Base-Catalyzed Isotopic Exchange of Molecular Hydrogen. 5.[1] The Potassium Anilide–Aniline System

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Isotopic exchange between molecular deuterium and aniline under catalysis by potassium anilide has been studied at 85 and 100 °C over a range of catalyst concentrations (0.03–0.1 M). Two consecutive processes occur, $D_2 \rightarrow HD \rightarrow H_2$, and rate constants have been evaluated; k_{D_2} and k_{HD} increase with increasing [PhNHK]. Plots of k_{D_2}/[PhNHK] vs. [PhNHK] and k_{HD}/[PhNHK] vs. [PhNHK] are linear in accord with second-order rate dependence on [PhNHK]. The kinetic behavior cannot be accommodated on the basis of free anilide ion and monomeric potassium anilide ion pairs as the main reactive species. Also the kinetic data serve to exclude a mechanism involving free deuteride ion as a reaction intermediate. The most probable mechanism is considered to be a preequilibrium formation of a catalyst–D_2 complex followed by rate-determining attack by a second molecule of potassium anilide in association with a solvent molecule via a cyclic transition state including participation of K^+. Less probable is reaction occurring via a dimer of the catalyst. Kinetic isotope effects, k_{HD}/k_{D_2}, are 1.82 at 85 °C and 2.12 at 100 °C (corrected for dependence on [PhNHK]). The small magnitude of the KIE and its inverse temperature dependence is consistent with a primary isotope effect involving concerted transfer of hydrogen (deuterium) in a nonlinear transition state. Comparison is drawn with exchange of D_2 in the RO^-/ROH and RNH^-/RNH_2 (R = H or Me) systems. It is concluded that the kinetic behavior in the $PhNH^-/PhNH_2$ system follows more closely the aqueous or alcoholic–base, than the ammonia or methylamine–base systems.

Isotopic exchange between molecular deuterium and a protic solvent under base catalysis is of interest regarding possible application of the principle for the separation of the deuterium isotope (e.g. from water, ammonia, or hydrocarbon feedstock) and also from a theoretical point of view.[3] In previous work we have studied the hydroxide ion catalyzed exchange of D_2 in dimethyl sulfoxide (Me_2SO) water mixtures.[4–6] While considerable enhancement over purely aqueous media was achieved, the rate increase was less than expected if the rate was directly dependent on the H_- function as a measure of medium basicity. Some mechanistic conclusions could be drawn from arguments based upon enthalpies of activation and transfer.[7]

In other studies of D_2 exchange a variety of basic systems were used in addition to aqueous hydroxide,[8,9] including methanolic methoxide,[10] ammonia,[11–14] and aliphatic amines[15–18] as catalyzed by the respective lyate ions. While isotopic exchange in aqueous or methanolic media is slow, with activation energies of ca. 24 kcal/mol, exchange in the $RNHK/RNH_2$ systems is very fast, with E_a values in the range of 3–7 kcal/mol being obtained.

TABLE I: Solubilities of D_2 and H_2 in Aniline as a Function of Temperature

temp, °C	solubility, (mol L^{-1}) × 10^3 D_2	solubility, (mol L^{-1}) × 10^3 H_2
0	1.76	1.65
35.0	2.15	
65.0	2.52	2.27, 2.34
85.0	2.70	
100.0	2.94	

TABLE II: Rate Constants for Exchange of D_2 and HD as a Function of Potassium Anilide Concentration and Temperature[a]

run no.	temp, °C	[PhNHK], M	$k_{D_2} \times 10^3$, s^{-1}	$k_{HD} \times 10^3$, s^{-1}	k_{HD}/k_{D_2}
24	85.0	0.0308	2.17	2.46	1.13
21	85.0	0.0568	5.80	7.67	1.32
23	85.0	0.0844	16.0	24.2	1.51
28	85.0	0.1072	22.8	36.9	1.62
29[b]	85.0	0.1072	21.3	33.0	1.55
25	100.0	0.0223	3.46	5.13	1.48
26	100.0	0.0422	18.2	30.1	1.65
27	100.0	0.0617	25.2	47.3	1.88

[a] In-solution rate constants are given. k_{D_2} values are corrected by the symmetry number of 2. [b] Run 29 was carried out after pumping H_2, HD, and D_2 at the end of run 28, followed by introducing fresh D_2.

