Chemical Reviews

Volume 73, Number 5 October 1973

The Kinetics of Atomic Hydrogen Reactions in the Gas Phase

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Received November 29, 1972 (Revised Manuscript Received March 7, 1973)

Contents

I. Introduction

A number of reviews of hydrogen atom reactions have appeared in the past. The most notable example is the excellent book by Steacie,[1] which includes a very detailed examination of the hydrogen atom reactions up to 1954. Although several reviews have appeared since 1954, they have generally been on specific aspects of hydrogen atom reactions or on particular areas where hydrogen atoms have played an important role. For example, in 1963, Cvetanović[2] reviewed the reactions of hydrogen atoms with olefins. Perhaps the most comprehensive review since Steacie's book was that by Thrush[3] in 1965 which includes work up to 1964.

Since 1964, mention of hydrogen atom work has been included in a number of more general articles, *e.g.*, ele-

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(1) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd ed, Reinhold, New York, N. Y., 1954.

(2) R. J. Cvetanović, *Advan. Photochem.*, 1, 115 (1963).

(3) B. A. Thrush, *Progr. React. Kinet.*, **3**, 63 (1965).

mentary gas phase reactions (Kaufman,[4] 1969) and atom reactions, including oxygen, hydrogen, sulfur, and halogen atoms (Wagner and Wolfrum,[5] 1971). In addition, the compilations of rate data of Trotman-Dickenson and coworkers,[6,7] Bahn,[8] and Schofield[9] include data on hydrogen atom reactions.

In this article, we have attempted to produce a concise up-to-date review of the kinetics of hydrogen atom reactions. An emphasis has been placed on the kinetic parameters of the various reactions discussed. In many cases, we have also included a discussion of the mechanism proposed for the reaction.

II. Hydrogen Atom Production

Since the first report of the dissociation of molecular hydrogen on hot tungsten filaments in 1911,[10] many methods have been developed for the generation of hydrogen atoms. Perhaps the most frequently used method is the so-called Wood's tube,[11] in which a low-pressure stream of molecular hydrogen passes over metallic electrodes held at a relatively high voltage. Other common methods include: (1) radiofrequency and high-frequency microwave discharges, (2) mercury-photosensitized decomposition of H_2 and hydrocarbons, (3) direct photolysis of several compounds, (4) radiolysis of paraffins, (5) certain flame reactions, and (6) shock tubes.

Tollefson and Le Roy[12] developed the pyrolytic method for kinetic studies of atomic hydrogen reactions. They obtained hydrogen atoms at partial pressures of the order of 5×10^{-3} Torr by passing hydrogen at 1 to 10 Torr over a tungsten filament maintained at 1700°.

In a Wood's tube (glow discharge), up to 25% dissociation of molecular hydrogen has been found over the pressure range 0.1 to 1.0 Torr.[11,13,14] This method has been extended to pressures as high as 20 Torr by Harteck and Roeder.[15] Contamination from the electrodes and the limited pressure range are the major disadvantages of the Wood's tube.

In order to avoid contamination by the electrodes, the electrodeless radiofrequency and microwave discharges have been used. The theory of the electrodeless discharge was outlined as early as 1928, but an efficient way of producing high concentrations of hydrogen atoms by this method was first described by Jennings and Linnett[16] in 1958. They were able to maintain the discharge with 350 W of 9.7-MHz radiation and a gas pressure of about 0.08 Torr. This gave about 50–60% dissociation of H_2 into H atoms. Knox and Dalgleish[17] found that mixtures of 10–15% H_2 in Ar (2 Torr), when passed through an 18-MHz radiofrequency discharge ($\sim$100 W), gave about 25% dissociation of H_2 into H atoms. Widespread use of microwave discharges for the dissociation of gases resulted from the development of powerful sources of microwave energy during World War II. Among the early users of this type of discharge were Nagle, *et al.*,[18] and Broida and Moyer,[19] who found that a microwave discharge provides an efficient, stable source of hydrogen atoms. The microwave source has the advantage of having the energy readily and efficiently coupled to the gaseous discharge. Corrigan and von Engel[20] have studied the electronic processes by which electron swarms in rf discharges attack H_2 to form H atoms. They found for a 5-MHz discharge 5×10^{-2} dissociations of H_2 for each electron volt of energy imparted. This was quite similar to the figures 5.8×10^{-2} and 6.5×10^{-2} obtained by Poole,[21] using a Wood–Bonhoeffer system, and Shaw,[22] using a microwave system. The similarity of the efficiencies for dissociation in the three discharge systems has prompted Shaw[22] to conclude that the collisional cross section of H_2 is about two to three times larger than predicted by theory.

The mercury (Hg $^3P_1$) photosensitized decomposition of H_2 has proven to be a convenient source of hydrogen atoms.[23,24] Hydrogen atoms may also be produced by the mercury (Hg $^3P_1$) photosensitized decomposition of hydrocarbons[25] and fluoro hydrocarbons.[26,27] The direct photolysis of many compounds, *e.g.*, HBr,[28,29] HI,[30,31] HCHO,[32] CH_3SH,[33] and H_2S,[34,35] results in the production of hot ground state ($^2S_{1/2}$) hydrogen atoms. These hot atoms have excessive translational energy (from 22 to 40 kcal/mol) depending on the wavelength of the photolysis source. In an excess of inert gas, these hot atoms will be deactivated rapidly by collisions and react as thermalized atoms.[36]

Hydrogen atoms may also be produced by radiolysis. Yang[37] produced H atoms by γ radiolysis of propane and studied the effect of C_2H_4 on the rate of H_2 production. Back[38] has used α radiolysis of hydrocarbons to produce H atoms. Bishop and Dorfman[39] produced H atoms in hy-

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(4) F. Kaufman, *Annu. Rev. Phys. Chem.*, **20**, 45 (1969).

(5) H. Gg. Wagner and J. Wolfrum, *Angew. Chem., Int. Ed. Engl.*, **10**, 604 (1971).

(6) A. F. Trotman-Dickenson and G. S. Milne, "Tables of Bimolecular Gas Reactions," Report NSRDS-NBS 9, U. S. Government Printing Office, Washington, D. C., 1967.

(7) E. Ratajczak and A. F. Trotman-Dickenson, "Supplementary Tables of Bimolecular Gas Reactions," University of Wales, Institute of Science and Technology, 1970.

(8) G. S. Bahn, "Reaction Rate Compilation for the H-O-N System," Gordon and Breach, New York, N. Y., 1968.

(9) K. Schofield, *Planet. Space Sci.*, **15**, 643 (1967).

(10) I. Langmuir, *Trans. Amer. Electrochem. Soc.*, **20**, 225 (1911).

(11) R. W. Wood, *Proc. Roy. Soc., Ser. A*, **102**, 1 (1923).

(12) E. L. Tollefson and D. J. Le Roy, *J. Chem. Phys.*, **16**, 1057 (1948).

(13) K. F. Bonhoeffer, *Z. Phys. Chem.*, **113**, 199 (1924).

(14) K. F. Bonhoeffer, *Z. Phys. Chem.*, **116**, 391 (1925).

(15) P. Harteck and E. Roeder, *Z. Phys. Chem., Abt. A*, **178**, 389 (1937).

(16) K. R. Jennings and J. W. Linnett, *Nature (London)*, **182**, 597 (1958).

(17) J. H. Knox and D. G. Dalgleish, *Int. J. Chem. Kinet.*, **1**, 69 (1969).

(18) D. E. Nagle, R. S. Julian, and J. R. Zacharias, *Phys. Rev.*, **72**, 971 (1947).

(19) H. P. Broida and J. W. Moyer, *J. Opt. Soc. Amer.*, **42**, 37 (1952).

(20) S. J. B. Corrigan and A. von Engel, *Proc. Roy. Soc., Ser. A*, **245**, 335 (1958).

(21) H. G. Poole, *Proc. Roy. Soc., Ser. A*, **163**, 404, 415, 424 (1937).

(22) T. M. Shaw, General Electric Microwave Laboratory Report TIS R58ELM 115, 1958; TIS R60ELM 178, 1960.

(23) H. W. Melville and J. C. Robb, *Proc. Roy. Soc., Ser. A*, **196**, 445, 466, 479, 494 (1949).

(24) R. J. Cvetanović and L. C. Doyle, *J. Chem. Phys.*, **50**, 4705 (1969).

(25) K. R. Jennings and R. J. Cvetanović, *J. Chem. Phys.*, **35**, 1233 (1961).

(26) P. M. Scott and K. R. Jennings, *J. Phys. Chem.*, **73**, 1513 (1969).

(27) P. M. Scott and K. R. Jennings, *J. Phys. Chem.*, **73**, 1521 (1969).

(28) R. M. Martin and J. E. Willard, *J. Chem. Phys.*, **40**, 3007 (1964).

(29) R. D. Penzhorn and H. L. Sandoval, *J. Phys. Chem.*, **74**, 2065 (1970).

(30) A. M. Rennert and M. H. J. Wijnen, *Ber. Bunsenges. Phys. Chem.*, **72**, 222 (1968).

(31) R. D. Penzhorn and B. de B. Darwent, *J. Chem. Phys.*, **55**, 1508 (1971).

(32) O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, **60**, 347 (1964).

(33) B. G. Dzantiev, A. V. Shishkov, and M. S. Unukovich, *Khim. Vys. Energ.*, **3**, 111 (1969); *Chem. Abstr.*, 71, 2772t (1969).

(34) B. de B. Darwent and R. Roberts, *Discuss. Faraday Soc.*, 14, 55 (1953).

(35) G. R. Woolley and R. J. Cvetanović, *J. Chem. Phys.*, **50**, 4697 (1969).

(36) B. de B. Darwent, R. L. Wadlinger, and M. J. Allard, *J. Phys. Chem.*, 71, 2346 (1967).

(37) K. Yang, *J. Amer. Chem. Soc.*, **84**, 719 (1962).

(38) R. A. Back, *J. Phys. Chem.*, **64**, 124 (1960).

(39) W. P. Bishop and L. M. Dorfman, *J. Chem. Phys.*, **52**, 3210 (1970).

drogen by a pulse of high-energy electrons from a febetron generator. In principle, the radiolysis technique is very similar to the two preceding photochemical methods. These techniques have been used primarily for measurements of competitive reactions, yielding ratios of the rate constants of the competing reactions.

Hydrogen atoms are present after ignition of mixtures of H_2 and O_2.[40] The presence of an added compound can change the explosion limits of the thermal reaction, and the relative rates of attack of H on the additive can be obtained by determining the relative rates of consumption of H_2 and the additive. Hydrogen atoms can be generated in the exhaust gas from low-pressure hydrogen, hydrogen–CO, and hydrocarbon flames. Atomic hydrogen reactions can be studied at very high temperatures (up to 1600°K) by this method.[41,42]

The thermal dissociation of hydrogen behind a shock wave was described by Gardiner and Kistiakowsky.[43] Determinations of the rate of dissociation of H_2 up to 3000°K have been made in shock tubes.[44]

III. Hydrogen Atom Detection and Concentration Measurement

The detection of H atoms and determination of their concentration has been made by both physical and chemical methods.

A. Physical Methods

1. Wrede Gauge Method

A fairly direct method of estimating the concentration of hydrogen atoms in a gas containing only H_2 and H has been devised by Wrede[45] and Harteck.[46] This method depends on the steady-state pressure difference which is established when the stream of gas containing hydrogen atoms and molecules is diffused onto a catalyst through a slit or capillary whose width is smaller than the mean free path of the gas. The H atoms recombine on the catalyst, and only molecules effuse back into the main system creating a small pressure difference across the orifice. This method can only be used at low pressures and for concentrations of atoms which are of the same order of magnitude as the concentration of molecules. Hence, it is only practical with the discharge tube method of H atom production. Groth and Warneck[47] have shown that with this method it is possible to obtain reasonable response times at pressures of 1 Torr or higher without loss of accuracy.

2. Calorimetric Method

Bonhoeffer[48] first investigated the calorimetric detection of atomic hydrogen. This method is dependent upon a measurement of the heat released when atoms recombine on an efficient catalyst. Linnett and Marsden[49] measured the relative concentrations of H atoms by mounting the catalyst on the tip of a fine thermocouple. Tollefson and Le Roy[12] obtained the absolute concentration by using an isothermal calorimetric probe in which the detector was a platinum spiral. The spiral was heated by the passage of a small current through it. The tendency for increased spiral temperature, due to atom recombination on its surface, was offset by lowering the current in the spiral. In this manner, heat losses present in a normal thermocouple probe were eliminated. The decrease in the power supplied to the detector gave a measure of the number of hydrogen atoms recombining on its surface per second. Fox, *et al.*,[50] found that elevated temperatures increased the efficiency and reduced the rate of surface poisoning of the catalyst. The possible errors, due to incomplete release of the heat of recombination on the surface and the change in thermal conductivity of the gas with its degree of dissociation, appeared to be small.[51] It was noted, however, that the diffusion effect could introduce serious errors if the gas flow was not rapid enough.[51] Shaw[22] has suggested the use of a triple-filament probe rather than the normal single-filament probe. Pospelova and Myasnikov[52] have used a calorimetric probe, with tip made of semiconductors to measure the recombination of hydrogen atoms.

3. Mass Spectrometric Method

The concentration of hydrogen atoms can be determined by mass spectrometry, provided that the molecular beam inlet is arranged so that the atoms can pass directly into the ionizing region of the spectrometer without surface collisions.[53] The mass spectrometer can be calibrated for hydrogen atoms by measuring the decrease in the H_2^+ peak before and after the production of H atoms.[54,55] Daby, *et al.*,[55] have also followed the H atom peak by using a time-of-flight mass spectrometer.

4. Lyman α Photometric Method

Hydrogen atoms have been measured by their absorption of the Lyman α line (121.578 nm) emitted from a hydrogen discharge lamp. This absorption can be measured by various vacuum ultraviolet detectors. This photometric technique has been found to be very sensitive and fast enough to follow the hydrogen atom decay.

Preston[56] was the first to use this method to determine hydrogen atom concentrations, with analysis by a vacuum spectrograph. Myerson, *et al.*,[57] were the first to use this method with a photomultiplier tube as the detection device. Michael, *et al.*,[58,59] have developed an ionization detector employing the ionization of NO as the detector. Braun and Lenzi[60] have used a slightly different tech-

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(40) R. R. Baldwin, D. E. Hopkins, and R. W. Walker, *Trans. Faraday Soc.*, **66**, 189 (1970).

(41) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **65**, 2200 (1961).

(42) C. P. Fenimore and G. W. Jones, *Symp. (Int.) Combust. Proc.*, *9th, 1962*, 597, (1963).

(43) W. C. Gardiner, Jr., and G. B. Kistiakowsky, *J. Chem. Phys.*, **35**, 1765 (1961).

(44) G. S. Bahn, *Pyrodynamics*, **5**, 221 (1967).

(45) E. Wrede, *Z. Phys.*, **54**, 53 (1929).

(46) P. Harteck, *Z. Phys. Chem.*, *Abt. A*, **139**, 98 (1928).

(47) W. Groth and P. Warneck, *Z. Phys. Chem. (Frankfurt am Main)*, **10**, 323 (1957).

(48) K. F. Bonhoeffer, *Z. Phys. Chem.*, **113**, 199, 492 (1924).

(49) J. W. Linnett and D. G. H. Marsden, *Proc. Roy. Soc., Ser. A*, **234**, 489, 504 (1956).

(50) J. W. Fox, A. C. H. Smith, and E. J. Smith, *Proc. Phys. Soc.*, **73**, 533 (1959).

(51) W. R. Schulz and D. J. Le Roy, *Can. J. Chem.*, **40**, 2413 (1962).

(52) I. N. Pospelova and I. A. Myasnikov, *Kinet. Katal.*, 7, 196 (1966); *Kinet. Catal. (USSR)*, 7, 178 (1966).

(53) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **21**, 1374, 1608 (1953).

(54) V. P. Strunin, A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, 7, 693 (1966); *Kinet. Catal. (USSR)*, 7, 610 (1966).

(55) E. E. Daby, H. Niki, and B. Weinstock, *J. Phys. Chem.*, **75**, 1601 (1971).

(56) W. M. Preston, *Phys. Rev.*, **57**, 1074 (1940).

(57) A. L. Myerson, H. M. Thompson, and P. J. Joseph, "Resonance Absorption Spectrophotometry of the Hydrogen Atom behind Shock Waves," Cornell Aeronautical Lab. Report AD-1689-A-3, 1964; *J. Chem. Phys.*, **42**, 3331 (1965).

(58) J. V. Michael and R. E. Weston, Jr., *J. Chem. Phys.*, **45**, 3632 (1966).

(59) J. V. Michael and D. T. Osborne, *Chem. Phys. Lett.*, **3**, 402 (1969).

(60) W. Braun and M. Lenzi, *Discuss. Faraday Soc.*, 44, 252 (1967).

nique by measuring the resonance fluorescence of the Lyman α excitation of H atoms. The atomic fluorescence arises from hydrogen (^2P) excited by absorption of the Lyman α line. This fluorescence is detected by a photomultiplier tube set at an angle so as not to be affected by the Lyman α lamp.

The Lyman α photometric method has been used in discharge flow,[58] mercury photosensitization,[59] shock tube,[57] photolysis,[60] and pulse radiolysis[39] systems.

5. *Electron Spin Resonance Method*

The validity of absolute hydrogen atom concentration measurement in the gas phase by electron spin resonance (esr) spectroscopy, using O_2 as a reference gas, has been established for many years.[61-64] The esr spectrum of the hydrogen atom consisting of a widely spaced doublet has proven to be a sensitive method for determining the concentration of H atoms.[65-67]

B. Chemical Methods

1. *Molybdenum Oxide Method*

Melville and Robb[23] used a molybdenum oxide film as a detector responsive to hydrogen atoms. MoO_3 film turns bluish when attacked by all types of atoms or radicals and is especially sensitive when attacked by hydrogen atoms.

2. *Chemiluminescence*

a. Emission from HNO*

Two methods based on the emission from excited HNO have been used to determine hydrogen atom concentrations.

The basic reaction was studied by Clyne and Thrush[68]

$$H\cdot + NO + M \rightarrow HNO^* + M \rightarrow HNO + M + h\nu \quad (1)$$

$$H\cdot + HNO \rightarrow H_2 + NO \quad (2)$$

where reaction 1 is the rate-determining step. They found that this reaction produced light in the visible and near-infrared region (500–800 nm).

Clyne and Thrush[69] also investigated the reaction of hydrogen atoms with NO_2. They suggested the mechanism as (3a) followed by (1).

$$H\cdot + NO_2 \rightarrow OH\cdot + NO \quad (3a)$$

$$H\cdot + NO + M \rightarrow HNO^* + M \rightarrow HNO + M + h\nu \quad (1)$$

The overall initial step has been found to be somewhat more complicated,[17,61,70,71] as shown in (3b).

$$2H\cdot + 3NO_2 \rightarrow H_2O + O_2 + 3NO \quad (3b)$$

$$H\cdot + NO + M \rightarrow HNO^* + M \rightarrow HNO + M + h\nu \quad (1)$$

From the above, it is seen that the extinction of the HNO* chemiluminescence occurs at an NO_2 flow rate of 1.5 times the hydrogen atom flow rate.

Clyne and Stedman[72] studied the reaction of hydrogen atoms with NOCl and suggested the initial step as (4), followed by (1).

$$H\cdot + NOCl \rightarrow NO + HCl \quad (4)$$

$$H\cdot + NO + M \rightarrow HNO^* + M \rightarrow HNO + M + h\nu \quad (1)$$

When the concentration of NOCl equaled that of hydrogen atoms, the HNO emission was extinguished, giving a measure of the hydrogen atom concentration. This same method has been used by other workers.[73,74]

b. Emission from Li*, Na*, and CuH

This technique[75-77] has been used in H_2–O_2–N_2 flames where the intensity of emission from the metal or metal hydride is proportional to the H atom concentration. The chemiluminescence is based on one of the equilibria

$$H\cdot + LiOH \rightleftarrows H_2O + Li^* \quad (5)$$

$$H\cdot + NaOH \rightleftarrows H_2O + Na^* \quad (6)$$

$$H\cdot + NaCl \rightleftarrows HCl + Na^* \quad (7)$$

In flames with temperatures from 1600 to 2400°K, the H atom concentration may be determined by a comparison of the emission from reactions 5 and 6. McEwan and Phillips[78] suggested the use of atomic absorption in association with these reactions for flames above 1600°K. Reaction 7 results from the addition of chlorine-containing substances to a flame containing free sodium. The change in the free sodium concentration gives a measure of the H atom concentration.

Bulewicz and Sugden[75] have also suggested the reaction

$$Cu + H\cdot + M \rightarrow CuH + M \quad (8)$$

where the CuH ($^1\Sigma$–$X^1\Sigma$, 428 nm 0–0 band) emission is proportional to the H atom concentration.

c. Shock Tube Studies

Investigations of the shock tube dissociation of H_2 have resulted in a number of interesting methods to determine the H atom concentration. Gardiner and Kistiakowsky[43] and Sutton[79] have measured the variation in gas density behind the shock front and determined the rate of dissociation of H_2 as a function of temperature and of the densities of the various species. Kistiakowsky and Gardiner used X-rays to measure the density, while Sutton used the technique of light interference. Patch[80] determined the loss of H_2 in the shock dissociation by observing the change in the ultraviolet absorption of the H_2 ($^1\Pi_u$–$^1\Sigma_g^+$) (Werner) transition. Jacobs, *et al.*,[81] ob-

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(61) A. A. Westenberg and N. deHass, *J. Chem. Phys.*, **43**, 1550 (1965).

(62) H. Wise, C. M. Ablow, and K. M. Sancier, *J. Chem. Phys.*, **41**, 3569 (1964).

(63) J. M. Brown and B. A. Thrush, *Trans. Faraday Soc.*, **63**, 630 (1967).

(64) A. A. Westenberg and N. deHass, *J. Chem. Phys.*, **50**, 707 (1969).

(65) R. Beringer and E. B. Rawson, *Phys. Rev.*, **87**, 228 (1952).

(66) T. M. Shaw in "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed., Academic Press, New York, N. Y., 1960, p 47.

(67) P. B. Davies, B. A. Thrush, and A. F. Tuck, *Trans. Faraday Soc.*, **66**, 886 (1970).

(68) M. A. A. Clyne and B. A. Thrush, *Discuss. Faraday Soc.*, **33**, 139 (1962).

(69) M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, **57**, 2176 (1961).

(70) L. F. Phillips and H. I. Schiff, *J. Chem. Phys.*, **37**, 1233 (1962).

(71) F. Kaufman, *Ann. Geophys.*, **20**, 106 (1964).

(72) M. A. A. Clyne and D. H. Stedman, *Trans. Faraday Soc.*, **62**, 2164 (1966).

(73) M. P. Halstead, D. A. Leathard, R. M. Marshall, and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, **316**, 575 (1970).

(74) D. O. Ham, D. W. Trainor, and F. Kaufman, *J. Chem. Phys.*, **53**, 4395 (1970).

(75) E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.*, **54**, 1855 (1958).

(76) E. M. Bulewicz, L. F. Phillips, and T. M. Sugden, *Trans. Faraday Soc.*, **57**, 921 (1961).

(77) E. M. Bulewicz, C. G. James, and T. M. Sugden, *Proc. Roy. Soc., Ser. A*, **235**, 89 (1956).

(78) M. J. McEwan and L. F. Phillips, *Combust. Flame*, **9**, 420 (1965).

(79) E. A. Sutton, *J. Chem. Phys.*, **36**, 2923 (1962).

(80) R. W. Patch, *J. Chem. Phys.*, **36**, 1919 (1962).

(81) T. A. Jacobs, R. R. Giedt, and N. Cohen, *J. Chem. Phys.*, 47, 54 (1967).

served infrared emission when small quantities of HCl were added to a shock front. The decrease in HCl emission as a result of reaction 9 was proportional to the H atom concentration. Myerson and coworkers[57,82] have used atomic resonance absorption spectrophotometry at the Lyman α line of both ^1H and ^2H to obtain a direct measurement of the rate of formation of atomic hydrogen behind the shock front.

$$H\cdot + HCl^* \rightarrow H_2 + Cl\cdot \qquad (9)$$

3. *Chemical Reaction Product Analysis*

The reactions of certain compounds with hydrogen atoms have been found useful for determining the hydrogen atom concentrations.

The reaction of hydrogen atoms with ethyl chloride[83-85] produces a titratable product, HCl, as shown in (10). It is suggested that the HCl produced at the temperature 125° in this reaction represents from 35 to 40% of the concentration of atomic hydrogen.[83]

$$H\cdot + C_2H_5Cl \rightarrow C_2H_5\cdot + HCl \qquad (10)$$

Hydrogen atom concentrations have been estimated from the maximum destruction of HBr and HI[86] and from the formation of HCN following the reactions with cyclic imines,[87] formamide,[88] and ethylenimine.[84]

Fenimore and Jones[89] have followed the H atom concentration in flames from the amount of HD formed after the addition of D_2 or D_2O to the flame.

Volpi and Zocchi[90] and Eberius, *et al.*,[91] suggested the determination of the atomic hydrogen concentration by chemical titration with excess ethylene. The stoichiometry of this reaction shows two hydrogen atoms consumed for each molecule of saturated hydrocarbons (CH_4, C_2H_6, and C_3H_8) formed. More recently, Purnell and coworkers[73] compared the NOCl titration method with the ethylene reaction. The two methods gave values for the H atom concentration which were in reasonable agreement. They found that values determined by the ethylene method were greater by about 10%.

IV. Chemical Reactions of Atomic Hydrogen with Organic Species

A. Reaction with Paraffins

1. *Methane*

The kinetics of the reaction of H atoms with CH_4 have been studied by many workers during the past years. The reaction has been studied using most of the methods of gas-phase kinetics including photochemical,[92] flow discharge,[93] flame,[41,94] catalytic H atom recombination,[95] esr,[96] and inhibition–combustion studies.[97-99]

Steacie[1] has reviewed values obtained prior to 1953 and arbitrarily selects an activation energy of about 12.5 kcal/mol with a steric factor of 0.1. Since then, numerous attempts have been made to measure the kinetic parameters for this reaction. The reported results fall into two distinct groups: (a) high activation energies (11 to 16 kcal/mol) with a correspondingly high preexponential factor, in the region 10^{14} cc mol^{-1} sec^{-1}, and (b) low activation energies (4–8 kcal mol^{-1}) coupled with a low preexponential factor, in the region 10^{10}–10^{13} cc mol^{-1} sec^{-1}. Table I presents sample data from various methods for various temperatures. (Table I also includes a summary of the kinetic data available on the reaction $H\cdot + CH_3\cdot\ (+M) \rightarrow CH_4\ (+M)$.)

Baldwin, *et al.*,[99] have obtained the expression $k = (1.26 \pm 0.25) \times 10^{14} \exp(-11{,}900 \pm 400/RT)$ cc mol^{-1} sec^{-1} from a critical review of the available data.

Most workers now agree on the following mechanism for the H + CH_4 reaction.

$$H\cdot + CH_4 \rightleftarrows CH_3\cdot + H_2 \qquad (11)$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \qquad (12)$$

2. *Ethane*

Numerous investigations[34,42,100-110] of the kinetics of the reactions of H atoms with C_2H_6 have been made. The kinetic parameters for this reaction are listed in Table II. Table II also includes a summary of the kinetic data available on the reaction of H atoms with ethyl radicals.

The activation energies presented in Table II vary from 6.8 to 14.1 kcal mol^{-1} and the preexponential factor from 3.43×10^{12} to 5.78×10^{14} cc mol^{-1} sec^{-1}. Baldwin and Melvin[107] reviewed the values prior to 1964. By combining three sets of values[34,42,107] over a wide temperature range (30–1280°), they found $\log A = 14.12 \pm 0.25$ cc mol^{-1} sec^{-1} and $E = 9.71 \pm 0.58$ kcal mol^{-1}. By the addition of C_2H_6 to slowly reacting mixtures of H_2 and O_2 at 500°, Baldwin, *et al.*,[40] calculated a value of $k = 2.01 \times 10^{11}$ cc mol^{-1} sec^{-1}. This value closely agrees with a value[107] of $k = 2.36 \times 10^{11}$ cc mol^{-1} sec^{-1} at 500° obtained from the parameters they calculated previously for the temperature range 30–1280°. Recently, Azatyan, *et al.*,[109,110] using an esr as a detection

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(82) A. L. Myerson and W. S. Watt, *J. Chem. Phys.*, **49**, 425 (1968).

