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Rates of Elementary Reactions: Measurement and Applications

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Summary. Modern experimental techniques for measuring rate parameters of elementary reactions have transformed the field of gas-phase reaction kinetics from one of indirect inference to one of direct determination. Recent progress in the principal techniques is described, a few examples are given of the hundreds of elementary reactions for which rate information has become available, and comparison with reaction rate theory is briefly discussed. Some generalizations regarding the dependence of rate parameters on structure and thermodynamics are drawn, and successful applications to atmospheric and combustion modeling and measurement are presented.

In the recent special issue of *Science* devoted to chemistry (22 February 1985), two articles (*1, 2*) described progress in chemical reaction dynamics and a third (*3*) advanced theoretical chemistry to full partnership with experimental measurement. For the most part, lasers and computers have made these advances possible, and these marvelous new toys have also brought exciting progress to the older field of gas-phase reaction kinetics. Now we use lasers and computers to monitor the appearance and disappearance of reactive species rather than peer at slowly rising or falling columns of mercury to measure the pressure changes due to bulk reactions.

Why rate constants of "elementary" reactions? Because we have known for more than a century that complicated overall reactions proceed via many elementary steps in which single chemical transformations, such as the transfer of an atom or group from molecule A to B, the breaking or forming of a chemical bond, or an intramolecular rearrangement, take place. Only quite recently have we been able to study these elementary steps directly, in isolation, rather than infer their rate parameters by measuring the rates of formation and removal of stable reactant and product species and then invoking reaction mechanisms. This latter, procrustean procedure is often not accurate. When we are successful in isolating a single elementary reaction and measuring its rate constant, our results come close to those of our colleagues, the state-to-state dynamicists (*1, 2*). To be sure, the reactant and product species undergo many collisions before we detect them, but the collisions are mainly with inert carrier gas (helium or argon) and thus chemically harmless. Such collisions keep kinetic and rotational energy distributions in thermal equilibrium but are inefficient in changing the species' electronic or vibrational energy, unless the vibrational quanta are small compared with the yardstick of thermal energy, k_BT (where k_B is the Boltzmann constant and T is temperature).

The reactions whose rates we investigate are usually very fast, because they involve reactive atomic or radical species that are produced in slow bond-breaking steps but then rapidly attack other molecules and thereby carry the overall reaction forward. These reactive species must therefore be produced in situ, their concentrations and that of other reactant and product species must be measured, and the reaction rate constants must be determined. As a consequence of the sensitive and specific detection methods used, we obtain partial state-to-state information, and we do so for a host of species ranging from hydrogen atoms to organic radicals.

Experimental Methods

Two general types of experimental methods may be distinguished. In the flash- or laser-photolysis (FP) method, a descendant of the work of Porter and Norrish (*4*), reactive species are produced in a short (10^{-6} to 10^{-8} second) light flash, and their decay resulting from a reaction is monitored in real time by spectroscopic means. In the flow reactor (flowing afterglow) discharge-flow (DF) method, a remote offspring of the work of Bonhöffer (*5*), the reactive species are produced continuously in steadily flowing carrier gas (helium or argon) and mixed with other reactants; the rate is determined either by changing the distance over which the reactants are in contact (the reaction time) or by changing the concentration of one reactant at constant reaction time.

How do these two methods compare? If they are both applicable to the study of a reaction, FP is the method of choice, because it provides direct measurements in real time and does not require corrections for surface and transport effects. Figure 1 shows the diagram of a high-temperature, flash photolysis–resonance fluorescence apparatus used by Ravishankara and colleagues (*6*) to measure the rate constants of the reactions $OH + H_2$ and $OH + D_2$ from about 250 K to 1050 K. Such data are most welcome for several reasons: (i) they give us insight into the essentials of a simple reaction event and may be compared with semiempirical and ab initio theoreti-

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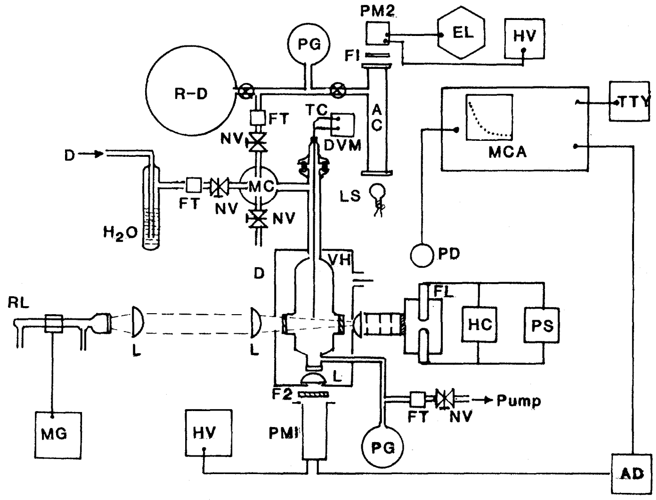

