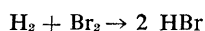


## Applications of Electron Spin Resonance to Gas-Phase Kinetics

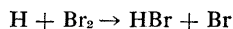
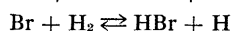
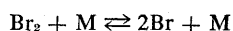
The quantitative detection of free radicals is used to measure elementary reaction rates.

A. A. Westenberg

Practically all (if not all) chemical reactions occurring to a measurable extent in the gas phase involve the unstable atoms or fragments of molecules which are designated generally as free radicals. The classic example used in most textbooks to illustrate this fact is the hydrogen-bromine reaction. The overall reaction of  $\text{H}_2$  and  $\text{Br}_2$  to give  $\text{HBr}$  according to



does not actually take place by the direct reaction of one molecule of  $\text{H}_2$  with one of  $\text{Br}_2$  to give two molecules of  $\text{HBr}$ . Fifty years ago it was shown that experimental data on the rate of  $\text{HBr}$  production could be interpreted satisfactorily if the actual chemical events occurring were



where  $\text{M}$  is any species present. The labile intermediates  $\text{Br}$  and  $\text{H}$  are the key ingredients in this simple chain mechanism, and the classical method of dealing with them is to assume that their concentrations are very small as compared to the other species, so that their net rates of change may be set equal to zero. This is the so-called "steady-state approximation" which has been applied in chemical kinetics but which is clearly a subterfuge that may or may not be valid in a given system.

Each of the chemical steps which actually takes place in a reacting system, as in the above example, is called an elementary reaction. The modern science of chemical kinetics is largely concerned with the measurement and theoretical prediction of the rates of these elementary reactions. In a complex practical situation the overall kinetic behavior is determined by the totality of all the individual elementary rates; if these are reliably known, it is a relatively trivial matter (1) to calculate the overall rate of reaction with modern computers. It is much more difficult (usually impossible) to deduce the rates of the elementary steps from overall measurements than it is to study the elementary reactions directly, provided that suitable techniques are available for the latter. The development and exploitation of new experimental techniques for isolating and measuring individual radical-molecule and radical-radical reaction rates have led to the striking progress which has characterized research in chemical kinetics in the last decade. One of these new techniques is the subject of this article. Since elementary gas reactions usually involve free radicals as reactants or products (or both), a reliable method for the detection and measurement of these species is clearly desirable for a study of their kinetics. Electron spin resonance (ESR) spectroscopy has proven very useful for this purpose.

### ESR as a Free Radical Detector

Several techniques have been used successfully for measuring the concentrations of atoms and radicals in kinetic applications, most of which have been reviewed by Jennings (2). Specific methods for oxygen atoms have been discussed by Kaufman (3), for hydrogen atoms by Thrush (4), and for nitrogen atoms by Brocklehurst and Jennings (5). Chemiluminescent photometry, which was reviewed by Thrush (6), is of value for measurements of relative atom concentrations in certain restricted cases. The glow associated with the addition of a trace of  $\text{NO}$  to a gas stream containing  $\text{O}$  atoms is proportional to the concentration of the latter, and this is perhaps the best known of the chemiluminescent techniques. The direct detection of free radicals by mass spectrometry, as discussed by Foner (7), has been used widely in kinetic studies. This method of detection has the advantage of considerable versatility and sensitivity, but it is not suitable for accurate absolute measurement of atoms and radicals because of the lack of suitable calibration methods. It also requires that the reacting system be physically sampled through a probe or pinhole of some sort, which can sometimes be an undesirable perturbation.

Recently there has been a strong surge of interest in the application of ESR spectroscopy to gas-phase kinetic studies. This type of spectroscopy has been enormously useful in the study of free radicals in the solid and liquid phases, trapped in inert matrices, and in biological systems; until the last few years practically all ESR work was confined to condensed phases. The first ESR detection of odd-electron species in the gas phase was carried out nearly 20 years ago by Beringer and his co-workers (8) on the paramagnetic gases  $\text{O}_2$  and  $\text{NO}$  (which may be thought of as stable free radicals); this work was followed by studies on free  $\text{H}$ ,  $\text{O}$ , and  $\text{N}$  atoms. Aside from its purely spectroscopic aspects, however, there

The author is supervisor of research in chemical physics at the Applied Physics Laboratory, Johns Hopkins University, 8621 Georgia Avenue, Silver Spring, Maryland.

was no exploitation of this technique in the gas phase until the paper by Krongelb and Strandberg (9) appeared in 1959. This paper, together with the greater availability of excellent commercial ESR spectrometers, has stimulated much of the ensuing flurry of activity associated with the application of ESR to kinetic problems.

The basic principles of ESR spectroscopy are well known, and only a few remarks will be given here. Several references are available (10), and Foner's article (7) discusses the fundamental principles. In its simplest form, as with free atoms such as H, for example, the phenomenon depends upon the species having one or more unpaired electrons and hence an electron spin magnetic moment. When the species is placed in a steady d-c magnetic field, its energy levels are split in accordance with the various allowed orientations of the electron spin moment (the Zeeman effect), and transitions between the split levels may be excited by the absorption of radiation of the proper frequency. Complications due to nuclear spin may sometimes occur, but these are easily taken into account. The ESR spectra of atoms are rather simple and uncluttered, consisting of only a few lines. In practice, the absorption is done with the sample contained in a resonant cavity at a fixed frequency, the lines being found by varying the d-c magnetic field. Since the frequencies used are in the microwave region ( $\sim 9000$  megacycles), all the power of modern electronic techniques can be brought to bear in controlling and measuring the spectra with great precision. The cavity is usually of cylindrical geometry (perhaps 3 to 4 cm in diameter and about 3 cm long)

with access holes in the end plates so that a sample tube can pass through coaxially.

The absorptions in simple atoms are brought about by coupling with the microwave magnetic field; that is, they are magnetic dipole transitions. This is also the case in molecular  $O_2$ , where the electron spin magnetic moment interacts with the angular momentum caused by rotation of the molecule and results in a very complex spectrum. The details have been thoroughly analyzed, however. When the free radical is diatomic and has a permanent electric dipole moment, as in OH and SO or the stable molecule NO, and also has a nonzero orbital angular momentum state ( $\pi$ ,  $\Delta$ , . . .), there is the possibility of coupling with the microwave electric field to get electric dipole transitions. These usually have much greater intensity than transitions of the magnetic dipole type (which may also be present) and may be very useful for this reason. In this case, possession of an unpaired electron is not a necessary condition for resonance absorption, and species with zero net electron spin ( $^1\Delta$  states, for example) have been detected. For this reason Carrington (11) has proposed the term "electron resonance" spectroscopy rather than "electron spin resonance" as being more general, since the Zeeman-type splittings can occur with either electron spin or orbital angular momentum.