(83) H. M. Chadwell and T. Titani, *J. Amer. Chem. Soc.*, **55**, 1363 (1933).

(84) J. W. S. Jamieson and C. A. Winkler, *J. Phys. Chem.*, **60**, 1542 (1956).

(85) J. W. S. Jamieson, G. R. Brown, and J. S. Tanner, *Can. J. Chem.*, **48**, 3619 (1970).

(86) D. M. Wiles and C. A. Winkler, *J. Phys. Chem.*, **61**, 620 (1957).

(87) J. W. S. Jamieson, G. R. Brown, and W. K. Hancock, *Can. J. Chem.*, **43**, 1973 (1965).

(88) J. W. S. Jamieson, *Can. J. Chem.*, 41, 1568 (1963).

(89) C., Fenimore and G. W. Jones, *J. Phys. Chem.*, **62**, 693 (1958).

(90) G. G. Volpi and F. Zocchi, *J. Chem. Phys.*, **44**, 4010 (1966).

(91) H. Eberius, K. Hoyermann, and H. Gg. Wagner, *Ber. Bunsenges. Phys. Chem.*, **73**, 962 (1969).

(92) R. Klein, J. R. McNesby, M. D. Scheer, and L. J. Schoen, *J. Chem. Phys.*, **30**, 58 (1959).

(93) J. W. S. Jamieson and G. R. Brown, *Can. J. Chem.*, **42**, 1638 (1964).

(94) G. Dixon-Lewis and A. Williams, *Symp. (Int.) Combust. Proc., 11th, 1966*, 951 (1967).

(95) M. R. Berlie and D. J. Le Roy, *Can. J. Chem.*, **32**, 650 (1954).

(96) M. J. Kurylo and R. B. Timmons, *J. Chem. Phys.*, **50**, 5076 (1969).

(97) A. B. Nalbandyan and N. I. Gorban, *Dokl. Akad. Nauk Arm. SSR*, **33**, 49 (1961); *Chem. Abstr.*, **57**, 1596i (1962).

(98) V. V. Azatyan, A. B. Nalbandyan, and T. Meng-yuan, *Kinet. Katal.*, **5**, 201 (1964); *Kinet. Catal. (USSR)*, **5**, 177 (1964).

(99) R. R. Baldwin, D. E. Hopkins, A. C. Norris, and R. W. Walker, *Combust. Flame*, **15**, 33 (1970).

(100) W. R. Trost and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 361 (1948).

(101) M. R. Berlie and D. J. Le Roy, *Discuss. Faraday Soc.*, 14, 50 (1953).

(102) N. I. Gorban and A. B. Nalbandyan, *Dokl. Akad. Nauk SSSR*, **132**, 1335 (1960); *Chem. Abstr.*, **55**, 13008b (1961).

(103) V. V. Voevodskii and V. N. Kondrat'ev, *Progr. React. Kinet.*, 1, 41 (1961).

(104) N. I. Gorban and A. B. Nalbandyan, *Zh. Fiz. Khim.*, **36**, 1757 (1962); *Russ. J. Phys. Chem.*, **36**, 946 (1962).

(105) K. Yang, *J. Phys. Chem.*, **67**, 562 (1963).

(106) R. R. Baldwin, *Symp. (Int.) Combust. Proc., 9th, 1962*, 604 (1963).

(107) R. R. Baldwin and A. Melvin, *J. Chem. Soc.*, 1785 (1964).

(108) G. B. Skinner and G. H. Ringrose, *J. Chem. Phys.*, **43**, 4129 (1965).

(109) V. V. Azatyan, S. B. Filippov, A. B. Nalbandyan, and L. B. Romanovich, *Arm. Khim. Zh.*, **22**, 193 (1969); *Chem. Abstr.*, 71, 90606v (1969).

(110) V. V. Azatyan and S. B. Filippov, *Dokl. Akad. Nauk SSSR*, **184**, 625 (1969); *Chem. Abstr.*, **70**, 91193z (1969).

TABLE I. Summary of the Published Arrhenius Parameters for the Methane and Methyl Radical Reactions

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + CH_4$		
372–436	4.5	10.0	Tungsten filament	95
620–738	7.8	13.0	Photolysis (D_2CO/CH_4)	92[a]
673–763	15.1	14.52	H_2/O_2 ignition	97
1220–1790	11.5	14.30	Flame (CH_4–H_2–O_2–N_2O)	41
883	$k = 2.9 \times 10^{10}$		H_2/O_2 ignition	98
500–803	7.4	11.78	Discharge (Wood's)	93
900	$k = 4.0 \times 10^{10}$		Flame (CH_4–H_2–O_2)	94
773	$k = 6.3 \times 10^{10}$		H_2/O_2 ignition	99
372–773	11.9	14.1	H_2/O_2 ignition	99
426–743	11.8	13.84	Discharge (microwave)	96
		$H\cdot + CH_3\cdot$		
298	$k = 2 \times 10^{12}$ to 4×10^{12}		(1.3 Torr of Ar)	b
296 ± 3	$k = (1.0 \pm 0.3) \times 10^{13}$		Discharge (high frequency) (6.7 Torr of Ar)	c
290 ± 3	$k = 2.3 \times 10^{12}$		Discharge (microwave) (8 Torr of Ar)	73
303–603	0.05	12.07	Discharge (microwave) (1.2 Torr of H_2)	123

[a] Refers to $D\cdot + CH_4$ reaction. [b] J. M. Brown, P. B. Coates, and B. A. Thrush, *Chem. Commun.*, 843 (1966). [c] A. F. Dodonov, G. K. Lavroskaya, and V. L. Tal'roze, *Kinet. Katal.*, 10, 477 (1969); *Kinet. Catal. (USSR)*, 10, 391 (1969).

method, found activation energies and preexponential factors of E = 9.1, 9.3 kcal mol^{-1} and log A = 13.61, 14.05 cc mol^{-1} sec^{-1}, respectively, which agree reasonably well with the results of Baldwin and Melvin.[107]

All the kinetic parameters were determined on the basis that the initial step was (13) and that it was the rate-controlling step.

$$H\cdot + C_2H_6 \rightarrow H_2 + C_2H_5\cdot \tag{13}$$

3. *Propane, n-Butane, Isobutane*

The kinetics of the reactions of hydrogen atoms with C_3H_8,[34,102-104,111-116] n-C_4H_{10},[34,105,111,115-118] and i-C_4H_{10}[34,102-105,116,118,119] have been extensively studied. A summary of the kinetic parameters of these reactions based on (14) as the primary step is given in Table III. (RH represents a paraffin.)

$$H\cdot + RH \rightarrow H_2 + R\cdot \tag{14}$$

4. *Other Paraffins*

Previous to 1958, few studies were reported of the reactions of hydrogen atoms with n-C_5H_{12},[111] *neo*-C_5H_{12},[100] and n-C_6H_{14}.[111,120] This was probably because of the large number of products and possible side reactions present in these reactions. The reactions were so complicated that a reliable determination of the primary step was almost impossible at that time. Since 1958, there have been no investigations of the reaction of hydrogen atoms with paraffins containing more than four carbon atoms.

B. Reaction with Olefins

When atomic hydrogen reacts with olefinic hydrocarbons, excited alkyl radicals are formed. The subsequent unimolecular dissociation of these radicals has been the subject of extensive experimental and theoretical studies.[121]

1. *Ethylene*

The kinetics and mechanism of the reaction of hydrogen atoms with ethylene have been extensively studied. Cvetanović[2] and Thrush[3] have reviewed the situation up to 1965, noting the conflicting results which have been obtained. It is generally agreed that the first step in this reaction is the addition of the H atom to form $C_2H_5\cdot$. The C_2H_5 radical so formed would be highly vibrationally excited and could contain up to 39.6 kcal mol^{-1} excess energy.[121] This radical may do one of two things: (1) it may decompose into the initial materials; (2) it may be deactivated by collisions with the resulting stabilized radical undergoing further reaction. The following mechanism[64,73,122,123] for the $H\cdot + C_2H_4$ reaction has been accepted by most workers.

$$H\cdot + C_2H_4 \rightleftarrows C_2H_5\cdot^* \rightarrow C_2H_5\cdot \tag{15}$$

$$H\cdot + C_2H_5\cdot \rightleftarrows C_2H_6^{**} \rightarrow 2CH_3\cdot \tag{16}$$

$$H\cdot + CH_3\cdot \rightleftarrows CH_4^* \xrightarrow{M} CH_4 \tag{17}$$

$$CH_3\cdot + CH_3\cdot \rightleftarrows C_2H_6^* \xrightarrow{M} C_2H_6 \tag{18}$$

$$CH_3\cdot + C_2H_5\cdot \rightarrow C_3H_8 \tag{19}$$

$$C_2H_5\cdot + C_2H_5\cdot \rightarrow n\text{-}C_4H_{10} \tag{20}$$

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(111) H. I. Schiff and E. W. R. Steacie, *Can. J. Chem.*, **29**, 1 (1951).

(112) K. Yang, *J. Amer. Chem. Soc.*, **84**, 3795 (1962).

(113) H. A. Kazmi, R. J. Diefendorf, and D. J. Le Roy, *Can. J. Chem.*, 41, 690 (1963).

(114) R. R. Baldwin, *Trans. Faraday Soc.*, **60**, 527 (1964).

(115) N. I. Parsamyan and A. B. Nalbandyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 750 (1968); *Chem. Abstr.*, **69**, 76297x (1968).

(116) R. R. Baker, R. R. Baldwin, and R. W. Walker, *Trans. Faraday Soc.*, **66**, 2812 (1970).

(117) H. A. Kazmi and D. J. Le Roy, *Can. J. Chem.*, **42**, 1145 (1964).

(118) R. R. Baldwin and R. W. Walker, *Trans. Faraday Soc.*, **60**, 1236 (1964).

(119) W. H. White, C. A. Winkler, and B. J. Kenalty, *Can. J. Res., Sect. B*, **20**, 255 (1942).

(120) R. G. W. Norrish and J. H. Purnell, *Proc. Roy. Soc., Ser. A*, **243**, 449 (1958).

(121) B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(122) J. R. Barker, D. G. Keil, J. V. Michael, and D. T. Osborne, *J. Chem. Phys.*, **52**, 2079 (1970).

(123) L. Teng and W. E. Jones, *J. Chem. Soc., Faraday Trans. 1*, **68**, 1267 (1972).

TABLE II. Summary of the Published Arrhenius Parameters for the Ethane and Ethyl Radical Reactions

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H + C_2H_6$		
298	9.0 ± 0.2		Discharge (Wood's)	100
353-436	6.8	12.53	Tungsten filament	101
297-478	9.0	14.4	Photolysis (D_2S/C_2H_6)	34[a]
682-823	12.0	13.17	H_2/O_2 ignition	102
773-898	14 ± 1	14.76	H_2/O_2 ignition	103
683-823	12.2	14.52	H_2/O_2 ignition	104
993-1433	9.7 ± 2	14.1	Flame (C_2H_6-H_2-O_2)	42
323-523	9.0	13.5	γ radiolysis	105
303-1553	9.9 ± 0.2	14.20 ± 0.1	H_2/O_2 ignition	106
304-1500	9.71 ± 0.58	14.12 ± 0.25	H_2/O_2 ignition	107
1025-1190	6.20	13.6	H_2/O_2 ignition	108
290-509	9.1	13.61	Discharge (microwave)	109
290-579	9.3	14.05	Discharge (microwave)	110
853-953	9.7	13.82	H_2/O_2 ignition	b
		$H\cdot + C_2H_5\cdot \rightarrow 2CH_3\cdot$		
290 ± 3	$k = 5.0 \times 10^{13}$		Discharge (microwave) (8 Torr of Ar)	73
303-603	0.87	14.04	Discharge (microwave) (1.2 Torr of H_2)	123
		$H\cdot + C_2H_5\cdot \rightarrow C_2H_6{}^* \rightarrow C_2H_6$		
298	$k = (3.6 \pm 1.2) \times 10^{13}$		Flash photolysis (50 Torr of He)	124

[a] Refers to $D\cdot + C_2H_6$ reaction. [b] N. I. Parsamyan, E. A. Arakelyan, V. V. Azatyan, and A. B. Nalbandyan, *Izv. Akad. Nauk SSSR*, 496 (1968); *Chem. Abstr.*, **69**, 76529z (1968).

TABLE III. Summary of the Published Arrhenius Parameters for C_3H_8, *n*-C_4H_{10}, and *i*-C_4H_{10} Reactions

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		Propane		
298	8.0	0.1[b]	Discharge (Wood's)	111[a]
300-500	7.2	14.5	Photolysis (D_2S/C_3H_8)	34[a]
683-823	8.5	13.43	H_2/O_2 ignition	102
773-898	8.3 ± 1	13.56	H_2/O_2 ignition	103
683-823	8.4	13.80	H_2/O_2 ignition	104
330-490	7.4	13.70	γ radiolysis	112
368-443	8.2	14.12	Tungsten filament	113
301-793	7.83 ± 0.78	13.8 ± 0.37	H_2/O_2 ignition	114
853-953	7.8	13.73	H_2/O_2 ignition	115
300-752	8.35	14.16	H_2/O_2 ignition	116
		n-Butane		
298	8.9	0.1[b]	Discharge (Wood's)	111
298	7.9	0.1[b]	Discharge (Wood's)	111[a]
300-500	7.1	14.5	Photolysis (D_2S/C_4H_{10})	34[a]
323-523	6.7	13.3	γ radiolysis	105
343-443	7.1	13.82	Tungsten filament	117
300-793	7.5 ± 0.5	13.9 ± 0.2	H_2/O_2 ignition	118
853-953	7.0	13.48	H_2/O_2 ignition	115
300-753	8.5	14.41	H_2/O_2 ignition	116
		Isobutane		
298	9.3	0.1[b]	Discharge (Wood's)	119
300-500	6.3	14.5	Photolysis (D_2S/C_4H_{10})	34[a]
683-823	6.1	13.47	H_2/O_2 ignition	102
773-898	5.6 ± 1	12.89	H_2/O_2 ignition	103
683-823	5.1	12.76	H_2/O_2 ignition	104
323-523	5.1	13.1	γ radiolysis	105
300-793	6.8 ± 0.5	14.0 ± 0.2	H_2/O_2 ignition	118
300-753	7.25	14.12	H_2/O_2 ignition	116

[a] Refers to D atom reactions. [b] Steric factor.

The kinetic data, determined by various workers, for the primary step in the $H\cdot + C_2H_4$ reaction are listed in the Tables IV, V, and VI. Since this reaction is found to be dependent upon experimental conditions (*e.g.*, pressure, concentration, reactants, etc.), an attempt has been made to outline the conditions under which the

TABLE IV. Summary of the Published Rate Constants for the Ethylene Reaction at Room Temperature and High Pressure

$k \times 10^{-11}$, cc mol^{-1} sec^{-1}	Pressure range, Torr	Method	Ref
6.0	435 (n-C_4H_{10})	Hg photosens	25
5-6[a]	∞ (He)	Discharge (microwave)	58
5.30 ± 0.84	6.56 (He)	Discharge (microwave)	54
6.00	75 (He)	Flash photolysis	60
2.20[a]	∞ (He)	Discharge (microwave)	64
1.40[a]	∞ (Ar)	Discharge (microwave)	64
8.43	24.4 (He)	Discharge (microwave)	*b*
1.5	16 (Ar)	Discharge (microwave)	73
5.48 ± 0.54	700-1500 (He)	Pulse radiolysis	c
8.19 ± 1.15[d]	∞ (He)	Flash photolysis	124
7.23 ± 0.60	500 (He)	Hg photosens	132
1.63	High pressure	Hg photosens	*e*
6.93	100 (CO_2)	Photolysis (HI/C_2H_4)	31
2.5	>305 (C_2H_6)	Hg photosens (C_2H_6)	*f*

[a] Refers to the extrapolated values from low pressures (5 Torr and 2 Torr). [b] A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, **10**, 22 (1969); *Kinet. Catal. (USSR)*, **10**, 14 (1969). [c] J. A. Eyre, T. Hikida, and L. M. Dorfman, *J. Chem. Phys.*, **53**, 1281 (1970). [d] Refers to the extrapolated values from high pressure (500 Torr). [e] A. B. Callear and J. C. Robb, *Trans. Faraday Soc.*, **51**, 638 (1955). [f] R. A. Back, *Can. J. Chem.*, **37**, 1834 (1959).

TABLE V. Summary of the Published Rate Constants for the Ethylene Reaction at Room Temperature and Low Pressure

$k \times 10^{11}$, cc mol^{-1} sec^{-1}	Conditions		Method	Ref
	Torr	Concn		
1.81	0.3-0.6 (H_2)	$[H\cdot] \sim [C_2H_4]$	Discharge	*a*
1.93 ± 0.10	2.1 (He)	$[H\cdot] < [C_2H_4]$	Discharge (microwave)	58
0.88	1.6-3.1 (Ar)	$[H\cdot] > [C_2H_4]$	Discharge (microwave)	63
2.29	2.3 (He)	$[H\cdot] \ll [C_2H_4]$	Discharge (microwave)	*b*
1.99 ± 0.60	5 (He)	$[H\cdot] \ll [C_2H_4]$	Flash photolysis	124
1.46	2.16 (He)	$[H\cdot] \gg [C_2H_4]$	Discharge (microwave)	122
2.34	1.51 (He)	$[H\cdot] \ll [C_2H_4]$	Discharge (microwave)	122
2.16	1.20 (H_2)	$[H\cdot] \geq [C_2H_4]$	Discharge (Wood's)	123

[a] H. Girouard, F. M. Graber, and B. F. Myers, General Dynamics Astronautic Report N64-13061, San Diego, Calif., 1963; NASA CR 52376. [b] A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, **10**, 22 (1969); *Kinet. Catal. (USSR)*, **10**, 14 (1969).

values presented have been determined. The rate constant determinations may be divided into two groups depending upon total pressure used: (a) high-pressure conditions (above 5 Torr) with $[C_2H_4] \gg [H\cdot]$ at room temperature (Table IV); (b) k_1 as determined at low pressures (0.3 to 5 Torr), various $[C_2H_4]/[H\cdot]$ ratios, and room temperature (Table V). Braun and coworkers,[124] using conditions where H atom reactions with radicals were minimal, determined rate constants over the pressure range 5 to 500 Torr. From their measurements, they determined an infinite pressure value of 8.19×10^{11} cc mol^{-1} sec^{-1}.

The activation energy and preexponential factor of reaction 15 have been determined by various workers, and their results are presented in Table VI. The two largest values (E = 6.6 and 7.2 kcal mol^{-1}),[101,125] based on the rather indirect approach of determining the effect of small concentrations of C_2H_4 on the first explosion limit of the H_2-O_2 reaction, are considered to be much too large. The value E = 3.18 kcal mol^{-1} was calculated by Baldwin, *et al.*,[126] based on a combination of the results of Yang[37] and Jennings and Cvetanović.[25]

The abstraction reaction of hydrogen atoms with C_2H_4

$$H\cdot + C_2H_4 \rightarrow C_2H_3\cdot + H_2 \quad (21)$$

$$H\cdot + C_2H_3\cdot \rightarrow C_2H_2 + H_2 \quad (22)$$

was suggested by Wartenberg and Schultze[127] in order to explain the formation of C_2H_2 found in their products. Klemenc and Patat[128] also found C_2H_2. In 1961, Jennings and Cvetanović[25] studied the ratio of the abstraction and addition reactions at room temperature by a competitive method and obtained the value of zero. This was recently reinvestigated[35] with similar results. Dzantiev and Shishkov[129] found the ratio of these reactions to be 0.25 when the H atoms were produced by photolysis of H_2S. They explained this high ratio by the presence of hot H atoms produced in the photolysis. Baldwin, *et al.*,[126] found no evidence that H atoms abstract H atoms from C_2H_4 at room temperature. They found the rate constant of the abstraction reaction to be $k = 2.5 \times 10^{11}$ cc mol^{-1} sec^{-1} at 813°, the activation energy to be E = 9.8 kcal mol^{-1} on the assumption that log A = 14 cc mol^{-1} sec^{-1}, and the value of the ratio of addition to abstraction to be 12.4 at 580°.

2. *High Carbon Olefins*

A number of measurements had been made of the relative rates[24,25,35,37,112,130,131] of these hydrogen atom-olefin reactions. With the exception of three independent photochemical studies by Cvetanović and coworkers, the values obtained vary considerably (Table VII). By using mercury-photosensitized decomposition of n-C_4H_{10} and observing the decrease in the rate of production of hydrogen in the presence and absence of olefins, Jennings and Cvetanović[25] measured the rates of addition of H· to olefins relative to the rate of abstraction of H· from the n-C_4H_{10}. In another group of reactions, Cvetanović and Doyle[24] used mercury-photosensitized decomposition of H_2 in the presence of small amounts of C_2H_4 or mixed with an added olefin. They obtained the rate constants from a comparison of the yields of n-butane in the two cases. The third method used by Woolley and Cvetanović[35] involved the photolysis of H_2S at 249 nm, while the relative rate constants were determined from a comparison of the yield of H_2 from H_2S alone and the yield of H_2

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(124) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **53**, 2776 (1970).

(125) V. V. Azatyan, A. B. Nalbandyan, and M. Y. Ts'ui, *Dokl. Akad. Nauk SSSR*, **149**, 1095 (1963); *Chem. Abstr.*, **59**, 12229f (1963).

(126) R. R. Baldwin, R. F. Simmons, and R. W. Walker, *Trans. Faraday Soc.*, **62**, 2486 (1966).

(127) H. v. Wartenberg and G. Schultze, *Z. Phys. Chem., Abt. B*, **2**, 1 (1929).

(128) A. Klemenc and F. Patat, *Z. Phys. Chem., Abt. B*, **3**, 289 (1929).

(129) B. G. Dzantiev and A. B. Shishkov, *Khim. Vys. Energ.*, 1, 192 (1967); *Chem. Abstr.*, **67**, 59566a (1967).

(130) P. E. M. Allen, H. W. Melville, and J. C. Robb, *Proc. Roy. Soc., Ser. A*, **218**, 311 (1953).

(131) J. N. Brady, H. W. Melville, and J. C. Robb, *Proc. Roy. Soc., Ser. A*, **236**, 318 (1956).

TABLE VI. Summary of the Published Arrhenius Parameters for the Ethylene Reaction

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
329-513	1.9	12.9	γ radiolysis	37
823-923	6.6	13.26	H_2/O_2 ignition	103
843-933	7.2	12.95	H_2/O_2 ignition	125
813	3.18	13.47	H_2/O_2 ignition	126
285-405	3.3	13.43	Discharge (radio freq.)	17
293-600	1.6 ± 0.8	13.27	Discharge (microwave)	*a*
298, 525	0.5		Discharge (microwave)	64
303-478	1.5 ± 0.1	12.9	Photolysis (HI/C_2H_4)	31
303-603	0.73	11.90	Discharge (Wood's)	123

[a] A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, 10, 22 (1969); *Kinet. Catal. (USSR)*, 10, 14 (1969).

TABLE VII. Summary of the Published Relative Rates for High Carbon Olefin Reactions

Olefin	Ref 130, 131	37, 112	24, 25, 35	132
C_3H_6	1.00	1.00	1.00	1.00
C_4H_8-1			1.04	1.38 ± 0.43
C_5H_{10}-1			0.89	1.37 ± 0.43
i-C_4H_8	0.48	9.52	2.52	3.60 ± 1.06
cis-C_4H_8-2	0.66	0.31	0.47	0.44 ± 0.11
trans-C_4H_8-2	0.52	0.35	0.59	0.57 ± 0.15
cis-C_5H_{10}-2			0.39	
trans-C_5H_{10}-2			0.44	
$(CH_3)_2C{=}CHCH_3$			1.03	
$(CH_3)_2C{=}C(CH_3)_2$	0.61	1.10	0.84	
1,3-C_4H_6		13.0	4.9	

TABLE VIII. Summary of the Published Absolute Rate Constants (10^{11} cc mol^{-1} sec^{-1}) for High Carbon Olefin Reactions

Olefin	Ref 55		a	60	*b*	17	134	*c*	132	*d*
C_3H_6	(4.6)[e]	6.2[f]	4.82		7.83		9.70		5.0	
C_4H_8-1	8.3	8.3			9.04				6.8	
C_5H_{10}-1									6.4	
i-C_4H_8	(4.2)	20		22.9		33.1				
cis-C_4H_8-2	4.8	4.1							3.9	
trans-C_4H_8-2	5.4	4.6		6.02					4.3	4.7 ± 1.2
$(CH_3)_2C{=}CHCH_3$	7.4	7.7								
$(CH_3)_2C{=}C(CH_3)_2$	7.0	8.6								
1,3-C_4H_6	(50)	32						17		
$CH_3HC{=}C(CH_3)_2$	7.8	9.2								
$H_2C{=}C(CH_3)CH_2CH_3$	(9.1)	21								
1,3-c-C_6H_8										12.7 ± 2.1
1,4-c-C_6H_8										9.8 ± 1.3
c-C_6H_{10}										4.4 ± 0.7

[a] A. B. Callear and J. C. Robb, *Trans. Faraday Soc.*, **51**, 638 (1955). [b] A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, **10**, 22 (1969); *Kinet. Catal. (USSR)*. **10**, 14 (1969). [c] S. Koda and T. Hikita, *Bull. Chem. Soc. Jap.*, **44**, 2888 (1971). [d] R. Knutti and R. E. Buhler, *Chimia*, **26**, 624 (1972). [e] In this column, the values in parentheses are uncertain. [f] In this column, all the values refer to D atom reactions.

when H_2S was mixed with an added olefin. Very good agreement was found for the values obtained in these experiments. These relative rate constants have been confirmed by Daby, *et al.*,[55] who used a fast flow discharge system coupled to a time-of-flight mass spectrometer. Table VIII gives the absolute rate constants determined by Daby, *et al.*,[55] as well as those obtained by a number of other workers.

Recently, Michael and coworkers[132] studied the kinetics for the reactions of hydrogen atoms with olefins (a) by obtaining the absolute rate constants using a fast flow discharge system similar to that of Daby, *et al.*,[55] and (b) by measuring the rates relative to the well-characterized H· + C_2H_2 reaction. They employed steady-state Hg photosensitization and Lyman α-photometry for the determination of H atoms. Their studies again confirmed the results of Cvetanović and coworkers and Daby, *et al.*[55] (see Tables VII and VIII).

Two early determinations of the activation energy for H atom addition to C_3H_6 have yielded values of 2.6[133] and 5.0[34] kcal mol^{-1}. The first of these was based on an assumed steric factor of 10^{-2}, and the second was determined from rate measurements at two temperatures (298 and 478°K). In 1971, Kurylo, *et al.*,[134] gave the value of 1.2 kcal mol^{-1} for the temperature range 177-473°K, under conditions where there was no interference from abstraction, nonterminal addition, or decomposition of excited propyl radicals. Their results can be compared to the value of 1.5 kcal mol^{-1} of Scheer and Klein[135] obtained for the temperature range 77-90°K. At the low temperature of 77°K, Hill, *et al.*,[136] gave a value for the rate constant of 1.8×10^6 cc mol^{-1} sec^{-1} for H atom addition to C_3H_6. This value is in good agreement with the value of the lower limit of 2.0×10^6 cc mol^{-1} sec^{-1} estimated by Scheer and Klein.[135] With the exception of work by Yang[37,112] (Table VII), no experimental determinations of activation energies of olefins other than C_3H_6 have been reported. As may be seen in Table VII, the values reported by Yang vary considerably from those of other workers. The reason for this is not immediately clear, but the noticeable deviation tends to throw some doubt on the work.

