REACTIONS OF HYDROGEN ATOMS IN AQUEOUS SOLUTIONS

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Contents

I. Introduction

In recent years the hydrogen atom has received an increasing amount of attention by investigators in various fields. Attempts have been made to measure its reaction rates and elucidate the mechanism of its reactions in the gas and solid phases and in hydrocarbon and aqueous solutions, and its radiobiological involvement was evaluated. It is an important intermediate in the radiolysis and photolysis of organic and aqueous systems, and as a result a considerable amount of research on the hydrogen atom has been carried out by radiation chemists trying to attain a better understanding of the chemistry of the H atom as well as its implications for other areas.

The development of radiation chemistry to a fairly precise science in the last decade, especially after establishing that two different reducing intermediates are produced in irradiated water, namely H and e_{aq}^- (the hydrated electron), has opened up many possibilities for studying the chemistry of the hydrogen atom. First, it has introduced a means of forming thermal hydrogen atoms practically homogeneously in a solvent that does not react with them and without the need of any solute that might interfere with their subsequent kinetics. Secondly, the development of the pulse radiolysis technique enabled the measurement of absolute rate constants for the reactions of hydrogen atoms by the spectrophotometric observation of the radicals produced by these reactions. The optical absorption of H atoms is very weak and at very short wavelengths; thus the use of this absorption for kinetic pur-

poses is impractical at present. The more recent development of the *in situ* radiolysis–electron spin resonance technique has broadened the scope of the research on the hydrogen atom in aqueous solutions, since the esr signals of the H atom can be observed directly and the changes in its concentration can thus be followed, resulting in unambiguous kinetic measurements. Furthermore, by the same technique the radicals produced by reactions of H can be positively identified in many cases. With all this recently developed sophisticated instrumentation, an appreciable contribution is still being made, however, by the good old-fashioned approach of product analysis of γ-irradiated solutions.
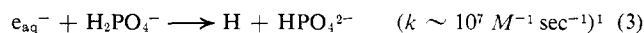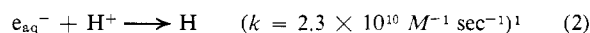
Before discussing the results of the various studies it would be helpful to summarize the reactions by which the hydrogen atom is formed in aqueous solutions and the types of reactions H undergoes with solutes. Studies of the intermediate and final products of these reactions will then be reviewed and followed by a discussion of the rate constants and the reaction mechanism.

II. Reactions

Hydrogen atoms are formed directly by radiolysis of water

$$H_2O \rightsquigarrow H, e_{aq}^-, OH, H_2, H_2O_2, H^+ \tag{1}$$
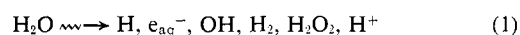
and from the reaction of hydrated electrons with acids, *e.g.*

$$e_{aq}^- + H^+ \longrightarrow H \qquad (k = 2.3 \times 10^{10} \ M^{-1} \ sec^{-1})[1] \tag{2}$$

$$e_{aq}^- + H_2PO_4^- \longrightarrow H + HPO_4^{2-} \qquad (k \sim 10^7 \ M^{-1} \ sec^{-1})[1] \tag{3}$$

Hydrogen atoms can also be formed by the direct photolysis of water at 184.9 nm,[2] but most solutes to be studied will interfere with this reaction by light absorption. Hydrogen atoms may be studied photolytically more conveniently by the photoionization of inorganic ions

$$X^- \xrightarrow{h\nu} X + e_{aq}^- \tag{4}$$

followed by reaction 2. In certain cases H atoms can also be directly produced by the photolysis of an organic solute, *e.g.*, from a thiol.

$$RSH \xrightarrow{h\nu} R\dot{S} + H \tag{5}$$

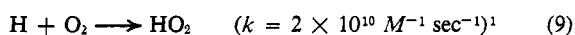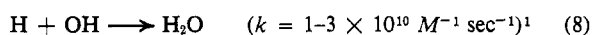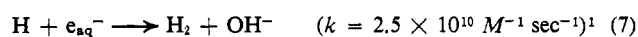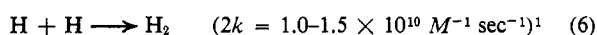Several investigators have produced hydrogen atoms in the gas phase by electric discharge in a stream of hydrogen gas. The H + H_2 mixture may be then bubbled through solutions.[3]

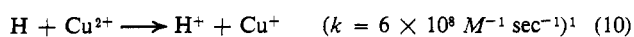(1) M. Anbar and P. Neta, *Int. J. Appl. Radiat. Isotop.*, **18**, 493 (1967).
(2) J. Barrett and J. H. Baxendale, *Trans. Faraday Soc.*, **56**, 37 (1960).
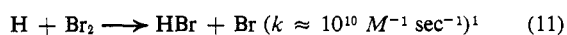(3) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959).

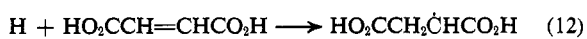The hydrogen atoms react very rapidly with radicals.

$$H + H \longrightarrow H_2 \quad (2k = 1.0\text{--}1.5 \times 10^{10} \; M^{-1} \sec^{-1})^1 \quad (6)$$

$$H + e_{aq}^- \longrightarrow H_2 + OH^- \quad (k = 2.5 \times 10^{10} \; M^{-1} \sec^{-1})^1 \quad (7)$$

$$H + OH \longrightarrow H_2O \quad (k = 1\text{--}3 \times 10^{10} \; M^{-1} \sec^{-1})^1 \quad (8)$$

$$H + O_2 \longrightarrow HO_2 \quad (k = 2 \times 10^{10} \; M^{-1} \sec^{-1})^1 \quad (9)$$

They can reduce by electron transfer

$$H + Cu^{2+} \longrightarrow H^+ + Cu^+ \quad (k = 6 \times 10^8 \; M^{-1} \sec^{-1})^1 \quad (10)$$

or react by atom transfer

$$H + Br_2 \longrightarrow HBr + Br \; (k \approx 10^{10} \; M^{-1} \sec^{-1})^1 \quad (11)$$

They add to olefinic compounds

$$H + HO_2CCH{=}CHCO_2H \longrightarrow HO_2CCH_2\dot{C}HCO_2H \quad (12)$$
$$(k = 9 \times 10^8 \text{ and } 6 \times 10^8 \; M^{-1} \sec^{-1}$$
$$\text{for fumaric and maleic acid, respectively})^4$$

and to aromatic rings

$$H + C_6H_5COOH \longrightarrow \dot{C}_6H_6COOH \quad (13)$$
$$(k = 1.0 \times 10^9 \; M^{-1} \sec^{-1})^5$$

and abstract atoms or radicals from saturated compounds.
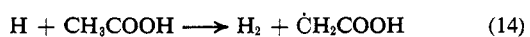
$$H + CH_3COOH \longrightarrow H_2 + \dot{C}H_2COOH \quad (14)$$
$$(k = 1 \times 10^5 \; M^{-1} \sec^{-1})^6$$

$$H + (CH_3)_2CHOH \longrightarrow H_2 + (CH_3)_2\dot{C}OH \quad (15)$$
$$(k = 7 \times 10^7 \; M^{-1} \sec^{-1})^6$$

$$H + ClCH_2COOH \longrightarrow \begin{array}{l} \longrightarrow H_2 + Cl\dot{C}HCOOH \quad (16) \\ \quad (k = 1.8 \times 10^5 \; M^{-1} \sec^{-1})^7 \\ \\ \longrightarrow HCl + \dot{C}H_2COOH \quad (17) \\ \quad (k = 8 \times 10^4 \; M^{-1} \sec^{-1})^7 \end{array}$$

$$H + BrCH_2COOH \longrightarrow HBr + \dot{C}H_2COOH \quad (18)$$
$$(k = 3 \times 10^8 \; M^{-1} \sec^{-1})^6$$

$$H + CH_3I \longrightarrow HI + \dot{C}H_3 \; (k \geq 2 \times 10^9 \; M^{-1} \sec^{-1})^6 \quad (19)$$

$$H + HSCH_2COOH \longrightarrow \begin{array}{l} \longrightarrow H_2 + \dot{S}CH_2COOH \quad (20) \\ \quad (k = 4 \times 10^9 \; M^{-1} \sec^{-1})^4 \\ \\ \longrightarrow H_2S + \dot{C}H_2COOH \quad (21) \\ \quad (k \approx 10^8 \; M^{-1} \sec^{-1})^1 \\ \\ \longrightarrow H_2 + HS\dot{C}HCOOH \quad (22) \\ \quad (k \approx 10^7 \; M^{-1} \sec^{-1})^1 \end{array}$$
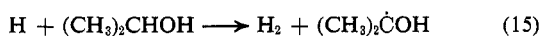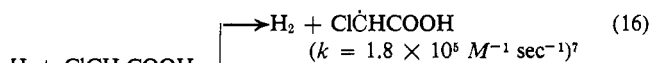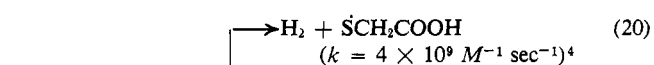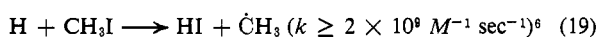
A unique reaction for the H atom is its generation of e_{aq}^-.

