

Mass Spectrometry of Inorganic Free Radicals

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Use of a mass spectrometer with a collision-free molecular beam sampling system has facilitated observations of certain free radicals, such as O atoms, and excited species which are readily destroyed by wall collisions. Data were obtained on the production of HO₂ by several reactions and on the rate constant for the homogeneous reaction of two HO₂ radicals. Electrical discharges in nitrogen compounds were used to produce N, NH₂, N₂H₃, and HN₂(CH₃)₂ radicals, and the unstable compounds N₂N₂, N₃H₃, N₄H₄, and HN₂CH₃. Metastable He and N atoms and N₂ molecules were obtained from electrical discharges. Substantial concentrations of N(²P) and N(²D) atoms were observed, in addition to ground state N(⁴S) atoms, from an electrical discharge in a mixture of N₂ with a large excess of helium. Nitrogen molecules in this system have excitation energies up to several electron volts.

Mass spectrometric studies have furnished considerable information on free radicals in gaseous systems. The scope of these studies includes: detection and identification of free radical species, measurement of radical concentrations, determination of radical ionization potentials, determination of bond-dissociation energies, and elucidation of the role of free radicals in chemical reactions. In addition, mass spectrometry has recently been extended to the investigation of electronically excited atoms and molecules. One aspect of information on a free radical which is not accessible to mass spectrometry is knowledge of its geometry (bond lengths and angles). Fortunately, for simple free radicals this information is often obtainable by optical spectroscopy.

A major problem in mass spectrometry of free radicals is the extraction of the gas sample from the reacting system and its transport into the ionization chamber without materially changing the composition of the sample and, in particular, avoiding loss of the free radicals in the process. In some cases, spurious free radical signals may be produced in the mass spectrometer by ion-molecule reactions and by reactions of incoming molecules with the heated filament. The mass spectrometer used in the studies reported here employs a collision-free molecular

beam sampling system to avoid loss of reactive chemical species, and is designed to discriminate strongly against background signals and extraneous effects generally present in conventional instruments.

Although this paper is primarily concerned with inorganic free radicals and reactions of inorganic free radicals, it also discusses some unstable nitrogen compounds, and metastable atoms and molecules. The production, detection, and identification of free radicals, and the determination of bond-dissociation energies for the radicals, are considered in some detail. Radicals produced by heterogeneous reactions, such as the catalytic reactions on heated filaments in the mass spectrometer ion source, are not considered.

Experimental

The mass spectrometer and its collimated molecular beam sampling system (6, 12) have been especially designed for the study of reactive free radicals.

The gas being sampled enters the molecular beam system shown in Figure 1 through a small circular aperture in a glass or quartz cone and is collimated by two additional slits. The three sections of the molecular beam sampling system are separately evacuated by high speed diffusion pumps, the pressures typically being 10^{-8} mm. of Hg in the first section, 10^{-6} in the second section, and 10^{-7} in the ion source section. The molecular beam traverses a distance of 10 cm. from the entrance aperture to the center of the ion source. This corresponds to a transit time of about 230 μ sec. for an oxygen molecule at room temperature. The molecular beam is mechanically interrupted at 170 cps. by a vibrating reed beam chopper in the first section in order to provide discrimination against background signals.

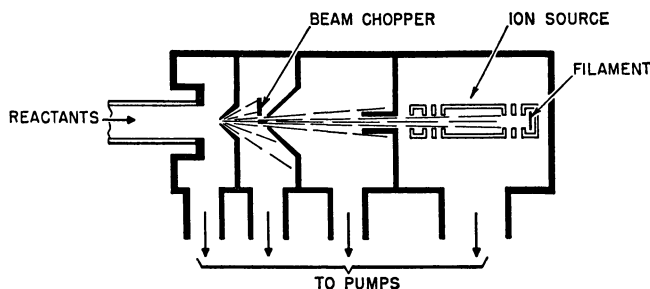


Figure 1. Molecular beam sampling system of mass spectrometer

A block diagram of the mass spectrometer and the ion detection system is shown in Figure 2.

Molecules that are ionized by electron impact in the ion source are accelerated, sent through a conventional 90° magnetic sector analyzer, postaccelerated by a few thousand volts, and arrive at the electron multiplier detector. The output of the electron multiplier detector consists of pulses of about 10^{-13} coulomb per ion. The pulses are amplified and sent through a gated amplifier and an electronic switch which is synchronized with the beam chopper so that one of the ion counters records ions only when the beam chopper is open, the other only when the beam chopper is closed. The difference between the two ion counts represents the ion intensity contributed by the molecular beam, while the square root of the sum of the two ion counts is approximately equal to the standard deviation of the measurement and serves as a useful indicator of the quality of the data being obtained.

With this arrangement it has been possible to measure ion currents as low as 0.01 ion per second under favorable conditions, and measurements are often made down to the 0.1-ion per second level.

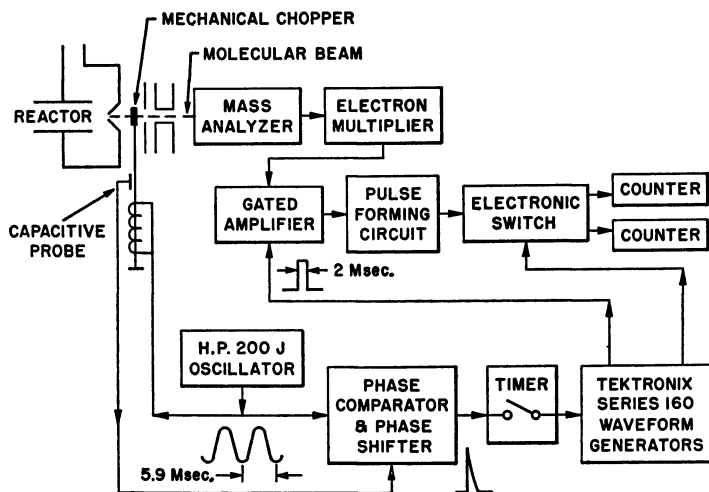


Figure 2. Block diagram of mass spectrometer and ion detector system

The lifetime of free radicals in very low pressure systems, such as mass spectrometer ion sources, is determined principally by the probability of destruction of the radical by surface reactions. The relative ease with which CH_3 radicals have been detected in conventional mass spectrometers and the corresponding difficulty in detecting O atoms are related to the speed of surface reactions, as shown by the following experiments.

