are well defined and that β is independent of ion energy as previously reported.[21] The only major sources of error are in the time interval measurement, which should be accurate to better than $\pm 5\%$, and in the determination of the concentration of reactant gas in the reaction region, which is probably accomplished within the same uncertainty. The absolute rate constant of $1.00 \pm 0.08 \times 10^{-9}$ cc sec^{-1} derived from these measurements is in good agreement with the value $1.09 \pm 0.09 \times 10^{-9}$ cc sec^{-1} reported by other investigators.[21]

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Rate Constants for Reaction of Hydrogen Atoms with Aromatic and Heterocyclic Compounds. The Electrophilic Nature of Hydrogen Atoms[1]

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Abstract: Rate constants for the reaction of H atoms with aromatic and nitrogen heterocyclic compounds in aqueous solutions have been measured by a steady-state *in situ* radiolysis–esr method. The rate constants for the aromatic compounds investigated vary between 2.4 and 26×10^8 M^{-1} sec^{-1} and those for the heterocyclic compounds between 0.6 and 3.3×10^8 M^{-1} sec^{-1}. Electron-donating substituents enhance the rate and electron-withdrawing groups retard the rate, qualitatively indicating an electrophilic character for the reaction. Correlation of the rate constants for a series of monosubstituted benzenes with Hammett's substituent constants shows a reasonably linear behavior ($\log k = 9.04 - 0.45\sigma$). Additivity of the σ constants was tested for the case of the acid form of the phenylenediamines and for the dicyanobenzenes. In the first instance the rate constants for all three isomers were found to be about one-half that for the anilinium ion, as expected from the Hammett plot. Additivity fails, however, in the case of the dicyanobenzenes where the rate constants for the three derivatives differ by a factor of two and those for the ortho and meta isomers are only slightly less than for cyanobenzene itself. In the case of pyridine the introduction of a nitrogen atom into the aromatic ring causes a considerable decrease in the rate constant. The effect of a second nitrogen atom is dependent on the position. The rate for pyrimidine is lower while the rates for pyridazine and pyrazine are higher than that for pyridine. These findings appear to reflect a reinforcement of the electron-withdrawing effect of the nitrogen atoms when they are in the 1 and 3 positions but a partial cancellation in the 1 and 2 or 1 and 4 positions.

It is known that, in general, aromatic compounds react with hydrogen atoms with rate constants of the order of 10^9 M^{-1} sec^{-1} and that the predominant pathway of this reaction is the addition to the aromatic ring.[2–8] Studies have been carried out by pulse radiolysis methods in which the formation of the cyclohexadienyl type radical was directly observed,[2–5] by competitive methods[6,7] and by a steady state esr method recently developed in these laboratories.[8,9] The former type of study specifically examines the addition reaction while the latter measures the total rate, but for most aromatic systems abstraction contributes little and the two types of measurements should give very similar rate constants. A previous intercomparison[6] of the relative rate constants for reaction of hydrogen atoms with the substituted aromatic compounds indicated that these rate constants could be correlated with the Hammett substituent constants and suggested an electrophilic behavior for the H atom in its attack on the aromatic ring. The rate constants measured were, in general, lower for compounds which had strong electron-withdrawing groups. These measurements were, however, made by a competitive method at pH 7 where the hydrogen atom yield is low and where precise measurements are difficult. The range of variation of rate constants was small and the deviations from a simple Hammett plot were relatively large. Recent pulse measurements, while generally giving rate constants which agreed with the competitive study, are not sufficiently extensive to corroborate the above suggestion. More detailed observations on the effect of substituents on the rate of reaction of hydrogen atom with aromatic systems are obviously in order. While either chemical competitive

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(1) Supported in part by the U. S. Atomic Energy Commission.

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or pulse methods, in their current refinements, could undoubtedly also furnish the desired information it was decided, for a number of reasons, to undertake a systematic survey by means of the steady-state radiolysis esr method.[9] These studies have also been extended to a number of nitrogen heterocyclic compounds.