The species which have thus far been detected in the gas phase by ESR include: H, N, O, S, P, F, Cl, Br, and I atoms; diatomic species  $O_2(^3\Sigma, ^1\Delta)$ , NO, OH, SH, SeH, TeH,  $SO(^3\Sigma, ^1\Delta)$ , ClO, BrO, and NS; triatomic species  $NO_2$  and  $NF_2$ ; and free electrons. The number and variety make it evident

why the technique is of such interest to kineticists. Only two species containing more than two atoms are mentioned. The prospects for the detection of polyatomic radicals are not very promising, although considerable effort has been made in this direction and will no doubt continue. There are basic reasons (11) why nonlinear polyatomic radicals are unlikely to give spectra which are either intense enough or in suitable regions of the magnetic field for easy detection, although measurement of radicals such as  $CH_3$ ,  $CH_2$ , and  $HO_2$  would be of great importance for kinetics. Free electrons give very intense signals in ESR spectrometers, although these arise from the classical phenomenon of cyclotron resonance absorption and have nothing to do with electron spin. The deuterium analogs D, OD, and SD have also been detected.

### Radical Concentration Measurement

For relative concentration measurements the ESR method is quite simple. With all instrumental variables of the spectrometer held fixed or suitably taken into account, the absorption signal is proportional to the number of radicals per unit volume present in the resonant cavity. The typical spectrometer displays the signal on a pen recorder in a form qualitatively similar to the first derivative of the absorption curve, so that relative concentrations are easily compared by monitoring the peak-to-peak height of the trace. In this type of display it is necessary that any time variation of the radical concentration in the cavity be slow as compared to the time required (1 minute, for example) for the recorder to trace out the signal; thus this method is usually employed with the steady-state flow systems to be discussed below. For transient concentration measurements a direct oscilloscope display may be used, although with considerably lower precision.

The problem of determining absolute concentrations is a more difficult one, and here the key suggestion was made by Krongelb and Strandberg (9). As with any spectroscopic technique, the way to circumvent the practically insurmountable problem of accounting for all of the many instrumental factors which affect the output signal is to convert the measurement to a relative one by comparing the unknown with a calibrating substance at known con-

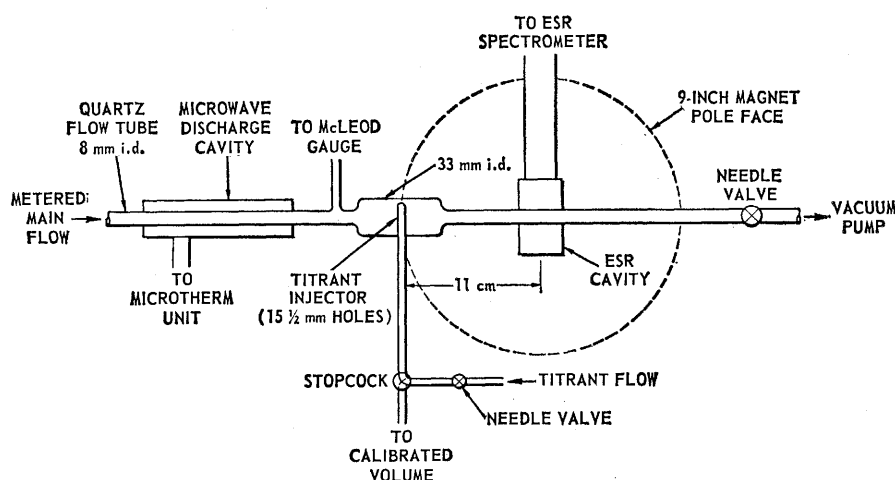


Fig. 1. Schematic diagram of fast flow apparatus used for comparing ESR concentration measurements with gas-phase titrations.

centration. The idea of Krongelb and Strandberg was that O<sub>2</sub> be used as a stable reference gas, since it could be readily introduced into the cavity at a known pressure. The importance of this suggestion lies in the fact that both O<sub>2</sub> and the free atoms of unknown concentration are gases and therefore fill the cavity in exactly the same way (12). This is an essential feature of a suitable reference substance, since the spectrometer signal depends upon the geometry of the sample in the cavity, that is, the volume of sample which the oscillating microwave field "sees." This must be identical in both the unknown and standard, and the only way to assure this practically is for the standard to be a stable gas. The solid standards used in condensed-phase ESR work are not suitable for gases.

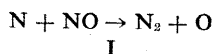
Since the ESR spectrum of O<sub>2</sub> is of the magnetic dipole type, it is a useful reference gas for simple atoms, which also have magnetic dipole spectra. Krongelb and Strandberg made their proposal in connection with determinations of O atoms and showed how the intensities of the O transitions could be rigorously related to those of O<sub>2</sub>. Similar relations were later developed for N and H atoms (13) and for the halogens Cl, Br, and I (14). For radicals that exhibit electric dipole transitions, the use of O<sub>2</sub> as a reference is not satisfactory, because the oscillating microwave radiation in the cavity has its magnetic- and electric-field vectors oriented at right angles to each other. This means that the crucial geometric factors for magnetic and electric dipole transitions are different. Even though the magnetic- and electric-field vectors may be related in principle, in practice the fields in the cavity are distorted for various reasons so that the theoretical calculation is not reliable. Thus, what is required for radicals with electric dipole transitions is a reference gas having the same type of spectrum. The stable gas NO is the obvious choice for this purpose, and the necessary intensity relations were worked out (14) for measuring absolute OH concentrations in this way. Since the cyclotron resonance absorption of free electrons also results from interaction with the microwave electric field, the theory relating electron signal intensity to NO was included in this paper. By proper orientation of a suitable cavity in the external magnetic field, both magnetic and electric dipole transitions can be detected with the same cavity.