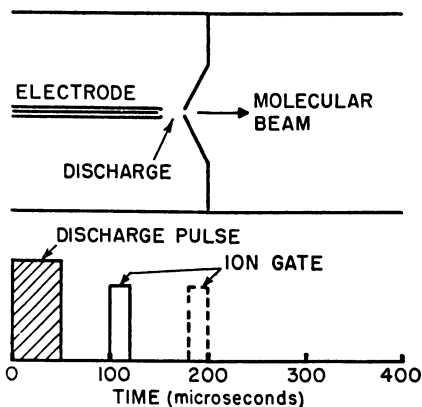


Figure 3. Pulsed discharge source of free radicals

Ion counter activated for 20- $\mu\text{sec.}$ interval by adjustable ion gate

An electrical discharge source of free radicals was set up as indicated in Figure 3. The selected gas was introduced at high flow rate through the small

center tube and was repetitively subjected to short discharge pulses ($50\ \mu\text{sec.}$) just in front of the pinhole, producing each time a burst of radicals. For this experiment the beam chopper was inactivated and the ion counter was controlled by an adjustable electronic gate of $20\text{-}\mu\text{sec.}$ width.

The CH_3 intensity as a function of time from a pulsed discharge in CH_4 is shown in Figure 4. The transit time of the radicals into the instrument is responsible for the time lag of about $0.2\ \text{msec.}$ between initiation of the discharge and the attainment of peak intensity. The decay of the CH_3 intensity with time is

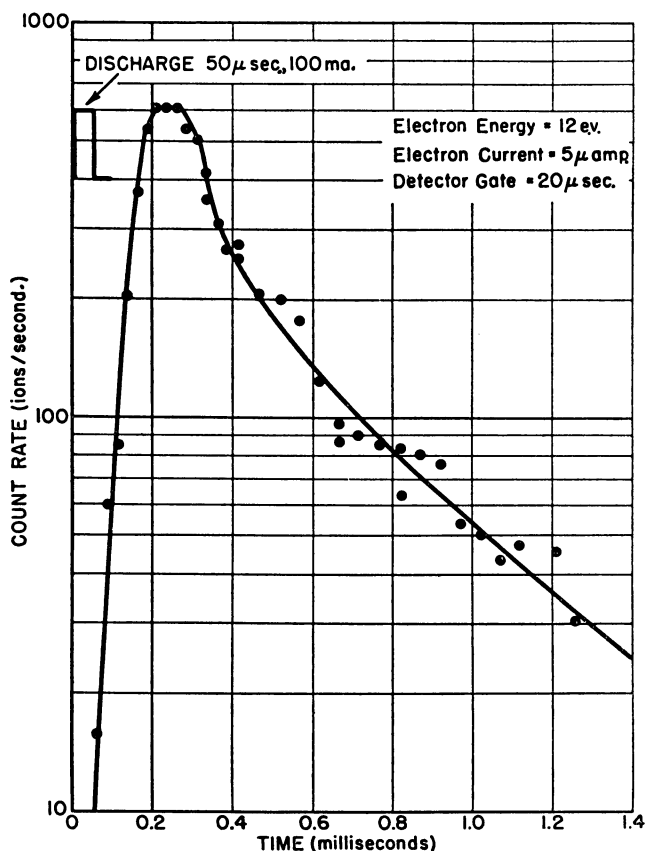


Figure 4. CH_3 radicals from pulsed electrical discharge in CH_4

much slower than predicted on the assumption that the molecules in the trailing part of the pulse are the slow molecules in a Maxwell-Boltzmann velocity distribution. In contrast, O atoms from an electrical discharge in O_2 follow the curve shown in Figure 5. Here the O atom intensity decays by a factor of 100 in $0.7\ \text{msec.}$ as compared to the decay by only a factor of 6 in this time for CH_3 radicals. The O atom curve is reasonably close to what is theoretically predicted for a step function of radicals having a Maxwell-Boltzmann distribution. This indicates that incoming O atoms are destroyed by single, or at most a few, collisions with the walls of the ion source. On the other hand, CH_3 radicals obviously survive many collisions with the walls. These experiments indicate why CH_3 radicals

can be readily observed in instruments that may often not detect comparable inputs of O atoms and other highly reactive species. Experiments have shown that propyl radicals can undergo many thousands of collisions with cold surfaces without reaction (5). The fact that many hydrocarbon free radicals are observed in mass spectrometers is probably due to their ability to survive many wall collisions.

