Very Fast Reactions in Solution

Elementary steps in chemical reaction mechanisms can now be studied.

Gordon G. Hammes

The use of kinetic investigations as an aid in understanding the mechanism of chemical reactions in solution has engaged chemists for over a century. The ultimate goal of such investigations is to understand chemical reactions on a molecular basis. Ideally, one would like to be able to specify the state—that is, the energy and structure—of a molecule (in a quantum mechanical sense) as a function of time as the molecule undergoes reaction. In practice, the presence of solvent molecules and the fact that single molecules cannot be observed directly prevents such a specification, but a realistic goal is to try to map out the time course of the reaction as the reacting molecules proceed through a series of intermediate states which are averaged with respect to energy and whose structure is specified in a rough classical sense. Such a procedure is not easy to carry out: classical kinetic techniques usually give information about the overall chemical reaction, and information about intermediate states can only be inferred in an indirect manner. In order to study the "elementary steps" in chemical mechanisms, techniques must be used which permit detection of reaction intermediates and permit kinetic studies in the time range from molecular physical motions (about 10^{-13} second) to some long time set by the patience of a particular investigator. Most of the steps prior to and after the rate-determining step in a chemical reaction occur very rapidly, and only in recent years has the time range of kinetic investigations been extended to times sufficiently short to bridge the gap between classical chemical kinetics and molecular spectroscopy. In this article, some of the new techniques employed are discussed, along with a few examples of applications to chemistry (see *1* for a more comprehensive coverage).

As a general frame of reference, a brief consideration of the maximum possible rate of chemical transformations at room temperature is useful. The rate of bimolecular reactions is limited by the rate at which the reactants can diffuse together. This process is concentration-dependent, but even if the reactants are present at high concentrations ($\sim 0.1M$), the reaction occurs in times of the order of magnitude of 10^{-10} second or longer. The reverse process, dissociation, is limited by the rate at which two molecules can diffuse apart, and again the associated time constant is usually 10^{-10} second or longer. The rates of intramolecular transformations are limited, in principle, by the rates of molecular vibration and hindered rotation. In this case, a clear dividing line between physical and chemical transformations does not exist, although we clearly do not want to call a single molecular vibration a chemical reaction, nor do we want to call a rotation which profoundly alters the chemical properties of a molecule a physical process. However, a fairly safe generalization is that chemical intramolecular transformations are associated with time constants of 10^{-10} to 10^{-11} second or longer. Therefore, techniques are needed which permit the study of reactions having time constants as short as 10^{-10} second; in point of fact, this need is now reasonably well met by existing methods. Some of the methods currently available for studying chemical reactions in the time range 1 to 10^{-10} second are now considered.

Flow Methods

The first extension of classical kinetic methods to times shorter than 1 second occurred with the innovation of flow methods by Hartridge and Roughton, in 1923 (*2*). They were able to achieve a time resolution of about a millisecond by driving the reactants under pressure into a special mixing chamber where mixing could occur in a few milliseconds. After mixing, the fluid enters an observation tube, and measurements at different times can be made either by observing the fluid at various distances along the observation tube or by observing at a constant distance along the tube while varying the velocity of the fluid. It is easy to see that, in either case, if the velocity is constant, the time of the observation relative to initiation of the reaction is simply d/v, where d is the distance from the mixing chamber and v is the velocity of the flowing reaction mixture. An even more useful device is a stopped-flow apparatus; with this method the reaction mixture is driven against a piston, which is stopped rapidly, usually by having the end of the piston hit a solid surface, and observations are made after the flow stops. Chance and his co-workers merit special mention for their part in the development of this technique (*3*). Various methods have been used for following the changes in concentration—for example, spectrophotometry, fluorimetry, and conductance measurements. Flow methods have proved very useful in studying a variety of different chemical reactions, but the flow method is inherently limited by the rate at which two fluids can mix, and mixing cannot be accomplished very readily in less than 1 millisecond. Thus, an entirely different experimental approach is needed for studying reactions with characteristic time constants of less than 1 millisecond.