It was of interest to extend the study of D_2 exchange to the use of potassium anilide/aniline, as the first examination of a basic system involving an aromatic amine. The basicity of $PhNH^-$ is about intermediate between that of HO^- and NH_2^- (RNH^-), which should have consequences on the kinetic behavior. As well, the low dielectric constant of aniline (ϵ = 7.0 at 25 °C; cf. for NH_3, ϵ = 22.4 at −33 °C)[19] would lead to ion pairing phenomena to be especially important, with possible consequences on mechanisms and on the role of free ions vs. ion pairs and aggregates. Previous exchange studies in ammonia or aliphatic amines have been variously considered as proceeding via the free amide ions

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(1) (a) Part 4: Buncel, E.; Symons, E. A.; More O'Ferrall, R. A. *J. Am. Chem. Soc.* **1978**, *100*, 1084. (b) The present paper is also part 17 of a series on Hydrogen Exchange Studies. Part 16: Davey, J. P.; Jones, J. R.; Buncel, E. *Can. J. Chem.* **1986**, *64*, 1246.

(2) Deceased.

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(18) Symons, E. A.; Clermont, M. J. *Can. J. Chem.* **1981**, *59*, 2386.

(19) *International Critical Tables*, Vol. 6, p 60 (NH_3); p 90 ($C_6H_5NH_2$).

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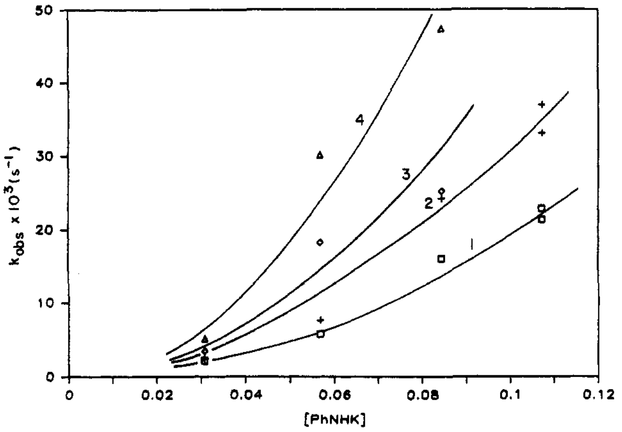

Figure 1. Plot showing rate dependence of D_2 and HD exchange at 85 and 100 °C on catalyst concentration in potassium anilide–aniline system: 1 (□), D_2 at 85 °C; 2 (+), HD at 85 °C; 3 (◇), D_2 at 100 °C; 4 (△), HD at 100 °C.

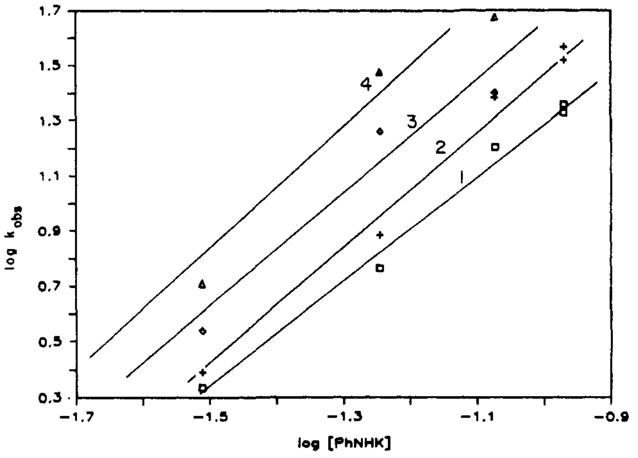

Figure 2. Plot of log k_{obsd} vs. log [PhNHK] for exchange of D_2 and HD at 85 and 100 °C: 1 (□), D_2 at 85 °C; 2 (+), HD at 85 °C; (3) ◇), D_2 at 100 °C; 4 (△), HD at 100 °C.

with possible contribution of alkali metal amide ion pairs. The results of the study using $PhNHK/PhNH_2$ in the exchange of D_2 reported herein reveal a kinetic behavior that is different from the ammonia or aliphatic amine base systems and are discussed in terms of possible mechanisms of these exchange processes.

