Carbanion Mechanisms. 6.[1] Metalation of Arylmethanes by Potassium Hydride/18-Crown-6 Ether in Tetrahydrofuran and the Acidity of Hydrogen

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Abstract: The metalation of a series of hydrocarbon acids in anhydrous tetrahydrofuran has been studied. Triphenylmethane, diphenylmethane, and di-*p*-tolylmethane are readily metalated by potassium hydride in the presence of 18-crown-6 ether in tetrahydrofuran. The metalation of di-2,4-xylylmethane occurs only to partial completion while *p*-phenyltoluene is unreactive. The acidity of hydrogen is therefore comparable to that of di-2,4-xylylmethane in this medium. The equilibrium constant for the reaction with di-2,4-xylylmethane can be calculated from the equilibrium carbanion concentration and the measured solubility of hydrogen and of potassium hydride under the experimental conditions. The equilibrium acidity of hydrogen in this medium can hence be derived. The roles of medium and of ion pairing effects in this system are considered.

The conversion of organic compounds into their metal derivatives constitutes an important intermediate stage in a variety of sequences which utilize organometallic compounds as reactive species.[2,3] Such processes also form the basis of determination of the acidities of weak acids, leading to an improved understanding of structure-reactivity relationships. Since the facility of the ionization of carbon acids is known to depend on the structure and constitution of the organic substrate,[4-7] the basic strength of the reagent required to effect this ionization must vary accordingly. For example, whereas nitromethane can be converted into its nitronate anion by means of aqueous sodium hydroxide or ethanolic sodium ethoxide, toluene requires the action of butyllithium for conversion to benzyllithium to occur.

We have undertaken a program aimed at determining the acidity of very weak acids, as a quantitative extension of our studies of hydrogen-deuterium exchange[8,9] and in order to investigate the pertinent rate-equilibrium relationships. Thus, in relation to our study of isotopic exchange in the D_2-OH^--H_2O-Me_2SO system[10] (cf. ref 11 and 12), we have undertaken to evaluate the pK_a of hydrogen (deuterium). The pK_a of H_2 has not been determined experimentally and estimates of this quantity in the literature vary between 29 and 38.[13,14] It appeared to us that the metalation of weak hydrocarbon acids by metal hydrides, as given in:

$$RH + MH \rightleftarrows RM + H_2 \qquad (1)$$

could potentially lead to evaluation of the pK_a of H_2. Thus, reaction 1 should proceed to the right provided that RH is a stronger acid than H_2. Therefore, if a series of weak hydrocarbon acids of increasing pK_a is taken, a break in reactivity will occur in the region of the pK_a of H_2. In a complementary study, we have sought to evaluate the pK_a of H_2 by investigating the reaction of organocesiums with hydrogen,[1] a process which in essence constitutes the reverse of reaction 1. Preliminary results of part of this work have been reported.[15]

Results and Discussion

Survey of Reaction of Potassium Hydride with Hydrocarbons. Metalation of a number of hydrocarbon acids in a medium of tetrahydrofuran (THF), at room temperature, was examined by two methods. In the first method carbanion formation was monitored spectrophotometrically, while in the second method evolution of hydrogen gas was followed using a gas buret. The same reaction flask was used for both types of experiments (see Experimental Section). The spectrophotometric method requires much smaller quantities of reagents and was used in the majority of the measurements (Table I), leaving the hydrogen gas method for some selected confirmatory experiments (Table II).