Experimental Section

The experiments at pH 1 reported here are essentially identical in type with those previously reported on aliphatic systems.[8,9] The instrumentation involved is identical with that described in the work of Eiben and Fessenden.[10] In certain instances measurements were made both at higher and at lower pH. For experiments at pH values between 0 and 3 an appropriate concentration of perchloric acid was added and the H atoms were produced by the reaction of e_{aq}^- with H^+. Experiments at pH 4-7 were carried out in a 0.08 *M* phosphate buffer ($H_2PO_4^- + HPO_4^{2-}$) and H atoms produced by the reaction of e_{aq}^- with $H_2PO_4^-$. The details of this latter experiment will be described separately.[11] In all cases parallel measurements on ethanol were made and the rate constants reported here are based on an absolute rate constant for ethanol of 2.5×10^7 M^{-1} sec^{-1} at all pH values.[12] In most cases appropriate amounts of a 10^{-2} *M* stock solution were added to the solution under study after determining the signal in the absence of solute. The dicyanobenzenes have only limited solubilities so that in their case the concentration was determined by spectrophotometric measurements.

The rate constants measured here are all very high and therefore had to be measured in very dilute solutions. In general they were measured under conditions where the signal was reduced to ~10% of that in the absence of solute. For solutes which react with a rate constant of 1×10^9 M^{-1} sec^{-1} the solute concentration was only ~10^{-4} *M*. Depletion did not cause any apparent problem at low beam current. For solutes less reactive than 10^9 M^{-1} sec^{-1} the accuracy of the relative rates is believed to be of the order of the reproducibility of the measurements which was ~10% (see ref 8 and 9). Depletion becomes an increasingly important problem with increased reactivity above 10^9 M^{-1} sec^{-1}. This problem would be manifest as an excessively low apparent rate constant. The higher rate constants given in Table I should, therefore, be regarded as lower limits. This difficulty is especially true of the measurement on aniline at pH 7 where the signal available to be examined was only ~50% of that at lower pH (see ref 11).

The solutes used were of the purest grade available commercially and the source of each is indicated in Table I. Impurities might result in apparently high rate constants. However, because the reactions under consideration are very fast it seems unlikely that reaction with impurities can cause any significant effect on the observed rates.

Results and Discussion

The rate constants determined at pH 1 for various derivatives of benzene are given in Table I. For the monosubstituted derivatives they vary from 4.5 for trimethylanilinium ion to 15×10^8 M^{-1} sec^{-1} for benzaldehyde. Aniline was measured both at pH 1, where it is present as the anilinium ion, and at pH 7, where it is in the basic form. The rate constants were respectively 4.9 and 26×10^8 M^{-1} sec^{-1}. Except for phenol the relative rate constants given here agree with those reported from a competitive study at pH 7,[6] within the relatively large error which must be assigned to this previous work.

Of the compounds reported in Table I absolute measurements by pulse radiolysis methods have previously been reported on phenol (18×10^8 M^{-1} sec^{-1}),[3] acetophenone (11×10^8 M^{-1} sec^{-1}),[2] phenylacetic acid (10×10^8 M^{-1} sec^{-1}),[2] benzoic acid (10×10^8 M^{-1} sec^{-1}),[2] and benzonitrile (6.8[2] and 3.1[13] $\times 10^8$ M^{-1} sec^{-1}). Except for the latter value for benzonitrile there is good agreement between the results of the present measurements and the pulse radiolysis measurements. This agreement is gratifying since the pulse method, in which the absorption of the hydrogen adduct was observed, required the presence of a scavenger to selectively eliminate the OH which would otherwise interfere by giving a product radical with a similar absorption spectrum. In all of the pulse experiments significant corrections had to be applied because this selectivity could not be made complete. The esr method is unquestionably more direct and less subject to artifacts which can result from insufficient understanding of the detailed kinetics.

Table I. Rate Constants for the Reactions of Hydrogen Atoms with Aromatic and Heterocyclic Compounds at pH 1

Compd	Rate constant $\times 10^{-8}$ M^{-1} sec^{-1} Present work[a]	Pulse radiolysis data[b]
Aniline[c,d]	26[c]	
Benzaldehyde[e]	15	
Phenol[e]	14	18
Anisole[d]	12	
Acetophenone[f]	12	11
Benzyl alcohol[e]	11	
Benzene		11
Acetanilide[d]	11	
Nitrobenzene		10.4
Phenylacetic acid[d]	9.6	10.1
Benzamide[d]	8.9	
Phenyl acetate[d]	8.6	
Benzoic acid[e]	8.5	10.0
Benzenesulfonic acid		8.2
Benzonitrile[g]	6.4	6.8
Anilinium ion[h]	4.9	
Trimethylanilinium ion[h]	4.5	
o-Dicyanobenzene[d]	5.5	
m-Dicyanobenzene[d]	5.2	
p-Dicyanobenzene[d]	2.8	
o-Phenylenediamine[h]	2.8[i]	
m-Phenylenediamine[h]	3.4	
p-Phenylenediamine[h]	3.0	
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine[h]	2.4	
Pyridine[e]	2.2	
Pyridazine[j]	2.9	
Pyrimidine[k]	1.0	
Pyrazine[j]	3.3	
Imidazole[k]	0.62	
Purine[k]	1.2	

