

**Fig. 1**—In 1960, a low pressure fuel-lean flame of methane and air was analyzed by Fristrom *et al*<sup>5</sup> for the appearance and disappearance of chemical species and for local temperature. The reaction zone was approximately 4 mm thick. Experimental results are shown as individual data points. Recently, J. Warnatz<sup>6</sup> was able to calculate composition and temperature profiles of the same flame from known reaction rates of approximately 80 of the important individual steps that are postulated to occur during the oxidation of methane (solid lines). The agreement between prediction and experiment is excellent.

inhibitors (methyl halides) into this bath, determine their rates of reaction with hydrogen atoms at the high temperature, and compare the results with extrapolations obtained with entirely different tech-

## THE SEARCH FOR HO<sub>2</sub>

In more than two hundred years, chemists have isolated and identified about 100 chemical elements and millions of compounds into which these elementary building blocks can be combined. This continuing and unending quest (the number of potential combinations of elements into compounds is virtually limitless) has been accompanied by an intensive effort to learn more about the bonds that hold these building blocks together in recognizable structures and shapes and to discover the rules that determine the rates and the pathways by which one chemical structure changes into another.

Until about 50 years ago, the study of chemistry was based on a belief in stability. To be sure, many

techniques at lower temperature.<sup>7,8</sup> For the first time it was demonstrated that these measurements give concordant results.

Many intriguing and important problems remain, especially in applied areas where fuel/oxidizer mixing limitations, catalytic surface effects, soot formation, and many other subtle interactions may lead to undesirable end effects. However, for the central problem of gas phase combustion, 200 years of flame research have, at long last, brought about a remarkable confluence of theory and experiment. Taking into account the dominant physical processes of diffusion and heat conduction and the numerous interacting chemical reaction steps, the structure of flames can now be viewed in its full intricacy. Complex flame systems can be constructed out of the many individual reactions that proceed within a flame and the overall behavior of such flames can, in principle, be predicted.

WALTER G. BERL

## REFERENCES

1. J. O. Hirschfelder, C. F. Curtiss, and D. E. Campbell, "The Theory of Flame Propagation," *J. Phys. Chem.* **57**, pp. 403-414 (1953).
2. R. M. Fristrom and A. A. Westenberg, *Flame Structure*, McGraw-Hill (1965).
3. G. Dixon Lewis, "Kinetic Mechanisms, Structure, and Properties of Premixed Flames in Hydrogen-Oxygen-Nitrogen Mixtures," *Phil. Trans. Roy. Soc.* **292**, pp. 45-99 (1979).
4. J. Warnatz, "Calculation of the Structure of Laminar Flat Flames II: Flame Velocity and Structure of Freely Propagating Hydrogen-Oxygen and Hydrogen-Air Flames," *Ber. Bunsenges. Phys. Chem.* **82**, pp. 643-649 (1978).
5. R. M. Fristrom, C. Grunfelder, and S. Favin, "Methane-Oxygen Flame Structure I: Characteristic Profiles in the Low-Pressure, Laminar, Lean, Premixed Methane-Oxygen Flame," *J. Phys. Chem.* **64** pp. 1386-1392 (1960).
6. J. Warnatz, "Flame Velocity and Structure of Laminar Hydrocarbon Flames," *Proc., Seventh International Colloq. on Gas Dynamics of Explosions and Reactive Systems* (to be published).
7. L. W. Hart, C. Grunfelder, and R. M. Fristrom, "The 'Point Source' Technique Using Upstream Sampling for Rate Constant Determinations in Flame Gases," *Combust. Flame* **23**, pp. 109-119 (1974).
8. A. A. Westenberg and N. de Haas, "Rates of H + CH<sub>3</sub>X Reactions," *J. Chem. Phys.* **62**, pp. 3321-3325 (1975).

levels of stability were identified and techniques were developed to move from one level to another. Some substances were so labile that they would barely survive at room temperature. At high temperatures most compounds would change into a relatively small number of stable products. A few elements like radium and polonium showed signs of instability. But once substances such as hydrogen (H<sub>2</sub>) and oxygen (O<sub>2</sub>) molecules reacted with each other, they were expected to form only water or, on occasion, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The details of how such transformations take place were but dimly perceived. It was generally assumed that a direct reaction (commonly written as 2H<sub>2</sub> + O<sub>2</sub> → 2H<sub>2</sub>O) occurs that involves no other chemical species.