Cvetanović and coworkers[25,35] determined the ratio k(H· abstraction)/k(H· addition) to be 0.082, 0.093, 0.032, and 0.015 for C_3H_6, 1-C_4H_8, *i*-C_4H_8, and 1,3-C_4H_6, respectively. In these results, the amount of the abstraction reaction never exceeded 10% of the total reaction at room temperature.

The addition of an H atom to an olefin results in the formation of a vibrationally excited alkyl radical. This excited radical can dissociate, forming either the original H atom and olefin or a new radical and olefin. It may also

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(132) J. A. Cowfer, D. G. Keil, J. V. Michael, and C. Yeh, *J. Phys. Chem.*, **75**, 1584 (1971).

(133) H. W. Melville and J. C. Robb, *Proc. Roy. Soc., Ser. A*, **202**, 181 (1950).

(134) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **54**, 4662 (1971).

(135) M. D. Scheer and R. Klein, *J. Phys. Chem.*, **65**, 375 (1961).

(136) C. G. Hill, Jr., R. C. Reid, and M. W. P. Strandberg, *J. Chem. Phys.*, **42**, 4170 (1965).

TABLE IX. Summary of the Published Rate Constants (10^{10} cc mol^{-1} sec^{-1}) for the Acetylene Reaction at Room Temperature

Pressure, Torr	Ref 138	137[a]	58	12	139	51	b	90
0.5		0.35					8.1	
1.0	0.90	0.70	0.78					1.2
1.9		1.10	1.11					2.3
3.0		1.40	1.17		0.81	1.10		2.2
4.0		1.75						
4.7		2.00	1.24					
5.2			2.02					
8.6		2.35	3.90					
10.3		2.55	5.93					
15		2.90		5.0 ± 1.2[c]				
20		3.20						
30		3.35						
50		3.50						

[a] All values in this column were adopted from the Figure 4 of ref 143. [b] H. Girouard, F. M. Graber, and B. F. Myers, General Dynamics Astronautical Report N64-13061, San Diego, Calif., 1963; NASA CR 52376. [c] Pressure range 1.0–15 Torr.

undergo collisional stabilization. The reaction of H atoms with olefins can be described by reactions 23 to 25.

$$\mathrm{H\cdot + (olefin)_{I} \rightleftarrows R_1\cdot^*} \qquad (23)$$

$$\mathrm{R_1\cdot^*}\begin{array}{l}\nearrow \mathrm{R_2\cdot + (olefin)_{II}} \\ \underset{\mathrm{M}}{\searrow} \mathrm{R_1\cdot}\end{array} \qquad (24)$$

$$\mathrm{H\cdot + (olefin)_{I} \rightarrow H_2 + R_2\cdot} \qquad (25)$$

C. Reaction with Alkynes

1. Acetylene

Steacie[1] described several investigations of this reaction which were made prior to 1953. In particular, results obtained in flow systems indicate that acetylene is not consumed but that it merely promotes the recombination of hydrogen atoms. The various rate constants obtained to date for the reaction H + C_2H_2 are listed in Table IX. The values given by Hoyermann, *et al.*,[137] and Michael and Weston[58] are considered to be most reliable. They studied the reaction over a wide pressure range and found a pressure dependence of the rate constant which has greatly assisted in establishing the mechanism of this reaction.

In 1967, Michael and Niki[138] proposed the following reaction mechanism based on isotopic studies.

$$\mathrm{H\cdot + C_2H_2 \rightarrow C_2H_3\cdot^*} \qquad (26)$$

$$\mathrm{C_2H_3\cdot^* \rightarrow C_2H_3\cdot} \qquad (27)$$

$$\mathrm{H\cdot + C_2H_3\cdot \rightarrow C_2H_4^* \rightarrow C_2H_2 + H_2} \qquad (28)$$

This mechanism has been confirmed recently by Hoyermann, *et al.*,[137] who found that, at high pressures (above 50 Torr), most of the vibrationally excited vinyl radicals (excess energy $E \sim 39$ kcal mol^{-1}) are deactivated to below the dissociation limit and can further react with H atoms. On the other hand, the vibrationally excited C_2H_4 in reaction 28 decomposes almost immediately, and much higher pressures are required to stabilize this species.

The activation energy of the addition reaction H· + C_2H_2 was first calculated by Dingle and Le Roy[139] over the temperature range 278–372°K. Their values of E = 1.5 kcal mol^{-1} and $P = 4 \times 10^{-4}$ (steric factor) are in good agreement with those predicted by collision theory. From their studies over the temperature range 243–473°K, Hoyermann, *et al.*,[137] found the expression $k_{26} = 2.3 \times 10^{12} \exp(-2500/RT)$ cc mol^{-1} sec^{-1} for the rate constant. They[140] also studied the reactions D· + C_2H_2 and H· + C_2D_2 over the temperature ranges 200–469°K and 300–470°K, respectively. They obtained the expressions $k = 3.1 \times 10^{13} \exp(-3700 \pm 200/RT)$ and $k = 2.0 \times 10^{13} \exp(-5300 \pm 500/RT)$ cc mol^{-1} sec^{-1}, respectively, for each reaction.

2. Methylacetylene

Methylacetylene (C_3H_4) is the only other member of the alkyne group that has received attention. Brown and Thrush[63] gave the rate constant $2.4 \pm 0.3 \times 10^{11}$ cc mol^{-1} sec^{-1} for the H· + C_3H_4 reaction at room temperature. They found that the rate constant was independent of pressure over the pressure range 0.9 to 2.4 Torr. In 1970, Solomon, *et al.*,[141] using a fast flow discharge system coupled to a mass spectrometer, gave a value for the rate constant of approximately 10^{11} cc mol^{-1} sec^{-1} at 283°K. The mechanism of the reaction is suggested to be similar to the H· + C_2H_2 reaction and is given in steps 29 to 31.

$$\mathrm{H\cdot + C_3H_4 \rightleftarrows C_3H_5\cdot^*} \qquad (29)$$

$$\mathrm{C_3H_5\cdot^* \rightarrow C_3H_5\cdot} \qquad (30)$$

$$\mathrm{H\cdot + C_3H_5\cdot \rightarrow H_2 + C_3H_4} \qquad (31)$$

D. Reaction with Halo Hydrocarbons

1. Halogen-Substituted Paraffins

Work on these reactions has been reviewed thoroughly by Steacie,[1] but few determinations of the kinetics for the various reactions have been made. In 1933, Chadwell and Titani[83] studied the reactions of hydrogen atoms with such saturated halo hydrocarbons as CH_3F, CH_3Cl, CH_3Br, CH_3I, C_2H_5Cl, and C_2H_5Br by product analysis. They produced their H atoms in a Wood's discharge flow system. Except for CH_3F, which was not found to react, they proposed a general reaction

$$\mathrm{H\cdot + R_IX \rightarrow HX + R_I\cdot} \qquad (32)$$

In the same year, Cremer, *et al.*,[142] studied the reactions

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(137) K. Hoyermann, H. Gg. Wagner, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*, **72**, 1004 (1968).

(138) J. V. Michael and H. Niki, *J. Chem. Phys.*, **46**, 4969 (1967).

(139) J. R. Dingle and D. J. Le Roy, *J. Chem. Phys.*, **18**, 1632 (1950).

(140) K. Hoyermann, H. Gg. Wagner, J. Wolfrum, and R. Zellner, *Ber. Bunsenges. Phys. Chem.*, **75**, 22 (1971).

(141) W. C. Solomon, K. H. Homann, and J. H. Warnatz, *Int. J. Chem. Kinet.*, **2**, 457 (1970).

(142) E. Cremer, J. Curry, and M. Polanyi, *Z. Phys. Chem., Abt. B*, **23**, 445 (1933).

TABLE X. Summary of the Published Arrhenius Parameters for the Halo Hydrocarbon Reactions

Compound	Ref 83[a]	142[a]	146	108	67[c]	147	149	143	144
CH_3F	>9		3.91[a] (11.88)[b]						
CH_3Cl	9	7.2					8.0[a] (14.49)[b]		
CH_3Br	6.5	3.2			4.3[a] (13.73)[b]		6.9[a] (14.55)[b]		
CH_3I	<5	<4.5							
CF_4						43.7[a] (14.85)[b]			
CF_3Br				17.5[a] (15.64)[b]					
CCl_4		<3.3						3.9[a] (12.77)[b]	
$CHCl_3$		<4.3							
CH_2Cl_2		5.8							
C_2H_5Cl	8								
C_2H_5Br	6								
C_2H_5I		<4.5							
1,2-$C_2F_4Br_2$				14.5[a] (15.0)[b]					
CF_3H				5.0[a] (12.70)[b]					11.2[a] (12.51)[b]

[a] Activation energy (kcal mol^{-1}). [b] Log A (cc mol^{-1} sec^{-1}). [c] D atom reaction.

TABLE XI. Relative Rates of Abstraction of Different Atoms from the Same Molecule

Halomethane	Rel rate constant	Numerical value
CCl_3F	k_F/k_{Cl}	0.21
CCl_3Br	k_{Br}/k_{Cl}	1.5
CCl_2HBr	k_{Br}/k_{Cl}	1.6
CCl_3D	k_D/k_{Cl}	3.3
CCl_2HBr	k_H/k_{Cl}	3.4

of atomic hydrogen with CH_3Cl, CH_3Br, CH_3I, C_2H_5I, CH_2Cl_2, $CHCl_3$, and CCl_4 by product analysis using a modified Wood's discharge tube system. In addition to reaction 32, they proposed reaction 33 as also being important. Both investigations gave values for the activation energies which are listed in Table X.

$$H\cdot + R_IX \rightarrow H_2 + R_{II}X \qquad (33)$$

Five years later, Vance and Bauman[143] investigated reaction 34. They determined the kinetic parameters by

$$H\cdot + CCl_4 \rightarrow HCl + CCl_3\cdot \qquad (34)$$

using a Wood's discharge flow system to produce H atoms and a calorimetric method to measure the atomic hydrogen concentration. They gave the activation energy and exponential factor as $E = 3.9$ kcal mol^{-1} and log $A = 12.77$ cc mol^{-1} sec^{-1} based on a steric factor of 7×10^{-3}. In 1965, Skinner and Ringrose[108] studied reactions 35 and 36 by inhibition of the H_2-O_2 reaction at 970–1300°K under shock-tube conditions.

$$H\cdot + CF_3Br \rightarrow CF_3\cdot + HBr \qquad (35)$$

$$H\cdot + 1,2\text{-}C_2F_4Br_2 \rightarrow C_2F_4Br\cdot + HBr \qquad (36)$$

They gave the activation energies and exponential factors shown in Table X. They proposed that the radical $C_2F_4Br\cdot$ from reaction 36 can be attacked by hydrogen atoms as in

$$H\cdot + C_2F_4Br\cdot \rightarrow C_2F_4 + HBr \qquad (37)$$

They gave the kinetic parameters of reaction 37 to be $E = 11.5$ kcal mol^{-1} and log $A = 16.30$ cc mol^{-1} sec^{-1}. It seems reasonable to suggest that the products of reaction 37 are produced by decomposition of vibrationally excited $C_2F_4BrH^*$.

Skinner and Ringrose[108] and Amphlett and Whittle[144] also obtained Arrhenius parameters for reaction 38 by studying the reverse reaction. The values are given in Table X.

$$H\cdot + CF_3H \rightarrow CF_3\cdot + H_2 \qquad (38)$$

Clark and Tedder[145] studied the reactions of hydrogen atoms with the halomethanes CCl_4, CCl_3Br, CCl_3D, CCl_3F, CCl_2HF, and CCl_2HBr by product analysis using a discharge fast-flow system. They found that the first step in these reactions was the abstraction of a halogen atom as shown in (32). The resulting radical added H atoms to form a vibrationally excited molecule which was either stabilized or decomposed by elimination of HX. The elimination of the more stable HX was always favored. Table XI gives their results for the relative rates of abstraction of different atoms from the same molecule.

(143) J. E. Vance and W. C. Bauman, *J. Chem. Phys.*, **6**, 811 (1938).

(144) J. C. Amphlett and E. Whittle, *Trans. Faraday Soc.*, **63**, 2695 (1967).

(145) D. T. Clark and J. M. Tedder, *Trans. Faraday Soc.*, **62**, 393, 399, 405 (1966).

Parsamyan, *et al.*,[146] studied the reaction

$$H\cdot + CH_3F \rightarrow HF + CH_3\cdot \quad (39)$$

over the temperature range 858–933°K using the flame method. The kinetic parameters obtained are given in Table X. The values of the kinetic parameters (Table X) for reaction 40 were obtained by Kochubei and Moin[147] using a flow system over the temperature range 1323–1523°K. Chadwell and Titani[83] found no reaction corresponding to (39) at room temperature, and Dacey and Hodgins[148] found no reaction at 573°K as shown in (40).

$$H\cdot + CF_4 \rightarrow HF + CF_3\cdot \quad (40)$$

Seidel[149] studied the reactions

$$H\cdot + CH_3Cl \rightarrow HCl + CH_3\cdot \quad (41)$$

$$H\cdot + CH_3Br \rightarrow HBr + CH_3\cdot \quad (42)$$

in crossed molecular beams at room temperature and gave the kinetic parameters shown in Table X. Recently, Davies and Thrush[67] studied the reaction

$$D\cdot + CH_3Br \rightarrow DBr + CH_3\cdot \quad (43)$$

using a discharge flow system coupled with an electron paramagnetic resonance spectrometer over the temperature range 297–480°K. They found that Seidel's value $k_{42} = 3.3 \times 10^9$ cc mol^{-1} sec^{-1} at 300°K was an order of magnitude below their value $k = 3.20 \pm 0.5 \times 10^{10}$ at 297°K, possibly because Seidel's value was obtained with a long extrapolation and also because the activation energy refers only to relative translational energy. Thrush considered that the isotopic effect should not be greater than a factor of 2, which would make Seidel's value still too high.

Scott and Jennings[26] investigated the mercury-photosensitized decomposition of C_2H_5F, 1,1-$C_2H_4F_2$, and 1,1,1-$C_2H_3F_3$. They proposed reactions 44, 45, and 46, in

$$H\cdot + C_2H_5F \rightarrow H_2 + CH_3CHF\cdot \quad (44)$$

$$H\cdot + 1,1\text{-}C_2H_4F_2 \rightarrow H_2 + CH_3CF_2\cdot \quad (45)$$

$$H\cdot + 1,1,1\text{-}C_2H_3F_3 \rightarrow H_2 + CH_2CF_3\cdot \quad (46)$$

each case using deuterium labeling and the variation of product yields with light intensity. The major products in each case arose from radical combination and disproportionation. They also found that, after the abstraction of an H atom, the resulting radical usually added an H atom to form a vibrationally excited molecule which decomposed by elimination of HF in preference to stabilization by collision.

Table X summarizes the various kinetic parameters obtained for the halo paraffin reactions. Because of rather large discrepancies and a general lack of information, comparison of the values is difficult.

2. *Halogen-Substituted Ethylenes*

Little attention has been given to the reaction of hydrogen atoms with halogen-substituted ethylenes. In an early investigation, Melville and Robb,[23] using the molybdenum oxide method, obtained collision efficiencies of 0.3 × 10^{-4} and $<10^{-4}$ for the reaction of hydrogen atoms with C_2F_4 and C_2Cl_4, respectively.

In 1968, Rennert and Wijnen[30] studied the reaction of hydrogen atoms with C_2H_3Cl by photolyzing HI in the presence of C_2H_3Cl. The following reactions were suggested.

$$H\cdot + C_2H_3Cl \rightarrow C_2H_4Cl\cdot^* \quad (47)$$

$$H\cdot + C_2H_3Cl \rightarrow C_2H_2Cl\cdot + H_2 \quad (48)$$

$$H\cdot + C_2H_3Cl \rightarrow C_2H_3\cdot + HCl \quad (49)$$

They also found the following ratios of rate constants, $k_{48}/k_{47} = 2.15$ and $k_{49}/k_{47} = 1.47$. Recently, Tanner and Jamieson[150] investigated the kinetics of the reaction of hydrogen atoms with C_2H_3Cl by using a Wood's discharge tube over the temperature range 305–767°K. They gave the specific reaction rate constants for HCl production to be $3.6 \times 10^{11} \exp(-2750/RT)$ cc mol^{-1} sec^{-1} and for C_2H_4 plus C_2H_6 production to be $1.8 \times 10^{11} \exp(-2800/RT)$. They found that the maximum yields of HCl at both 601 and 767°K exceeded the flow rates of atomic hydrogen, indicating that the reaction had limited chain characteristics.

Scott and Jennings[27] studied the products formed by the addition of hydrogen atoms to C_2H_3F, 1,1-$C_2H_2F_2$, and 1,1,2-C_2HF_3 using the mercury-photosensitization method. Hydrogen atoms have been shown to add largely or exclusively to the less fluorinated carbon of these fluoroethylenes. The major reaction products are formed by combination and disproportionation reactions of the resulting radicals. Less important products are formed by addition of H atoms to the original radicals forming vibrationally excited molecules which stabilize by collision or decompose by elimination of HF.

More recently, Penzhorn and Sandoval[29] studied the addition and abstraction reactions of thermal hydrogen atoms with fluorinated ethylenes using a photolysis method. They found that the relative rates of addition for *cis*-$C_2F_2H_2$:C_2FH_3:C_2H_4:*trans*-$C_2F_2H_2$:1,1-$C_2F_2H_2$:C_2F_3H:C_2F_4 are 1.00:1.12:1.43:1.67:2.08:2.36:2.42, while those of abstraction for C_2FH_3:C_2F_3H:*cis*-$C_2F_2H_2$:*trans*-$C_2F_2H_2$:1,1-$C_2F_2H_2$ are 1.00:1.78:1.94:3.61:6.60. They suggested steps 50 to 52 as the mechanism for these reactions. In each case, they assumed that both k_{50} and k_{51} are very much greater than k_{52}.

$$H\cdot + C_2F_xH_y \rightarrow C_2F_xH_{y+1}\cdot \quad (50)$$

$$H\cdot + C_2F_xH_y \rightarrow C_2F_xH_{y-1}\cdot + H_2 \quad (51)$$

$$H\cdot + C_2F_xH_y \rightarrow C_2F_{x-1}H_y\cdot + HF \quad (52)$$

Teng and Jones[151,152] studied the products formed in the reactions of H atoms with C_2F_4 and C_2HF_3 using a Wood's discharge tube. The determination of the reaction mechanism was complicated by the large number of products formed.

The kinetics of the reactions of hydrogen atoms with C_2H_3F and 1,1-$C_2H_2F_2$ have been studied[123,153] from 303 to 603°K using a Wood's discharge tube and fast flow system. For comparison purposes, the reaction with C_2H_4 was studied under identical conditions. Table XII gives the mechanistic steps applicable to these reactions and the kinetic parameters for each step as calculated by numerical integration of the differential equations pertaining to each reactive species in the mechanism. Very good agreement was obtained between product yields calculat-

(146) N. I. Parsamyan, V. V. Azatyan, and A. B. Nalbandyan, *Arm. Khim. Zh.*, **20**, 950 (1967); *Chem. Abstr.*, **69**, 76218x (1968).

(147) V. F. Kochubei and F. B. Moin, *Kinet. Katal.*, **10**, 494 (1969); *Kinet. Catal. (USSR)*, **10**, 405 (1969).

(148) J. R. Dacey and J. W. Hodgins, *Can. J. Res., Sect. B*, **28**, 173 (1950).

(149) W. Seidel, *Z. Phys. Chem. (Frankfurt am Main)*, **65**, 95 (1969).

(150) J. S. Tanner and J. W. S. Jamieson, *Can. J. Chem.*, **49**, 1023 (1971).

(151) L. Teng and W. E. Jones, *Can. J. Chem.*, 47, 1696 (1969).

(152) L. Teng, M.Sc. Thesis, Dalhousie University, Halifax, Canada, 1968.

(153) (a) L. Teng, Ph.D. Thesis, Dalhousie University, Halifax, Canada, 1972; (b) L. Teng and W. E. Jones, *J. Chem. Soc., Faraday Trans. 1*, **69**, 189 (1973).

TABLE XII. Summary of the Arrhenius Parameters for the Reactions of H Atoms with C_2H_4, C_2H_3F, and 1,1-$C_2H_2F_2$ (ref 123, 153a,b)

Reactions	Log *A* (cc mol^{-1} sec^{-1})	*E*, kcal mol^{-1}
$H\cdot + C_2H_2F_2 \rightleftarrows C_2H_3F_2\cdot^* \xrightarrow[M]{} C_2H_3F_2\cdot$	11.07	1.63
$H\cdot + C_2H_3F_2\cdot \rightleftarrows C_2H_4F_2^{**} \rightarrow C_2H_3F + HF$	14.10	1.00
$H\cdot + C_2H_2F_2 \rightleftarrows C_2H_3F_2^* \rightarrow C_2H_2F\cdot + HF$	10.79	2.05
$H\cdot + C_2H_3F \rightleftarrows C_2H_4F\cdot^* \rightarrow C_2H_4F\cdot$	11.08	0.91
$H\cdot + C_2H_4F\cdot \rightleftarrows C_2H_5F^{**} \rightarrow C_2H_4 + HF$	14.01	0.87
$H\cdot + C_2H_4 \rightleftarrows C_2H_5\cdot^* \xrightarrow[M]{} C_2H_5\cdot$	11.89	0.73
$H\cdot + C_2H_5\cdot \rightleftarrows C_2H_6^{**} \rightarrow CH_3\cdot + CH_3\cdot$	14.04	0.87
$H\cdot + CH_3\cdot \rightleftarrows CH_4^* \xrightarrow[M]{} CH_4$	12.07	0.05
$CH_3\cdot + CH_3\cdot \rightleftarrows C_2H_6^* \xrightarrow[M]{} C_2H_6$	13.42	0.43
$CH_3\cdot + C_2H_5\cdot \rightarrow C_3H_8$	13.40	0.40
$C_2H_5\cdot + C_2H_5\cdot \rightarrow C_4H_{10}$	12.87	0.19
$H\cdot \xrightarrow{\text{wall}} \tfrac{1}{2}H_2$	1.50	0.69
$H\cdot + C_2H_3F \rightarrow C_2H_2F\cdot + H_2$	10.03	1.08
$H\cdot + C_2H_2F\cdot \rightleftarrows C_2H_3F^{**} \rightarrow C_2H_2 + HF$	13.77	0.95
$CH_3\cdot + C_2H_4F\cdot \rightleftarrows i\text{-}C_3H_7F^{**} \rightarrow C_3H_6 + HF$	13.99	0.86

ed with these parameters and experimentally determined yields.

E. Reaction with Aldehydes and Ketones

1. Aldehydes

Several studies[154-158] have been made of the reaction of H atoms with HCHO. The two major products, CO and H_2, are formed according to the reactions

$$H\cdot + HCHO \rightarrow H_2 + HCO\cdot \tag{53}$$

$$H\cdot + HCO\cdot \rightarrow H_2 + CO \tag{54}$$

The kinetic parameters for the H + HCHO reaction are listed in Table XIII.

The kinetics of the reaction of H atoms with CH_3CHO have been given by Lambert, *et al.*,[159] and McKnight, *et al.*[160] (Table XIII). Based on a detailed analysis of the reaction with deuterated acetaldehyde, the latter group proposed the mechanism given in eq 55–58.

$$H\cdot + CH_3CHO \rightarrow CH_3CO\cdot + H_2 \tag{55}$$

$$H\cdot + CH_3CO\cdot \rightarrow CH_2CO + H_2 \tag{56}$$

$$H\cdot + CH_2CO \rightleftarrows CH_3CO\cdot^* \rightarrow CH_3\cdot + CO \tag{57}$$

$$H\cdot + CH_3\cdot \xrightarrow{\text{wall}} CH_4 \tag{58}$$

2. Ketones

Kinetic parameters have been given (Table XIII) for two ketones CH_2CO[161] and CH_3COCH_3.[162] The major products CH_4, CO, and C_2H_6 from the H atom ketene reaction have been accounted for by reactions 57, 58, and 59.

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \tag{59}$$

TABLE XIII. Summary of the Published Arrhenius Parameters for the Reactions of H Atoms with Aldehydes and Ketene

Compounds	Temp, °K	*E*, kcal mol^{-1}	Log *A* (cc mol^{-1} sec^{-1})	Method	Ref
HCHO	525–670	2.6	13.21	Photolysis (H_2CO/D_2)	154
	525–670	2.7	13.21	Photolysis (H_2CO/D_2)	154[a]
	523–673	3.26	13.29	H_2/O_2 ignition	155
	600–700	3.49	13.46	H_2/O_2 ignition	155
	300	$k = (2.7 \pm 0.7) \times 10^{10}$		Discharge (microwave)	156
	720	$k = 3.5 \times 10^{12}$		Pyrolysis (HCHO)	157
	297	$k = (3.25 \pm 0.3) \times 10^{10}$		Flash photolysis (~170–176 nm)	*b*
	297–652	3.76	13.13	Discharge (microwave)	c
DCDO	581–614	3.0	13.3	Photolysis (D_2CO)	158
	525–670	3.6	13.21	Photolysis (H_2CO/D_2CO)	154
	525–670	3.6	13.21	Photolysis (H_2CO/D_2CO)	154[a]
CH_3CHO	297	$k \sim 2 \times 10^{10}$		Discharge (microwave)	159
	297	≤ 6		Discharge (Wood's)	*d*
CD_3CDO	300	$k = (1.9 \pm 0.3) \times 10^{10}$		Discharge (microwave)	160
CH_2CO	298	$k = 7.8 \times 10^{10}$		Discharge (microwave)	161
CH_3COCH_3	298	8.8		Discharge (Wood's)	162[e]
	298	8.0		Discharge (Wood's)	162[a,e]

[a] Refers to D atom reaction. [b] B. A. Ridley, J. A. Davenport, L. J. Stief, and K. H. Welge, *J. Chem. Phys.*, **57**, 520 (1972). [c] A. A. Westenberg and N. deHaas, *J. Phys. Chem.*, **76**, 2213 (1972). [d] W. R. Trost, B. de B. Darwent, and E. W. R. Steacie, *J. Chem. Phys.*, **16**, 353 (1948). [e] A steric factor of 1 was assumed.

The activation energy for the reaction with acetone, the only other ketone studied to date, is the value given in Table XIII as determined by Harris and Steacie[162] on the basis of a steric factor of unity.

F. Reaction with Alcohols and Amines

1. Alcohols

During the last 7 years, the reactions with alcohols have been extensively studied.[163-167] Reactions 60 to 63

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(154) J. R. McNesby, M. D. Scheer, and R. Klein, *J. Chem. Phys.*, **32**, 1814 (1960).

(155) R. R. Baldwin and D. W. Cowe, *Trans. Faraday Soc.*, **58**, 1768 (1962).

(156) W. R. Brennen, I. D. Gay, G. P. Glass, and H. Niki, *J. Chem. Phys.*, **43**, 2569 (1965).

(157) R. Klein, M. D. Scheer, and L. J. Schoen, *J. Amer. Chem. Soc.*, **78**, 50 (1956).

(158) R. Klein, J. R. McNesby, M. D. Scheer, and L. J. Schoen, *J. Chem. Phys.*, **30**, 58 (1959).

(159) R. M. Lambert, M. I. Christie, and J. W. Linnett, *Chem. Commun.*, 388 (1967).

(160) C. McKnight, H. Niki, and B. Weinstock, *J. Chem. Phys.*, 47, 5219 (1967).

(161) R. W. Carr Jr., I. D. Gay, G. P. Glass, and H. Niki, *J. Chem. Phys.*, **49**, 846 (1968).

(162) G. M. Harris and E. W. R. Steacie, *J. Chem. Phys.*, **13**, 554 (1945).

(163) Z. G. Dzotsenidze, K. T. Oganesyan, and A. B. Nalbandyan, *Arm. Khim. Zh.*, **21**, 370 (1968); *Chem. Abstr.*, **70**, 28217v (1969).

