, when the results were expressed relative to the hydrogen burned (y) the maximum disappeared (cp. fig. 3).

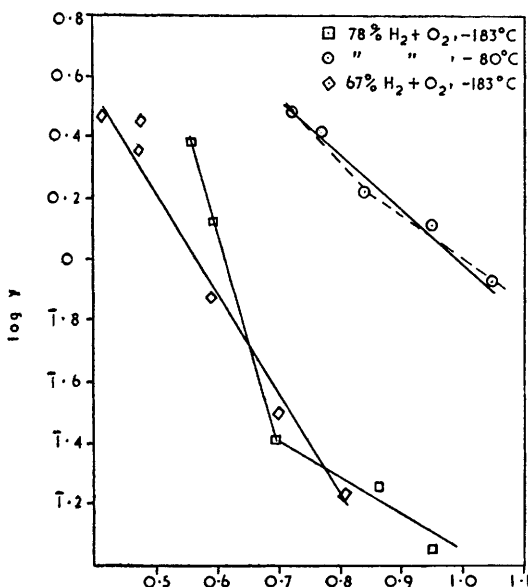


FIG. 4.—Relation between $\log y$ and $\log P$.

The dependence of the yield y on the pressure p is of the type $y = kp^{-n}$, where k and n are constants. A similar relation was found from ethylene explosions by Veinshtein.¹¹ It was well obeyed by stoichiometric mixtures, but complications were found with other mixtures (e.g. fig. 4).

EFFECT OF COMPOSITION OF MIXTURE

As shown in fig. 5 the yield (relative to hydrogen burned) increases with hydrogen concentration (at a constant total pressure of 5 cm, when combustion is complete). The agreement for the 25, 50 and 78 % mixtures between boric-acid-coated single explosions, uncoated single explosions and multistatic after nearly 400 explosions is satisfactory.

The power of p_{H_2} in the relation $y \propto p_{H_2}^n$ changes gradually from just above 1 to nearly 3. This agrees with the conclusion of the next section in indicating that peroxide formation is favoured by hydrogen and inhibited by oxygen.

The stoichiometric yield lies on the curve for large numbers of explosions in the multistatic system, where the surface anomalies are at a minimum. In single explosions,

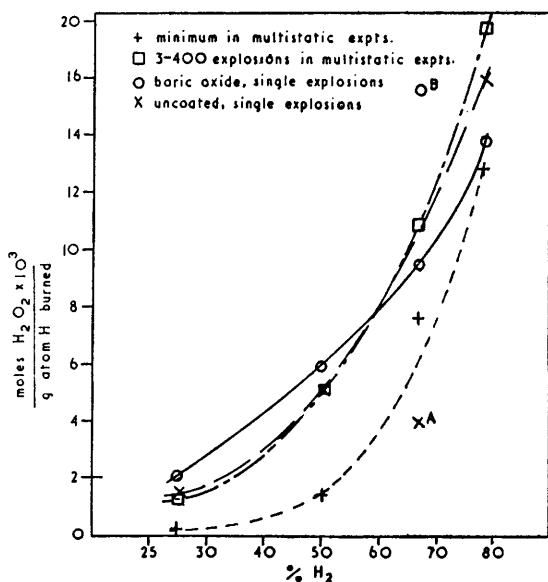


FIG. 5.—The effect of mixture composition with various surfaces.

