

MASS SPECTROMETRY of VERY FAST CHEMICAL REACTIONS

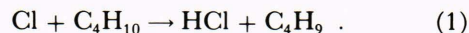
S. N. Foner and R. L. Hudson

A mass spectrometer employing a crossed molecular beam reactor has been developed for studying very fast elementary gas phase reactions. With this system it has been possible to obtain direct identification of free radicals and unstable molecules formed in hydrogenation, oxidation, and chlorination reactions.

Although it has been established that chemical reactions usually proceed by a series of elementary steps involving atoms and free radicals as intermediates, information on these elementary steps is far from complete. Indeed, most of the information on the elementary reaction steps has been *indirectly* deduced from kinetic data on overall reaction rates, without the benefit of direct observational evidence that the free radicals supposed to be participating in the reactions are actually present.

In many simple reactions, the deductive evidence for the radicals produced is so strong that there is no reason to doubt the correctness of the assignments. For example, in the reaction of

atomic chlorine with butane (which we shall discuss in detail later) one confidently expects the Cl-atom to abstract a hydrogen atom from the butane to form HCl and leave a butyl (C_4H_9) radical, according to the equation



Although the rate constants for this reaction are quite well known from competitive chlorination experiments,¹ direct observation of the butyl radical product of the reaction had not been reported prior to our study, and, therefore, was one of the targets of the experimental program.

On the other hand, there are many reactions that have been proposed to explain experimental results that, to state it mildly, are highly speculative. In complex reactions it is not too difficult to suggest several alternative mechanisms that

¹G.C. Fettes and J.H. Knox, "The Rate Constants of Halogen Atom Reactions," *Progress in Reaction Kinetics*, Volume 2, Macmillan Company, New York, 1966, 1-38.

Studies of very fast bimolecular reactions have been carried out with a mass spectrometer incorporating a high intensity crossed molecular beam system. At the low pressures involved, the products observed are the result of single molecular collisions. Free radicals formed in a variety of elementary reactions have been directly observed, and an unusual reaction has been discovered in which an oxygen atom, in a single step, removes two hydrogen atoms from opposite ends of a molecule.

could possibly explain the results, and in the absence of direct observations of the intermediates it is not possible to establish which one is the correct mechanism.

One effective approach that has been used to elucidate mechanisms of chemical reactions has been to analyze the reacting systems by mass spectrometry, first, to see if the theoretically postulated radicals and stable molecules are actually present and second, to measure their concentrations. Mass spectrometer sampling times have ranged from many seconds for static systems, in which case the more interesting highly reactive components have completely disappeared, down to the order of a millisecond for fast flow reactors, in which case free radicals and other intermediates can be readily observed.

For studying the details of very fast elementary reactions, a fast flow reactor with a millisecond sampling system does not provide adequate time resolution, as can be seen from the following considerations. If the reaction takes place at room

temperature and one atmosphere pressure, the molecular collision rate would be about 5×10^9 /sec, so that a molecule would undergo several million collisions before sampling. Marked improvement in resolution can be obtained by reducing the pressure from one atmosphere (760 Torr) to about 1 Torr, in which case only several thousand collisions would occur before analysis. Further significant reduction in pressure to limit the number of collisions runs into two problems: (1) diffusion to the walls of the apparatus becomes important and wall reactions have to be considered, and (2) the mass spectrometer sensitivity decreases monotonically along with the reactor pressure, so that detection of radicals becomes more difficult. Some of the reactions we have been interested in studying take place within 10 to 100 collisions, so that a different approach is needed.

A potentially powerful technique for studying very fast reactions is to employ crossed molecular beams. Crossed molecular beams have been used to study elastic scattering and reactive scattering

of alkali atoms with halogen compounds² (for example, the reaction of potassium atoms with methyl iodide has been studied in great detail³). In a typical experiment, collimated molecular beams of the reactants are directed at right angles to each other and the molecules interact in the region where the beams intersect. There is a finite probability that a molecule will suffer a single collision in the region where the beams cross, but negligible likelihood for two or more collisions occurring. The characteristic time resolution for a crossed beam experiment is the duration of a bimolecular collision, which is typically less than 10^{-12} sec (for an assumed chemical interaction distance of 2 \AA and a mean relative velocity of 4×10^4 cm/sec, one obtains a collision time of 5×10^{-13} sec).