Results and Discussion

Kinetic Behavior. The change in composition of isotopic species (D_2, HD, H_2) as a function of time during the course of a given run in the reaction of D_2 in the $PhNHK/PhNH_2$ system, as followed mass spectrometrically, is consistent with a consecutive pseudo-first-order kinetic system shown in eq 1. The D_2 concentration decreased in an exponential manner, HD increased to a maximum value thereafter declining, while the H_2 concentration increased steadily. A curve-fitting computer method has been used to evaluate the constituent rate constants. The vapor-phase rate constants so obtained were converted into in-solution rate constants by multiplying by the factor (total moles of D_2 in system)/(moles of D_2 dissolved in liquid phase) and using the measured solubility data for D_2 in aniline as given in Table I. The resulting in-solution rate constants (k_{D_2} values corrected for the symmetry number of 2)[20] for a series of runs at varying catalyst concentrations and at two temperatures are given in Table II and plotted in Figure 1. The data at 85 °C show that the variation of the rate constant with catalyst concentration is clearly nonlinear and increases more rapidly than for a first-order dependence on [PhNHK]. At 100 °C, where the experimental technique is more difficult and consequently the scatter of points is greater, the same trend is observed.

$$D_2 \xrightarrow{k_{D_2}} HD \xrightarrow{k_{HD}} H_2 \qquad (1)$$

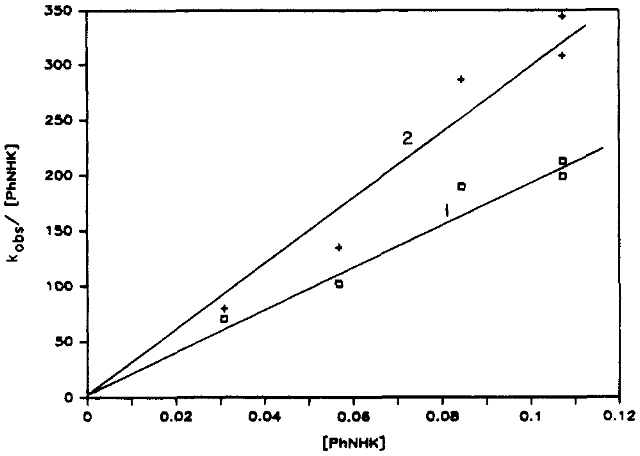

Figure 3. Plot of k_{obsd}/[PhNHK] vs. [PhNHK] for D_2 and HD exchange at 85 °C: 1 (□), D_2; 2 (+), HD.

TABLE III: Concentrations of Free Anilide Ions and Potassium Anilide Ion Pairs[a]

run no.	temp, °C	[PhNHK], M	$[PhNH^-] \times 10^5$, M	$[PhNH^-K^+]_{ip}$, M
24	85.0	0.0308	6.56	0.0307
21	85.0	0.0568	8.91	0.0567
23	85.0	0.0844	10.86	0.0843
28	85.0	0.1072	12.25	0.1071
29	85.0	0.1072	12.25	0.1071
25	100.0	0.0223	3.09	0.0222
26	100.0	0.0422	4.26	0.0421
27	100.0	0.0617	5.15	0.0616

[a] Data calculated by using the dissociation constant values for PhNHK, $K_d = 1.4 \times 10^{-7}$ M at 85 °C and $K_d = 4.3 \times 10^{-8}$ M at 100 °C, via the Fuoss eq 4. [PhNHK] is the stoichiometric concentration.

The nonlinear nature of the plots in Figure 1 is indicative of a rate dependence which is not first order in potassium anilide. However, plots of log k vs. log [PhNHK] are linear with slope 2.1 ± 0.1 (Figure 2) which indicates that the reaction is second order with respect to PhNHK. Hence eq 2 and 3 follow:

$$\text{rate} = k_{obsd}[D_2] = k[D_2][PhNHK]^2 \qquad (2)$$

$$k_{obsd}/[PhNHK] = k[PhNHK] \qquad (3)$$

The plot according to eq 3 is shown in Figure 3 for the D_2/PhNHK and HD/PhNHK data at 85 °C. The plots shown in Figures 2 and 3 are in accord with the observation that no exchange takes place in the absence of potassium anilide.