Table 1. Comparison of absolute N concentrations determined by NO titration with initial N and product O (after titration with NO) concentrations measured by ESR.

| Total pressure (mm) | Percent atoms |         |         |
|---------------------|---------------|---------|---------|
|                     | N (titration) | N (ESR) | O (ESR) |
| 0.41                | 0.96          | 0.88    | 0.90    |
| .54                 | .62           | .67     | .68     |
| .66                 | .46           | .41     | —       |
| 1.04                | .41           | .46     | .37     |
| 1.07                | .20           | —       | .19     |

The general procedure for measurements of absolute concentrations, therefore, is to obtain a recorder trace of a suitable line in the spectrum of the atom or radical, along with a total pressure measurement of the mixture. The system is then filled with pure O<sub>2</sub> (or NO) at a known pressure, and one or more of its spectral lines is recorded. The ratio of the experimental integrated intensities is obtained, usually by straightforward numerical means (the first moments of the recorded signals are actually required), and this, together with the two pressures and the theoretical intensity relations, permits the concentration of the unknown radical to be determined. Careful attention to certain instrumental variables in the two measurements is necessary, of course (13).

In any fairly sophisticated technique such as this, which has a number of possible experimental and theoretical pitfalls, it is comforting to test it in some way. Thus, after the procedure had been outlined in principle, Westenberg and deHaas tried to formulate an appropriate test (13). The only good approach which suggested itself was to compare the absolute concentration measurements made by the ESR technique with those of another entirely independent technique, and the most reliable alternative seemed to be the method of gas-phase titration (3). The trick here is to add a "titrating" gas with which the atom being measured reacts with great speed in a simple, known way. For example, N atoms react cleanly and very rapidly with NO according to



Therefore, if NO is metered into a flowing N-containing gas stream at a gradually increasing rate until the N just vanishes, at this end point the NO flow is equal to the original flow rate of N atoms. Since the end points of

such reactions are often accompanied by characteristic chemiluminescent color changes, the analogy with the more familiar acid-base titrations is apparent.

In our work the titration reaction could be followed by the ESR signals themselves. The apparatus (Fig. 1) consists of a conventional fast flow system in which linear gas velocities up to about 5000 cm/sec can be attained at pressures of the order of 1 mm. The system is constructed entirely of quartz, this material being essential to minimize dielectric losses in the section passing through the ESR cavity. In a typical experiment N<sub>2</sub> gas was fed into the system through the microwave discharge cavity (2450 megacycles), where the N<sub>2</sub> was dissociated to a small extent so that it contained less than 1 mole percent N atoms. The gas then flowed past the titrant injector (consisting of several small holes for good mixing), through the ESR cavity in the magnetic field, and then to the pump. The ESR cavity was located as close to the titrant injector as physically possible, so that there was no significant recombination of atoms on the wall between the two points. With the ESR spectrometer tuned to one of the resonance lines of the N atom, the N signal was monitored as gradually increasing flows of NO were metered into the injector. Figure 2 shows that the N signal decreased linearly with NO flow as required by the simple one-step titration reaction I. At the same time the product O atom was generated in corresponding fashion; this was demonstrated by tuning to the O line and repeating the NO addition (Fig. 2). The end point where N vanishes is sharply defined. The gradual decrease in O beyond this point is caused by a subsequent reaction (O + NO + M → NO<sub>2</sub> + M) that is of no consequence here.

The significant comparison was between the absolute concentration of N, as determined from the metered NO rate at the titration end point, and the initial N and product O concentrations from ESR using the O<sub>2</sub> standard. Results of this test are given in Table 1 for several different flow pressures and atom concentrations. The agreement between the results based upon the two independent techniques is good (±10 percent) and strongly supports the validity of both. Similar successful tests have been made directly on O and H atoms by use of other titration reactions, so that the reliability of the ESR method for the measurement of

absolute concentrations may be regarded as well established.

The advantages of ESR spectroscopy for gas-phase work may be summarized as follows:

1) It is reliable. The spectra of atoms and radicals are quite simple and generally well analyzed. Interfering spectra or ambiguities in identification practically never occur; thus there is no doubt about the identity of the radical being measured.

2) Concentration measurements can be quite precise and accurate. Absolute concentrations can be measured to an accuracy of about  $\pm 10$  percent, errors being introduced mainly in the required numerical integration of the signals. The precision of relative measurements is better than this.

3) It is fairly sensitive. Roughly  $10^{12}$  radicals per cubic centimeter can be accurately measured, which corresponds to about 0.003 percent at 1 mm pressure and room temperature. Other techniques are considerably more sensitive in specific cases, for example, the NO photometric detection of O.

4) It is versatile.

The disadvantages are:

1) It requires rather complex and expensive instrumentation. The kineticist interested only in ESR applications need not worry much about the complexities, since these have been largely

overcome in commercial spectrometers which are now routinely available in many laboratories. A major investment in equipment is involved, however.

2) Concentration measurements are averaged over a fairly large volume in the cavity (several cubic centimeters, typically). Where sharp concentration gradients are involved, this lack of spatial resolution could be a problem, although this may sometimes be alleviated by combining with probe sampling prior to detection.

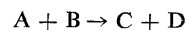
3) Careful attention to a number of subtle experimental details is essential for the achievement of reliable results. This is true of other methods as well, but the complexity of the basic phenomena involved in ESR detection makes it particularly important that they be thoroughly understood and considered.

From the foregoing remarks it seems fair to say that ESR spectroscopy is probably the most powerful of the available techniques for the detection and quantitative measurement of gas-phase free radicals.

#### Applications to OH Kinetics

The goal of experimental chemical kinetics at a fairly fundamental level is the elucidation of the elementary steps

which take place in a given reacting system and the measurement of the rate of each elementary reaction (15). The latter involves determining the rate coefficient for the reaction. Thus in the bimolecular step



the basic equation for the time rate of change of concentration may be written

$$-d[A]/dt = -d[B]/dt = d[C]/dt = d[D]/dt = k[A][B] \quad (1)$$

where concentrations (in moles per cubic centimeter) are denoted by brackets and  $k$  is the rate coefficient (or rate constant, an unfortunate misnomer). The quantity  $k$  is a function of temperature  $T$ , and an important part of kinetic research concerns the determination of this temperature dependence.