Relaxation Methods

In the early 1950's the development of a new kind of method for studying rapid reactions in solution was begun by M. Eigen and his coworkers (*4*). Subsequent development of these relaxation methods has extended the time range of kinetic investigations to times as short as 10^{-10} second. The principle of these methods is quite simple: rather than trying to mix the reactants together very rapidly, the investigator perturbs an equilibrium mixture of reactants by varying some external parameter such as temperature or pressure. If the equilibria are dependent upon the external parameter,

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The author is professor of chemistry at Cornell University, Ithaca, New York.

the equilibrium concentrations will vary, and the rate at which the concentrations vary is a measure of the rates of the chemical reactions coupling the concentrations. This can be most easily visualized by considering a step-function perturbation. Suppose, for example, the temperature is changed instantaneously from T_1 to T_2. If the chemical equilibria are temperature-dependent, the concentrations will all change from their equilibrium values at T_1 to their respective values at T_2. The rate at which the concentrations change from one equilibrium state to another is a measure of the kinetics of the reactions occurring. This type of behavior is depicted schematically in Fig. 1. In practice, of course, an instantaneous step-function perturbation is not possible, but the time during which the perturbation occurs need only be short compared to the rates of the chemical reactions in order for an effective step perturbation to be achieved.

Any type of perturbation can be utilized if it causes detectable deviations in concentration from some arbitrary reference state. Effective step-function perturbations, periodic perturbations, and pulsewise perturbations of various forms have been utilized. The state being perturbed need not necessarily be an equilibrium state; any stationary state is suitable if this state does not have an overall net change in concentrations. The manner in which the state of a system depends on certain external parameters is dictated by the laws of thermodynamics; temperature, pressure, and electric field have proved to be particularly useful external parameters.

Four relaxation methods have been used extensively: the temperature jump, the pressure jump, an electric field jump, and ultrasonic attenuation measurements. In the temperature jump method a rapid rise in temperature is utilized to perturb the system. A temperature jump of approximately 10°C can be brought about by charging a condenser with a high voltage (20 to 100 kilovolts) and then discharging the condenser rapidly through the reaction mixture. To insure uniform and rapid heating, an inert electrolyte is added to the reaction mixture. With this method, temperature rises of 10° can be achieved in about 10^{-6} second, so reactions with characteristic time constants longer than 1 microsecond can be studied. Changes in concentration have been detected with absorption spectrophotometry, polarimetry, and fluorimetry. Dielectric heating and heating by light pulses have also been utilized, but these methods have not proved as useful as a high-voltage condenser discharge.

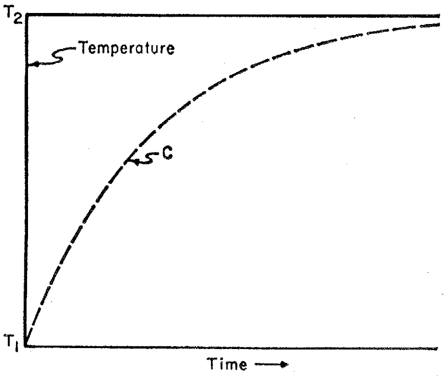


Fig. 1. Change in concentration, c, following a step-function perturbation from temperature T_1 to temperature T_2.

In the pressure jump method a diaphragm is inserted over the reaction mixture and a pressure of 50 to 100 atmospheres is applied by means of either a liquid or a gas. If the diaphragm is then burst, a pressure jump of 50 to 100 atmospheres is achieved. Because chemical equilibria are relatively insensitive to pressure, only very sensitive conductance methods have been used for detecting changes in concentration.

Changes in electric field are most often used to perturb equilibria involving the production or destruction of ions. Electric-field changes are usually accomplished by discharging a condenser through the reaction mixture; in this case the resistance of the solution must be very high to minimize heating effects which might mask the effect of the electric field. Changes in concentration are followed conductometrically.

An ultrasonic wave is an adiabatic pressure wave, so generally both a temperature and a pressure change accompany the propagation of a sound wave through solution. In aqueous solution, temperature fluctuations are nearly absent because the thermal expansion coefficient of water is very small (zero at 4°C). As early as 1920, Einstein suggested the use of an ultrasonic wave for the study of gas phase reactions (*5*). Unfortunately, only recently have technological advances permitted the use of ultrasonics for kinetic studies. Kinetic information generally is obtained by measuring the absorption coefficient of the ultrasonic wave at various frequencies. The absorption coefficient is related to the energy dissipation of ultrasound in the liquid, and the energy dissipation goes through maxima at frequencies characteristic of the processes occurring. This method permits measurement of time constants as short as 10^{-10} second.

Table 1. Methods for studying fast reactions in solution, and time range covered.