A change in this simplistic view came about in the 1920's. Researchers working in the area between physics and chemistry became familiar with the details of explosions and flames where chemical reactions proceed at speeds well beyond the leisurely pace of the conventional chemical reaction. Puzzling observations were made. For example, if a container is filled with hydrogen and oxygen at a high enough temperature, its contents would always explode during mixing. But by lowering the temperature below a critical level, the reaction between the two gases settles down to a slow rate of water formation that might take hours to go to completion. However, when one starts to withdraw such a slowly reacting mixture from the container by means of a vacuum pump, the remaining mixture of hydrogen, oxygen, and water vapor suddenly (and always at a precisely reproducible pressure designated the "explosion limit") explodes with a bright flash and the reaction is completed instantly.

This extraordinary behavior of a sudden transition from a slow reaction to a very fast one by a mere change in pressure became a turning point in the interpretation of chemical reactions. A general explanation was provided by the Russian chemist, N. N. Semenov,<sup>1</sup> who proposed that highly reactive atoms and so-called "free" radicals mediate the transformation among the reactants. These intermediaries, whose concentration depended on the particular conditions of the experiment, were, in fact, crucial participants in the reaction. Their very reactivity made it impossible (at the then-existing state of the art) to detect or to isolate them by conventional chemical means. Because of their inaccessibility, they had not been thought of by chemists as being important in chemical reactions even though physicists had been aware of their existence in many experiments in which gases were exposed to either high temperatures or electric discharges.

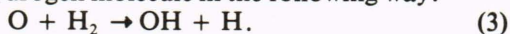
For the hydrogen-oxygen system, not many choices of intermediaries are possible. Hydrogen atoms (H), oxygen atoms (O), and hydroxyl radicals (OH) were already known in physics. One could postulate that water is formed by the elementary reaction



in which one reactive substance (OH) disappears but another one (H) appears. This atom, in turn, would react with oxygen



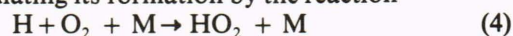
The OH formed in (2) would react as in (1) with more hydrogen to form another molecule of water. The oxygen atom, on the other hand, can react with a hydrogen molecule in the following way:



According to this scheme, once a reactive substance is provided to initiate the process, water can be formed in a simple series of chain reactions in which the key radicals are regenerated endlessly. In fact, in reactions (2) and (3) the number of "chain carriers" increases in each reaction step.

However, these three reactions are inadequate by themselves to explain the observed events. Since more chain carriers are formed than are used up, the formation of water would be expected to become progressively faster with time and always end up in an explosion. A way had to be proposed to remove the chain carriers as quickly as they are formed in the region where the reaction proceeds slowly and to let them build up at a rapidly increasing rate only at the explosion limit.

A careful analysis of the experimental observations on how the explosion limit is affected by gas temperature, container size, pressure, mixture ratio, and the presence of inert diluents led to a reaction scheme that forced the postulation of one additional intermediary, the hydroperoxo radical ( $\text{HO}_2$ ), which has the extraordinary properties of being a stable enough free radical to compete with the chain reaction involving hydrogen atoms (reaction (2)) but also unstable enough to be destroyed once it reaches the wall of the reaction vessel. Only by postulating its formation by the reaction



(where M can be any of the stable participants in the reaction) was it possible to account for the observed system behavior in detail. One of the proponents of  $\text{HO}_2$  said about its existence "These conclusions are inescapable."<sup>2</sup>

When this "inescapable" interpretation was proposed in the 1930's, there was no experimental evidence from any source for the physical existence of  $\text{HO}_2$  nor would there be for 20 years. Yet after studying reactions involving the oxidation of hydrogen-containing materials that included the entire family of hydrocarbon fuels and of myriad other organic compounds, physical chemists had few doubts that the proposed free radical must exist. Without  $\text{HO}_2$ , the observed system behavior simply could not be interpreted; with it, the observations became understandable.