Catalytic Species. The nature of the catalytic species which is responsible for exchange has direct bearing on the efficiency of the process as well as the observed rate law. Due to the very small dielectric constant of aniline (6.0 at 85 °C and 5.4 at 100 °C),[19] the extent of dissociation of PhNHK into the free ions will be quite small. Nevertheless, since free ions are generally much more reactive than ion pairs,[21] it is possible that $PhNH^-$ could be the main contributing species in the exchange process.[11,22]

In the potassium anilide/aniline system the dissociation constant of PhNHK has not been determined but it can be estimated from the Fuoss eq 4,[23] where a is sum of the ionic radii in Å of the ion

$$K_d^{-1} = 2.52 \times 10^{-3} a^3 \exp(e^2/a\epsilon kT) \qquad (4)$$

pair species, e the electronic charge, k is Boltzmann's constant,

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ϵ is the dielectric constant of the medium, and T is the absolute temperature. Using an estimate of $a = 4.5$ Å for PhNHK based on individual bond lengths and ionic radii (which compares with $a = 3.0$ Å for KNH_2 used in Delmas work[14]), one obtains $K_d = 1.4 \times 10^{-7}$ M at 85 °C and $K_d = 4.3 \times 10^{-8}$ M at 100 °C,[24] from which values of $[PhNH^-]$ have been calculated for the various kinetic runs (Table III). However, a plot of k_{obsd} vs. $[PhNH^-]$ shows strong upward curvature for the $D_2 \rightarrow HD$ as well as $HD \rightarrow D_2$ processes, at both temperatures, indicating that $PhNH^-$ is not the sole catalytic species in the exchange process. Moderate variation in a and K_d values did not result in linear k_{obsd} vs. $[PhNH^-]$ plots.

Next we examine the possibility that catalysis occurs by both free anilide ion and potassium anilide ion pairs, for which eq 5 is applicable. Substituting for $K_d = [PhNH^-][K^+]/[PhNH^-K^+]$

$$k_{obsd} = k_1[PhNH^-] + k_2[PhNH^-K^+] \qquad (5)$$

$= [PhNH^-]^2/[PhNH^-K^+]$ one obtains eq 6 which is rearranged to eq 7. According to eq 7 a plot of $k_{obsd}/[PhNH^-]$ vs. $[PhNH^-]$

$$k_{obsd} = k_1[PhNH^-] + k_2[PhNH^-]^2/K_d \qquad (6)$$

$$k_{obsd}/[PhNH^-] = k_1 + k_2[PhNH^-]/K_d \qquad (7)$$

should be linear with k_1 as intercept and k_2/K_d as slope. The relevant plots showed appreciable scatter and the best-fit straight lines in all cases gave large negative intercepts, contrary to requirement according to eq 7. The qualitative nature of these plots remained unaffected when somewhat different K_d values were used, further indicating the inapplicability of the treatment.

Mechanism of Exchange. It has been shown that there is a second-order rate dependence on potassium anilide concentration in this system (eq 2 and 3). This is clearly not consistent with a deuteride ion mechanism

$$PhNH^- + D\text{-}D \rightarrow PhNHD + D^- \qquad (8)$$

$$D^- + PhNH_2 \rightarrow DH + PhNH^- \qquad (9)$$

analogous to that which had been considered by Wilmarth[8,11] to apply to the OH^-/H_2O as well as NH_2^-/NH_3 systems.

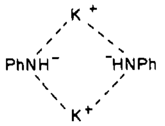
The simplest process requiring a second-order dependence on potassium anilide is probably a termolecular process in which rate-determining formation of an intermediate between two molecules of PhNHK and a D_2 molecule is followed by fast exchange with a solvent molecule. Since termolecular processes are generally considered unlikely, one of the following possibilities is preferred.

We consider first a process involving a preequilibrium formation of dimer $(PhNHK)_2$ which reacts in the rate-determining step with D_2 and a molecule of aniline that could be present as a solvate of the catalyst, to give the exchanged products:

$$2PhNHK \rightleftarrows (PhNHK)_2 \qquad (10)$$

$$(PhNHK)_2 + D_2 + PhNH_2 \rightarrow \text{exchanged products} \qquad (11)$$

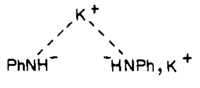
Of various structural formulations of the dimer such as **1**–**3**, the symmetrical species **1** would be unreactive but **2** and **3** could both be reactive in exchange. The transition structures **4** and **5** would apply to these species, with **5** favored on symmetry grounds.