Almost all of the previous reaction studies with crossed molecular beams have been done with alkali atoms as one of the reactants, principally because these atoms can be detected readily with a surface ionization detector consisting of a heated tungsten wire or ribbon that converts the impinging alkali atoms into positive ions. For other atoms or molecules there are no high efficiency detectors available, so that achieving adequate beam intensity becomes a very serious problem in the design of experiments.

Since we shall be concerned with elementary bimolecular reactions, some discussion is in order on the general characteristics of bimolecular reactions and the rate constants associated with very fast reactions.

Bimolecular Reactions

Bimolecular reactions can be classified into two general types: (1) association reactions, in which the two colliding molecules combine to form a new molecule, and (2) exchange reactions, in which the two colliding molecules react to produce two new product molecules.

The association reaction:



in which the molecules (or atoms) designated by A and B combine to form the molecule C, is only of academic interest for the very low pressure experiments which we are concerned with because the molecule C, in the absence of a stabilizing collision with another molecule to remove excess energy, is not a persistent entity and will decompose back into A and B. The time for unimolecular decomposition of molecule C is extremely short; for a diatomic molecule, decomposition would take place in the time needed to execute a molecular

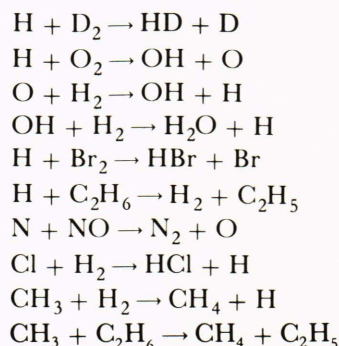
vibration or about 10^{-13} sec, while for a more complicated molecule the decomposition time would depend in a complex way on the number of degrees of freedom of the system and the amount of excitation energy, but in any event decomposition would occur long before the molecule could be detected in the mass spectrometer.

In an exchange reaction, which can be written in most general form as



where A and B are the reacting molecules and C and D are the product molecules, there is no problem in satisfying momentum and energy conservation requirements, and collisional stabilization of the products to prevent back reaction is unnecessary. All of the bimolecular reactions observable with crossed molecular beams are of this type.

A very important subclass of exchange reactions is the metathetical reaction of atom transfer, in which one of the colliding molecules snatches an atom away from the other molecule. The most common type encountered is that in which a hydrogen atom is transferred. Atom transfer reactions in which one of the reacting molecules is an atom or free radical occur very frequently in chain reactions. Some examples of atom transfer reactions involving atoms and free radicals are:



In most of the reactions listed above, a radical reacts with a stable molecule to produce a different radical and molecule. Exceptions are the second and third reactions, in which a radical reacts with a stable molecule to produce two radicals. These two chain branching reactions, incidentally, are responsible for the rapid proliferation of radicals in mixtures of hydrogen and oxygen leading to explosions.

Rate Constants and Steric Factors

The rate equation for the bimolecular reaction $A + B \rightarrow C + D$ can be written as

$$-\frac{d[A]}{dt} = k[A][B] = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}, \quad (4)$$

where k is the rate constant, and $[A]$, $[B]$, $[C]$,

²D.R. Herschbach, "Reactive Scattering in Molecular Beams," *Advances in Chemical Physics*, Volume 10, Interscience Publishers, New York, 1966, 319-393.

³E.F. Greene and J. Ross, "Molecular Beams and a Chemical Reaction," *Science* **159**, 1968, 587-595.

and [D] are the concentrations of A, B, C, and D, respectively. Bimolecular reactions are usually interpreted either in terms of classical collision theory or the transition-state theory of chemical kinetics. While the transition-state theory is more sophisticated than the collision theory and should, in principle, allow one to calculate rate constants from detailed knowledge of the partition functions of the activated complex, a more descriptive picture emerges from the collision theory.

