## An hydration scale for ketones in polar aprotic solvents<sup>1</sup>

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An hydration scale ( $W_0$ ) for aqueous sulfolane and dimethyl sulfoxide (DMSO) has been developed that represents the effect of the solvent on the equilibrium hydration of a series of trifluoroaceto-

phenones;  $ZH_2O \rightleftharpoons Z + H_2O$ . The equilibrium constants are correlated with the substituent parameter  $\sigma^+$ ;  $\rho^+ = -1.62$  for dehydration. The function  $W_0$ , defined as  $W_0 = pK_d + \log [Z]/[ZH_2O]$  $= -\log (f_Z|f_{ZH_2O} \cdot a_{H_2O})$  is zero for pure water and rises to a value of 2.72 in 99 mole% sulfolane.  $W_0$  in aqueous DMSO is negative from 0 to 85 mole% DMSO, meaning that these systems hydrate the ketones to a greater extent than does pure water.

[3]

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Carbonyl compounds undergo hydration reactions to give gem diols provided that the attached groups are small or contain strongly electronegative atoms (1). We have used the general Hammett overlap method (2) to determine (a) the thermodynamic equilibrium constants for the hydration of a series of ring-substituted trifluoroacetophenones (standard state, water) and (b) the hydrating ability of solvent mixtures that range from pure water to 99 mole% tetramethylene sulfone (sulfolane) or dimethyl sulfoxide (DMSO). To preserve the analogy with Hammett-type acidity functions the equilibrium equation is written so that the hydrate is on the left and the ketone on the right.



The dehydration constant,  $K_d$ , takes the form

[1]  $K_{d} = \frac{[Z]}{[ZH_{2}O]} \cdot \frac{f_{Z}}{f_{ZH_{2}O}} \cdot a_{H_{2}O}$ Therefore [2]  $pK_{d} = -\log\left(\frac{[Z]}{[ZH_{2}O]}\right) - \log\left(\frac{f_{Z}a_{H_{2}O}}{f_{ZH_{2}O}}\right)$ We define  $W_{0}$  as

<sup>1</sup>Taken from the Ph.D. thesis of J. D. Van Dyke, 1970. <sup>2</sup>Present address: Polymer Corporation, Sarnia, Ontario.

$$W_0 = -\log\left(\frac{f_Z a_{H_2O}}{f_{ZH_2O}}\right)$$

Combining [2] and [3] gives

[4] 
$$W_0 = pK_d + \log \frac{[Z]}{[ZH_2O]}$$

The symbol  $W_0$  seems appropriate for this function since water is a component of the equilibrium. The subscript indicates the substrate's charge.

Values of log  $[Z]/[ZH_2O]$  were obtained at 31.4 ° using both <sup>19</sup>F n.m.r. and ultraviolet (u.v.) spectroscopy, the latter being used at high water concentrations where solubility problems made n.m.r. measurements difficult or impossible. Excellent agreement between the two techniques was achieved.

The only ketone not previously prepared (3), 3-methoxy- $\alpha$ , $\alpha$ , $\alpha$ -trifluoroacetophenone, was obtained by the action of 3-methoxyphenylmagnesium bromide on trifluoroacetic acid; b.p. 60° at 2 Torr.

Anal. Calcd. for C<sub>9</sub>H<sub>7</sub>OF<sub>3</sub>: C, 52.95; H, 3.45; F, 27.92. Found: C, 52.74; H, 3.49; F, 28.1.

The anchor compound is 4-methoxy- $\alpha,\alpha,\alpha$ trifluoroacetophenone whose  $pK_d$  in water was found to be 0.84. (This value was obtained by adding a solution of this ketone in aqueous sulfolane to water so that the concentration of water was actually 99.90 mole%.) Methanesulfonic acid was added as catalyst to most of the solutions, because equilibrium was reached extremely slowly in solutions whose water content was low. Experiments at higher water content showed the position of the hydration equilibrium to be unaffected by acid, except for the dimethylamino compound. Table 1 lists the  $pK_d$  values (in water) determined by the overlapping technique and Fig. 1 shows the effect of substituents on  $pK_d$  (4). It is interesting to note that the substituent parameter that governs the hydration equilibrium is  $\sigma^+$  rather than  $\sigma$  (5), and this presumably reflects the importance of resonance interaction between para substituents and the carbonyl group (5).

Figure 2 shows the variation of  $W_0$  with solvent composition for aqueous sulfolane and aqueous DMSO. It is clear that sulfolane has a greater dehydrating action in these systems than does DMSO, in sharp contrast to their effect on hydroxide ion basicity (6). Figure 2 reveals that aqueous systems containing up to 85 mole% DMSO are more hydrating with respect to trifluoroacetophenones than is pure water.