Almost all of the significant kinetic applications of ESR have involved steady-state flow systems of some sort, since the full precision and power of the method can be best exploited in this way. The reaction can then be followed as a function of distance instead of time, which permits the radical concentrations to be observed at leisure, so to speak, since for any fixed reaction distance the concentration in the ESR cavity is constant in time. The use of fast flow reactors has been de-

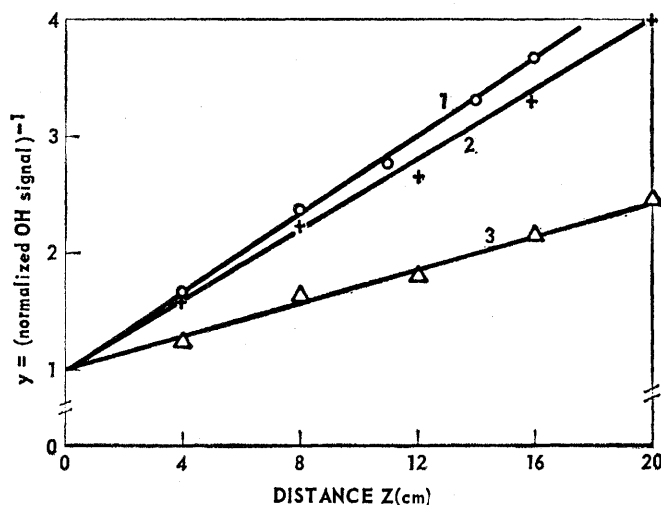
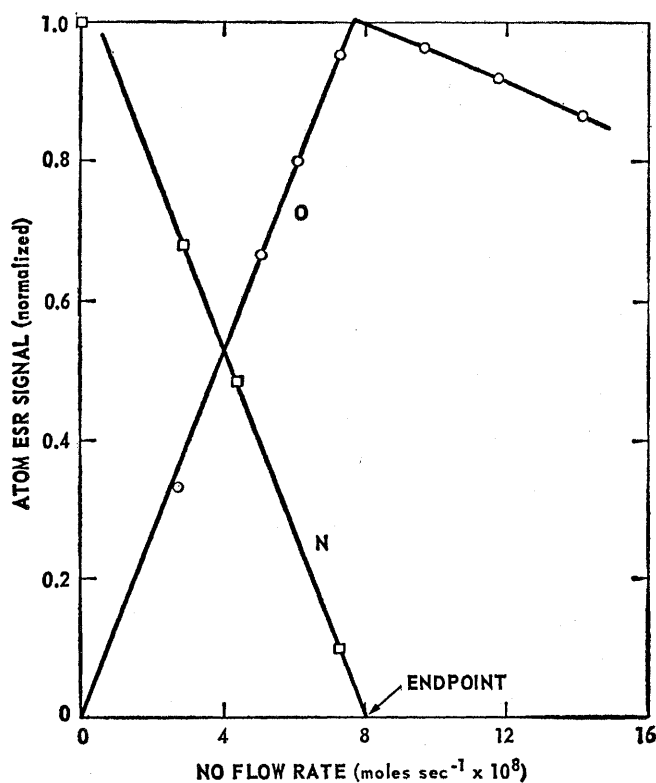
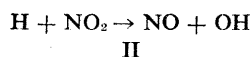


Fig. 2 (left). Disappearance of N and appearance of O as measured by ESR during titration with NO for the reaction  $N + NO \rightarrow N_2 + O$ . Pressure = 1.0 mm; total flow rate ( $N_2$ ) =  $1.5 \times 10^{-5}$  mole/sec; initial N concentration = 0.52 mole percent.

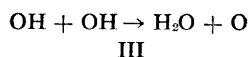
Fig. 3 (above). Plots showing linear dependence of reciprocal OH concentration on reaction distance  $z$  due to reactions III and IV;  $y = [OH]_0/[OH]$ . Curve 1: Pressure = 1.03 mm; velocity = 3370 cm/sec;  $[OH]_0 = 1.22 \times 10^{-10}$  mole/cm<sup>3</sup>; argon carrier. Curve 2:  $P = 0.93$  mm;  $v = 3050$  cm/sec;  $[OH]_0 = 1.06 \times 10^{-10}$  mole/cm<sup>3</sup>; argon carrier. Curve 3:  $P = 1.26$  mm;  $v = 4870$  cm/sec;  $[OH]_0 = 0.72 \times 10^{-10}$  mole/cm<sup>3</sup>; helium carrier.

scribed by Thrush (6). As far as the author is aware, the first reliable measurements of well-defined gas-phase rate coefficients by ESR detection were those involving OH radicals performed in our laboratory in 1965 (16), although Krongelb and Strandberg (9) had made a preliminary attempt to determine the recombination rate of O atoms and Marshall (17) had reported a similar measurement on N atoms which is now known to be in error (13). The study of OH reactions requires, first of all, a convenient source of radicals; Del Greco and Kaufman (18) showed that the very fast reaction

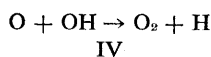


was a satisfactory way of producing OH. This OH source was used in our kinetic work, which was done in a flow system essentially the same as that shown in Fig. 1 except that the NO<sub>2</sub> injector was simply a ring of holes around the circumference of a flow tube of uniform diameter, so that the linear gas velocity could be accurately calculated from the total flow rate, pressure, and temperature. The ESR cavity and its associated magnet could be moved along the tube downstream of the NO<sub>2</sub> injector for a distance of about 20 cm.

The OH experiments were carried out as follows. A steady flow of inert gas (usually helium) containing a trace of H<sub>2</sub> was passed through the discharge where the H<sub>2</sub> was dissociated. The NO<sub>2</sub> was added through the injector until all the H was "titrated" and converted to OH by reaction II. The decay of OH was then followed by ESR at a series of positions down the flow tube. The OH decays by reaction with itself according to



which has a rate coefficient  $k_3$ ; the O generated then consumes another OH in the much faster reaction



Thus each occurrence of reaction III is followed immediately by an occurrence of reaction IV, and the net rate equation for the decay of the OH concentration is

$$-d[\text{OH}]/dt = 3k_3[\text{OH}]^2 \quad (2)$$

which has the simple solution

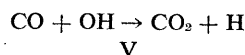
$$[\text{OH}]_0/[\text{OH}] = 1 + 3k_3[\text{OH}]_0 z/v \quad (3)$$

Table 2. Rate coefficients for various reactions of the OH radical measured by ESR. Temperature = 300°K.