(164) W. K. Aders and H. Gg. Wagner, *Z. Phys. Chem. (Frankfurt am Main)*, 7, 224 (1971).

TABLE XIV. Summary of the Published Arrhenius Parameters for the Alcohol and Amine Reactions

Compound	Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
CH_3OH	843–943	8.6 ± 1.0	12.21	D_2/O_2 ignition	7, 163[a]
	295–653	5.3 ± 0.3	13.36	Discharge (microwave)	167
C_2H_5OH	843–963	8.1 ± 0.6	13.08	H_2/O_2 ignition	7, 165
	423	$k = 1.3 \times 10^{10}$		γ radiolysis	166
	843–943	6.9 ± 1.0	12.65	D_2/O_2 ignition	7, 163[a]
n-C_3H_7OH	843–943	5.6 ± 1.0	12.64	D_2/O_2 ignition	7, 163[a]
	863–963	6.5 ± 0.5	13.44	H_2/O_2 ignition	7, 167
i-C_3H_7OH	863–963	6.4 ± 0.5	13.39	H_2/O_2 ignition	7, 167
n-C_4H_9OH	863–963	5.1 ± 0.6	13.30	H_2/O_2 ignition	7, 167
	843–943	4.9 ± 1.0	12.72	D_2/O_2 ignition	7, 163[a]
t-C_4H_9OH	773–963	5.3 ± 0.5	13.23	H_2/O_2 ignition	7, 167
$C_2H_5NH_2$	883–963	8.7 ± 0.8	13.10	H_2/O_2 ignition	*b*, 7
n-$C_3H_7NH_2$	883–963	8.0 ± 0.8	13.14	H_2/O_2 ignition	*b*, 7
$(CH_3)_2NH$	863–963	10.8 ± 0.7	13.21	H_2/O_2 ignition	7, 169
$(CH_3)_3N$	863–963	11.8 ± 0.7	13.87	H_2/O_2 ignition	7, 169
c-C_3H_7N	328–573	4.8 ± 0.5	12.48	Discharge (Wood's)	84

[a] Refers to D atom reaction. [b] K. T. Oganesyan, T. G. Mkryan, G. A. Sachyan, and A. B. Nalbandyan, *Arm. Khim. Zh.*, **21**, 737 (1968); *Chem. Abstr.*, 71, 33808p (1969).

present the general mechanism for the alcohol reactions. The main products from subsequent reaction steps are paraffins, H_2O, aldehydes, and CO. The kinetic parameters for the reaction with various alcohols are given in Table XIV.

$$H\cdot + ROH \rightarrow R_1OH + H_2 \qquad (60)$$

$$H\cdot + ROH \rightarrow RO + H_2 \qquad (61)$$

$$H\cdot + ROH \rightarrow R\cdot + H_2O \qquad (62)$$

$$H\cdot + ROH \rightarrow RH + OH\cdot \qquad (63)$$

2. *Amines*

Few studies have been made of the reactions with amines. H atom abstraction from both the H–N bonds and H–C bonds has been proposed.[168] Oganesyan, *et al.*,[169] found the activation energy for the reaction $H\cdot + HN(CH_3)_2$ to be greater than that for $H\cdot + N(CH_3)_3$, suggesting that $D(N\text{–}H) < D(N\text{–}C)$. It was noted[170] that the reactivity with D atoms followed the order $NH_3 > CH_3NH_2 > C_2H_5NH_2 > C_3H_7NH_2$. The various results for amine reactions are included in Table XIV.

G. Reaction with CN-Containing Compounds

Haggart and Winkler[171,172] showed that the reaction of H atoms with C_2N_2 in the presence of excess H_2 involves the chain process

$$H\cdot + C_2N_2 \rightarrow HCN + CN\cdot \qquad (64)$$

$$CN\cdot + H_2 \rightarrow HCN + H\cdot \qquad (65)$$

Dunn, *et al.*,[173] explained the CN·* luminescence by the termolecular process

$$H\cdot + H\cdot + CN\cdot \rightarrow H_2 + CN\cdot^* \qquad (66)$$

The polymer which results from the C_2N_2 reaction is believed[173] to form by the reaction

$$CN\cdot + C_2N_2 \rightarrow C_3N_3 \qquad (67)$$

The rate constants were given[173] as $k_{64} = 5.2 \pm 1.8 \times 10^8$, $k_{65} = 1.8 \times 10^{10}$, and $k_{67} = 6 \times 10^9$ cc mol^{-1} sec^{-1} at 300°K.

Claridge, *et al.*,[174] proposed the steps

$$H\cdot + ICN \rightarrow HCN^* + I\cdot \qquad (68)$$

$$H\cdot + ICN \rightarrow HI + CN\cdot \qquad (69)$$

for the $H\cdot + ICN$ reaction. They estimated $k_{69} \cong 6 \times 10^{11}$ cc mol^{-1} sec^{-1}.

The reaction with CH_3CN was suggested[85] to follow the mechanism

$$H\cdot + CH_3CN \rightarrow CH_4 + CN\cdot \qquad (70)$$

$$H\cdot + CH_3CN \rightarrow CH_3\cdot + HCN \qquad (71)$$

$$CN\cdot + H_2 \rightarrow HCN + H\cdot \qquad (65)$$

$$2CH_3\cdot \rightarrow C_2H_6 \qquad (59)$$

The rate constants representing the formation of HCN, C_2H_4, and C_2H_6 were calculated as $k_{HCN} = 2.14 \times 10^{12} \exp(-5816/RT)$, $k(CH_4) = 1.00 \times 10^{11} \exp(-2990/RT)$, and $k(C_2H_6) = 1.02 \times 10^{12} \exp(-7857/RT)$.

H. Reaction with Aromatic Hydrocarbons

1. *Benzene*

The Arrhenius parameters reported for the reaction with benzene and alkyl-substituted benzenes are given in Table XV. Based on the work of Benson and Shaw[175] and of Yang,[112] the primary step is

$$H\cdot + C_6H_6 \rightarrow C_6H_7\cdot^* \qquad (72)$$

This reaction is followed by H atom attack on the cyclo-

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(165) K. T. Oganesyan, A. B. Nalbandyan, and N. I. Parsamyan, *Dokl. Akad. Nauk Arm. SSR*, **40**, 159 (1965); *Chem. Abstr.*, **63**, 13017g (1965).

(166) K. N. Bansal and G. R. Freeman, *J. Amer. Chem. Soc.*, **90**, 7183 (1968).

(167) K. T. Oganesyan and A. B. Nalbandyan, *Izv. Akad. Nauk Arm. SSR, Khim. Nauki*, **18**, 237 (1965); *Chem. Abstr.*, **63**, 17844c (1965).

(168) A. N. Wright, J. W. S. Jamieson, and C. A. Winkler, *J. Phys. Chem.*, **62**, 657 (1958).

(169) K. T. Oganesyan and A. B. Nalbandyan, *Arm. Khim. Zh.*, **19**, 150 (1966); *Chem. Abstr.*, **65**, 3701c (1966).

(170) Z. G. Dzotsenidze, K. T. Oganesyan, and A. B. Nalbandyan, *Soobshch. Akad. Nauk Gruz. SSR*, **50**, 379 (1968); *Chem. Abstr.*, **69**, 61909z (1968).

(171) C. Haggart and C. A. Winkler, *Can. J. Chem.*, **37**, 1791 (1959).

(172) C. Haggart and C. A. Winkler, *Can. J. Chem.*, **38**, 329 (1960).

(173) M. R. Dunn, C. G. Freeman, M. J. McEwan, and L. F. Phillips, *J. Phys. Chem.*, **75**, 2662 (1971).

(174) R. F. C. Claridge, F. T. Greenaway, and M. J. McEwan, *J. Phys. Chem.*, 74, 3293 (1970).

TABLE XV. Summary of Published Arrhenius Parameters for the Aromatic Reactions

Compound	Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
C_6H_6	298	$k = 1.1 \times 10^{11}$		Hg photosens	130
	329-513	3.9	13.1	γ radiolysis	112
	298	$k = 2.9 \times 10^{12}$		Discharge	a
	300-357	4.3 ± 0.8	13.77 ± 0.5	Pulse radiolysis	177
	Room temp	$k = (1.55 \pm 0.14) \times 10^{10}$		Discharge (microwave)	b
$(C_6H_5)_2$	298-393	4.3 ± 0.8	14.2 ± 0.5	Pulse radiolysis	177
$C_6H_5CH_3$	298	$k = 2.4 \times 10^{10}$		Hg photosens	130
	298	$k = 1 \times 10^{11}$		Pulse radiolysis	c
	329-513	3.9	13.1	γ radiolysis	112
	635-694	1.5	12.3		175
m-$C_6H_4(CH_3)_2$	635-694	1.5	12.6		175
	298	$k = 4.4 \pm 0.9 \times 10^{11}$		Pulse radiolysis	177
o-$C_6H_4(CH_3)_2$	635-694	0.6	12.6		175
	298	$k = 3.5 \pm 1.0 \times 10^{11}$		Pulse radiolysis	177
p-$C_6H_4(CH_3)_2$	635-694	1.5	12.6		175
	298	$k = 3.5 \pm 0.7 \times 10^{11}$		Pulse radiolysis	177
$C_6H_5NH_2$	298-393	2.6 ± 0.8	13.22 ± 0.5		177
$C_6H_5C_2H_5$	298	$k = 2.0 \pm 0.4 \times 10^{11}$			177
C_6H_5CN	298-393	5.2 ± 0.8	14.02 ± 0.5		177
$C_6H_5CF_3$		5.1 ± 0.8	13.98 ± 0.5		177
C_6H_5F		3.2 ± 0.8	12.98 ± 0.5		177
C_6H_5Cl		2.4 ± 0.8	12.74 ± 0.5		177
$C_6H_5NO_2$		4.0 ± 0.8	13.71 ± 0.5		177
$C_6H_5OCH_3$		5.7 ± 0.8	14.9 ± 0.5		177
$C_6H_5CH_2Cl$		3.0 ± 0.8	13.1 ± 0.5		177
Naphthalene			14.93 ± 0.5		177
Pyridine	298	$k = 1.8 \pm 0.3 \times 10^{11}$			177

[a] H. Girouard, F. M. Graber, and B. F. Myers, General Dynamics Astronautical Report N64-13061, San Diego, Calif., 1963; NASA CR 52376. [b] R. Knutti and R. E. Bühler, *Chimia*, **26**, 624 (1972). [c] M. C. Sauer, Jr., and B. Ward, *J. Phys. Chem.*, 71, 3971 (1967).

hexadienyl radicals to form H_2 and various C_6 cyclic hydrocarbons.

2. *Toluene and Xylenes*

Reaction 73 was suggested by Benson and Shaw[175] as the most probable step for attack of the H atom on toluene. They found that since the H atoms can add to the benzene ring and the methyl position at about equal rates, the preexponential factor for addition to toluene is six times the rate of addition to benzene.

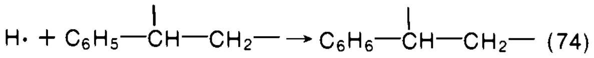
$$H\cdot + C_6H_5CH_3 \rightarrow C_6H_6 + CH_3\cdot \qquad (73)$$

The relative rate of addition of hydrogen has been found[176] to be 3:2:2:1 for o-xylene:m-xylene:p-xylene:toluene. Table XV includes kinetic parameters for these compounds.

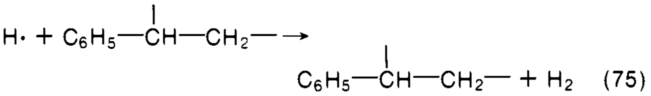
3. *Substituted Aromatics*

Sauer and Mani[177] have completed an extensive survey of the reactions with substituted benzenes (see Table XV). They found that H atoms have an electrophilic character in these reactions as compared to the electroneutral character claimed by Cvetanović in the olefin reactions.

Wall and Ingalls[178] treated polystyrene with H and D atoms as proposed in eq 74 and 75.



$$H\cdot + C_6H_5-\overset{|}{C}H-CH_2- \rightarrow C_6H_6-\overset{|}{C}H-CH_2- \qquad (74)$$



$$H\cdot + C_6H_5-\overset{|}{C}H-CH_2- \rightarrow C_6H_5-\overset{|}{C}H-CH_2- + H_2 \qquad (75)$$

As for the $H\cdot + C_6H_6$ reaction, the principal reaction appeared to be the H atom addition to the phenyl ring, where $k_{74} = 4 \times 10^6$ cc mol^{-1} sec^{-1} and $k_{75} = 1 \times 10^9$ cc mol^{-1} sec^{-1} at room temperature.

V. *Chemical Reactions of Atomic Hydrogen with Inorganic Species*

A. Recombination Reactions

1. *Heterogeneous Recombination*

Wood[11] found in his early studies that water in the H_2 stream or on the surface of the discharge and reaction vessels increased the concentration of H atoms. The water inhibited the wall-catalyzed recombination of H atoms and was referred to as a "poison." Poole,[21] in his investigation of the Wood discharge, found that water gave a variable and unpredictable H atom concentration, while syrupy phosphoric acid acted as an efficient and stable poison. Later workers have used other acids, such as H_3BO_4,[179,180] HNO_3,[180] and HF,[91] as poisons. Unfortunately, these poisons contain water which tends to react with certain compounds producing erroneous results. In order to counteract this, Wittke and Dicke[181] used a mixture of $(CH_3)SiCl_3$ and $(CH_3)_2SiCl_2$, which formed a water-resistant polymeric coating called "Drifilm." Berg and Kleppner[182] were the first to suggest the

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(175) (a) S. W. Benson and R. Shaw, *J. Chem. Phys.*, 47, 4052 (1967); (b) *J. Amer. Chem. Soc.*, **89**, 5351 (1967).

(176) A. Tsuchiya, A. Hashimoto, H. Tominage, and S. Masamune, *Bull. Jap. Petrol. Inst.*, **2**, 85 (1960), as quoted by ref 175a.

(177) M. C. Sauer, Jr., and I. Mani, *J. Phys. Chem.*, 74, 59 (1970).

(178) L. A. Wall and R. B. Ingalls, *J. Chem. Phys.*, 41, 1112 (1964).

(179) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **48**, 4405 (1968).

(180) M. Green, K. R. Jennings, J. W. Linnett, and D. Schofield, *Trans. Faraday Soc.*, **55**, 2152 (1959).

(181) J. P. Wittke and R. H. Dicke, *Phys. Rev.*, **103**, 620 (1956).

(182) H. C. Berg and D. Kleppner, *Rev. Sci. Instr.*, **33**, 248 (1962).

TABLE XVI. Surface-Catalyzed Recombination of H Atoms: $H\cdot + \text{wall} \rightarrow \frac{1}{2}H_2 + \text{wall}$

Surface	Temp, °K	k, sec^{-1}	$\gamma = 2rk/\bar{c}$	Ref
Pyrex + Teflon	300	0.17 ± 0.24[a]	$8.0 \pm 11.3 \times 10^{-7}$	192
Pyrex + Teflon	300	0.22 ± 0.21	$7 \pm 6.7 \times 10^{-7}$	192
Pyrex + Drifilm	298	14.6 ± 1.4		*b*
Pyrex + *m*-H_3PO_4	298	1.7 ± 0.2[a]		c
Pyrex + *o*-H_3PO_4 + P_2O_5	278–352	4.8–2.6		139
Pyrex + 5% Drifilm in CCl_4	298	30		17
Pyrex + o-H_3PO_4	303–603	10–17		153
Pyrex + 10% HF	300	0.21 ± 0.15		193
Pyrex + 5% HF	303	10.8–30.0		91
Acid-washed quartz	293	4.1–5.5	1.8×10^{-5}	*d*
Pyrex + Al_2O_3	300		4.5×10^{-1}	185
Pyrex + Na_3PO_4	300		$\geq 10^{-1}$	185
Pyrex + K_2CO_3	300		$\geq 10^{-1}$	185
Pyrex + KCl	300		$> 10^{-5}$	185
Pyrex + K_2SiO_3	300		$> 10^{-2}$	185
"Clean" Pyrex	300		4×10^{-3}	185
Pyrex	298		$< 3 \times 10^{-5}$	e
Pyrex + HNO_3	298		2×10^{-5}	180
Pyrex + NH_4OH	298		$2.5\text{–}4.5 \times 10^{-3}$	180
Pyrex + H_3BO_4	298–823		$1.2\text{–}8 \times 10^{-4}$	180
"Clean" Pyrex	298		$\sim 10^{-4}$	180
Pyrex + Al_2O_3	298–723		$1.8\text{–}5 \times 10^{-4}$	180
Pyrex	298	$KH_2PO_4 > K_2HPO_4 \sim K_3PO_4$		180
Pyrex + type of Drifilm	77		$4.3 \pm 1.1 \times 10^{-4}$	183
Pyrex + polytrifluoro-chloroethylene	77		4.2×10^{-4}	183
Pyrex + Teflon	77		$1.0 \pm 0.2 \times 10^{-4}$	183
"Clean" Pyrex	77		$2.9 \pm 0.7 \times 10^{-4}$	183
Pyrex + H_3PO_4 (cc)	77–300		$10^{-5}\text{–}10^{-6}$	196
Pyrex	119–527	$3.2\text{–}1.3 \times 10^{3}$	$5 \times 10^{-5} - 9.6 \times 10^{-3}$	190
Quartz	300	2.8×10^{2}	2.8×10^{-3}	190
Pyrex + Drifilm	293		$\sim 1.8 \times 10^{-5}$	*f*
Pyrex	298		7.5×10^{-4}	*g*
Pyrex	~190		9.3×10^{-4}	188

[a] D atom reaction. [b] J. R. Barker, D. G. Keil, J. V. Michael, and D. T. Osborne, *J. Chem. Phys.*, **52**, 2079 (1970). [c] S. Toby and H. I. Schiff, *Can. J. Chem.*, **34**, 1061 (1956). [d] K. M. Sancier and H. Wise, *J. Chem. Phys.*, **51**, 1434 (1969). [e] H. Wise and C. M. Ablow, *ibid.*, **29**, 634 (1958). [f] F. S. Larkin, *Can. J. Chem.*, **46**, 1005 (1968). [g] B. J. Wood and H. Wise, *J. Chem. Phys.*, **29**, 1416 (1958).

use of fused Teflon as a poison. Polytrifluorochloroethylene has also been suggested.[183]

The wall-catalyzed recombination of H atoms is a first-order process strongly dependent upon surface conditions and on certain characteristics of the system. The recombination coefficient, γ, which is in effect the surface efficiency, may be expressed as

$$\gamma = 2rk/\bar{c} \tag{76}$$

where k is the first-order recombination rate constant, r the vessel diameter, and $\bar{c}$ the average velocity of the atoms to the wall. Diffusion effects must be considered in this calculation. These have been discussed by Kaufman[184] and Wise and Wood.[185]

In many of the earlier studies, γ has been calculated from flow characteristics and, by using eq 76, the first order rate constant has been determined. More recently, direct measurements or estimates of k have been possible.[139] From these measurements, the surface efficiency can be calculated.

Table XVI presents various values of k and γ. By plotting log γ *vs.* temperature ($1000/T$), Gelb and Kim[186] have found that γ has maximum values at 48.5 and 833°K and a minimum value at 111°K. These temperatures correspond to maxima and minima in the reaction rate. Gelb and Kim's plot was based upon the data of earlier workers.[187–189]

Two mechanisms have been postulated to explain the wall-catalyzed recombination.[190] The Rideal mechanism proposes that the reaction occurs between a surface-adsorbed atom and a gas-phase atom. This is considered to be the basic mechanism for the temperature range 120–500°K. The Hinshelwood mechanism suggests that the reaction takes place between two surface-adsorbed atoms and is considered to be the basic mechanism for temperatures below 120°K and above 500°K. Since both of the above reactions depend upon adsorbed species, the wall-catalyzed recombination rate must be dependent upon the binding energy of the adsorption sites.[186]

The H atoms can be held by strong chemisorption or by physical adsorption which may be either weak or strong. The weakly adsorbing sites have a binding energy of about 2 kcal/mol,[185,186] while the strongly adsorbing sites have a binding energy of about 45 kcal/mol.[185,186] The recombination coefficients presented in Table XVI probably represent a combination of the efficiencies of these two sites in promoting recombination.[186]

In a recent study, Bader and Gesser[191] noted that the H atom adsorption site on any surface is identified with

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(183) E. B. Gordon, A. N. Ponomarev, and V. L. Tal'roze, *Kinet. Katal.* 7, 577 (1966); *Kinet. Catal. (USSR)*, 7, 511 (1966).

(184) F. Kaufman, *Progr. React. Kinet.*, 1, 1 (1961).

(185) H. Wise and B. J. Wood, *Advan. At. Mol. Phys.*, 3, 291 (1967).

(186) A. Gelb and S. K. Kim, *J. Chem. Phys.*, **55**, 4935 (1971).

(187) B. J. Wood and H. Wise, *J. Phys. Chem.*, **65**, 1976 (1961).

(188) K. Tsu and M. Boudart, *Can. J. Chem.*, **39**, 1239 (1961).

(189) W. V. Smith, *J. Chem. Phys.*, 11, 110 (1943).

(190) B. J. Wood and H. Wise, *J. Phys. Chem.*, **66**, 1049 (1962).

(191) L. W. Bader and H. D. Gesser, *Can. J. Chem.*, **50**, 2305 (1972).

TABLE XVII. Termolecular Recombination of H Atoms:[a] $H\cdot + H\cdot + M = H_2 + M$

M	Temp, °K	k, cc^2 mol^{-2} sec^{-1}	Method	Ref
H_2	298	$3.01 \pm 0.15 \times 10^{15}$	Tungsten filament	196
H_2	300	4.6×10^{15}	(Estimate)	194
He	300	3.3×10^{15}	(Estimate)	194
Ar	300	3.2×10^{15}	(Estimate)	194
H_2	300	$4.2 \pm 1 \times 10^{15}$	Discharge (microwave)	192
H_2	300	$2.7 \pm 0.4 \times 10^{15}$	Discharge (microwave)	193
D_2	300	$5.4 \pm 0.7 \times 10^{15\,b}$	Discharge (microwave)	192
H_2O	303	$9 \pm 2 \times 10^{16}$	Discharge (microwave)	91
H_2	298	3.2×10^{15}	Discharge (microwave)	307
Ar	298	5.4×10^{15}	Discharge (microwave)	307
He	298	4.0×10^{15}	Discharge (microwave)	307
CO_2	298	5.1×10^{15}	Discharge (microwave)	307
N_2	298	3.5×10^{15}	Discharge (microwave)	307
CH_4	298	5.3×10^{15}	Discharge (microwave)	307
N_2O	298	2.9×10^{16}	Discharge (microwave)	307
H_2	293	$1.2 \pm 0.1 \times 10^{16}$	Discharge (rf)	c
Ar	293	$0.81 \pm 0.08 \times 10^{16}$	Discharge (rf)	c
He	293	$0.47 \pm 0.07 \times 10^{16}$	Discharge (rf)	c
Ar	~3500	$1 \times 10^{18}\,T^{-1}$	Best value from known exptl values	224
N_2	1900	3.6×10^{15}	Flame ($H_2/O_2/-$)	*d*
Ar	1900	2.2×10^{15}	Flame ($H_2/O_2/-$)	*d*
He	1900	4.7×10^{15}	Flame ($H_2/O_2/-$)	*d*
$CO + CO_2$	1900	5×10^{15}	Flame ($H_2/O_2/-$)	*d*
Ar	~1600	4×10^{14}	Shock tube	e
N_2	~1600	6×10^{14}	Shock tube	e
H_2O	~1600	$\leq 1.3 \times 10^{15}$	Shock tube	e
He	296	$7.26 \pm 0.58 \times 10^{15}$	Discharge (rf)	*f*
Ar	296	$5.62 \pm 0.36 \times 10^{15}$	Discharge (rf)	*f*
H_2	2500-7000	$\log k = 15.243 - 1.95 \times 10^{-4}T$	Shock tube	*g*
Ar	2500-7000	$\log k = 15.787 - 2.75 \times 10^{-4}T$	Shock tube	*g*

[a] Values prior to 1968 are compiled in ref 44. [b] D atom reaction. [c] F. S. Larkin, *Can. J. Chem.*, **46**, 1005 (1968). This paper also reports that the temperature variation of the rate constant was approximately $T^{-1/2}$ for 190–350°K. [d] C. J. Halstead and D. R. Jenkins, *Symp. (Int.) Combust. Proc.*, *12th, 1968*, 979 (1969). [e] R. W. Getzinger and L. S. Blair, *Combust. Flame*, **13**, 271 (1969). [f] V. V. Azaytan, L. B. Romanovich, and S. B. Filippov, *Kinet. Katal.*, **9**, 1188 (1968); *Kinet. Catal. (USSR)*, **9**, 986 (1968). [g] I. R. Hurle, A. Jones, and J. L. J. Rosenfeld, *Proc. Roy. Soc., Ser. A*, **310**, 253 (1969).

an electron-deficient atom on the surface. Any poison applied must "neutralize" these sites. Thus, it is essential that neutralizing substances be Lewis bases capable of strong adsorption at the electron-deficient sites. Poisons, such as H_3PO_4 (acid) or Na_3PO_4 (salt), fulfill this requirement. Polymeric coatings, such as Drifilm or Teflon, isolate the impinging atoms from the electron-deficient sites on the glass surface.

2. *Homogeneous Recombination*

The termolecular recombination of H atoms in the gas phase has been studied over a wide range of temperatures and experimental conditions. Myerson, *et al.*,[57] have graphically represented the results determined prior to 1964. (Jacobs, *et al.*,[81] have partially reviewed the results obtained during the period 1962–1966.) Bahn[44] has compiled the data for the period 1957–1968. An examination of all of these results leads to the general conclusion that when the third body is an inert gas (Ar or He) or H_2, the rate constant is about 10^{15} cc^2 mol^{-2} sec^{-1} at 300°K. Previous to 1968, H_2 or an inert gas has been used as the third body. Recently, other third bodies have been considered. Table XVII presents the rate constants for termolecular recombination published since 1968 for various third bodies.

The heterogeneous and homogeneous recombination rate constants for both H and D atoms appear to be inversely related (*i.e.*, as one value decreases the other increases).[192] Recently, Bennett and Blackmore[193] have discussed values obtained for the termolecular rate constant in flow systems at room temperature. They concluded that some of the earlier authors erred in their determination of the termolecular rate constant, since they did not consider the interaction between the surface and gas recombination reactions.

A number of theoretical studies of the termolecular recombination have been made. Two of the most prominent recent studies are: (1) the resonance theory of Roberts, *et al.*,[194] and (2) the modified phase space theory of Shui, *et al.*[195] Roberts, *et al.*,[194] predicted a low-temperature maximum (at about 70°K) for the rate constant. Later, Ham, *et al.*,[196] studied the termolecular reaction in a flow system at temperatures down to 77°K. They[196] found no evidence of the maximum rate constant predicted by Roberts, *et al.*[194] Furthermore, an extrapolation of their[196] data to lower temperatures did not indicate the maximum predicted by Roberts, *et al.*[194]

B. Reaction with H_2, D_2, and HD

The following series of exchange reactions is of con-

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(192) J. E. Bennett and D. R. Blackmore, *J. Chem. Phys.*, **53**, 4400 (1970).

(193) J. E. Bennett and D. R. Blackmore, *Proc. Roy. Soc., Ser. A*, **305**, 553 (1968).

(194) R. E. Roberts, R. B. Bernstein, and C. F. Curtiss, *Chem. Phys. Lett.*, **2**, 366 (1968); *J. Chem. Phys.*, **50**, 5163 (1969).

(195) V. H. Shui, J. P. Appleton, and J. C. Keck, *Symp. (Int.) Combust. Proc., 13th, 1970*, 21 (1971).

(196) D. O. Ham, D. W. Trainor, and F. Kaufman, *J. Chem. Phys.*, **53**, 4395 (1970).

