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Mass Spectrometry of the HO₂ Free Radical*

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Mass spectrometric studies on the production, identification, and determination of thermochemical energies of HO₂ radicals are reported. Reactions found to produce HO₂ radicals, and examined in some detail, were: (1) reaction of H with O₂, (2) reaction of H with H₂O₂, (3) reaction of O with H₂O₂, (4) reaction of OH with H₂O₂, (5) photolysis of H₂O₂, and (6) low-power electrical discharge in H₂O₂. Of the reactions studied, the low-power electrical discharge in H₂O₂ provided the most intense and convenient source of HO₂ radicals. Ion-molecule reactions, which are negligible in normal operation of our mass spectrometer, are shown to be a potentially serious source of interference in studies of HO₂ with conventional mass spectrometers.

The ionization potential of HO₂, $I(\text{HO}_2)$, and the appearance potential of HO₂⁺ from H₂O₂, $A(\text{HO}_2^+)$, have been redetermined, and the bond dissociation energies $D(\text{H}-\text{OOH})$ and $D(\text{H}-\text{O}_2)$ have been recalculated. The measured values are: $I(\text{HO}_2) = 11.53 \pm 0.02$ ev, $A(\text{HO}_2^+) = 15.36 \pm 0.05$ ev with an estimated absolute accuracy of ± 0.1 ev. The derived thermochemical energies are: $D_0(\text{H}-\text{OOH}) = 88.4 \pm 2$ kcal/mole, $D_0(\text{H}-\text{O}_2) = 45.9 \pm 2$ kcal/mole, $\Delta H_0^\circ(\text{HO}_2) = 5.7 \pm 2$ kcal/mole for the values at 0°K; and $D(\text{H}-\text{OOH}) = 89.6 \pm 2$ kcal/mole, $D(\text{H}-\text{O}_2) = 47.1 \pm 2$ kcal/mole, $\Delta H_{298}^\circ(\text{H}-\text{O}_2) = 5.0 \pm 2$ kcal/mole for the corresponding values at 25°C. Possible sources of error are examined and their effect on these values is discussed.

I. INTRODUCTION

THE HO₂ radical is an important intermediate in theories of oxidation, combustion, and explosion processes. The existence of HO₂ was apparently first suggested by Marshall¹ in order to explain the formation of hydrogen peroxide by uv irradiation of a mixture of hydrogen and oxygen. Indirect evidence for the participation of HO₂ in reactions is rather extensive. The thermal reaction of hydrogen and oxygen² probably provides the strongest indirect evidence for HO₂ in a gas-phase reaction. In this reaction, HO₂ is necessary as a radical chain breaking species to explain the second explosion limit.

Direct experimental proof of the existence of HO₂ was obtained by Foner and Hudson³ in a mass spectrometric study of the reaction of hydrogen atoms with oxygen molecules. Mass spectrometric detection of HO₂ has also been reported by Robertson⁴ in the reaction of hydrogen atoms with oxygen, by Ingold and Bryce⁵ in reactions of hydrogen and methyl radicals with oxygen, and by Fabian and Bryce⁶ in the methane-oxygen reaction. The ionization potential of the HO₂

radical and the H—O₂ bond dissociation energy have been measured.⁷

Because of the general interest in the physical and chemical properties of the HO₂ radical, serious efforts have been made to study the radical by optical spectroscopy, microwave spectroscopy, and electron spin resonance. Although the infrared detection of the HO₂ radical has been reported in absorption⁸ and emission,⁹ the identifications have not been confirmed by subsequent work.¹⁰ Electron spin resonance studies on (1) electrical discharge products from water and hydrogen peroxide, condensed at liquid nitrogen temperature^{11,12} and at liquid helium temperature¹³ and (2) products generated by uv irradiation of hydrogen peroxide-water solutions at 77°K¹⁴ and 90°K,¹⁵ consistently show a broad asymmetrical line (with variations in shape depending on experimental conditions) near the free-electron position which is probably due to HO₂ radicals trapped in the solid.

In this paper, mass spectrometric studies are presented on the production, identification, and determination of energies of HO₂ radicals. A number of reactions for generating HO₂ radicals are discussed. Because of its importance to the thermochemistry of

* This work was supported by the Bureau of Naval Weapons, Department of the Navy.

¹ A. L. Marshall, *J. Phys. Chem.* **30**, 34, 1078 (1926).

² See B. Lewis and G. von Elbe, *Combustion, Flames and Explosions of Gases* (Academic Press Inc., New York, 1961), 2nd ed., Chap. 2, and W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide* (Reinhold Publishing Corporation, New York, 1955), Chap. 2, for discussions of this reaction and other references.

³ S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **21**, 1608 (1953).

⁴ A. J. B. Robertson, *Applied Mass Spectrometry* (Institute of Petroleum, London, 1954), p. 112.

⁵ K. U. Ingold and W. A. Bryce, *J. Chem. Phys.* **24**, 360 (1956).

⁶ D. J. Fabian and W. A. Bryce, *Seventh International Symposium on Combustion* (Butterworths Scientific Publications, London, 1958), p. 150.

⁷ S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **23**, 1364 (1955).

⁸ P. A. Giguère, *J. Chem. Phys.* **22**, 2085 (1954).

⁹ R. B. Tagirov, *Zhur. Fiz. Khim.* **30**, 949 (1956).

¹⁰ P. A. Giguère and K. B. Harvey, *J. Chem. Phys.* **25**, 373 (1956).

