Studies of Gaseous Atom–Molecule Reactions by Electron Paramagnetic Resonance Spectroscopy

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Gaseous atom–molecule reactions have been investigated by a technique that combines magnetic-dipole and electric-dipole e.p.r. spectroscopy. This technique has been used to study some elementary reactions that produce OH, to detect e.p.r. spectra of SH, SD, and SO, and to examine transient species in a number of other atom–molecule reactions.

Introduction

The ability of electron paramagnetic resonance (e.p.r.) spectroscopy to detect and measure low concentrations of free radicals in dynamic systems and to identify and elucidate molecular structure provides a potentially important tool for investigations of mechanisms and kinetics of gaseous, free-radical reactions. Such studies of gaseous reactions by e.p.r. techniques become more feasible as the number of gaseous species with well-characterized e.p.r. spectra increases. Spectra of several gaseous atomic species[1-9] and of a few stable molecular species[10-15] have been detected by conventional e.p.r. techniques. Achievement of detectable concentrations of transient molecular paramagnetic species has proved difficult, not only because of the short lifetimes of such species in most gaseous environments, but because of excessive pressure-broadening of resonance lines, except at very low pressures, and also because of the distribution of free radical populations among several rotational states that exhibit individual e.p.r. spectra. Magnetic-dipole transitions between adjacent Zeeman levels are studied in conventional e.p.r. spectroscopy, but certain paramagnetic diatomic molecules[16] can also exhibit electric-dipole transitions between Zeeman levels. If these molecules have large electric-dipole moments, they are detectable by electric-dipole e.p.r. spectroscopy at much smaller concentrations than are required for magnetic-dipole spectroscopy since the intensity ratio of electric to magnetic transitions is μ_e^2/μ_0^2 (where μ_e and μ_0 represent the permanent electric dipole moment and magnetic dipole moment of the molecule). Electric-dipole e.p.r. spectroscopy was first used[13] to study NO and has recently been utilized by Radford[17a,b] to detect OH in the effluent gas stream from a discharge in H_2O vapor. We present here a technique that combines electric-dipole and magnetic-dipole e.p.r. spectroscopy for studying gaseous atom–molecule reactions

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[1] R. Beringer and M. A. Heald, *Phys. Rev.*, **95**, 1474 (1954).

[2] E. B. Rawson and R. Beringer, *ibid.*, **88**, 677 (1952).

[3] V. W. Hughes and J. S. Geiger, *ibid.*, **99**, 1842 (1955).

[4] M. A. Heald and R. Beringer, *ibid.*, **96**, 645 (1954).

[5] H. G. Dehmelt, *ibid.*, **99**, 527 (1955).

[6] H. E. Radford, V. W. Hughes, and V. Beltran-Lopez, *ibid.*, **123**, 153 (1961).

[7] V. Beltran-Lopez and H. G. Robinson, *ibid.*, **123**, 161 (1961).

[8] J. S. M. Harvey, R. A. Kamper, and K. R. Lea, *Proc. Phys. Soc.* (London), **76**, 979 (1960).

[9] K. D. Bowers, R. A. Kamper, and C. D. Lustig, *ibid.*, **B70**, 1176 (1957).

[10] R. Beringer and J. G. Castle, *Phys. Rev.*, **81**, 82 (1951).

[11] M. Tinkham and M. W. P. Strandberg, *ibid.*, **97**, 951 (1955).

[12] R. Beringer and J. G. Castle, *ibid.*, **78**, 581 (1950).

[13] R. Beringer, E. B. Rawson, and A. F. Henry, *ibid.*, **94**, 343 (1954).

[14] J. G. Castle and R. Beringer, *ibid.*, **80**, 114 (1950).

[15] L. H. Piette, F. A. Johnson, K. A. Booman, and C. B Colburn, *J. Chem. Phys.*, **35**, 1481 (1961).

[16] Diatomic molecules that are not in Σ-electronic states have doubly degenerate Zeeman levels, designated ±λ-states, that become nondegenerate in a magnetic field. Electric-dipole transitions are allowed between +λ- and −λ-states of different Zeeman levels, whereas magnetic-dipole transitions are allowed between λ-states of the same sign. For a further discussion of λ-doubling, see G. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

[17] (a) H. E. Radford, *Phys. Rev.*, **122**, 114 (1961); (b) *ibid.*, **126**, 1035 (1962).

and demonstrate this technique by some qualitative observations on several elementary gaseous reactions.