1

$$[PhNHK_2^+]\ PhNH^-$$

2



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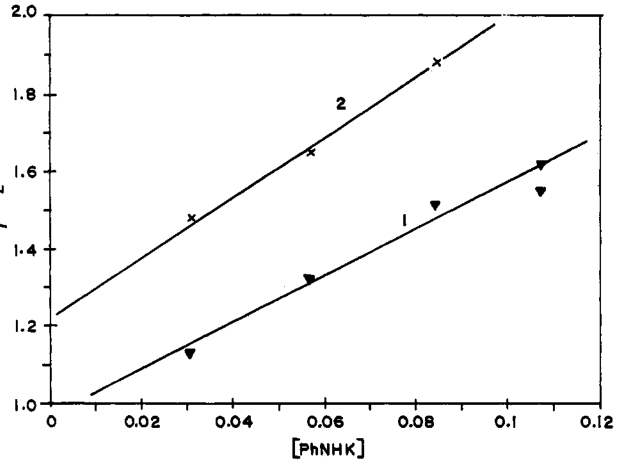
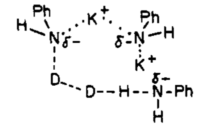


Figure 4. Kinetic isotope effect, k_{HD}/k_{D_2}, as function of catalyst concentration and temperature for exchange of HD and D_2 in potassium anilide–aniline system: 1 (▼), 85 °C; 2 (×), 100 °C.



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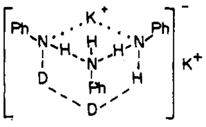

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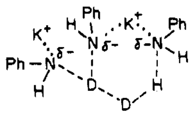

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Reaction via a $PhNH\text{-}D_2$ complex is considered next. The complex formed in a preequilibrium would undergo attack in the rate-determining step by a second molecule of PhNHK in association with a solvent molecule:

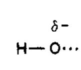
$$PhNHK + D_2 \rightleftarrows PhNHK\text{-}D_2 \qquad (12)$$

$$PhNHK\text{-}D_2 + PhNHK + PhNH_2 \rightarrow \text{exchanged products} \qquad (13)$$

This mechanism is depicted in structure **6** for the transition state.

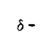
The following characteristics of eq 12 and 13 lead to this process being favored. (1) The initially formed (weak) $PhNHK\text{-}D_2$ complex would serve to polarize the D–D bond for attack by PhNHK + $PhNH_2$ in the second step. (2) Electrophilic assistance would be rendered by the solvent molecule and the K^+ counterion of the attacking PhNHK species in the rate-determining step via a cyclic six-centered transition state.

An associative mechanism involving formation of a complex between catalyst and D_2 was proposed in the hydroxide/D_2, methoxide/D_2,[10] amide/D_2,[12] and cyclohexylamide/D_2[17] systems and has received support from theoretical work of Ritchie and King.[25] In the KNH_2/D_2 and $KNHMe/D_2$ systems, with the much more strongly basic NH_2^- and $MeNH^-$ anions, initial polarization of D_2 may not be required, nor participation by K^+, and in these systems the transition state for exchange would be as shown in **7**, corresponding to attack of a solvated amide ion on D_2 being concerted with electrophilic assistance provided by an aniline molecule. The formation of the energetically unfavorable free deuteride ion is circumvented in **7**, as it is also in the mechanisms of eq 10, 11, and 12, 13.



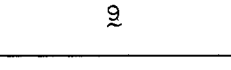
$$\overset{\delta-}{\underset{\mathrm{H}}{\mathrm{Me{-}N}}}\cdots\overset{\delta+}{\mathrm{D}}\cdots\overset{\delta-}{\mathrm{D}}\cdots\mathrm{H}\cdots\overset{\delta-}{\underset{\mathrm{H}}{\mathrm{N{-}Me}}}$$

7



$$\mathrm{H{-}}\overset{\delta-}{\mathrm{O}}\cdots\mathrm{D}\cdots\mathrm{D}\cdots\mathrm{H}\cdots\overset{\delta-}{\mathrm{O}}\mathrm{{-}H}$$

8



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(24) (a) The decrease in the estimated K_d values as the temperature is raised and the negative ΔH_d and ΔS_d values for the dissociation process are paralleled by results reported by Hogen-Esch and Smid[24b] for the dissociation of fluorenyl alkali metal salts in tetrahydrofuran. It was considered that the negative value for the enthalpy of dissociation of the contact ion pair results from the gain in solvation enthalpy on formation of the solvent-separated ion pair. Similarly, the large decrease in entropy on dissociation would result from the greater ordering effect of solvent molecules on free ions (or solvent separated ion pairs) relative to contact ion pairs. These considerations would presumably apply to the present system as well. (b) Hogen-Esch, T. E.; Smid, J. *J. Am. Chem. Soc.* **1966**, *88*, 318.