¹¹ R. Livingston, J. Ghormley, and H. Zeldes, *J. Chem. Phys.* **24**, 483 (1956).

¹² A. I. Gorbanev, S. D. Kaitmazov, A. M. Prokhorov, and A. B. Tsentsiper, *Zhur. Fiz. Khim.* **31**, 515 (1957).

¹³ C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, *Phys. Rev.* **112**, 1169 (1958).

¹⁴ S. D. Kaitmazov and A. M. Prokhorov, *Zhur. Eksptl. i Teoret. Fiz.* **36**, 1331 (1959).

¹⁵ R. C. Smith and S. J. Wyard, *Nature* **186**, 226 (1960).

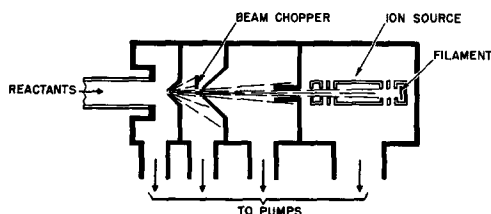


Fig. 1. Molecular beam sampling system.

systems involving hydrogen and oxygen, the bond-dissociation energy $D(\text{H}-\text{O}_2)$ has been redetermined and a critical evaluation is given of the data and possible sources of error.

II. MASS SPECTROMETER

The essential features of the mass spectrometer have been described.¹⁶ The gas sampling system, shown in Fig. 1, uses a collimated molecular beam input which is modulated at 170 cps by a vibrating-reed beam chopper. The entrance aperture of the molecular beam in these experiments was a Pyrex cone with a 0.03-cm-diameter hole pierced in the tip which was ground to a feather edge.

A number of modifications have been made to improve the sensitivity and precision of measurement. Phase detection of the electron multiplier collector current in the original design, has been replaced by a system using synchronized ion counters. The arrangement is shown in the block diagram, Fig. 2. The output of the electron multiplier, consisting of pulses of about 10^{-13} coul/ion, is converted by a preamplifier into a series of voltage pulses of 0.2- μsec duration. The voltage pulses are sent to a gated amplifier which is controlled by pulse generators synchronized with the molecular beam chopper. The gated amplifier is on for 2 msec during each half-cycle of the modulation period, corre-

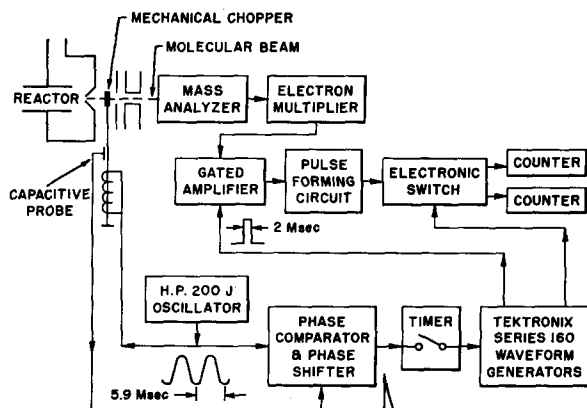


Fig. 2. Block diagram of the mass spectrometer ion detection system. Separate ion counters, synchronized with the molecular beam chopper, record ions with chopper open and chopper closed, respectively.

¹⁶ S. N. Foner and R. L. Hudson, J. Chem. Phys. **21**, 1374 (1953).

sponding to times when the mechanical chopper is either completely open or completely closed. The transit time of the molecules into the ion source is about 250 μsec and an appropriate phase shift is introduced into the gating circuits to compensate for this.

An electronic switch directs the pulses to separate electronic counters during alternate half cycles. Thus one of the counters integrates the ion count N_1 when the beam chopper is open, while the other registers the ion count N_2 when the beam chopper is closed, i.e., the background count. The difference between the two ion counts, $N_1 - N_2$, is the ion intensity contributed by the molecular beam, while $(N_1 + N_2)^{1/2} = \sigma$ is a measure of the statistical error and is equal to the standard deviation for large ion counts. The timer is arranged to give precisely reproducible counting periods of 10 sec, 50 sec, or multiples of these periods.

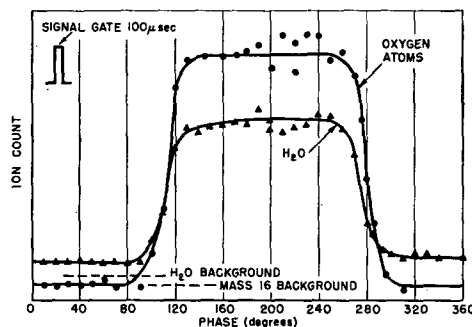


Fig. 3. Waveform of the modulated molecular beam for O atoms and H_2O molecules. Modulation period is 5.9 msec.

The waveform of the modulated molecular beam was determined by shortening the amplifier gate to 100 μsec and measuring the ion intensity as a function of phase angle in the modulation cycle. The waveforms for oxygen atoms and water are shown in Fig. 3. It will be noted that the background of H_2O is increased by the introduction of H_2O , while the mass 16 background is unaffected by the introduction of O atoms, indicating the complete destruction of O atoms in a time very short compared to a half-period of the modulation (3 msec).