Fig. 1. Schematic diagram of the high-temperature flash photolysis–resonance fluorescence apparatus (*6*). Abbreviations: AD, amplifier discriminator; D, diluent gas; DVM, digital voltmeter; F2, 309.5-nm band-pass filter; FL, flash lamp; FT, flow transducer; HC, high-voltage capacitor; HV, high voltage; L, lens; MC, mixing chamber; MCA, multichannel analyzer; MG, microwave generator; NV, needle valve; PD, photodiode; PG, pressure gauge; PM1, photomultiplier; PS, high-voltage power supply; R-D, reactant-diluent gas; RL, resonance lamp; TC, thermocouple; TTY, teletype; and VH, vacuum housing. [From (*6*); courtesy of the American Chemical Society]

cal predictions (see Fig. 2 for such a comparison); (ii) they are used directly in the modeling of atmospheric photochemistry; and (iii) they may be extrapolated with confidence to combustion temperatures and may be used to model combustion processes.

The flow reactor DF method is used widely (and has been championed by this author) because of its versatility. In DF, radicals are produced, react, and are detected in separate regions of the instrument, whereas in FP, these processes usually occur in the same region. Consequently, in DF, many different methods may be used to produce radicals (electrical discharges, thermal dissociation, infrared-laser multiphoton dissociation, and prereaction of other atoms or radicals) or to detect them (resonance or laser-induced fluorescence, long path absorption, infrared or visible chemiluminescence, laser magnetic resonance, mass spectrometry, and catalytic probe calorimetry). The price that must be paid for this diversity is twofold: a transport equation must be solved, and the surface boundary condition (that is, the reaction or removal of reactive species at the flow reactor surface) may be ill-defined, variable, and poorly controlled. The first condition is now well characterized. The transport equation for a single, pseudo–first-order reaction in a cylindrical flow reactor in steady-state, laminar flow is given by

$$2\bar{v}\left(1-\frac{r}{r_0}\right)^2\frac{\partial[X]}{\partial z} - D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial[X]}{\partial r}\right)+\frac{\partial^2[X]}{\partial z^2}\right]+k^1[X]=0$$

where $\bar{v}$ is the average flow velocity; r and z, the radial and axial coordinates; r_0, the flow tube radius; $[X]$, the radical concentration; D, the molecular diffusion coefficient of the radical; and k^1, the apparent first-order rate constant. This equation has been solved by the use of various approximations (*7–9*) as well as by numerical integration (*10, 11*). If the surface boundary condition is well behaved, the interpretation of flow reactor DF data is straightforward. In earlier studies, it was assumed that DF experiments had to be run at relatively low pressures, say less than 10 torr, because of transport effects, but this limitation is overly conservative as Keyser's work (*9*) on the OH + HCl reaction at pressures up to 100 torr has shown. The surface boundary conditions are determined by

$$D\left.\frac{\partial[X]}{\partial r}\right|_{r=r_0} = -\frac{r_0k_s}{2}[X]_{r=r_0}$$

where k_s (in inverse seconds) is the effective first-order radical-removal rate constant at the surface. When the surface conditions are not well controlled, as is sometimes the case for some radical species (often at very low or very high temperatures), the method becomes unworkable until the surface problem is resolved. That these surface problems are by no means insoluble has been shown by Howard (*12*) who has studied reactions of OH and HO_2 radicals in a clean quartz flow tube up to 1270 K, by Silver and Kolb (*13*) who have studied reactions of NH_2 radicals in an Al_2O_3 flow tube (*14*) to 1215 K, and by others.

Two apparatuses from our laboratory are shown in Figs. 3 and 4. The apparatus in Fig. 3 has a movable, concentric double-injector tube that allows a prereaction to generate a reactive species in the larger injector tube, for example, HO_2 from

$$F + H_2O_2 \rightarrow HO_2 + HF$$

and uses both laser-induced fluorescence and vacuum-ultraviolet resonance fluorescence to monitor molecular and atomic reactant or product species. The apparatus in Fig. 4 uses infrared-laser multiphoton dissociation of suitable precursors in an upstream cell to generate radical species and makes use of three detection methods at the downstream end of the flow reactor: vacuum-ultraviolet resonance fluorescence, laser-induced fluorescence, and modulated molecular-beam mass spectrometry. The temperature range of these two systems is now only moderate, about 200 to 500 K, but this range depends strongly on the reactive species to be monitored. In our earlier work on hydrogen atom recombination (*15, 16*), for example, good data were collected down to 77 K, but this would not be possible for most molecular radicals. In brief summary, then, although FP is the more desirable method, it often cannot be used because of difficulties with radical generation and detection by optical methods and because of interference from other reactants. The flow reactor DF technique, on the other hand, is nearly universally applicable and allows us to investigate atom-radical or radical-radical reaction rates as described below. There are still other methods, such as molecular modulation, stirred flow reactor, and very low pressure pyrolysis, which are not discussed here for lack of space. Nor is it possible to describe hybrids of FP and DF in which the FP cell is part of a flow reactor such that certain reactive species are generated upstream, pass through the FP cell, and react with flash-generated species on a time scale that is short compared to the residence time in the cell. Several dozen FP and DF apparatuses are now in use, here and abroad, in university, government, and other types of research laboratories.