(25) Ritchie, C. D.; King, H. F. *J. Am. Chem. Soc.* **1968**, *90*, 833. **1968**, *90*, 838.

TABLE IV: Activation Parameters for D_2 Exchange in Various Base and Solvent Systems

solvent	catalyst	pK_a	E_a, kcal mol^{-1}	$\Delta S^{\ddagger}$, eu	ref
H_2O	KOH	15.7	24	7	8, 9
CH_3OH	CH_3OK	16[a]	24	4	10
$C_6H_5NH_2$	C_6H_5NHK	27[a]	31	15	present work
NH_3	KNH_2	37[b]	8	−9	12, 14
CH_3NH_2	CH_3NHK	38[b]	7	−5	15, 16
$(CH_3)_2NH$	$(CH_3)_2NK$	38[c]	7	−2	16
$C_6H_{11}NH_2$	$C_6H_{11}NHNa$	41.6[d]	3	−47	17

[a] Reference 30. [b] Reference 31. [c] Estimated value. [d] Reference 32.

Kinetic Isotope Effects. The results on kinetic isotope effects, k_{HD}/k_{D_2}, are presented in Table II for the various runs. It is seen that there is an appreciable dependence of the KIE on potassium anilide concentration as well as on temperature (see also ref 8 where similar observations were made). Plots of k_{HD}/k_{D_2} vs. [PhNHK] are linear as shown in Figure 4. The variation of the KIE with catalyst concentration could possibly arise from different contributions of free ions and ion pairs to the overall rate as the total base concentration is varied.

One can make correction for the catalyst concentration dependence of the KIE as follows. Since it was shown that the variation of k_{obsd} with [PhNHK] adheres to eq 3, it follows that

$$\text{for } D_2 \rightarrow HD \qquad k^{D_2}_{obsd}/[\text{PhNHK}] = k'_{D_2}[\text{PhNHK}]$$

$$\text{for } HD \rightarrow H_2 \qquad k^{D_2}_{k_{obsd}}/[\text{PhNHK}] = k'_{HD}[\text{PhNHK}]$$

The corrected isotope effect is hence given by $(\text{KIE})_{cor} = k'_{HD}/k'_{D_2}$, which is the ratio of the slopes of the plots in Figure 3. Thus we obtain $(\text{KIE})_{cor} = 1.82$ at 85 °C and $(\text{KIE})_{cor} = 2.12$ at 100 °C.

The relatively small values of the KIE, in comparison with typical systems involving C–H/C–D rupture, is striking and the inverse temperature dependence of the KIE is also noteworthy. In a theoretical analysis[1a] of the KIE for the hydroxide ion exchange of D_2 in Me_2SO–water mixtures, which also exhibited small KIE values (1.18–1.65 depending on the solvent composition), it was concluded that the small isotope effects are indeed consistent with rate-determining hydrogen transfer.[26-29] The zero point energy (ZPE) contribution to the KIE in the $D_2/HD/H_2$ system is very much smaller than in the case of C–D/C–H bonds. Model calculations for the transition state indicated a concerted mechanism with the base and a solvent molecule participating in the rate-determining step as shown in **8**. Further reduction in the KIE arose from a nonlinear configuration, **9**. An inverse temperature dependence of the isotope effect was predicted for these processes.[30] The transition structure **6** shows some analogy with **9** since a concerted transfer of hydrogen (deuterium) occurs in both cases in a nonlinear fashion. Thus the small value of the KIE in the present study and the inverse temperature dependence are both consistent with theoretical expectations for the mechanism in eq 12 and 13.

Activation Parameters. Although evaluation of accurate activation parameters is not warranted by the results in the present work, approximate estimates can be useful for comparison with other systems. From the data in Table II one obtains an average E_a value of 31.2 ± 2.4 kcal/mol for the $D_2 \rightarrow HD$ process and 31.0 ± 1.8 kcal/mol for the $HD \rightarrow H_2$ processes. Average $\Delta S^{\ddagger}$ values for the two processes are 14.6 ± 6.0 and 15.3 ± 4.9 eu, respectively.

