in eq 9. The diffusion coefficient of e_s^- is similar to that of RO⁻, and that of NO₃⁻ is similar to Cl⁻³⁶ The values of ηD of e_s⁻ and Cl⁻, reflected in $\eta \lambda_0$ (Figure 7), change with solvent composition. We conclude that the values of r_e and $r_{NO_3^-}$ are larger in ethanol than in water and that the reaction radius $(R_e + R_{NO_1})$ is also larger in ethanol by a similar factor. A larger reaction radius in an alcohol than in water might be necessitated by the fact that both e^- and NO₃⁻ are solvated by the hydroxy ends of the molecules, and when the two solvated species come together, they are buffered by the alkyl groups. The same effect might explain the larger effective radii for diffusion.

Summary

1. Reports that the diffusion coefficients of solvated electrons are approximately equal to those of RO⁻ ions in alcohols^{3,13} are supported by analysis of electron reaction rate constants in these solvents

2. The dielectric permittivity and viscosity of the solvent each affect the rate constant of electron reaction with both charged and noncharged solutes. However, the variation of electron mobility with solvent dielectric permittivity is much smaller than suggested earlier.²⁴

3. The effective radii of solvated electrons for diffusion (Stokes) and for reaction with NO_3^- ions are both larger in ethanol than in water. This is related to the solvation structures of e⁻ and NO₃⁻ in these solvents.

Further Work

A better understanding of diffusion of the electrons and solutes through the solvents, and of solvent rearrangement about the reacting pair, requires information about rotational relaxation times of the solvent molecules. Measurement of relaxation times in mixed solvents would be particularly fruitful.

Rate Constants and Mechanism for the Reaction of Hydrogen Atoms with Aniline

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The hydrogen atom induced decomposition of aniline was studied by using a heated single-pulse shock tube. Hydrogen atoms were generated from hexamethylethane decomposition at sufficiently high aniline to hexamethylethane concentration so that the main reactions were abstraction of the amine hydrogen and displacement of the amino group. The rate expressions are $k_{a}(H+C_{6}H_{5}NH_{2}\rightarrow C_{6}H_{5}NH+H_{2}) = 1.8 \times 10^{11} \exp(-5846/T) L/(mol s) \text{ and } k_{d}(H+C_{6}H_{5}NH_{2}\rightarrow C_{6}H_{6}+NH_{2}) = 2.2 \times 10^{10}$ exp(-3735/T) L/(mol s) over the temperature range of 1000-1140 K and at pressures near 3.3 atm of argon. These rate expressions are compared to earlier results on toluene and phenol.

Introduction

This is the third of a series of papers on the mechanisms and rates of hydrogen atom attack on substituted aromatic compounds. Previously, we reported on the reactions of hydrogen atoms with toluene¹ and phenol.² In each of these systems the reaction paths are abstraction of the hydrogen from the substituent and the displacement of that moiety. These studies demonstrated that through final product analysis and under conditions which can be uniquely generated in a single pulse shock tube definitive results on the rate constants and expressions for these reactions can be obtained. We now consider the analogous reactions with aniline. For the abstraction process the main interest is the effect of the resonance stability of the anilino radical on the rate constants and rate expressions. In the case of displacement, the thermochemistry and the larger A factor for expulsion of the amine from the cyclohexadienyl adduct (compared to H-atom ejection) cause virtually every hydrogen addition to lead to displacement. This site-specific rate constant contrasts with that of lower temperature studies, where addition to all the sites³ can occur, and it is difficult to make an unambiguous interpretation of the mechanism. At the temperatures of this study, addition to a nonsubstituted site would be immediately reversed since the cyclohexadienyl radical is unstable at our temperatures.⁴

The methodology involves carrying out experiments on the decomposition of trace quantities of hexamethylethane in the presence of a large excess of aniline. Under ideal limiting conditions, the hydrogen atoms must react exclusively with the aniline. Any other reactive radical that is generated during the hydrogen