TABLE XVIII. Reaction with H_2, D_2, and HD

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + p\text{-}H_2 \rightarrow o\text{-}H_2 + H\cdot$		
300–444	$\log k = 15.45 - 349(10^3/T) + 3.83(10^5/T^2)$		Tungsten filament	198
274–468	$k = 1.18 \times 10^{15} T^{1/2} \Gamma \exp(-9.2 \times 10^3/RT)$		Γ is the tunneling factor	201
	8.812	13.86	(Estimate)	204
300–1000	6.750	13.46	(Estimate)	203
300–1000	7.726	13.65	(Review)	224
1000	$k = 1.1 \times 10^{12}$		H_2/D_2 thermal reaction	a
1000	8.00 ± 0.5	14.17	(Estimate)	205
		$H\cdot + HD \rightarrow D\cdot + H_2$		
300–1000	7.0	13.15	(Estimate)	203
1000	$k = 3.7 \times 10^{11}$		H_2/D_2 thermal reaction	a
		$H\cdot + D_2 \rightarrow HD + D\cdot$		
1000	$k = 6.1 \times 10^{11}$		H_2/D_2 thermal reaction	a
368–468	7.30	12.63	Tungsten filament	199
300–1000	8.00	13.40	(Estimate)	203
300–1000	8.560	13.51	(Review)	9
300–750	9.390	14.00	Discharge (microwave)	202
		$D\cdot + p\text{-}D_2 \rightarrow o\text{-}D_2 + D\cdot$		
300–1000	$k = 2 \times 10^{13}$		(Estimate)	203
1000	$k = 5.7 \times 10^{11}$	H_2/D_2 thermal reaction		a
358–468	7.63 ± 0.10	13.09	Tungsten filament	200
		$D\cdot + HD \rightarrow D_2 + H\cdot$		
300–1000	7.100	13.04	(Estimate)	203
1000	$k = 4.0 \times 10^{11}$		H_2/D_2 thermal reaction	a
		$D\cdot + H_2 \rightarrow HD + D\cdot$		
274–468	$k = 3.63 \times 10^{15} T^{1/2} \Gamma \exp(-9.4 \times 10^3/RT)$		Tungsten filament, Γ is the tunneling factor	201
1000	$k = 9.8 \times 10^{11}$		H_2/D_2 thermal reaction	a
300–1000	6.400	13.40	(Estimate)	203
275–1000	6.780	13.42	(Review)	9
250–750	7.610	13.64	Discharge (microwave)	202
295	(1) $H\cdot + D_2 \rightarrow HD + D\cdot$ (2) $H\cdot + HCl \rightarrow H_2 + Cl\cdot$	$k_1/k_2 = 14 \pm 4$	Photolysis (HCl/D_2)	b
295	(1) $D\cdot + HD \rightarrow D_2 + H\cdot$ (2) $D\cdot + DCl \rightarrow D_2 + Cl\cdot$	$k_1/k_2 = 65$	Photolysis (DCl/H_2)	b
295	(1) $H\cdot + D_2 \rightarrow HD + D\cdot$ (2) $H\cdot + HBr \rightarrow H_2 + Br\cdot$	$k_1/k_2 = 0.55$	Photolysis (D_2/HBr)	b

[a] G. Boato, G. Careri, A. Cimino, E. Molinari, and G. G. Volpi, *J. Chem. Phys.*, **24**, 783 (1956); A. Cimino, E. Molinari, and G. G. Volpi, *ibid.*, **33**, 616 (1960). [b] A. E. DeVries and F. S. Klein, *ibid.*, 41, 3428 (1964).

siderable interest to both experimental and theoretical chemists

$$H\cdot + p\text{-}H_2 \rightarrow o\text{-}H_2 + H\cdot \quad (77)$$

$$H\cdot + HD \rightarrow H_2 + D\cdot \quad (78)$$

$$H\cdot + D_2 \rightarrow HD + D\cdot \quad (79)$$

$$D\cdot + p\text{-}D_2 \rightarrow o\text{-}D_2 + D\cdot \quad (80)$$

$$D\cdot + HD \rightarrow D_2 + H\cdot \quad (81)$$

$$D\cdot + H_2 \rightarrow HD + H\cdot \quad (82)$$

The work prior to 1955 has been reviewed by Steacie[1] and Trotman-Dickenson.[197] References to these reactions can also be found in most books on chemical kinetics. Kinetic results, determined for these reactions since 1955, are presented in Table XVIII.

Most of the experimental determinations have been made over a fairly wide temperature range (~298–800°K). Le Roy and coworkers have examined reactions 77,[198] 79,[199] 80,[200] and 82[201] by using a hot tungsten filament to produce the reacting atoms and an isothermal calorimetric probe to determine the atom concentrations. Their Arrhenius plots for reactions 77 and 82 were curved at the low temperature end which indicated a tunneling effect. Therefore, they included a tunneling factor, Γ, in

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(197) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworths, London, 1955.

(198) W. R. Schulz and D. J. Le Roy, *J. Chem. Phys.*, **42**, 3869 (1965).

(199) W. R. Schulz and D. J. Le Roy, *Can. J. Chem.*, **42**, 2480 (1964).

(200) D. J. Le Roy, B. A. Ridley, and K. A. Quickert, *Discuss. Faraday Soc.*, 44, 92 (1967).

(201) B. A. Ridley, W. R. Schulz, and D. J. LeRoy, *J. Chem. Phys.*, **44**, 3344 (1966).

their expression for the rate constants for these two reactions. When reactions 79 and 80 were studied over slightly higher temperature ranges, the curvature in the Arrhenius plots was not as noticeable.

More recently, Westenberg and deHaas[202] have studied reactions 79 and 82 by using a microwave discharge to produce the atoms and epr to detect the atoms. Their temperature range was about twice that covered by Le Roy and coworkers. Above 450°K, Westenberg and deHaas found that the Arrhenius plots were linear, while below this temperature, curvature in the plots for reactions 79 and 82 indicated a tunneling effect. Contrary to theory, they predicted that the tunneling factor for reaction 79 was larger than the tunneling factor for reaction 82. Also, the results of Westenberg and deHaas show less curvature in the Arrhenius plot for reaction 82 than do the results of Le Roy and coworkers.

During the period 1955–1972, there were a number of theoretical interpretations of reactions 77[203-205] and 78 to 82[203] where calculated results for the rate constants and the activation energies were compared with experimental results. Weston[206] has recently reviewed the exchange reactions and has compared theoretical and experimental findings. A comparison of the London–Eyring–Polanyi (LEP) calculation with experimental results gave poor agreement. The London–Eyring–Polanyi–Sato (LEPS), bond-energy-bond-order (BEBO), and Boys–Shavitt calculations were found to give reasonable agreement with the experimental rate constants but predicted activation energies higher than found experimentally. This good agreement only occurs if tunneling corrections are not considered in the theoretical calculations. If the tunneling indicated in the experimental results is considered, agreement is very poor.

More recently, Shavitt[207] has theoretically calculated an activation energy in the range 9.8 ± 0.2 kcal/mol^{-1} for hydrogen exchange reactions. This value agrees well with the value of 9.39 found by Westenberg and deHaas[202] for reaction 79 but is higher than the value usually reported for the exchange reactions.

C. Reaction with Halogen-Containing Compounds

Because of the interest in the use of HBr and HI as photolytic H atom sources, the $H\cdot + Br_2$ and $H\cdot + I_2$ reactions have been more extensively studied than the analogous chlorine and fluorine reactions. However, owing to the recent interest in fluorine-containing rocket propellants and the interest in the hydrogen halide chemical lasers, the $H\cdot + F_2$ and $H\cdot + Cl_2$ reactions are now being studied quantitatively. The early work on the reactions with HI, I_2, HBr, and Br_2 has been reviewed by Steacie,[1] and work on these systems prior to that publication will not be mentioned here.

1. Iodine and Hydrogen Iodide

The photolysis of HI at the appropriate wavelength (*e.g.*, 253.7 nm) yields an H atom containing excess translational energy and an I atom.

$$HI + h\nu\ (253.7\ \text{nm}) \rightarrow H\cdot^* + I^*\ (^2P_{1/2})\ \text{or}\ I\cdot\ (^2P_{3/2}) \qquad (83)$$

The "hot" H atoms produced by this reaction are quenched by large amounts of inert gas added to the system. By adding some other reactant, *e.g.*, C_2H_4, a relative rate constant is obtained by comparing the reactions: $H\cdot + HI$ and $H\cdot +$ reactant.[208] Therefore, most of the absolute rate constants which have been calculated by using the photolysis of HI as the source of H atoms are based on the rate constants for the $H\cdot + HI$ reaction as determined by Sullivan[209-211] in a thermal system.

Polanyi and coworkers[212,213] have found that the photolysis of HI yields an electronically excited I atom ($^2P_{1/2}$) which emits infrared radiation (~1.3 μ) as it goes to the ($^2P_{3/2}$) state. They have also found that a similar process occurs in the $H\cdot + HI$ reaction.

$$H\cdot + HI \rightarrow H_2 + I^*\ (^2P_{1/2}) + I\cdot\ (^2P_{3/2}) \qquad (84)$$

From their measurements, they have concluded that about 98% of the I was formed in the ground state ($^2P_{3/2}$) and about 2% in the excited state ($^2P_{1/2}$).

The values published for reactions 84[210,211,214] and 85[211] are given in Table XIX.

$$H\cdot + I_2 \rightarrow HI + I\cdot \qquad (85)$$

Several determinations have been made of the ratio k_{84}/k_{85} and these are given in Table XX.

2. Bromine and Hydrogen Bromide

Fass[215] has studied the photolysis of HBr–Br_2 mixtures and has postulated a mechanism which includes both "hot" and thermal H atoms

$$HBr \rightarrow H\cdot^* + Br\cdot(^2P_{3/2}) \qquad (86)$$

$$H\cdot^* + HBr \rightarrow H_2 + Br\cdot \qquad (87)$$

$$H\cdot^* + Br_2 \rightarrow HBr + Br\cdot \qquad (88)$$

$$H\cdot + HBr \rightarrow H_2 + Br\cdot \qquad (89)$$

$$H\cdot + Br_2 \rightarrow HBr + Br\cdot \qquad (90)$$

$$H\cdot^* + M \rightarrow H\cdot \qquad (91)$$

By studying the photolysis of HBr with and without the presence of moderating gas, Fass found that the ratio of reaction probabilities for the hot H atom reactions, k_{88}/k_{87}, was approximately the same as the ratio of preexponential factors for the thermalized H atom reactions, A_{90}/A_{89}. This is consistent with the collision theory interpretation of the Arrhenius preexponential factor as being directly proportional to the probability that a collision at an energy above the reaction threshold will result in a chemical reaction.

A summary of the published Arrhenius parameters for the absolute and relative rate constants of reactions 89 and 90 is given in Tables XIX and XX.

3. Chlorine and Hydrogen Chloride

The H_2–Cl_2 system has been recently reviewed by Cohen, *et al.*[216] The two basic reactions of this system have been found to be eq 92 and 93.

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(202) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, 47, 1393 (1967).

(203) I. Shavitt, *J. Chem. Phys.*, **31**, 1359 (1959).

(204) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **40**, 2033 (1964); **43**, 3259 (1965).

(205) R. E. Weston, Jr., *J. Chem. Phys.*, **31**, 892 (1959).

(206) R. E. Weston, Jr., *Science*, **158**, 332 (1967).

(207) I. Shavitt, *J. Chem. Phys.*, **49**, 4048 (1968).

(208) R. D. Penzhorn and B. deB. Darwent, *J. Phys. Chem.*, **72**, 1639 (1968).

(209) J. H. Sullivan, *J. Chem. Phys.*, **49**, 1155 (1968).

(210) J. H. Sullivan, *J. Chem. Phys.*, **36**, 1925 (1962).

(211) J. H. Sullivan, *J. Chem. Phys.*, **30**, 1292 (1959).

(212) P. Cadman, J. C. Polanyi, and I. W. M. Smith, *J. Chim. Phys. Physicochim. Biol.*, 111 (1967).

(213) P. Cadman and J. C. Polanyi, *J. Phys. Chem.*, **72**, 3715 (1968).

(214) S. W. Mayer and L. Schieler, *J. Phys. Chem.*, **72**, 236 (1968).

(215) R. A. Fass, *J. Phys. Chem.*, 74, 984 (1970).

(216) N. Cohen, T. A. Jacobs, G. Emanuel, and R. L. Wilkins, *Int. J. Chem. Kinet.*, 1, 551 (1969).

TABLE XIX. Reaction with Halogen-Containing Compounds

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + HI \rightarrow H_2 + I\cdot$		
667-800	0.7 ± 0.25	13.70	H_2/I_2 thermal reaction	210
667-738	1.17 ± 0.35	13.80	H_2/I_2 thermal reaction	211
298-2500	1.60	12.18 + 0.67 log T	(Estimate)	214
		$H\cdot + I_2 \rightarrow HI + I\cdot$		
667-738	0 ± 0.50	14.60	H_2/I_2 thermal reaction	211
		$H\cdot + HBr \rightarrow H_2 + Br\cdot$		
1105-1284	2.2	13.79	H_2/O_2 ignition	108
1100-2000	3.0	13.72	Flame ($H_2/O_2/N_2/-$)	*a*
298-2500	2.7	11.92 + 0.67 log T	(Estimate)	214
77	0.35		Photolysis (HBr)	*b*
		$H\cdot + Br_2 \rightarrow HBr + Br\cdot$		
1100-2000	3.0	14.65	Flame ($H_2/O_2/N_2/-$)	*a*
		$H\cdot + HCl \rightarrow H_2 + Cl\cdot$		
	4.50		Molecular beam	c
195-497	3.50	13.36	Discharge (microwave)	219
901-1071	5.20	13.86	(Estimate)	*d*
298-2500	4.80	11.40 + 0.77 log T	(Estimate)	214
195-373	2.9 ± 0.3	11.54 ± 0.18 + 0.5 log T	Discharge (rf)	72
295-425	0.9 ± 1.3		HCl/D_2 and DCl/H_2 photolysis	*e*
		$H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$		
	1.90		Molecular beam	c
294-565	1.8 ± 0.3	14.57 ± 0.06	Discharge (rf)	225, 226
	2.7	12.94 ± 0.68 log T	(Estimate)	*f*, 223
300-1100	2.2	15.11	(Estimate)	*g*
	2.7	12.64 + 0.68 log T	(Estimate)	*h*, 223
298	$k = 5.7 \times 10^{11}$		Discharge (microwave)	218
298	$k = 2 \pm 0.1 \times 10^{11}$		Discharge (microwave) D atom	218
273-358	<2.5		$H_2/Cl_2/O_2$ photolysis	197
		$H\cdot + HF \rightarrow H_2 + F\cdot$		
1000-3500	17.6	13.08	(Estimate)	*i*, *j*
	17.21	12.04 + 0.67 log T	(Estimate)	*j*, *k*
	17.6	12.98	(Estimate)	*j*, *l*
3700-6100	35.0	12.30	Shock tube	*m*
3800-5300	35.50	13.0	Shock tube	*n*
		$H\cdot + F_2 \rightarrow HF + F\cdot$		
288	$k = 1.8 \times 10^{12}$	$E_a = 1.5 \pm 0.3$	H_2–F_2 thermal reaction	222
294-565	2.4 ± 0.2	14.08 ± 0.01	Discharge (rf)	225, 226
	4.2	>13.48		o, 227
	1.5	12.82 + 0.68 log T	(Estimate)	*f*, 223
	4.0	12.72 + 0.5 log T		*p*, 227
	1.5	12.32 + 0.67 log T	(Estimate)	*q*
	2.4	13.97	(Estimate), $k_{300°K} = 1.66 \times 10^{12}$	*r*
300	$k = 2.5 \pm 2 \times 10^{12}$	$E_a = 2.6$	Discharge (microwave)	*s*
		$H\cdot + F\cdot + M \rightarrow HF + M$ (in cc^2 mol^{-2} sec^{-1})		
	$k = 2.5 \times 10^{18}T^{-1}$		M = Ar	*j*, *t*
1000-3500	$k = 3.6 \times 10^{19}T^{-1}$		M = any, $k_{1000°K} = 3.6 \times 10^{15 \pm 1}$	*i*, *j*
	$k = 7.2 \times 10^{18}T^{-1}$		M = any, estimate from $H\cdot + H\cdot + M = H_2 + M$	*j*, *u*
	$k = 4.6 \times 10^{18}T^{-1.5}$		M = H_2O, $k_{1000°K} = 1.4 \times 10^{17}$	*j*, *l*
	$k = 7.2 \times 10^{17}T^{-0.5}$		M = H_2, $k_{1000°K} = 2.3 \times 10^{16}$	*j*, *l*
	$k = 3.5 \times 10^{17}T^{-0.5}$		M = H, $k_{1000°K} = 1.5 \times 10^{16}$	*j*, *l*
	$k = 4.6 \times 10^{18}T^{-0.5}$		M = OH, $k_{1000°K} = 1.4 \times 10^{17}$	*j*, *l*
	$k = 7.2 \times 10^{18}T^{-1}$		M = any, based on $H\cdot + H\cdot + M = H_2 + M$	224
	$k = 1 \times 10^{19}T^{-0.5}$		M = HF	*v*, 223
	$k = 1 \times 10^{18}T^{-1}$		M = not specified	*n*, 223
	3.05	15.69	M = not specified	*x*, 223
	$k = 1 \times 10^{19}T^{-0.5}$		M = HF	*y*, *z*, 223
	$k = 7 \times 10^{17}T^{-0.5}$		M = H_2	*y*, 223
	$k = 3.5 \times 10^{17}T^{-0.5}$		M = H	*y*, 223

TABLE XIX (*Continued*)

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
	$k = 1 \times 10^{19}T^{-0.5}$		M = H_2O	*y*, 223
	$k = 1 \times 10^{19}T^{-0.5}$		M = OH	*y*, 223
		$H\cdot + Cl\cdot + M \rightarrow HCl + M$ (in cc^2 mol^{-2} sec^{-1})		
	$k = 1 \times 10^{19}T^{-0.5}$		M = not specified	*z*, 223
	$k = 8.8 \times 10^{17}T^{-1}$		M = not specified	*w*, 223
		$H\cdot + Cl_2O \rightarrow HCl + ClO\cdot$ *or* $HOCl + Cl\cdot$		
298	$k = 1.3 \pm 0.2 \times 10^{13}$		Discharge (microwave)	229
300	$k \sim 2 \times 10^{13}$		Based on HCl ir chemiluminesence compared to that from $H\cdot + Cl_2$	230, 231
		$H\cdot + ClO\cdot \rightarrow Cl\cdot + OH\cdot$		
	1.9	12.88 + 0.68 log T	(Estimate)	*f*, *h*, 223
		$H\cdot + ClO\cdot \rightarrow O\cdot + HCl$		
	1.3	12.77 + 0.67 log T	(Estimate)	*f*, *h*, 223
		$H\cdot + ClF \rightarrow F\cdot + HCl$		
	1.9	12.75 + 0.68 log T	(Estimate)	*f*, *h*, 223
		$H\cdot + ClF \rightarrow HF + Cl\cdot$		
	3.2	12.26 + 0.68 log T	(Estimate)	*f*, *h*, 223
		$H\cdot + HOCl \rightarrow ClO\cdot + H_2$		
1000–3500	0	12.78 ± 2.0	(Estimate), $k_{1000°\mathrm{K}} = 6 \times {}^{12 \pm 2}$	*i*, *j*

[a] M. J. Day, D. V. Stamp, K. Thompson, and G. Dixon-Lewis, *Symp. (Int.) Combust. Proc., 13th, 1970*, 705 (1971). [b] W. E. Falconer and W. A. Sunder, *Can. J. Chem.*, **46**, 3789 (1968). [c] W. Seidel, H. Martin, H. Rehling, and F. G. Mietzner, *Ber. Bunsenges. Phys. Chem.*, **68**, 504 (1964). [d] E. S. Fishburne, *J. Chem. Phys.*, **45**, 4053 (1966). [e] A. E. deVries and F. S. Klein, *ibid.*, 41, 3428 (1964). [f] S. W. Mayer and L. Schieler, Aerospace Corp. Report, TDR-669-(9210-02)-2 (SSD-TR-66-78), 1966, as quoted in ref 223. [g] J. Lin and J. Light, *J. Chem. Phys.*, **45**, 2545 (1966). [h] L. Schieler and S. W. Mayer, Chemical Propulsion Information Agency Publication 108, 1966, p 131, as quoted in ref 223. [i] D. E. Jensen and S. C. Kurzius, Aero Chem Research Laboratory Report TP-149, 1967, as quoted in footnote *j*. [j] D. Garvin, National Bureau of Standards Report 9884, U. S. Government Printing Office, Washington, D. C., 1968. [k] S. W. Mayer and L. Schieler, Chemical Propulsion Information Agency Publication, 146(1), 121 1967, *J. Phys. Chem.*, **72**. 236 (1968), as quoted in footnote *j*. [l] R. Tunder, S. Mayer, E. Cook, and L. Schieler, Aerospace Corporation, Thermochemistry Research Dept., Aerospace Corp. Report, TR-1001 (9210-02)-1, 1967, as quoted in footnote *j*. [m] J. A. Blauer, *J. Phys. Chem.*, **72**, 79 (1968). [n] T. A. Jacobs, R. R. Giedt, and N. Cohen, *J. Chem. Phys.*, **43**, 3688 (1965). [o] S. S. Penner, *J. Franklin Inst.*, **249**, 441 (1950), as quoted in ref 227. [p] R. Dunlap and R. Hermsen, United Aircraft Corp. Report UTC-2032-FR, 1963, as quoted in ref 227. [q] S. W. Mayer, L. Schieler, and H. S. Johnson, *Symp. (Int.) Combust. Proc., 11th, 1966*, 837 (1967). [r] R. Wilkins, Aerospace Corp. Report TR-0059 (6753-20)-1, 1971. [s] S. W. Rabideau, H. G. Hecht, and W. B. Lewis, *J. Magn. Resonance*, **6**, 384 (1972). [t] T. A. Jacobs, R. R. Giedt, and N. Cohen, AIAA 2nd Propulsion Joint Specialist Conference Paper 66-637, June 1966, as quoted in footnote *j*. [u] S. S. Cherry, P. I. Gold, and L. J. VanNice, TRW System Report 08832-6001-T0000, 1967 as quoted in footnote *j*. [v] P. I. Gold, T. R. W. Systems Report 5435-6005-TU000, 1965, as quoted in ref 223. [w] C. T. Crowe, R. Dunlap, R. W. Hermsen, M. Rogers, P. G. Willoughby, H. Woolff, and R. Woolfolk, United Technical Center Report U.T.C-2128-FR, 1966, as quoted in ref 223. [x] W. G. Burwell, V. J. Sarli and T. F. Zupnik, 3rd Conference on Performance of High Temperature Systems, 1964, as quoted in ref 223. [y] S. W. Mayer, E. A. Cook, and L. Schieler, Aerospace Corp. Report TDR-269(4210-10)-6 (SSD-TDR-64-139), 1964, as quoted in ref 223. [z] E. A. Cook and L. Schieler, Aerospace Corp. Report TDR-269(9210-02)-1 (SSD-TDR-64-183), 1964, as quoted in ref 223.

TABLE XX. Relative Rates of Reaction with Halogen-Containing Compounds

Temp, °K	k_1/k_2	$E_1 - E_2$, kcal mol^{-1}	Method	Ref
	(1) $H\cdot + HI \rightarrow H_2 + I\cdot$; (2) $H\cdot + I_2 \rightarrow HI + I\cdot$			
667	0.070 ± 0.02		H_2/I_2 thermal reaction	210
800	0.082 ± 0.012		H_2/I_2 thermal reaction	210
973	0.06			*a*
303–533	0.20	0.64	Photolysis ($HI/I_2/CO_2$)	208
323–473	0.083 ± 0.007	0 ± 0.35	Photolysis (HI)	*b*
800	0.073[c]		D_2/I_2 thermal reaction	*d*
	(1) $H\cdot + HBr \rightarrow HBr + Br\cdot$; (2) $H\cdot + Br_2 \rightarrow H_2 + Br\cdot$			
573–800	0.15	0.8 ± 0.3	H_2/Br_2 thermal reaction	215
1300–1700	0.099 ± 0.007		H_2/Br_2 thermal reaction	*e*
	(1) $H\cdot + HCl \rightarrow H_2 + Cl\cdot$; (2) $H\cdot + Cl_2 \rightarrow HCl + Cl\cdot$			
273–335	0.147 ± 0.033	1.54 ± 0.13	Photolysis (H_2/Cl_2)	217
	≤0.05		Photolysis (H_2/Cl_2)	*f*
196	$1.6 \pm 0.05 \times 10^{-3}$		γ radiolysis (HCl/SF_6)	*g*
274	$7.5 \pm 0.5 \times 10^{-3}$		γ radiolysis (HCl/SF_6)	*g*
293	$8.7 \pm 0.5 \times 10^{-3}$		γ radiolysis (HCl/SF_6)	*g*

[a] O. Horie, Y. Ishii, and A. Amano, *J. Phys. Chem.*, **68**, 1264 (1964). [b] J. L. Holmes and P. Rodgers, *Trans. Faraday Soc.*, **64**, 2348 (1968). [c] D atom reactions. [d] J. H. Sullivan, *J. Chem. Phys.*, **39**, 3001 (1963). [e] D. Britton and R. M. Cole, *J. Phys. Chem.*, **65**, 1302 (1961). [f] J. Bigeleisen, F. S. Klein, R. E. Weston, and M. Wolfsberg, *J. Chem. Phys.*, **30**, 1340 (1959). [g] R. S. Davidow, R. A. Lee, and D. A. Armstrong, *ibid.*, **45**, 3364 (1966).

$$H\cdot + HCl \rightarrow H_2 + Cl\cdot \qquad (92)$$

$$H\cdot + Cl_2 \rightarrow HCl + Cl\cdot \qquad (93)$$

Klein and Wolfsberg[217] obtained a ratio of k_{92}/k_{93} which they based upon a competitive rate study.

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(217) F. S. Klein and M. Wolfsberg, *J. Chem. Phys.*. **34**, 1494 (1961).

Stedman, *et al.*,[218] using a microwave discharge to produce H atoms, gave a value for the rate constant of reaction 93 as 5.75×10^{11} cc mol^{-1} sec^{-1}. They suggested that possible reaction of Cl atoms with H_2^* which formed in the microwave discharge caused their value to be slightly higher than that of Klein and Wolfsberg.

The H· + HCl reaction has been studied by Clyne and Stedman[72] in a fast-flow system over a temperature range 195–373°K. Two models were considered: (1) a model having a simple collison theory of temperature dependence with a steric factor of ~0.025 and (2) a model having a transition complex with a complicated temperature dependence. Westenberg and deHaas[219] suggested that discrepancies between the experimental rate constant and that determined from the equilibrium constant for the $H\cdot + HCl \rightarrow Cl\cdot + H_2$ reaction were due to the formation of HCl* in the reverse reaction, whereas H_2^* did not form in the forward reaction.

The results published since 1954 for reactions 92 and 93 are presented in Table XIX.

4. *Fluorine and Hydrogen Fluoride*

The reactions with fluorine and hydrogen fluoride may be represented as

$$H\cdot + F_2 \rightarrow HF + F\cdot \qquad (94)$$

$$H\cdot + HF \rightarrow H_2 + F\cdot \qquad (95)$$

Levy and Copeland[220,221] were among the first to study reaction 94 in a thermal system. The reaction was found to involve the chain step

$$F\cdot + H_2 \rightarrow HF + H\cdot \qquad (96)$$

The pyrolysis and photolysis reactions of H_2–F_2 mixtures were found to be inhibited to a limiting value by oxygen.[222] The inhibition was considered to be due to such reactions as

$$H\cdot + O_2 + M \rightarrow HO_2\cdot + M \qquad (97)$$

$$F\cdot + O_2 + M \rightarrow FO_2\cdot + M \qquad (98)$$

Bahn, *et al.*,[223,224] have made estimates of the rate constants for the various reactions of shock heated H_2–F_2–O_2 mixtures. They found that the rate constant for the reaction

$$H\cdot + F\cdot + M \rightarrow HF + M \qquad (99)$$

was comparable to, if not the same as, the rate constant for the termolecular recombination of H atoms. From the analysis of third body efficiencies, they obtained the following pattern

$$\begin{array}{l} Ar : F_2 : HF : N_2 : F\cdot : H_2O : H_2 : O_2 : H\cdot \quad O : OH\cdot = \\ 1 : 1 : 2 : 2.8 : 4 : 4 : 8 : 13 : 20 : 40 : 40 \end{array}$$

The most recent determination for reaction 94 is that of Dodonov and coworkers[225,226] who used a fast-flow system connected to a mass spectrometer. Recently Cohen[227] has reviewed the H_2–F_2 system.