Comparing with other exchange systems, it is recalled that, for OH^-/H_2O and CH_3O^-/CH_3OH, $E_a \approx 24$ kcal/mol and $\Delta S^{\ddagger} \approx 7$ eu (CH_3O^-/CH_3OH).[8,10] In contrast, in the RNH^-/RNH_2 systems very low E_a values (3–7 kcal/mol) and negative $\Delta S^{\ddagger}$ values are obtained (−2 to −47 eu depending on the cation and amine).[12,14,17] The data are summarized in Table IV.

It is apparent from the results that the potassium anilide/aniline system does not resemble the amide/ammonia or aliphatic amide/amine systems, which have associated very small E_a's and negative $\Delta S^{\ddagger}$ values. There is more resemblance between the $PhNHK/PhNH_2$ and the OH^-/H_2O or CH_3O^-/CH_3OH systems, although the former has an even higher E_a and more positive $\Delta S^{\ddagger}$. However, in making such comparisons it should be borne in mind that the systems being considered are quite disparate, not only as far as chemical species are concerned, but also their physical state (free ions, ion pairs, aggregates) as a result of the very large changes in dielectric constants of the media as well as the temperatures under which the experiments are carried out.

Concluding Remarks

The present results for D_2 exchange in the potassium anilide/aniline system contrast with previous work in other basic systems. Medium basicity and dielectric constant differences are thought to be mainly responsible for the different kinetic behaviors and activation parameters in these various systems. Since H_2 is an exceedingly weak acid,[33] with an estimated pK_a of ca. 36, a very strong base is required to effect proton transfer, albeit in a concerted manner with electrophilic assistance provided by a solvent molecule. With regards to the $RNHK/RNH_2$ vs. $PhNHK/PhNH_2$ comparison, we have proposed that different mechanisms apply to D_2 exchange in these systems, largely as a result of basicity differences. Comparing further HO^-/H_2O with $PhNHK/PhNH_2$ in D_2 exchange, the vastly different dielectric constants of solvents water and aniline must clearly have important consequences, with ion pairing and consequent participation of the counterion being much more likely in the latter case, as we have proposed.

Experimental Section

Materials. Aniline (Baker) was first converted into the hydrochloride which was recrystallized from ethanol and treated with NaOH solution and the generated aniline was dried and distilled from zinc powder. Deuterium gas (Matheson) was used as received.

A stock solution of potassium anilide in aniline was prepared in a glass vessel fitted with a Rotaflo stopper and O ring joint.[34] Potassium metal (1.3 g) and aniline (25 mL) were introduced under vacuum, venting the H_2 evolved. The solution of $PhNHK/PhNH_2$ (ca. 1.3 M) was purple.

Determination of Potassium Anilide Concentration. A known volume (0.1–0.2 mL) of the $PhNHK/PhNH_2$ stock solution was syringed into a 2.0-mL volumetric flask fitted with a septum and the solution made up to mark with $PhNH_2$. Freshly distilled MeI was added in small portions by syringe until the purple color changed into reddish brown with precipitation of KI: $C_6H_5NHK + CH_3I \rightarrow C_6H_5NHCH_3 + KI$. One milliliter of the clear solution was transferred into another flask and 6.0 μL of *p*-xylene was syringed in as external reference. The NMR spectrum of this solution showed peaks at δ 3.64 (m, aromatic H), 6.84 (br, s, NH), and 7.83 (s, $N{-}CH_3$). In dry aniline the $N{-}CH_3$ protons of $C_6H_5NHCH_3$ appear as a doublet centered at δ 7.83 (*J* = 5.0

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Hz).[35] The ratio of the peak heights, N–Me/Xy–Me, is then compared with a calibration curve obtained for a series of standard solutions of varying $C_6H_5NHCH_3/C_6H_5NH_2$ concentrations containing constant amounts (6.0 μL) of *p*-xylene and the concentration of anilide in the original $PhNHK/PhNH_2$ stock solution calculated.

Solubility of Deuterium in Aniline. This was determined by a gas chromatographic method[36,37] and data are given in Table I, together with some values for H_2 for comparison.