Potassium hydride has been found to metalate compounds in the intermediate acidity range (e.g., acetone)[16] and to be superior to both lithium hydride and sodium hydride in its effectiveness.[16] In order to test our proposed method of attack, the interaction between triphenylmethane and potassium hydride, in THF solvent, was first examined. Using the spectrophotometric method, it was found that metalation did not occur as there was no development of color characteristic of the trityl anion, which is in agreement with Brown's conclusion.[16] However, when the experiment was performed in the presence of 18-crown-6 ether (see Table I, run 1, for concentrations of reagents), a facile metalation reaction (eq 2) was observed as evidenced by the development of the spectral absorption characteristic of the trityl anion, with a major peak appearing at 496 nm and a secondary peak at 430 nm. The trityl anion is formed in near quantitative yield, as judged by the solution absorbance value (Table I). When the experiment was performed using the gas buret method, the volume of hydrogen evolved was found once again to be almost quantitative (Table II).

$$Ph_3CH + KH \xrightarrow[\text{THF}]{\text{18-crown-6}} Ph_3CK + H_2 \qquad (2)$$

Since alkali metal hydrides are considered to be virtually insoluble in typical organic solvents,[17] it is presumed that the role of the crown ether in the present system is to partially solubilize the hydride by complexation of K^+, thereby increasing the reactivity of H^- toward the hydrocarbon. This is in accord with findings of other workers on enhanced reactivity resulting from the use of crown ethers,[18-21] especially in nucleophilic substitution by potassium halides, hydroxide, and methoxide in a variety of substrates and using various aprotic organic solvents. However, to our knowledge, the present observation is the first reported case of the use of crown ethers to effect acid-base equilibria. Very recently, the use of diamine-chelated phenylsodium in hydrocarbon solvents was reported in the determination of equilibrium ion-pair acidities of a number of hydrocarbons.[22]

From the observed reaction between TPM and KH, it could be concluded that H_2 is a weaker acid than TPM. Therefore, to evaluate the range of applicability of eq 1, it was decided to study a series of hydrocarbon acids of increasing pK_a and those selected are shown below together with their abbreviated notation and pK_a values[23] as determined in the cesium cyclohexylamide/cyclohexylamine (CsCHA/CHA) system.

The results that we obtained for the interaction of KH/

Table I. Spectrophotometric Data for Reaction between Hydrocarbon Acids (RH) and Potassium Hydride in the Presence of 18-Crown-6 Ether in Tetrahydrofuran at Room Temperature

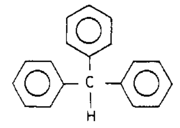
Run no.	RH	$[RH]_0 \times 10^3$, M	$[KH]_0$,[a] M	[Crown], M	λ_{max},[b] nm	A[c]
1	TPM	0.908	0.0286	0.0280	496 (430) sh	1.93 (1.00)
2		0.393	0.0281	0.0312		0.85 (0.50)
3		0.298	0.0322	0.0316		0.63 (0.34)
4	DPM	0.328	0.0304	0.0315	448	1.34
5		0.167	0.0277	0.0291		0.73
6	DPTM	0.490	0.0258	0.0250	450	1.85
7		0.298	0.0297	0.0287		0.91
8		0.157	0.0194	0.0197		0.55
9	DXM	1.616	0.0256	0.0248	448	0.84
10		0.816	0.0233	0.0237		0.34
11		0.391	0.0349	0.0311		0.26
11a						(0.38)[d]
11b						(0.46)[d]
12	PPT	1.469	0.0302	0.0298		

[a] The potassium hydride is present as a suspension; the $[KH]_0$ values given represent the overall stoichiometric quantities based on the weight of KH taken and the volume of THF used, and are given for purposes of comparison only. The measured solubility of KH in the THF/crown ether system is $(21.5 \pm 9.5) \times 10^{-6}$ M. [b] The λ_{max} values for R^-K^+ experience a shift to longer wavelengths due to the presence of 18-crown-6 ether in this system. [c] Absorbance data (at λ_{max}) are the maximum values obtained and correspond to the following reaction times: TPM, 1 h; DPM, 10 h; DPTM, 48 h; DXM, 72 h (PPT, 168 h). For TPM, DPM, and DPTM the A values correspond to 100% conversion to R^-K^+; for DXM the extent of conversion in runs 9, 10, and 11 is 17, 14, and 22%, respectively, on the basis of an ϵ value for DXM^-K^+ of 29 000.[24] [d] These values were obtained after consecutive degassing of the reaction solution from run 11 and standing for further periods of 72 h in order to allow the maximum absorbance to be reached.