Experimental

A Varian V-4500 e.p.r. spectrometer and 12-in. magnet were used for this investigation. The spectrometer cavity was replaced by a cavity designed to operate in the TE-011 mode with components of both the electric and magnetic fields of the microwave radiation normal to the steady magnetic field—a necessary condition for detection of both electric-dipole and magnetic-dipole Zeeman transitions. The TE-011 cavity consisted of a hollow cylinder (7-cm. o.d., 3.8 cm. high) that was positioned in the spectrometer magnet with the flat cylinder ends facing the pole pieces. The cylinder wall was fabricated from copper, 1 cm. thick, while the top and bottom of the cavity were closed with glass plates, 0.6 cm. thick and silvered on the inside. The silver layer was sufficiently thin to admit a magnetic field, alternating at 100 kc.p.s., to the cavity but was thick enough to act as a reflecting surface for X-band microwave radiation supplied to the cavity *via* a tuning iris in the cavity wall. Copper tubes (1.2 cm. square, 3 cm. long) projected from either side of the cylinder to provide ingress and egress for quartz tubing used to conduct gas through the cavity without substantial losses of microwave radiation. Gas was contained in the cavity by a quartz vessel of 35-cc. volume, fitted snugly to the inner cavity surface. Quartz tubes (12-mm. o.d.) projected from either side of the cavity liner through the copper ports to provide for gas flow through the cavity. The cavity separated along a median plane between the end plates to permit removal of the quartz liner and was also provided with an insulated slot across the cavity wall to reduce impedance to the 100-kc.p.s. modulating field. Field modulation coils on both cavity faces were driven by a 50-w. amplifier supplied in turn by the Varian 100-kc.p.s. power supply. From observation of "modulation broadening" of resonances of atomic hydrogen, we estimate that a modulation field amplitude of 3.5 gauss could be attained in the cavity. Cavity Q was about 8000 without the quartz liner and 1600 with the liner in place.

The frequency of the microwave radiation supplied to the cavity was monitored with a Hewlett-Packard wavemeter (Model X 350 A). The steady magnetic field was measured with a proton n.m.r.-type gaussmeter (Nuclear Magnetics Corp. precision gaussmeter Model M-2) at a position adjacent to the cavity in the magnet gap. Relative intensities of e.p.r. absorption lines were estimated by comparison of the first derivative absorption curves recorded at constant, low-microwave power levels, taking the intensity of a resonance line as proportional to the product of the square of the separation of the points of maximum slope of the absorption and the maximum amplitude of the derivative curve. Absolute concentrations of paramagnetic species cannot be inferred from intensities of their electric-dipole e.p.r. spectra without a knowledge of their electric-dipole moments.

Gas flow through the cavity was controlled and measured by conventional high-vacuum techniques. Gas entered the cavity through 12-mm. o.d. quartz tubing (inlet A) at low pressure and high velocity ($\approx 10^3$ cm./sec.). A few centimeters upstream from the cavity, the gas passed through an electrodeless discharge induced by 2450-Mc.p.s. radiation from a 125-w. Raytheon diathermy power supply. The discharge-dissociated gas was made to traverse two sharp turns before entering the cavity to prevent strong cyclotron resonance from free electrons produced through photoionization of gas in the cavity by radiation from the discharge.[18] Provision was made to admix a second gas (inlet B) to the discharge-dissociated gas stream at the entrance to the cavity. The two gas streams were mixed in the cavity and pumped out through the outlet tube on the opposite side of the cavity. Gas pressure was measured in the outlet tube a few centimeters downstream from the cavity.