According to the kinetic theory of gases, the number of collisions ζ per unit volume per unit time between molecules A and B is given by

$$\zeta = \pi \sigma_{AB}^2 \left(\frac{8RT}{\pi\mu} \right)^{1/2} [A] [B], \quad (5)$$

where $\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$ is the mean collision diameter of molecules A and B, μ is the reduced mass $\left(\frac{1}{\mu} = \frac{1}{M_A} + \frac{1}{M_B} \right)$, where M_A and M_B are the molecular weights of A and B, R is the gas constant, and T is the absolute temperature. If all collisions were effective in producing reaction, ζ would be the rate of reaction, and by comparison with Eq. (4) we would have $\zeta = k[A][B]$. In terms of specific collision frequency, $\zeta' = \zeta/[A][B]$, i.e., the collision rate for unit concentrations of A and B, we would have $k = \zeta'$.

In a reactive collision there is a potential energy barrier, known as the activation energy, that must be surmounted in order for the reaction to take place. This is depicted schematically in Fig. 1 for an exothermic bimolecular reaction having an activation energy E . The reason atom and free radical reactions are favored over molecule-molecule reactions is that the former generally have much lower activation energies. Among the exchange reactions involving atoms and free radicals there is great variation in the activation energy; some reactions take place with zero or near zero activation energy, while others have activation energies ranging upwards of 20 kcal/mole. Very fast bimolecular reactions at room temperature are characterized by having low activation energies.

For a reaction with an activation energy E , the number of collisions with adequate energy is obtained by multiplying the collision rate by the Arrhenius factor $e^{-E/RT}$. Since all collisions with adequate energy are not necessarily effective in producing reaction, a steric factor P is usually introduced to express the ratio between the actual rate and that predicted by collision theory. The rate constant can, therefore, be written as

$$k = P \zeta' e^{-E/RT} = P \pi \sigma_{AB}^2 \left(\frac{8RT}{\pi\mu} \right)^{1/2} e^{-E/RT}. \quad (6)$$

From an experimental standpoint, the rate con-

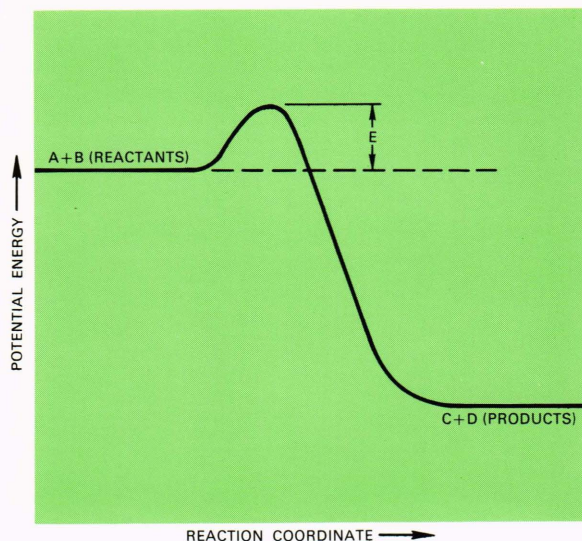


Fig. 1—Schematic representation of an exothermic bimolecular reaction with an activation energy E .

stant is usually simply written in the two parameter form

$$k = A e^{-E/RT}, \quad (7)$$

where A is an experimentally determined constant called the frequency factor and E is the activation energy.

To get a feeling for the magnitudes of the rate constants that are involved in fast reactions, we can calculate the maximum value for the rate constant by setting the activation energy equal to zero and the steric factor equal to unity. For a typical set of parameters, $T = 300^\circ\text{K}$, $\sigma_{AB} = 4 \times 10^{-8} \text{ cm}$, and reduced mass $\mu = 32$, one obtains $k = 2.25 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} = 1.35 \times 10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$. Therefore, we have as a rule of thumb that reactions with rate constants of the order of $10^{14} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ take place at almost

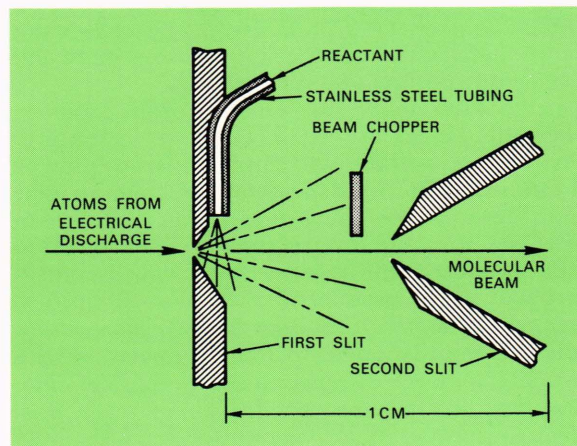


Fig. 2—Diagram of the crossed molecular beam apparatus.