$$H + OH^- \longrightarrow e_{aq}^- + H_2O \quad (k = 2 \times 10^7 \; M^{-1} \sec^{-1})^{7,8} \quad (23)$$

$$H + F^- \longrightarrow e_{aq}^- + HF \quad (k = 1 \times 10^4 \; M^{-1} \sec^{-1})^{9,10} \quad (24)$$
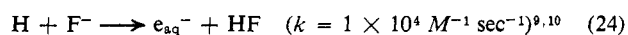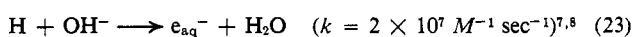
III. Products of Hydrogen Atom Reactions

A. STABLE PRODUCTS

Little study has been done on the organic end products of the reactions of hydrogen atoms. Reaction mechanisms or rate constants in many cases have been studied by observation of the intermediate radicals, and when stable products have been determined these were usually H_2, HD, or X^-. A great

deal of information has been gained from the measurement of the hydrogen yield and from the determination of the isotopic composition of the hydrogen produced from irradiated solutions containing isotopically labeled compounds. Much of this information involves rate constant determination and will be discussed below. In general the ratio H_2/HD is used as a measure of hydrogen abstraction from a compound compared to deuterium abstraction from a deuterated compound or from a deuterated site of the same compound. The total yield of molecular hydrogen is used as a measure of abstraction compared to reactions that do not produce hydrogen. These experiments rely on the reproducibility of the γ-radiolysis results which is most satisfactory. Except for competiti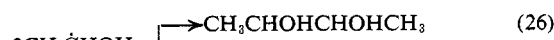on kinetics the yield of hydrogen has been used to distinguish between hydrogen abstraction which yields H_2 and other modes of H atom reaction. For example, it was determined that the reaction of H with benzoic acid and acetonitrile favors addition $(\geq 97\%)^{11}$ over abstraction, whereas that with acetone favors abstraction $(\sim 66\%)^{11}$ The reaction of H with organic halogen compounds largely depends on the halogen. Bromo compounds suppress the yield of H_2 from H completely, demonstrating that practically no hydrogen abstraction takes place from these compounds,[12] whereas the chloro compounds undergo both hydrogen abstraction and chlorine abstraction, in certain cases at comparable rates.[7,12]

The study of the reactions of H atoms with organic halogen compounds has been complemented by determination of the yield of the halide ions.[7,12,13] The measurement of the yield of chloride ions in aqueous solutions of chloroacetic acid provided one of the first tools to distinguish between reactions of hydrated electrons and of hydrogen atom.[7,13] The reaction of e_{aq}^- with an alkyl chloride, bromide, or iodide results in the formation of the halide ion by dissociative electron attachment. The reaction of H can result in both hydrogen abstraction and halogen abstraction. However, halogen abstraction is much more effective in the case of the bromo and iodo compounds and only with chloro compounds has substantial hydrogen abstraction been demonstrated. The mechanism of dehalogenation by H atoms has been suggested to be an atom abstraction process and not an electron transfer.[12]

Some organic end products which result from H atom reactions have been determined. For example, it was found that the radicals formed by hydrogen abstraction from acetic acid dimerize to yield succinic acid.[14]

$$2\dot{C}H_2COOH \longrightarrow HOOCCH_2CH_2COOH \quad (25)$$
$$(2k = 1.8 \times 10^9 \; M^{-1} \sec^{-1})^{15}$$
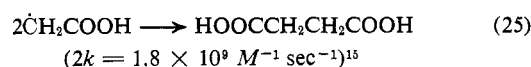
The radicals formed by reaction of H with ethanol are mainly the α radicals,[16] and these radicals were found to undergo both dimerization to a glycol and disproportionation to acetaldehyde and ethanol.[17]

$$2CH_3\dot{C}HOH \longrightarrow \begin{array}{l} \longrightarrow CH_3CHOHCHOHCH_3 \quad (26) \\ \longrightarrow CH_3CHO + CH_3CH_2OH \quad (27) \end{array}$$
$$(2k = 2.3 \times 10^9 \; M^{-1} \sec^{-1})^{18}$$

(4) P. Neta and R. H. Schuler, *Radiat. Res.*, **47**, 612 (1971).

(5) P. Neta and L. M. Dorfman, *J. Phys. Chem.*, **73**, 413 (1969).

(6) P. Neta, R. W. Fessenden, and R. H. Schuler, *ibid.*, **75**, 1654 (1971).

(7) J. Jortner and J. Rabani, *ibid.*, **66**, 2078, 2081 (1962).

(8) J. Rabani, *Advan. Chem. Ser.*, No. **50**, 242 (1965).

(9) M. Anbar and P. Neta, *Trans. Faraday Soc.*, **63**, 141 (1967).

(10) M. Anbar and E. J. Hart, *J. Phys. Chem.*, **71**, 4163 (1967).

(11) P. Neta, G. R. Holdren, and R. H. Schuler, *ibid.*, **75**, 449 (1971).

(12) M. Anbar and P. Neta, *J. Chem. Soc. A*, 834 (1967).

(13) E. Hayon and A. O. Allen, *J. Phys. Chem.*, **65**, 2181 (1961).

(14) W. M. Garrison, W. Bennett, S. Cole, H. R. Haymond, and B. M. Weeks, *J. Amer. Chem. Soc.*, **77**, 2720 (1955).
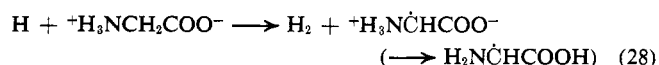
(15) P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, **73**, 4207 (1969).

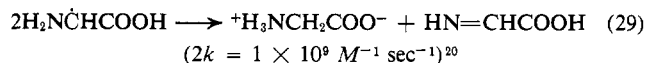(16) C. Lifshitz and G. Stein, *J. Chem. Soc.*, 3706 (1962).

(17) G. G. Jayson, G. Scholes, and J. Weiss, *ibid.*, 1358 (1957).

(18) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, **73**, 3794 (1969).
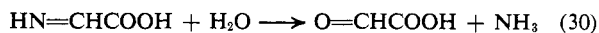
The radicals from isopropyl alcohol undergo disproportionation only. The radicals from glycine

$$H + {}^+H_3NCH_2COO^- \longrightarrow H_2 + {}^+H_3N\dot{C}HCOO^-$$
$$(\longrightarrow H_2N\dot{C}HCOOH) \quad (28)$$

disproportionate[19]

$$2H_2N\dot{C}HCOOH \longrightarrow {}^+H_3NCH_2COO^- + HN{=}CHCOOH \quad (29)$$
$$(2k = 1 \times 10^9 \ M^{-1} \ sec^{-1})[20]$$

and the unstable imino acid hydrolyzes mainly to glyoxylic acid which was identified.[19]

$$HN{=}CHCOOH + H_2O \longrightarrow O{=}CHCOOH + NH_3 \quad (30)$$

The reaction of H atoms with cysteine takes place mainly by hydrogen abstraction from the SH group (as in reaction 20), and the resulting R$\dot{S}$ radicals dimerize to form cystine

$$2R\dot{S} \longrightarrow RSSR \quad (31)$$

the yield of which has been determined confirming this mechanism.[21,22]

B. INTERMEDIATE PRODUCTS

Much information on the mechanism of reaction of H atoms has been gathered from observation of the short-lived intermediates initially produced by these reactions. Intermediates produced in aqueous solutions have been generally monitored through their optical absorption by pulse radiolysis techniques or identified by electron spin resonance spectroscopy.