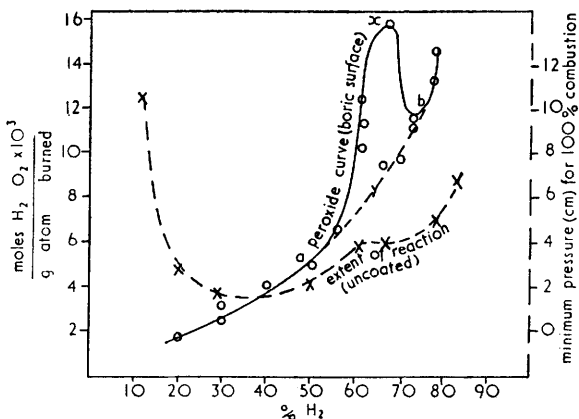


FIG. 6.—The effect of mixture composition on percentage reaction and on peroxide at -180°C .

however, the stoichiometric yield is very low (point A), compared with the curve for uncoated vessels, but for explosions in boric-acid-coated vessels, the yield can lie well above the line (point B). With the stoichiometric mixture in boric-acid-coated vessels, however, the yield was either normal (9.4) or high (15.8); the individual values were reproducible to ± 0.05 , but not predictable (cp. fig. 6). The fundamental process is probably the line $a-y-b$, but under special conditions, another process also operates which leads to the peninsula $a-x-b$. Although these experiments were all at $p = 5$ cm where combustion was complete (i.e. $> 90\%$), a similar peninsula (also in fig. 6) occurs in the curve relating extent of reaction (in uncoated vessels) with mixture composition.

At -80° , the peninsula is at 62 % H_2 at 8 cm initial pressure in coated vessels. In the absence of coating, the yields are greatly reduced, and a shallow maximum only is observed at 67 % H_2 .

THE EFFECT OF EXTERNAL TEMPERATURE

In order to obtain strictly comparable results, the coated reaction vessel was filled at room temperature to the constant pressure of 12.0 cm, and then cooled to the appropriate temperature. The value of $y \times 10^3$ fell from 27.2 at $-196^{\circ}C$ to 15.0 at $-183^{\circ}C$, and eventually to 8.0 at $-80^{\circ}C$.

In flow experiments which are less dependent on pressure, the concentration of the product fell from 10 % to 3 % when the cooling temperature was raised from -183° to -80° (table 2). A similar trend was shown in flow experiments in which the greater part of the heat was removed by a water jacket, and only the bottom of the vessel was refrigerated.

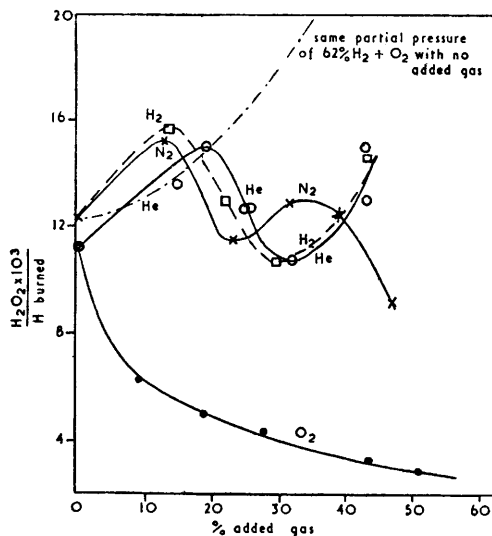


FIG. 7.—The effect of added gases, at a constant total pressure of 5 cm, and the yield corresponding to the same partial pressure of 62 % $H_2 + O_2$.

in a boric-acid-coated vessel at -183° using varying proportions of 62 % H_2 mixture, and either nitrogen or helium added to provide the same total pressure, the latter being high enough to ensure complete combustion. The results are shown in fig. 7 which includes earlier results recalculated so as to show the effect of hydrogen and of oxygen on a comparable basis. Several deductions can be made. First, oxygen behaves differently from the inert gases, so that its inhibitive effect must be due to a chemical reaction which removes a chain carrier which normally leads to peroxide formation. Secondly, the peninsula is not due solely to the increase in hydrogen concentration, but also to an "inert gas" effect.