Results and Discussion

The sensitivity of our apparatus for detecting electric-dipole Zeeman transitions was tested by observation of the spectrum[13] of NO flowing through the cavity. A spectrum for NO($^2\pi_{3/2}$, J = $^3/_2$) at 0.15 mm. is shown in Figure 1. Since the nine Zeeman lines show λ-doubling, the resonances arise primarily from electric-dipole transitions. In this experiment

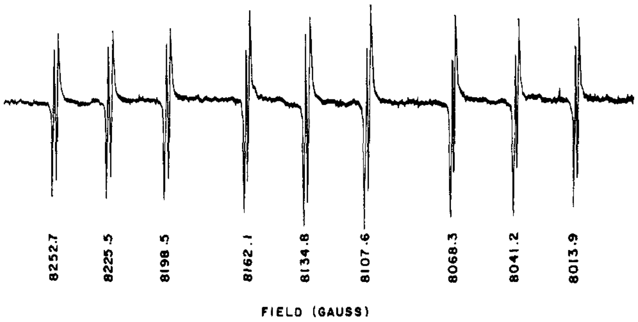

Figure 1. Electric-dipole e.p.r. spectrum of NO($^2\pi_{3/2}$, J = $^3/_2$) at 8.842 × 10^9 c.p.s.

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[18] R. L. Collins, *J. Chem. Phys.*, **34**, 1425 (1961).

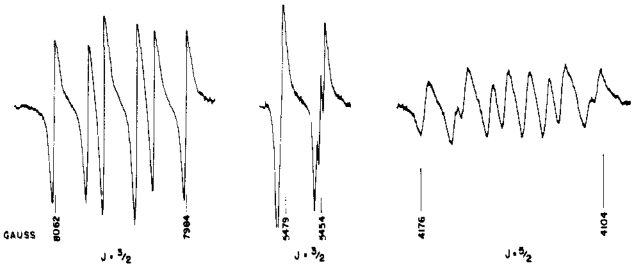

Figure 2. Electric-dipole e.p.r. spectrum of $OH(^2\pi_{3/2}, J = {}^3/_2, {}^5/_2)$ at 8.842×10^9 c.p.s.

the partial pressure of NO in the $^2\pi_{3/2}$, $J = {}^3/_2$ state was 1.5×10^{-3} mm., and it is estimated that a partial pressure of 1×10^{-4} mm. would have been detectable. The sensitivity of the instrument for detecting electric-dipole transitions of other species is modified, of course, by the values of the respective electric dipole moments relative to the dipole moment of NO.

When the effluent gas stream from a discharge in H_2O vapor in inlet A was permitted to flow through the cavity at a pressure of 0.50 mm., magnetic-dipole spectra of $H(^2S_{1/2})$[1] and $O(^3P_2, ^3P_1)$[2] were detected, as well as electric-dipole spectra of $OH(^2\pi_{3/2}, J = {}^3/_2$ and $J = {}^5/_2)$.[17a] Representative spectra of OH are shown in Figure 2. Effluent gas streams from discharges in other gases (*e.g.*, CH_4, CF_4, CCl_4, NH_3, H_2S, and H_2S–H_2O) were examined in a similar way. Although strong magnetic-dipole spectra of atomic species (H, O, N, F, and Cl) were detected, no transient molecular species, other than OH, were observed. We conclude that the lifetimes of most transient molecular radicals are so short that the concentrations of such species obtained in a discharge outside of the e.p.r. cavity decrease to undetectable levels before the dissociated gas reaches the cavity. Indeed, although Radford[17a] inferred that the OH that he detected by e.p.r. originated in a discharge some distance upstream from the spectrometer cavity, other work[19] indicates that the lifetime of OH is too short to permit detectable concentrations of OH to survive more than a few millimeters from the discharge and suggests that OH detected by e.p.r. results from reactions in the cavity of other relatively long-lived reactive species from the discharge. Thus, we were led to attempt to produce transient molecular radicals in the cavity by admixing a gas stream containing high concentrations of atoms (such as H from dissociated H_2O or H_2) from inlet A with a molecular gas from inlet B at the entrance to the cavity. This technique was used, in experiments described below, to show that OH is formed in detectable quantities by atom–molecule reactions of species in discharge-dissociated water vapor, to detect some new e.p.r. spectra, and to make some qualitative observations on elementary atom–molecule reactions.