Radicals produced by hydrogen abstraction from saturated aliphatic compounds, e.g., alcohols,[18] carboxylic acids,[15] and amino acids,[20] have been observed by pulse radiolysis. However, in most cases the same radicals have been produced by the reactions of both H and OH with the organic solute. Both of these reactants form the same radical by H abstraction, and only when abstraction can take place from different positions of the molecule is there a distinction between the products of H and OH reactions. H atoms are more selective than OH radicals and will, therefore, produce the different organic radicals with different relative yields. Radicals produced by H abstraction from alcohols[18] show optical absorption in the far-ultraviolet region, and the absorption maxima were not observed in most cases. The pK's of the OH groups in the α radicals formed from alcohols were found to be 4–6 units below those for the parent compounds. The radicals formed by H abstraction from position α of carboxylic acids[15] have absorption maxima at 300–350 nm, and their pK values are comparable to those of the parent molecules. Further, those produced by H abstraction from hydroxy[23] and amino acids[20] absorb at ~250 nm with high extinction coefficient, and their dissociation constants are greatly different from those for the parent compounds.

Radicals formed by the addition of a hydrogen atom to aromatic or heterocyclic compounds have absorption spectra only slightly different from those of the analogous OH adducts. The H adducts have been observed with benzene,[24]

benzoic acid,[5] several other aromatic compounds,[25-27] and several pyrimidine bases.[28-31] From these spectrophotometric studies the position at which the hydrogen atom adds was not determined, and in most cases it was suggested that addition takes place with comparable yields at all available positions (ortho, meta, and para in benzoic acid and 5, 6 in the pyrimidine bases). In the same pulse radiolysis experiments the kinetics of formation and disappearance of these radicals was followed. The kinetics of formation can usually be studied under pseudo-first-order conditions so that they give a direct absolute measurement of the rate constant for the reaction of H with the organic solute as will be discussed below. The decay of the transient absorption followed in most cases a second-order decay, indicating a radical–radical reaction. The rate constants for the latter reactions were found to be of the order of 10^8 to $10^9 \ M^{-1} \ sec^{-1}$ for neutral or singly charged radicals.

Transient absorption spectra of the cyclohexadienyl radicals produced by the addition of H to several aromatic compounds have been measured and the absorption maxima were found to be in the region of 300 to 400 nm depending on the substituent.[5,24-27] The bathochromic shifts caused by substitution on these radicals are similar to those for the corresponding substituted benzenes.[25]

The transient absorptions of the H adducts of thymine and uracil have maxima at 400 and 420 nm, respectively,[28,29] whereas the H adduct of orotic acid shows an absorption peak at 345 nm.[30] In the case of the 5-halouracils H atoms were found to react both by addition and by halogen abstraction to yield a mixture of several radicals which show very broad absorption spectra centered at ~370 nm.[31]

Optical pulse radiolysis experiments have also been used to observe species formed by reaction of H with inorganic compounds. For example, silver atoms formed by

$$Ag^+ + H \longrightarrow Ag^0 + H^+ \quad (k = 1.1 \times 10^{10} \ M^{-1} \ sec^{-1})[32] \quad (32)$$
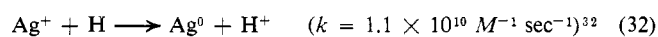
have been observed at 310 nm and from their rate of formation k_{32} has been determined.[32] The rate constant for the reaction

$$MnO_4^- + H \longrightarrow MnO_4^{2-} + H^+ \quad (33)$$
$$(k = 2.4 \times 10^{10} \ M^{-1} \ sec^{-1})[33]$$
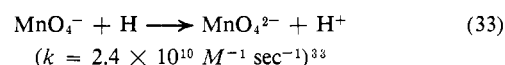
has been determined by following the disappearance of MnO_4^- at 545 nm.[33] The perhydroxyl radical formed by reaction 9 shows optical absorption with a maximum at 230 nm and has a relatively slow disappearance rate.[34] And finally the generation of e_{aq}^- from H by reactions 23 and 24 has also been confirmed by pulse radiolysis,[10,35] where an increase

(19) B. M. Weeks and W. M. Garrison, *Radiat. Res.*, 9, 291 (1958).

(20) P. Neta, M. Simic, and E. Hayon, *J. Phys. Chem.*, 74, 1214 (1970).

(21) F. E. Littman, E. M. Carr, and A. P. Brady, *Radiat. Res.*, 7, 107 (1957).

(22) G. Navon and G. Stein, *Isr. J. Chem.*, 2, 151 (1964).

(23) M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 73, 4214 (1969).

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(25) B. Chutny, *Nature (London)*, 213, 593 (1967).

(26) E. J. Land and M. Ebert, *Trans. Faraday Soc.*, 63, 1181 (1967).

(27) K.-D. Asmus, B. Cercek, M. Ebert, A. Henglein, and A. Wigger, *ibid.*, 63, 2435 (1967).

(28) L. S. Myers, Jr., and L. M. Theard, *J. Amer. Chem. Soc.*, 92, 2868 (1970).

(29) C. L. Greenstock, J. W. Hunt, and M. Ng, *Trans. Faraday Soc.*, 65, 3279 (1969).

(30) C. L. Greenstock, *ibid.*, 66, 2541 (1970).

(31) L. K. Patterson and K. M. Bansal, *J. Phys. Chem.*, 76, 2392 (1972).

(32) J. H. Baxendale and P. L. T. Bevan in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 253.

(33) J. H. Baxendale, J. P. Keene, and D. A. Stott in "Pulse Radiolysis," J. H. Baxendale, M. Ebert, J. P. Keene, and A. J. Swallow, Ed., Academic Press, New York, N. Y., 1965, p 107.

(34) D. Behar, G. Czapski, J. Rabani, L. M. Dorfman, and H. A. Schwarz, *J. Phys. Chem.*, 74, 3209 (1970).

(35) M. S. Matheson and J. Rabani, *ibid.*, 69, 1324 (1965).

in the optical absorption by e_{aq}^- or an effect on its decay rate was observed.

A more positive identification of the radicals formed by the reactions of H atoms with organic compounds is achieved by electron spin resonance spectroscopy. Much of the esr work on hydrogen atoms has been done with acid glasses because, unfortunately, only few laboratories are equipped with adequate esr equipment to study the fast reactions which occur immediately after irradiation. The experiments with aqueous solutions helped identify the radicals produced by reaction of H with benzene, oxalic, fumaric, maleic, and muconic acids, nitriles, amines, and amino acids. Substituted furan and other compounds are currently being studied. In the case of benzene,[36] furans,[37] and the fumarate,[38] maleate,[39] and muconate ions,[39] the H adducts have been identified. With nitriles the hydrogen atom was found to add to the carbon atom.[40]

$$R\!-\!C\!\equiv\!N + H \longrightarrow R\!-\!CH\!=\!N\cdot \qquad (34)$$
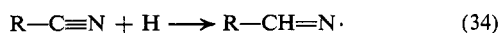
With oxalic acid the reaction is addition to the carboxyl group[36]

$$H + HO\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!OH \longrightarrow HO\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle OH}{|}}{C}\!-\!OH \qquad (35)$$
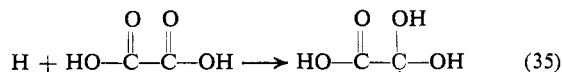
The same radical was found to be formed from glyoxylic acid probably by hydrogen abstraction from the hydrate[36]

$$H + HO\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}\!-\!OH \longrightarrow H_2 + HO\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\overset{\overset{\displaystyle OH}{|}}{C}\!-\!OH \qquad (36)$$
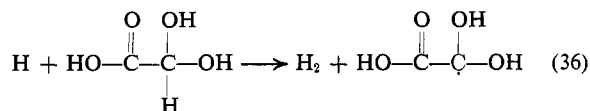
Except for providing positive identification of radicals and determination of the site of attack of H on the molecule, one of the main advantages of esr over the optical studies lies in the fact that hydrogen atoms can be observed directly and their kinetics followed.[6]
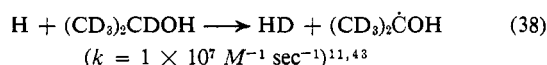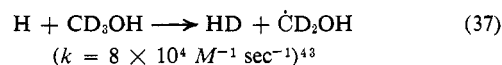
IV. Determination of Rate Constants for Hydrogen Atom Reactions

Several methods have been developed for the determination of absolute or relative rate constants for the reactions of hydrogen atoms with organic and inorganic compounds. Most methods utilize ionizing radiation for the production of H in aqueous solutions, and the main volume of data has been obtained by competition kinetics. The relative rates are then put on an absolute scale by reference to an absolute rate constant determined directly. Absolute rates have been measured by pulse radiolysis using optical or esr spectroscopy. Relative measurements have been carried out by both of these techniques and also by product analysis. In what follows the various techniques will be described and compared.