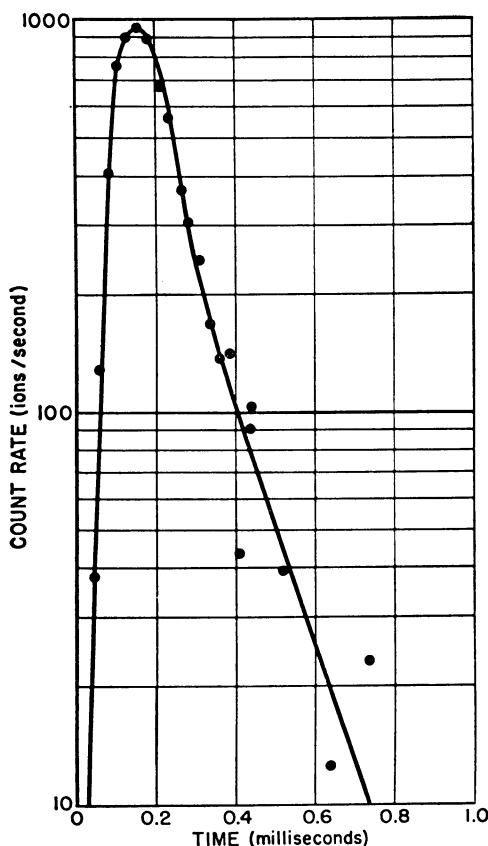


Figure 5. O atoms from pulsed electrical discharge in O_2

Appearance Potential Measurements

The detection and identification of free radicals are intimately connected with measurements of appearance potentials. The appearance potential, $A(R_1^+)$, of the R_1^+ ion from the molecule R_1R_2 in the ionization process



is given by

$$A(R_1^+) \geq I(R_1) + D(R_1 - R_2) \quad (2)$$

where $I(R_1)$ is the ionization potential of the radical R_1 , $D(R_1 - R_2)$ is the dissociation energy of the $R_1 - R_2$ bond, and the inequality indicates that in some cases the fragments may possess excess energy. Since bond-dissociation energies are usually of the order of a few electron volts, it is possible in principle to detect the presence of the free radical R_1 by using electron energies well below the

appearance potential of the R_1^+ ion from all stable molecules in the system that are potential sources of this ion. In many instances, the ionization potential of the radical can be measured rather accurately. This is useful not only in clearly establishing the identity of the radical, but by application of Equation 2 may lead to the determination of bond-dissociation energies. When the radicals are present in large concentrations, they can be analyzed as ordinary components in a gas mixture using electrons with 50- to 75-e.v. energy (19). However, for radicals at low concentration, operation of the mass spectrometer at reduced electron energy results in a much higher effective sensitivity for radical detection.

An example of an ionization potential measurement of a free radical is illustrated in Figure 6, where the radical being studied is OH produced by an electrical discharge in H_2O (9). In this method, which is one of several currently in use for appearance potential measurement, the ionization curve of the unknown is compared with the ionization curve of a reference gas, argon in this case, whose ionization potential is known spectroscopically. From the voltage scale shift required to match the curves in Figure 6, 2.59 e.v., and the ionization potential of argon, $I(\text{Ar}) = 15.76$ e.v., the ionization potential of OH was determined in this experiment as 13.17 e.v. Thus far, although the OH radical has been extensively studied by optical spectroscopy, a spectroscopic check on the value of $I(\text{OH})$ quoted here has not been available. The appearance potential of the OH^+ ion

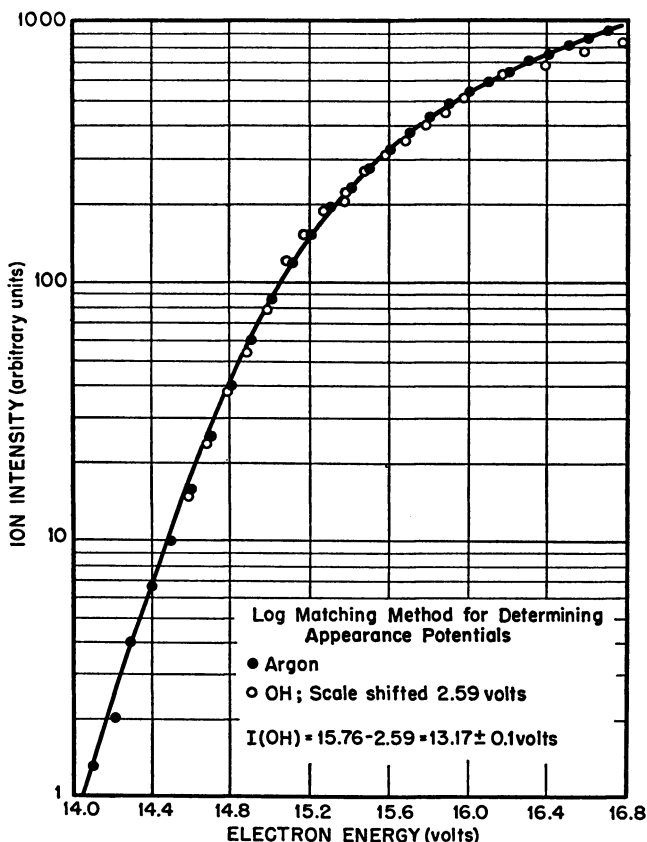


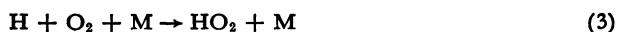
Figure 6. Determination of ionization potential of OH free radical

from H_2O was measured to be 18.19 e.v. This leads to a value of $D(\text{H}-\text{OH}) = 5.02 \pm 0.15$ e.v., and in combination with thermochemical data to $D(\text{O}-\text{H}) = 102.9 \pm 3$ kcal. per mole, which is in good agreement with the spectroscopic determination of $D(\text{O}-\text{H}) = 101.3 \pm 0.3$ kcal. per mole (2).

Studies of HO_2 Free Radical

Because the HO_2 free radical plays an important role in oxidation, combustion, and explosion phenomena, substantial efforts have been made by optical spectroscopy and mass spectrometry to establish the participation of HO_2 in various reactions, to determine its structure, and to measure the thermochemical energies associated with it. As one phase of the mass spectrometric investigation of HO_2 , a series of experiments was carried out to find reactions producing significant concentrations of HO_2 radicals in relatively simple chemical systems. Reactions found to produce HO_2 were: H atoms with O_2 , H atoms with H_2O_2 , O atoms with H_2O_2 , OH with H_2O_2 , photolysis of H_2O_2 , and electrical discharge in H_2O_2 .

