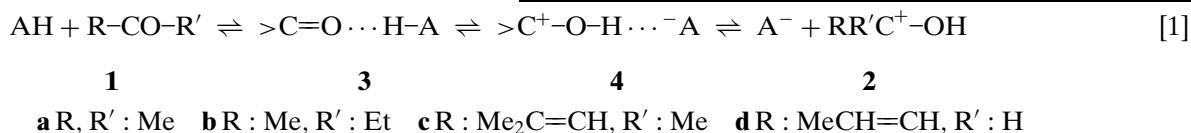# NOTE

Solid Acids and Acids in Solution: The Reversible Transfer of Hydrons to Carbonyl Groups

Formation of hydronated ketones (**1** → **2**, Eq. [1]) as reaction intermediates (1) or long-lived species in solution (2) has been established for a long time.

in the static complex, rather than displace a dynamic equilibrium like Eq. [1] (10b). Accordingly, aldol condensation (one of the examples given) was presented as the attack of

$$AH + R-CO-R' \rightleftharpoons\ >C=O \cdots H-A \rightleftharpoons\ >C^+-O-H \cdots\ ^-A \rightleftharpoons\ A^- + RR'C^+-OH \qquad [1]$$

$$\mathbf{1} \qquad\qquad \mathbf{3} \qquad\qquad \mathbf{4} \qquad\qquad \mathbf{2}$$

a R, R′ : Me   **b** R : Me, R′ : Et   **c** R : Me$_2$C=CH, R′ : Me   **d** R : MeCH=CH, R′ : H

In polar, hydroxylic solvents, a direct encounter of AH and **1** is not necessary, because the hydrogen transferred is relayed by the solvent. Free (solvated) ions result. In nonhydroxylic solvent, even polar (e.g., SO$_2$), a preassociation by hydrogen bonding (**3**) intervenes and the hydron transfer gives an ion pair (**4**) which dissociates reversibly to the free ions. Ionization and dissociation are thus separate kinetic steps (3).

More recently, three groups have examined ^{13}C NMR spectra of ketones in acid zeolites. Bosáček *et al*. saw a sizable downfield shift of the C-2 (C=O) signal of acetone (**1a**) in HZSM-5 and concluded that partial hydronation (Eq. [1]) occurred (4). Xu *et al*. found that δ(C-2) of **1a** does not change for 0 < [**1a**]/[acid sites] < 1, but decreases afterward (5), paralleling the change of heat of adsorption of nitrogen bases on HZSM-5 (6). Contrastingly, δ(C-2) decreases steeply with the increase in **1a** concentration on HY well below the 1 : 1 ratio (5). This is as expected for a solid acid with sites far apart, chemically noninteracting (HZSM-5), and for a solid acid with chemically interacting sites (HY), respectively (7). Among various reaction products identified, the spectrum of mesityl oxide (**1c**) was interpreted based on Eq. [1] and used to evaluate the acid strength of zeolites (5) by a method developed earlier (7a, 8).

Biaglow *et al*. noted a lack of mobility (also reported by Xu *et al*. (5)) of adsorbed molecules for [**1a**]/[acid sites] < 1 on HZSM-5 and studied the chemical shift anisotropy of the C=O signal (9). Later, they measured isotropic δ values for **1a** (10) similar to those reported before (4, 5), but offered a novel interpretation, rejecting the reversible hydron transfer of Eq. [1] in favor of *static* hydrogen-bonded complexes (**3**), in which "the fluctuations of the delocalized proton . . . are not so large as to lead to exchange between a protonated and unprotonated from. . . ." An increase in acid strength was thus said to increase the strength of hydrogen bond

the enol at the hydrogen-bonded C=O, with no charged intermediate intervening ((10b), Scheme 8). The description of "complexes" of α,β-unsaturated ketones is ambiguous: compounds **1c,d** were shown in a table as cations but were considered to result from the condensation reaction as static hydrogen-bonded complexes with the acid sites (cf. **1d** in Scheme 8 of Ref. (9b)); at another point it was stated that "there is no equilibrium between. . . species (**1c,d** and **4c,d**) in the HZSM-5." The much more basic α,β-unsaturated imines were shown in the table as H-bonded complexes (10b), although it was stated in the text that the "complex in this case is in all probability protonated" (10b, c). The authors did not consider that the two reactions are mechanistically similar (reversible hydron transfer) and differ only by the position of the equilibrium favoring hydrogen-bonded neutrals for ketones and hydrogen-bonded ion pairs for imines. The authors even spoke about "similar, hydrogen-bonded complexes in magic acid solutions. . .," in which ". . .the proton is almost completely transferred to the molecule. . ." (10b), thus implying that even in those media the substrates under consideration are not present in the form of their conjugate acids (hydronated species).