Ion currents as low as 0.01 ions/sec have been measured under very favorable conditions; and measurements at the 0.1-ion/sec level are not uncommon. A practical upper limit to the ion intensity that can be recorded is about 50 000 ions/sec. This is due to the difficulty of accurately correcting for coincident counting losses at high counting rates. Of course, considerable range extension can be obtained by reducing the electron current or by using low-abundance isotopic mass peaks. For very large ion intensities, which are rarely encountered in free radical studies, the original arrangement¹⁶ using the electron multiplier as a wide-band ion current amplifier probably would be more satisfactory.

The mass spectrometer has been designed to greatly reduce extraneous effects generally present in conventional instruments. Discrimination against background molecules is provided by the modulated molecular beam system. Ion-molecule reactions which can be a disturbing factor and source of error in conventional instruments are negligible in normal operation because of the low ion source pressure (10^{-6} to 10^{-7} mm Hg) developed by the molecular beam.

III. REACTIONS FOR PRODUCTION OF HO₂

The principal mechanisms for producing HO₂ radicals can be divided into two classes: (1) addition reactions, $H+O_2+M\rightarrow HO_2+M$ and $OH+O+M\rightarrow HO_2+M$, and (2) bimolecular abstraction reactions, such as $OH+H_2O_2\rightarrow HO_2+H_2O$, $CH_4+O_2\rightarrow CH_3+HO_2$, etc. The requirement of a third body M to remove excess energy in an addition reaction makes this process relatively inefficient at low gas pressures. Bimolecular abstraction reactions are not limited by the requirement of a third body, and consequently can be employed for the production of HO₂ in homogeneous gas-phase reactions at low pressures. Since a controlling factor in the detection and analysis of a radical by mass spectrometry is the mole fraction of radicals present, rather than their absolute concentration in the gas, reactions which do not require high concentrations of stabilizing gas molecules are favored. In the studies of HO₂ reported here, bimolecular reactions were found to be the best sources of HO₂.

A. Reaction of H Atoms with O₂

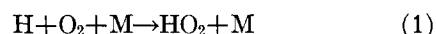
The classical reaction for producing HO₂ is a three-body collision of a hydrogen atom, an oxygen molecule, and a third body which may be either another molecule or the wall of the apparatus. The HO₂ radical was, in fact, first detected in a study of this reaction.³ We have reported on the room temperature reaction of H atoms with O₂ at low pressures¹⁷ and at moderately high pressures,³ and on the reaction at liquid-nitrogen temperature.¹⁷ Hydrogen atoms were produced by dissociating dry hydrogen in a conventional Wood's discharge tube. Reaction times were varied by changing the position where the oxygen was added to the gas stream.

In the low-pressure (~ 1 mm Hg) room-temperature reaction in the time interval 0.002 to 0.02 sec, neither HO₂ nor H₂O₂ was observed, but OH and H₂O were found in substantial quantities. As the pressure was reduced, the relative yield of OH remained approximately constant, indicating that the OH production was taking place primarily on the surface of the reactor, rather than by reaction in the gas phase.

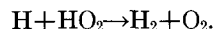
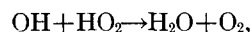
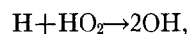
Recently, Charters and Polanyi¹⁸ reacted H atoms with O₂ in a much larger vessel (16 cm diameter, vs

1.2 cm diameter in our case) and observed the emission spectrum of OH. They concluded that the vibrationally excited OH[†] radicals were being produced in the gas phase reaction: $H+HO_2\rightarrow OH^\dagger+OH$. This reaction, which apparently is an important source of OH in their experiments, would play a considerably smaller role in our low pressure experiments because of the much larger surface-to-volume ratio and the ease of diffusion of radicals to the wall. In their experiments at low temperature they observed an increase in OH intensity on cooling the walls with liquid air. This is in marked contrast with our experiments in which OH disappeared completely when the reactor was cooled to liquid-nitrogen temperature. It is quite likely that the temperature of the gas in their experiments was substantially above that of the cooled walls (particularly since the internal mirrors were estimated by them to be at only -10° to -20°C) and, therefore, the experiments are not comparable. This explanation is further strengthened by other experiments which we have done showing that OH radicals are effectively removed by a liquid nitrogen trap.

At higher pressures (1–4 cm Hg), the formation of HO₂ by the reaction



was observed.³ The concentration of HO₂ attained in these experiments was about 0.001% and corresponded to conversion of 1% of the H atoms into HO₂ in a reaction time of 0.01 sec. Attempts to increase the concentration of HO₂ radicals by using higher H atom concentrations and by increasing the reaction time have not been successful. This limitation is apparently due to competition from the destructive reactions:



It is rather easy to see that the net effect of these reactions is to make the HO₂ concentration quite insensitive to H-atom input. Increasing reaction time is not effective because of the loss of HO₂ radicals by recombination reactions.

B. Reactions Involving Hydrogen Peroxide

In searching for more intense sources of HO₂ than the addition reaction of H atoms with O₂, we investigated a series of reactions involving hydrogen peroxide, and found several useful sources of HO₂ radicals. The following systems were studied in some detail: (1) reaction of H atoms with H₂O₂, (2) reaction of O atoms with H₂O₂, (3) reaction of OH with H₂O₂, (4) photolysis of H₂O₂, and (5) low-power electrical discharge in H₂O₂.

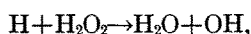
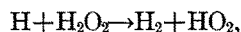
¹⁷ S. N. Foner and R. L. Hudson, J. Chem. Phys. **23**, 1974 (1955).

¹⁸ P. E. Charters and J. C. Polanyi, Can. J. Chem. **38**, 1742 (1960).