The reaction of H atoms with O_2 molecules, the classical method for HO_2 production and the reaction used in the mass spectrometric detection of the HO_2 radical (7), does not yield high concentrations of HO_2 radicals. This is partly due to the requirement of a third-body M to remove excess energy, which makes the reaction inefficient at low pressures. However, the introduction of stabilizing gas molecules into the reaction has the undesirable effect of reducing the sensitivity of the mass spectrometer, because the ion source pressure is approximately the same for the various experiments and, therefore, the detectability of a free radical is essentially determined by its mole fraction in the gas rather than by its absolute concentration. Furthermore, H atoms can react with HO_2 radicals, and attempts to increase the HO_2 concentration by increasing the H atom input were unsuccessful, probably for this reason. Typically, the concentration of HO_2 obtained by the reaction

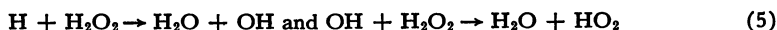


at pressures of 1 to 4 cm. of Hg was of the order of 0.001% and corresponded to the conversion of about 1% of the H atoms in a reaction time of about 0.01 second.

Reactions involving H_2O_2 were found to be rather useful sources of HO_2 radicals. The reactions of H and O atoms and OH radicals with H_2O_2 to produce HO_2 are not limited by third-body requirements and, therefore, are operable at low pressure. It is not always possible to decide on the particular primary reaction involved, because radicals may be generated in subsequent reactions. For example, in the reaction of H with H_2O_2 the HO_2 can be produced either by



or by the sequence of reactions



The concentration of HO_2 obtained from the $\text{H} + \text{H}_2\text{O}_2$ reaction at a pressure of about 0.5 mm. of Hg and reaction time of about 0.01 second was of the order of 0.1%. The reaction of O atoms with H_2O_2 was found to generate HO_2 radicals, but at substantially lower concentration. The reaction involved is



The yield of HO_2 was only about 0.01%, probably because of destruction of HO_2 radicals by O atoms which were necessarily present in large concentration. The

reaction of H_2O_2 with OH radicals from an electrical discharge in H_2O or H_2O_2 proceeds very rapidly by the reaction



and has yielded HO_2 in concentrations of about 0.3%. It was also determined that small quantities of HO_2 could be generated by photolysis of H_2O_2 . This was not particularly surprising, since the primary photolytic decomposition step is the production of OH radicals which had been shown in our previous experiments to produce HO_2 radicals.

A generally applicable technique for the generation of free radicals and other unstable species is the use of a confined low power electrical discharge in a high speed gas stream of a suitable compound. By the partial decomposition of the compound in the discharge an assortment of free radicals, ions, and excited molecules are generated which can react immediately with the undecomposed parent compound. The reaction products are quickly removed from the discharge zone by the streaming gas. The apparatus used is rather simple, consisting of two wire loop electrodes wrapped around the quartz or glass reactor tube, spaced about 1 cm. apart, and connected to a radio-frequency generator. While it is desirable to operate discharges at high power levels when generating simple radicals such as atoms, it is essential in attempting to manufacture complex radicals to be able to operate at low power levels in order to avoid complete decomposition of the parent compound.

The yield of HO_2 radicals from an electrical discharge in H_2O_2 as a function of decomposition is shown in Figure 7. The 0.003- and 0.006-second curves were taken by positioning the electrodes at appropriate distances from the molecular beam entrance aperture. Two features are worth noting. First, the production of HO_2 , which attains a peak value of 0.4%, is relatively insensitive to H_2O_2 decomposition over the range from about 5 to 30%. Secondly, OH radicals are not observable at 0.003 second for decomposition less than 60%, indicating that the removal of OH by reaction with H_2O_2 is very rapid. A lower limit of 4×10^{-18} cc. per molecule per second has been deduced for the rate constant of the $\text{OH} +$

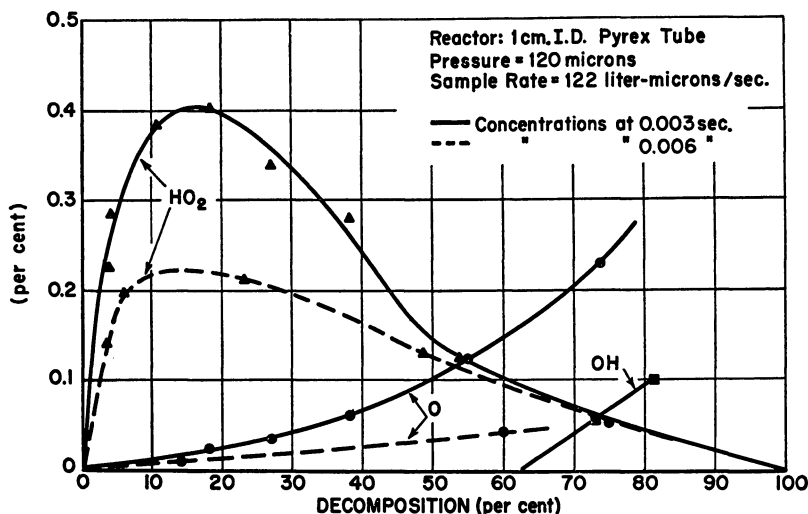


Figure 7. HO_2 radical production by electrical discharge in H_2O_2 .

H_2O_2 reaction. O atoms which are formed in the discharge are considerably less reactive than OH radicals, since they persist long after OH has disappeared. If the discharge power is low, the system after a few milliseconds becomes extremely simple chemically, the major radical component being HO_2 flowing in a stream of H_2O_2 with small amounts of H_2 , O_2 , and H_2O , all of which are nonreactive toward HO_2 .