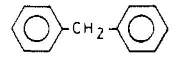
Table II. Reaction between Hydrocarbon Acids (RH) and Potassium Hydride/Crown Ether in Tetrahydrofuran as Followed by Evolution of Hydrogen Gas

RH	$[RH]_0$, M	$[KH]_0$,[a] M	[Crown], M	Time for 90% rxn, h	H_2 produced, %
TPM	0.0535	0.1025	0.0928	7	97
DPM	0.0475	0.0817	0.0879	18	104
DPTM	0.0500	0.1020	0.0920	87	94
DXM	0.0336	0.0760	0.0719		35[b]

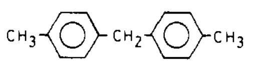
[a] As in Table I, footnote a. [b] Yield of H_2 after 87 h; no further increase was observed after prolonged reaction times.



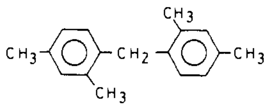
triphenylmethane
(TPM 31.5)



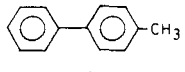
diphenylmethane
(DPM 33.1)



di-p-tolylmethane
(DPTM 35.1)



di-2,4-xylylmethane
(DXM 36.3)



p-phenyltoluene
(PPT 38.6)

18-crown-6/THF with DPM and DPTM are analogous to the result with TPM, namely, that the reaction leading to the organometallic derivative occurs to completion in all these cases. The extent of the conversion of RH to RK was estimated by performing several experiments using increasing concentrations of RH (Table I, runs 1-3, 4-5, and 6-8). On plotting the absorbance at λ_{max} vs. [RH], linear plots passing through the origin were obtained showing that Beer's law was obeyed. From the slopes of these plots the following molar extinction coefficient values (ϵ in M^{-1} cm^{-1} at the wavelengths of the absorption maxima) of the alkylpotassiums were obtained: TPM^-K^+, 21 300 (496 nm), 11 600 (430 nm); DPM^-K^+, 43 000 (448 nm); $DPTM^-K^+$, 37 800 (450 nm). A noteworthy point, however, was that the rate of the RH/KH/18-crown-6 reaction was observed to decrease in the order TPM, DPM, DPTM; the times required for 90% completion were 0.5, 5, and 30 h, respectively.

The reaction of KH/18-crown-6/THF with DXM assumed different characteristics from those described above for TPM, DPM, and DPTM. In the DXM/KH case (Table I, runs 9-11) the plot of the maximum in absorbance vs. [RH] exhibited considerable scatter and from the approximate slope an apparent extinction coefficient of ca. 6000 was calculated, whereas in other work[24] we have obtained for DXM^-K^+ in THF an ϵ value of 29 000. Using this figure, an estimate of 22% conversion in 72-h reaction time can be made for run 11 in Table I.

The next hydrocarbon in the series of increasing pK_a being PPT, its reaction with the KH/18-crown-6/THF system was examined. Metalation did not occur to any extent even after prolonged reaction times. However, when PPT in THF was treated with *n*-butyllithium, the spectrum of the PPT^- anion (λ_{max} 430 nm) was obtained, as expected on using the stronger base.

To summarize the results recorded hitherto, the metalation of the hydrocarbons TPM, DPM, and DPTM by reaction with KH/18-crown-6 in THF proceeds to completion, but conversion of DXM occurs only to ca. 20% and there is no reaction

Table III. Calculation of K_{rel} and $pK_a(H_2)$ for Reaction between Di-2,4-xylylmethane (DXM) and Potassium Hydride/Crown Ether in Tetrahydrofuran Using Data in Table I