THE ADDITION OF CARBON MONOXIDE

Carbon monoxide behaved differently from the inert gases. The first 30 % had little effect either on the peroxide yield or on the extent of oxidation of the hydrogen at constant total pressure (fig. 8). Further additions of carbon monoxide decreased the conversion of the hydrogen and doubled the peroxide yield (relative to hydrogen burned). In all experiments, combustion of either fuel or oxygen, whichever was in excess, was complete. Since CO diminishes the partial pressure of the 62 % H_2 mixture, the effect of the total pressure and of partial pressure on the yield are compared, and in fig. 9, $\log y$ against $\log p$ have been plotted. They resemble each other closely in form, and have identical "transition pressures" (3.24 cm at -183°). The value of n below this pressure for the CO mixture is equal to that above it for the explosions of the hydrogen + oxygen mixture.

TABLE 2

58 % H_2 ; $p = 6.7$ cm

$T^{\circ}C$	$[H_2O_2]/[H] \times 10^3$ burned	% (weight/volume)
- 30	0.19	0.07
- 58	2.44	0.8
- 80	7.95	3.0
- 183	36.4	10.0

These experiments show at least one marked difference between the results from the explosion system and those from the discharge-through-water and atomic hydrogen + oxygen systems, since the latter produce no peroxide at $-80^{\circ}C$.

EFFECT OF INERT GASES

In order to test whether the peninsula in the stoichiometric region is due specifically to reactions involving hydrogen, explosions were carried out

However, for a fixed partial pressure of 62 % $\text{H}_2 + \text{O}_2$, the addition of CO decreases the yield of peroxide.

FIG. 8.—The effect of carbon monoxide on peroxide yield and on the extent of reaction, together with the peroxide yield corresponding to the same partial pressure of 62 % $\text{H}_2 + \text{O}_2$.

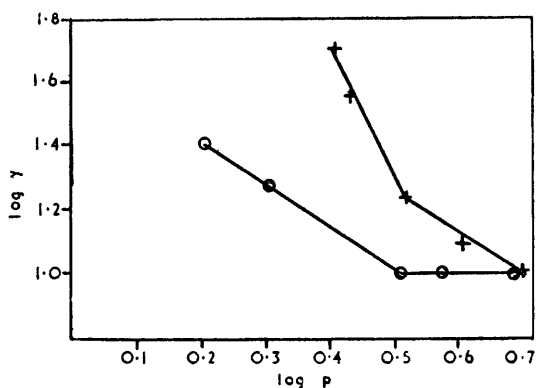
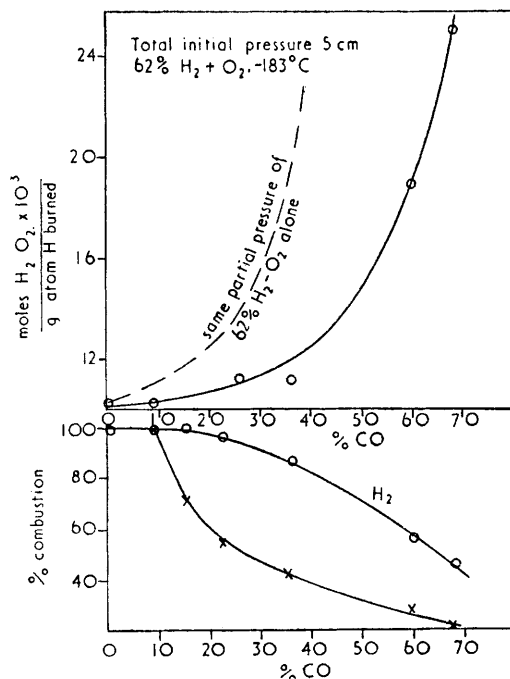


FIG. 9.—Plots of $\log \gamma$ against $\log P$ for explosion in the presence and absence of added carbon monoxide.

THE EFFECT OF VESSEL GEOMETRY

Most of the measurements reported above were made with a reaction vessel 19 mm wide and 20 cm long. The effects observed previously by Egerton and Minkoff were confirmed, i.e. a decrease in vessel diameter raised the yield slightly, and for each diameter, there was an optimum length.