The ionization potential of HO_2 has been measured using the low-power electrical discharge in H_2O_2 as the radical source. Ionization curves for HO_2 and argon are shown in Figure 8, from which it is found that $I(\text{HO}_2) = 11.53$ e.v. with a precision of measurement of ± 0.02 e.v. The bond-dissociation energy, $D(\text{H}-\text{O}_2)$, can be calculated from $I(\text{HO}_2)$ and the appearance potential of HO_2^+ from HO_2 , $A(\text{HO}_2^+) = 15.36 \pm 0.05$ e.v., together with some well established thermochemical energies. The bond-dissociation energy, $D(\text{H}-\text{O})_2$, thus calculated is 45.9 ± 2 kcal. per mole at 0°K ., and 47.1 ± 2 kcal. per mole at 25°C .

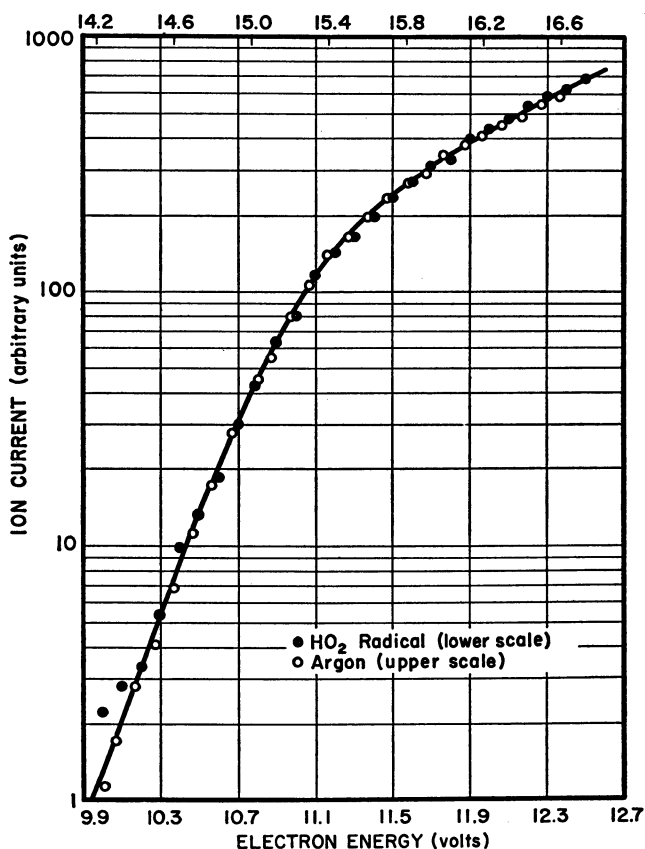


Figure 8. Determination of ionization potential of HO_2 . Voltage scales for HO_2 radical and argon (standard) indicated on lower and upper scales, respectively

The recombination reaction of HO_2 radicals by the gas phase reaction



is, in principle at least, one of the simplest HO_2 reactions to study. Estimates for

the collisional efficiency of this reaction vary from about 10^{-6} (18) to unity (4). A comprehensive series of experiments was carried out to measure the recombination of HO_2 radicals (13). The concentration of HO_2 radicals was followed as a function of time in a flow system. A typical concentration *vs.* time curve is given in Figure 9, which presents data for a borosilicate glass tubing reactor 1.9 cm. in diameter. The decrease in HO_2 radical concentration follows approximately a second-order rate law, as expected, for Reaction 8. However, measurements taken

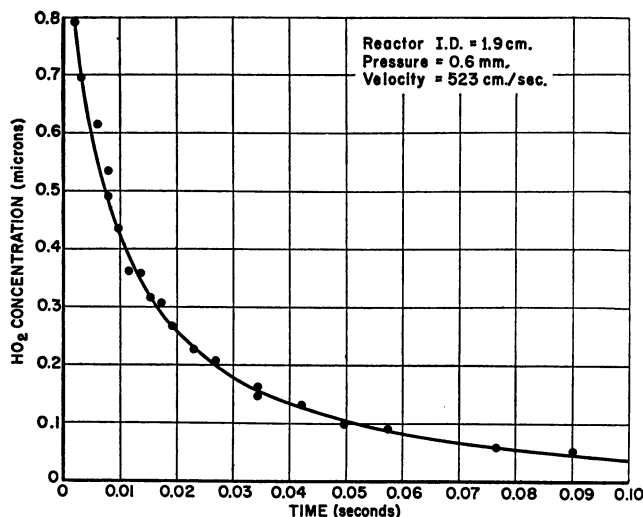


Figure 9. HO_2 concentration as a function of time in a 1.9-cm. diameter borosilicate glass

at different pressures and in reactors of different surface-volume ratios showed conclusively that HO_2 radicals were being consumed not only by the homogeneous reaction but also by a heterogeneous reaction, which also followed a second-order rate law. The surface reaction is very complicated, and is experimentally found to be a function of the partial pressures of the condensable components in the system, indicating that HO_2 radicals and condensable molecules are competing for surface sites. The data have been analyzed to give a value of about 3×10^{-12} cc. per molecule per second for the rate constant of the homogeneous Reaction 8. This corresponds to a collisional efficiency of about 1% for the gas phase reaction of two HO_2 radicals.

Radicals and Unstable Molecules from Nitrogen Compounds

In some instances the distinction between inorganic and organic free radicals will be interpreted loosely—for example, when we consider the reaction of H atoms with a methyl-substituted hydrazine. The radicals discussed were produced either by mixing the products of an electrical discharge with a suitable reactant or by applying an electrical discharge directly to the reactant.

The NH_2 radical was observed in several reactions, including OH with NH_3 , H atoms with N_2H_4 , N atoms with N_2H_4 , H atoms with $\text{H}_2\text{N}_2(\text{CH}_3)_2$, and electrical discharge in N_2H_4 . As expected from bond-energy considerations, the NH_2 radical was not produced by reaction of NH_3 with H, O, or N atoms. The ionization potential of the NH_2 radical has been measured to be 11.4 ± 0.1 e.v.