A. COMPETITION KINETICS BY PRODUCT ANALYSIS

This method was the first one used for determination of rate constants for H atom reactions in aqueous solutions. It dates

back to the 1950's[41] and is still being widely used.[11,42] Its advantage lies in the simplicity and availability of the instrumentation necessary and in the relatively accurate results this method can yield. Generally, H atoms are produced in aqueous solutions, either neutral (G_H = 0.6 atom per 100 eV absorbed) or acid ($G(H)$ = G_H + $G_{e_{aq}^-}$ = 3.4), by steady-state irradiation with X-rays or γ-rays. Competition for the H atoms between a compound that undergoes hydrogen abstraction to yield hydrogen (e.g., reactions 14 and 15) and a compound that reacts with H with no subsequent formation of H_2 (e.g., reactions 10, 12, 13, 18, and 22) is followed, and the yield of hydrogen at different concentration ratios is a measure of the relative rate constants. Another type of competition is carried out between a deuterated compound which yields HD such as

$$H + CD_3OH \longrightarrow HD + \dot{C}D_2OH \qquad (37)$$
$$(k = 8 \times 10^4\ M^{-1}\ \text{sec}^{-1})^{43}$$

$$H + (CD_3)_2CDOH \longrightarrow HD + (CD_3)_2\dot{C}OH \qquad (38)$$
$$(k = 1 \times 10^7\ M^{-1}\ \text{sec}^{-1})^{11,43}$$

and another compound that either yields H_2 or no hydrogen at all. Measurements of the total yield of hydrogen and the isotopic composition H_2/HD give the relative rate constants for all the reactions involved in the competition (for details see, e.g., ref 11, 42, 43). The only complication in this work is the production of "molecular hydrogen" in a constant yield that should be taken into account.

Competition kinetics has also been used in experiments where the hydrogen atoms have been produced by methods other than radiolysis. A large number of rate constant measurements in aqueous solutions were carried out using hydrogen atoms produced in the gas phase by an electrodeless discharge and introduced into the solution in a stream of molecular hydrogen.[3] In these experiments nonvolatile products such as chloride,[7] ferrocyanide,[44] nitrite,[44] and cobaltous ions[45] were analyzed. Comparison of results obtained by this technique with those from irradiated solutions helped distinguish between H and e_{aq}^- and establish the interconversion of these species.[7] Rate constants determined by this method are based on competition with the H + H reaction and are usually in agreement with other determinations despite mechanistic difficulties.[44]

Another technique recently developed utilizes the photolysis of thiols[46,47] or of tert-butyl peroxyformate[48] to produce hydrogen atoms in solution. Different competition systems were examined in a way that the isotopic composition of the hydrogen evolved (HD/D_2) serves as a measure of the competition. These systems, however, seem to be extremely complicated and some of the complications have been discussed.[47] One drawback of this technique lies in the fact that one of the competing reactants is used as solvent, and, although in one experiment the addition of 50 mol % water did not change the result, one cannot expect an agreement between rate constants in dilute aqueous solutions and in a large variety of

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organic solvents. Another difficulty in this technique is the uncertainty as to what percentage of the H atoms react with the solvent as hot atoms, since no unreactive solvent is used which can effectively thermalize the H atoms before reaction. Despite these uncertainties the relative rate constants determined in these experiments[46-48] were usually in fair agreement with those measured by other techniques.

B. PULSE RADIOLYSIS METHODS

The pulse radiolysis technique has been used for the measurement of H atom rate constants both absolutely and by competition kinetics. Direct kinetic spectrophotometric observation of H atoms as they react is extremely difficult because of the very short wavelength of their absorption and their low extinction coefficient.[49] Absolute rate constant determinations were, therefore, made by observing the formation rate of a transient absorption resulting from H atom reactions. This method was successful with aromatic[5,24,26,27] and heterocyclic compounds,[29-31] where the H adducts absorb in the region of 300–400 nm, and with some inorganic ions such as silver.[32] The difficulty with many of these experiments is that e_{aq}^- and OH also react with the same solutes to give products with an absorption similar to that of the H adduct.[25] To eliminate interference by e_{aq}^-, measurements were carried out in acid solutions where the e_{aq}^- is readily converted into H (reaction 2). This method is, however, not applicable to neutral or basic media. The interference by OH is more serious and more difficult to overcome. An additional solute is necessary in many cases which would scavenge OH but not H. The compounds that fulfill this requirement best are tert-butyl alcohol and deuteriomethanol. The ratio between their rate of reaction with OH and with H is about 5000, and in most experiments corrections of only $\leq 10\%$ were necessary. Using these modifications the absolute rate constants for the reaction of H atoms with several aromatic compounds have been measured in acid solution by following the formation of the transients at their corresponding absorption maxima.[5,24,26,27] These measurements are the most accurate absolute determinations of H atom rate constants carried out to date and serve as a reference to put other relative rate constants on an absolute scale.

Compounds which do not form an easily observable absorbing transient by their reaction with H can be studied by competition kinetics. For example, the effect of added solutes on the optical density of the transients formed from reaction of H with p-nitrobenzoic acid[5,50] or with silver ions[32] was used to determine their relative rates of reaction with H atoms.

C. ELECTRON SPIN RESONANCE METHODS

The esr signals of hydrogen atoms are easily observable in irradiated aqueous solutions as a result of their enhancement by spin-polarization effects (i.e., nonequilibrium population of the electron-nuclear spin levels) which are present at times shortly after the H atom formation.[6,36,51,52] These signals decrease with time as a result of relaxation processes which are, because of the high degree of initial polarization,

essentially exponential in character. This relaxation can serve as an internal reference against which chemical rates can be measured competitively by observing the reduction in the esr signal caused by added solutes under steady-state conditions.[6] This method has provided rapid and accurate determinations of relative rate constants, and a large volume of data has been collected using this technique.[4,6,53,54]

The esr method can also be used for direct measurement of absolute rate constants if the time dependence of the H atom signal after a short pulse of radiation is followed in the presence of a reactive solute.[51,52] The range of applicability of this technique is, however, limited to cases where the pseudo-first-order rate is faster than the relaxation period of the polarization ($\sim$50 μsec) and slower than the spectrometer response ($\sim$1 μsec). Thus the steady-state method is applicable to a wider range of concentrations and rate constants than the pulse method. Only a few compounds have been studied by this latter method,[51,52] and the agreement between the two types of measurements is generally very good.

Both of these esr experiments have an advantage over all the previous techniques in that the hydrogen atoms are directly observed, and their disappearance is a direct measure of their reaction. It is not necessary to know the reaction mechanism or the nature of the species formed in order to measure the rate constant by esr. This method is, therefore, less prone to misinterpretation of results or to kinetic complications. Where several simultaneous reaction paths exist, one measures, however, the overall rate, and the information on the partial rates of the individual paths is not available.

V. Kinetics and Mechanism of Hydrogen Atom Reactions

The present article deals only with reactions in aqueous solutions, and no attempt is made to discuss hydrogen atom reactions in other media. A very large number of studies dealing with H atom reactions in gases and in organic solvents have been published. It should be mentioned, however, that in those cases where comparison is possible the rate constants in the gas phase were found to be more than an order of magnitude lower than those in aqueous solutions.[24,55] This effect is thought to result from the solvation of the solute or from the caging of the reactants. There are also indications that the rate constants in a hydrocarbon solvent[56] are lower than those in water, which might emphasize the solvation effects on both the solute and the H atom.

Rate constants for hydrogen atom reactions with several hundred compounds in aqueous solutions have been reported (e.g., ref 1, 4, 6), and some generalizations on the behavior of the H atom were suggested.[4,6,12,57] The effect of substituents on the reactivity of organic substrates is quite complex. A semiquantitative correlation was possible for a series of substituted benzenes.[53,58] For most other compounds, however, any attempt at correlation is made difficult by the fact that many of the substituent groups react directly with the H, and, therefore, their effect on abstraction cannot be estimated.

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Such substituents include the halogens, nitro, cyano, sulfur, and also the carboxyl, keto, and aldehydo groups in certain compounds as will be discussed below.