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atom induced decomposition of the aniline can also react with aniline. The result is the generation of large quantities of the most stable and unreactive radical, the anilino radical. At the concentration levels of concern here the anilino radical cannot react with the hexamethylethane. The mechanism for hexamethylethane decomposition⁵ is known to involve the cleavage of the weakest carbon-carbon bond leading to the formation of tert-butyl radicals followed by their rapid decomposition to form isobutene and a hydrogen atom. The rate expression for this rate-limiting process is

$$k(C_8H_{18} \rightarrow 2t - C_4H_9) = 3 \times 10^{16} \exp(-34500/T)/s = k_{dec,hex}$$

Thus every isobutene that is detected implies the release of a hydrogen atom into the system. The benzene that is detected is due to the displacement reaction. The difference between the isobutene and the benzene that is formed is the contribution from the abstraction processes. The abstraction of a ring hydrogen is endothermic and has a rate constant that is far smaller⁶ than the number we will be assigning for the abstraction of the anilino hydrogen. The ratio of the rate constants for abstraction and displacement is thus equal to the quantity (isobutene/benzene) -1. This can be placed on a temperature scale through the use of the total isobutene yields and the rate expression for hexamethylethane decomposition given above. The entire procedure is similar to the comparative rate method that we have used in

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the case of unimolecular reactions⁷ and removes the major source of error from this type of shock tube work. Finally, in order to determine the absolute values of the rate constants and expressions, we carry out experiments with an excess of methane. This results in a lowering of the yield of benzene since some of the hydrogen atoms are now removed from the systems by the abstraction reaction with methane, $H + CH_4 \rightarrow CH_3 + H_2$. The decrease in yield is directly related to the relative rates of hydrogen attack on methane and aniline. Since the rate expression for the former process is well-known^{1,8}

$$k(\text{H+CH}_4 \rightarrow \text{CH}_3 + \text{H}_2) = k_{a,CH_4} =$$

2.4 ×10¹¹ exp(-7000/T) L/(mol s)

we can now convert all of our results to an absolute basis.

The above analysis is based on experiments carried out in the limiting regions of low ratios of hexamethylethane to aniline concentrations. In the intermediate region there are always contributions from hydrogen atom attack on hexamethylethane. This is easily corrected for and in the studies for both toluene and phenol we found that rate constants for H + hexamethylethane on a per atom basis are the same as that for H-attack on ethane. An added complication is the reaction of the hydrogen atom with the resonance-stabilized radical that is an end product of the reaction. In the case of phenol we used chemical kinetic modeling to fine tune our results and obtain a value for this rate constant.² Anticipating the possibility of hydrogen attack on such a radical, we carried out a series of experiments near our limiting low hexamethylethane-phenol ratio and extrapolated to obtain the final results.

Aniline was used as a radical scavenger by Esteban et al.⁹ and their collaborators for studying the thermal decomposition of a variety of organic compounds. The fact that quite acceptable results were obtained is indicative of the stability and low reactivity of the anilino radical. Direct evidence of this is furnished by the bond strength of $368 \pm 8 \text{ kJ/mol}$ for the N-H bond in aniline.¹⁰ Recently Michael and co-workers¹¹ have determined the rate expression for hydrogen atom attack on ammonia to be

 $k(H+NH_3 \rightarrow H_2+NH_2) =$ 1.8 × 10¹¹ exp(-8067/T) L/(mol s)

in the temperature range appropriate to these experiments. This can be compared with the expression that we have used for hydrogen atom attack on CH₄. Values of the former are distinctly larger over all temperature ranges due to the 9.6 kJ/mol higher N-H bond strength¹⁰ in ammonia in comparison to that of the C-H bond in methane. Note, however, that the bond strength of the benzylic hydrogen in toluene is 373 kJ/mol or, within the uncertainty, the same as that for aniline.

Inherent in all the above is the assumption that hexamethylethane is far more thermally labile than aniline. We estimate that under our conditions the relative rate constants for thermal decomposition are close to 40 000 to 1 in favor of the former. A consequence of this is that we can probably work at aniline to hexamethylethane ratios of 1000 to 1 without confusing contributions from aniline decomposition.