Run no.	$[DXM]_0$[a] × 10^3, M	$[DXM^-K^+]_e$[b] × 10^3, M	$[H_2]_t$[c] × 10^3, M	$[H_2]_e$[d] × 10^3, M	$[DXM]_e$[e] × 10^3, M	[KH][f] × 10^6, M	K_{rel}[g]	pK_{rel}[g]	$pK_a(H_2)$[g]
9	1.616	0.289	0.289	0.0219	1.327	21.5 ± 9.5	0.257 ± 0.125	0.62 ± 0.21	35.67 ± 0.21
10	0.816	0.117	0.117	0.0088	0.699	21.5 ± 9.5	0.079 ± 0.038	1.13 ± 0.21	35.17 ±0.19
11	0.391	0.089	0.089	0.0067	0.302	21.5 ± 9.5	0.106 ± 0.051	1.01 ± 0.21	35.30 ± 0.21
11a[h]	0.302	0.131	0.041	0.0031	0.261	21.5 ± 9.5	0.083 ± 0.040	1.11 ± 0.21	35.19 ± 0.21
11b[i]	0.262	0.158	0.027	0.0020	0.235	21.5 ± 9.5	0.072 ± 0.035	1.17 ± 0.21	35.11 ± 0.22

[a] Initial concentration of DXM. [b] Spectrophotometrically measured carbanion concentration at equilibrium. [c] Total hydrogen produced. [d] Equilibrium concentration of hydrogen in solution phase. [e] Equilibrium concentration of DXM, i.e. $[DXM]_0 - [DXM^-K^+]_e$. [f] Measured concentration of potassium hydride in the THF/crown ether system. [g] The error limits given for K_{rel}, pK_{rel}, and $pK_a(H_2)$ are derived from the experimental error in the determination of the solubility of potassium hydride in the THF/18-crown-6 system. [h] Obtained by degassing the solution at the end of run 11. [i] Obtained by degassing the solution at the end of run 11a.

at all in the case of PPT. On the basis of the above discussion, and from consideration of eq 1, it can be concluded that while TPM, DPM, and DPTM are stronger acids than H_2, DXM and H_2 have comparable acidities.

Further evidence concerning the comparable acidity of DXM and H_2 could be obtained by degassing the solution from the reaction of DXM with KH/18-crown-6, after the equilibrium absorbance value had been reached. This experiment was performed on completion of run 11 in Table I and resulted in an increase in absorbance, from 0.26 to 0.38 (run 11a). Another degassing cycle led to a further increase in absorbance to 0.46 (run 11b). These experiments therefore establish that reaction 1 with R = di-2,4-xylylmethyl and M = potassium, in the presence of 18-crown-6 in THF, proceeds to equilibrium.

The experiments performed by monitoring the hydrogen gas evolved (Table II) gave results which are qualitatively similar to the spectrophotometric results described above (Table I). It was noted, however, that the reaction solutions in the former method tended to become discolored on prolonged reaction times and in some of the experiments the volume of gas decreased slightly after reaching the maximum values which are recorded in Table II. These observations indicate that decomposition reactions set in at the higher carbanion concentrations required in the H_2 gas method as compared to the spectrophotometric method. The calculations described in the following section will hence be limited to the results obtained by the spectrophotometric method.

An Estimate of the pK_a of H_2. The results obtained in this work, relating to reaction 1 with RH = DXM, can in principle be used to calculate the pK_a of hydrogen. However, the calculations are based on certain assumptions being valid, namely that ion association and medium effects do not materially affect the derived pK_a values. We will show subsequently that these assumptions hold in the present system.

An estimate of the pK_a of H_2 can be made using the data obtained with DXM (Table I). The equilibrium constant K_{rel} for eq 1 is related to the K_a values of RH and H_2 via eq 3 and 4:

$$K_{rel} = K_a^{RH}/K_a^{H_2} \tag{3}$$

$$pK_a^{H_2} = pK_a^{RH} - pK_{rel} \tag{4}$$

The problem reduces therefore to evaluation of K_{rel} from eq 5:

$$K_{rel} = \frac{[RK]_e[H_2]_e}{[RH]_e[KH]_e} \tag{5}$$

Of the equilibrium concentration terms in eq 5, $[RK]_e$ is the spectrophotometrically measured carbanion concentration while $[KH]_e$ is given by the solubility of potassium hydride in the THF/crown ether system, which has been determined (21.5 ± 9.5 × 10^{-6} M, see Experimental Section and discussion below for effect of error limit on derived pK_a values). The $[RH]_e$ term is also known, being equal to $[RH]_0 - [RK]_e$. From the stoichiometry of reaction 1 we have $[RK]_e = [H_2]_t$, the total hydrogen produced. This will be partitioned between the solution and gaseous phases, so that the equilibrium concentration of H_2 in solution is $[H_2]_e = [H_2]_t - [H_2]_g$. From the measured solubility of H_2 in THF, the ratio of the concentrations of H_2 in solution and in the gas phase is given by $[H_2]_e/[H_2]_g = 0.082$, so that for any given value of $[H_2]_t$ one can calculate $[H_2]_e$ and hence K_{rel}. Thus, for run 11 with DXM we have $[RH]_0 = 0.391 \times 10^{-3}$ M and $[RK]_e = 0.089 \times 10^{-3}$ M, so that $[RH]_e = 0.302 \times 10^{-3}$ M. Also, $[H_2]_t = 0.089 \times 10^{-3}$ M, which gives $[H_2]_e = 0.082 \times 0.089 \times 10^{-3}/1.082 = 0.0067 \times 10^{-3}$ M. One then obtains $K_{rel} = 0.106 \pm 0.051$ so that $pK_{rel} = 1.01 \pm 0.21$ and $pK_a(H_2) = 35.30 \pm 0.21$. The error limits given for K_{rel}, pK_{rel}, and $pK_a(H_2)$ are derived from the experimental error in the determination of the solubility of potassium hydride in the THF/18-crown-6 ether system. For runs 9 and 10 one obtains comparable $pK_a(H_2)$ values. The detailed results are presented in Table III.

The calculation of K_{rel} according to eq 5 is also applicable to the experiments performed with DXM/KH/18-crown-6 in which the hydrogen was removed by degassing after equilibrium had been reached (runs 11a,b). This perturbation procedure resulted in a new equilibrium position being established, as shown by the observed increase in carbanion concentration. In the case of run 11a, the absorbance increase from 0.26 to 0.38 corresponds to an increase in concentration of carbanion from 0.089×10^{-3} to 0.131×10^{-3} M. The change in carbanion concentration (0.041×10^{-3} M) corresponds to the total H_2 produced, so that the resulting equilibrium concentration of H_2 is given by $[H_2]_e = 0.082 \times 0.041 \times 10^{-3}/1.082 = 0.0031 \times 10^{-3}$ M. One then obtains $K_{rel} = 0.083 \pm 0.040$ and $pK_a(H_2) = 35.19 \pm 0.21$. Similar treatment (Table III) of run 11b for the second degassing procedure yields $K_{rel} = 0.072 \pm 0.035$ and $pK_a(H_2) = 35.11 \pm 0.22$. The combined data in Table III yield an average $pK_a(H_2) = 35.3 \pm 0.3$ for the THF/18-crown-6 ether system.

Effect of Ion Pairing on Derived pK_a of H_2. In media of low dielectric constant, ion pairing phenomena can have profound effects on equilibria, including the evaluation of pK_a values.[25] The possible influence of this factor on our derived value of the pK_a of H_2 must therefore be examined. Two points need to be considered in this regard: the effect of the presence of crown ether, and the effect of change of solvent, from CHA for which the pK_a values have been given,[23] to THF as used in the present work.

There has been ample evidence presented[26] that crown ethers, through their capacity for complexing metal cations, convert originally "tight" ion pairs into "loose" ion pairs. Thus, in the presence of crown ether (X) the reaction under study may be represented by eq 6 in which $(\mathrm{H}^-,\mathrm{X},\mathrm{K}^+)$ and $(\mathrm{R}^-,\mathrm{X},\mathrm{K}^+)$ represent loose ion pairs:

$$\mathrm{RH} + (\mathrm{H}^-,\mathrm{X},\mathrm{K}^+) \overset{K_6}{\rightleftharpoons} (\mathrm{R}^-,\mathrm{X},\mathrm{K}^+) + \mathrm{H}_2 \tag{6}$$