Kinetics of Deuterium Exchange. The reaction vessel used in the kinetic studies has been described before.[5,37] The side arms permitted connection of the flask to a vacuum pump and, by a septum and syringe needle, to a manometer and deuterium gas cylinder. The reaction vessel was evacuated and transferred to a drybox, and appropriate volumes of the $PhNHK/PhNH_2$ stock solution (1.0–4.0 mL) were introduced through the septum by a gas-tight syringe, followed by 25.0 mL of freshly distilled aniline. After mixing, 2.0 mL of the diluted $PhNKH/PhNH_2$ solution was withdrawn by syringe for determination of the anilide concentration. The reaction vessel was then cooled to 0 °C, degassed, and placed in the constant temperature bath. Following equilibration, D_2 was introduced to a pressure of 1 atm and stirring (500 rpm) started. Samples of gas (0.5 mL) were withdrawn periodically by the gas-tight syringe equipped with a 6-in. needle and two-way valve and analyzed as previously[5] by using a Picker Nuclear MS10 mass spectrometer which was calibrated with a standard mixture of $D_2/HD/H_2$ before each run.

Rate constants for exchange were obtained by a computer curve-fitting method. A program was set up which gave a best fit between experimental values of mole % D_2, HD, and H_2 and theoretical values calculated by assuming two consecutive pseudo-first-order processes (eq 1).[37] The resulting vapor-phase rate constants were converted into in-solution first-order rate constants as previously[5] by using the solubilities of D_2 in aniline.

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Rate Coefficients for N(^{2}D) Reactions

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We have measured rate coefficients for the reactions of N(^{2}D) with O_2, CO_2, N_2O, CO, and H_2 in a discharge-flow reactor. The values are 4.6 ± 0.5, 0.35 ± 0.03, 2.2 ± 0.3, 1.7 ± 0.4, and 2.3 ± 0.5 in units of 10^{-12} cm^3 molecule^{-1} s^{-1} for O_2, CO_2, N_2O, CO, and H_2, respectively. A resonance-fluorescence diagnostic having an ultimate sensitivity of better than 1×10^8 atoms cm^{-3} monitors the number density of N(^{2}D). The extreme sensitivity of the diagnostic allows kinetic measurements to be made in regions of the flow reactor far downstream from the source of the metastables. This feature removes fluid dynamic complications which plague most flow reactor studies of metastable kinetics. The diagnostic sensitivity also affords over two orders of magnitude in N(^{2}D) number density decays, thereby ensuring the accurate determination of kinetic decay rates. A movable injector for the reactants allows measurements at a variety of reactions times, thereby eliminating uncertainties caused by imperfect mixing in the reactor.

Introduction

Metastable atomic nitrogen, N(^{2}D, ^{2}P), plays an important role in the chemistry of the nonequilibrium upper atmosphere and of systems employing nitrogen or air discharge plasmas. N(^{2}D), through its chemiluminescent reaction with molecular oxygen

$$N(^2D) + O_2 \rightarrow NO(v) + O \qquad (1)$$

controls the production of NO in the thermosphere and provides a key source of vibrationally excited NO (and perhaps electronically excited O) in electron-irradiated air.[1,2] Similarly, quenching of N(^{2}D) by other common atmosphere species such as CO_2, N_2O, CO, H_2, or H_2O may proceed by chemical or energy-transfer reactions to form internally excited molecular products.

Several investigators[3-8] have studied the quenching kinetics of N(^{2}D) using either discharge-flow or flash photolysis techniques. Most of these studies employed relatively insensitive and error-prone techniques for detecting the commonly obtained, low concentrations of N(^{2}D), viz. resonance absorption,[4,5,8] electron-spin resonance (ESR) spectroscopy,[6] and tracer fluorescence.[7] Since the maximum obtainable N(^{2}D) number densities are typically only slightly above the detection limits of techniques such as resonance absorption or ESR, it is difficult to obtain the factor of 10 to 100 first-order N(^{2}D) decays which are required not only for precise rate-coefficient determinations but also to rule out interference from secondary reactions. The limitation in dynamic range imposes additional uncertainties on the flow reactor studies,[4,6,8] where the measurements must be made at fairly short flow distances under conditions of poorly characterized flow development. As a result, N(^{2}D) quenching rate coefficients available in the literature still exhibit considerable disparity, often as much as a factor of 3.

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