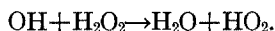
(1) *Reaction of H Atoms with H₂O₂*

Two types of reaction were studied: the reaction of H atoms with solid H₂O₂, and the reaction of H atoms with gaseous H₂O₂. In the reaction of H atoms with solid H₂O₂, H₂O₂ was first condensed on the walls of the reactor maintained at -30°C and then H atoms from a Wood's discharge were admitted. The products observed were H₂O and O₂ in roughly equal amounts. No evidence was found of HO₂ or OH (less than 0.05% of the O₂ produced).

The reaction of H atoms with gaseous H₂O₂ was studied at a total pressure of about 0.4 mm Hg with an H₂O₂ partial pressure of 0.1 mm Hg. The HO₂ radical was observed as a product along with large amounts of O₂ and H₂O. In the reaction time of 0.01 sec almost all the H atoms were consumed. The concentration of HO₂ obtained was of the order of 0.1%. The production of HO₂ proceeds by either or both of the following reactions:



followed by

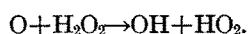


The apparent rate constant for the disappearance of H atoms is approximately 1×10^{-13} cm³/molecule sec. This is an overestimate of the rate of the H+H₂O₂ reaction, since it neglects consumption of H atoms in subsequent radical reactions.

(2) *Reaction of O Atoms with H₂O₂*

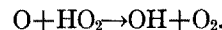
In the reaction of O atoms with H₂O₂ at 1 mm Hg total pressure and reaction time of 0.01 sec, H, OH, and HO₂ radicals were observed accompanied by a small amount of H₂ and large amounts of H₂O and O₂. No ozone was produced in the reaction. Less than half of the O atoms were consumed, showing that this reaction is much slower than the reaction of H with H₂O₂. The apparent rate constant for the disappearance of O atoms, 4×10^{-15} cm³/molecule sec is an upper limit for the rate of the O+H₂O₂ reaction since it neglects other reactions of O atoms. There was no significant decrease during the reaction in the concentration of metastable O₂(¹Δ_g) molecules produced in the discharge.¹⁹ This is not unexpected, since any plausible reaction involving O₂ and H₂O₂ would require more than the 22.5 kcal/mole excitation energy of the metastable molecules.

The HO₂ concentration obtained was only about 0.01%. The HO₂ radical is undoubtedly produced by the reaction

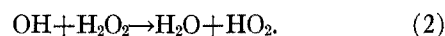


The fact that very few HO₂ radicals were observed is

probably due to their rapid removal by the competing O-atom reaction:

(3) *Reaction of OH with H₂O₂*

When hydroxyl radicals, produced by an intense electrical discharge in H₂O or H₂O₂, were mixed with H₂O₂ it was found that the OH radicals were very quickly destroyed. The production of HO₂ radicals was found to be comparable to the amount of OH destroyed. The rapid destruction of OH radicals by H₂O₂ has been confirmed in microwave experiments at this Laboratory by Massey and Cannon²⁰ who observed the immediate extinction of the OH spectrum when H₂O₂ was introduced into their microwave absorption cell. These observations are consistent with the generation of HO₂ radicals by the reaction:



The maximum concentration of HO₂ obtained by this method was about 0.3%, which is a few hundred-fold higher than obtained in the reaction of H with O₂. A discharge in H₂O₂ or the equivalent stoichiometric mixture, H₂O+ $\frac{1}{2}$ O₂, produced a higher HO₂ concentration than a discharge in pure water. This correlates with the higher OH radical yield from electrical discharges in H₂O₂ or the mixture H₂O+ $\frac{1}{2}$ O₂.

(4) *Photolysis of H₂O₂*

The production of HO₂ by photodecomposition of H₂O₂ was expected since the primary photolytic step²¹ is $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\text{OH}$, and the reaction of OH with H₂O₂ to form HO₂ had been established. In this experiment, the reactor was a Vycor tube 3.4 cm in diameter through which H₂O₂ at a pressure of 0.4 mm Hg flowed at a speed of 100 cm/sec. Small concentrations of HO₂ were obtained at the mass spectrometer, located 30 cm (0.3 sec) downstream, when a 15-w GE mercury resonance lamp (G15T8) placed parallel to the Vycor tube was excited with about 300 w of 6 Mc/sec rf power. The photolytic method probably would be more suitable to higher-pressure experiments, in which case more of the uv radiation would be absorbed by the gas.

(5) *Low-Power Electrical Discharge in H₂O₂*

A confined low-power glow discharge in a rapidly flowing stream of H₂O₂ vapor was found to be an excellent source of HO₂ radicals. The electrodeless discharge used for this purpose restricted the discharge to a small volume, eliminated the possibility of decomposition at electrodes, and permitted the position of the discharge to be easily changed.

The apparatus essentially consisted of a Pyrex or

¹⁹ S. N. Foner and R. L. Hudson, J. Chem. Phys. **25**, 601 (1956).

²⁰ J. T. Massey and S. M. Cannon (private communication).

²¹ D. J. Volman, J. Chem. Phys. **17**, 947 (1949).

quartz tube with two aluminum or wire loop electrodes wrapped around the tube, spaced about 1 cm apart, and connected to an rf generator as shown in Fig. 4. A useful feature of the transmitter used is a built-in antenna matching network which permits the discharge power to be varied continuously over the range of from less than 1 to 100 w. Substantial quantities of HO_2 radicals are produced at power levels of the order of 1 w in a discharge which is barely visible in a darkened room. It is essential to be able to operate the discharge at low power levels in order to avoid completely decomposing the H_2O_2 . Microwave diathermy generators were found to be unsuitable for these low power experiments because they would not maintain a discharge at sufficiently low power levels.