Experimental Section

The experiments were carried out in a heated single-pulse shock tube that is maintained at 110 °C. This permits us to work with such nonvolatile compounds as aniline. We carried out experiments with six mixtures. The compositions of the mixtures studied are listed in the legend for Figure 1. Also included are the range of experimental conditions encountered. These have been cal-



Figure 1. Rate constant ratio for abstraction and displacement (in the form of log ((isobutene/benzene) – 1)) versus rate constant for hexamethylethane decomposition, for the following mixtures (ppm): 1, aniline/hexamethylethane 21000/909 (+); 2, aniline/hexamethylethane 20000/54 (*); 3, aniline/hexamethylethane 40000/79 (Δ); 4, aniline/hexamethylethane/methane 25600/66/143000 (\Box); 5, aniline/hexamethylethane 24000/176/192000 (\blacksquare); 6, aniline/hexamethylethane 63000/66 (\diamond). Conditions: temperature, 1000–1140 K; pressure, 2.7–4.0 atm argon; heating time, 500 μ s.

TABLE I:	Summary	of Re	esults ir	ı Terms	of Re	lation	log	(log
((Isobutene	/Benzene	- 1))	= M l	og k _{bex,d}	_{ec} + 1	3		

\ ,	//	•	
mixture	М	В	
1	0.0788 ± 0.019	$+0.251 \pm 0.049$	
2	0.0904 ± 0.014	-0.072 ± 0.037	
3	0.0799 ± 0.010	-0.087 ± 0.026	
4	0.0762 ± 0.010	$+0.400 \pm 0.27$	
5	0.0785 ± 0.005	$+0.495 \pm 0.011$	
6	0.0613 ± 0.007	-0.094 ± 0.019	

culated on the basis of the internal standard and the gas dynamic properties of the mixtures. The rationale for such variations in reaction conditions is to establish the optimum conditions for obtaining definitive rate expressions. An unexpected feature of the results was the large scatter in the first two sets of experiments. We are uncertain as to the source. It may well be that some "conditioning" of our gas handling system was necessary before reproducible transfer of the aniline could be affected. Most of the quantitative results were derived from the last four sets of data. Analysis was by gas chromatography with a packed Carbopack column and with flame ionization detection. The aniline and hexamethylethane were from Aldrich Chemicals.¹² Except for vigorous degassing and a single bulb-to-bulb distillation it was used without further purification. The methane and argon were from Matheson and were of Research Grade and UHP quality, respectively.

Results

A summary our experimental results can be found in Figure 1. Table I gives quantitative data in the form of linear leastsquares fits of the data. The y axis in Figure 1 is the ratio of the rate constants for all reactions, other than displacement, that remove H atoms from the system, to that for the displacement process. The variations in aniline to hexamethylethane concentrations are intended to isolate the abstraction reaction for study. It can be seen that, as the aniline to hexamethylethane ratio increases, the displacement reaction, as expected, becomes more important. At low extents of reaction or at the lower temperatures this is due to the decreasing importance of hexamethylethane as a source of abstractable hydrogen atoms. The x axis is given in terms of the rate constants for hexamethylethane decomposition

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and is derived from the relation

$$k_{\text{dec,hex}} = (\ln (1 - [(\text{isobutene})_f/2(\text{hexamethylethane})_f]))/t$$

where the subscripts i and f refer to initial and final concentrations, respectively, and t is the residence time of about 500 μ s. This serves as the internal standard for these studies. Such a direct measurement as opposed to a calculated temperature is necessary due to the extremely nonideal conditions behind the reflected shock through these mixtures. A small error is introduced from the reaction of H atoms with hexamethylethane, since this also forms isobutene. It is not of serious consequence since the abstraction to displacement ratio is not strongly dependent on $k_{hex,dec}$.