The present investigation showed that the length of the electrodes had a profound influence both on the extent of reaction and on the yield of peroxide. The effect with uncoated tubes 15.3 cm long, 1.3 cm diam., is shown in table 3.

The wide scatter obtained with the medium length electrode was also observed by Egerton and Minkoff. The results show clearly (fig. 10) that the yield of peroxide linearly increased by a decrease in the extent of reaction. The effect of the electrodes is presumably to interfere with the flame propagation, and so to leave pockets of unburned gas. At the same time, the longer electrodes may also act as cold probes which trap additional quantities of peroxide.

TABLE 3

P_{initial}	electrode length, cm	% H_2 burned	$\text{H}_2\text{O}_2/\text{H}$ burned $\times 10^3$
4.00	1.8	102	10.4
4.00	1.8	103	10.9
4.02	4.8	76.8	22.2
3.97	4.8	87.4	18.7
3.98	4.8	98.6	15.8
4.01	4.8	64.8	33.1
3.97	7.0	62	32.3
3.99	7.0	60.2	34.6
3.98	7.0	79.8	26.2
3.96	7.0	61.2	32.9

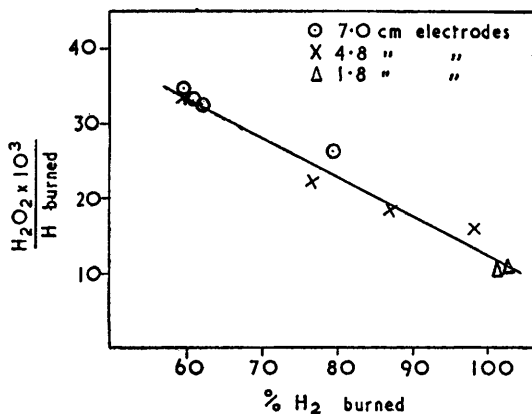
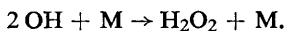


FIG. 10.—The relation between peroxide yield and the extent of reaction.

DISCUSSION

Egerton and Minkoff had concluded that the surface reaction, in agreement with the conclusions of workers concerned with reactions of the products of the water discharge on cold walls, contributed part of the peroxide,



This process was assumed to occur readily at -180°C but not at -80°C . Two aspects must be considered. First, the comparatively large amounts of peroxide found in the present experiment at -80°C seem at first sight to be independent of this mechanism, which, it is stated, is inoperative at -80°C . However, the evidence for this deduction has been strongly criticized by Oldenburg,⁷ who concluded that, in those experiments, all the OH was dissociated. If this is correct, the reaction, $2\text{OH} + \text{wall} \rightarrow \text{H}_2\text{O}_2 + \text{wall}$, cannot be excluded.

However, even at -180°C , peroxide formation was shown to be independent of OH concentration. Thus, Townes *et al.*⁹ found that when the OH concentration (measured by microwave absorption) was increased 50 times, the peroxide in the solution changed from 14.4 to 14.6 % in one set of experiments, and from 25 to 23 % in another.

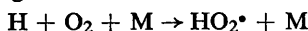
This mechanism should therefore be eliminated. The gas phase part of the mechanism involved the formation of HO_2^* , with a comparatively long life, in the bimolecular association reaction, $\text{H} + \text{O}_2 \rightarrow \text{HO}_2^*$. Independent evidence has now been obtained, by Robb and by Robertson, of the formation of HO_2^* by such a reaction, under pressure conditions where three-body collisions were very infrequent. Patrick and Robb showed, for example, that hydrogen atoms

were "trapped" by oxygen molecules for at least 10^{-7} sec. Unlike Egerton and Minkoff, however, Robertson¹² assumed that the association complex was stabilized by one collision with H_2 , within approximately 5×10^{-12} sec at pressures below 10 mm mercury. The stable HO_2^* could then exist for at least 10^{-3} sec, the time required for it to diffuse from his reaction system into the mass spectrometer. He also showed that with a similar assumption, Patrick and Robb's¹³ observations would indicate a similar lifetime for the unstabilized radical.