[a] From relative rates determined by esr. [b] Absolute rates taken from ref 2, except phenol (ref 3) and benzene (ref 4). [c] Measured at pH 7 by use of phosphate (see text). [d] Eastman Organic Chemicals. [e] Baker Analyzed Reagent. [f] Fisher Certified Reagent. [g] Baker Grade Reagent. [h] Eastman Organic Chemicals; in the form of hydrochloride or dihydrochloride. [i] Measured at pH 0. The values measured at pH 1, 2.0, 3.1, and 4.2 were, respectively, 7.3, 10, 11, and 16 (see text). [j] Aldrich Chemical Co. [k] Cyclo-Chemical Division, Travenol Laboratories.

It is readily seen in Table I that strong electron-donating groups such as NH_2 accelerate whereas strong electron-withdrawing groups such as NH_3^+ decelerate the rate of the hydrogen atom addition to the ring. We have attempted in Figure 1 to correlate the reaction rate with the electron density on the ring, using as a semiquantitative measure of the latter the Hammett sub-

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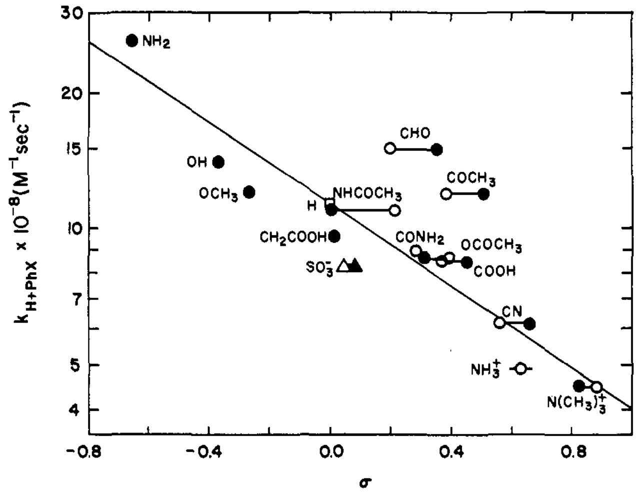

Figure 1. A plot of the rate constants for reaction of hydrogen atoms with monosubstituted benzenes as a function of the Hammett substituent constants σ. The values of σ_{para} (●) and σ_{meta} (○) were taken from ref 14 and used as discussed in the text. The rate constants for benzene (□) and benzenesulfonic acid (△) were taken from ref 4 and 2, respectively.

stituent constant σ. The values of σ used in Figure 1 were taken from the summary by Ritchie and Sager.[14] For substituents with a deactivating effect (positive σ values) both σ_{meta} and σ_{para}, which are in most cases similar, are plotted in Figure 1. For substituents with an activating effect only σ_{para} was used because the contribution of σ_{meta} is very small in these cases. This choice of σ values is made also because in the case of the activating substituents the reaction is expected to take place mainly in the ortho and para positions, whereas in the case of the deactivating substituents addition of the hydrogen atoms could be expected to take place at all positions more or less statistically.[15] It should be pointed out, however, that σ values relate normally to a reaction on the side chain. Although in this case the reaction is on the ring itself, the Hammett correlation is used and is expected to help in drawing general conclusions about the polar nature of the reaction but is not expected to yield detailed quantitative agreement.