(*1*) *Production of OH by Reactions of H and O with H_2, O_2, and H_2O.* When partially dissociated H_2 flowed through the cavity at 0.30 mm. pressure, a strong magnetic-dipole spectrum of H was detected. When sufficient O_2 was added to the gas stream at the cavity entrance to raise the pressure to 0.40 mm., OH was detected. Further addition of O_2 caused the intensity of the OH spectrum to increase until the pressure was 0.54 mm. and to decrease at higher pressures. The intensity of the H spectrum also increased as O_2 was added as pressure increased from 0.30 to 0.40 mm. but decreased at higher O_2 flow rates. Atomic oxygen was not detected. These observations can be explained in terms of the following reactions

$$H + O_2 \longrightarrow OH + O \quad (1)$$

$$O + H_2 \longrightarrow OH + H \quad (2)$$

$$2OH \longrightarrow H_2O + H \quad (3)$$

Hydroxyl radicals are produced from O_2 and H_2 by reactions 1 and 2 without diminishing the H concentration. Reaction 3 causes an increase in the H concentration. Other reactions among these species are possible and undoubtedly occur. When the O_2 flow becomes large, back diffusion of O_2 into inlet A occurs, and the transient paramagnetic species react before they reach the cavity.

When H_2O was added to discharge-dissociated H_2 at 0.30 mm. pressure, no OH was detected until the total pressure reached 0.60 mm. The intensity of OH increased as the H_2O flow was increased while the intensity of H remained constant, and O was not detected. It is suggested that the following equilibrium is established in the gas stream through the cavity.

$$H + H_2O \rightleftarrows H_2 + OH \quad (4)$$

The bond energies of these species require that the equilibrium be strongly displaced in favor of H and H_2O. Consequently, the addition of H_2O can cause large increases in the OH concentration while only producing a very small decrease in the H concentration.

Partially dissociated O_2 flowing through the cavity at 0.45 mm. pressure gave rise to a detectable spectrum of $O(^3P_2)$. When H_2 (25% H_2 in argon) was added to this gas stream at the cavity entrance, the intensity of O decreased, but neither OH nor H was detected. However, addition of H_2O to discharge-dissociated O_2 at 0.50 mm. caused the O spectrum to disappear and the spectrum of OH to appear when the total pressure

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[19] K. Kaufman and F. P. Del Greco, *J. Chem. Phys.*, **35**, 1895 (1961).

had increased to only 0.55 mm. The hydroxyl radicals detected in this experiment may arise from the endothermic reaction

$$O + H_2O \longrightarrow 2OH \tag{5}$$

or from reaction of H_2O with O_3 in the oxygen stream.

E.p.r. spectra of H, O, and OH were detected in the gas stream from a discharge in H_2O. When O_2 was added to this gas stream at the cavity entrance, the intensity of the OH spectrum increased.

It is concluded from these experiments that OH is indeed produced in detectable quantities *in situ* in the gas stream by reactions among the species (H, O, H_2, O_2, and H_2O) in the effluent stream from a discharge in H_2O.

(*2*) *Production of* $SH(^2\pi_{3/2})$, $SD(^2\pi_{3/2})$, *and* $SO(^3\Sigma)$. When H_2S was added at the cavity entrance to a stream of partially dissociated H_2O, a 12-line spectrum attributed to electric-dipole transitions of $SH(^2\pi_{3/2}, J = {}^3/_2)$ was detected. The spectrum of SH, shown in Figure 3, was most intense when the H_2O pressure was 0.5 to 0.6 mm. and sufficient H_2S was added to just quench the spectrum of H (a pressure increment of about 30%). The production of SH is attributed to the reaction

$$H + H_2S \longrightarrow H_2 + SH \tag{6}$$

When H_2S was added to dissociated D_2O in a similar manner, spectra of both SH and SD were detected, presumably as a consequence of the reactions

$$D + H_2S \longrightarrow HD + SH \tag{7}$$

$$D + SH \longrightarrow H + SD \tag{8}$$

Four other e.p.r. lines were detected when H_2S was added to dissociated H_2O or D_2O. These lines are believed to arise from electric-dipole transitions between Zeeman levels of *different* rotational states of $SO(^3\Sigma)$ which is produced by elementary reactions such as

$$SH + OH \longrightarrow SO + H_2 \tag{9}$$

$$SH + H \longrightarrow S + H_2 \tag{10}$$

$$SH + O \longrightarrow S + OH \tag{11}$$

$$SH + OH \longrightarrow S + H_2O \tag{12}$$

$$S + O \longrightarrow SO \tag{13}$$

Details of the e.p.r. spectra of SH, SD, and SO have been presented elsewhere.[20] The assignment of the spectrum of $SO(^3\Sigma)$ has been confirmed and extended by Daniels and Dorain[21] through observations of SO from discharge-dissociated SO_2.