Discussion of the effect of structure on reactivity will be made for various groups on the basis of the reported rate constants. It is beyond the scope of this paper to summarize all the rate constants. The data available up to 1967 have previously been summarized[1] and a more complete current compilation is underway elsewhere.[59] To facilitate discussion, some representative rate constants are shown in Figure 1. Most of these rate constants have been determined by the steady-state *in situ* radiolysis–esr technique[4,6] and put on an absolute scale using the rate constants for benzoic acid determined by pulse radiolysis.[5] A few of the rate constants shown in Figure 1 have been determined only by other techniques, and these are marked by dashed lines. Many of the rates in Figure 1 have also been obtained by methods other than esr, and the agreement in most cases is quite satisfactory.

A. ALIPHATIC COMPOUNDS

In the homologous series of normal hydrocarbons, carboxylic acids, and alcohols, the rate constants increase with chain length and approach a plateau at $\sim 10^8$ M^{-1} sec^{-1}. It has been also noted that the effect of functional groups on the reactivity of the molecule toward H atoms decreases as the chain length increases because the hydrogen atoms adjacent to the functional group have only a small contribution to the overall reactivity of the long-chain molecule.[4,6]

It can be seen from the results for hydrocarbons and carboxylic acids that the methyl and the carboxyl groups by themselves are relatively very unreactive, i.e., $\leq 10^5$ M^{-1} sec^{-1}, so that where other reactive sites are present reaction is not expected to occur to any significant extent on the CH$_3$ or COOH group. This conclusion is also supported by results for the other groups of compounds. The CH$_2$ and CH groups are progressively more reactive ($k_{CH_3} \ll k_{CH_2} < k_{CH}$) as seen from both the carboxylic acid and the alcohol data. It has not been possible to assign partial reactivities for each of these groups and predict all of the experimental results. However, a fairly good agreement with many of the rate constants can be obtained if it is assumed that the partial reactivities of CH$_3$, CH$_2$, and CH are 0.1, 1, and 2 × 10^7 M^{-1} sec^{-1}.[4] These values yield a ratio of 1:15:60 for the relative reactivities of a primary, secondary, and tertiary hydrogen, respectively. Hydrogen atoms seem, therefore, to react more selectively in water than in organic solvent,[47] and they are also more selective than organic radicals toward abstraction.

Other generalizations supported by the results for carboxylic acids and alcohols are that the reactivity of the hydrogen atom to be abstracted is enhanced by a factor of ~ 1.6 by an OH or CH$_3$ group attached to the same carbon and is retarded by a factor of 1.5 by a OH or OR group at position β. These rules are based on the facts that ethanol and 1-propanol react with the same rates, that ethylene glycol, glycerol, and the sugars are, respectively, less reactive than ethanol, 2-propanol, and hexanol, and that tartaric is less reactive than malic acid.

The effect of the carboxyl group on the reactivity is more difficult to assess. At the first glance it is seen that the reactivities of acetic and malonic acids are similar to those of

methane, the reactivities of propionic and succinic acids to those of ethane, and the reactivities of butyric acid to that of propane. An attempt to assign to the carboxyl group a deactivating factor of two, based on comparison between lactic acid and 2-propanol, fails if one considers the reactivity of glycolic acid. Dissociation of a carboxyl group increases the rate of abstraction from position α by a factor of ~ 3.[54]

Representative rate constants for amines, amino acids, and derivatives are shown in the third column of Figure 1. All these rates were measured in acid solution where the amino group is protonated. The NH$_3^+$ group strongly deactivates adjacent hydrogen atoms. Thus glycine and alanine are two orders of magnitude less reactive than their hydroxylated analogs glycolic and lactic acids. The reactivity of the group $-CH(NR_3^+)COOH$ is very small, $\sim 10^5$ M^{-1} sec^{-1}, but the amino group exerts an effect also on the β and γ hydrogens. The β hydrogens are deactivated by a factor of ~ 10, judging from the very low reactivities of β-aminoethanol, β-alanine, and valine compared with those of ethanol, propionic acid, and isobutane, respectively. The low reactivity of leucine, where a tertiary hydrogen is in the γ position, demonstrates the deactivating effect of the NH$_3^+$ group even at this distant position. The same effect is also seen from the comparison of the rate constant of 1,6-hexanediamine with that of 1-hexylamine.

Since the effect of the amino group in acid solution appears to be caused mainly by its charge, this effect should be minimal when the amino group is acetylated so that it does not protonate at pH 1. Indeed, N-acetylglycine, glycylglycine, and N-acetylalanine are over an order of magnitude more reactive than glycine and alanine. These findings also indicate that the attack of the hydrogen atom is at the position α to NH rather than that α to NH$_3^+$ in glycylglycine. In line with these suggestions glycylglycylglycine is twice as reactive as glycylglycine and not three times.[4]

It is also expected that when the amino group is not protonated (in basic solutions) it will exert an activating effect on the abstraction instead of the strong deactivating effect shown by NH$_3^+$. This was experimentally verified for aniline[53] (see below) and aminoacetonitrile[54] and also for hydrogen abstraction by OH radicals.[60] Since the effect of dissociation of the carboxyl group causes only a small change in its deactivating effect and since the reactivity of the amino acids is mainly determined by the effect of the amino group, it can be expected that the reactivity of the zwitterion form (in neutral solution) will be only slightly higher than that of the acid form but much lower if it is compared with that of the basic form. Indeed, the rate constants for glycine, valine, aspartic acid, and glutamic acid are respectively only 1.1, 1.4, 3.6, and 3.3 times greater in neutral than in acid solution.[54]

B. REACTIVE FUNCTIONAL GROUPS

Certain functional groups were found to increase the reactivity of the molecule by their being targets for direct reaction with the H atoms. These groups include CN, CO, CHO, NO$_2$, and others. The cyano group for instance is expected to have a deactivating effect on the C–H bonds similar to that of the carboxyl group. Instead, it is found that acetonitrile and cyanoacetic acid are about an order of magnitude