Method	Time range (sec)
Flow	10^{-3}–1*
Temperature jump	10^{-6}–1
Pressure jump	10^{-5}–1*
Electric field jump	10^{-8}–10^{-4}
Ultrasonic	10^{-10}–10^{-5}
Nuclear magnetic resonance	10^{-7}–1
Electron spin resonance	10^{-9}–10^{-5}
Flash photolysis	10^{-6}–1*
Fluorescence	10^{-10}–10^{-8}
Electrochemical	10^{-4}–1 *

* Or longer.

Relaxation methods have a unique feature: because the deviations from equilibrium are small, the kinetic behavior of the system can always be described by a set of linear differential equations. For example, for a one-step mechanism such as

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AB}$$

the rate equation (a step-wise perturbation being assumed) is

$$-\frac{d\Delta c}{dt} = \frac{1}{\tau}\,\Delta c \qquad (1)$$

where Δc is the deviation of the concentration of all components from their equilibrium values and τ is the relaxation time of the system. In this case

$$1/\tau = k_1\,(\bar{\mathrm{A}} + \bar{\mathrm{B}}) + k_{-1} \qquad (2)$$

where the bars above A and B designate equilibrium concentrations. If the mechanism is complex, a system of rate equations of the general form

$$-\frac{d\Delta c_i}{dt} = \sum_j a_{ij}\Delta c_j \qquad (3)$$

is obtained, where the a_{ij} are known functions of rate constants and equilibrium concentrations. If the system of simultaneous equations is solved, a spectrum of relaxation times is obtained, each relaxation time having its own particular dependence on the equilibrium concentrations. This type of analysis is mathematically analogous to the normal-mode analysis commonly used in vibrational spectroscopy. The relaxation times can be viewed as normal-mode relaxation times, similar in concept to normal-mode vibrational frequencies. In principle, determination of all the relaxation times of a system as a function of the equilibrium concentrations permits postulation of a chemical mechanism and evaluation of all the rate constants associated with the mechanism.

Table 2. Rate constants of selected protolytic reactions.*

Reaction	$k_f (M^{-1}\ \text{sec}^{-1})$ †	$k_r (\text{sec}^{-1})$ ‡	Reference
$H^+ + OH^- \rightleftharpoons H_2O$	1.4×10^{11}	2.6×10^{-5}	(*8*)
$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$	4.5×10^{10}	8×10^{5}	(*9*)
$NH_3 + H^+ \rightleftharpoons NH_4^+$	4.3×10^{10}	24	(*10*)
$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$	3.4×10^{10}	5×10^{5}	(*9*)
$C_3N_2H_4 + H^+ \rightleftharpoons C_3N_2H_5^+$	1.5×10^{10}	1.7×10^{3}	(*11*)
$C_3N_2H_5^+ + OH^- \rightleftharpoons C_3N_2H_4 + H_2O$	2.3×10^{10}	2.5×10^{3}	(*11*)
$OH^- + EDTA^{3-} \rightleftharpoons EDTA^{4-} + H_2O$	3.8×10^{7}	6.9×10^{3}	(*12*)
$OH^- + PAS^- \rightleftharpoons PAS^{2-} + H_2O$	3×10^{7}	3×10^{4}	(*12*)

* All reactions in water around room temperature (20° ± 10°C). † Rate constant for the reaction in the forward direction. ‡ Rate constant for the reaction in the reverse direction.

Magnetic Resonance Methods

The advent of magnetic resonance methods has also extended the range of accessible times in kinetic investigations. If nuclei which possess a magnetic moment (that is, have non-zero nuclear spin) are placed in a magnetic field, they precess around the direction of the field with a radial frequency, ω, which is proportional to the strength of the magnetic field, H_{local}, at the nucleus. The exact resonance condition is

$$\omega = \gamma H_{\text{local}} \qquad (4)$$

where γ is the gyromagnetic ratio of the nucleus in question. In practice, the frequency is held constant and the strength of the magnetic field is varied until the resonance condition is satisfied. In liquids, very sharp lines are obtained. The magnetic field at each particular nucleus depends strongly on the exact chemical environment, so nuclei with different electronic shielding exhibit resonance at slightly different applied magnetic fields. In addition, interactions with neighboring nuclei through orbital electrons cause a splitting of the resonance lines. These two phenomena give rise, respectively, to chemical shifts and spin-spin splitting (see *1*). For example, the two possible orientations (spin up and spin down) of the proton in the hydroxol of methanol cause a splitting of the resonance due to the protons in the methyl group. In order for this splitting to occur, the OH proton must go "on" and "off" slowly relative to the reciprocal of the frequency of the splitting. When sufficient HCl is added to methanol, the OH proton goes "on" and "off" very rapidly because of rapid proton-transfer reactions, and the splitting of the CH_3 protons disappears. The transition between a complex spectrum, in which peaks with different chemical shifts or with spin-spin splittings are observed, and the simpler spectrum produced by rapid exchange occurs when