Experimental Results

Before we discuss a few specific reactions, it is useful to examine the scope of recent work on elementary reaction rate measurements. A review by Baulch *et al.* (*17*) in 1982 on evaluated kinetic and photochemical data for atmospheric chemistry listed approximately 180 reactions of (mostly) ground-state species of simple radicals or molecules containing hydrogen, oxygen, nitrogen, carbon, sulfur, and the halogens. An update of this review (*18*) in 1984 listed about 220 reactions. If each reaction was studied by two or three different groups, this would amount to about 500 investigations of elementary reaction rates pertinent to atmospheric reactions. If we add nonatmospheric reactions, the number is perhaps doubled. Clearly, there has been rapid progress in the measurement of rate parameters. Furthermore, the accuracy has also been improved. In most studies, it is now expected that single standard deviation uncertainties are about 3 to 10 percent for random statistical error in a measured rate constant and 10 to 20 percent when errors of all other independent variables are included. The uncertainties are larger for derived parameters that describe the temperature dependence; these are, of course, strongly dependent on the magnitude of the temperature range of the measurements.

Two examples may be cited for hydrogen atom transfer reactions with small energy barriers and "tight," well-defined transition states. The reaction

$$\begin{gathered} OH + H_2 \rightarrow H_2O + H \\ (\Delta H_0^0 = -61.6 \text{ kJ mol}^{-1}) \end{gathered} \tag{1}$$

has been mentioned earlier (Figs. 1 and 2) (ΔH_0^0 is the specific heat of the reaction). Although the data shown come from one investigation (*6*), there have been eight other investigations since the early 1970's with different experimental techniques that cover smaller temperature ranges but agree on the value of k_1(298 K) within 13 percent (k_n is the rate constant for Eq. *n*). The Arrhenius plot (Fig. 2) is curved as expected from first principles (the specific heat of the transition state rises more rapidly than that of the reactants) and the activation energy is close to 17 kJ mol^{-1} near 300 K. The comparison with ab initio calculations will be discussed in the next section.

The reaction

$$\begin{gathered} OH + CH_4 \rightarrow H_2O + CH_3 \\ (\Delta H_0^0 = -61.8 \text{ kJ mol}^{-1}) \end{gathered} \tag{2}$$

is also well characterized. Eight independent studies conducted since 1974 have given $k_2(298\text{ K}) = 7.9 \times 10^{-15}$ cm^3 sec^{-1} ± 12 percent. Three recent investigations have shown upward curvature in their Arrhenius plots, and the activation energy near 300 K is about 16 kJ mol^{-1}. Since OH is an important species in atmospheric chemistry, a large effort has gone into the laboratory measurement of its rate constants for reactions with more than 200 organic compounds, roughly half by absolute and half by competitive techniques (*19*). About 100 of these reactions proceed by hydrogen atom abstraction, similar to Eqs. 1 and 2 above, but about 80 to 90 reactions with olefins and aromatics have been studied in which OH addition takes place. Either may be followed by further reaction of the radical so formed or by elimination of a more weakly bonded atom or group, such as chlorine or bromine, before the radical has been collisionally stabilized.

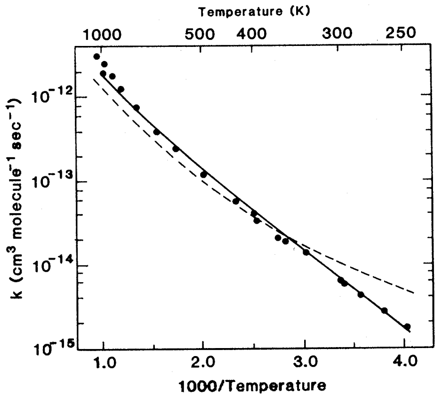

Fig. 2. Comparison of experimental data (*6*) (solid points and full line) and ab initio theoretical calculation (*39*) (broken line) for the $OH + H_2$ reaction.

Atom-radical and radical-radical reaction rates have been measured directly in recent experiments. In our laboratory, the reactions of HO_2 with H (*20*), O (*20*), and OH (*21, 22*) were studied in the movable double-injector apparatus (Fig. 3). The HO_2 radicals were produced by the reaction $F + H_2O_2$ in the double injector and made to react with H or O at variable times in the range of ~10 to 40 msec, the atoms having been produced in microwave discharges from traces of H_2 or O_2 in He far upstream of the vacuum-ultraviolet resonance fluorescence detector. For HO_2 + H, all three product channels were identified and their rates measured

$$\begin{gathered} HO_2 + H \rightarrow OH + OH \\ (\Delta H_0^0 = -151.6 \text{ kJ mol}^{-1}) \end{gathered} \tag{3a}$$

$$\begin{gathered} HO_2 + H \rightarrow H_2O + O \\ (\Delta H_0^0 = -221.2 \text{ kJ mol}^{-1}) \end{gathered} \tag{3b}$$

$$\begin{gathered} HO_2 + H \rightarrow H_2 + O_2 \\ (\Delta H_0^0 = -220.2 \text{ kJ mol}^{-1}) \end{gathered} \tag{3c}$$

The interesting result was that the least exothermic channel, Eq. 3a, accounted for 87 percent and the other two, Eqs. 3b and 3c, for 4 and 9 percent, respectively, of the overall rate constant of $(7.4 \pm 1.2) \times 10^{-11}$ cm^3 sec^{-1}.