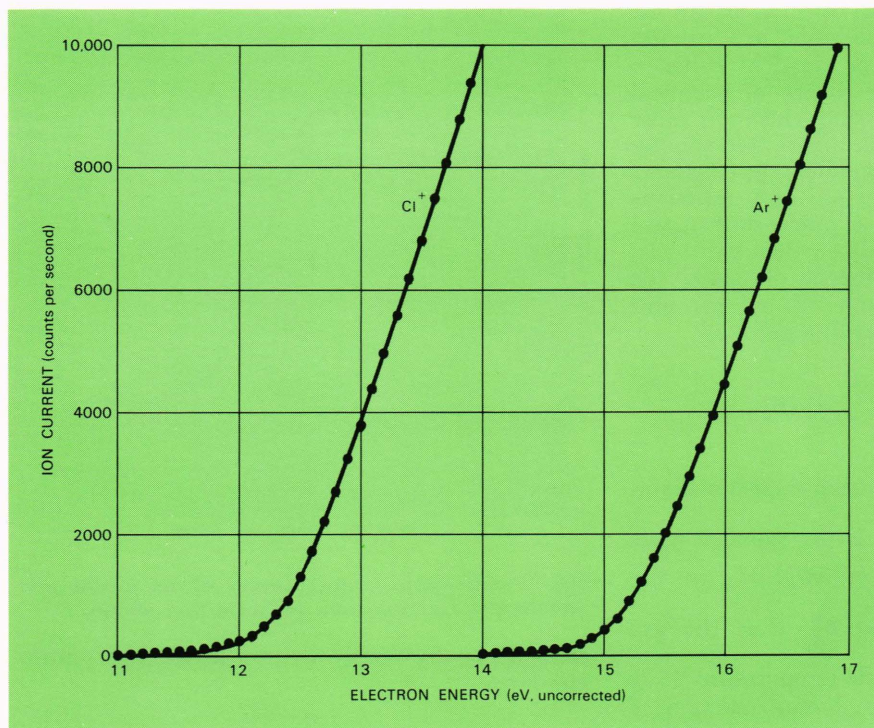


Fig. 3—Ionization curve for chlorine atoms produced by an electrical discharge along with an argon reference curve.

every collision, and reactions with rate constants of the order of $10^{12} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}$ take place every few hundred collisions.

Experimental Arrangement

The crossed molecular beam system is shown schematically in Fig. 2. Atoms generated by an electrical discharge enter through a small circular orifice 0.0118 cm in diameter in a conically divergent aperture in a stainless steel plate 0.0915 cm thick, while a cross beam of stable molecules effuses from the end of a stainless steel hypodermic needle tube. The hypodermic needle tubing has an inside diameter of 0.020 cm and is placed in a slot milled halfway through the stainless steel plate and fastened in position by spotwelding.

In contrast to typical crossed beam systems, where the beams are well collimated, in the present apparatus the two closely spaced sources (1 mm separation) radiate beams of large angular divergence. Since the intensity of each beam decreases with the inverse square of the distance from its source, the reaction rate, which is proportional to the product of the beam intensities, becomes a maximum between the two sources and falls off rapidly (inverse fourth power of the distance) for large distances from the sources. The net effect is that the reaction takes place predominantly in a small volume between the two sources and the reaction products can be considered as radiating from a small secondary source about 0.5 mm in diameter. The slit system which

defines the molecular beam entering the mass spectrometer has been designed to accept molecules coming from a circular zone about 0.75 mm in diameter. Therefore, reaction products that happen to have the proper direction can travel directly into the ion source and be detected.