Except for the two carbonyl compounds studied, the points in Figure 1 appear to obey a Hammett plot reasonably well. The linear relationship of the figure can be expressed by the equation

$$\log (k/1.1 \times 10^9) = -0.45\sigma \qquad \text{(I)}$$

The general decrease in reactivity with increase in σ value is taken to demonstrate a small but definite electrophilic nature in the attack of the hydrogen atoms on the aromatic ring. While the slope of the plot is not pronounced it must be remembered that the rates are of the order of 10% of the diffusion-controlled limit so that even small changes reflect a significant change in the nature of the reactants. The value of ρ (= -0.45) determined here is somewhat lower than the value -0.7 previously given.[6] The reaction of OH radicals with aromatic compounds has a similar value of ρ (-0.4 to -0.5)[16,17] although the absolute rate constants are about seven times higher.[17] This fact would indicate that the reactions of hydrogen atoms are less sensitive than the reactions of OH to the electron density around the aromatic nucleus.

Pryor and Henderson[18] have recently determined the effect of substituents on the relative rates of hydrogen abstraction from the methyl group of a series of substituted toluenes. They conclude that the rate is not strongly affected by substitution (a 25% difference between *m*-fluorotoluene and *m*-xylene was reported) and give a ρ value of -0.13. If a comparison with the present study is valid this indicates that the effect of substitution is magnified considerably when the reaction takes place on the ring itself. It should be pointed out that Pryor and Henderson's measurements were made in organic solvents. There are a number of indications, however, that the rates of hydrogen atom reactions in water are considerably greater than those in the gas phase[4,19] and in organic solvents[20] so that comparison of the two sets of results is extremely tenuous.

The constant 1.1×10^9 in eq I represents the rate for the unsubstituted system, *i.e.*, benzene. Sauer and Ward[4] have reported a rate constant for benzene of 1.1×10^9 M^{-1} sec^{-1} from direct observations on the production of cyclohexadienyl radical in pulse experiments. Michael and Hart[7] report a somewhat lower value of 0.53×10^9 M^{-1} sec^{-1} obtained from more indirect experiments. The rate constant for benzene-sulfonic acid which would be predicted from eq I is 1.05×10^9 M^{-1} sec^{-1} in good agreement with the absolute value of 0.82×10^9 M^{-1} sec^{-1} previously determined.[2] A discrepancy exists, however, in the case of nitrobenzene where values of 1.04 and 5.6×10^9 M^{-1} sec^{-1} have been reported[2,5] from pulse measurements as compared to a value of 0.5×10^9 M^{-1} sec^{-1} expected from the strong deactivating effect of the nitro group ($\sigma_{meta} = 0.71$ and $\sigma_{para} = 0.78$).[14] The relatively high rate for the reaction of H atoms with nitrobenzene has previously been noted[2,6] and ascribed to a direct reaction with the nitro group. A contribution of the nitro group of about 0.5×10^9 M^{-1} sec^{-1} to the total reactivity is suggested. It has since been observed, however, that in aliphatic compounds the nitro group is not particularly reactive. For example, a rate constant of only 4.4×10^7 M^{-1} sec^{-1} is observed for reaction of nitromethane.[9] The apparent high reactivity of a nitro group in the aromatic systems, if real, must be a result of its activation by the aromatic nucleus. A similar situation appears to exist for benzaldehyde and acetophenone, both of which lie above the values predicted from eq I by about 0.5×10^9 M^{-1} sec^{-1}. Since the carbonyl group is relatively unreactive toward H atom addition in aliphatic compounds (rate constants of only 2.8×10^6 and 3.4×10^7 M^{-1} sec^{-1} are observed for reaction of H atoms with acetone and acetaldehyde respectively),[9] an activating effect of the aromatic nucleus on the carbonyl group must exist for this excess reactivity to be attributed to reaction with the substituent.

Disubstituted Compounds. Two series of disubstituted compounds were examined, the phenylenedi-

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amines and the dicyanobenzenes. Because of the large difference between the acid and the basic form of the amino group, measurements had to be made at pH 0 in the case of *o*-phenylenediamine where the first p*K* is below 2.[21] The first p*K* values of the meta and para isomers are, respectively, 2.7 and 3.3[21] so that these substances are, as far as the kinetics are affected, completely protonated at pH 1. In all three cases the rate constant of the fully protonated form was found to be $\sim 3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. If one assumes that the σ values are additive a value of $3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ is predicted from eq I and only a very slightly lower value would be predicted if the experimentally measured value for NH_3^+ is used. In this case the effect of electron withdrawal by the NH_3^+ appears to be additive. A similar effect is seen in the correspondence between the value of $2.4 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ determined for tetramethylphenylenediamine at pH 1 and the predicted value, $\sim 2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$.