The yield of HO_2 as a function of H_2O_2 decomposition in a 1-cm tube is shown in Fig. 5. The gas velocity was about 1250 cm/sec. The HO_2 radical concentrations were computed from measurements taken near the ionization threshold assuming an ionization cross section for HO_2 midway between O_2 and H_2O_2 . The pro-

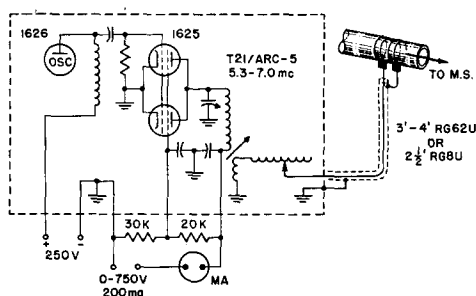


FIG. 4. Electrodeless discharge arrangement. Foil or wire loop electrodes wrapped around the glass tube are connected to the rf generator through a matching network.

duction of HO_2 is relatively insensitive to H_2O_2 decomposition over the range 5% to 40%, changing by less than a factor of 2. The 0.003- and 0.006-sec curves were taken by placing the electrodes at the corresponding distances from the molecular beam entrance aperture. It should be noted that OH was not observed at 0.003 sec for H_2O_2 decomposition less than 60%, and at 0.006 sec the OH produced at 80% decomposition had been completely destroyed. This again points to the rapidity with which OH reacts with H_2O_2 . Assuming that the principal radical constituent in the discharge is OH which then reacts with H_2O_2 to produce HO_2 , the nonobservance of OH at 0.003 sec for low decompositions implies a lower limit of 4×10^{-13} cm³/molecule sec for the rate constant of reaction (2). Oxygen atoms formed in the discharge are considerably less reactive than OH, as is evident from their persistence for times in excess of 0.006 sec.

From the mass spectrometric standpoint, the low-power electrical discharge in H_2O_2 is an exceptional source of HO_2 because very little O_2 is produced in the reaction and, therefore, interference at mass 33 from

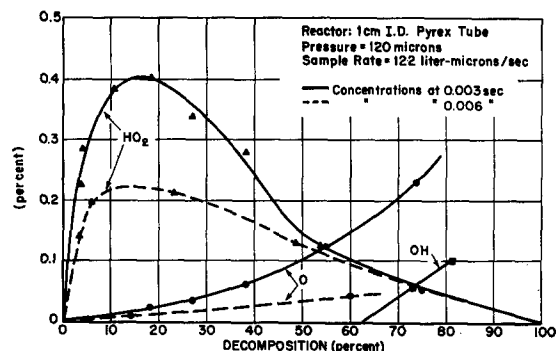


FIG. 5. Radical concentrations at 0.003 and 0.006 sec as a function of H_2O_2 decomposition by an electrical discharge.

the $\text{O}^{16}\text{O}^{17}$ isotope is virtually absent. The usual conditions of operation in our work corresponded to 5–10% decomposition of H_2O_2 .

The use of an electrical discharge to partially decompose a chemical compound, so that the various free radicals, ions, excited molecules, etc., generated by the discharge can almost immediately react with the undecomposed parent compound to generate specific free radicals or compounds is a technique which should have general applicability. This method has already been applied, for example, to the production of diimide²² and various hydronitrogen compounds and radicals.²³

IV. ION-MOLECULE REACTIONS

The generation of the HO_2^+ ion by ion-molecule reactions in the mass spectrometer ionization chamber is

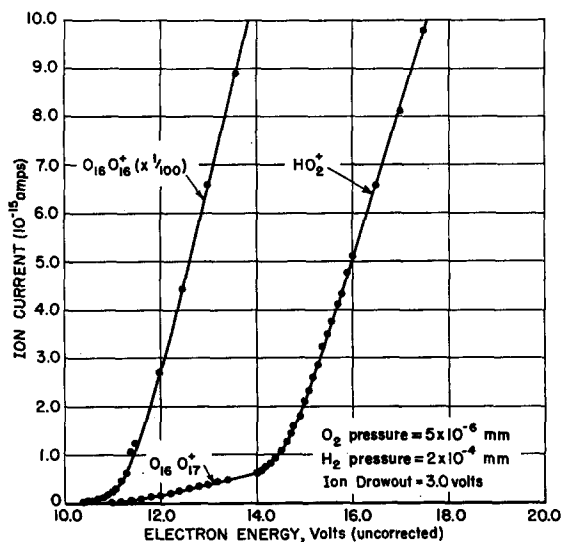


FIG. 6. Appearance potential curves for mass 32 and mass 33 at high ion source pressures showing the production of HO_2^+ by the ion-molecule reaction of H_2^+ and O_2 .

²² S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **28**, 719 (1958).

²³ S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **29**, 442 (1959).