Conversion of the data in Table I to rate constants is based on the procedure described in the earlier papers.^{1,2} We begin by considering the ideal situation. The specific reactions of interest are

$$H + C_6H_5NH_2 \rightarrow C_6H_5NH + H_2 \qquad k_a$$
$$H + C_6H_5NH_2 \rightarrow C_6H_6 + NH_2 \qquad k_d$$

We use the data at the highest aniline to hexamethylethane ratio to derive the ratio of rate constants for abstraction displacement. Implicit in this is the assumption that at the 955 to 1 aniline to hexamethylethane ratio we have indeed approached the limiting value. This is supported from the data in Figure 1 where the results of mixtures with aniline to hexamethylethane from 370 to 955 to 1 are very close to each other. Substituting the rate expression for hexamethylethane decomposition into the leastsquares relation, we obtain

 $(isobutene/benzene) - 1 = k_a/k_d = 8.3 \exp(-2114/T)$

In the presence of large quantities of methane, the methane abstraction process decreases the benzene yield (displacement product). Our results are related to rate constants on the basis of the following relation

(isobutene/benzene) - 1 =

$$(k_a(aniline) + k_{a,CH_4}(CH_4))/k_d(aniline)$$

Since we have determined k_a/k_d previously, substitution leads to the equation

$$\log ((8.3 \exp(-2114/T) + k_{a,CH_4}(CH_4))/k_a(aniline)) = 0.0762 \log (k_{dec,hex}) + 0.400$$

$$\log ((8.3 \exp(-2114/T) + k_{a,CH_4}(CH_4))/k_a(aniline)) = 0.0785 \log (k_{dec,hex}) + 0.495$$

where the first relation is for the experiments for the mixture with 14.3% methane and the second from the mixture with 19.2% methane. With the appropriate methane to aniline ratios, we then numerically solve for a linear relation relating the logarithm of the ratio of rate constants of hydrogen abstraction from methane and aniline to that of the logarithm of the rate constant for hexamethylethane decomposition. The results are as follows

for mixture 4

$$\log (k_{a,CH_4}(CH_4)/k_a(aniline)) = 0.0224 \log (k_{dec,hex}) - 0.444$$

for mixture 5

$$\log (k_{a,CH_4}(CH_4)/k_d(aniline)) = 0.0211 \log (k_{dec,hex}) - 0.421$$

The agreement between the results from the different mixtures is very satisfactory. Note that we are able to use lower aniline to hexamethylethane ratios in these cases since the methane also serves to protect the hexamethylethane from radical attack. Substituting into the above rate expression for hexamethylethane decomposition leads to the relation

for mixture 4

$$k_{a,CH_4}(CH_4)/k_a(aniline) = 0.84 \exp(-772/T)$$

for mixture 5

$$k_{a,CH_4}(CH_4)/k_a(aniline) = 0.85 \exp(-728/T)$$

From the rate expression for hydrogen atom attack on methane we obtain

$$k_a = 2.8 \times 10^{11} \exp(-6228/T) \text{ L/(mol s)}$$

 $k_d = 3.4 \times 10^{10} \exp(-4113/T) \text{ L/(mol s)}$

where we have used an average of the results from mixtures 4 and 5.

The experiments carried out with mixture 1 contain the highest relative quantity of hexamethylethane. From the data in Figure 1, it can be seen that there must be a major contribution from hydrogen atom attack on the hexamethylethane. The relationship joining the appropriate rate constants is similar to that for methane except for the substitution of hexamethylethane

$$(isobutene/benzene) - 1 =$$

$$(k_{a}(aniline) + k_{a,C_{8}H_{18}}(HME))/k_{d}(aniline)$$

where $k_{a,C_8H_{18}}$ is the rate constant for the reaction

$$\mathbf{H} + \mathbf{C}_{8}\mathbf{H}_{18} \rightarrow \mathbf{H}_{2} + \mathbf{C}_{8}\mathbf{H}_{17} \rightarrow \mathbf{C}_{4}\mathbf{H}_{8} + t \cdot \mathbf{C}_{4}\mathbf{H}_{9} \rightarrow \mathbf{C}_{4}\mathbf{H}_{8} + \mathbf{H}$$

Each hydrogen atom reacted in this reaction produces 2 additional isobutenes. Proceeding as before we then obtain

$$k_{\rm a,C_8H_{18}}/k_{\rm a} = 14$$

Although as noted earlier there is considerable scattering in this set of data we find, at 1032 K ($k_{\text{dec,hex}} = 100$), $k_{a,C_8H_{18}} = 8.7 \times$ 10^9 L/(mol s). This can be compared with our value of 4.9 × $10^9 L/(mol s)$ from the toluene study. This suggests another loss mechanism under these conditions. In the case of phenol this was identified as the reaction of phenoxyl with hydrogen atoms, since combination products of phenoxyl radicals will not be stable under the reaction conditions. In the case of toluene, the rapid combination of benzyl with itself and with methyl reduces the pool of radicals since bibenzyl and ethylbenzene have long lifetimes in the 1000-1140 K range. In the present case, the situation is rendered more complex because we have presumably anilino and amine radicals. The combination products have lifetimes shorter than or close to the heating time and there is the possibility of disproportionation. The general situation is thus too complex to model properly.