Only one product channel exists for

$$\begin{gathered} HO_2 + O \rightarrow OH + O_2 \\ (\Delta H_0^0 = -221.1 \text{ kJ mol}^{-1}) \end{gathered} \tag{4}$$

This reaction is also very fast [$k_4 = (5.4 \pm 0.9) \times 10^{-11}$ cm^3 sec^{-1}], and recently we clarified its detailed course (*23*) by means of ^{18}O isotope studies. It proceeds not by hydrogen atom transfer but by formation of an HO_3 adduct that breaks up into $OH + O_2$ such that the labeled ^{18}O ends up in the O_2 rather than in the OH molecule. The HO_2 + OH reaction

$$\begin{gathered} HO_2 + OH \rightarrow O_2 + H_2O \\ (\Delta H_0^0 = -290.6 \text{ kJ mol}^{-1}) \end{gathered} \tag{5}$$

was studied (*21*) by preparing (excess) HO_2 as above but by using the sequence of reactions

$$H + F_2 \rightarrow HF + F$$
$$F + H_2O \rightarrow OH + HF$$

to generate OH instead of the reaction

$$H + NO_2 \rightarrow OH + NO$$

because NO would react with excess HO_2 to regenerate OH. The point is, of course, that under the chosen DF conditions, side reactions (either in parallel or in series with the desired step) are effectively minimized. The rate constant was found to be very large [k_5(298 K) = $(7.1 \pm 1.2) \times 10^{-11}$ cm^3 sec^{-1}], and its temperature dependence was found to be negative, corresponding to $\exp[(416 \pm 86)/T]$ or $T^{(-1.33 \pm 0.13)}$, where *T* is the temperature over the range 252 to 420 K. Other groups, too, have investigated several of these reactions. Keyser (*24*) and Temps and Wagner (*25*) reported values of 6.4×10^{-11} and 6.6×10^{-11} cm^3 sec^{-1} for k_5(298 K), in good agreement with our value of 7.1×10^{-11}. For k_4(298 K), excellent agreement exists among four studies performed at the Jet Propulsion Laboratory (*26*), Harvard University (*27*), the Georgia Institute of Technology (*28*), and the University of Pittsburgh (*20*). Finally, a brief account of the present status of the atom-radical reaction

$$\begin{gathered} O + ClO \rightarrow Cl + O_2 \\ (\Delta H_0^0 = -229 \text{ kJ mol}^{-1}) \end{gathered} \tag{6}$$

is the rate-limiting step in the stratospheric ozone removal by ClO_x species. In the most recent study of this reaction, Margitan (*29*) used an ingenious combination of DF and laser FP techniques, in which oxygen atoms were detected by vacuum-ultraviolet resonance fluorescence and ClO was detected by multipass ultraviolet absorption to determine k_6. The result [$k_6(298\ \mathrm{K}) = 4.2 \times 10^{-11}$ cm^3 sec^{-1}] is in good agreement with Leu's value of 3.6×10^{-11} (*30*) and Zahniser and Kaufman's value of 4.2×10^{-11} cm^3 sec^{-1} (*31*), but lower than two earlier values, 5.3×10^{-11} and 5.2×10^{-11}, from Clyne's group (*32*, *33*).

What we learn from this small sample of recent results is this: it is now possible to make direct measurements of the rate parameters of most elementary gas-phase reaction steps of atoms, small radicals, and molecules and to do so with respectable accuracy. This is also true for other types of reactions such as radical-molecule recombinations or complex rearrangements proceeding via strongly bound adducts.

Comparison with Theory

The problem of calculating an ab initio rate constant for an elementary reaction is extraordinarily difficult. It consists of two parts: the quantum chemical calculation of potential-energy surfaces corresponding to the reaction event (that is, representing the structure and energy of all intermediate stages between reactants and products) and calculation of the dynamics of the system as it evolves from reactants to products. Although much progress has been made in both parts of the problem, the calculation of dynamics has advanced more than the calculation of the potential energy surface, because the latter is limited to simple (few electron) systems, requires massive amounts of computer time, and becomes repetitious, since a great many points on the potential energy surface must be calculated to define it with sufficient accuracy to do the dynamics. The BAC-MP4 method of Melius and Binkley (*34*) has been used with success in the calculation of binding energies for molecules, radicals, and transition states, but it contains a semiempirical bond additivity correction and cannot be used to calculate full potential-energy surfaces. Earlier work by Dunning and co-workers has provided moderately accurate potential energy surfaces for H + CH_4 (*35*), OH + H_2 (*36*), and other reactions.