| Reaction                                                  | $k$<br>(cm <sup>3</sup> mole <sup>-1</sup> sec <sup>-1</sup> ) |
|-----------------------------------------------------------|----------------------------------------------------------------|
| OH + OH → H <sub>2</sub> O + O                            | 1.55 ± 0.12 × 10 <sup>12</sup> (16)                            |
| OH + CO → CO <sub>2</sub> + H                             | 1.15 ± 0.05 × 10 <sup>11</sup> (16)                            |
| OH + H <sub>2</sub> → H <sub>2</sub> O + H                | 3.9 ± 0.2 × 10 <sup>9</sup> (16)                               |
| OH + CH <sub>4</sub> → H <sub>2</sub> O + CH <sub>3</sub> | 6.5 ± 1.5 × 10 <sup>9</sup> (19)                               |
| OD + OD → D <sub>2</sub> O + O                            | 9.5 ± 1.0 × 10 <sup>11</sup> (20)                              |
| OD + CO → CO <sub>2</sub> + D                             | 3.3 ± 0.1 × 10 <sup>10</sup> (20)                              |

where time has been converted to distance  $z$  by means of the constant linear flow velocity  $v$  (that is,  $dz/dt = v$ ), and  $[\text{OH}]_0$  is the absolute OH concentration at some reference position  $z = 0$ . Thus a curve of  $[\text{OH}]_0/[\text{OH}]$  plotted against  $z$  should be linear with a slope given by  $3k_3[\text{OH}]_0/v$ ; knowledge of  $v$  and the absolute  $[\text{OH}]_0$  allows  $k_3$  to be determined. Figure 3 illustrates some experimental confirmation of this predicted behavior under various conditions. Using the NO calibration procedure described above, we measured the  $[\text{OH}]_0$  values by ESR; the slopes of several such linear plots give the average  $k_3$  at room temperature listed in Table 2.

Once  $k_3$  has been determined it is possible to measure other rates involving OH. If another gas, CO, for example, is added through a second injector (not shown in Fig. 1) at a flow rate in large excess as compared to that of NO<sub>2</sub>, the OH will undergo the reaction



in addition to reactions III and IV. The OH decay equation then becomes

$$-d[\text{OH}]/dt = 3k_3[\text{OH}]^2 + k_5[\text{CO}][\text{OH}] \quad (4)$$

Since  $[\text{CO}]$  is very much greater than  $[\text{OH}]_0$ , the  $[\text{CO}]$  is effectively constant during the reaction. Under these circumstances Eq. 4 has a simple analytic solution which may be used to determine  $k_5$  from a knowledge of  $[\text{OH}]_0$ ,  $[\text{CO}]$ ,  $k_3$ , and the measured  $[\text{OH}]$  decay along the tube. The rate coefficient for reaction V (Table 2) was obtained in this way. The rates for the reactions of OH with H<sub>2</sub> and CH<sub>4</sub> (16, 19) (also listed in Table 2) were determined in a similar manner by injecting either H<sub>2</sub> or CH<sub>4</sub> in excess instead of CO. The two reactions of the deuterated analog OD were studied (20) by generating OD from the reaction of NO<sub>2</sub> with D from discharged D<sub>2</sub> instead of H<sub>2</sub>. Isotope effects on the

rate coefficients, as discussed by Weston (21), were measurable, both OD cases being considerably slower than their OH counterparts.

The results for reaction V at room temperature were of particular significance to combustion chemists, because this reaction is the major step by which CO is converted to CO<sub>2</sub> in flames and other combustion systems. For many years the room temperature value of  $k_5$  was thought to be about four orders of magnitude lower than we found it to be. This erroneous estimate was based entirely on some earlier flow-tube work (22) in which the OH was generated from a discharge in H<sub>2</sub>O, a favorite OH source at one time. It was shown later (23), however, that OH in such a system is generated slowly by complex reactions downstream of the discharge itself, which makes rate measurements of OH with other species appear much too slow. These incorrect low-temperature data on  $k_5$ , combined with high-temperature data obtained by other techniques in flames, made it appear that  $k_5$  had a much more pronounced temperature dependence, that is, an activation energy, than was really the case. The ESR results showed that  $k_5$  actually changes very little (factor of 3 or 4) from 300° to 2000°K.

## Applications to Atom-Molecule

### Kinetics

All of the work described above was confined to room temperature. Since the temperature dependence of rate coefficients is one of their most interesting and important aspects, it is desirable to adapt the ESR technique, with all its advantages, to an apparatus with as wide a temperature range as possible. The method used for the OH reactions, in which the ESR cavity was actually moved along the flow tube, is not suitable to high or low temperatures because of the difficulty of accomplishing cavity movement on a heated or cooled tube. There are many reasons why this

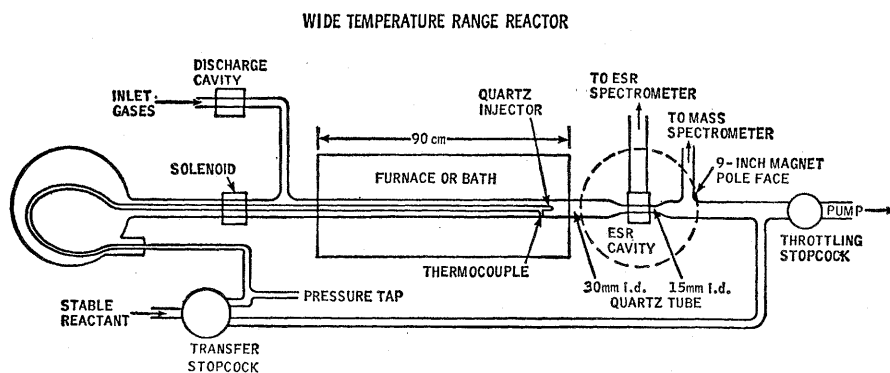


Fig. 4. Schematic diagram of fast flow apparatus used for atom-molecule rate measurements from 200° to 1000°K.

is not feasible. Thus a method was sought whereby the ESR detection cavity could be physically located outside the heated or cooled region.

A good deal of success has been achieved with the arrangement shown in Fig. 4. This is a fast flow system with provision made for furnishing a trace concentration of some reactive atom A from a discharge highly diluted in an inert gas. This mixture flows through a reactor section, which can be maintained at some uniform temperature by means of a furnace or cooling bath, and then through the ESR cavity at a fixed position outside the reactor. The cavity thus remains at room temperature. The reactor is provided with a movable injector for the addition of a metered flow of a stable reactant molecule B. The injector carries a thermocouple for temperature measurement and also serves as a pressure probe. At the injector exit, B rapidly mixes and starts reacting with A, and the reaction distance is varied by moving the injector relative to the ESR cavity. The concentration of B is

maintained in large excess as compared to the concentration of A so that [B] is essentially constant. The rate equation (Eq. 1) then applies with the product  $k[B]$  a constant at a given temperature and pressure.