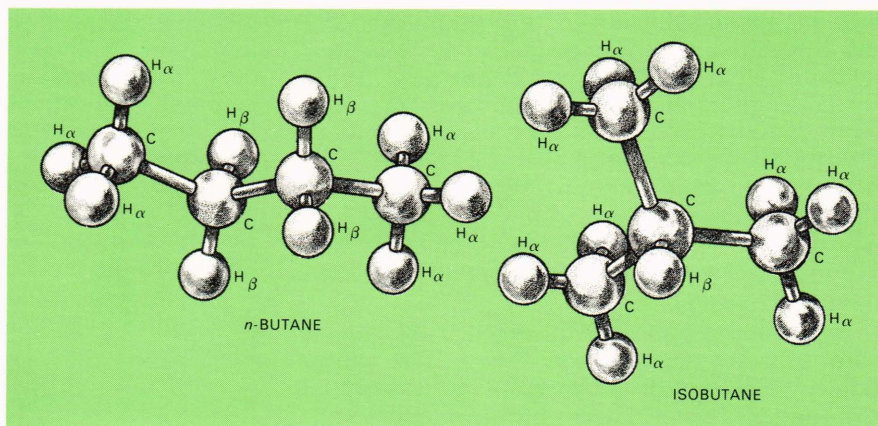
The essential features of the free radical mass spectrometer have been described.^{4, 5, 6} The instrument incorporates a molecular beam sampling system with three stages of differential pumping and uses modulation of the molecular beam to discriminate against background interferences. To achieve high ultimate sensitivity the ions are detected by an electron multiplier and counted in synchronism with the beam chopper so that one measures both the signal plus background and the background. The difference of the two numbers gives the signal due to the molecular beam, while the square root of their sum is the standard deviation of the measurement due to statistical fluctuations. In the latest version of the apparatus, a reversible counter is synchronized with the beam chopper to give direct readout of the signal,

⁴S.N. Foner and R.L. Hudson, "The Detection of Atoms and Free Radicals in Flames by Mass Spectrometric Techniques," *J. Chem. Phys.* **21**, 1953, 1374-1382.

⁵S.N. Foner and R.L. Hudson, "Mass Spectrometry of Free Radicals and Vibronically Excited Molecules Produced by Pulsed Electrical Discharges," *J. Chem. Phys.* **45**, 1966, 40-48.

⁶S.N. Foner and R.L. Hudson, "Mass Spectrometry of Free Radicals and Metastable Molecules," *APL Technical Digest*, **5**, No. 4, March-April 1966, 2-11.

Fig. 4—Structure of *n*-butane and isobutane.



updating the results with the chopper frequency (170 Hz), which considerably simplifies some of the operations, such as focusing the instrument and searching for small peaks.

Chlorine Atom Reactions

Among the fastest bimolecular reactions at room temperature are those involving atomic chlorine. As mentioned earlier, despite the extensive kinetic information available on these reactions, including measurements of rate constants and activation energies, direct observation of the radicals produced had not been reported.

Atomic chlorine was produced by dissociating a rapidly flowing stream of Cl_2 diluted with helium at about 1 Torr pressure by a 2450 MHz microwave discharge. The Cl-atoms were monitored by the mass spectrometer. In the absence of a cross beam of reactant, the mass spectrometer functions as a typical free radical mass spectrometer with the molecular beam of atoms from the electrical discharge going directly into the mass spectrometer.

An ionization curve for Cl-atoms from the microwave discharge is shown in Fig. 3 along with an ionization curve for the reference gas, argon, which was used to standardize the electron energy scale. The ionization potential of Cl-atoms

obtained in this experiment was in agreement with the spectroscopic value, 13.01 eV, proving that Cl-atoms were being produced and transmitted through the instrument. Chlorine atom yields of about 50% have been routinely produced in our experiments.