The dynamics is treated either by classical or semiclassical trajectory calculations (*37*) or by variational transition state theory (*38*). Quantum mechanical corrections for tunneling are then grafted onto the semiclassical solution, since an ab initio, three-dimensional, quantum mechanical calculation of all but the simplest reactions such as

$$\mathrm{H} + ortho\text{-}\mathrm{H}_2 \rightarrow para\text{-}\mathrm{H}_2 + \mathrm{H}$$

is out of reach and is likely to remain so for some time. A comparison of the best experimental data (*6*) and the best theoretical calculations (*39*) for Eq. 1 is shown in Fig. 2. The agreement is fairly good, but we must remember that the calculated energy barrier is uncertain to ±8 kJ mol^{-1} (which would change k_1 near 300 K by a factor of 25) and that the tunneling correction is very large, amounting to more than 99 percent of the total rate constant at 200 K, to 94 percent at 298 K, and to 51 percent at 600 K. This large correction is probably responsible for the crossover of the two lines in Fig. 2 and for their increasing divergence at low temperatures. We may conclude that, as a test case or benchmark exercise, such a calculation is very valuable; however, the necessarily approximate treatment of the potential energy surface, both of the barrier height and of the details near the transition state configuration, and the semiquantitative treatment of quantum effects make it unlikely that such theoretical calculations will soon become full partners (*3*) with experimental measurements. The OH + H_2 reaction is very simple. It involves one heavy atom and three hydrogen atoms, and it is a "direct" reaction with a well-defined transition state of short lifetime (about 10^{-14} second) at the top of an energy barrier. Yet to bring the experimental and calculated rate constants for this reaction into congruence seems an impossible task. Incorporating this degree of sophistication into theoretical calculations for more complicated sys-

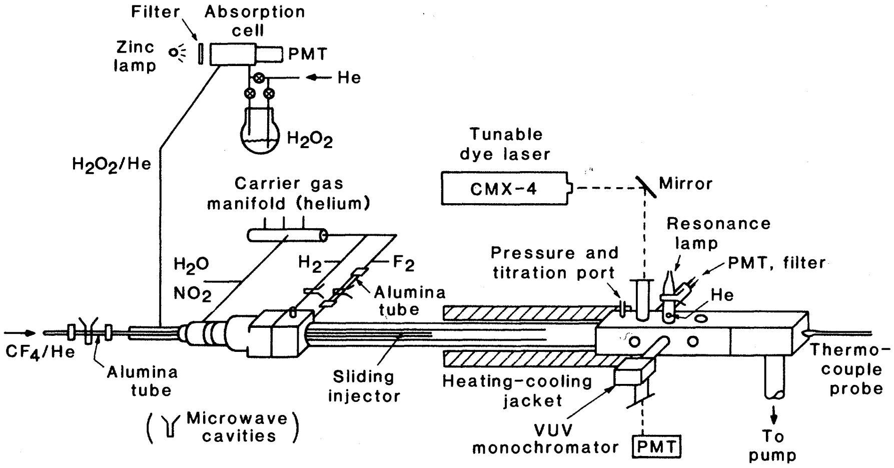

Fig. 3. Diagram of double-injector, flow reactor apparatus with laser-induced fluorescence and vacuum-ultraviolet resonance-fluorescence detection of atom-radical species (*19–22*). [From (*66*); courtesy of the American Institute of Physics]

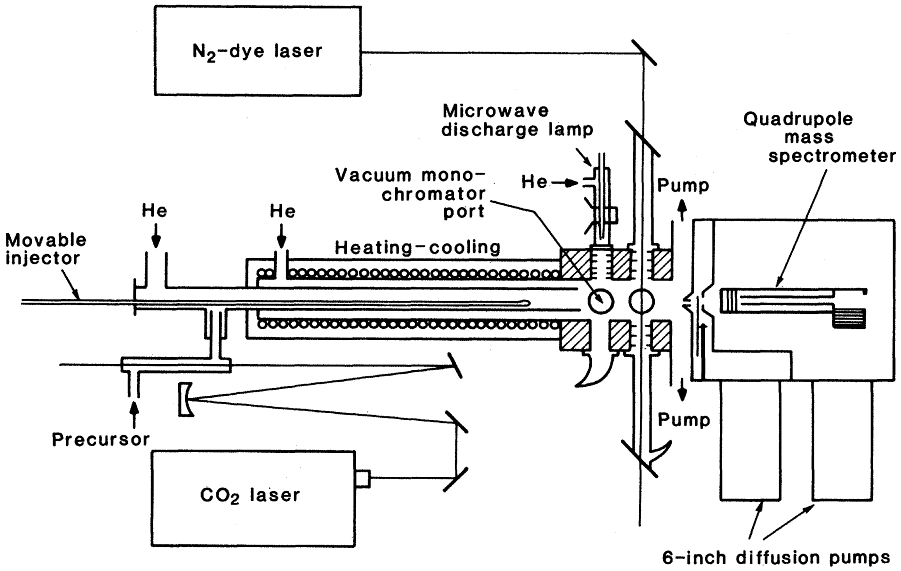

Fig. 4. Diagram of flow reactor apparatus that uses three detection techniques: laser-induced fluorescence, vacuum-ultraviolet resonance fluorescence, and modulated molecular-beam mass spectrometry. The apparatus also employs infrared-laser multiphoton dissociation to generate radical species in an upstream cell.

tems is still out of reach, particularly for ab initio calculations of potential energy surfaces. Since the experimental measurement of rate parameters is relatively easy and accurate, it is important that theorists and experimenters work closely together on the selection of other benchmark systems to maximize the contribution of theory to our understanding of elementary rate processes.

