value of this maximum rate is somewhat greater than can be accounted for by comparison with the rate of reaction of chlorine trioxide and ozone. However, we have found it necessary to consider two forms of the chlorine trioxide molecule, one of which is much more reactive than the other. If we assume that all or at least a large portion of these molecules are formed in this reactive state it would be possible to account for a much higher rate. It seems, therefore, that the quantitative elucidation of the behavior of chlorine–ozone mixtures is dependent on the chlorine trioxide molecule. The data available are not sufficient for such treatment at present but it must be emphasized that in all these studies it is necessary to do more than measure the pressure change as a function of time.

Summary

It has been shown that when mixtures of chlorine and ozone are illuminated with blue light two oxides of chlorine having the formulas ClO_3 and Cl_2O_7 are formed in appreciable quantities. The Cl_2O_7 is relatively inert chemically and tends to remain in the system unchanged once it is formed. The factors influencing the amount of this oxide formed have been studied. The ClO_3 undergoes a thermal decomposition, a chlorine-sensitized photodecomposition, and a reaction with ozone. One product of the latter reaction is Cl_2O_7. Evidence has been presented that one of the primary products in the thermal decomposition is ClO_2. The bearing of all these reactions on the previous observations of the chlorine-sensitized decomposition of ozone has been discussed.

BERKELEY, CALIFORNIA RECEIVED JULY 10, 1934

[CONTRIBUTION NO. 143 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

The Influence of Lead Tetraethyl upon the Combination of Hydrogen and Oxygen

BY H. G. TANNER

M. V. Poljakow and P. Stadnik[1] recently have reported that yields of hydrogen peroxide as high as 8 to 10% were obtained by the simple expedient of exploding electrolytic gas at reduced pressure in a vessel surrounded by liquid air. They attributed their success in part to the catalytic action of the platinum filament which was used to ignite the gas mixture. Their results and conclusions are novel and deemed of sufficient importance to warrant confirmatory experiments.

Using a 2:1 mixture of hydrogen and oxygen at total pressures between 40 and 120 mm., and apparatus built according to their specifications, the formation of hydrogen peroxide was confirmed qualitatively by the $TiCl_4$ test. Quantitative determinations, however, made by permanganate titration, showed that the yields obtained were only 0.2 to 0.3% of the weight of water simultaneously produced. In most of these experiments the reaction of the elements was practically complete. The theory advanced by Poljakow and Stadnik would attribute these lower yields to a lesser activity of the platinum filament. That any catalytic property of platinum was involved, either in their experiments or those mentioned above, does not appear probable, particularly in view of the fact that Poljakow and Stadnik reported that the temperature to which the filament was heated had very little effect upon the reaction. Heterogeneous catalytic reactions are usually quite sensitive to the temperature of the catalyst, and, therefore, the extent to which the filament functioned catalytically appears to be very small. This conclusion was checked experimentally by employing a spark to explode the mixture. Sparks were produced between tungsten terminals, and also between platinum terminals, but the yields of hydrogen peroxide were the same as before. These experiments prove that the platinum filament had no catalytic action and indicate that the formation of hydrogen peroxide under these conditions took place in the gas phase.

The latter conclusion led to the thought that the yield of hydrogen peroxide might be enhanced by the addition of catalysts which would function in the gas phase. From current theories of knock-inducing substances for engine fuels, one would expect to raise the peroxide yield by addition of knock-inducing reagents. Four experiments were performed in which nitrogen peroxide (obtained from the decomposition of lead nitrate) was introduced with the hydrogen–oxygen mixture into the reaction vessel. Explosions with this oxide present reduced the yield of hydrogen peroxide to zero. These results were not altogether surprising, since experimental conditions were not all that could be desired. The liquid air around the reaction vessel could have removed all but a trace of the nitrogen peroxide vapor prior to explosion. Furthermore, the nitrous acid which could have formed with the water condensed on the reaction vessel wall might have been just sufficient to destroy all the hydrogen peroxide simultaneously condensed. Therefore, conclusions about any effect which nitrogen peroxide may have had on this reaction cannot be drawn from these negative results.

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(1) Poljakow and Stadnik, *Phys. Z. Sowjetunion*, **3**, 227, 617 (1933).

Theories regarding the action of knock-inhibiting substances in motor fuel explosions,[2] if applicable to the hydrogen–oxygen reaction, do not lead one to anticipate that an increase of hydrogen peroxide would be obtained by the presence of such substances during the explosion. Nevertheless, the following experiments in which lead tetraethyl was added to electrolytic gas were performed.