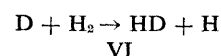
Under these conditions it is possible to show rigorously (24) that, if any extraneous atom losses (usually on the walls) depend only upon the first power of the atom concentration (so-called first-order atom wall loss), the changes in [A] measured at the cavity as the B injector is moved to various positions  $z$  are due only to reaction with B in the gas phase. The simple solution to Eq. 1 may then be used, that is,

$$\log [A]_0/[A] = k[B] z/\nu \quad (5)$$

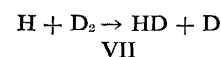
where  $k$ , [B], and  $\nu$  all pertain to their values at the reactor temperature. Only relative atom concentrations are required in Eq. 5, which is a significant simplification. Any loss of atoms on the walls is canceled out, therefore, when the detection point is fixed and the B injector is movable. This is a very important advantage which is not realized

in the opposite situation, that is, with movable detector and fixed injector. The requirement that the atom wall loss must be first-order is not a serious restriction, since the available evidence indicates that this is fulfilled under most conditions. It is thus possible to measure atom-molecule rate coefficients over a wide range of temperature; the apparatus of Fig. 4 has been operated from 195°K to nearly 1000°K. Rate coefficients as low as  $10^7$  and as high as  $10^{13} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$  have been measured in this way.

An interesting example of the use of this technique is provided by the results obtained (25) on the exchange reactions of isotopic hydrogen



and



These are two of the most fundamental elementary reactions in chemistry, involving the simplest of reactants. They are a crucial proving ground for chemical kinetic theories, since one must be able to understand these reactions thoroughly before one can hope to handle more complicated cases. Thus it is most important to have accurate experimental data on these rates. Fortunately, their study has provided a nearly ideal application of the ESR-fast flow technique. For reaction VI about 1 percent of the D atoms in helium gas carrier were passed down the reactor, and an excess of  $\text{H}_2$  was metered in through the injector. The logarithmic plots of the D signal at the ESR cavity were excellent linear functions of injector position, as required by Eq. 5. Figure 5 shows some typical cases. From the slopes of such plots the value of  $k_6$  could be obtained with considerable precision ( $\pm 10$  percent), and similar results were possible for  $k_7$ . It is customary to give results for rate coefficients as a function of temperature in the Arrhenius form

$$k = A \exp(-E/RT) \quad (6)$$

where  $E$  is the activation energy,  $R$  is the gas constant, and  $A$  is called the preexponential factor. If this simple form is obeyed, a plot of  $\log k$  against  $T^{-1}$  should be linear with a slope given by  $E/R$ . The experimental results for  $k_6$  and  $k_7$  plotted in this way are shown in Fig. 6. The circled points are the ESR data for both rate coefficients up to 750°K, and down to 250°K for  $k_6$

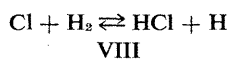
Table 3. Arrhenius parameters for atom-molecule reactions measured by the ESR-fast flow technique;  $k = A \exp(-E/RT)$ .

| Reaction                                                                            | $10^{-13} \times A$<br>( $\text{cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ ) | $E$<br>(kcal/mole) | Range of validity<br>(°K) |
|-------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|--------------------|---------------------------|
| $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$ (25)                       | 4.4                                                                         | 7.6                | 350-750                   |
| $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ (25)                       | 4.9                                                                         | 9.4                | 450-750                   |
| $\text{O} + \text{H}_2 \rightarrow \text{OH} + \text{H}$ (31)                       | 3.2                                                                         | 10.2               | 450-950                   |
| $\text{O} + \text{D}_2 \rightarrow \text{OD} + \text{D}$ (32)                       | 2.0                                                                         | 11.0               | 400-950                   |
| $\text{O} + \text{CH}_4 \rightarrow \text{OH} + \text{CH}_3$ (31)                   | 2.0                                                                         | 9.2                | 400-700                   |
| $\text{O} + \text{C}_2\text{H}_6 \rightarrow \text{OH} + \text{C}_2\text{H}_5$ (24) | 1.8                                                                         | 6.1                | 300-500                   |
| $\text{O} + \text{C}_2\text{H}_4 \rightarrow ?$ (33)                                | .59                                                                         | 1.5                | 230-380                   |
| $\text{O} + \text{OCS} \rightarrow \text{CO} + \text{SO}$ (31)                      | 1.9                                                                         | 4.5                | 270-800                   |
| $\text{O} + \text{CS}_2 \rightarrow \text{CS} + \text{SO}$ (31)                     | 1.2                                                                         | 1.0                | 230-540                   |
| $\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$ (31)                    | 1.0                                                                         | .6                 | 300-540                   |
| $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$ (34)                       | 1.5                                                                         | 7.9                | 400-900                   |
| $\text{Cl} + \text{H}_2 \rightarrow \text{HCl} + \text{H}$ (27)                     | 1.2                                                                         | 4.3                | 250-450                   |
| $\text{H} + \text{HCl} \rightarrow \text{H}_2 + \text{Cl}$ (27)                     | 2.3                                                                         | 3.5                | 200-500                   |

and 300°K for  $k_7$ . The plots are linear for the most part, but they exhibit definite curvature at lower temperature. The curvature is qualitatively what one would expect of quantum mechanical tunneling through the potential barrier separating reactants and products (21), but the entire explanation of the phenomenon is not yet clear. The triangle points are data by LeRoy and his colleagues (26) which were obtained by an entirely different technique; the agreement, for the most part, is quite remarkable, although there is some discrepancy at lower temperatures which requires additional study. The degree to which these completely independent determinations confirm each other is a very encouraging sign that the data are not only of good precision but are also probably about as accurate. Table

3 gives the Arrhenius parameters  $A$  and  $E$  for reactions VI and VII in the temperature ranges where the plots of Fig. 6 are linear. Westenberg and deHaas have considered some of the theoretical implications of these results (25).