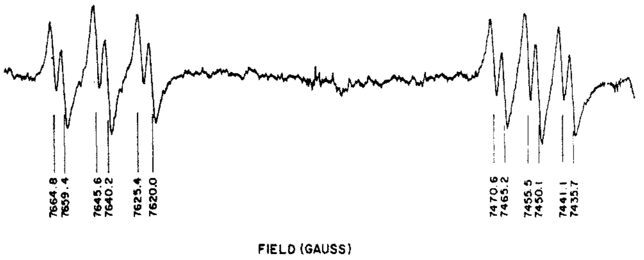

Figure 3. Electric-dipole e.p.r. spectrum of $SH(^2\pi_{3/2}, J = {}^3/_2)$ at 8.850×10^9 c.p.s.

(*3*) *Other Atom–Molecule Reactions.* The fast, stoichiometric reaction[22]

$$H + NO_2 \longrightarrow NO + OH \tag{14}$$

was chosen for a further test of the technique that has been presented here for the study of atom–molecule reactions. Nitrogen dioxide was added at the cavity inlet to a stream of partially dissociated H_2 at 0.40 mm. The spectrum of OH was detected and increased in intensity as NO_2 was added until the total pressure of the flowing gas reached 0.50 mm. The intensity of the spectrum of H decreased uniformly as the NO_2 flow rate was increased. No attempt was made to follow the concentrations of NO or NO_2 by e.p.r. although this should be quite feasible.[13,14] When NO_2 was added in a similar manner to dissociated H_2O, the intensity of the OH spectrum increased, and the intensity of H decreased as expected.

In other experiments, various gases were added at the cavity entrance to a stream of partially dissociated nitrogen at 0.60 mm. Addition of H_2O to the nitrogen stream caused a decrease in the intensity of the e.p.r. spectrum[4] of N, but spectra of H, O, or OH were not detected. Small amounts of CS_2 or *n*-propane quenched the spectrum of N, but again no other species were detected. When NO was added to the nitrogen stream, the intensity of N decreased, and O was detected in accordance with the known reaction[23]

$$N + NO \longrightarrow N_2 + O \tag{15}$$

The spectrum of O reached maximum intensity when sufficient NO was added to just quench the spectrum of N.

When *n*-propane was added to a stream of partially dissociated H_2 at 0.60 mm., the intensity of the H spectrum decreased, but no new species were detected.

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(20) C. C. McDonald, *J. Chem. Phys.*, **39**, 2587 (1963).

(21) J. M. Daniels and P. B. Dorain, *ibid.*, **40**, 1160 (1964).

(22) W. A. Rosser and H. Wise, *J. Phys. Chem.*, **65**, 532 (1961).

(23) P. Harteck, R. R. Reeves, and G. Mannella, *J. Chem. Phys.*, **29**, 608 (1958).

However, when *n*-propane was added to a stream of dissociated D_2O, the intensity of D decreased, and a spectrum of H appeared and then was quenched at higher propane flow rates. These observations can be accounted for by the reactions

$$D + C_3H_8 \longrightarrow HD + C_3H_7 \qquad (16)$$

$$D + HD \longrightarrow D_2 + H \qquad (17)$$

Addition of *n*-propane to dissociated O_2 resulted in the disappearance of O and the appearance of a weak spectrum of OH, presumably as a consequence of the reaction

$$O + C_3H_8 \longrightarrow OH + C_3H_7 \qquad (18)$$

In summary, it appears that the technique that has been presented here, combining magnetic-dipole and electric-dipole e.p.r. spectroscopy to examine atom–molecule reactions taking place in the gas within the spectrometer cavity, can be used for quantitative studies of species for which e.p.r. spectra have been established. It also offers an approach for detecting new e.p.r. spectra of other species. For example, molecules such as CF, CCl, CH, NS, PO, SiH, and TiO should exhibit electric-dipole transitions between Zeeman levels within rotational states of these species. This list can be expanded considerably if one considers molecules such as SO in which electric-dipole transitions between Zeeman levels of different rotational states are possible.