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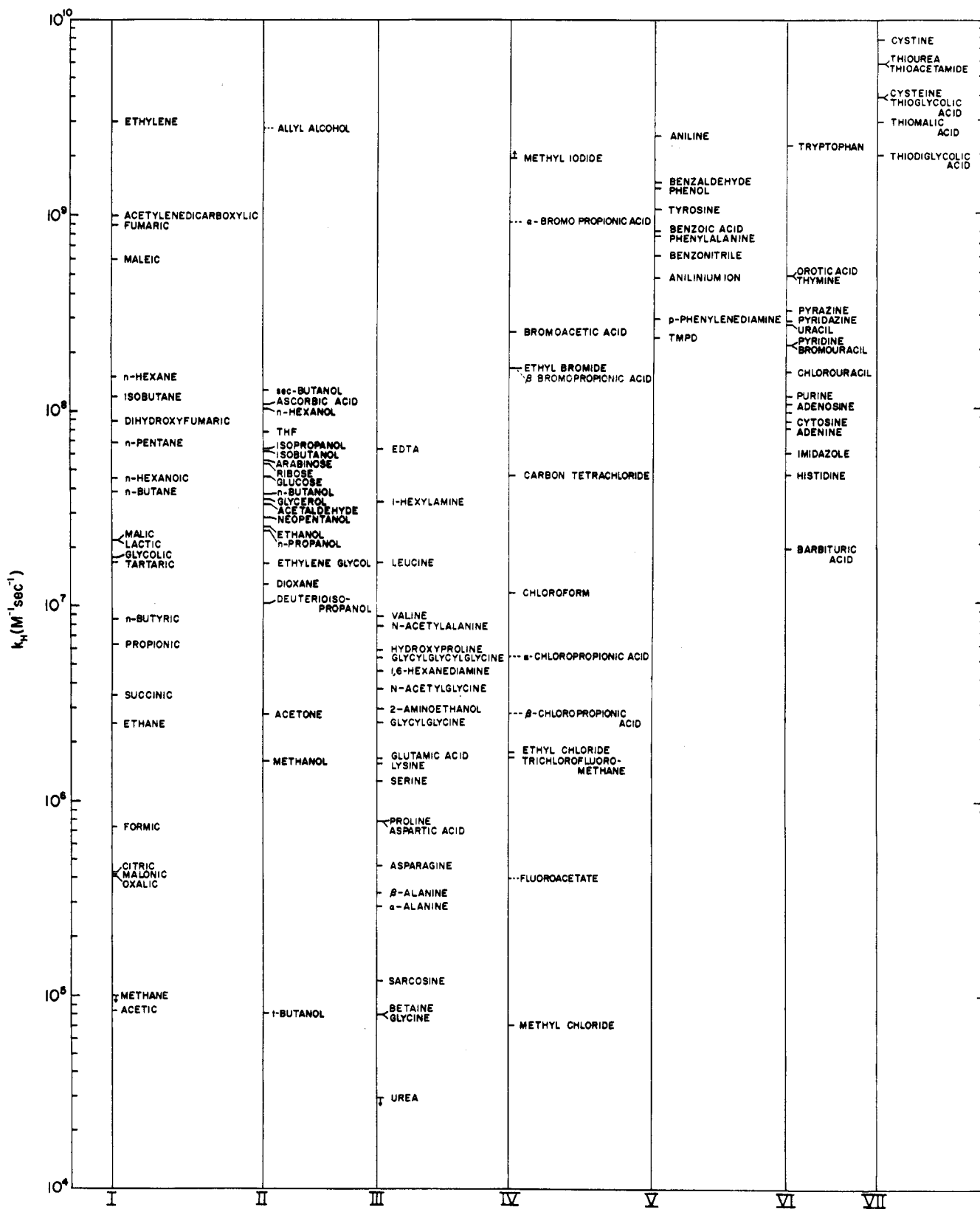
Figure 1. Representative rate constants for the reactions of hydrogen atoms with organic compounds in aqueous solutions. Most values were determined by the esr technique.[4,6,53] The values marked by dashed lines were determined by competition kinetics.[1] The columns include representative compounds of the following groups: (I) hydrocarbons and carboxylic acids; (II) alcohols, glycols, sugars, ethers, and carbonyl compounds; (III) amines, amino acids, and derivatives; (IV) halogen compounds; (V) aromatic compounds; (VI) heterocyclic compounds; (VII) sulfur compounds.
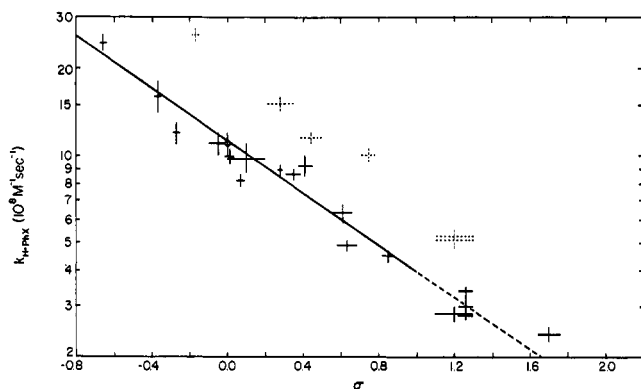
Figure 2. A plot of the rate constants for reaction of hydrogen atoms with substituted benzenes as a function of the Hammett substituent constant σ. The vertical lines represent the range of rate constants reported in ref 5, 24, 26, 53, and 58, and the horizontal lines represent the range between σ_{para} and σ_{meta} for the deactivating groups. For activating groups only σ_{para} were used.[53,58] The σ values are taken from C. D. Ritchie and W. F. Sager *Progr. Phys. Org. Chem.*, **2**, 323 (1964). The solid line represents $\log(k/1.1 \times 10^9) = -0.45\sigma$ for monosubstituted benzenes. The dotted line is an extension for disubstituted benzenes. The substituents shown in the figure by solid lines are in order of increasing average σ: NH_2, OH, OCH_3, COO^-, H, CH_2COOH, SO_3^-, $NHCOCH_3$, $CONH_2$, $OCOCH_3$, COOH, CN, NH_3^+, $N(CH_3)_3^+$, p-$(CN)_2$, o-, m-, p-$(NH_3^+)_2$, p-$(NH$-$(CH_3)_2^+)_2$. The substituents shown by dotted lines do not fit the Hammett plot and they are in order of increasing average σ: CH_3 (rate constant uncertain because of solubility difficulties); CHO, $COCH_3$, and NO_2 (direct reaction with these groups causes an increased rate constant); o- and m-$(CN)_2$ (additivity is not expected because both inductive and mesomeric effects are involved).

more reactive than acetic and malonic acid, respectively, with the reactivity of acetonitrile similar to that of methanol. This effect was explained by direct addition of the H atoms to the $C\equiv N$ bond[6,11] which was, in turn, confirmed by measuring the decrease in hydrogen yield[11] and by observing the H adduct by esr.[40]

The carbonyl group adds hydrogen atoms with a relatively low rate constant and contributes only 35% to the total reactivity of acetone.[11] The aldehyde group shows a much higher reactivity; acetaldehyde is 12 times more reactive than acetone.[6] Apparently hydrogen abstraction from this group must be important and will hopefully be checked experimentally. The nitro group scavenges H atoms rapidly, and the reactivities of nitro compounds, both aliphatic[6,61] and aromatic,[27,58] are much higher than expected for the rest of the molecule. It also appears that H addition to a nitro or a carbonyl group is enhanced by an adjacent aromatic ring.[53]

The reactivities of the halogen compounds largely depend on the halogen atom (Figure 1, column IV). Fluoroacetate undergoes H abstraction at a very low rate, but no fluorine abstraction could be detected.[12] Chloro compounds undergo chlorine abstraction and hydrogen abstraction at comparable rates.[7,12] Multiple chlorination enhances the total reactivity. $CHCl_3$ is 170 times and CCl_4 is 700 times more reactive than CH_3Cl.[6] Monobromo compounds react with H atoms to undergo mainly bromine abstraction ($\geq 98\%$)[11,12] with rate constants of the order of 10^8 M^{-1} sec^{-1}. Iodo compounds are all expected to be very reactive ($>10^9$ M^{-1} sec^{-1}) similarly to methyl iodide, and the contribution of hydrogen abstrac-

tion in these compounds is negligible compared to iodine abstraction. The effect of structure on the rate of halogen abstraction has been found[12] to be small (a factor of 5) for bromo compounds and much larger (>100) for chloro compounds, most probably because of the lower C–Br bond energy compared to that of C–Cl. The mechanism of these halogen abstraction reactions has been suggested to involve an atom transfer rather than a charge transfer because no correlation was found between the reactivities of e_{aq}^- and H with haloaliphatic compounds.[12]

Compounds containing sulfur in –SH, –S—S–, –S–, or C=S bonds react very rapidly with hydrogen atoms; all rate constants are very close to the diffusion-controlled limit (Figure 1, column VII). Variations of rate constants between these groups of compounds are relatively small. The –SH group undergoes H abstraction ($\sim 4 \times 10^9$ M^{-1} sec^{-1}), the –S—S– group forms –S + HS– ($\sim 8 \times 10^9$ M^{-1} sec^{-1}), and the C=S group adds H atoms ($\sim 6 \times 10^9$ M^{-1} sec^{-1}). These very high rate constants might contribute to the explanation of the radioprotective properties of sulfur-containing compounds.

Unsaturated hydrocarbons, alcohols, and acids add hydrogen atoms very rapidly. Although H abstraction from these compounds is feasible, its contribution to the overall rate is usually very small compared to the addition to the double bond. Some effect of substituents on the rate constant for addition can be noticed. It appears that a C=C bond bearing no functional groups on these carbons reacts very rapidly ($\sim 3 \times 10^9$ M^{-1} sec^{-1} for ethylene[6] and allyl alcohol[42,62]), substitution with two carboxyl groups lowers the rate constant (down to 9×10^8 M^{-1} sec^{-1} for fumaric and 6×10^8 M^{-1} sec^{-1} for maleic acid[4]), and substitution with two hydroxyl groups lowers the rate constant even further (to 9×10^7 M^{-1} sec^{-1} for dihydroxyfumaric acid and 1.1×10^8 M^{-1} sec^{-1} for ascorbic acid[4]).