The semiempirical method of thermochemical kinetics (*40, 41*) uses Eyring's transition state theory (*42*), often in its thermodynamic form, and drastically reduces the calculational task through clever use of empirical analogy. This method does not require ab initio quantum calculations of the potential energy surface; instead it takes the barrier height from experiment and estimates the detailed properties of the transition state by analogy with known chemical species. It does not minimize the reactive flux through variation of the hypersurface corresponding to the transition state and usually does not apply tunneling corrections. The method's strength lies in its empiricism, that is, the power of interpolation or extrapolation from known sets of molecular properties. Its predictive power, however, is difficult to estimate. A factor-of-two accuracy has been claimed for it; but recent experimental tests in our laboratory (*43*) have suggested larger uncertainties in the comparison of measured and calculated values of A in the Arrhenius expression for bimolecular rate constants, $k = A \exp(-E/RT)$. Even so, such guidelines are valuable in making a priori decisions on the importance of individual steps in a large mechanism and in weeding out implausible rate parameters deduced from indirect experimental work.

Since this semiempirical technique requires little computational effort, it should always accompany experimental determinations of rate constants. Lest we become overconfident, two recent examples may be cited where apparently simple reactions are difficult to explain in terms of simple transition state theory. The rates of the reaction

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$

and its deuterium analog have been accurately measured (*44*) as functions of temperature and pressure, yet to fit these data with thermochemical transition state theory (*45*) it is necessary to invoke an unusually loose H_2O_4 intermediate. Similarly, the reaction

$$OH + HNO_3 \rightarrow H_2O + NO_3$$

may be expected to be a simple, exothermic hydrogen-atom transfer, but its rate parameters show that it is not. Because of this reaction's great importance in stratospheric chemistry, its rate constant has been measured by eight groups since 1981. The very small value of A in its Arrhenius expression and its negative temperature dependence show that it is not a direct hydrogen atom transfer. The most recent explanation (*46*) of these unexpected experimental results invokes the formation of a complex in which OH attacks from above or below the $HONO_2$ plane to form a four-center transition state. In both of these cases we seem to be stretching the ground rules of the semiempirical theory to their limit.

Before we discuss some of the applications of laboratory measurements, a general summary is in order. Most important, the rates of several hundred single-step, elementary reactions have been measured with reasonable accuracy, many over sizable temperature ranges. These include the rates of both direct and complex-intermediate reactions, as well as bond-forming associations. Because the most sensitive detection techniques are spectroscopic, the radical species whose rates have been measured are small, but the molecular reactants are often quite large, as the extensive studies of hydroxyl radical reactions have shown (*19*). The products of these elementary steps are not easily identified. The increasing complexity of the chemical systems is leading to the reemergence of mass spectrometry as a major detection method, particularly with modulated molecular-beam sampling and phase-sensitive detection. In general, progress is rapid, and the studies are being extended in many directions, for example, to more complex reactants, to metal compound reactions, and to wider temperature ranges. The field of gas-phase reaction kinetics has thus matured and made excellent use of modern instrumentation and data analysis.

Applications in Atmospheric Science

Measurement of elementary reaction rates has advanced atmospheric science in two ways: it has made possible the modeling of chemically complicated mechanisms for certain regions of the atmosphere, such as the stratosphere and the clean or polluted troposphere, and it has stimulated the measurement of minor species in situ through adaptation of laboratory techniques to field measurements.

No one would have predicted 20 years ago that critical evaluations (*18, 47*) would soon become available that list hundreds of elementary chemical and photochemical reactions. Our understanding of stratospheric chemistry progressed from the four reactions of the Chapman mechanism (*48*)

$$O_2 + h\nu \rightarrow O + O \qquad (7)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (8)$$

$$O_3 + h\nu \rightarrow O^* + O^*_2 \qquad (9)$$

$$O + O_3 \rightarrow O_2 + O_2 \qquad (10)$$

(where M is any third collison party) to the presently known 100 to 150 reaction mechanisms by the addition of catalytic cycles based on HO_x, NO_x, and ClO_x species. In broad outline, the chemistry is simple: each catalytic cycle is the equivalent of the odd-oxygen removal step (Eq. 10), for example

$$OH + O_3 \rightarrow HO_2 + O_2 \qquad (11)$$

$$HO_2 + O \rightarrow OH + O_2 \qquad (12)$$

or

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (13)$$

$$NO_2 + O \rightarrow NO + O_2 \qquad (14)$$

or

$$Cl + O_3 \rightarrow ClO + O_2 \qquad (15)$$

$$ClO + O \rightarrow Cl + O_2 \qquad (16)$$

In each cycle, one reaction is usually rate-limiting (for example, Eq. 14 for the NO_x cycle).