The suggestion that the excess energy of formation can be dissipated by one collision with hydrogen seems improbable for two reasons. First, measurements of the collision efficiencies of inert gases in the transfer of energy to decomposing cyclobutane, or isomerizing cyclopropane (the reverse process), shows that hydrogen is one of the least efficient molecules for effecting this process.¹⁴

Thus an estimate of 100 to 1000 collisions of HO_2^* with H_2 would seem more probable for the dissipation of the energy. The lifetime of the unstabilized HO_2^* would then be nearer to 10^{-8} - 10^{-9} sec, which is similar to the lifetime deduced by Rosen assuming that the energy in the newly-formed bond is momentarily shared with other vibrational degrees of freedom within the molecule.¹⁵

More direct evidence is provided by the effects of inert gases on the second limit of the hydrogen + oxygen explosion. This is a measure of the efficiency of the inert gas M in effecting the reaction



in one stage. Satisfactory correlations have been made between the efficiency and the number of collisions¹⁶ for monatomic and diatomic gases. Water and carbon dioxide are much more effective than would have been expected (14 and 5 times respectively), due to these molecules having frequencies¹⁷ also present in HO_2^* (see also Giguère,¹⁸ Minkoff¹⁵). These facilitate the stabilization by the transfer of a quantum of vibrational energy, a mechanism not possible with the simpler gases.

There is thus no strong reason for rejecting the idea that HO_2^* unstabilized (hence retaining its energy of formation) as distinct from HO_2^* stabilized and unreactive, can exist for 10^{-7} - 10^{-8} sec, a conclusion which would have removed the basis of the mechanism.

The authors wish to thank Sir Alfred Egerton for his constant help and encouragement, and the Admiralty for financial support to one of them (A. J. E.). The award of an I.C.I. Fellowship to G. J. M. by the University of London is gratefully acknowledged.

¹ e.g. Poljakow *et al.*, *Acta physicochim.*, 1939, **11**, 453.

² Egerton and Minkoff, *Proc. Roy. Soc. A*, 1947, **191**, 145.

³ Everett and Minkoff, *Fuel*, 1954, **33**, 66.

⁴ Everett and Minkoff, *Fuel*, 1954, **33**, 184.

⁵ Broida, Everett and Minkoff, *Fuel*, 1954, **33**, 251.

⁶ Broida, Everett and Minkoff, *5th Symp. on Combustion* (Rheinhold, New York, 1955), 779.

⁷ Oldenberg, *J. Chem. Physics*, 1949, **17**, 1059.

⁸ Minkoff, *Faraday Soc. Discussions*, 1953, **14**, 141.

⁹ Townes *et al.*, *J. Chem. Physics*, 1954, **22**, 245.

¹⁰ Egerton, Everett, Minkoff, Rudrakanchana and Salooja, *Anal. Chim. Acta*, 1954, **10**, 422.

¹¹ Veinshtein, *J. Physic. Chem. Soc. (Russia)*, 1938, **12**, 137.

¹² Robertson, *Faraday Soc. Discussions*, 1954, **17**, 98, 99.

¹³ Robb and Patrick, *Faraday Soc. Discussions*, 1954, **17**, 98.

¹⁴ Pritchard, Sowden and Trotman-Dickenson, *Proc. Roy. Soc. A*, 1953, **218**, 416.

¹⁵ Minkoff, *Faraday Soc. Discussions*, 1947, **2**, 151.

¹⁶ Williams and Singer, *Ann. Reports*, 1948, **45**, 75.

¹⁷ Walsh, *Fuel*, 1954, **33**, 247.

¹⁸ Giguère, *J. Chem. Physics*, 1954, **22**, 2085.