where X = 18-crown-6. Since with X in the reaction system equilibra 7 and 8 are established (i.e. tight ion pairs are converted into loose ion pairs):

$$(\mathrm{H}^-,\mathrm{K}^+) + \mathrm{X} \overset{K_7}{\rightleftharpoons} (\mathrm{H}^-,\mathrm{X},\mathrm{K}^+) \tag{7}$$

$$(\mathrm{R}^-,\mathrm{K}^+) + \mathrm{X} \overset{K_8}{\rightleftharpoons} (\mathrm{R}^-,\mathrm{X},\mathrm{K}^+) \tag{8}$$

it follows that K_6 will be given by:

$$K_6 = \frac{K_8}{K_7}\frac{[\mathrm{R}^-,\mathrm{K}^+][\mathrm{H}_2]}{[\mathrm{H}^-,\mathrm{K}^+][\mathrm{RH}]} \tag{9}$$

The concentration terms in eq 9 represent the equilibrium constant K_{10} for the reaction between KH and RH in THF in the absence of X:

$$(\mathrm{H}^-,\mathrm{K}^+) + \mathrm{RH} \overset{K_{10}}{\rightleftharpoons} (\mathrm{R}^-,\mathrm{K}^+) + \mathrm{H}_2 \tag{10}$$

Equation 11 follows from the above:

$$K_6 = K_{10}(K_8/K_7) \tag{11}$$

It is seen from eq 11 that K_6 which corresponds to the experimentally measured K_{rel} value for the loose ion pair equilibrium in the THF/KH/crown ether system differs from K_{10} which is applicable to the contact ion pair equilibrium. The latter may be used in calculating the ion pair acidity of H_2. Direct information on the magnitude of the K_8/K_7 ratio is not available but from literature data on related systems[27] one would expect this to range between 1 and 10^{-2}. For the case that $K_8/K_7 = 1$ we have $K_{10} = K_6$ and the ion pair acidity of H_2 in THF, as given by eq 12, becomes $\mathrm{p}K_\mathrm{a}{}^{\mathrm{H}_2} = \mathrm{p}K_\mathrm{a}{}^{\mathrm{RH}} - \mathrm{p}K_6 = \mathrm{p}K_\mathrm{a}{}^{\mathrm{RH}} - \mathrm{p}K_{\mathrm{rel}}$, as in eq 4:

$$\mathrm{p}K_\mathrm{a}{}^{\mathrm{H}_2} = \mathrm{p}K_\mathrm{a}{}^{\mathrm{RH}} - \mathrm{p}K_{10} \tag{12}$$

Now the THF and CHA media are believed to be comparable in terms of loose and contact ion pair equilibria,[25,26] which justifies our use of Streitwieser's $\mathrm{p}K_\mathrm{a}{}^{\mathrm{RH}}$ values determined in the CsCHA/CHA system and applicable to ion pair acidities.[23] The pK_a value of 35.3 ± 0.3 for H_2 which we have obtained would thus be applicable to the CHA medium as well. Considering the other limit, $K_8/K_7 = 10^{-2}$, one now obtains from eq 11 $K_{10}/K_6 = 10^2$. Using this value in eq 12 leads to $\mathrm{p}K_\mathrm{a}{}^{\mathrm{H}_2} = \mathrm{p}K_\mathrm{a}{}^{\mathrm{RH}} - \mathrm{p}K_6 + 2 = \mathrm{p}K_\mathrm{a}{}^{\mathrm{H}_2} - \mathrm{p}K_{\mathrm{rel}} + 2$. Therefore, the ion pair acidity of H_2 will increase by up to 2 pK_a units compared to the situation when $K_8/K_7 = 1$, and this will be applicable to the THF as well as the CHA media according to the above reasoning.