The possibility of contributions from another hydrogen removal channel is confirmed from a comparison of the results from mixtures 6 with that of mixtures 2 and 3. If one remembers that the ratios of aniline to hexamethylethane are 950 to 1, 506 to 1, and 370 to 1, respectively, for these mixtures, then if the difference between the results of these experiments is solely due to the contributions due to abstraction of a hydrogen from hexamethylethane leading to 2 additional isobutenes, our rate constant for H + hexamethylethane leads to the conclusion that the differences should be barely observable. From Figure 1 it can be seen that the differences are particularly noticeable at high extents of decomposition. This is fully in agreement with the possibility of the alternative loss mechanism being hydrogen combination with the long-lived radicals in the system. In view of the difficulties in properly characterizing the anilino and amine radical system, we have resorted to a simple extrapolation at the high extents of reaction. This leads to a decrease of our k_a/k_d ratio by about 6% at the high conversion end. It is unchanged at low extents of reaction. The corrected rate expressions then become

$$k_{\rm a} = 1.8 \times 10^{11} \exp(-5846/T) \text{ L/(mol s)}$$

 $k_{\rm d} = 2.2 \times 10^{10} \exp(-3735/T) \text{ L/(mol s)}$

Note that the overall change is small and is well within the uncertainties of the measurements. Nevertheless, we expect that these numbers are the best values and will be so used in subsequent discussion.

Discussion

We have now completed studies on the mechanisms and rates of hydrogen atom attack on toluene, phenol, and aniline, and it

 TABLE II: Comparison of Rate Expressions and Rate Constants for Hydrogen Atom Attack on Some Organic Compounds

		1075 K			
compound	rate expressions ^a	rate constants at 1075 K	rate constants, per H atom		
	A: Abstraction				
methane (ref 1,8)	$2.4 \times 10^{11} \exp(-7000/T)$	3.6×10^{8}	9 × 10 ⁷		
ammonia (ref 11)	$1.8 \times 10^{11} \exp(-8067/T)$	1×10^{8}	3.3×10^{7}		
water (ref 8)	$2.4 \times 10^{11} \exp(-11310/T)$	6.4×10^{6}	3.2×10^{7}		
hexamethylethane (ref 1)		6.1 × 10 ⁹	3.4×10^{8}		
toluene (ref 1)	$1.2 \times 10^{11} \exp(-4138/T)$	2.56×10^{9}	8.5×10^{8}		
phenol (ref 3)	$1.1 \times 10^{11} \exp(-6240/T)$	3.3×10^{8}	3.3×10^{8}		
aniline (this work)	$1.8 \times 10^{11} \exp(-5846/T)$	7.8×10^{8}	3.9×10^{8}		
	B: Displacement				
toluene (ref 1)	$1.2 \times 10^{10} \exp(-2578/T)$	1.1×10^{9}			
phenol (ref 2)	$2.2 \times 10^{10} \exp(-3990/T)$	5.4×10^{8}			
aniline (this work)	$2.2 \times 10^{10} \exp(-3735/T)$	6.8×10^{8}			

^a Units of L/(mol s).

is instructive to make comparisons. Table II contains a summary of all the rate expressions, the rate constants at an intermediate temperature in the studies, and for the abstraction rate constants, the values normalized to a per hydrogen basis. For the abstraction process we have also included the rate expressions and constants for H attack on methane, ammonia, water, and hexamethylethane.