(11), which when combined with the appearance potential of NH_2^+ from NH_3 , 16.0 ± 0.1 e.v., leads to the dissociation energy $D(\text{NH}_2\text{-H}) = 106 \pm 3$ kcal. per mole, in good agreement with the value 104 ± 2 kcal. per mole reported by Altschuller (1).

The N_2H_3 radical was observed as a product of an electrodeless electrical discharge in N_2H_4 , and also when N_2H_4 reacted with the products of a high power microwave discharge in H_2 or N_2 . The N_2H_3 radical has a low ionization potential, $I(\text{N}_2\text{H}_3) = 7.88 \pm 0.2$ e.v., and as a result it has been detected in concentrations of about 1 part in 10^7 .

A related free radical, $\text{HN}_2(\text{CH}_3)_2$, was obtained by an electrical discharge in unsymmetrical dimethylhydrazine. An appearance potential curve for this radical is shown in Figure 10. The ionization potential of the radical is 6.6 ± 0.3 e.v. If the radical is assumed to be $\text{HN}_2(\text{CH}_3)_2$, then one finds from appearance potentials that $A[\text{HN}_2(\text{CH}_3)_2^+] - I[\text{HN}_2(\text{CH}_3)_2] = D[\text{H} - \text{HN}_2(\text{CH}_3)_2] = 3.4 \pm 0.3$ e.v. = 78 ± 8 kcal. per mole. The N-H bond-dissociation energy thus calculated is in good agreement with a similar calculation for hydrazine, which gives $A(\text{N}_2\text{H}_3^+) - I(\text{N}_2\text{H}_3) = D(\text{H-N}_2\text{H}_3) = 3.3 \pm 0.2$ e.v. = 76 ± 5 kcal. per mole. The close agreement of the N-H bond-dissociation energies indicates that the radical observed is $\text{HN}_2(\text{CH}_3)_2$ rather than $\text{H}_2\text{N}_2\text{CH}_3\text{CH}_2$.

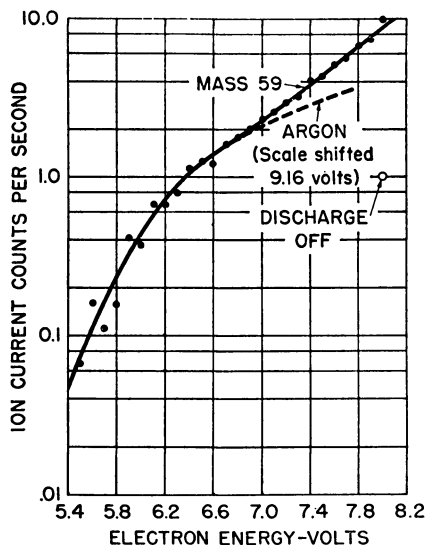


Figure 10. Appearance potential curve for $\text{HN}_2(\text{CH}_3)_2$ radical from discharge in $\text{H}_2\text{N}_2(\text{CH}_3)_2$

The NH radical has not yet been observed mass spectrometrically, despite its demonstrated presence by optical spectroscopy in systems that have also been examined by mass spectrometry. The difficulty is apparently due to the low concentrations of NH radicals in these systems, coupled with the interference generally present at mass 15 from CH_3 and isotopic ^{15}N .

A number of unstable nitrogen compounds have been produced by electrical discharges. These include diimide (N_2H_2), triazene (N_3H_3), tetrazene (N_4H_4), and methylimide (HN_2CH_3), none of which had been previously identified. Di-

imide was discovered (10) during an unsuccessful search for the NH radical in the decomposition of hydrazoic acid. The other compounds were discovered in the products of electrical decomposition of hydrazine and dimethylhydrazine. The discharge arrangement was similar to the one used for HO_2 production from H_2O_2 . The yield of N_2H_2 and N_3H_3 from an electrical discharge in N_2H_4 is given in Figure 11. The similarity of these curves with the HO_2 production curves in Figure 7 is apparent. The maximum concentration of N_2H_2 was obtained with radio-frequency power of about 5 watts. The conversion efficiency of N_2H_4 into N_2H_2 is high at low values of decomposition—for example, at 5% decomposition, 30% of the reacted N_2H_4 shows up as N_2H_2 , while at the peak of the curve about 15% of the N_2H_4 is converted to N_2H_2 .