The results for these reactions are presented in Table XIX.

5. *Interhalogens and Other Simple Halides*

Until recently, very little work has been done on the interhalogens. Bahn[228] has studied the following H· + ClF reactions

$$H\cdot + ClF \rightarrow HF + Cl\cdot \qquad (100)$$

$$H\cdot + ClF \rightarrow HCl + F\cdot \qquad (101)$$

He obtained the rate constants $k = 1.8 \times 10^{12}T^{0.68} \exp(-3200/RT)$ cc mol^{-1} sec^{-1} and $k = 5.6 \times 10^{12}T^{0.68} \exp(-1900/RT)$ cc mol^{-1} sec^{-1} for reactions 100 and 101, respectively.

Freeman and Phillips[229] have used a mass spectrometer to study the reaction

$$H\cdot + Cl_2O \rightarrow HOCl + Cl\cdot \qquad (102)$$

$$\rightarrow HCl + ClO\cdot \qquad (103)$$

They were unable to prove which step (eq 102 or 103) was the initial step of the reaction. Both reactions have similar values of ΔH and would eventually lead to similar end products. They obtained a rate constant based on the consumption of Cl_2O in the presence of excess H atoms. Setser and coworkers[230,231] approximated the rate constant for reaction of $H\cdot + Cl_2O$ by comparing the HCl infrared emission with the amount of HCl* produced in the $H\cdot + Cl_2$ reaction, the rate constant of which was known.

By comparing the HCl* emission from reaction 103 with the HOCl* emission from reaction 102, they approximated a value of $k_{103} = 4 \times 10^{12}$ cc mol^{-1} sec^{-1}, which is about one-fifth the rate constant given by Freeman and Phillips for the overall rate constant.

A summary of the published Arrhenius parameters for the interhalogen and oxygen-containing halogen compounds is given in Table XIX.

6. *Infrared Chemiluminescence from H· + X_2 and H· + HX Reactions*

Polanyi and coworkers have investigated the infrared chemiluminescence from reactions of H atoms with Cl_2,[232] HCl,[233] Br_2,[234] HBr,[234] I_2,[212,213] and HI.[212,213] Polanyi and coworkers[235] were one of the first research groups to predict that the species formed in this reaction would be vibrationally excited in the ground electronic state and that a large percentage of the energy of the reaction would go into the vibrational excitation of one of the products.

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(218) D. H. Stedman, D. Steffenson, and H. Niki, *Chem. Phys. Lett.*, 7, 173 (1970).

(219) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **48**, 4405 (1968).

(220) J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **67**, 2156 (1963).

(221) J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **69**, 408 (1965).

(222) J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **72**, 3168 (1968).

(223) G. S. Bahn, *Pyrodynamics*, 4, 371 (1966).

(224) G. S. Bahn, S. S. Cherry, P. I. Gold, R. C. Mitchell, and J. Q. Weber, *AIAA J.*, 7, 181 (1969).

(225) A. F. Dodonov, G. K. Lavrovskaya, I. I. Morozov, R. G. Albright, V. L. Tal'roze, and A. K. Lyubimova, *Kinet. Katal.*, 11, 821 (1970); *Kinet. Catal. (USSR)*, 11, 677 (1970).

(226) R. G. Albright, A. F. Dodonov, G. K. Lavrovskaya, I. I. Morozov, and V. L. Tal'roze, *J. Chem. Phys.*, **50**, 3632 (1969).

(227) N. Cohen, Aerospace Report No. TR-0172 (2779)-2, Sept 1971.

(228) G. S. Bahn, *Pyrodynamics*, **6**, 297 (1969).

(229) C. G. Freeman and L. F. Phillips, *J. Phys. Chem.*, **72**, 3031 (1968).

(230) M. J. Perona, D. W. Setser, and R. J. Johnson, *J. Chem. Phys.*, **52**, 6384 (1970).

(231) M. J. Perona, D. W. Setser, and R. J. Johnson, *J. Phys. Chem.*, 73, 2091 (1969).

(232) P. D. Pacey and J. C. Polanyi, *Appl. Optics*, **10**, 1725 (1971), and references to earlier work therein.

(233) J. K. Cashion and J. C. Polanyi, *Proc. Roy. Soc., Ser. A*, **258**, 529 (1960).

(234) J. R. Airey, P. D. Pacey, and J. C. Polanyi, *Symp. (Int.) Combust. Proc., 11th, 1966*, 85 (1967).

(235) K. G. Anlauf, P. J. Kuntz, D. H. Maylotte, P. D. Pacey, and J. C. Polanyi, *Discuss. Faraday Soc.*, 44, 183 (1967).

Other workers have made similar studies on the reactions of H atoms with F_2,[236] SCl_2,[230,237] S_2Cl_2,[230,237] $SOCl_2$,[230] SO_2Cl_2,[230] and OF_2.[238,239]

The theoretical studies of Polanyi and coworkers have been used as a basis for the construction of chemical lasers. The reactions $H\cdot + X_2$ or $F\cdot + H_2$ may be used as chemical laser systems when the vibrationally excited products (*i.e.*, HF*) have sufficient population inversion in their vibrational levels. A comprehensive bibliography has recently been published.[240]

D. Reaction with Sulfur-Containing Compounds

1. Hydrogen Sulfide

The reaction of H atoms with H_2S has been extensively studied because of the use of H_2S as a photolytic source of H atoms.

The products of the photolytic decomposition of H_2S are determined by the intensity and wavelength of the irradiating light,[241] as shown in the following reactions.

$$H_2S + h\nu\ (\lambda > 200\text{ nm}) \rightarrow H\cdot(^2S) + HS\cdot(^2\Pi) \quad (104)$$

$$H_2S + h\nu\ (\lambda < 200\text{ nm}) \rightarrow H_2 + S \quad (105)$$

$$H_2S + h\nu\ (\lambda < 163\text{ nm}) \rightarrow 2H\cdot + S \quad (106)$$

The H atoms, produced in this way, are in the ground state. However, they have excess translational energy. The H atoms in reaction 104 have about 23 kcal mol^{-1} excess translational energy, and those in reaction 106 have about 42 kcal mol^{-1} excess translational energy. These "hot" atoms are thermalized by large quantities of inert gas (*e.g.*, CO_2[36]). Darwent, *et al.*,[36] have concluded that when these "hot" atoms are insufficiently thermalized, they react with the reactant, thus causing an error in the rate measured for the reaction $H\cdot$ + reactant. This was believed to have been the case in the reactions studied by Darwent and Roberts.[34]

Several studies[241-246,33] have been made of the reaction of H atoms with H_2S. In a typical fast-flow system, the following basic mechanism has been suggested.[247]

$$H\cdot + H_2S \rightarrow H_2 + HS\cdot \quad (107)$$

$$H\cdot + HS\cdot \rightarrow S + H_2 \quad (108)$$

$$S(^3P) + S(^3P) + M \rightarrow S_2^*(B^3\Sigma_u^-) + M \quad (109)$$

$$S \rightarrow \text{wall deposit} \quad (110)$$

Fair and Thrust[247] have observed the $S_2(B^3\Sigma_u^- - X^3\Sigma_g^-)$ emission in the above system. Cupitt and Glass[242] found that, when H_2S was in excess, a sulfur deposit formed on the walls of the reaction vessel. They found that when H atoms were in excess this did not occur. Mihelcic and Schindler[243] have suggested that the following reactions should also be included in the mechanism.

$$2HS\cdot \rightarrow H_2S + S \quad (111)$$

$$S + HS\cdot \rightarrow S_2 + H\cdot \quad (112)$$

Table XXI shows that the values obtained by using several different methods are in fair agreement with an average value of $k_{107} = 6 \times 10^{11}$ cc mol^{-1} sec^{-1} at 298°K.

Cupitt and Glass[242] have estimated a value of $k = (3.6 \pm 1.8) \times 10^{13}$ cc mol^{-1} sec^{-1} for reaction 108 at 298°K. Mayer and Schieler[214] have calculated an Arrhenius expression for the same reaction by using the Johnson–Parr method. They obtained a value of k at 298°K which was several magnitudes lower than the value estimated by Cupitt and Glass. Darwent and Roberts[248] have suggested that reaction 108 is fast. Thus, it is a significant reaction only at low pressures and high light intensities.

Fair and Thrush[245] added O_2 to the $H\cdot + H_2S$ reaction in a fast-flow system at room temperature and observed a pale blue afterglow which was attributed to the SO_2 (240.0–480.0 nm) continuum. They also detected SO bands ($B^3\Sigma^- - X^3\Sigma^-$, 244.2–282.7 nm), which were attributed to the reaction

$$S + O + M \rightarrow SO^*\ (B^3\Sigma^-) + M \quad (113)$$

Cupitt and Glass[242] suggested that the basic mechanism was altered by such reactions as

$$S + O_2 \rightarrow SO + O \quad (114)$$

$$O + HS\cdot \rightarrow H\cdot + SO \quad (115)$$

2. Sulfur Dioxide

Except for the work of Fair and Thrush,[249] this reaction has only been studied at high temperatures (*i.e.*, > 700°K). The results of these studies are in reasonable agreement. The mechanism

$$H\cdot + SO_2 + M \rightarrow HSO_2\cdot + M \quad (116)$$

$$H\cdot + HSO_2\cdot \rightarrow H_2 + SO_2 \quad (117)$$

indicates that under high temperature conditions, the SO_2 acts as a catalyst for radical recombination. Fenimore and Jones[250] considered reaction 116 as the rate-controlling step. Fair and Thrush[249] studied the reaction in a typical fast-flow system at 298°K. At this temperature, they found an efficient heterogeneous reduction of SO_2 in the presence of H atoms. However, they found no evidence of reaction 116 at higher temperatures. They suggested that the reduction mechanism involved reactions which had the overall stoichiometry as follows.

$$2H\cdot + SO_2 \rightarrow H_2O + SO \quad (118)$$

$$2H\cdot + SO \rightarrow H_2O + S \quad (119)$$

The results for reactions 116 and 117 are presented in Table XXI.

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(236) N. Jonathan, C. M. Melliar-Smith, and D. H. Slater, *J. Chem. Phys.*, **53**, 4396 (1970).

(237) R. L. Johnson, M. J. Perona, and D. W. Setser, *J. Chem. Phys.*, **52**, 6372 (1970).

(238) M. J. Perona, *J. Chem. Phys.*, **54**, 4024 (1971).

(239) D. H. Levy, *J. Chem. Phys.*, **56**, 1415 (1972).

(240) A. N. Chester and L. D. Hess, *IEEE J. Quantum Electron.*, **8**, 1 (1972). The bibliography of this paper gives reference to all work on HF or DF chemical lasers prior to Aug 1970.

(241) M. J. Kurylo, N. C. Peterson, and W. Braun, *J. Chem. Phys.*, **54**, 943 (1971).

(242) L. T. Cupitt and G. P. Glass, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970, No. PHYS-48.

(243) D. Mihelcic and R. N. Schindler, *Ber. Bunsenges. Phys. Chem.*, 74, 1280 (1970).

(244) D. Perner and Th. Franken, *Ber. Bunsenges. Phys. Chem.*, **73**, 897 (1969).

(245) R. W. Fair and B. A. Thrush, *Trans. Faraday Soc.*, **65**, 1557 (1969).

(246) R. L. Wadlinger and B. deB. Darwent, *J. Phys. Chem.*, 71, 2057 (1967).

(247) R. W. Fair and B. A. Thrush, *Trans. Faraday Soc.*, **65**, 1208 (1969).

(248) B. de B. Darwent and R. Roberts, *Proc. Roy. Soc., Ser. A*, **216**, 344 (1953).

(249) R. W. Fair and B. A. Thrush, *Trans. Faraday Soc.*, **65**, 1550 (1969).

(250) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **69**, 3593 (1965).

TABLE XXI. Reaction with Sulfur-Containing Compounds

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + H_2S \rightarrow H_2 + HS\cdot$		
190–464	1.79 ± 0.60	12.89	Flash photolysis	241
298	$k = 7.7 \pm 1.5 \times 10^{11}$		Pulse radiolysis	244
298	$k = 9 \times 10^{11}$		Discharge (rf)	242
243–368	1.68 ± 0.05	13.03 ± 0.78	Discharge (microwave)	243
300–550	5.0[a]	14.65	Photolysis (D_2S)	34
298	$k = 2.3 \times 10^{11}$		Discharge (microwave)	*b*
298	$k = 9.2 \times 10^{11}$		Discharge (microwave)	c
		$H\cdot + HS\cdot \rightarrow H_2 + S$		
298	$k = 3.6 \pm 1.8 \times 10^{13}$		Discharge (rf)	242
298–2500	2.8	11.66 ± 0.67 log T	(Estimate), $k_{298°K} = 2.0 \times 10^{11}$	214
		$H\cdot + SO + M \rightarrow HSO + M$ (in cc^2 mol^{-2} sec^{-1})		
300	$k > 10^{17}$		(Estimate)	245
		$H\cdot + SO_2 + M \rightarrow HSO_2\cdot + M$ (in cc^2 mol^{-2} sec^{-1})		
298	$k < 5 \times 10^{14}$		M = Ar, discharge (rf)	249
1480–1660	$k = 7.2 \times 10^{16}$		M = total press., flame ($H_2/O_2/N_2/-$)	250
<2000	$k = 1 \times 10^{16}$		M = H_2O, flame ($H_2/O_2/-$)	*d*
784	$k = 1.4 \times 10^{16}$		M = H_2, H_2/O_2 ignition	e
		$H\cdot + HSO_2\cdot \rightarrow H_2 + SO_2$		
2000	$k = 3 \times 10^{12}$		Flame ($H_2/O_2/N_2/SO_2$)	*f*
2110	$k = 1.56 \pm 0.48 \times 10^{12}$		Flame ($O_2/N_2/C_3H_8/SO_2$)	*g*
		$H\cdot + SF_6 \rightarrow SF_5\cdot + HF$		
1030–1670	30 ± 5	15.30	Flame ($H_2/O_2/N_2/SF_6$)	252
(1) $H\cdot + H_2S$ (2) $H\cdot + HS\cdot$		$k_1/k_2 = 40 \pm 20$	Discharge (microwave)	242

[a] D atom reaction. [b] H. Rommel and H. I. Schiff, *Int. J. Chem. Kinet.*, 4, 547 (1972). [c] L. T. Cupitt, *Diss. Abstr. B*, 33, 1477 (1972); Ph.D. Thesis, Rice University, 1972. [d] A. S. Kallend, *Trans. Faraday Soc.*, **63**, 2442 (1967). [e] P. Webster and A. D.Walsh, *Symp. (Int.) Combust. Proc., 10th, 1964*, 463 (1965). [f] C. J. Halstead and D. R. Jenkins, *Symp. (Int.) Combust. Proc., 12th, 1968*, 979 (1969). [g] R. A. Durie, G. M. Johnson, and M. Y. Smith, *Combust. Flame*, 17, 197 (1971).

3. *Sulfur Hexafluoride*

SF_6 has not been found to react with H atoms at low temperature. However, it appears to have an inhibiting effect on high-temperature flame reactions. Miller, *et al.*,[251] have found that the addition of small quantities of SF_6 decreased the burning velocity of fuel-rich hydrogen flames by about 30%. Fenimore and Jones[252] have postulated the following reaction as the primary step.

$$H\cdot + SF_6 \rightarrow HF + SF_5\cdot \qquad (120)$$

They estimated the rate constant of the reaction by sampling the concentration of H atoms in various sections of the flame. Since the SF_6 inhibited the flame, they concluded that the SF_6-H atom reaction did not regenerate H atoms in subsequent steps in the mechanism. This conclusion was based upon the comparison of H atom concentrations in the SF_6 flame with H atom concentrations in O_2 or N_2O flames, where the H atoms were regenerated in subsequent steps (*e.g.*, reactions 121 and 122).

$$H\cdot + N_2O \rightarrow N_2 + OH\cdot \qquad (121)$$

$$OH\cdot + H_2 \rightarrow H_2O + H\cdot \qquad (122)$$

Table XXI presents the rate constants obtained from reactions of H atoms with sulfur-containing compounds. A review of the kinetics of combustion of gas-phase sulfur-containing compounds, which includes some H atom reactions, has recently been published.[253]

E. Reaction with Nitrogen-Containing Compounds

1. *Nitrogen*

Varney[254] has shown that nitrogen does not react with ground-state H atoms.

Tanaka and McNesby[255] have found that nitrogen reacts with H atoms in the excited (^2P) state when the H atoms are produced by the irradiation of H(^2S) atoms with Lyman α (121.6 nm) light. Since ammonia and a small amount of hydrazine were found as products of this reaction, they proposed that the mechanism involved either an energy transfer as in reactions 123 and 124 or an atom transfer as in reaction 125. They suggested that the NH_3 resulted from either a reaction of NH with H_2 or H· or from some type of reaction of N with H atoms. The energy-transfer mechanism was suggested from earlier work on the krypton photosensitized reaction of mixtures of N_2 and H_2,[256] while the atom-transfer reaction was suggested from spectroscopic evidence for the NH($^3\Pi$-$^3\Sigma$) emission band.[257] Later, Koyano and Tanaka[258] re-

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(251) D. R. Miller, R. L. Evers, and G. B. Skinner, *Combust. Flame*, 7, 137 (1963).

(252) C. P. Fenimore and G. W. Jones, *Combust. Flame*, **8**, 231 (1964).

(253) C. F. Cullis and M. F. R. Mulcahy, *Combust. Flame*, **18**, 225 (1972).

(254) R. N. Varney, *J. Chem. Phys.*, **23**, 866 (1955).

(255) I. Tanaka and J. R. McNesby, *J. Chem. Phys.*, **36**, 3170 (1962).

(256) W. E. Groth, *J. Chem. Phys.*, **23**, 729 (1955).

(257) H. P. Broida and I. Tanaka, as quoted in ref 255.

(258) I. Koyano and I. Tanaka, *J. Chem. Phys.*, **40**, 895 (1964).

peated the work of Tanaka and McNesby but were unable to distinguish which of the reactions, (123) and (124) or (125), was the primary reaction. They presented no kinetic measurements for these reactions.

$$H\cdot(^2P) + N_2(^1\Sigma_g^+) \rightarrow H\cdot(^2S) + N_2^* \qquad (123)$$

$$N_2^* \rightarrow 2N(^4S) \qquad (124)$$

$$H\cdot(^2P) + N_2(^1\Sigma_g^+) \rightarrow NH(^3\Pi_i) + N(^4S) \qquad (125)$$

In the early 1930's a few studies were made of the H· + N + M reaction. In all cases, a small amount of NH_3 was found as the end product. Some hydrazine was also detected. A recent kinetic determination by Mavroyannis and Winkler[259] gave an upper limit for the rate constant for the reaction

$$H\cdot + N + M \rightarrow NH + M \qquad (126)$$

as $k = 4.8 \times 10^{14}$ cc^2 mol^{-2} sec^{-1} at room temperature.

2. *Nitric Oxide*

The reaction of H atoms with NO as in the reaction

$$H\cdot + NO + M \rightarrow HNO + M \qquad (127)$$

has been extensively studied by Thrush and coworkers,[68,260,261] in a fast flow system. They have suggested that the reaction is a third-order process which yields both ground-state and electronically excited HNO which leads to the following mechanism for the reaction

$$H\cdot + NO + M \rightarrow HNO^*(^1A'') + M \qquad (128a)$$

$$H\cdot + NO + M \rightarrow HNO(^1A') + M \qquad (128b)$$

$$HNO^*(^1A'') \rightarrow HNO(^1A') + h\nu \text{ (red continuum)} \qquad (129)$$

$$HNO^*(^1A'') + M \rightarrow HNO(^1A') + M \qquad (130)$$

$$H\cdot + HNO \rightarrow H_2 + NO \qquad (131)$$

They found that both the light intensity and the rate constant of the reaction were dependent upon the nature of the third body.

Strausz and Gunning[262] have studied the H· + NO reaction in a static system by using either mercury photosensitization of H_2 or photolysis of HCHO as the H atom source. They found N_2 and N_2O as the main products which they explained by the following reactions.

$$H\cdot + NO + M \rightarrow HNO + M \qquad (127)$$

$$2HNO + M \rightarrow N_2O + H_2O + M \qquad (132)$$

$$HNO + 2NO \rightarrow N_2 + HNO_3 \qquad (133)$$

Clyne and Thrush also found N_2O, but to a much lesser extent than was found by Strausz and Gunning. The results of Strausz and Gunning were later confirmed by Kohout and Lampe.[263]

A summary of Arrhenius parameters for reactions 127 and 131 is given in Table XXII.

3. *Nitrogen Dioxide*

On the basis of the observations and kinetic determinations of a number of workers,[61,70,260] the following reaction scheme has been proposed for the reaction of H atoms with NO_2 in the absence of H_2.

$$H\cdot + NO_2 \rightarrow NO + OH\cdot \qquad (134)$$

$$H\cdot + NO + M \rightarrow HNO^* + M \qquad (127)$$

$$HNO^* \rightarrow HNO + h\nu \text{ (red continuum)} \qquad (129)$$

$$2OH\cdot \rightarrow H_2O + O \qquad (135)$$

$$O + OH\cdot \rightarrow H\cdot + O_2 \qquad (136)$$

The overall stoichiometry for the reaction has been established by Westenberg and deHass[61] as

$$2H\cdot + 3NO_2 \rightarrow 3NO + H_2O + O_2$$

In all studies, the H + NO_2 reaction was performed at temperatures of 300°K or higher. Even above room temperature small amounts of N_2O_4 are mixed with NO_2 because of the equilibrium

$$N_2O_4 \rightarrow 2NO_2 \qquad (137)$$

In all cases the presence of N_2O_4 has been considered. Sherwood[264] has recently studied the reaction of H atoms with solid N_2O_4 (77°K). From the products formed, he suggested that the primary step was

$$N_2O_4 + 2H\cdot \rightarrow O_2N\text{-}N(OH)_2 \rightarrow O_2N\text{-}NO + H_2O \qquad (138)$$

4. *Nitrosyl Chloride*

Clyne and Stedman[72] have suggested reactions 139, 127, and 129 as the mechanism for the reaction of H atoms with ONCl. They studied the kinetics of the reaction by means of the HNO* emission formed in reaction 127. Phillips and coworkers[265] have studied reaction 139 by using a mass spectrometer. Their results are in good agreement with those of Clyne and Stedman[72] and Niki, *et al.*[266] They do suggest, however, that the walls of the reaction vessel must be freshly poisoned to inhibit the H or Cl atom wall-catalyzed recombinations.

$$H\cdot + ONCl \rightarrow NO + HCl \qquad (139)$$

$$H\cdot + NO + M \rightarrow HNO^* + M \qquad (127)$$

$$HNO^* \rightarrow HNO + h\nu \text{ (red continuum)} \qquad (129)$$

5. *Nitrous Oxide*

The following reaction has been proposed as the primary step in the reaction with N_2O.

$$H\cdot + N_2O \rightarrow OH\cdot + N_2 \qquad (140)$$

Three determinations[267-269] of the rate constant for reaction 140 have been made at temperatures greater than 1200°K and predict an activation energy of about 16 kcal mol^{-1}. The lower temperature flame study[270] (900°K) predicts an activation energy of about 13 kcal mol^{-1}, which compares well with the high-temperature determinations. The poor agreement shown between the

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(259) C. Mavroyannis snd C. A. Winkler, *Can. J. Chem.*, **40**, 240 (1962).

(260) M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, **57**, 1305 (1961).

(261) D. B. Hartley and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **297**, 520 (1967).

(262) O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, **60**, 347 (1964).

(263) F. C. Kohout and F. W. Lampe, *J. Amer. Chem. Soc.*, **87**, 5795 (1965); *J. Chem. Phys.*, **46**, 4075 (1967).

(264) P. M. A. Sherwood, *J. Chem. Soc. A*, 2478 (1971).

(265) M. R. Dunn, M. M. Sutton, C. G. Freeman, M. J. McEwan, and L. F. Phillips, *J. Phys. Chem.*, **75**, 722 (1971).

(266) H. Niki, D. H. Stedman, and D. Steffenson, Abstracts 160th National Meeting of American Chemical Society, Chicago, Ill., Sept 1970, No. PHYS.-116.

(267) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **63**, 1154 (1959).

(268) G. Dixon-Lewis, M. M. Sutton, and A. Williams, *Symp. (Int.) Combust. Proc., 10th, 1964*, 495 (1965).

(269) H. Henrici and S. H. Bauer, *J. Chem. Phys.*, **50**, 1333 (1969).

(270) G. Dixon-Lewis, M. M. Sutton, and A. Williams, *J. Chem. Soc.*, 5724 (1965).