C. AROMATIC COMPOUNDS

Aromatic compounds undergo H atom addition to the ring with relatively high rate constants. These compounds were studied by competition kinetics,[58] by pulse radiolysis,[5,24,26,27] and by esr.[53] Most rate constants determined by the various methods are in good agreement. An effect of substituents on the rate of reaction was found.[53,58] Trimethylanilinium ion, with a rate constant of 4.5×10^8 M^{-1} sec^{-1},[53] is the least reactive monosubstituted benzene while aniline, with a rate constant of 2.6×10^9 M^{-1} sec^{-1},[53] is the most reactive. The anilinium ion is only slightly more reactive than trimethylanilinium and a factor of 5 less than aniline itself. Disubstituted benzenes cover a wider range of rate constants; e.g., $N,N,$-N',N'-tetramethyl-p-phenylenediammonium ion has a rate constant of only 2.4×10^8 M^{-1} sec^{-1}.[53] Correlation of the rate constants for substituted benzenes with Hammett's substituent constants is shown in Figure 2 (partly presented in ref 53). This linear behavior [$\log(k/1.1 \times 10^9) = -0.45\sigma$] shows that the H atom attack on the aromatic ring exhibits a small but definite electrophilic character. Only several compounds deviate from this behavior, and these deviations can, in most cases, be explained by a direct reaction of H atoms with the substituent group. The aromatic nitro group reacts with H atoms directly, and as a result the rate constant for

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(62) A. Appleby, G. Scholes, and M. Simic, *J. Amer. Chem. Soc.*, **85**, 2370 (1963).

nitrobenzene is higher by a factor of $\sim$2 than expected from the Hammett plot. The aldehydo group of benzaldehyde most probably undergoes H addition quite rapidly, $\sim$5 $\times$ 10^8 M^{-1} sec^{-1}, judging from its deviation from the plot in Figure 2. Disubstitution shows additivity of the σ values for the case of the phenylenediammonium ions, as expected for substituents having inductive effect only, but the dicyanobenzenes show additivity only for the para isomer (Figure 2).

D. HETEROCYCLIC COMPOUNDS

Nitrogen heterocyclic compounds (Figure 1, column VI) react considerably more slowly than aromatic compounds. The rate for pyridine is only one-fifth that for benzene, in line with the expected retardation of electrophilic reactions by the ring nitrogen. The additional effect of a second nitrogen in position 3 is clear from the additional decrease observed for pyrimidine. Pyridazine and pyrazine, however, react more rapidly than pyridine because the effects of the nitrogens are partially cancelled when they are at positions 1,2 or 1,4. Other heterocyclic compounds shown in Figure 1 are of biological interest. Uracil has a rate constant three times higher than that of pyrimidine as a result of the substitution by two activating OH groups. Further activation seems to take place with methyl substitution; thymine and 6-methyluracil react more rapidly than uracil. Barbituric acid, however, reacts very slowly, and this fact was explained[4] by the presence of this compound in acid solution in a keto form which does not contain a 5,6 double bond, the site at which H atoms add to these pyrimidine bases. Barbiturate ion, on the other hand, has a rate constant 100 times greater than that of the acid.[54]

E. INORGANIC COMPOUNDS

Most of the known rate constants for inorganic compounds have been summarized previously,[1] and very few additional ones have been measured since then. Mechanistic studies on reactions of H with inorganic compounds are scarce. The most thorough investigation was done on complexes of cobalt.[45,63,64] From the rate constants for a series of complexes of the type $Co(NH_3)_5X^{n+}$, where X was a halogen or a pseudohalogen, it has been concluded that the mechanism of this reaction involves an atom transfer and not an electron transfer. Among the other inorganic substrates studied, the most reactive ones are Ag^+, Hg^{2+}, $Fe(CN)_6^{3-}$, MnO_4^-, CrO_4^{2-}, CN^-, N_3^-, Br_2, I_2, O_2, all reacting with a rate constant close to the diffusion-controlled limit, $\sim$$10^{10}$ M^{-1} sec^{-1}. Other inorganic compounds were found very unreactive, e.g., CO_2, N_2O, F^-, Ni^{2+}, Zn^{2+}.

H_2O_2 reacts only moderately with H with a rate constant of $\sim$$10^8$ M^{-1} sec^{-1}, in contrast with its fast reaction ($\sim$$10^{10}$ M^{-1} sec^{-1}) with e_{aq}^-.[1] Oxygen, on the other hand, reacts very rapidly with both H and e_{aq}^-.[1] The reaction of O_2 with e_{aq}^- is evidently a fast electron transfer process while that of O_2 + H is the addition reaction of a H atom to a biradical which again is a very fast process. Although the products are the acid and basic forms of the same species, their mechanism of formation is very different. In the case of H_2O_2 the reaction with e_{aq}^- is a reduction reaction leading to the formation of $H_2O_2^-$ as an intermediate which breaks down within $<$$10^{-10}$ sec to OH + OH$^-$. The reaction with H is a hydrogen

abstraction resulting in the formal oxidation of H_2O_2 to HO_2; therefore this is a much slower process as expected.

Another interesting difference is between nitrite and nitrate ions. The first reacts relatively rapidly with both H and e_{aq}^-, whereas nitrate reacts with H with a rate constant three orders of magnitude lower than that with e_{aq}^-.[1] The lower reactivity of H with NO_3^- is predictable if one remembers that the resonance structure of NO_3^- has relatively little π electron density in the N–O bond, which is required for the addition of a H atom. The observed slow rate is in accord with the reluctance of H atoms to react by an electron transfer mechanism. In fact, there is not a single well-established case where H atoms react as electron transfer donors.

The reactions of H with OH$^-$ and with F$^-$ are unique as they form a hydrated electron (reactions 23 and 24).

VI. Summary

The radiolysis of aqueous solutions seems to be the method most utilized for the study of H atoms. Besides the advantages of these systems already mentioned, i.e., the production of thermal H atoms in a homogeneous solution of an inert solvent, it should be pointed out that the various radiolysis techniques have been developed to a fairly precise science and can give reproducible quantitative results. Sufficient information has been collected from the study of aqueous solutions on reaction rates and products of reactions that it has become possible to predict with a fair degree of certainty the behavior of certain systems not yet studied.

The reactions of H atoms have already been studied with a large number of organic compounds, many of biological interest, and most systems are fairly well understood. Since most rate measurements were carried out in acid solutions, there is a need for additional studies in neutral solutions, especially of compounds that undergo an acid–base dissociation. Studies in alkaline solutions become complicated by the interference of the reaction of H with OH$^-$. Therefore, it would seem difficult to measure the rate constants for H with the basic forms of amines and amino acids with reasonable accuracy, although this rate is expected to be an order of magnitude higher than that of the acid forms.[54]

Comparisons have been made between reactions of H atoms and those of e_{aq}^-, OH, and organic radicals. The reactions of H and OH were found to follow the same pattern whenever hydrogen abstraction from an aliphatic compound[60] or addition to an aromatic ring take place.[65] The rate constants for abstraction are usually higher for OH than for H, and the selectivity of OH is lower. The isotope effect in the abstraction of H or D atoms from an aliphatic compound is also much larger for abstraction by H[43] than for abstraction by OH.[60] In their addition to an aromatic ring both H and OH behave as electrophiles, although the latter seems to have a more pronounced electrophilic character. Some functional groups react differently with H and OH mostly because of the redox properties of these radicals. Differences also exist between their reactivities toward inorganic compounds. By and large, H behaves as a reducing agent in these systems, but there are exceptions like the reaction of H with ferrous ions where an efficient oxidation takes place. In a way the H + OH$^-$ reaction may be looked upon as an acid–base process.

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(64) J. Halpern and J. Rabani, *J. Amer. Chem. Soc.*, **88**, 699 (1966).

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Table I

Rate Constants for the Reactions of Hydrogen Atoms with Organic Compounds in Aqueous Solutions[a]