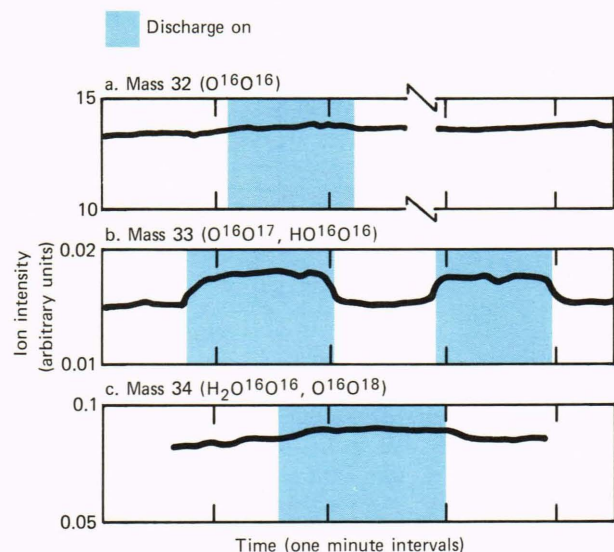
In the middle 1940's there was a brief report from the Shell Research Laboratories that when a hydrogen/oxygen flame is placed in front of the sampling port of a mass spectrometer, it would produce a molecular fragment of the correct mass (33) attributable to  $\text{HO}_2$ . But the evidence was flimsy. The system was too complex and too difficult to analyze. Convincing experimental evidence for  $\text{HO}_2$  was still lacking.

It was another 10 years before the definitive experiments that would identify  $\text{HO}_2$  were made by Samuel N. Foner and Richard L. Hudson at APL in 1953.<sup>3</sup> This was done by combining a sensitive mass spectrometer with a reliable "molecular beam" inlet and a reacting system that could leave little doubt about the events that were occurring. The reaction scheme was to generate hydrogen atoms in a separate electric discharge, mix them rapidly with oxygen molecules before all the hydrogen atoms had time to recombine, and analyze the reaction products for  $\text{HO}_2$ . In this in-

initial effort, the mass spectrometer, despite its sensitivity, was hard pressed to show a peak at mass 33 caused by  $\text{HO}_2$ . The peak was there, nevertheless, disappearing when the hydrogen atoms were shut off and reappearing when they were turned on again (Fig. 1).

Once such a trailblazing discovery is made, a veritable flood of additional information commonly comes to light quickly.<sup>4</sup> Other reactions were found (mainly involving hydrogen peroxide) that proved to be more convenient sources of  $\text{HO}_2$  in much higher concentration. Many rates of  $\text{HO}_2$  reactions with itself, with other simple molecules, and with hydrocarbons have now been measured.<sup>5</sup> The spectra of  $\text{HO}_2$  were obtained, from which many of its structural properties have been estimated.<sup>6</sup> Its terrestrial existence is beyond question. Only its presence in interstellar gas clouds, where so many other free radicals have recently been discovered, has yet to be established.<sup>7</sup>

Nearly 20 years later,  $\text{HO}_2$  made one more appearance in the APL research effort. The reaction of  $\text{HO}_2$  with carbon monoxide was proposed at one time as an important link in atmospheric chemistry research. If the reaction proceeded rapidly, it would offer an attractive pathway for eliminating the carbon monoxide that is generated when fossil fuels are burned and for whose scavenging from the atmosphere no really satisfac-