The very fast reactions of Cl-atoms with butane were used to check out the apparatus and to obtain direct identification of the butyl radicals produced. There are two isomeric forms of butane, *n*-butane and isobutane, having the structural formulas indicated in Fig. 4. In each of the butanes there are two classes of hydrogen atoms. In the diagrams, all of the H-atoms labelled H_α are indistinguishable chemically, as are the H-atoms labelled H_β . Removal of an H_α -atom from *n*-butane leaves the *n*-butyl radical, while removal of an H_β -atom produces the *sec*-butyl radical. In the case of isobutane, removal of one of the nine H_α -atoms produces the isobutyl radical, while removal of the H_β -atom produces the *tert*-butyl radical. All of these butyl radicals are chemically distinct and have different ionization potentials.

The frequency factors and activation energies (see Eq. 7) for the four reactions of Cl-atoms with the *n*-butane and isobutane have been determined.¹ Thus, instead of the simplified reaction (Eq. 1) discussed at the beginning of the paper, we have the four reactions listed in Table I along

TABLE I. ATOMIC CHLORINE REACTIONS WITH THE BUTANES

Reaction	$A(\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1})$	$E(\text{kcal mole}^{-1})$	$k(\text{cm}^3 \text{mole}^{-1} \text{sec}^{-1})$ at 300°K
$n\text{-C}_4\text{H}_{10} + \text{Cl} \rightarrow n\text{-C}_4\text{H}_9 + \text{HCl}$	8.4×10^{13}	0.77 ± 0.14	2.3×10^{13}
" " $\rightarrow \text{sec-C}_4\text{H}_9 + \text{HCl}$	9.6×10^{13}	0.30 ± 0.14	5.8×10^{13}
			$k_{\text{total}} = 8.1 \times 10^{13}$
$\text{iso-C}_4\text{H}_{10} + \text{Cl} \rightarrow \text{iso-C}_4\text{H}_9 + \text{HCl}$	1.2×10^{14}	0.80 ± 0.14	3.1×10^{13}
" " $\rightarrow \text{tert-C}_4\text{H}_9 + \text{HCl}$	2.1×10^{13}	0.10 ± 0.16	1.8×10^{13}
			$k_{\text{total}} = 4.9 \times 10^{13}$

with the tabulated rate equation parameters and the calculated rate constants for the reactions taking place at 300°K (room temperature). From the large values of the total rate constants, it is clear that these reactions take place with high probability, the steric factors for the reactions (see Eq. 6) being close to unity. We have estimated that in the case of *n*-C₄H₁₀ about 1 in 3 collisions with a Cl-atom leads to reaction, while in the case of *iso*-C₄H₁₀ about 1 in 5 collisions with a Cl-atom results in reaction.

Experimental results for the reaction of Cl-atoms with isobutane are shown in Fig. 5. The ionization curve gives clear evidence for the presence of two species of butyl radicals having different ionization potentials. The initial portion of the curve is due to *tert*-butyl radicals, which have an ionization potential of about 7.1 eV. Above 8.4 eV the curve is the result of superposition of ionization of both *tert*-butyl and isobutyl radicals. From the slopes of the linear sections of the ionization curve one can estimate the ratio of isobutyl to *tert*-butyl production in the reaction. We find the ratio of *iso*-C₄H₉/*tert*-C₄H₉ = 2.0, which is in good agreement with, and well within the uncertainty of, the tabulated rate constant data, which predict the ratio $3.1 \times 10^{13} / 1.8 \times 10^{13} = 1.7$.

In the case of the Cl-atom reaction with

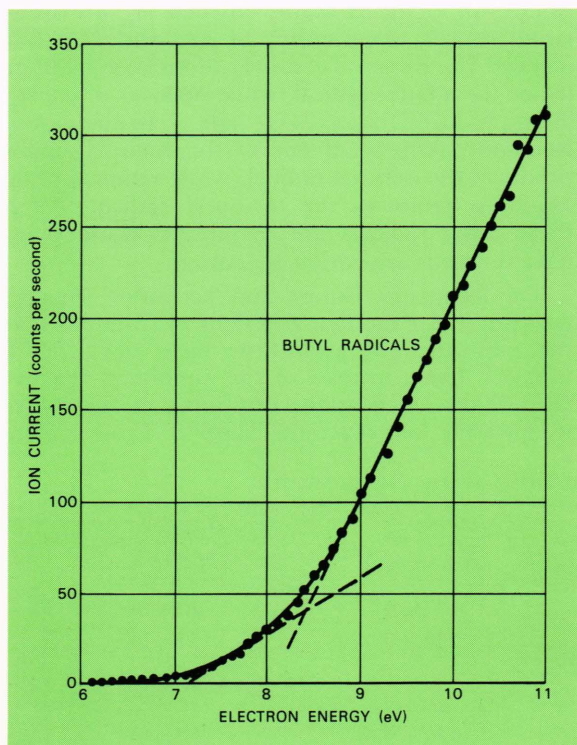
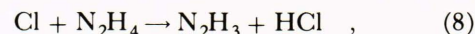