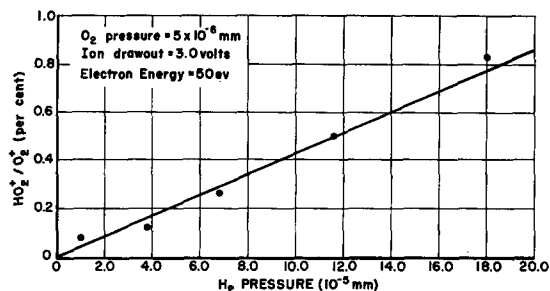
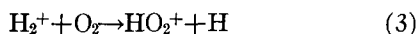


FIG. 7. HO_2^+ ion intensity produced by ionic reaction as a function of H_2 pressure in the ion source.

potentially a serious source of error in studies of the HO_2 radical. The ionic reaction



has a particularly large cross section, and is readily observed in conventional mass spectrometers when mixtures of H_2 and O_2 are introduced at pressures of the order of 10^{-4} mm Hg. The HO_2^+ produced by the ionic reaction is characterized by an onset at the ionization potential of H_2 , $I(\text{H}_2) = 15.422$ ev, rather than at $I(\text{HO}_2) = 11.53$ ev.

Although ionic reactions are negligible in normal operation of our mass spectrometer because the molecular beam develops very low pressures (10^{-6} to 10^{-7} mm Hg) in the ion source, it was decided to study this ionic reaction by operating the mass spectrometer as a conventional instrument. Hydrogen and oxygen were introduced directly into the ion source through a controlled leak. Appearance potential curves are shown in Fig. 6 for mass 32 and mass 33 when the O_2 pressure was 5×10^{-6} mm Hg and the H_2 pressure was 2×10^{-4} mm Hg. The initial portion of the mass 33 curve is $\text{O}^{16}\text{O}^{17}$ ionization. The break in the curve at about 14.0 ev, corresponds to 15.5 ev on an absolute energy scale and correlates with the onset of H_2 ionization.

The dependence of HO_2^+ ion intensity on H_2 pressure is shown in Fig. 7. It is seen that even at H_2 ion source pressures as low as 10^{-5} mm Hg, the ionic reaction (3) is a significant source of the HO_2^+ ion, amounting to 0.043% of the O_2^+ peak or half of the mass 33 isotopic oxygen peak. These data have been analyzed to give for the specific rate constant of reaction (3), $k = 8.3 \pm 0.9 \times 10^{-9}$ cm³/molecule sec, in good agreement with the more precise value 7.56×10^{-9} cm³/molecule sec obtained by Stevenson and Schissler.^{24,25}

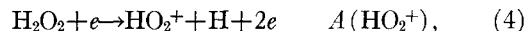
The HO_2^+ ion has also been observed as a secondary product in more complicated chemical systems. For example, Đông and Cottin²⁶ reported the HO_2^+ ion as a product of the reaction of H_2O^+ and O_3 , which they interpreted as a reaction involving electronically ex-

cited H_2O^+ . We have observed that a mass 33 peak, probably HO_2^+ , is produced by an undetermined reaction when a mixture of CH_4 and O_2 is sent into the mass spectrometer at high pressure.

Some of the observations of HO_2 reported in the literature were apparently made under conditions favorable for the production of HO_2^+ by ion-molecule reactions. In studying the HO_2 radical by mass spectrometry, it is necessary to exclude possible interference from ion-molecule reactions by: (1) carrying out an independent study to assess the role of pertinent ion-molecule reactions, or (2) operating at low ion source pressures, or (3) the most definitive method, measuring the appearance potential of the ion.

V. IONIZATION POTENTIALS AND BOND DISSOCIATION ENERGIES

The ionization potential of the HO_2 free radical has been measured directly.⁷ The bond dissociation energy $D(\text{H}-\text{O}_2)$ can be calculated from the appearance potential of the HO_2^+ ion from H_2O_2 , the ionization potential of HO_2 , and the known enthalpy of formation of H_2O_2 . The important processes in the determination of $D(\text{H}-\text{O}_2)$ are



where $A(\text{HO}_2^+)$ is the appearance potential of the

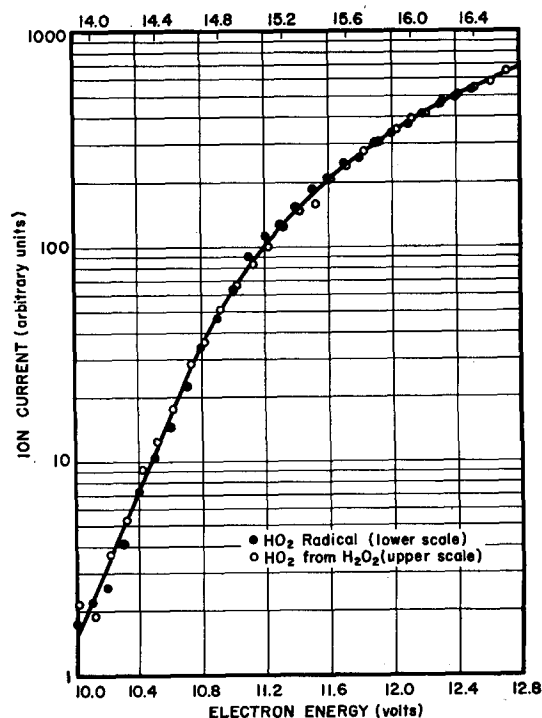


FIG. 8. Appearance potential curves for HO_2^+ from the HO_2 radical and HO_2^+ from H_2O_2 using the semilog matching method. The voltage scales for HO_2 ionization and HO_2^+ from H_2O_2 are indicated on the lower and upper scales, respectively.

²⁴ D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.* **29**, 282 (1958).

²⁵ G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.* **29**, 294 (1958).

²⁶ P. Đông and M. Cottin, *J. Phys. Chim.* **57**, 557 (1960).