Probably the most reliable data are the rate constants at an intermediate point (1075 K) in our determinations. The most interesting feature is the small variation in these quantities for each type of reaction. Toluene is the most and phenol the least reactive. For the displacement process, this ordering is contrary to what one would expect if purely steric factors are operative. For the abstraction reaction,^{1,2} as noted earlier, the resonance energy is clearly not manifested in either the rate constants or the rate expression. The ordering of the rate constants follows the pattern of bond energies ranging from water to ammonia to methane. Nevertheless, the differences from the most to the least reactive is only a factor of 2.5. We suspect that the actual bond energies for the bonds being broken (anilino, benzyl, and phenoxyl) are not known to sufficient accuracy so as to draw conclusions between rate constants and bond energies. Certainly, the closeness of the rate constants is a reflection of the similarity in bond energies and thermodynamics. To put these factors in proper perspective, the difference in rate constants on a per hydrogen basis for the abstraction of a hydrogen from methane and hexamethylethane, where the variation in bond energies is 16 kJ/mol, is close to a factor of four.

The rate expressions for these processes are subject to considerably larger uncertainties than the rate constants. Nevertheless, some general trends are clear. The displacement reactions involve tighter transition states (lower A factor) and lower energy channels than the abstraction processes. For the latter, the A factors are very close to those for the unsubstituted hydride analogues of the aromatic compounds. In the case of aniline and ammonia for example, the A factors per hydrogen are 0.9×10^{11} and 0.6×10^{11} L/(mol s), respectively. Thus, most of the difference upon phenyl substitution is due to differences in the activation energies. Indeed, for all these systems the A factors for the abstraction reactions are strikingly similar. The total variation for all these systems is less than a factor of 3. Similarly, the variation in the A factors for displacement is only a factor of 2. Note that in this case the elementary process is the site-specific

 TABLE III: Rate Expressions for Hydrogen Displacement and Abstraction from Benzene

attacking	rate expressions ^a			
group	displacement	abstraction		
CH3	$1.2 \times 10^9 \exp(-8023/T)$ (ref 1)	$3 \times 10^{8} \exp(-5590/T)$ (ref 14)		
NH ₂	$7.9 \times 10^9 \exp(-9123/T)$ (this work)			
ОН	$3.4 \times 10^9 \exp(-5330/T)$ (ref 2)	$1.4 \times 10^{10} \exp(-2260/T)$ (ref 15)		

^aUnits of L/(mol s).

addition of hydrogen atoms. Considering the differences in the nature of the substrates this constancy is remarkable. In the case of unimolecular decompositions, we have found for homologous compounds very small variations in A factors when the data at these temperatures are represented in the Arrhenius form. In the present case there is of course a much larger variation in the range of compounds. We are fortunate that for the hydride there now exist sufficient data so that one can consider rate expressions near a particular temperature. It may well be that by focusing on results at a particular temperature it will be possible to derive some generalizations with respect to transition-state structures and energies for a particular class of compounds. Finally, note that the comparisons in Table II are between the aromatics and the hydrides. A more proper comparison for the effect of resonance is with the ethyl-substituted compound. The difference in rate constants can therefore be expected to be considerably smaller.

The rate expression for the displacement of the amino group by the hydrogen atom can be used to derive the rate expression for the reverse reaction, the displacements of a hydrogen from benzene by NH_2 , through the equilibrium constant. This result should be of the same accuracy as the measured value since the thermodynamic properties¹³ of all the quantities are well-known. The results and comparable results for phenol and toluene can be found in Table III. It should be noted that in all these cases the displacement rate constants are composites of elementary rates, since the thermodynamics dictate that the reverse of the initial addition process should be the more rapid than the hydrogen displacement. These numbers are of most interest with respect to the mechanism for radical attack on benzene. Unfortunately, data for the abstraction of a hydrogen from benzene by the amino radical do not exist. For the other systems, abstraction is most favored over displacement for hydroxyl, while for methyl, displacement can make a small but significant contribution. The rate constant for displacement of a hydrogen atom by an amino radical from benzene is not very much different than the analogous process for methyl. After taking into account the small increase in reaction endothermicity between abstraction by amino and methyl radicals, we suspect that the branching ratio between abstraction and displacement for amino attack on benzene will be similar to that for methyl attack.

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