Fig. 5—Ionization curve for butyl radicals produced by the reaction of Cl-atoms with isobutane. The electron energy scale has been corrected for instrumental effects.

n-butane, the *sec*-butyl radical, which has a lower ionization potential than the *n*-butyl radical, has been clearly identified. Because of the high rate constant for *sec*-butyl radical production relative to *n*-butyl production and the close spacing of their ionization potentials, it has been difficult to resolve the ionization curve to show a distinct break due to onset of *n*-butyl radical ionization. However, the experimental data are consistent with the generation of two species of butyl radicals in the reaction.

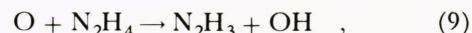
The reaction of Cl-atoms with hydrazine was also studied. The reaction is the hydrogen atom transfer reaction



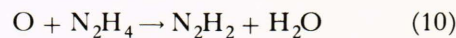
and the hydrazyl (N₂H₃) radical was observed in the experiment.

Oxygen Atom Reactions

The most surprising reaction we have studied thus far is that of oxygen atoms with hydrazine.⁷ The expected reaction was the atom transfer reaction

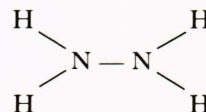


and the N₂H₃ radical was, indeed, observed. However, a substantially larger intensity of N₂H₂ was also observed, indicating that the reaction



was a competitive reaction occurring with much higher probability. The experimental data are shown in Fig. 6. The solid curve drawn for N₂H₃⁺ is an ionization curve for N₂H₃ obtained by us in other experiments carried out on this particular radical. The scatter in the N₂H₃⁺ data points in the present experiment reflects the statistical fluctuations in measurements at these low counting rates (1 count per second or less). Assuming that the ionization cross sections for the two molecules are equal, one finds that the yield of N₂H₂ is approximately 25 times that of N₂H₃.

Aside from kinetic considerations in the apparent removal of two hydrogen atoms in a single elementary reaction, the most pressing question to be answered was which two hydrogens were removed. If the reaction took the H-atoms from one end of the hydrazine molecule,



the diradical NNH₂ would be produced, while removal of H-atoms from opposite ends of the

⁷S.N. Foner and R.L. Hudson, "Mass Spectrometry of Very Fast Reactions: Identification of Free Radicals and Unstable Molecules Formed in Atom-Molecule Reactions," *J. Chem. Phys.* 1968 (in press).

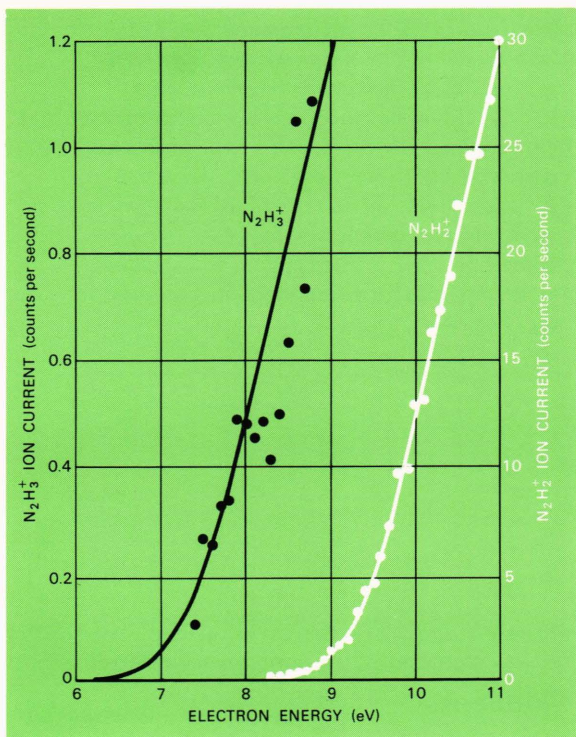
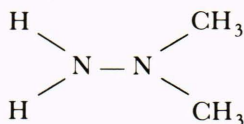