TABLE XXII. Reactions with Nitrogen-Containing Compounds

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		H· + N· + M → NH + M (in cc^2 mol^{-2} sec^{-1})		
298	$k \leq (4.87 \pm 0.8) \times 10^{14}$		Discharge (Wood's)	259
		H· + NO + M → HNO + M (in cc^2 mol^{-2} sec^{-1})		
231–704	-0.6 ± 0.2	$14.0 + (0.9 \pm 0.3) \log T$	Discharge (rf), M = H_2	68, 260
293	$k = (1.48 \pm 0.15) \times 10^{16}$		Discharge (rf), M = H_2	68, 260
293	$k = (0.87 \pm 0.15) \times 10^{16}$		Discharge (rf), M = Ar	68, 260
293	$k = (0.72 \pm 0.10) \times 10^{16}$		Discharge (rf), M = Ne	68, 260
293	$k = (0.66 \pm 0.10) \times 10^{16}$		Discharge (rf), M = He	68, 260
298	$k = 1.1 \times 10^{16}$		Discharge (microwave)	*a*
298	$k = (1.4 \pm 0.2) \times 10^{16}$		Pulse radiolysis, M = H_2	308
298	$k = 1 \times 10^{16}$		(Review), M = H_2	*b*
298	$k = (1.11 \pm 0.15) \times 10^{16}$		Discharge (rf), M = Ar	261
298	$k = (1.28 \pm 0.21) \times 10^{16}$		Discharge (rf), D atom, M = Ar	261
298	$k = (2.07 \pm 0.18) \times 10^{16}$		Discharge (rf), M = H_2	261
298	$k = (2.26 \pm 0.23) \times 10^{16}$		Discharge (rf), M = CO_2	261
298	$k = (2.45 \pm 0.44) \times 10^{16}$		Discharge (rf), M = N_2O	261
298	$k = (3.96 \pm 0.46) \times 10^{16}$		Discharge (rf), M = SF_6	261
298	$k = (6.82 \pm 1.22) \times 10^{16}$		Discharge (rf), M = H_2O	261
	0.700	$17.0 - 0.5 \log T$	(Estimate)	c, 287
		H· + HNO → NO + H_2		
226	$k > 3 \times 10^{10}$		Discharge (rf), $E_a < 4.0$	68, 260
293	$k > 6 \times 10^{9}$		Discharge (rf)	68, 260
1600–2000	$k = (6 \pm 3) \times 10^{12}$		Flame ($H_2/N_2/O_2$)	*d*
2000	$k = (4.8 \pm 1.2) \times 10^{12}$		Flame ($H_2/N_2/O_2$)	*e*
	0.90	$12.59 + 0.5 \log T$	(Estimate)	*f*, 287
	$k = 12.59T^{0.5}$		(Estimate)	c, 287
2110	$k = (2.34 \pm 1.14) \times 10^{12}$		Flame ($H_2/O_2/NO_2$)	*g*
		H· + HNO → NH + OH·		
	13.0	$11.30 + 0.5 \log T$	(Estimate)	c, 287
		H· + NO_2 → NO + OH·		
300	$k = 6 \times 10^{12}$		Derived from 254 by (*a*)	*h*, *i*
500–540	$k = 3 \times 10^{13}$		Photolysis ($H_2/NO_2/Cl_2$)	*h*
633	$k = 2.2 \times 10^{14}$[j]		H_2/O_2	*k*
633	$k = 5.5 \times 10^{13}$[l]		H_2/O_2 mixture + NO_2	*k*
500–540	$k = 3 \times 10^{13}$		Discharge (rf)	*m*
630	$k = 2 \times 10^{14}$		Discharge (rf)	*m*
300	$k = (2.88 \pm 0.3) \times 10^{13}$		Discharge (microwave)	70
	5.0	$11.70 + 0.5 \log T$	(Estimate)	c, 287
		H· + ONCl → HCl + NO		
300	$k > 1 \times 10^{12}$		Discharge (rf)	72
296	$k = (1.6 \pm 0.5) \times 10^{13}$		Discharge (microwave)	265
	$k = (1.9 \pm 1) \times 10^{13}$		Discharge (microwave)	266
		H· + N_2O → N_2 + OH·		
423	$k \sim 10^{7}$	($E_a \sim$ 10–15)	Discharge (microwave)	271
1260–1780	16.3 ± 2	14.62	Flame ($N_2/N_2O/H_2$)	267
1357	$k = 2.9 \times 10^{11}$		Flame ($N_2/N_2O/H_2$)	268
900	$k = 4.3 \times 10^{10}$		Flame ($N_2/N_2O/H_2$)	268
Flame T	16.0	14.48	(Review of premixed flames)	*n*
900	13.0 ± 1.5	13.7 ± 0.4	Flame ($H_2/N_2/O_2/N_2O$)	270
1700–2600	12.0	13.60	Shock tube	269
		H· + N_2O → NH + NO		
	30.0	$11.0 + 0.5 \log T$	(Estimate)	c, 287
		H· + HNO_3 → OH· + HNO_2		
298	$k < 6 \times 10^{10}$		Discharge (microwave)	272
298	$k = 6 \times 10^{11}$		Photolysis (HNO_3/H_2)	273
		H· + NH_3 → H_2 + NH_2·		
423	$k \sim 10^{7}$	($E_a \sim$ 10–15)	Discharge (microwave)	271
843–963	13.7 ± 0.6	13.61	H_2/O_2 ignition	o
		D· + NH_3 = NH_2D + H·		
423–741	10.1 ± 0.15	13.28	Discharge (microwave)	275

TABLE XXII (*Continued*)

Temp, °K	*E*, kcal mol^{-1}	Log *A* (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + NH \rightarrow N + H_2$		
1000	1.5	$11.85 + 0.68 \log T$	(Estimate), $k_{1000°K} = 3.3 \times 10^{13}$	281
		$H\cdot + HN_3 \rightarrow$ products		
298	$k > 7.2 \times 10^{10}$		Relative to $O + C_2H_2$	280
		$H\cdot + N_2H_3\cdot \rightarrow 2NH_2\cdot$		
300	$k = (1.6 \pm 0.8) \times 10^{12}$		Discharge (microwave)	276
		$H\cdot + N_2H_4 \rightarrow H_2 + N_2H_3\cdot$		
298-423	2.0	11.54	Discharge (microwave)	271
243-463	$k = (1.7 \pm 0.2) \times 10^{11}$ [p]		Discharge (microwave)	278
213-473	2.5	13.11	Discharge (microwave)	276
300-540	1.3 ± 0.20	12.18	Discharge (microwave)	277
		$H\cdot + N_2H_4 \rightarrow NH_2\cdot^* + NH_3$		
293-349	2.6	8.08	Based on k_{77} of 232	279
213-473	3.1	9.65	Based on k_{77} of 238	276

[a] R. Simonaitis, *J. Phys. Chem.*, **67**, 2227 (1963). [b] J. Heicklen, *AIAA J.*, **5**, 4 (1967). [c] Thermochemistry Research Dept., Aerospace Corp. Report TR-100(9210-02)-1, 1966, as quoted in ref 287. [d] E. M. Bulewicz and T. M. Sugden, *Proc. Roy. Soc., Ser. A*, **277**, 143 (1964). [e] C. J. Halstead and D. R. Jenkins, *Chem. Phys. Lett.*, **2**, 281 (1968). [f] S. W. Mayer and L. Schieler, Aerospace Corp. Report TR-669(9210-02)-3, 1966, as quoted in ref 287. [g] M. Y. Smith, *Combust. Flame*, **18**, 293 (1972). [h] W. A. Rosser and H. Wise, *J. Phys. Chem.*, **65**, 532 (1961). [i] P. Harteck and B. R. Reeves "Chemical Reactions in the Lower and Upper Atmosphere," Interscience, New York, N. Y., 1961, pp 219–238. [j] Value based on a value of $k = 2.2 \times 10^{16}$ cm^6 mol^{-2} sec^{-1} for $H + O_2 + M \rightarrow HO_2 + M$. [k] P. G. Ashmore and B. J. Tyler, *Trans. Faraday Soc.*, **58**, 1108 (1962). [l] Value based on value of $k = 5.5 \times 10^{15}$ cm^6 mol^{-2} sec^{-1} for $H + O_2 + M \rightarrow HO_2 + M$. [m] M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, **57**, 2176 (1961). [n] C. P. Fenimore, "Chemistry in Premixed Flames," Pergammon Press, New York, N. Y., 1964, p 36. [o] K. T. Aganesyan and A. B. Nalbandyan, *Dokl. Akad. Nauk. SSSR*, **160**, 162 (1965); *Proc. Acad. Sci. USSR*, **160**, 18 (1965). [p] Same value for D atom reaction.

high-temperature results and the extrapolated result of the one low-temperature determination[271] has led Henrici and Bauer[269] to suggest that these inconsistencies cannot be reconciled by reaction 140.

Owing to the high activation energy (E = 30 kcal mol^{-1}) for reaction 141, it would seem probable that this reaction would only occur in high-temperature systems.

$$H\cdot + N_2O \rightarrow NH + NO \qquad (141)$$

6. Nitric Acid

Morris and Niki[272] have studied the following reaction in a fast-flow system by mass spectroscopy.

$$H\cdot + HNO_3 \rightarrow OH\cdot + HNO_2 \qquad (142)$$

By comparing the rate of the H· + *trans*-butene-2 reaction under similar conditions as used in reaction 142, they estimated the rate constant for reaction 142 to be 6×10^{10} cc mol^{-1} sec^{-1}.

Bérces, *et al.*,[273] photolyzed HNO_3 directly in a static system. They determined the ratio k_{142}/k_{134} to be 60. If the value of k_{134} determined by Phillips and Schiff[70] is used, the value of Bérces, *et al.*, of k_{142} is slightly higher than that determined by Morris and Niki.

7. Ammonia

Early workers[271] have suggested that ammonia acts as a catalyst for recombination of H atoms as shown in the following reactions

$$H\cdot + NH_3 \rightarrow NH_2\cdot + H_2 \qquad (143)$$

$$NH_2\cdot + H\cdot \rightarrow NH_3 \qquad (144)$$

Moore, *et al.*,[274] found no emission bands in their spectroscopic study of the reaction, which could be attributed to the formation of either NH or NH_2 radicals. Furthermore, they found that more than 95% of the original NH_3 was recovered.

Recently, Kurylo, *et al.*,[275] studied reaction 143 in a fast-flow system observing the decay of H and D atoms by epr. Since they observed no net consumption of H atoms as was suggested by reactions 143 and 144, they suggested the following reaction as the primary step.

$$NH_3 + D\cdot \rightarrow (NH_3D)\cdot \rightarrow \dot{N}H_2D + H\cdot \qquad (145)$$

They also suggested that reaction 145 would make the activation energies found by most workers seem more plausible since an exchange reaction is indicated rather than an abstraction reaction. This agrees with the suggestion of Moore, *et al.*,[274] of an exchange reaction.

8. Hydrazine

Several workers[271,276] have suggested the following reactions as the basic mechanism for the $H + N_2H_4$ reaction.

$$H\cdot + N_2H_4 \rightarrow N_2H_3\cdot + H_2 \qquad (146)$$

$$H\cdot + N_2H_3\cdot \rightarrow 2NH_2\cdot \qquad (147)$$

$$2N_2H_3\cdot \rightarrow 2NH_3 + N_2 \qquad (148)$$

$$2NH_2\cdot + M \rightarrow N_2H_4 + M \qquad (149)$$

$$2NH_2\cdot \rightarrow NH_3 + NH \qquad (150)$$

The main products of the reaction were NH_3, N_2, and H_2. By using long reaction times (*i.e.*, greater than 5 msec), small amounts of N-containing compounds such as N_2H_2 and HN_3 were also found.[276] It has also been suggested that the formation of N-containing compounds is due to reactions of NH or NH_2 radicals produced in the early stages of the reaction (reactions 147 or 150).

Schiavello and Volpi[271] studied this reaction in a stirred-

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(271) M. Schiavello and G. G. Volpi, *J. Chem. Phys.*, **37**, 1510 (1962).

(272) E. D. Morris and H. Niki, *J. Phys. Chem.*, **75**, 3193 (1971).

(273) T. Bérces, S. Förgeteg, and F. Márta, *Trans. Faraday Soc.*, **66**, 648 (1970).

(274) G. E. Moore, K. E. Shuler, S. Silverman, and R. Herman, *J. Phys. Chem.*, **60**, 813 (1956).

(275) M. J. Kurylo, G. A. Holliden, H. F. LeFevre, and R. B. Timmons, *J. Chem. Phys.*, **51**, 4497 (1969).

(276) M. Gehring, K. Hoyermann, H. Gg. Wagner, and J. Wolfrum, *Ber. Bunsenges. Phys. Chem.*, **75**, 1287 (1971).

flow reactor. They obtained an activation energy of about 2 kcal $\mathrm{mol^{-1}}$. Francis and Jones[277] obtained a larger rate constant, but a similar activation energy, when they studied reaction 146 by monitoring the H atom decay by epr in the presence of excess N_2H_4. More recently, Gehring, *et al.*,[276,278] have made a thorough investigation of the reaction by following both the H atom decay by epr and the product formation by mass spectroscopy. Gehring, *et al.*,[278] first predicted no temperature dependence for this reaction. However, in a later report,[276] they gave an activation energy of 2.5 kcal $\mathrm{mol^{-1}}$. Their overall Arrhenius expression for reaction 146 differed from that of Francis and Jones.[277] However, the two rate constants at 300°K determined by Gehring, *et al.*,[276,278] and the rate constant at 300°K determined by Francis and Jones[277] lie in the range of $k = 1.2 \times 10^{11}$ cc $\mathrm{mol^{-1}\ sec^{-1}}$.

Ghosh and Bair[279] observed a greenish emission in the H atom–N_2H_4 reaction which they attributed to excited NH_2 radicals formed in reaction 151. On the basis of Schiavello and Volpi's[271] value for k_{146}, they calculated a rate constant for reaction 151 as $1.2 \times 10^8 \exp(-2600/RT)$ cc $\mathrm{mol^{-1}\ sec^{-1}}$. Gehring, *et al.*,[276] recalculated the rate constant for reaction 151 as $k = 4.5 \times 10^9 \exp(-3100/RT)$ cc $\mathrm{mol^{-1}\ sec^{-1}}$ based on their value for k_{146}.

$$\mathrm{H\cdot + N_2H_4 \rightarrow NH_2\cdot^* + NH_3} \qquad (151)$$

9. Other N–H Compounds

Combourieu, *et al.*,[280] have estimated the rate constant for reaction 152 by comparing the rate for reaction 152 with the rate of reaction of atomic O (free of O_2) with C_2H_2 under similar conditions. They found that $k_{152} > 7.2 \times 10^{10}$ cc $\mathrm{mol^{-1}\ sec^{-1}}$.

$$\mathrm{H\cdot + HN_3 \rightarrow products} \qquad (152)$$

Gehring, *et al.*,[276] have estimated the rate constant for reaction 147 as $k = (1.6 \pm 0.8) \times 10^{12}$ at 300°K. Their value was based on a matching of computer-simulated and experimental concentration profiles. They also determined the ratio $k_{149}/k_{150} = 4.7 \times 10^6$ cc $\mathrm{mol^{-1}}$.

$$\mathrm{H\cdot + N_2H_3\cdot \rightarrow 2NH_2\cdot} \qquad (147)$$

Mayer, *et al.*,[281] have calculated the preexponential factor and activation energy for the following reaction.

$$\mathrm{H\cdot + NH \rightarrow N\cdot + H_2} \qquad (153)$$

10. Nitrogen Fluorides

Clyne and White[282] have made a spectroscopic investigation of the reaction of H atoms with NF_2 radicals. They found some emission bands which they attributed to the $(^1\Sigma^+\text{-}X^3\Sigma^-)$ and $(^1\Delta\text{-}X^3\Sigma^-)$ bands of NF. They also found an intense yellow afterglow which they attributed to the nitrogen afterglow. The emissions can be explained by the following reactions.

$$\mathrm{H\cdot + NF_2\cdot \rightarrow HF + NF(^1\Sigma,\ ^1\Delta)} \qquad (154)$$

$$\mathrm{NF(^1\Sigma) \rightarrow NF(^3\Sigma)} + h\nu \qquad (155)$$

$$\mathrm{NF(^1\Delta) \rightarrow NF(^3\Sigma)} + h\nu \qquad (156)$$

$$\mathrm{H\cdot + NF \rightarrow HF + N(^4S)} \qquad (157)$$

$$\mathrm{2N(^4S) + M \rightarrow N_2^*(B^3\Pi_g) + M} \qquad (158)$$

$$\mathrm{N_2^*(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)} + h\nu \qquad (159)$$

Recently Kuhn and Wellman[283] studied the H_2–N_2F_4 thermal explosion. They found that an explosive chain reaction occurred and that there was a variation in the product type and stoichiometry depending on whether the H_2/N_2F_4 ratio was 2, 1, or 0.5. However, they gave no kinetic values for any of the reactions.

Some HF chemical laser work has been done on the reaction of H_2 with NF_3[284] or N_2F_4.[285] This process is initiated by flash photolysis or discharge with the initiating reaction involving F atoms.

A complete summary of the Arrhenius parameters for the reactions of H atoms with N-containing compounds is given in Table XXII.

F. Reaction with Oxygen-Containing Compounds

Many reviews on the reactions of the H_2–O_2 system have been written since Steacie's review[1] in 1954. Kaufman[71,286] has twice reviewed atmospheric reactions and has included the reactions of some H· + oxygen-containing compounds (1964, 1969). Compilations of data for these reactions have been written by Bahn,[44,287] Baulch and coworkers,[288] Trotman-Dickenson and coworkers,[6,7] and Schofield.[9] The reactions have been studied under a wide variety of conditions and temperatures. A most extensive review, covering all the reactions of the H_2–O_2 system up to 1966, has been written by Venugopalan and Jones.[289] Therefore, discussion here will cover only work presented since 1966.

1. Oxygen

The basic mechanism for the reaction of H atoms with O_2 is given in the following reactions.

$$\mathrm{H\cdot + O_2 \rightarrow OH\cdot + O} \qquad (160)$$

$$\mathrm{O + H_2 \rightarrow OH\cdot + H\cdot} \qquad (161)$$

$$\mathrm{OH\cdot + H_2 \rightarrow H_2O + H\cdot} \qquad (162)$$

$$\mathrm{H\cdot + O_2 + M \rightarrow HO_2\cdot + M} \qquad (163)$$

The overall reaction with O_2 has been found to be a chain reaction with a regeneration of H atoms by reactions 161 and 162.

Under certain conditions of temperature and pressure, H_2 and O_2 react spontaneously. This phenomenon has been used in the investigation of the reaction of H atoms with various substances where the effect of additives on the explosion limit is measured. Baldwin, *et al.*,[40] have suggested that reactions 160 to 170 occur in the explosion. Inhibition of the explosion is caused by the reaction of H atoms with the additive rather than with O_2 (eq 160). Furthermore, the additives may react with other chain carriers such as O (eq 161) or OH· (eq 162). Since this mechanism is too complicated to be considered kinetically, Baldwin, *et al.*,[40] have suggested that reactions

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(277) P. D. Francis and A. R. Jones, *J. Chem. Phys.*, **54**, 5085 (1971).

(278) M. Gehring, K. Hoyermann, H. Gg. Wagner, and J. Wolfrum, *Ber. Bunsenges, Phys. Chem.*, 73, 956 (1969).

(279) P. K. Ghosh and E. J. Bair, *J. Chem. Phys.*, **45**, 4738 (1966).

(280) J. Combourieu, G. LeBras, and G. Laverdet, *C. R. Acad. Sci., Ser. C*, **268**, 1335 (1969).

(281) S. W. Mayer, L. Schieler, and H. S. Johnson, *J. Chem. Phys.*, **45**, 385 (1966).

(282) M. A. A. Clyne and I. F. White, *Chem. Phys. Lett.*, **6**, 465 (1970).

(283) L. P. Kuhn and C. Wellman, *Inorg. Chem.*, **9**, 602 (1970).

(284) W. H. Green and M. C. Lin, *IEEE J. Quantum Electron.*, 7, 98 (1971).

(285) L. E. Brus and M. C. Lin, *J. Phys. Chem.*, **75**, 2546 (1971).

(286) F. Kaufman, *Can. J. Chem.*, 47, 1917 (1969).

(287) G. S. Bahn, *Pyrodynamics*, **5**, 375 (1967).

(288) D. L. Baulch, D. D. Drysdale, and A. C. Loyd (also D. G. Horne, No. 4), "High-Temperature Reaction Rate Data," Department of Physical Chemistry, The University, Leeds, England, 1968–1971, No. 1–6.

(289) V. Venugopalan and R. A. Jones, "Chemistry of Dissociated Water Vapour and Related Systems," Interscience, New York, N. Y., 1966.

$$H\cdot + O_2 \rightarrow OH\cdot + O \quad (160)$$

$$O + H_2 \rightarrow OH\cdot + H\cdot \quad (161)$$

$$OH\cdot + H_2 \rightarrow H_2O + H\cdot \quad (162)$$

$$H\cdot + O_2 + M \rightarrow HO_2\cdot + M \quad (163)$$

$$H_2O_2 + M' \rightarrow 2OH\cdot + M' \quad (164)$$

$$H\cdot + HO_2\cdot \rightarrow 2OH\cdot \quad (165)$$

$$2HO_2\cdot \rightarrow H_2O_2 + O_2 \quad (166)$$

$$HO_2\cdot + H_2 \rightarrow H\cdot + H_2O_2 \quad (167)$$

$$H\cdot + H_2O_2 \rightarrow H_2O + OH\cdot \quad (168)$$

$$H\cdot + H_2O_2 \rightarrow H_2 + HO_2\cdot \quad (169)$$

$$OH\cdot + H_2O_2 \rightarrow HO_2 + HO_2\cdot \quad (170)$$

165, 167, 169, and 170 might be neglected. However, it has been shown that reaction 165 plays an important part in the mechanism at the second-explosion limit, even though it is not significant at the first-explosion limit. Values determined since 1968 (values published between 1966 and 1968 for reaction 160 are given in ref 7) for the reaction 160 and since 1966 for reaction 163 are given in Table XXIII. These values are in good agreement with each other and with previous determinations. Reaction 160 has been found to have an activation energy of about 14–16 kcal mol^{-1} and a preexponential factor of about 10^{14} cc mol^{-1} sec^{-1}.

The stable ground state of O_2 is ($^3\Sigma_g{}^-$). A discharge through O_2 is capable of producing excited species, for example, $O_2(^1\Delta_g)$. Glass[290] has treated $O_2(^1\Delta_g)$ with H atom as shown in the following reaction.

$$H\cdot(^2S) + O_2(^1\Delta_g) \rightarrow OH\cdot(^2\Pi) + O(^3P) \quad (171)$$

He has reported a rate constant of $k_{max} = 1.2 \times 10^9$ cc mol^{-1} sec^{-1} which agrees quite well with the estimate of Brown,[291] who gave $k_{171} = 3.9 \times 10^9$ cc mol^{-1} sec^{-1}. More recently Schofield[292] has estimated a higher value of 1.8×10^{11}.

2. *Water*

Although the primary reactions of the H_2–O_2 system have been extensively studied (*i.e.*, $H\cdot + O_2$ and $O + H_2$), only a few studies have been made of other reactions in the chain mechanism.

In the gas-phase system, water has been found to be an efficient catalyst for the termolecular recombination of H atoms. A few estimates,[9] based on the K_{eq} of reaction 172 and the k of the reverse reaction, have been made for the biomolecular reaction of H_2O with H atoms as in the following reaction.

$$H\cdot + H_2O \rightarrow OH\cdot + H_2 \quad (172)$$

3. *Hydrogen Peroxide*

The reaction of H atoms with hydrogen peroxide has been studied most recently by Albers, *et al.*,[293] by using a typical fast-flow system. They found that (1) there was a chain reaction and (2) H_2O was an important product of the reaction. They also found that the addition of O atoms to the reaction suppressed the chain reaction of $H\cdot + H_2O_2$ as well as the formation of water.

The basic mechanism of this reaction has been suggested as

$$H\cdot + H_2O_2 \rightarrow OH\cdot + H_2O \quad (168)$$

$$H\cdot + H_2O_2 \rightarrow H_2 + HO_2\cdot \quad (169)$$

followed by the rapid reactions[294,295]

$$H\cdot + HO_2\cdot \rightarrow 2OH\cdot \quad (165)$$

$$H\cdot + HO_2\cdot \rightarrow H_2 + O_2 \quad (173)$$

$$H\cdot + HO_2\cdot \rightarrow H_2O + O \quad (174)$$

$$OH\cdot + H_2O_2 \rightarrow H_2O + HO_2\cdot \quad (170)$$

By substituting D atoms for H atoms, Albers, *et al.*,[293] found that $k_{169D}/k_{168D} \sim 10$ at 421°K.

Baldwin, *et al.*,[296] have determined the ratio k_{169}/k_{168} as 0.16 (713°K) and 0.13 (773°K). Comparison of their result with those of Albers, *et al.*, shows that the path of the reaction is noticeably temperature dependent.

A summary of the published Arrhenius parameters for the H atom reactions with O-containing compounds that have been reported since 1966 (since 1968 for $H\cdot + O_2 \rightarrow OH\cdot + O$ reaction) are given in Table XXIII.

4. *$H(^2P)$ Reactions with Oxygen-Containing Compounds*

Wauchop and Phillips[297,298] have treated $H(^2P)$ atoms with the O-containing compounds: O_2, NO, N_2O, CO, CO_2, and SO_2. The $H(^2P)$ atoms were produced by the irradiation of normal $H(^2S)$ atoms by Lyman α (121.6 nm) radiation.

This work was similar to that of Tanaka and McNesby.[255] The emission from the resulting diatomic hydrides produced in the above reactions was observed spectroscopically, and the results are presented in Table XXIV.

G. Reaction with Carbon, CO, CO_2, and Silicon-Containing Compounds

1. *Carbon*

Although graphite readily promotes surface recombination of H atoms (with an activation energy of ~2 kcal mol^{-1}), it also produces small amounts of hydrocarbons (principally CH_4) by chemical reaction with the H atoms. This chemical reaction was estimated to have an activation energy in the range of 7–9 kcal mol^{-1} from a study[299] between 365 and 500°K.

Recently, Wood and Wise[300] have investigated the reaction of H atoms with graphite at higher temperatures (450–1200°K) and have found that, up to 700°K, the rate constant increased as the temperature of the graphite increased. Since the principal product, CH_4, is thermodynamically unstable at temperatures above ~800°K, the main products for the $H\cdot$ + graphite reaction above this temperature were H_2 and carbon.

Gill, *et al.*,[301] found that, at 77°K, when more H atoms were present, the CH_4 which formed on the surface was

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(290) G. P. Glass, Abstracts, 160th National Meeting of The American Chemical Society, Chicago, Ill., 1970, No. PHYS.-51.

(291) R. L. Brown, *J. Geophys. Res.*, **75**, 3935 (1970).

(292) K. Schofield, *Int. J. Chem. Kinet.*, **4**, 255 (1972).

(293) E. A. Albers, K. Hoyermann, H. Gg. Wagner and J. Wolfrum, *Symp. (Int.) Combust. Proc., 13th, 1970*, 81 (1971).

(294) N. R. Greiner, *J. Phys. Chem.*, **72**, 406 (1968).

(295) M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **275**, 559 (1963).

(296) R. R. Baldwin, D. Jackson, R. W. Walker, and S. J. Webster, *Symp. (Int.) Combust. Proc., 10th, 1964*, 423 (1965).

(297) T. S. Wauchop and L. F. Phillips, *J. Chem. Phys.*, **47**, 4281 (1967).

(298) T. S. Wauchop and L. F. Phillips, *J. Chem. Phys.*, **51**, 1167 (1969).

(299) A. B. King and H. Wise, *J. Phys. Chem.*, **67**, 1163 (1963).

(300) B. J. Wood and H. Wise, *J. Phys. Chem.*, **73**, 1348 (1969).

(301) P. S. Gill, R. E. Toomey, and H. C. Moser, *Carbon (Oxford)*, **5**, 43 (1967).