It is to be noted that measurement of equilibrium acidities in solvents of low dielectric constant such as CHA and THF is subject to greater uncertainty than comparable measurements in solvents of high dielectric constant such as dimethyl sulfoxide ($\mathrm{Me_2SO}$) or water. As has been pointed out recently by Bordwell and co-workers,[28] the former type of solvent system is limited not only by the uncertainty with respect to ion association phenomena but also by the necessity of choosing a reference ("anchor") base as a standard state (see also ref 29-31). Nevertheless, $\mathrm{Me_2SO}$ is limited to determination of acidities with p$K_\mathrm{a} < 35$, and study of still weaker acids requires use of solvents with extremely small autoprotolysis constants, CHA, THF, or benzene being commonly used for this purpose.[4-7]

It is interesting to comment on the relative rates of the metalation process observed in this study. The observed reactivity order for the RH + KH reaction has been found to be TPM > DPM > DPTM > DXM ≫ PPT. This relative order is in accord with Eigen's[32] postulate, since the rate of proton transfer between RH and H^- will be dependent on the relative magnitudes of the pK_a values of RH and H_2, decreasing as p$K_\mathrm{a}(\mathrm{H}_2)$ − pK_a(RH) decreases. By the same token, it follows from Eigen's principle that the reverse reaction, namely proton transfer between H_2 and R^-, should follow the reverse order of reactivity. In fact, in the complementary study[1] we have found for the RCs + H_2 reaction (eq 13) in cyclohexylamine solvent the reactivity order $\mathrm{PPT^-Cs^+} \gg \mathrm{DXM^-Cs^+}$, $\mathrm{DPM^-Cs^+}$. However, our analysis of the results of that study[1] did not include an assignment of the pK_a of hydrogen due to an inherent uncertainty as to the effect of ion association phenomena. The degree of association into ion pairs or aggregates is expected to differ for the species RCs and CsH in the cyclohexylamine solvent, requiring caution in the assignment of pK_a values.[25] In the present study, in contrast, the use of crown ether leads to "loose" ion pairs for both the RM and MH species and this situation has enabled us to make an assignment of the pK_a value of hydrogen.

$$\mathrm{RCs} + \mathrm{H}_2 \rightleftharpoons \mathrm{RH} + \mathrm{CsH} \tag{13}$$

The acidities of binary hydrides, XH, and of more complex hydrides, RH, where R is composite, have been the subject of extensive discussion.[4-7] Since such hydrides can be considered as derivatives of H_2, the availability of the pK_a for this primary acid should make it possible to reach a better understanding of structural effects in ionization processes.

Experimental Section

Materials. Tetrahydrofuran (THF) was dried by distilling first from calcium hydride followed by repeated distillation from lithium aluminum hydride under argon. The dry THF was stored over *n*-butyllithium prior to distillation into the reaction vessel in vacuo. 18-Crown-6-ether (Aldrich) was dried in vacuo before use. Potassium hydride (Ventron-Alfa or Pressure Chemicals) was obtained as an oil suspension and was washed repeatedly with dry petroleum ether under nitrogen before use. The hydrocarbon acids were commercial samples, other than DXM which was prepared according to published procedure.[33] The commercial compounds were purified by crystallization or distillation as appropriate.

Procedure. Reactions were performed in a cylindrical vessel (~120 mL) fitted with a 1-mm quartz cuvette and a greaseless vacuum (Rotaflo) stopcock.[1] A known weight of potassium hydride was introduced under a nitrogen atmosphere and THF solvent (20-25 mL) was distilled into the reaction vessel in vacuo. The hydrocarbon and the crown ether were then introduced in turn in glass ampules under nitrogen. In the spectrophotometric method, the vessel was shaken vigorously to effect mixing and placed into the sample compartment of a Unicam SP800B spectrophotometer, and the spectrum was scanned intermittently over the region 300-650 nm until the maximum in absorbance was reached. In the case of very slow reactions, the vessel was shaken mechanically in-between scanning.

In the hydrogen gas method, the reaction vessel was attached to a mercury filled gas buret after introduction of the KH and THF. The system was then flushed with nitrogen and the hydrocarbon and crown ether were added in turn. The reaction mixture was stirred magnetically and the evolution of gas followed with time.