The activity of water in aqueous DMSO de-

Y	p <i>K</i> <sub>d</sub>
4-(CH₃)₂N	-0.86
4-CH₃O	0.84
4-CH₃	1.46
3-CH <sub>3</sub>	1.77
H	1.89
	1.91
	1.99
3-NO <sub>2</sub>	3.15
4-(CH <sub>3</sub> ) <sub>2</sub> N	







FIG. 2. Plots of  $W_0$  determined with trifluoroacetophenone indicators against solvent composition for sulfolane-water mixtures ( $\bigcirc$ ) and DMSO-water mixtures ( $\bigcirc$ ) containing 0.1*M* methanesulfonic acid.

creases faster than does the water concentration and in aqueous sulfolane it decreases more slowly than does the water concentration (7). The  $W_0$ values are in the reverse order and this must result from the  $f_Z/f_{ZH_2O}$  term in eq. 3 being strongly solvent dependent. We believe that the ketone hydrate, because of its *gem* diol character, fits into the water structure without greatly perturbing it whereas the presence of sulfolane tends to exclude the ketone hydrate from the association pattern, causing  $f_{ZH_2O}$  to rise. DMSO, on the other hand, appears to form stronger associations with the hydrate than does water, causing  $f_{ZH_2O}$  in these solutions to fall (8).

Acidity scales have been found to be more substrate dependent than was originally thought (9) and we have little hope that hydration scales will be better behaved. Nonetheless, the concept should be of considerable value for determining hydration equilibrium constants in water (or any other standard state) of compounds whose degree of hydration is too high or too low for direct measurement.

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## Bromination and chlorination of exo, exo-5, 6- and endo, endo-5, 6dideuterionorbornene; on the mechanism of nortricyclyl bromide and chloride formation

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Proton (deuteron) loss from C-6 to form tricyclic product occurs with exo and endo stereoselectivity when bromine and chlorine, respectively, are added to exo, exo-5, 6- and endo, endo-5, 6-dideuterionorbornene. These data strongly suggest that elimination occurs predominately from 6 in bromination and from 4 in chlorination or alternatively from the unsymmetrically bridged ions 2 and 3, respectively.

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Typically, the addition of a polar reagent  $E^+Y^-$  electrophilically to norbornene yields 3-Enortricyclene as one of the major products (1a-j)<sup>2</sup> Although bridged ions of the type 1a and 1b have been considered as possible intermediates in the additions, no information about the mechanism of tricyclic product formation has been available. To gain information on this problem, a study of the complete set of additions has been undertaken. This communication reports new and interesting mechanistic information obtained from a preliminary study with the electrophilic reagents Br2 and Cl2 and the substrates exo, exo-5,6- and endo,endo-5,6-dideuterionorbornene (2). The results are listed in Tables 1 and 2.

To interpret the observed exo and endo stereoslectivities in bromination and chlorination, respectively, the data already accumulated on 1,3 elimination in norbornyl systems are used. That is, endo stereoselectivity at least should be observed if proton loss occurs prior to a 1,2 Wagner-Meerwein shift or complete participation of the  $C_1$ --- $C_6$  bond (1, 3-5). Importantly also, Berson and Grubb (6) have shown that the 6,2 hydrogen shift occurs endo  $\rightarrow$  endo in the 2-carboxy-3-methyl-5-norbornyl cation.

That a radical process does not contribute to tricyclic product formation in this study is seen from (a) the data accumulated on the reaction of radicals with norbornene (7-11), (b) Poutsma's study (1h) on the chlorination of norbornene, and (c) the data in entries 6 and 7, Table 1. That scrambling of deuterium via hydrogen shifts is not important is indicated by the following facts. The products of the reactions are 70% syn-2,7dibromide, 10% 2,3-trans-dibromide, 10% nortricyclyl bromide, and 10% other dibromides in CCl<sub>4</sub>-Br<sub>2</sub>; 40% syn-2,7-dichloride, 55% nortricyclyl chloride, and 5% other dichlorides in CCl<sub>4</sub>-Cl<sub>2</sub>. Furthermore, n.m.r. integration data from endo, endo-5, 6-dideuterio-syn-7-norbornenyl bromide, (C-1 and -2 protons) prepared via the bromination of exo, exo-5, 6-dideuterion orbornene (2) has shown that extensive deuterium scrambling does not occur within the limits of detection (5-10%).

Therefore, if exo, exo-5, 6-di-deuterion orborn-

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<sup>&</sup>lt;sup>2</sup>In ref. 1: (c) bromine and N-bromosuccinimide; (d) N,N-dibromosulfonamide; (e) N-bromosuccinimide in wet DMSO; (f) N-bromosuccinimide in H<sub>2</sub>SO<sub>4</sub>, t-BuOH; (g) 2,4-dinitrobenzenesulfonylbromide and chloride; (h) chlorine and hypochlorous acid; (i) iodo-baragnedichleride; (i) load totracestate benzenedichloride; (j) lead tetraacetate.