TABLE XXIII. Reaction with Oxygen-Containing Compounds[p]

Temp, °K	*E*, kcal mol^{-1}	Log *A* (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + O + M \rightarrow OH\cdot + M$ (cc^2 mol^{-2} sec^{-1})		
1400–3000	0	14.48	Shock tube	*a*
		$H\cdot + O_2 + M \rightarrow HO_2\cdot + M$ (cc^2 mol^{-2} sec^{-1})		
1400–3000	0	18.51	Shock tube	*a*
203–404	0.473 ± 0.092	15.38	Flash photolysis, M = He, $\lambda > 105$ nm	*b*
		$H\cdot + O_2 \rightarrow OH\cdot + O$[c]		
1150–1400	16.3	14.10	Shock tube	*d*
650–1000	16.8	14.36	Flame (H_2/O_2)	e
1000–2500	$k = 8.6 \times 10^{11} \times$ $\{\exp\ [-(\frac{12,300}{R})(\frac{1}{T} - \frac{1}{1600})]\}$		Shock tube	*f*
1600	$k = 8.64 \times 10^{11}$		Shock tube	*f*
1400–3000	16.6525	14.30	Shock tube	*a*
975–2060	14.70	13.98	Shock tube	*g*
298	16.8	14.78	(Review)	286
300–2500	16.790	14.40	(Review)	9
1000–1700	16.700	14.30	C_2H_2-O_2 flame	*h*
		$H\cdot + O_2(^1\Delta_g) \rightarrow OH\cdot + O$		
	$k = 1.2 \times 10^9$		Combined H_2 and O_2 discharges	290
	$k \leq 3.9 \times 10^9$		Discharge (microwave)	291
	$k \leq 1.8 \times 10^{11}$		(Estimate)	292
	4.7	13.37	Discharge (microwave)	*i*
298	$k = 9.4 \times 10^9$		Discharge (microwave)	*j*
		$H\cdot + O_2 + M \rightarrow HO_2\cdot + M$ (in cc^2 mol^{-2} sec^{-1})		
298	$k = 5.87 \pm 0.68 \times 10^{15}$		Pulse radiolysis, M = Ar, $k^{H_2}/k^{Ar} = 2.9$	308
225–1500	0.870 ± 0.70	15.30 ± 0.60	Shock tube, M = Ar	*g*
298	$k = (2.16 \pm 0.65) \times 10^{16}$		Discharge (microwave), M = He	*k*
298	$k = 1.7 \pm 0.4 \times 10^{16}$		Pulse radiolysis, M = H_2, $k^{H_2}/k^{Ar} = 2.0$	*l*
	$k = 1.1 \times 10^{16}$		(Review), M = Ar	286
743–813	−1.3 ± 0.5	15.70	$H_2/O_2/N_2$ thermal reaction	*m*
225–1500	$k = 1.1 \times 10^{16}(273/T)$	1.3	(Review), M = Ar	9
1400–3000	0	18.51 − 1 log *T*	Shock tube, M = total gases	*a*
600	$k \sim 3 \times 10^{16}$		Flame (H_2/O_2) (estimate)	e
		$H\cdot + HO_2\cdot \rightarrow 2OH\cdot$		
1400–3000	0	13.78	Shock tube	e
	$k \geq 1.8 \times 10^{11}$		(Review), $E_a \leq 2$	286
		$H\cdot + HO_2\cdot \rightarrow H_2 + O_2$		
1400–3000	0	13.78	Shock tube	*a*
$H + HO_2\cdot$	$\rightarrow \begin{cases} a\ \ H_2 + O_2 \\ b\ \ H_2O + O \\ c\ \ 2OH \end{cases}$	$k_a:k_b:k_c = 1.0:1.2:0.11$		*k*
		$H\cdot + O_3 \rightarrow OH\cdot + O_2$		
300	$k = (1.6 \pm 0.3) \times 10^{13}$		(Review)	71, 286
1400–3000	0	12.78	Shock tube	*a*
		$H\cdot + OH\cdot \rightarrow H_2 + O$		
1400–3000	8.0525	13.29 + 0.03 log *T*	Shock tube	*a*
	8.3	13.26	Review	286
1000–1700	8.0525	13.20 + 0.3 log *T*	Flame ($H_2/O_2/C_2H_2/CO$)	*h*
298–2500	4.3	11.20 + 0.79 log *T*	(Estimate), $k_{1000°\,K} = 4.3 \times 10^{12}$	214
		$H\cdot + OH\cdot + M \rightarrow H_2O + M$ (in cc^2 mol^{-2} sec^{-1})		
1400–3000	0	17.18 − 0.5 log *T*	Shock tube	*a*
<2130	$k[M] = 4.4 \times 10^{10}$ cc mol^{-1} sec^{-1}		Flame ($H_2/O_2/N_2$)	o
		$H\cdot + H_2O \rightarrow OH\cdot + H_2$		
296–3000	20.1 ± 0.5	13.92	(Review, calculated)	288
296–3000	20.66	14.25	(Review, calculated)	9
296–2000	19.90	14.04	(Review, calculated)	*n*

TABLE XXIII *(continued)*

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + H_2O_2 \rightarrow \begin{cases} OH\cdot + H_2O \\ H_2 + HO_2\cdot \end{cases}$		
743–813	11.8 ± 2	14.62	$H_2/O_2/N_2$ thermal reaction	*m*
300–2000	9.2	13.36	(Review)	288
294–464	4.2 ± 0.4	12.85	Discharge (microwave)	293

[a] W. G. Browne, D. R. White, and G. R. Smookler, *Symp. (Int.) Combust. Proc., 12th, 1968*, 557 (1969). [b] M. J. Kurylo, *J. Phys. Chem.*, **76**, 3518 (1972). [c] Values for this reaction published between 1966 and 1968 are given in ref 7. [d] T. A. Brabbs, F. E. Belles and R. S. Brokaw, *Symp. (Int.) Combust. Proc., 13th, 1970*, 128 (1971). [e] K. H. Eberius, K. Hoyermann, and H. Gg. Wagner, *Symp. (Int.) Combust. Proc., 13th, 1970*, 713 (1971). [f] G. L. Schott, *Symp. (Int.) Combust. Proc., 12th, 1968*, 569 (1969). [g] D. Gutman, E. A. Hardwidge, F. A. Dougherty, and R. W. Lutz, *J. Chem. Phys.*, 47, 4400 (1967). [h] W. G. Browne, R. P. Porter, J. D. Verlin, and A. H. Clark, *Symp. (Int.) Combust. Proc., 12th, 1968*, 1035 (1969). [i] J. E. Breen Jr., *Diss. Abstr. B*, **33**, 1476 (1972); Ph.D. Thesis, Rice University, 1972. [j] L. T. Cupitt, *Diss. Abstr. B*, **33**, 1477 (1972); Ph.D. Thesis, Rice University, 1972. [k] A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, **10**, 701 (1969); *Kinet. Catal. (USSR)*, **10**, 573 (1969). [l] W. P. Bishop and L. M. Dorfman, *J. Chem. Phys.*, **52**, 3210 (1970). [m] R. R. Baldwin, D. Jackson, R. W. Walker, and S. J. Webster, *Trans. Faraday Soc.*, **63**, 1676 (1967). [n] D. Garvin, National Bureau of Standards Report 9884, U. S. Government Printing Office, Washington, D. C., 1968. [o] N. J. Friswell and M. M. Sutton, *Chem. Phys. Lett.*, **15**, 108 (1972). [p] Values prior to 1967 are compiled in ref 44.

TABLE XXIV. Reaction of H(^{2}P) with Oxygen-Containing Compounds[a]

Reactant	Process	Bands	Origin, nm
O_2	$H(^2P) + O_2(^3\Sigma) \rightarrow OH(^2\Sigma) + O(^3P)$	OH, $A^2\Sigma \simeq X^2\Pi$	306.4
NO	$H(^2P) + NO(^2\Pi) \rightarrow NH(^3\Pi) + O(^3P)$	NH, $A^3\Pi \simeq X^3\Sigma$	336.0
N_2O	$H(^2P) + N_2O(^1\Sigma) \rightarrow NH(^3\Pi) + NO(^2\Pi)$	NH, $A^3\Pi \simeq X^3\Sigma$	336.0
CO	$H(^2P) + HCO(^2A) \rightarrow CH(^2\Sigma) + OH(^2\Pi)$	CH, $C^2\Sigma \simeq X^2\Pi$	314.3
CO_2	$H(^2P) + HCO(^2A) \rightarrow CH(^2\Sigma) + OH(^2\Pi)$	CH, $C^2\Sigma \simeq X^2\Pi$	314.3
SO_2	$H(^2P) + SO_2(^1A_1) \rightarrow SH(^2\Sigma) + O_2(^3\Sigma)$	SH, $A^2\Sigma \simeq X^2\Pi$	323.7

[a] Compiled from ref 298.

converted to higher molecular weight hydrocarbons (*e.g.*, C_2H_6, C_3H_8).

2. *Carbon Dioxide and Carbon Monoxide*

The reaction of H atoms with CO_2 (reaction 175) has been studied in only a few systems. Early workers[302-304]

$$H\cdot + CO_2 \rightarrow OH\cdot + CO \qquad (175)$$

have given an activation energy exceeding 30 kcal mol^{-1}, while more recent workers[260,305] have given an activation energy of about 23 kcal mol^{-1}. After reviewing the various activation energies obtained up to 1968, Bahn[306] felt that most of the early data were too high. Following interpretation of the various rate constants, he suggested the value

$$k = 1.99 \times 10^{16} T^{-0.76623} \exp(-25117/RT) \text{ cc mol}^{-1} \text{ sec}^{-1}$$

for the H + CO_2 reaction. This value agrees reasonably well with the value of Baulch, *et al.*[288]

Only two determinations of the termolecular reaction of H atoms with CO have been published.[307,308] CO has been found to assist in the recombination of H atoms as shown in the following mechanism.

$$H\cdot + CO + M \rightarrow HCO\cdot + M \qquad (176)$$

$$H\cdot + HCO\cdot \rightarrow H_2 + CO \qquad (177)$$

The rate constant given by Bennett and Blackmore[307] for reaction 176 is larger by a factor of 3 than that given by Hikida, *et al.*[308] However, Bennett and Blackmore have suggested that their value is an upper limit for the rate constant of reaction 176.

3. *Silicon-Containing Compounds*

The reactions of H or D atoms with four silicon-containing compounds, SiH_4,[309-311] $(CH_3)_3SiH$,[312,313] $(CH_3)_4Si$,[312,313] and $(C_2H_5)_4Si$,[314] have been studied. The results of these studies are included in Table XXV.

The reaction with SiH_4 has been reported to have an activation energy of about 0.5 kcal mol^{-1}.[309,310] Moortgat[311] has given a lower limit for the rate constant as 1.3 × 10^{11} cc mol^{-1} sec^{-1} (298°K) with an estimated activation energy of about 4 kcal mol^{-1}.

Schindler and coworkers[312,313] have treated $(CH_3)_3SiH$ and $(CH_3)_4Si$ with D atoms as shown in the following reactions

$$D\cdot + (CH_3)_3SiH \rightarrow (CH_3)_3Si\cdot + HD \qquad (178)$$

$$D\cdot + (CH_3)_3Si\cdot \rightarrow (CH_3)_3SiD \qquad (179)$$

$$D\cdot + (CH_3)_4Si \rightarrow (CH_3)_3Si(CH_2)\cdot + HD \qquad (180)$$

They found a net consumption of two D atoms for both compounds. In the trimethylsilane reaction, D atom abstraction resulted almost completely from the Si–H bond.

Baldwin, *et al.*,[314] have given a value of k = 2.18 × 10^{12} cc mol^{-1} sec^{-1} at 793°K for the reaction of H atoms with $(C_2H_5)_4Si$.

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(302) C. P. Fenimore and G. W. Jones, *J. Phys. Chem.*, **62**, 1578 (1958).

(303) H. Wise and W. A. Rosser, *Symp. (Int.) Combust. Proc., 9th, 1962*, 733 (1963).

(304) E. I. Intezarova, V. N. Kondratiev, and M. Z. Mukhoyan, *Kinet. Katal.*, **5**, 585 (1964); *Kinet. Catal. (USSR)*, **5**, 517 (1964).

(305) W. F. Hassel, G. S. Bahn, and J. L. Harp, Arnold Engineering Development Centre, Report AECD-TR-67-104, 1967.

(306) G. S. Bahn, *Pyrodynamics*, **6**, 101 (1968).

(307) J. E. Bennett and D. R. Blackmore, *Symp. (Int.) Combust. Proc., 13th, 1970*, 51 (1971).

(308) T. Hikida, J. A. Eyre, and L. M. Dorfman, *J. Chem. Phys.*, **54**, 3422 (1971).

(309) Yu. L. Spirin, *Russ. J. Phys. Chem.*, **36**, 636 (1962).

(310) H. Niki and G. J. Mains, *J. Phys. Chem.*, **68**, 304 (1964).

(311) G. K. Moortgat, *Diss. Abst. B*, **31**, 1879 (1970); Ph.D. Thesis, University of Detroit, 1970.

(312) M. A. Contineanu, D. Mihelcic, R. N. Schindler, and P. Potzinger, *Ber. Bunsenges. Phys. Chem.*, **75**, 426 (1971).

(313) D. Mihelcic, R. N. Schindler, and P. Potzinger, *Ber. Bunsenges. Phys. Chem.*, **75**, 1137 (1971).

(314) R. R. Baldwin, C. J. Everett, and R. W. Walker, *Trans. Faraday Soc.*, **64**, 2708 (1968).

TABLE XXV. Reaction with Carbon, HCO, CO, CO_2, COS, and Silicon-Containing Compounds

Temp, °K	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
		$H\cdot + C \text{ (graphite)} \rightarrow H_2 + CH_4$		
365-500	7-9		Discharge (rf)	299
450-1200	5.55		Discharge (rf) Rate = $k[H_2][H]^{0.5}$	300
		$H\cdot + C_2 \rightarrow C + CH\cdot$		
	10.0	11.7 + 0.5 log T	(Estimate)	214
		$H\cdot + C_2 \rightarrow C_2H\cdot$		
	0	11.7 + 0.5 log T	(Estimate)	214
		$H\cdot + HCO\cdot \rightarrow H_2 + CO$		
1000-1700	0	13.30	Flame ($H_2/O_2/C_2H_2/CO$)	*a*
1400-3000	0	13.30	Shock tube	*b*
		$H\cdot + CO + M \rightarrow HCO\cdot + M$ (in cc^2 mol^{-2} sec^{-1})		
298	$k = (2.6 \pm 0.4) \times 10^{13}$		Pulse radiolysis, M = Ar	308
298	$k = (4 \pm 0.06) \times 10^{13}$		Pulse radiolysis, M = H_2	308
298	$k \leq 1.2 \times 10^{14}$		Discharge (microwave), M = H_2	307
1000-1700	0	13.76 + 0.11 log T	Flame ($H_2/O_2/C_2H_2/CO$)	*a*
1400-3000	0	13.76 + 0.11 log T	Shock tube	*b*
		$H\cdot + CO_2 \rightarrow OH\cdot + CO$		
1200-1350	33.3	15.48	Flame ($H_2/O_2/CO_2$)	302
	33.0	15.47		303
1304-1735	29.7	14.89	Flame (CH_4/O_2)	304
	33.0	15.11	Flame (CH_4/O_2)	*c*
	30.7	11.43 + 0.79 log T	(Estimate)	*d*, 306
	33.0	13.43 + 0.5 log T	(Estimate)	*e*
1072	$k = 8.3 \times 10^8$		Flame ($H_2/O_2/CO_2$)	268
	30.7423	17.48	(Estimate)	302
	25.117	16.30	(Estimate)	305, 306
727-3727	23.50	13.75	(Review)	288
1000-1700	25.142	16.54 + 0.80 log T	Flame ($H_2/O_2/C_2H_2/CO$)	*a*
		$H\cdot + COS \rightarrow CO + HS\cdot$		
298	$k = 1.3 \times 10^{10}$		Discharge (microwave)	*f*
		$H\cdot + SiH_4 \rightarrow H_2 + SiH_3\cdot$		
298	~0.5		Hg photosens (SiH_4/SiD_4)	309, 310
298	$k > 1.32 \times 10^{11}$ [g]		Photolysis (SiH_4/SiD_4) $E_a \sim 4.1$	311
		$H\cdot + SiH\cdot \rightarrow Si + H_2$		
	0.4	12.11 + 0.5 log T	(Estimate)	214
		$D\cdot + (CH_3)_3SiH \rightarrow HD + (CH_3)_3Si\cdot$		
295-555	2.30 ± 0.05	12.73	Discharge (microwave)	312
		$D\cdot + (CH_3)_4Si \rightarrow HD + (CH_3)_3Si(CH_2)\cdot$		
603	$k = 2.5 \times 10^{10}$		Discharge (microwave)	312
		$H\cdot + (C_2H_5)_4Si \rightarrow H_2 + (C_2H_5)_3Si(C_2H_4)\cdot$		
793	$k = 2.8 \times 10^{12}$		H_2/O_2 ignition, $E_a \sim 5.9$	314

[a] W. G. Browne, R. P. Porter, J. D. Verlin, and A. H. Clark, *Symp. (Int.) Combust. Proc., 12th, 1968,* 1035 (1969). [b] W. G. Browne, D. R. White, and G. R. Smookler, *ibid.*, 557 (1969). [c] R. M. Fristrom, *Symp. (Int.) Combust. Proc., 9th, 1962,* 560 (1963). [d] W. E. Kaskan and W. G. Browne, General Electric Co., Missile Space Division Report R64SD37 (1964), as quoted in ref 306. [e] W. Chinitz, *Pyrodynamics*, 3, 197 (1965). [f] H. Rommel and H. I. Schiff, *Int. J. Chem. Kinet.*, 4, 547 (1972). [g] D atom reaction.

A summary of the published results for the reactions of H atoms with C, CO, CO_2, and Si-containing compounds is given in Table XXV.

H. Reaction with Miscellaneous Compounds

This section presents the rather sparse data which have been published on a number of reactions of H atoms with compounds which have not already been discussed. A summary of a number of these reactions is presented in Table XXVI. Most of the values given in this table have been obtained from theoretical considerations, and, since very few experimental investigations have been made of the H atom reactions with these inorganic compounds, no comparison is possible.

After discharging mixtures of H_2 with PCl_3, PBr_3, or $POCl_3$, Gutmann[315] found that the compounds reduced to red phosphorus. The compounds $TiCl_4$, $ZnCl_4$, $SbCl_5$,

TABLE XXVI. Reaction with Miscellaneous Compounds

Reaction	E, kcal mol^{-1}	Log A (cc mol^{-1} sec^{-1})	Method	Ref
$H\cdot + AlCl_2 \rightarrow AlCl + HCl$	5.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + AlF_2 \rightarrow AlF + HF$	6.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + AlH \rightarrow Al + H_2$	4.0	11.74 + 0.68 log T	(Estimate)	214
$H\cdot + AlOCl \rightarrow AlCl + OH$	8.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + AlOH \rightarrow AlO + H_2$	5.0	11.1 + 0.7 log T	(Estimate)	*a, b*
$H\cdot + AlO_2H \rightarrow AlO + H_2O$	5.0	10.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + AsCl_3 \rightarrow$ $As_4 + As_2 + HCl^c$	21.7		$H_2/AsCl_3$ Thermal reaction	317–319
$H\cdot + BeCl \rightarrow Be + HCl$	6.0	11.7 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + BeF \rightarrow Be + HF$	8.0	11.6 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + BeH \rightarrow Be + H_2$	1.3	12.20 + 0.5 log T	(Estimate)	214
$H\cdot + BeH_2 \rightarrow BeH + H_2$	5.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + BeOH \rightarrow BeO + H_2$	5.0	11.7 + 0.7 log T	(Estimate)	*a, b*
$H\cdot + BeO_2H_2 \rightarrow BeOH + H_2O$	5.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + BF_2 \rightarrow BF + HF$	6.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + BH \rightarrow B + H_2$	4.4	11.59 + 0.71 log T	(Estimate)	214
$H\cdot + BH_2 \rightarrow BH + H_2$	6.0	11.0 + 0.5 log T	(Estimate)	214
$H\cdot + BH_2 \rightarrow BH_3$	0	11.0 + 0.5 log T	(Estimate)	214
$H\cdot + BO_2H \rightarrow BOH + OH$	7.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H\cdot + BO_2H \rightarrow BO + H_2O$	7.0	11.0 + 0.5 log T	(Estimate)	214
$H\cdot + KH \rightarrow K + H_2$	4.6	11.75 + 0.70 log T	(Estimate)	214
$H + KCl \rightarrow K + HCl$	7.0	11.7 + 0.5 log T	(Estimate)	*a, b*
$H + KF \rightarrow K + HF$	7.0	11.7 + 0.5 log T	(Estimate)	*a, b*
$H + LiF \rightarrow Li + HF$	7.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H + LiH \rightarrow Li + H_2$	6.1	11.61 + 0.71 log T	(Estimate)	214
$H + LiO \rightarrow LiH + O$	5.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H + MgH \rightarrow Mg + H_2$	1.8	12.32 + 0.5 log T	(Estimate)	214
$H + NaF \rightarrow Na + HF$	6.0	11.0 + 0.5 log T	(Estimate)	*a, b*
$H + NaH \rightarrow Na + H_2$	4.0	11.81 + 0.68 log T	(Estimate)	214
$H + NaOH \rightarrow NaO + H_2$	19.2	12.08 + 0.7 log T	(Estimate)	*a, b*
$H + PH \rightarrow P + H_2$	1.92	11.84 + 0.67 log T	(Estimate)	214

[a] R. Tunder, S. Mayer, E. Cook, and L. Schieler, Aerospace Corp., Thermochemistry Research Dept., Aerospace Report TR-1001 (9210-02)-1, 1967, as quoted in footnote *b*. [b] D. Garvin, National Bureau of Standards Report 9884, U. S. Government Printing Office, Washington, D. C., 1968. [c] 700–800°.

$AsCl_3$, and VCl_4 were also found[316] to reduce to their respective metals.

Recently, a number of Russian workers[317–319] have found that the reaction $H\cdot + AsCl_3$ produces HCl and As. A short induction period indicated a radical chain mechanism. The reaction produced As_4 and As_2 as shown in the following reactions.

$$AsCl_3 + 1.5H_2 \rightarrow 0.25As_4 + 3HCl \quad (181)$$

$$AsCl_3 + 1.5H_2 \rightarrow 0.5As_2 + 3HCl \quad (182)$$

Reaction 181 was considered the dominant step.

Wiles and Winkler[86] found that the reaction of H with PH_3 led to the formation of red phosphorus on the walls. Owing to reaction of gas-phase H atoms with the surface-adsorbed phosphorus, determination of a mechanism for this reaction was impossible.

Polanyi and coworkers[320,321] have investigated the reaction of H atoms with sodium. They determined the rate constant to be $k = 10^{21}$ cc^2 mol^{-2} sec^{-1} for the reaction

$$H\cdot + H_2{}^* + Na \rightarrow NaH + H_2 \quad (183)$$

$$(H_2{}^* \text{ in } v \geq 6)$$

This value was about 10^4 times larger than previous measurements. They accounted for this difference by suggesting that the Na reacts with both H atoms and $H_2{}^*$ as shown in reaction 183.

VI. Concluding Remarks

We have attempted in this review to present a comprehensive summary of the kinetic data available on hydrogen atom reactions in the gas phase. For reactions with organic species, all data published to mid-1972 have been included, while for the inorganic reactions the data published since Steacie's book[1] have been stressed. We hope that this review will be particularly useful to those presently working in the field of hydrogen atom chemistry. Brief sections on production and detection of hydrogen atoms have been included in the hope that they will prove beneficial to those who might be contemplating research in this area.

Acknowledgments. We acknowledge Graduate Scholarships awarded to L. T. and S. D. M. by the Faculty of Graduate Studies, Dalhousie University. Financial assistance from the National Research Council of Canada is also acknowledged. We are especially grateful to Miss P. Lutley and the staff of the Dalhousie Science Library for checking the bibliography.

VII. Addendum

A number of papers have come to our attention since this article was submitted for publication. Of particular note is

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(315) V. Gutmann, *Monatsh. Chem.*, **86**, 98 (1955).

(316) V. Gutmann, *Monatsh. Chem.*, **86**, 765 (1955).

(317) V. V. Krapukhin, I. A. Sokolov, V. P. Potepolov, and S. G. Mnatsakan'yan, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.*, **10**, 86 (1967); *Chem. Abstr.*, **68**, 108348n (1968).

(318) V. V. Krapukhin, I. A. Sokolov, and M. N. Kostyuchenko, *Izv. Vyssh. Ucheb. Zaved., Tsvet. Met.*, **10**, 95 (1967); *Chem. Abstr.*, **68**, 5150n (1968).

(319) V. V. Krapukhin and I. A. Sokolov, *Met. Tsvet. Redk. Metal.*, 65 (1967); *Chem. Abstr.*, **68**, 65263m (1968).

(320) J. C. Polanyi and C. M. Sadowski, *J. Chem. Phys.*, **36**, 2239 (1962).

(321) E. M. Nemeth, J. C. Polanyi, and C. M. Sadowski, *J. Chem. Phys.*, **40**, 2054 (1964).

the reference book by Kondratiev,[322] which has recently appeared in English translation. It contains a list of rate constants for those reactions studied up to 1969.

Michael, *et al.*,[323] have studied the pressure dependence of the apparent bimolecular rate constant for the reaction of H atoms with C_2H_4 at room temperature. From experiments at high pressures of helium they were able to extrapolate a value for the high-pressure limit of the rate constant as $(9.7 \pm 1.9) \times 10^{11}$ cc mol^{-1} sec^{-1}. This value may be compared with the values obtained by other workers as listed in Table IV.

The coefficient (γ) for the heterogeneous recombination of H atoms was determined by Azatyan, *et al.*,[324] as 0.6×10^{-5}. They used a continuous-flow quartz apparatus and generated the atomic species by a 13.6-MHz discharge.

Mitchell and Le Roy[325] extended the measurements of the rate constant for the reaction of D atoms with H_2 from 346 down to 167°K. By combining their results with those of Westenberg and deHaas,[202] between 297 and 745°K, they have obtained the expression $k = (1.64 \pm 0.10) \times 10^7 T^2 \exp[(-5360 \pm 40)/RT]$ cc mol^{-1} sec^{-1}.

Takacs and Glass[326] gave the rate constant $(2.0 \pm 0.5) \times 10^{12}$ cc mol^{-1} sec^{-1} for the reaction of H atoms with HBr. This value was obtained from studies at 295°K in a fast discharge flow system using epr to monitor $H(^2S_{1/2})$ and $Br(^2P_{3/2})$ at a number of different reaction times. The value obtained may be compared with those presented in Table XIX.

From an esr study of the reaction of H atoms with H_2S, Bradley, *et al.*,[327] have determined the rate constants 5.0 $\times 10^{11}$ and 2.5×10^{13} cc mol^{-1} sec^{-1} for the reactions $H\cdot + H_2S \longrightarrow H_2 + SH\cdot$ and $H\cdot + SH\cdot \longrightarrow H_2 + S$, respectively. They point out that the latter reaction is very important in this system and that previous measurements which have neglected this reaction may require correction. Previous values for these reactions are reported in Table XXI.

The rate constant for the reaction of H atoms with NO has been determined by Atkinson and Cvetanovič[328] by a modulation technique. The H atoms were generated by mercury photosensitization of H_2 in a flow system; 253.7-nm mercury resonance radiation was emitted by a modulated rf powered low-pressure mercury arc. H atom concentrations were monitored by the observation of the red HNO emission. A value of $(2.15 \pm 0.13) \times 10^{16}$ cc mol^{-2} sec^{-1} was obtained for the reaction $H\cdot + NO + M \longrightarrow HNO + M$ at 298°K ($M = H_2$). This value is in excellent agreement with the value determined by Hartley and Thrush[261] as shown in Table XXII. Atkinson and Cvetanović also obtained values of $\log A = 15.95$ in units of cc^2 mol^{-2} sec^{-1} and $E = 0.54 \pm 0.15$ kcal mol^{-1}.

Baldwin, *et al.*,[329] by adding N_2O to slowly reacting mixtures of $H_2/O_2/He$ determined the value 2.6×10^9 cc mol^{-1} sec^{-1} for the reaction $H\cdot + N_2O \longrightarrow N_2 + OH\cdot$ at 773°K. From a combination of their data with other measurements they gave $\log A = 13.88$ in units of cc mol^{-1} sec^{-1} and $E = 15.1 \pm 1.0$ kcal mol^{-1}. These values may be compared with other measurements presented in Table XXII.

From a shock tube study of the reaction $H\cdot + O_2 + Ar \longrightarrow HO_2\cdot + Ar$, Jachimowski and Houghton[330] obtained a value of $k = 2.3 \times 10^{15}$ cc^2 mol^{-2} sec^{-1}. Other values for this reaction are given in Table XXIII.

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(322) V. N. Kondratiev, "Rate Constants of Gas Phase Reactions," Translated by L. J. Holtschlag, R. M. Fristrom, Ed., U. S. Government Printing Office, Washington, D. C., NSRDS-NBS, COM-72-10014, 1972.

(323) J. V. Michael, D. T. Osborne, and G. N. Suess, *J. Chem. Phys.*, **58**, 2800 (1973).

(324) V. V. Azatyan, F. A. Grigorgan, and S. B. Filippov, *Kinet. Katal.*, **13**, 1389 (1972).

(325) D. N. Mitchell and D. J. Le Roy, *J. Chem. Phys.*, **58**, 3449 (1973).

(326) G. A. Takacs and G. P. Glass, *J. Phys. Chem.*, 77, 1060 (1973).

(327) J. N. Bradley, S. P. Trueman, D. A. Whytock, and T. A. Zaleski, *J. Chem. Soc., Faraday Trans. 1*, **69**, 416 (1973).

(328) R. Atkinson and R. J. Cvetanovič, *Can. J. Chem.*, **51**, 370 (1973).

(329) R. R. Baldwin, A. Gethin, and R. W. Walker, *J. Chem. Soc., Faraday Trans. 1*, **69**, 352 (1973).

(330) C. J. Jachimowski and W. M. Houghton, *NASA Tech. Note.* NASA TN D-6990 (1972).