Solubility of Potassium Hydride and of Hydrogen. A known weight (ca. 50 mg) of potassium hydride was introduced into a glass vessel (~120 mL) fitted with a side arm consisting of a Rotaflo stopcock attached to an O ring joint. THF (ca. 30 mL) was distilled in vacuo and a weighed amount of 18-crown-6 ether (0.3-0.4 g) was added by means of a glass ampule under nitrogen. After shaking for 1 h, the vessel was attached to a cylindrical glass piece with a built-in fritted disk equipped with an O ring joint at either end. The lower end of this piece was connected to a reaction vessel fitted with a 1-cm quartz cuvette and containing triphenylmethane (1-2 mg). Prior to filtration, the lower part of the apparatus (consisting of the fritted disk and the reaction vessel) was evacuated and the fritted disk was flamed out.

On filtration a red colored solution was obtained and from the absorbance value (using $\epsilon_{496} = 21\,300$) the concentration of TPM^-K^+, and hence of KH, was obtained. The resulting values of the solubility of KH showed appreciable variation in six determinations, as may be expected for a very sparingly soluble substance. The overall result for the solubility of potassium hydride in the THF/crown ether system is $(21.5 \pm 9.5) \times 10^{-6}$ M.

The solubility of H_2 in THF was determined by the GLC method described by Symons[34] under conditions analogous to those pertaining to the reaction under study. Thus, H_2 gas was introduced to 1 atm into the reaction vessel containing ~20 mL of THF after freezing with liquid nitrogen and evacuating the system. The vessel was then closed off from the H_2 source, allowed to reach room temperature, and shaken thoroughly. Aliquots (4 mL) of the solution were then removed with a gas-tight syringe and the gas stripped off by the technique described previously.[34] Analysis was performed by GLC using a prior calibration with a known volume of H_2. The solubility of H_2 in THF at 25 °C was thus obtained as $(3.66 \pm 0.20) \times 10^{-3}$ M. The solubility coefficient can then be expressed as the volume of gas dissolved by unit volume of liquid, i.e., $22.4 \times 3.66 \times 10^{-3} = 0.082$.

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Hydrazine Lone Pair–Lone Pair Interactions. X-Ray Crystallographic Structure Determination of Two Six-Membered Ring Hydrazines

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Abstract: The structures, determined by x-ray crystallography, are reported for 3,4-dimethyl-3,4-diazabicyclo[4.4.0]decane (**2**) and for 2,3-dimethyl-2,3-diazatricyclo[$8.4.0.0^{4,9}$]tetradec-9-ene (**3**). Crystals of **2** are triclinic, $P\bar{1}$, with $a = 9.618$ (2), $b = 10.435$ (2), $c = 5.440$ (1) Å, $\alpha = 102.55$ (2), $\beta = 94.38$ (1), $\gamma = 74.88$ (2)°, $V = 514.4$ (2) Å^3, and $Z = 2$. The structure was solved by direct methods and refined to $R_1 = 4.6\%$ and $R_2 = 5.7\%$ for 666 independent observed reflections. Crystals of **3** are monoclinic, $P2_1/n$, with $a = 14.343$ (3), $b = 6.672$ (1), $c = 14.073$ (2) Å, $\beta = 104.29$ (1)°, $V = 1304.9$ (3) Å^3, and $Z = 4$. Solution by direct methods and refinement gave $R_1 = 5.4\%$ and $R_2 = 5.7\%$ for 1398 independent observed reflections. Compound **2** has the methyl groups substituted diequatorial on the six-membered ring and **3** has the axial,equatorial conformation. The implications of these results for the interpretation of photoelectron spectroscopic experiments and equilibrium constant measurements are discussed.

The conformations of hydrazine derivatives have received a great deal of study by a wide range of experimental techniques.[1] The angle of rotation about the N–N bond has been of particular interest, and it is well established that for many acyclic hydrazine derivatives, the preferred conformation is that which has the lone-pair orbitals nearly perpendicular (I, θ near 90°), although this is clearly not the sterically least hindered conformation. A large change in the energy separa-