Since the explosion had to occur in a vessel surrounded by liquid air, the introduction of any readily condensable vapor, such as lead tetraethyl, into the gas phase presented a difficulty. This introduction was made by connecting the spark terminals in the reaction vessel with a short piece of very fine platinum wire, and wetting this wire with some lead tetraethyl. Evaporation was negligible until the wire was heated suddenly by a heavy current at the moment desired. The lead tetraethyl was thus instantly vaporized practically simultaneously with the explosion and hence had little or no time to be condensed on the wall by the liquid air. A considerable portion of the lead tetraethyl may have been decomposed by the flashing of the wire; nevertheless, the yield of hydrogen peroxide was found to have been increased from 0.2 to values between 0.9 and 1.2% of the weight of water formed simultaneously. The anti-knock effect of the lead tetraethyl was also noticeable. The noise of the explosion was reduced from a violent snap to a soft puff which in many cases was barely audible.

In one experiment the liquid air was removed from around the reaction vessel and placed around a trap adjacent to the reaction vessel. A series of explosions was conducted in the usual manner with lead tetraethyl present. The contents of the trap were examined for hydrogen peroxide, but none was found. Evidently the hydrogen peroxide was decomposed in transit between the reaction vessel and the trap. The chief point of interest in this experiment was the failure of the condensate in the trap to reveal the presence of hydrogen peroxide. Reaction mechanisms are frequently interpreted upon the basis of findings obtained from a trap condensate, or a motor exhaust condensate. This experiment shows how unreliable such data may be if unstable compounds such as hydrogen peroxide are concerned.

Since the bridge-wire used in the above experiments was vaporized, other experiments were performed to determine the effect, if any, which this filament vapor had on the hydrogen peroxide yield. The apparatus was cleaned of all traces of lead tetraethyl by a 1% solution of bromine in carbon tetrachloride. A platinum bridge-wire was used as before, but no lead tetraethyl added. Explosion of electrolytic gas yielded only 0.2% of hydrogen peroxide. Variations in the length and diameter of the bridge-wire, also the voltage applied to the terminals, did not alter the yield of hydrogen peroxide. A bridge-wire of pure lead was tried. At the moment of applying the heating current the lead was instantly vaporized, but the yield of hydrogen peroxide remained at 0.2%. Other wires were used, including iron, molybdenum, nickel, silver, gold, nichrome, magnesium, copper, tungsten and aluminum, but no catalytic effect was detected. The yield of hydrogen peroxide was always near 0.2%. Occasionally, the series would be interrupted by an experiment employing lead tetraethyl on the bridge-wire and a large increase in the yield of hydrogen peroxide was always obtained. Following such an experiment, rigorous cleaning of the apparatus with the bromine solution was found necessary before consistent results again could be obtained with omission of lead tetraethyl. This illustrates how effective are even traces of lead tetraethyl contributed from the walls of the apparatus in changing the course of the reaction.

There remained the possibility that lead tetraethyl itself could increase the apparent yield of hydrogen peroxide by virtue of burning to lead peroxide, which, if present, would respond to the $TiCl_4$ test, and also would consume potassium permanganate during titration. An experiment was made in which the bridge-wire coated with lead tetraethyl was flashed in pure oxygen (at its usual partial pressure). Lead peroxide formation, if it had occurred, would thus be accentuated. A negative test, however, was obtained for hydrogen peroxide by the usual procedures. Similarly, the filament coated with lead tetraethyl and flashed in pure hydrogen yielded no product which consumed potassium permanganate nor responded to the $TiCl_4$ test for hydrogen peroxide. These experiments prove that the increase in hydrogen peroxide yield was real, and not due to extraneous effects.

Discussion

The above experiments have established that a trace of lead tetraethyl can increase the yield of hydrogen peroxide formed during the explosion of electrolytic gas as much as sixfold. The mechanism by which this is accomplished is not entirely clear.