Furthermore, the catalytic minor species are interrelated by other fast reactions such as

$$HO_2 + NO \rightarrow OH + NO_2$$

or

$$ClO + NO \rightarrow Cl + NO_2$$

and they may be converted into "reservoir" species that are unreactive toward O and O_3, for example

$$Cl + CH_4 \rightarrow HCl + CH_3$$

or

$$OH + NO_2 + M \rightarrow HNO_3 + M$$

The reservoir species may, in turn, be converted back into active catalysts, as in

$$HCl + OH \rightarrow Cl + H_2O$$

Add to this chemical complexity the effects of vertical and horizontal transport, of solar radiation as function of altitude (that is, the filtering action of absorbing species) and solar zenith angle, and of pressure (roughly from 100 to 200 torr at the tropopause to 1 torr at the stratopause), and the immense complexity of the problem becomes apparent. Without detailed laboratory results for the more than 100 chemical and photochemical steps, it would be impossible to model the entire process on computers. Yet, in spite of the advances in laboratory measurement, the uncertainties in the predictions of one-dimensional models for the reduction of the total ozone column by continued chlorofluorocarbon release (*49*) have mainly been due to uncertainties or errors in rate parameters or due to the omission of certain elementary steps.

Our understanding of tropospheric chemistry is less advanced than that of stratospheric chemistry for several reasons: (i) transport effects are both more important and more prominent than those in the stratosphere and require three-dimensional modeling; (ii) the chemistry is more complex, that is, many more trace species are present both in the clean and polluted troposphere; and (iii) it is more difficult to monitor the reactive species because they are present at extremely small mixing ratios (mole fractions), often less than 10^{-12} of total pressure. For example, the most important radical species, OH, has not yet been reliably measured in the troposphere or in the lower stratosphere. Its mixing ratio in the lower troposphere is about 10^{-14}.

The second contribution of reaction rate measurements to atmospheric science, namely the adaptation of laboratory techniques to the detection of radical species in situ, has been immensely successful. The work of Anderson and his co-workers serves as an excellent example. Starting with the development of atom and radical resonance fluorescence (*50–52*) as a sensitive monitoring method in DF studies, they adapted and improved these methods for balloon-parachute experiments in which O, O_3, OH, HO_2, Cl, and ClO concentrations were measured in the stratosphere. This fast-drop parachute method has now been superseded by a reel-down technique in which the payload is lowered and raised repeatedly from a platform attached to a stationary balloon (*53*), as shown in Fig. 5. Recent data for stratospheric ClO measured by this new technique are now available (*54*).

Applications in Combustion Science

Combustion processes are, in general, more exothermic than atmospheric ones, less dependent on a photochemical driving force, operate at higher temperatures, and often consist of even larger numbers of elementary reactions (*55*). The modeling of hydrocarbon pyrolysis (*56*), oxidation (*57*), and inhibition (*58*), for example, has recently been described in terms of mechanisms consisting of 80 to 100 elementary steps. Although such numbers seem large, they are much smaller than the true total number of steps. That many of these modeling studies successfully calculate experimental quantities such as flame speeds, induction times, and composition profiles means that the authors have made use, intuitively or by formal calculation, of a sensitivity analysis that reduces an essentially intractable problem to a size that allows computer analysis while still making chemical sense. The importance of mathematical sensitivity analysis (*59*) cannot be overemphasized, nor can its limitations. By the latter, we mean that the desired sensitivity coefficients (for example, the ranking of elementary steps in order of their importance) is highly dependent on such boundary conditions of the problem as initial composition, reaction time, and temperature constraints.

Turning now to the supply and demand of elementary reaction rate parameters, we see that the present state of affairs for combustion processes is not nearly as satisfactory as it is for atmospheric processes. Rate data are needed for high temperatures, say, 1000 to 2500 K, but relatively little experimental work has been done in that range, and few of the radical species of C–H–O or C–H–O–N systems have been generated and monitored by direct methods. Warnatz (*60*) has reviewed the rate data for the C–H–O system up to C_4-hydrocarbons that were published up to 1981, and Hanson and Salimian (*61*) have reviewed the data for the N–H–O system. A major evaluation of elementary-reaction rate data for combustion processes is now under way at the National Bureau of Standards.