Another significant set of data was that on the reaction



which was measured separately in both directions (27). Let us designate the rate coefficient for the forward direction as  $k_8$  and that for the reverse direction as  $k_{-8}$ . One of the results of the fundamental principle of microscopic reversibility derived from the statistical mechanics of chemical reactions (28) is that the forward and re-

verse rate coefficients at equilibrium should be related to the equilibrium constant  $K$ , that is

$$k_8/k_{-8} = K_8 \quad (7)$$

This is easily derived by equating the rate expressions for the forward and reverse reactions.

$$k_8[\text{Cl}]_{\text{eq}}[\text{H}_2]_{\text{eq}} = k_{-8}[\text{H}]_{\text{eq}}[\text{HCl}]_{\text{eq}}$$

which is true by definition at equilibrium, and by the definition

$$K_8 = \{[\text{H}][\text{HCl}]/[\text{Cl}][\text{H}_2]\}_{\text{eq}}$$

Relations like Eq. 7 are widely used in various kinetic applications to enable one to derive a rate coefficient in one direction from that in the other direction. Since rates are always measured when the reactants are not at equilibrium (usually very far re-

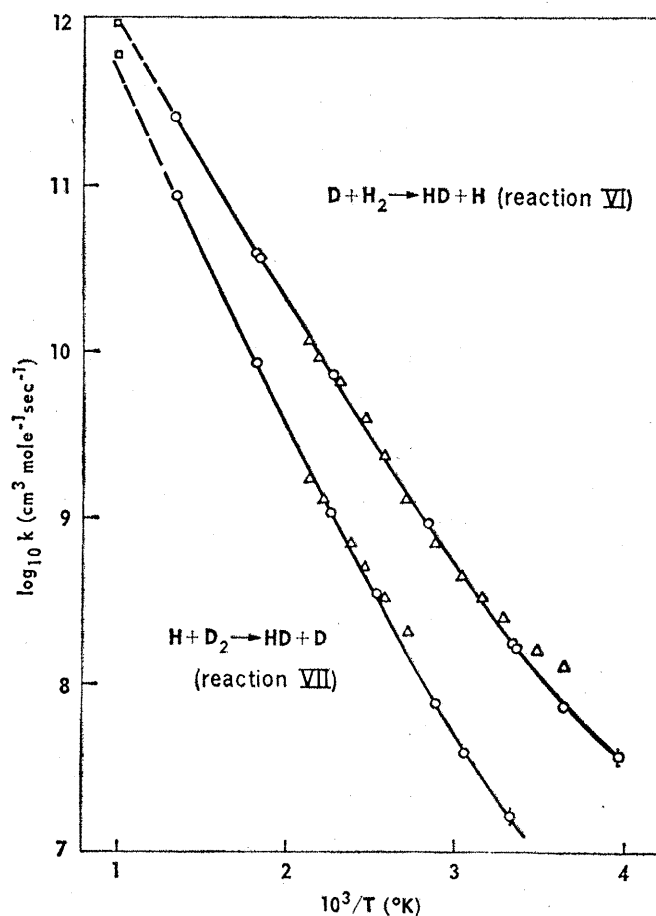
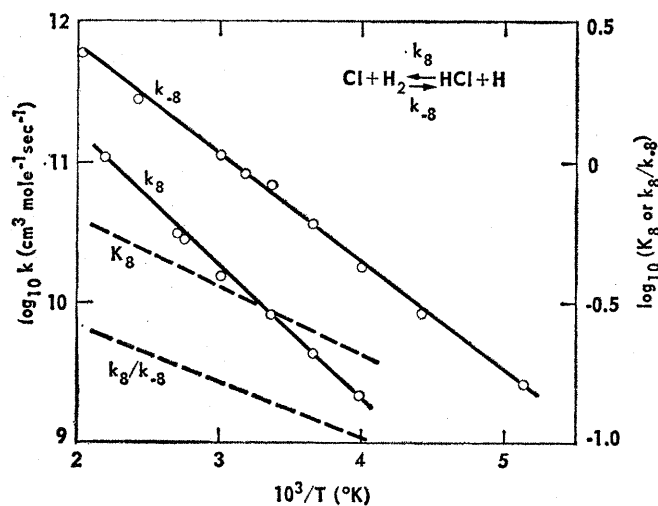
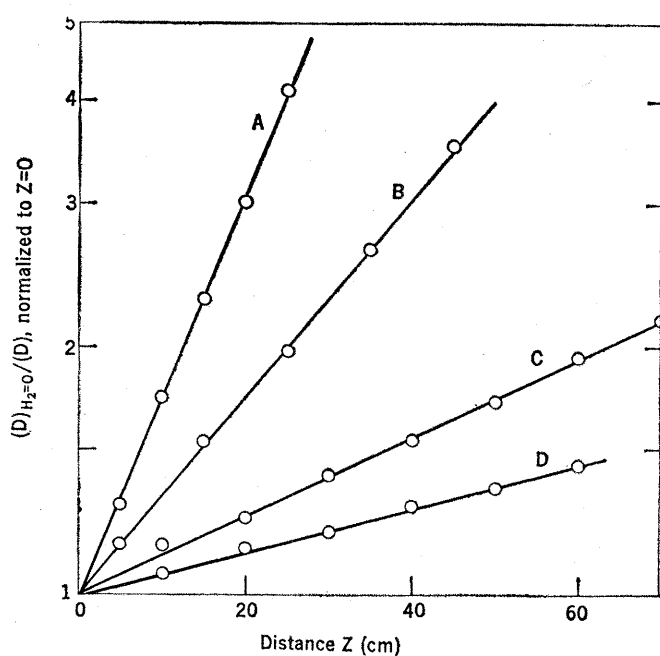


Fig. 5 (top left). Examples of D-atom decay in the reaction  $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$  under various flow conditions. Curve A: Temperature = 548°K. Curve B:  $T = 543^\circ\text{K}$ . Curve C:  $T = 274^\circ\text{K}$ . Curve D:  $T = 252^\circ\text{K}$ . Fig. 6 (above). Arrhenius plots of  $\log k$  against  $T^{-1}$  for the reactions  $\text{D} + \text{H}_2 \rightarrow \text{HD} + \text{H}$  (reaction VI) and  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$  (reaction VII). Open circles, data using ESR detection (25); open triangles, data of LeRoy and co-workers (26). Fig. 7 (left). Arrhenius plots of rate coefficients for the reaction  $\text{Cl} + \text{H}_2 \rightleftharpoons \text{HCl} + \text{H}$  (reaction VIII) measured separately in both directions. Broken lines compare experimental  $k_8/k_{-8}$  with the equilibrium constant  $K_8$ .

moved), the use of an equilibrium expression such as Eq. 7 in these circumstances is open to question. The ESR technique offered an excellent way to test the applicability of Eq. 7 to reaction VIII, since  $k_8$  and  $k_{-8}$  are roughly equal and either one can be measured without appreciable error due to back reaction by adding very large excesses of either  $H_2$  or  $HCl$ . Results of these separate measurements of  $k_8$  and  $k_{-8}$  over a substantial temperature range are given in Fig. 7; this represents the first time such a comparison of forward and reverse rates could be made at the same temperatures. Both plots show good linearity. The ratio  $k_8/k_{-8}$  is also plotted along with the equilibrium constant  $K_8$ . The discrepancy of about a factor of 2 to 3 is apparent. A possible explanation has been offered (27) in terms of the greater probability of rotational excitation of  $HCl$  as a product than of  $H_2$  as a product; however, much additional theoretical study is needed.