$$\tau \simeq 1/\delta\omega \qquad (5)$$

Here τ is the mean lifetime for chemical exchange and $\delta\omega$ is the splitting (in radians per second) between lines obtained when there is no exchange. (This is essentially a manifestation of the uncertainty principle.) The relaxation time is defined by

$$1/\tau_i = \frac{\text{Rate of removal of molecules from } i\text{th state by exchange}}{\text{Number of molecules in } i\text{th state}} \qquad (6)$$

Thus, kinetic studies can be made if some parameter, such as temperature or catalyst concentration, can be varied so that the rate of chemical exchange is increased to the point where peaks associated with different chemical shifts coalesce, or, alternatively, to the point where spin-spin splitting is eliminated. A more detailed analysis shows that, even if exchange is rapid, the width of the resonance line will be dependent on the rate of exchange. The time range covered by nuclear magnetic resonance techniques is approximately 10^{-1} to 10^{-7} second.

Electron spin resonance is understandable in terms similar to those of nuclear magnetic resonance. In electron spin resonance the spin of an electron interacts with the field, and the resonance condition is

$$h\nu = g\beta H_{\text{local}} \qquad (7)$$

where ν is the frequency, g is a constant related to the spin and orbital motions of an electron, and β is the Bohr magneton. In order for an electron spin signal to be observable, the system must contain unpaired electrons. In general, electron spin resonance spectra are quite complex, because of interactions between nuclei and electron spins, but, again, kinetic studies can be made if resonance lines can be made to coalesce or if line widths can be made to change. The time range covered by this method is about 10^{-5} to 10^{-9} second.

Many other methods, not discussed here, are available for the study of fast reactions. Table 1 gives a summary of some of the methods currently in use and the time ranges that they cover (see *1* for details).

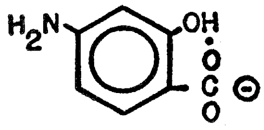
Many different kinds of reactions have been studied by fast reaction techniques. Let us consider a few examples. Fifteen years ago the reactions between (i) protons and (ii) acids and bases were thought to occur instantaneously. However, a large number of such reactions have now been studied in aqueous solution; some typical results are given in Table 2. For many acids and bases, the association reactions with protons and hydroxyl ions are diffusion-controlled —that is, a reaction occurs every time the two reaction partners collide. (This behavior can be used to define the concept of "normal" acids and bases.) The reason for this can be found in the structure of water: a hydrogen-bonded bridge is formed between reaction partners which permits rapid transfer of a proton. For a proton and a base, B, this can be depicted as

$$\mathrm{B\ \overset{H}{H}O \cdots \overset{H}{H}OH^+}$$

while for an acid, AH, and a hydroxyl ion, the situation can be visualized as

$$\mathrm{AH \cdot \overset{H}{O}H \cdots \overset{H}{O}H \cdots \overset{H}{O}^-}$$

The rate of proton jumps in a hydrogen-bonded lattice has been inferred, from measurements on ice, to be about 10^{13} jumps per second. Thus, reaction occurs very rapidly after the reactant partners diffuse together. If the water structure around the reactants is perturbed in such a manner that rapid proton transfer cannot occur, the reaction is no longer diffusion-controlled. This situation prevails, for example, in the reaction of OH^- with trivalent ethylenediaminetetraacetic acid (EDTA), because the high charge density around EDTA disrupts the water structure, and in the reaction of OH$^-$ with *p*-aminosalicylic acid (PAS), where one of the reactants is "blocked" from the solvent by an internal hydrogen bond:



For normal acids and bases, the acidity or basicity is determined almost entirely by the rate of dissociation, since the association rates are all diffusion-controlled. Proton exchange reactions between different acids and bases have also been studied in considerable detail. (In the cases just discussed, water was one of the acids or bases.) The overall reaction can be written

$$AH + B \rightleftharpoons A^- + BH^+$$

For normal acids and bases the rate is diffusion-controlled as long as the proton is bound more tightly at the proton acceptor than at the donor. The rate of the reverse reaction is then determined by the overall equilibrium constant. A great many protolytic reactions have now been studied, and the influence of electrostatic interactions, electronic structure, and molecular structure on reaction rates has been probed (see *6*).