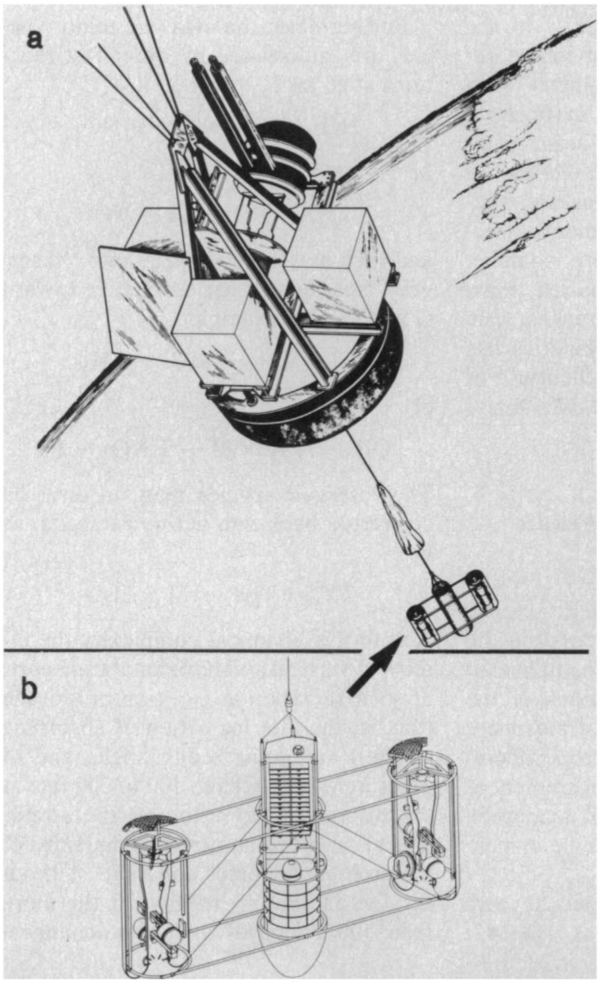

Fig. 5. Rendering of the reel-down experimental apparatus (*54*) showing the winching system and suspended payload. A helium-filled research balloon is used to lift the combination to any altitude up to 40 kilometers. (a) The geometry of the experiment at float altitude in the docked position. (b) A diagram of the suspended instrument array including the optical system and flow system used to observe the free radical in situ. [From (*53*)]

Since the most direct experimental methods are limited to temperatures lower than about 1500 K and since most of the active research groups have confined their studies to the range 200 to 500 K, there is a great need for direct measurements over wider ranges. It is particularly important that such measurements be performed with one apparatus for consistency and comparability. In the usual evaluation of rate data of a given elementary step, say,

$$H + O_2 \rightarrow OH + O$$

which is probably the single most important reaction in combustion, the results of many investigations are plotted together where each covers only a small temperature range. The trouble is, of course, that uncertainty limits are often underestimated and systematic errors not recognized. When a single FP or DF study provides data over a sufficient temperature range (a factor of three to five in degrees Kelvin) the extrapolation to combustion temperatures is straightforward. This is best done within the framework of thermochemical transition state theory (*40, 41*), as Cohen (*62*) has shown for reactions of OH with alkanes. Caution must be exercised in the case of hydrogen atom transfer reactions over (and through) "thin" barriers where tunneling increases the rate at low but not at high temperatures (*39*). A recent FP–resonance fluorescence study (*63*) of the OH + CH_4 reaction from 298 K to 1512 K serves as a fine example of a single, direct study whose results may be extrapolated with confidence to about 2000 K. Fontijn and co-workers (*64*) have developed high-temperature flow reactors for rate studies up to 2000 K.

In summary, the H_2 and O_2 combustion system is reasonably well characterized, although even there some elementary steps such as the formation of HO_2 by way of H + O_2 + M (where M is the inert carrier gas) have uncertain temperature- and M-dependence. As the complexity grows from CO–H_2–O_2 to CH_4–O_2 to larger saturated hydrocarbons, olefins, and aromatics, the mechanisms become much more complicated, and the total number of steps becomes unmanageable. However, simplifications do exist, such as the overall sequence in the oxidation of alkanes (C_4H_{10}) to olefins (C_2H_4, C_3H_6), to CO, and to stable combustion products, as Dryer and Glassman (*65*) have shown in their turbulent flow reactor apparatus. Much further work needs to be done on measurements of the rates of direct radical reactions. For example, the rates and products of hydrocarbon radical disproportionation reactions are still uncertain.

Conclusions

The experimental science of measuring the rates of elementary chemical reactions has advanced to a point where hundreds of such rates either have been determined or are within reach. In a sense, these data give us a global view of chemical reactivity for gas-phase reactions. What this information lacks in detailed, state-to-state insight it more than makes up for in chemical diversity. It is essential that this research be pursued for its own sake rather than just for the sake of providing input data for atmospheric and combustion chemistry, however important these applications are. The existing data bases of elementary-reaction rate constants have not yet been systematically examined for what they tell us about chemical reactivity. In the light of present advances in the techniques for the generation and detection of reactive species, the number of accessible reactions and the range of temperatures and pressures being studied are rapidly increasing and the accuracy of the rate measurements is rapidly improving.

The field of elementary-reaction kinetics has suffered somewhat from benign neglect in comparison with its fashionable cousin, state-to-state dynamics, yet the latter is less applicable to larger chemical species. Applications in atmospheric science have made it possible to model increasingly complicated reaction systems successfully. Strong interaction between theorists and experimentalists has developed but needs to be expanded. What is needed more than anything else is the full realization by the academic community that elementary reaction kinetics is an intellectually exciting field that gives insight into why, how, and how fast chemical reactions take place.

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