Table 3 summarizes results for the reactions studied to date by the ESR technique in our laboratory. The temperature range given is that for which a plot of  $\log k$  against  $T^{-1}$  is linear, although in most cases the reaction has been studied over a wider range. In some cases the product atom or radical could also be followed as it was generated in the reactor; this technique was of great aid in establishing the identity of the elementary reaction being measured. The connection to the mass spectrometer (Fig. 4) was also a valuable adjunct in some systems (particularly the hydrocarbons) if secondary reactions which consumed the atom reactant occurred after the initial step. The net rate of decay of the atom was then some multiple of that characterized by the rate coefficient for the initial reaction, and the establish-

ment of an absolute  $k$  required that this stoichiometry be separately determined with the mass spectrometer. For example, in the reaction of O with  $CH_4$ , four O atoms are consumed per  $CH_4$ ; two O atoms are consumed per  $C_2H_4$  in the reaction of O with  $C_2H_4$ ; and so forth.

Other ESR applications to kinetics have been made. Mulcahy and co-workers (29) have used a double cavity to monitor the atom concentrations at the inlet and outlet of a stirred reactor type of apparatus. Westenberg and Fristrom demonstrated the feasibility of withdrawing samples directly from a flame through a fine quartz probe and passing the gas through an ESR cavity for analysis of its free radical content (30). It is clear that the possibilities of ESR spectroscopy in gas kinetic studies have only begun to be tapped.

## Summary

Electron spin resonance spectroscopy is a reliable and versatile means for the quantitative detection of a variety of free atoms and simple radicals. Coupled with carefully controlled fast flow reactors, the use of this technique in many cases allows the rates of elementary chemical reactions to be determined with unprecedented reliability.

## References and Notes

1. This is not to say that the complete prediction of some complex reacting systems (such as flames, for example) is trivial even now, since the chemical kinetics may be strongly coupled with other phenomena of gas flow, diffusion, and turbulence. When only chemical reactions are important, the gross rates are easily computed from the elementary reaction rates.
2. K. R. Jennings, *Quart. Rev. London* **15**, 237 (1961).
3. D. Kaufman, in *Progress in Reaction Kinetics*, G. Porter, Ed. (Pergamon, New York, 1961), vol. 1, p. 3.
4. B. A. Thrush, in *ibid.* (1965), vol. 3, p. 65.
5. B. Brocklehurst and K. R. Jennings, in *ibid.* (1967), vol. 4, p. 1.
6. B. A. Thrush, *Science* **156**, 470 (1967).
7. S. N. Foner, *ibid.* **143**, 441 (1964).
8. R. Beringer and J. G. Castle, Jr., *Phys. Rev.* **75**, 1963 (1949); *ibid.* **76**, 868 (1949); R. Beringer and E. B. Rawson, *ibid.* **87**, 228 (1952); E. B. Rawson and R. Beringer, *ibid.* **88**, 677 (1952); M. A. Heald and R. Beringer, *ibid.* **96**, 645 (1954).
9. S. Krongelb and M. W. P. Strandberg, *J. Chem. Phys.* **31**, 1196 (1959).
10. See, for example, D. J. E. Ingram, *Free Radicals as Studied by Electron Spin Resonance* (Butterworth, London, 1958); C. P. Poole, Jr., *Electron Spin Resonance* (Wiley, New York, 1967); A. Carrington and A. D. McLachlan, *Introduction to Magnetic Resonance* (Harper & Row, New York, 1967).
11. A. Carrington, D. H. Levy, T. A. Miller, *Proc. Roy. Soc. London Ser. A* **293**, 108 (1966).
12. The assumption must be made here that there are no losses of atoms serious enough to set up an appreciable concentration gradient in the cavity (there being no gradient in the reference  $O_2$  concentration, of course). This assumption is easily fulfilled in most practical applications.
13. A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **40**, 3087 (1964).
14. A. A. Westenberg, *ibid.* **43**, 1544 (1965).
15. At the most fundamental level one would hope to measure the reaction probability for reactants and products in specific quantum states. This does not seem imminent, although some molecular beam experiments (either accomplished or conceived) are aimed in this direction.
16. G. Dixon-Lewis, W. E. Wilson, A. A. Westenberg, *J. Chem. Phys.* **44**, 2877 (1966).
17. T. C. Marshall, *Phys. Fluids* **5**, 743 (1962).
18. F. P. Del Greco and F. Kaufman, *Discuss. Faraday Soc.* **33**, 128 (1962).
19. W. E. Wilson and A. A. Westenberg, *Eleventh Symposium on Combustion* (Combustion Institute, Pittsburgh, 1967), p. 1143.
20. A. A. Westenberg and W. E. Wilson, *J. Chem. Phys.* **45**, 338 (1966).
21. R. E. Weston, Jr., *Science* **158**, 332 (1967).
22. L. I. Avramenko and R. V. Lorentso, *Zh. Fiz. Khim.* **24**, 207 (1950).
23. F. Kaufman and F. P. Del Greco, *J. Chem. Phys.* **35**, 1895 (1961).
24. A. A. Westenberg and N. deHaas, *ibid.* **46**, 490 (1967).
25. ———, *ibid.* **47**, 1393 (1967).
26. B. A. Ridley, W. R. Schulz, D. J. LeRoy, *ibid.* **44**, 3344 (1966); W. R. Schulz and D. J. LeRoy, *Can. J. Chem.* **42**, 2480 (1964).
27. A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **48**, 4405 (1968).
28. An illuminating review of rate coefficients and their relation to equilibrium has been given by B. Widom, *Science* **148**, 1555 (1965).
29. M. F. R. Mulcahy, J. R. Steven, J. C. Ward, *J. Phys. Chem.* **71**, 2124 (1967).
30. A. A. Westenberg and R. M. Fristrom, *Tenth Symposium on Combustion* (Combustion Institute, Pittsburgh, 1965), p. 473.
31. A. A. Westenberg and N. deHaas, *J. Chem. Phys.* **50**, 707 (1969).
32. ———, *ibid.* **47**, 4241 (1967).
33. ———, *Twelfth Symposium on Combustion*, in press.
34. W. E. Wilson, *J. Chem. Phys.* **46**, 2017 (1967).