When a spark ignites electrolytic gas, atoms of hydrogen and oxygen, ions and electrons are produced. Their collisions with each other and with molecules of hydrogen and oxygen give a "sphere of reaction" in which is produced a variety of unstable substances including hydroxyl, ozone and superoxide (HO_2). The local temperature rises tremendously. The various products, therefore, attain high velocities. They penetrate the surrounding gas. Some of these particles penetrate farther than others. A heavy molecule like ozone would not be likely to go very far before collision occurred. The penetration of ions and electrons would be relatively small because their electric fields would increase the probability of energy exchanges. The neutral atoms of hydrogen would probably greatly surpass all others in depth of penetration into the surrounding gas mixture. A hydrogen atom leaving a point of reaction at high temperature may have a path of flight measurable in millimeters, whereas other species of particles probably have comparatively short ranges. At the point where the hydrogen

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(2) A review of the various theories of knock and anti-knock effects in motor fuels is to be found in "Catalytic Oxidation of Organic Compounds in the Vapor Phase," Marek–Hahn, Chemical Catalog Co., New York, 1932, pp. 302–364.

atom collides with oxygen inelastically, a second center of reaction is started. Hydroxyl, ozone, hydrogen peroxide, water, hydrogen atoms, etc., are again formed; in fact, the various so-called "chain reactions" take place in this second sphere of action as in the first. The high-speed hydrogen atoms from this second sphere will likewise penetrate, in random directions, the surrounding gas. Some atoms will advance in line with the original atom to carry the reaction forward. Others will dart backward to ignite unburned gas which may remain between the two spheres of reaction, or may even penetrate the first sphere which has since expanded, and there react with whatever may be available such as a hydrogen peroxide molecule, ozone, etc.

Suppose now that lead tetraethyl molecules be "stationed" throughout the hydrogen-oxygen mixture, and assume that they can act as effective barriers to the travel of the high speed hydrogen atoms. When an explosion is started hydrogen atoms are shot out of the zone of reaction, but a large percentage of them is captured by the intervening "screen" of lead tetraethyl molecules. Only relatively few escape to start the secondary reaction zones. Burning (explosion) is accordingly slower, and in consequence the violence (temperature and pressure) of the reaction is subdued. This explains the anti-knock effect observed.

In each reaction zone the usual "chain" reactions occur. The chief difference, however, is that the hydrogen atom concentration would be lowered by the presence of the lead tetraethyl. Hence, reactions such as

$$H + H_2O_2 = HO_2 + H_2, \text{ or}$$
$$H + H_2O_2 = H_2O + OH$$

would be less likely to occur and the net result would be an increase in the amount of hydrogen peroxide which could be recovered.

The above picture of the manner in which the explosion is propagated is in harmony with the various "chain reaction" theories. The latter are merely supplemented by the assumption that the hydrogen atom may have an exceptionally long free path. The further assumption is made that lead tetraethyl has a relatively high "absorption coefficient" for hydrogen atom. A direct determination of this coefficient for hydrogen atom, also for oxygen atom, and for free radicals from organic compounds could probably be made readily. Such data might assist in the development of a satisfactory explanation of anti-knock action of general application.

Summary

Lead tetraethyl added to electrolytic gas was found to increase the yield of hydrogen peroxide formed in an explosion at reduced pressure. A theory consistent with the anti-knock effect is presented in explanation of this result.

WILMINGTON, DEL. RECEIVED JULY 13, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Some Physical Constants of Methyl Ethyl Ketone and an Investigation of its Addition Compound with Sodium Iodide Dihydrate

BY W. A. FELSING, LOUISE SHOFNER AND N. B. GARLOCK

Introduction.—Lochte[1] studied some of the derivatives of methyl ethyl ketone and proposed for the purification of this substance the sodium iodide dihydrate addition compound scheme so successfully used for acetone by Shipsey and Werner.[2] Wadsworth and Dawson[3] questioned the validity of Lochte's method, their contention being based upon a study of the system sodium iodide–methyl ethyl ketone. Since Lochte's method involved the system sodium iodide–methyl ethyl ketone–water, it has seemed desirable to prepare pure methyl ethyl ketone by the two methods (bisulfite and sodium iodide dihydrate), to compare their vapor pressures, densities and indices of refraction, and to determine the composition of the solid product formed when sodium iodide dihydrate reacts with methyl ethyl ketone.

Methods and Apparatus.—The *vapor pressures* were determined by the static method used and described by Felsing and Thomas,[4] all the usual precautions for high accuracy being observed.

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[1] Lochte, *Ind. Eng. Chem.*, **16**, 956 (1924).

[2] Shipsey and Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[3] Wadsworth and Dawson, *ibid.*, 2784 (1926).

[4] Felsing and Thomas, *Ind. Eng. Chem.*, **21**, 1269 (1929).