Fig. 6—Oxygen atom reaction with hydrazine showing the yields of the $N_2H_3^+$ radical and the $N_2H_2^+$ molecule. Note that the intensity scale for $N_2H_2^+$ is 25 times that of $N_2H_3^+$.

molecule would produce the diimide (N_2H_2) molecule.⁸

To resolve this question, we studied the reaction of O-atoms with unsymmetrical dimethyl hydrazine,



If the O-atom abstracts the hydrogens from one end of the hydrazine molecule, a similar reaction should also occur with unsymmetrical dimethyl hydrazine with the production of $N_2(\text{CH}_3)_2$. When the experiment was carried out we observed the $\text{HN}_2(\text{CH}_3)_2$ radical, but did *not* observe any $N_2(\text{CH}_3)_2$. This is strong kinetic evidence that in the O-atom reaction with N_2H_4 the two hydrogen atoms are actually removed from opposite ends of the molecule.

Additional evidence to confirm the production of diimide in the $\text{O} + N_2H_4$ reaction was obtained from ionization potential studies, which showed that within experimental error the reaction product had the same ionization potential as diimide.⁸ It would be an accidental coincidence if the ionization potential of the diradical NNH_2 had the

same ionization potential as N_2H_2 . The overall evidence is, therefore, rather strong that diimide is the product of the reaction.

There is considerable mystery concerning the collisional mechanics involved in the O-atom reaction removing the two H-atoms from hydrazine. There is no problem with regard to energy available in the reaction, since the production of diimide by the reaction (Eq. 10) is exothermic by 90 kcal/mole. From considerations of molecular geometry it would have been easier to have formed the H_2O molecule by snatching the two H-atoms from a single end of the hydrazine molecule, since the distance between the two hydrogens in water, 1.52 Å, is very close to the distance between the end hydrogens of hydrazine, 1.60 Å, and, therefore, no molecular distortion would have been required to carry out the reaction. Forming the H_2O product molecule by taking H-atoms from opposite ends of the hydrazine molecule requires considerable molecular bending of the N_2H_4 molecule during the collision if the reaction proceeds by sequential formation of first an O-H bond with an H-atom at one end, followed by reaching out across the molecule to complete the second O-H bond. An alternative possibility is the initial formation of an OH radical that tumbles through the hydrazine molecule, picking up a hydrogen atom from the other end to complete the formation of a water molecule. At the present time the collisional mechanics of this reaction is a speculative topic.

Hydrogen Atom Reactions

Some studies have been carried out on the reactions of H-atoms with various compounds. Most of these reactions do not have high collisional yields at 300°K and, therefore, it is usually difficult to detect the products formed in single bimolecular reactions. Thus far, none of the systems studied have shown any unexpected behavior. The H-atom transfer reaction has been observed. In the case of unsymmetrical dimethyl hydrazine, for example, the reaction is $\text{H} + \text{H}_2\text{N}_2(\text{CH}_3)_2 \rightarrow \text{H}_2 + \text{HN}_2(\text{CH}_3)_2$, and the expected $\text{HN}_2(\text{CH}_3)_2$ radical has been observed.

Summary

Mass spectrometry of very fast elementary gas phase reactions using crossed molecular beams is providing a deeper insight into the mechanisms of chemical reactions. By furnishing direct observational evidence for the presence of free radicals in reactions, it has substantiated indirectly-deduced information on the role of free radicals in reactions. The observation of the unexpected reaction in which an oxygen atom, apparently in a single step, removes two H-atoms from opposite ends of a hydrazine molecule, suggests that more surprises may be in store as additional reactions are investigated.

⁸S.N. Foner and R.L. Hudson, "Diimide—Identification and Study by Mass Spectrometry," *J. Chem. Phys.* **28**, 1958, 719-720.