As the understanding of the interaction between an acid molecule or site and a substrate is needed for the description of reactions on solids and in solution, a discussion of the pertinent data is offered here.

Unquestionably, ketones are hydronated in strong and superacids (2). The possibility, however, that in HZSM-5 ketones are present as complexes (**3**) and hydronated species do not intervene even in ion pairs (**4**), as unstable intermediates of enolization (10b), needs careful consideration. Elucidation of the nature of interaction is important also for any attempt to use NMR spectroscopy for acidity evaluation (4, 9), because it was found that in the absence of a measurable extent of hydron transfer,

there is no correlation between the strength of hydrogen bond to the indicator base and the acid strength of the H bond donor (11). Several possible reasons for such an interaction mechanism can be extracted from Ref. (10b): (a) hydron transfer does not occur for acids significantly below superacidic strength; (b) hydron transfer is prohibited in nonpolar environments; (c) hydron transfer does not occur in solid state; (d) zeolites have some unique features preventing hydron transfer. In each case we deal with reversible transfer between electronegative atoms and each will be examined in the following.

(a) Hydron transfers from acids of moderate strengths to ketones. Reference (10) describes the acid–base reaction as a static complex **3**, rather than a *dynamic* equilibrium (Eq. [1]). An increase in acid strength of the medium would bring only a strengthening of the hydrogen bond and (not stated explicitly in Ref. (10)) a concomitant weakening of the A–H bond. Stated differently, the new model describes the acid–base interactions involving **1** as an energy surface with one minimum, rather than with two energy minima (not counting the initial and final states **1** and **2**) in Eq. [1]: "... in moderately acidic solvents such as trifluoroacetic acid... (t)he valence bond description...is represented by a superposition of...resonance structures, but *not* by any exchange process involving chemical equilibria" (10a). The authors consider that zeolites should behave similarly to these liquid acids: "Given that the magnitude of the isotropic shift in zeolites (relative to the pure liquids) is comparable to that in weak acids, it should be possible, in a similar manner, to determine the varying tendencies to form hydrogen bonds in different zeolites" (10a). Therefore, examination of hydronation reactions in solution becomes necessary in the present discussion.

Ketones were used as indicators by Hammett (1b). UV–visible spectra in strong acids (1b, 2b, c) showed a significant change of the molecular orbitals of ketones, especially the conjugated ones, which cannot be rationalized by the static complex **3**. At intermediate acidities the spectrum is a superposition of the spectra in strong acid and in nonacidic solvent. The relative intensities of these two components of the spectrum change with the acid strength (2b), which is incompatible with the static complex **3**.

From the observation that the extent of hydronation of **1a** in acids weaker than pK_a −4 as solvents is unimportant (12), it was later assumed that in a solvent of the acid strength of trifluoroacetic (TFA) no reversible hydron transfers (i.e., Eq. [1]) occur, only formation of complexes **3** (10a). This assumption can be checked by an evaluation of the rate of hydron transfer form an acid (AH) to **1** as a function of the relative values of $pK_{a(AH)}$ and $pK_{a(2)}$.

Hydron transfer is inherently fast, unless it involves a change in electron distribution and molecular structure in, one of the reactants (13). Thus, hydron transfers between
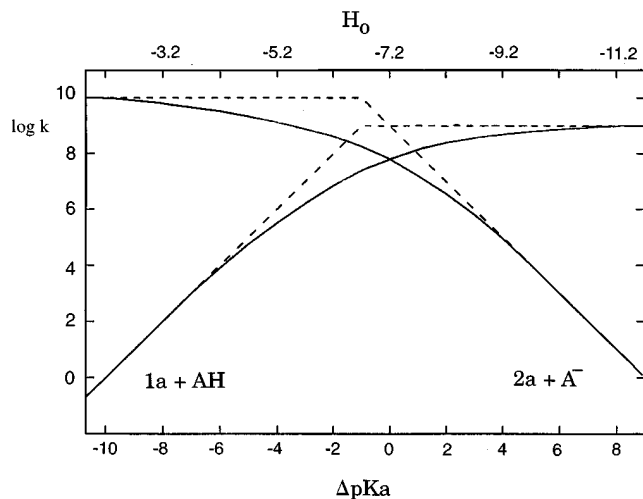

FIG. 1. Dependence of rate of hydron transfer reactions (**1a** + AH and **2a** + A⁻) upon ΔpK_a.