Compound	Rate constant, $M^{-1}\,sec^{-1}$	Ref	Compound	Rate constant, $M^{-1}\,sec^{-1}$	Ref
Acetaldehyde	3.4×10^7	6	Dichloromethane	4×10^6	6
Acetamide	1.3×10^6	6	o-Dicyanobenzene	5.5×10^8	53
Acetanilide	1.1×10^9	53	m-Dicyanobenzene	5.2×10^8	53
Acetate (pH 7)	4.2×10^6	54	p-Dicyanobenzene	2.8×10^8	53
Acetic acid	8.4×10^4	6	Diethyl ether	4.7×10^7	6
Acetone	2.8×10^6	6	2,3-Dihydroxyfumaric acid	9×10^7	4
Acetonitrile	1.5×10^6	6	Dioxane	1.3×10^7	6
Acetophenone	1.2×10^9	53	Dithiodiglycolic acid	1.0×10^{10}	4
N-Acetylalanine	8.0×10^6	6	Ethane	2.5×10^6	6
N-Acetylglycine	3.8×10^6	6	Ethyl alcohol (pH 1, pH 7)	2.6×10^7	6, 54
Acetylenedicarboxylic acid	1.0×10^9	4	Ethyl bromide	1.7×10^8	6
Adenine	8.3×10^7	4	Ethyl chloride	1.8×10^6	6
Adenine (pH 7)	0.9–1.5×10^8	54	Ethylene	3×10^9	6
Adenosine	1.1×10^8	4	Ethylenediaminetetraacetic acid	6.5×10^7	4
Adenosine (pH 7)	1.4–2×10^8	54	Ethylene glycol	1.7×10^7	6
α-Alanine	2.9×10^5	6	5-Fluorouracil	1.8×10^8	4
β-Alanine	3.4×10^5	6	Formate (pH 7)	1.3×10^8	54
Aminoacetonitrile	6.6×10^6	54	Formic acid	7.4×10^5	6
Aminoacetonitrile (pH 7)	5.6×10^7	54	Formic acid (pH 0)	4.5×10^5	54
2-Aminoethanol	3.0×10^6	4	Fumaric acid	9×10^8	4
α-Aminoisobutyric acid	8×10^4	6	Glucose	4.7×10^7	4
Aniline	4.9×10^8	53	Glutamate (pH 7)	5.6×10^6	54
Aniline (pH 7)	2.6×10^9	53	Glutamic acid	1.7×10^6	4
Anisole	1.2×10^9	53	Glycerol	3.6×10^7	4
Arabinose	5.7×10^7	4	Glycine	8×10^4	6
Arginine	4.9×10^6	4	Glycine (pH 7)	9×10^4	54
Ascorbate (pH 7)	3–6×10^8	54	Glycolate (pH 7)	4.0×10^7	54
Ascorbic acid	1.1×10^8	4	Glycolic acid	1.8×10^7	6
Asparagine	4.7×10^5	4	Glycylglycine	2.6×10^6	4
Aspartate (pH 7)	2.9×10^6	54	Glycylglycylglycine	5.5×10^6	4
Aspartic acid	8×10^5	4	Guanidine	1.3×10^6	4
Barbiturate (pH 7)	2.0×10^9	54	Hexamethylenimine	1.5×10^7	4
Barbituric acid	2.0×10^7	4	Hexane	1.5×10^8	6
Benzaldehyde	1.5×10^9	53	1,6-Hexanediamine	4.7×10^6	4
Benzamide	8.9×10^8	53	Hexanoate (pH 7)	5.3×10^7	54
1,3,5-Benzenetricarboxylic acid	6.5×10^8	6	Hexanoic acid	4.6×10^7	6
Benzoate (pH 7)	9.2×10^8	54	Hexyl alcohol (pH 1, pH 7)	1.0×10^8	6, 54
Benzoic acid	8.5×10^8	6	Hexylamine (pH 1, pH 7)	3.5×10^7	4, 54
Benzonitrile	6.4×10^8	53	Hippuric acid	1.0×10^9	4
Benzyl alcohol	1.1×10^9	53	Histidine	4.8×10^7	4
Betaine	8×10^4	4	Histidine (pH 3)	5.1×10^7	54
Bromoacetic acid	2.6×10^8	6	Histidine (pH 7)	2.5×10^8	54
5-Bromoorotic acid	2.1×10^8	4	4-Hydroxyproline	6.0×10^6	4
5-Bromouracil	2.2×10^8	4	Imidazole	6.2×10^7	4
Butane	3.9×10^7	6	Iminodiacetic acid	4.0×10^6	4
Butyl alcohol	3.8×10^7	6	Isobutane	1.2×10^8	6
sec-Butyl alcohol	1.3×10^8	6	Isobutyl alcohol	6.4×10^7	6
tert-Butyl alcohol	8×10^4	6	Isobutyrate (pH 7)	5.9×10^7	54
Butyric acid	8.6×10^6	6	Isobutyric acid	2.6×10^7	6
Carbon tetrachloride	4.8×10^7	6	Isobutyronitrile	2.2×10^7	6
Chloroform	1.2×10^7	6	Isoleucine	8×10^6	4
Chlorotrifluoromethane	$<10^6$	6	Isoorotic acid	9×10^7	4
5-Chlorouracil	1.6×10^8	4	Isopropyl alcohol	6.5×10^7	6
Citric acid	4.3×10^5	4	Isopropyl-d_7 alcohol	1.05×10^7	6
Cyanoacetic acid	3.2×10^6	6	Lactic acid	2.2×10^7	6
Cyclohexane	3×10^7	6	Leucine	1.7×10^7	4
Cyclopentane	3×10^7	6	Lysine	1.6×10^6	4
Cyclopropane	7×10^5	6	Maleic acid	6×10^8	4
Cysteine	4×10^9	4	Malic acid	2.2×10^7	4
Cystine	8×10^9	4	Malonic acid	4.2×10^5	6
Cytosine	9×10^7	4	Methane	$<10^5$	6
Cytosine (pH 7)	1.0–1.5×10^8	54	Methyl alcohol (pH 1, 7)	1.6×10^6	6, 54
Dichlorodifluoromethane	$<10^6$	6	Methyl chloride	7×10^4	6

Table I (Continued)

Compound	Rate constant, $M^{-1} sec^{-1}$	Ref	Compound	Rate constant, $M^{-1} sec^{-1}$	Ref
Methyl iodide	$\geq 2 \times 10^9$	6	Pyridine	2.2×10^8	53
6-Methyluracil	7×10^8	4	Pyridine (pH 7)	6.5×10^8	54
Neopentyl alcohol	2.9×10^7	6	Pyrimidine	1.0×10^8	4
Nitrilotriacetic acid	7.5×10^6	4	Ribose	5.5×10^7	4
Nitromethane	4.4×10^7	6	Sarcosine	1.2×10^5	4
Orotic acid	5×10^8	4	Serine	1.3×10^6	4
Oxalate (pH 7)	$\leq 4 \times 10^4$	54	Succinate (pH 7)	1.1×10^7	54
Oxalic acid	4.1×10^5	6	Succinic acid	3.5×10^6	6
Pentane	7×10^7	6	Tartaric acid	1.7×10^7	6
Phenol	1.4×10^9	53	Tartronic acid	2.3×10^7	4
Phenyl acetate	8.6×10^8	53	Tetrahydrofuran	7.8×10^7	6
Phenylacetic acid	9.6×10^8	53	N,N,N',N'-Tetramethyl-p-	2.4×10^8	53
Phenylalanine	8.0×10^8	4	phenylenediamine		
o-Phenylenediamine (pH 0)	2.8×10^8	53	Thioacetamide	6×10^9	4
o-Phenylenediamine	7.3×10^8	53	Thiodiglycolic acid	2×10^9	4
o-Phenylenediamine	1.6×10^9	53	Thioglycolic acid	4×10^9	4
(pH 4.2)			Thiomalic acid	3×10^9	4
m-Phenylenediamine	3.4×10^8	53	Thiourea	6×10^9	4
p-Phenylenediamine	3.0×10^8	53	Threonine	8×10^6	4
Proline	8×10^5	4	Thymine	5×10^8	4
Propane	2.2×10^7	6	Trichlorofluoromethane	1.7×10^6	6
Propionate (pH 7)	1.8×10^7	54	Trimethylanilinium	4.5×10^8	53
Propionic acid	6.4×10^6	6	Tryptophan	$\geq 2.3 \times 10^9$	4
Propionitrile	1.1×10^7	6	Tyrosine	1.1×10^9	4
Propyl alcohol	2.5×10^7	6	Uracil	2.8×10^8	4
Purine	1.2×10^8	4	Urea	$<3 \times 10^4$	6
Pyrazine	3.3×10^8	53	Valine	9×10^6	4
Pyridazine	2.9×10^8	53	Valine (pH 7)	1.3×10^7	54

a Determined by the esr technique. Solutions at pH 1 unless otherwise stated.

The H atoms in aqueous solutions appear to be more selective than organic radicals, probably because of the slightly electrophilic nature of H.

The reactions of H parallel those of e_{aq}^- only to a limited extent because the latter are pure electron transfer reactions whereas H atoms can react both by electron transfer and mainly by atom transfer. Differences between these two reactants, which may be considered as the acid and base of the same species, were found for several inorganic compounds (mainly cobalt complexes), for aromatic compounds, for halo-aliphatic and other aliphatic compounds, but it is beyond the scope of the present article to discuss these studies.

For a summary of the rate constants for the reactions of hydrogen atoms with organic compounds in aqueous solutions, determined by the esr method, see Table I.