The rate of hydrogen bond formation has been studied in a few cases. Some typical results are shown in Table 3. In relatively inert solvents (such as carbon tetrachloride and benzene), the rate of formation of benzoic acid and 2-pyridone dimers is essentially diffusion-controlled, while the rate of dissociation is relatively slow, reflecting how poorly the solvent competes with benzoic acid for the hydrogen bonding sites. In dioxane, the rate of formation of 2-pyridone dimers is again diffusion-controlled, but the rate constant for the reverse process is quite large, because dioxane, a good hydrogen bond acceptor, competes very effectively with 2-pyridone for hydrogen bonds. The fact that the association rate is diffusion-controlled implies that the formation of the hydrogen bonds after the reactants come together is more rapid than the separation of the reactants by diffusion. The associated rate constant must be greater than 10^{10} per second.

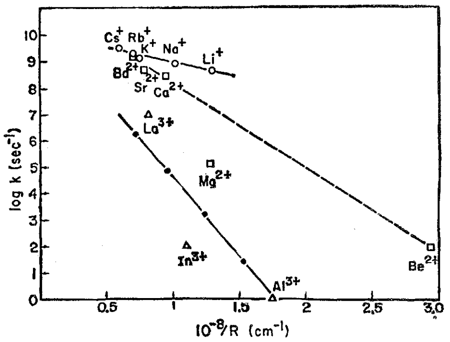


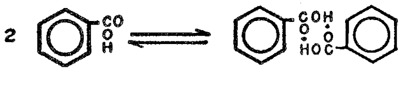
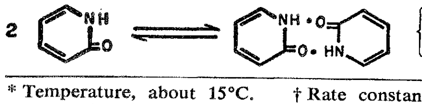
Fig. 2. Correlation between the rate constant, *k*, for the dissociation of inner-sphere water molecules of metal ions and the ionic radius *R* (see *15*). The lines show the approximate correlation between *k* and $1/R$ for ions of different valencies.

Metal ions in aqueous solution exist as positively charged ions usually surrounded by a layer of water molecules whose properties are markedly different from those of the bulk solvent. When the metal forms a complex with a ligand other than solvent, the overall reaction consists of substitution of the new ligand for solvent. The kinetics of literally hundreds of metal-complex reactions has been studied. A general mechanism has emerged from these studies: rapid formation of a complex between ligand and solvated metal followed by the rate-determining step, which is the release of one or more of the "inner"-sphere solvent molecules. (Successive substitution of two layers of solvent molecules has been observed in several cases.) Thus, the rate of formation of a metal complex is mainly determined by the particular metal ion and is relatively independent of the particular ligand involved. The rate constants characteristic of the dissociation of water from the inner hydration shell of several metal ions and the dependence of these rate constants on ionic size are shown in Fig. 2. From these results it is clear that the charge density around the metal ion is of importance: generally the rate constant decreases as the ionic charge increases, and at constant ionic charge the rate constant increases as the radius increases. For some metals of high charge density (for example, Al^{3+}), water dissociation is so slow that hydrolysis of the water molecule usually occurs before substitution. Also, transition metals do not conform well to the correlation shown in Fig. 2. In this case the properties of the *d*-electronic orbitals play a predominant role in binding of the hydration shell, but the general mechanism of metal-complex formation is still a substitution, whose rate is limited by the rate of dissociation of water molecules from the inner hydration shell.

For all the examples discussed thus far, the mechanisms and rates of reaction are mainly determined by the discrete solvent structure and the interaction of the solvent with the reactants. These mechanisms are applicable in a large majority of cases, but some exceptions to the general mechanisms occur.

As an illustration of a class of reactions still not well understood, the mechanism of enzyme catalysis is briefly discussed. Enzymes are amazing catalysts in that their catalytic efficiencies are generally greater by a factor of at least 10^6 than the efficiencies of corresponding synthetic catalysts. Several regularities for these mechanisms, in terms of the elementary steps involved, have become apparent (*7*). The initial combination of enzyme and substrate is quite rapid, although the rate constants usually fall somewhat below the values expected for a diffusion-controlled process. Once the substrate is combined with the enzyme, different types of reactions are possible, including macromolecular conformational changes, local acid-base catalysis (proton transfer), and electron transfer. All these elementary steps have now been studied in simple systems; they can be quite rapid, and therefore they may be involved in enzyme catalysis. Kinetic investigations of enzymatic reactions, coupled with structural studies, will, hopefully, lead to a molecular picture of enzyme catalysis in the near future.