If one assumes additivity, a rate constant of $3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ is predicted for the case of the dicyanobenzenes. While the rule of additivity does appear to hold in the case of *p*-dicyanobenzene it breaks down in the cases of the ortho and meta isomers which are twice as reactive as the para derivative and only slightly less reactive than benzonitrile itself.

The rates for phenylalanine and its *p*-hydroxy derivative have previously been measured by this esr method.[8] The respective rate constants are 8 and $11 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. The relative rates are about in the ratio of 1.5 expected from Figure 1 for OH substitution. In both cases there is little effect of the amino acid group on the rate of H addition to the ring although a substantial effect has been noted on the rate of abstraction from aliphatic systems.

Pulse radiolytic measurements have been made on three disubstituted benzenes.[2] The rate measured for *p*-hydroxybenzoic acid ($14.5 \times 10^8\ M^{-1}\ \text{sec}^{-1}$) is slightly higher than the value of $11 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ expected from the rule of additivity. The rates for *p*-chlorobenzoic acid ($11.3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$) and *p*-nitrobenzoic acid ($9.8 \times 10^8\ M^{-1}\ \text{sec}^{-1}$) are, however, two and three times the expected rates of 6 and $3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. Additivity appears to break down here although the latter may reflect an increased reactivity similar to that noted above for nitrobenzene.

pH Effects in the Aromatic Amines. The rate observed for the reaction of H atoms with aniline is strongly pH dependent. The basic form is five times more reactive than the acid form. This fact is as expected since the NH_2 group has a large negative σ value whereas that for the NH_3^+ group is positive. A ratio of the two forms of approximately 4 is indicated from the difference in σ values of 1.29. This effect of pH on the rate constant should be even more pronounced in the case of the phenylenediamines. If additivity is assumed, neutralization of the first NH_3^+ group should increase the rate from 3 to $11 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ and neutralization of the second NH_3^+ group to $\sim 45 \times 10^8\ M^{-1}\ \text{sec}^{-1}$. Rates in the latter region, which are expected at pH >5, are difficult to measure accurately by the present method. The pH effect on the rate of H atom reaction with *o*-phenylenediamine was studied over the range of pH 0–4. A plateau value of $10\text{–}11 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ was observed over the pH range of 2–3 which is as expected if the reacting substance is $H_2N\text{–}C_6H_4\text{–}NH_3^+$. The rate observed at pH 1 ($7.3 \times 10^8\ M^{-1}\ \text{sec}^{-1}$) corresponds to approximately 50% protonation of the second amino group and suggests that the p*K* is indeed close to 1. The rate observed at pH 4.2 ($16 \times 10^8\ M^{-1}\ \text{sec}^{-1}$) should have about 30% contribution from $H_2N\text{–}C_6H_4\text{–}NH_2$. The calculated rate at pH 4.2 is $21 \times 10^8\ M^{-1}\ \text{sec}^{-1}$ if the rate for reaction with $H_2N\text{–}C_6H_4\text{–}NH_2$ is as high as was suggested above. It is very likely, however, that this limiting rate is in fact somewhat lower either because additivity does not hold or because the rate is approaching very near to the diffusion-controlled limit.

Nitrogen Heterocyclic Compounds. It is seen in Table I that the rate constant for pyridine is $2.2 \times 10^8\ M^{-1}\ \text{sec}^{-1}$, *i.e.*, only $^1/_5$ that for benzene. The presence of nitrogen in the ring strongly retards the addition reaction. The three related dinitrogen heterocyclic compounds were also studied. The reinforcing effect of a second nitrogen in position 3 is demonstrated by the low rate observed for pyrimidine. The other two isomers, however, exhibit rates which are faster than that of pyridine. Apparently the retarding effect of the nitrogen atoms are partially cancelled when the two are present in the 1,2 or the 1,4 positions. These effects are taken to also indicate that the rate of the hydrogen atom reaction is controlled, to some extent at least, by details of the electron density distribution in the system with which it is reacting.

The rates for imidazole and purine are also given in Table I. The rates for uracil and a number of other pyrimidine and purine bases are given in Table III of ref 8. The observed rates are mostly of the order of $10^8\ M^{-1}\ \text{sec}^{-1}$, again indicating the strong retarding effect of a heterocyclic nitrogen atom on the H atom addition rate.

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