HO₂⁺ ion from H₂O₂, and $I(\text{HO}_2)$ is the ionization potential of the radical. The values of $A(\text{HO}_2^+)$ and $I(\text{HO}_2)$ have been redetermined, the value of $D(\text{H}-\text{O}_2)$ has been recalculated, and the sources of error have been critically examined.

The appearance potentials were determined by measuring the voltage shift required to match the initial portion of the ionization efficiency curve of the unknown with that of the standardizing gas whose ionization potential is known spectroscopically. The method used was to plot the log of the ion intensity as a function of electron energy for both the unknown and the standard and then match the curves by permitting arbitrary displacements along the ion intensity and electron energy axes. The intensity scale shift normalizes the ion intensities in a straightforward and precise manner. Various forms of this semilog matching technique have been effectively used by Honig,²⁷ by Lossing, Tickner, and Bryce,²⁸ by Dibeler and Reese,²⁹ by Foner and Hudson,³⁰ and others.

The shape of the HO₂ ionization curve is very close to that of argon and the precision of measurement was about ± 0.02 ev. The appearance potential curve for HO₂⁺ from H₂O₂ and the ionization curve for HO₂ are shown in Fig. 8. The appearance potential curve for HO₂⁺ from H₂O₂ has a longer tail than the ionization curves for HO₂ and argon, and, therefore, it is possible to obtain a good match over a smaller electron energy range and more uncertainty is involved in the measurement. In view of this uncertainty, an independent analysis of the data was made by the deboltzmannization procedure of Foner, Kossiakoff, and McClure.³¹ The results for $A(\text{HO}_2^+)$ and $I(\text{HO}_2)$ were consistent with those obtained by the semilog matching method.

The ionization energies obtained from several sets of data, using $I(\text{Ar}) = 15.76$ ev, are³²

$$I(\text{HO}_2) = 11.53 \pm 0.02 \text{ ev}, \quad (6)$$

$$A(\text{HO}_2^+) = 15.36 \pm 0.05 \text{ ev}. \quad (7)$$

These results are in very good agreement with those obtained in the earlier study.

The principal source of uncertainty in the calculations of the bond dissociation energies, $D(\text{H}-\text{OOH})$ and $D(\text{H}-\text{O}_2)$, is the possibility that the fragments in the dissociative ionization process (4) may possess excess kinetic and/or excitation energy. According to

Stevenson's empirical rule,³³ this should be a process with zero kinetic energy since $I(\text{HO}_2) = 11.53$ ev is less than $I(\text{H}) = 13.595$ ev. A direct proof that the fragments do not possess excess energy would be extremely difficult to obtain experimentally since the H atom, which is not observed, would take away 97% of the translational energy. Assuming that the dissociative ionization process takes place with the fragments separating with zero relative velocity and that the HO₂⁺ ion is not vibronically excited, the difference $A(\text{HO}_2^+) - I(\text{HO}_2) = D_0(\text{H}-\text{OOH})$, the bond dissociation energy at 0°K.

Combining the enthalpy of formation of H₂O₂(g) at 0°K, $\Delta H_0^0 = -31.04$ kcal/mole³⁴ and the dissociation energy of H₂ at 0°K, $D_0(\text{H}_2) = 103.24$ kcal/mole,³⁵ we have the thermochemical relationship:

$$D_0(\text{H}-\text{OOH}) + D_0(\text{H}-\text{O}_2) = 134.28 \text{ kcal/mole}. \quad (8)$$

From the experimental values of $I(\text{HO}_2)$ and $A(\text{HO}_2^+)$ we obtain:

$$D_0(\text{H}-\text{OOH}) = 3.83 \pm 0.1 \text{ ev} = 88.4 \pm 2 \text{ kcal/mole}, \quad (9)$$

$$D_0(\text{H}-\text{O}_2) = 45.9 \pm 2 \text{ kcal/mole}, \quad (10)$$

with the limits of error based on the estimated ± 0.1 -ev accuracy in the measurement of the difference, $A(\text{HO}_2^+) - I(\text{HO}_2)$. Any correction for excess energy in the dissociative ionization process (4) would decrease the value of $D_0(\text{H}-\text{OOH})$ and by Eq. (8) result in a corresponding increase in the value of $D_0(\text{H}-\text{O}_2)$. The calculated value 45.9 ± 2 kcal/mole is, therefore, a lower limit for the H—O₂ bond dissociation energy. The enthalpy of formation of HO₂ at 0°K is

$$\Delta H_0^0(\text{HO}_2) = 5.7 \pm 2 \text{ kcal/mole}. \quad (11)$$

The difference between the value $D_0(\text{H}-\text{O}_2)$ reported here and the previously published value⁷ is primarily due to the use of enthalpies at 25°C in the earlier calculation.

The thermochemistry of the HO₂ radical has been discussed by Gray.³⁶ The dissociation energy $D(\text{X}-\text{Y})$ is defined there as the standard enthalpy increase ΔH_{298}^0 of the reaction in which the gaseous molecule is decomposed at 25°C and 1 atm into two gaseous fragments by fission of the X—Y bond. With this definition, which is often used in discussing heat of reactions, $D(\text{H}-\text{O}_2)$ should exceed $D_0(\text{H}-\text{O}_2)$ by about $2RT$ since the dissociation process adds one mole of gas and three translational degrees of freedom to the system at the expense of one rotational degree of freedom. A more exact calculation taking into account vibrational

²⁷ R. E. Honig, J. Chem. Phys. **16**, 105 (1948).