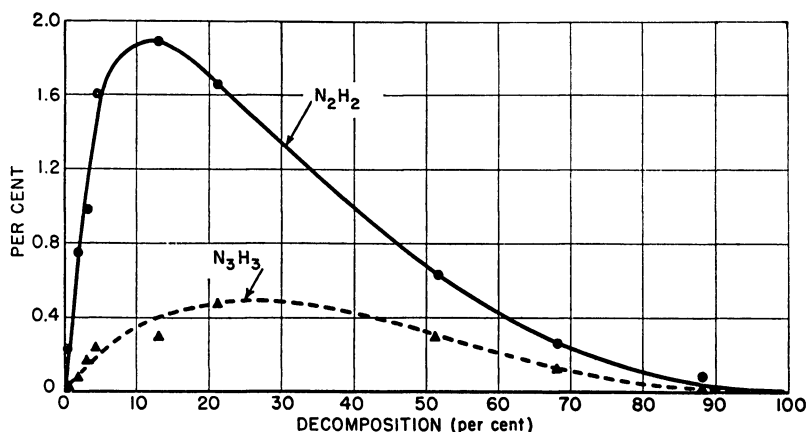


Figure 11. Diimide and triazene production by electrical discharge in hydrazine

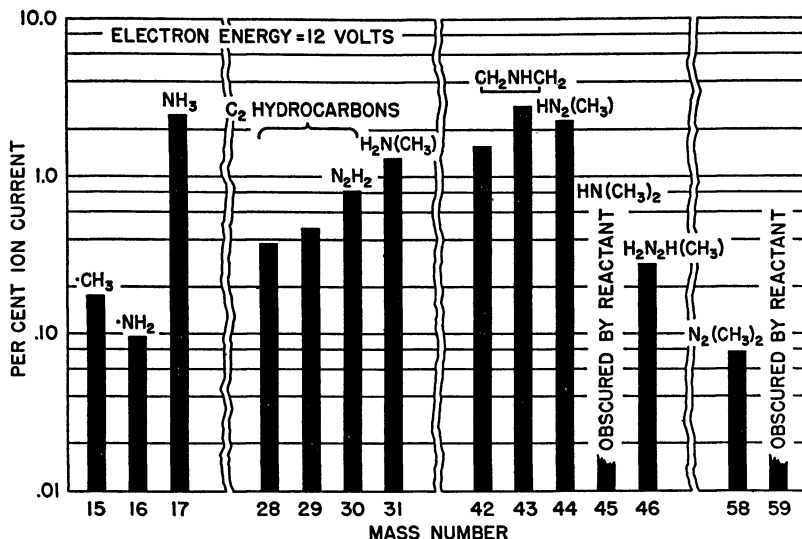


Figure 12. Products of reaction of H atoms with 1, 1-dimethylhydrazine
Low electron energy (12 e.v.) used to reduce dissociative-ionization interferences

The reaction of H atoms from an intense microwave discharge in hydrogen with unsymmetrical dimethylhydrazine produced an interesting array of products. In Figure 12 the ion intensities are referred to the parent hydrazine peak, whose intensity is arbitrarily taken as 100. The reaction reduces the parent peak by about 2%. Except for the dissociative-ionization peaks at mass 45 and mass 59, the ion intensities at the various mass numbers represent ion currents obtained from discharge products. Since the ionization potentials of the components are different, the relative intensities should not be directly used to infer relative concentrations. The presence of the NH_2 and CH_3 radicals is easily recognized. Among the stable components, the identification of NH_3 , N_2H_2 , H_2NCH_3 , and $\text{N}_2(\text{CH}_3)_2$ is straightforward. The peak at mass 44 has been assigned to methylimide (HN_2CH_3) rather than to a free radical. This assignment is substantiated by the fact that some of this material survives condensation and re-evaporation from a cold trap. The other identifications in Figure 12 represent the most probable assignments of the components.

The ionization potentials of the nitrogen compounds discussed above are collected in Table I.

Table I. Ionization Potentials

<i>Radical or Compound</i>	<i>Ionization Potential, E.V.</i>
NH_2	11.4 ± 0.1
N_2H_3	7.88 ± 0.1
$\text{HN}_2(\text{CH}_3)_2$	6.6 ± 0.3
N_2H_2	9.85 ± 0.1
NH_2CH_3	9.27 ± 0.1
N_3H_3	9.6 ± 0.1

Metastable Atoms and Molecules

The study of electronically excited atoms and molecules by mass spectrometry is a relatively recent development. In our mass spectrometer the flight time of a molecule from entrance slit to ionization chamber is a few hundred microseconds, so that only those excited states whose transitions to lower electronic states are highly forbidden can be investigated. Since these metastable species are often readily destroyed by wall collisions, it is generally necessary to employ a collision-free sampling system.

In testing the capability of the mass spectrometer to detect metastable components, we excited helium in a discharge and looked for metastable $\text{He}(2^3\text{S})$ atoms. The ionization curve in Figure 13 shows the presence of metastable He atoms. A rough value of the ionization potential obtained from these data was 5 e.v., which correlates with the spectroscopically calculated ionization potential of $\text{He}(2^3\text{S})$ atoms of 4.77 e.v. In order to observe these atoms it is necessary to maintain the discharge close to the sampling orifice, indicating very rapid destruction of the metastables by wall collision.

The detection of a substantial percentage (10 to 20%) of O_2 molecules in the $^1\Delta_g$ state (0.9772 e.v. above the ground state) when O_2 was passed through an electrical discharge has been reported by us (8) and confirmed in subsequent experiments by Herron and Schiff (16). The O_2 metastable molecules were not readily deactivated by collisions and were studied without difficulty 0.05 second after leaving the discharge and being pumped through 30 cm. of glass tubing.

Active nitrogen has been the subject of a large number of investigations. The principal energetic species in the afterglow are ground state N atoms and

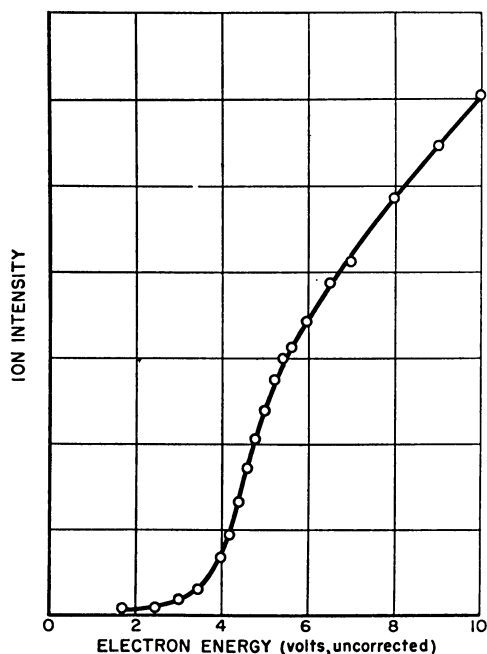


Figure 13. Ionization curve of metastable He atoms from electrical discharge in He

vibrationally excited N_2 molecules. Previous mass spectrometric studies of nitrogen subjected to electrical discharge have indicated only the presence of unexcited $N(^4S)$ atoms and unexcited N_2 molecules (3, 15, 17). Optical absorption