**Fig. 1**—The mass spectrometric ion intensities for (a) mass number 32 (due to  $\text{O}^{16}\text{O}^{16}$ ), (b) mass number 33 (due to  $\text{O}^{16}\text{O}^{17}$  and  $\text{HO}^{16}\text{O}^{16}$ ), (c) mass number 34 (due to  $\text{O}^{16}\text{O}^{18}$  and  $\text{HHO}^{16}\text{O}^{16}$ ) show that the pronounced plateaus for mass 33 must have been due to a molecular fragment ( $\text{HO}_2$ ) that is produced only during the period when hydrogen atoms generated in an electric discharge subsequently react with oxygen. Much of the intensity background at mass 33 and 34 comes from the ever-present oxygen isotopes  $\text{O}^{16}\text{O}^{17}$  and  $\text{O}^{16}\text{O}^{18}$ . Since no notable changes at mass 34 are observed with the discharge on, hydrogen peroxide was not formed in appreciable amounts. Consequently, its fragments could not have been responsible for any of the peaks at mass 33.

tory mechanism had been known. In a series of elegant experiments,<sup>8</sup> A. Westenberg and Newman de Haas measured free radical reactions at low pressure in simple systems in which the rates of appearance or disappearance of these radicals could be determined with great precision by using electron spin resonance techniques. The hydrogen atom/oxygen molecule reaction was a seemingly straightforward pathway that, in the presence of carbon monoxide, should permit rate measurements of the latter with  $\text{HO}_2$ . The results indicated a very fast reaction, quite in contrast to earlier, more indirect results deduced from more conventional explosion experiments.

In order to resolve this conflict, people elsewhere (particularly at the University of Maryland) carried out independent measurements on the  $\text{HO}_2$ -CO reaction using isotope tracer techniques and higher pressures.<sup>9</sup> There is now a consensus that  $\text{HO}_2$  is not as effective a scavenger of carbon monoxide as was believed by Westenberg, even though its role in reacting quickly with other atmospheric contaminants such as nitric oxide and sulfur dioxide is important.  $\text{HO}_2$  may have formed in Westenberg's experiment so as to produce a nonequilibrated species with unusually high energy content and great reactivity. If this is so, a new chapter of reaction research is opening where reactants are not in equilibrium with their surroundings. Such nonequilibrium conditions may prevail at high altitudes (low pressure) or in combustion situations where reactions occur at very high speed.

The detection of  $\text{HO}_2$  validated a theoretical prediction of great subtlety. For two decades experimenters were challenged to devise experiments that would provide convincing evidence. Foner and Hudson met the challenge.

WALTER G. BERL

#### REFERENCES

- <sup>1</sup>N. N. Semenov, *Chemical Kinetics and Chain Reactions*, Oxford (1935).
- <sup>2</sup>B. Lewis and G. Von Elbe, *Combustion, Flames, and Explosions of Gases*, Cambridge (1938).
- <sup>3</sup>S. N. Foner and R. L. Hudson, "Detection of the  $\text{HO}_2$  Radical by Mass Spectrometry," *J. Chem. Phys.* **21**, pp. 1608-1609 (1953).
- <sup>4</sup>S. N. Foner and R. L. Hudson, "Mass Spectrometry of the  $\text{HO}_2$  Free Radical," *J. Chem. Phys.* **36**, pp. 2681-2688 (1962).
- <sup>5</sup>A. C. Lloyd, "Evaluation and Estimated Kinetic Data for Phase Reactions of the Hydroperoxyl Radical," *Int. J. Chem. Kin.* **6**, pp. 169-228 (1974).
- <sup>6</sup>T. T. Pankert and H. J. Johnson, "Spectra and Kinetics of Hydroperoxyl Free Radicals in the Gas Phase," *J. Chem. Phys.* **56**, pp. 2824-2838 (1972).
- <sup>7</sup>S. Saito, "Microwave Spectroscopy of Short-Lived Molecules," *Proc. XXVIIth International Congress of Pure and Applied Chemistry: Vol. 2, Physical Chemistry*, pp. 1239-1250 (1977).
- <sup>8</sup>A. A. Westenberg and N. de Haas, "Steady State Intermediate Concentration and Rate Constants, Some  $\text{HO}_2$  Results," *J. Phys. Chem.* **76**, pp. 1586-1593 (1972).
- <sup>9</sup>D. D. Davis, W. A. Payne, and L. J. Stief, "The Hydroperoxyl Radical in Atmospheric Chemical Dynamics: Reaction with Carbon Monoxide," *Science* **179**, pp. 280-282 (1973).