²⁸ F. P. Lossing, A. W. Tickner, and W. A. Bryce, J. Chem. Phys. **19**, 1254 (1951).

²⁹ V. H. Dibeler and R. M. Reese, J. Research Natl. Bur. Standards **54**, 127 (1955).

³⁰ S. N. Foner and R. L. Hudson, J. Chem. Phys. **25**, 602 (1956).

³¹ S. N. Foner, A. Kossiakoff, and F. T. McClure, Phys. Rev. **74**, 1222 (1948).

³² The error limit quoted is a measure of the precision of determination in several runs. An uncertainty of ± 0.10 ev is our estimate of the absolute accuracy of ionization potential measurements by electron impact methods that do not use monoenergetic electron sources to resolve fine structure in the curves.

³³ D. P. Stevenson, Discussions Faraday Soc. **10**, 35 (1951).

³⁴ P. A. Giguère and I. D. Liu, J. Am. Chem. Soc. **77**, 6477 (1955).

³⁵ Selected Values of Chemical Thermodynamic Properties (NBS Circ. 500, Washington, D. C., 1952).

³⁶ P. Gray, Trans. Faraday Soc. **55**, 408 (1959).

excitation is not warranted by the data. At 25°C we have, therefore,

$$D(\text{H}-\text{O}_2) = 47.1 \pm 2 \text{ kcal/mole}, \quad (12)$$

$$D(\text{H}-\text{OOH}) = 89.6 \pm 2 \text{ kcal/mole}, \quad (13)$$

$$\Delta H_{298}^0(\text{HO}_2) = 5.0 \pm 2 \text{ kcal/mole}. \quad (14)$$

In considering the agreement between the published values of $A(\text{HO}_2^+)$ and $I(\text{HO}_2)$ on which the bond dissociation energy $D(\text{H}-\text{O}_2)$ is based, Gray³⁶ commented on the disagreement between our values and those of Robertson,³⁷ noting that the difference, $A(\text{HO}_2^+) -$

$I(\text{HO}_2)$, was in better agreement than the individual values, and expressed the hope that the measurements would be repeated. To set the record straight, it should be noted that Robertson measured only $A(\text{HO}_2^+)$, obtaining the value 16.1 ± 0.4 ev by linear extrapolation of the ion current curve from energies considerably above threshold. The ionization potential of HO_2 was not measured, but assumed to be intermediate between $I(\text{O}_2)$ and $I(\text{H}_2\text{O}_2)$ and taken as 12.2 ev. This assumed value, by comparison with our direct measurement, is in error by 0.7 ev. Thus, Robertson's datum using his expression $I(\text{HO}_2) - (235 \pm 9)$ kcal/mole for the heat of formation of HO_2 would lead to the value $D(\text{H}-\text{O}_2) = 30 \pm 9$ kcal/mole which is rather different from our value.

³⁷ A. J. B. Robertson, *Trans. Faraday Soc.* **48**, 228 (1952).

Adsorption of Gases on Quartz Single Crystals*

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Approximate adsorption isotherms of hexane and argon on the crystal face perpendicular to the Y axis of quartz have been obtained, making use of the alteration of the mechanically resonant frequency of a 10-Mc, Y-cut quartz crystal as a measure of the mass adsorbed. The "area" of the hexane molecule was found to be 50 \AA^2 and the heat of adsorption at (B.E.T.) monolayer coverage was 1.5 kcal/mole in excess of the heat of liquefaction. A piezoelectric crystal vibrating in a thickness-shear mode appears to constitute a microbalance of sensitivity sufficient to permit measurement, in favorable cases, of isotherms on adsorbents of very low specific area.

I. INTRODUCTION

THE interpretation of adsorption data in terms of a microscopic model is complicated by the effects of surface heterogeneity at low relative pressures and capillary condensation at high relative pressures. Therefore, studies of physical adsorption on oriented crystalline substrata would usefully complement the large body of data concerned with adsorption by powdered or highly porous materials. However, the limited sensitivity of conventional adsorption techniques makes it difficult to work with samples of very low specific area. In this connection it has been observed¹ that the deposition of a film of foreign matter on the surface of a quartz crystal vibrating in a thickness-shear mode will produce an alteration in resonant frequency $\Delta\nu$ which is proportional to the mass adsorbed, the pertinent relation being $\Delta\nu/\nu = \Delta m/m$, where m is the mass of the crystal. Since changes in the frequency generated by a crystal-controlled oscil-

lator may be measured with considerable accuracy, changes in the surface density of mass of 10^{-10} g/cm^2 or less might be detected provided that frequency shifts due to factors other than physical adsorption can be minimized or corrected for.

In this paper the effect of the adsorption of hexane and argon on the resonant frequency of a 10-Mc Y-cut crystal is discussed and some approximate isotherms and related thermodynamic quantities are reported. The Y cut, although it is crystallographically the simplest of the thickness-shear crystals, is, owing to its large temperature coefficient of frequency, not the most suitable orientation, nor is hexane the most suitable adsorbate. However this method does appear to provide the possibility of measuring, in favorable cases, accurate isotherms on single crystals, or on nonporous films evaporated on to single crystals.

II. EXPERIMENTAL PROCEDURE

The quartz crystals used in this work were obtained in the form of disks 1 cm in diameter polished flat

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¹ G. Sauerbrey, *Z. Physik* **155**, 206 (1959).