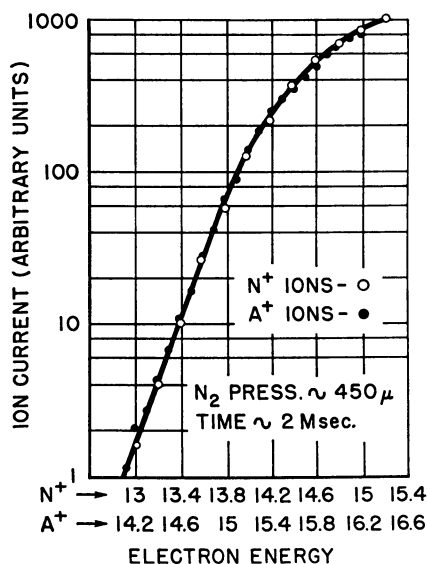


Figure 14. N atom ionization curve
Voltage scales for N atom and argon
(standard) indicated

studies (20) have shown that metastable $N(^2P)$ and $N(^2D)$ atoms are present in the afterglow at concentrations much lower than $N(^4S)$ atoms.

We have observed $N(^4S)$, $N(^2P)$, and $N(^2D)$ atoms and have found N_2 molecules with excitation energies up to several electron volts when nitrogen was subjected under certain conditions to an electrical discharge (14). Under normal discharge conditions these highly excited species are not observed. A typical ionization curve for N atoms produced by an electrical discharge in N_2 is shown in Figure 14. The atomic nitrogen in this case was produced by a high power (80-watt) microwave discharge in N_2 at a pressure of 0.45 mm. of Hg and was observed about 2 msec. after leaving the discharge. The N-atom ionization curve is very closely matched by an argon ionization curve scale shifted by 1.20 e.v., giving an N-atom ionization potential of 14.56 e.v., in excellent agreement with the spectroscopic value, 14.54 e.v.

If nitrogen with a large excess of added helium is subjected to electrical discharge and observed very shortly thereafter, one finds excited N atoms. This is illustrated in Figure 15 for a discharge in N_2 at 0.16 mm. of Hg plus He at 2.2 mm. of Hg observed within 1 msec. The synthetic N^+ curve was fitted to the experimental curve, using the spectroscopically known energies of the $N(^4S)$,

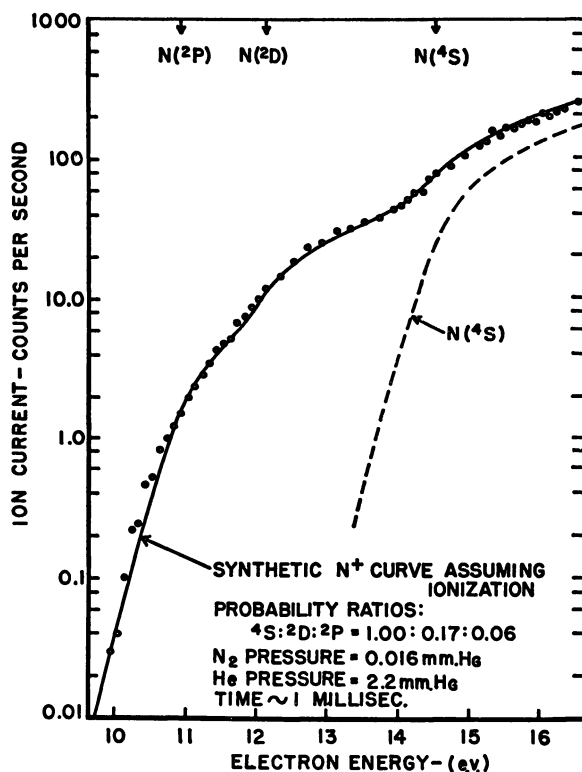


Figure 15. Metastable N atoms from electrical discharge in mixture of N_2 and He

— Calculated from known ionization potentials, indicated in figure, of 4S , 2P , and 2D states
 - - - Estimated ion current due to unexcited $N(^4S)$ atoms

$N(^2D)$, and $N(^2P)$ states and assuming that the ionization cross-section curves for atoms in these states were identical in shape. For convenience in calculation, the atomic ionization probability functions were assumed to be linear. The dashed curve represents the contribution of $N(^4S)$ ionization to the total ion current. The relative concentrations of N atoms in the 4S , 2D , and 2P states are estimated from this analysis to be in the ratio 1.00 to 0.17 to 0.06. The excited atoms were not observed except within a millisecond or so after leaving the discharge, presumably because they diffuse to the walls of the reactor and are destroyed there. Metastable N atoms have also been obtained from a high power discharge in pure N_2 , although in this case the concentrations of $N(^2D)$ and $N(^2P)$ relative to $N(^4S)$ were lower than those obtained in the N_2 -He mixture by a factor of about 25.

The N_2 molecules from the discharge in the N_2 -He mixture have also been studied and found to have excitation energies up to several electron volts. The ionization curve for N_2 is complex and can be explained by the presence of N_2 molecules in known metastable electronic states and in various vibrational levels.

Conclusion

The application of mass spectrometry to the study of inorganic free radicals has been illustrated by several examples from current research. Considerable information has been obtained on the presence, identity, and concentration of free radicals in gaseous systems, and on the mechanism of reactions involving free radicals. From appearance potential measurements a number of bond-dissociation energies have been calculated. The extension of the study of free radicals to include electronically excited species, as illustrated by the study of metastable N atoms and N_2 molecules from electrical discharges, is an area of investigation which may prove to be very interesting. The production of unstable chemical compounds by electrical discharges in high speed gas streams is an area of research which merits further exploration.

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RECEIVED May 3, 1962. Work supported by the Bureau of Naval Weapons, Department of the Navy, under NOrd 7386.