Table 3. Rate constants for selected hydrogen bonding reactions.*

Reaction	Solvent	k_f (M^{-1} sec^{-1})†	k_r (sec^{-1})‡	Reference
	CCl_4	3.9×10^9	3.4×10^5	(*13*)
	Benzene	$\sim 10^9$	$\sim 3 \times 10^5$	(*14*)
	Dioxane	1.7×10^9	0.9×10^8	(*14*)

* Temperature, about 15°C. † Rate constant for the reaction in the forward direction. ‡ Rate constant for the reaction in the reverse direction.

Summary

As a result of investigations using these methods, the molecular details of many solution reactions are becoming apparent. However, these techniques have not yet been applied to many types of reactions. They promise to be of considerable further usefulness in revealing the mechanism of many chemical reactions.

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NEWS AND COMMENT

M.I.T.: New President Will Pursue Broadened Goals

Cambridge. The Massachusetts Institute of Technology has been evolving rapidly during the postwar years toward what its leaders call a "university polarized around science and technology." In July, M.I.T. will have a new president, one who promises to continue in the path of his predecessors and make "no right angle turns." The presidency of M.I.T. is, most would agree, a position of unusual significance because of the Institute's leadership in technology and its major role in government-sponsored "big science."

As one Massachusetts newspaper has observed, a computer assigned to the screening of candidates for the presidency might have passed over Howard W. Johnson, the 43-year-old president-elect. Johnson is neither scientist nor engineer, but an economist whose reputation rests chiefly on his work as dean of M.I.T.'s Alfred P. Sloan School of Management. He will succeed President Julius A. Stratton, a physicist who did outstanding work in electromagnetic theory during the 1930's and 1940's.

However, it is not unprecedented for M.I.T. to choose its president from outside the ranks of scientists and engineers. The Institute's third president, Francis Amasa Walker, who served from 1881 to 1897, was a political economist. Stratton's predecessor, James R. Killian, Jr., now chairman of the Corporation of M.I.T., came to the presidency from a career primarily as an academic administrator. Moreover, the selection of a social scientist as president does not seem inappropriate for an institution which, though emphasizing science and technology, is concerned with the "totality of the human experience."

The New York *Times*, in a lead editorial on Johnson's election shortly after it was announced in December, observed that Sir Charles Snow, in taking a second look at his "two cultures" hypothesis, has perceived that the social scientists might lead in bridging the gap between humanists and physical scientists. The *Times* suggested that Johnson could be expected to continue the cultural bridge building already well under way at M.I.T.

Lord Snow's "two cultures" may be, as some believe, a moribund and scarcely accurate cliché. But there is no gainsaying the fact that at M.I.T., or any other institution, establishing a measure of common understanding between various fields of specialization is an endless task for which a social scientist may be as well fited as anyone. According to Killian, Johnson caught the attention of the M.I.T. Corporation and its selection committee because of exceptional personal qualities, not because of his professional identity as dean of the School of Management. Or, as Stratton put it, "It was not a choice based on the theology, but on a man."

The search for a new president began last November after it had been announced that Stratton would depart at the end of the current academic year. (Nearing M.I.T.'s retirement age of 65, Stratton will leave the Institute and devote himself to the chairmanship of the Ford Foundation board of trustees, a post which he assumed on 1 January.) The M.I.T. Corporation appointed a Committee on Succession, whose members were James B. Fisk, president of Bell Telephone Laboratories, Inc., chairman; Vannevar Bush, former vice president and dean of engineering of M.I.T. and former president of the Carnegie Institution; Crawford H. Greenwalt, chairman of E. I. du Pont de Nemours and Company, Inc.; Robert C. Gunness, executive vice president of Standard Oil Company (Indiana); and Edward J. Hanley, chairman and president of Allegheny Ludlum Steel Corporation. It was on this group's recommendation that the Corporation elected Johnson.

According to Killian, the committee assumed that, whoever became the new president, M.I.T. would not be making any radical shifts of direction or basic policy. All else being equal, the committee would favor someone from inside the Institute who understood M.I.T.'s complexities and whose selection would spare the Institute a long interregnum. There was no disposition to pass over the scientists and engineers. "It would be natural to think that the head of the Institute would come from engineering or science," Killian said. "This was the assumption at the beginning." But, he added, the most important quality sought was a gift for leadership, regardless of academic specialty.

Campus speculation on the chief contenders for the presidency pointed to Charles H. Townes, M.I.T.'s provost, and Jerome B. Wiesner, dean of the School of Science. Townes, co-winner of the 1964 Nobel prize in physics for