oxygen and nitrogen atoms, or from acetylene (14), are fast, and the transfer from the C–H of **1** to a base is slow. For inherently fast transfers, the rate (reciprocal of lifetime, in s^{-1}) depends characteristically upon the difference in strength between the acids on the two sides of the equation. A representation of this dependence for reaction of **1a** with various acids (Eq. [1]) is constructed in Fig. 1, as described by Eigen (13). It is similar with the diagrams obtained for reactions of phenol (acid) with PO_4^{3-}, piperidine, propylamine, CO_3^{2-}, NH_3, N_2H_4, and imidazole (bases), or of aniline (base) with CH_3COOH, $PhCOOH$, $HCOOH$, and $ClCH_2COOH$ (acids) (13). In Fig. 1, ΔpK_a is $(pK_{a(2a)} - pK_{a(AH)})$; the H_o values for which the extent of hydronation of **1a** at equilibrium is the same as for a given ΔpK_a value are shown at the top. The horizontal parts of the curves are not at the same level, because the limiting rate is faster for the reaction neutralizing charges ($2a \rightarrow 1a$) than for the reaction separating charges ($1a \rightarrow 2a$) (13). From $pK_{a(2a)} = -7.2$ (2b) (by NMR: ca. −7.1 (3f)), Fig. 1 gives $\log k = 1.8$, 2.2, and 2.5 for reactions of **1a** with the acids HSO_4^- (pK_a 0.92 (15), ΔpK_a −8.12), CCl_3COOH (pK_a 0.60 (12), ΔpK_a −7.80), and TFA (pK_a 0.23 (12), ΔpK_a −7.43), respectively, in water. For pure TFA (H_o −3.0 (8c)), Fig. 1 gives $\log k$ ca. 1.75. All these transfers are fast on NMR as well as chemical time scale, even though the amount of **2a** at equilibrium is extremely small (form Fig. 1 one evaluates **2/1** ca. 10^{-8} in TFA, but for the reaction $2a \rightarrow 1a$ $\log k > 9.5$). The representation to the contrary expressed by previous authors (10) is in error.

The position of the hydronation equilibrium (Eq. [1]) is determined by the effective strength of the acid and base ("effective" means as manifested in the reaction medium). Thus, in 70% H_2SO_4 (H_o − 5.9 (8c)), a medium of interest for the discussion below, the hydronation equilibrium constant **2/1** (or **4/3**) is estimated from Fig. 1 as ca. 10^{-2} ($\Delta G°$ 2.6 kcal/mol at RT) for **1a** and 450 ($\Delta G°$ −3.6 kcal/mol at

RT) for **1c** (p$K_{a(2c)}$ − 4.4 (8c)). In either case, however, the reaction of the ketone is described by an energy surface with two minima; a static hydrogen-bonded complex corresponds to a one-minimum energy surface. For **1a** in TFA, the two minima differ by 10.7 Kcal/mol at 293 K. Considering that the reverse reaction has a very low barrier, the barrier for hydronation of **1a** in TFA should be ca. 12 kcal/mol which is still low enough to assure a fast reaction at this temperature ($k(\mathbf{1a} \to \mathbf{2a})$ ca. $50\,\mathrm{s}^{-1}$), even though no **2a** can be evidence in TFA by usual spectroscopic techniques.

(b) Hydron transfers in nonpolar environments. The acid zeolites' cavities could be described as made of hydrophobic walls in which acid sites are embedded, being thus equivalent to molecules of acid isolated in a nonpolar solvent. Because of the rigidity of the lattice, the anion formed from the acid site cannot be stabilized by hydrogen bonding (16) with OH groups existing elsewhere in the channel. This model is adequate for HZSM-5, but less so for HY, for which the spectrum of adsorbed acetone (5) indicates closely situated, interacting acid sites, as discussed above (7). In any event, if the parallelism invoked by the previous authors between solution and solid state (10a) holds, the inability of acids to transfer hydrons to bases in nonpolar medium could explain a similar behavior for HZSM-5.

It is obvious that the acidic strength of any compound AH is weaker in nonpolar than in polar solvents. There are examples, however, of acid–base reactions in nonpolar (or rather non-hydrogen-bond-forming) media, provided the anion is stabilized. Stabilization is achieved by hydrogen bonding with the cation (17) in an undissociated ion pair (3). Where structural or steric factors in the cation hinder this interaction, dimeric anions $(A–H\cdots A)^-$ are formed (3, 16, 18). There are also data on fast (equilibrium) hydronation of weak *oxygen* bases in non-hydrogen-bond-forming media. Thus, the interaction of ketones with anhydrous HBr in CBr_2F_2 was studied by ^1H NMR spectroscopy (19). For 2-butanone (**1b**), the (averaged) proton signal seen at room temperature broadened on deep cooling and split below 163 K into a signal for HBr at −0.3 ppm and a signal for the OH in **2a** at ca. 13 ppm (19), a similar chemical shift with that found in superacid (2g–k). For **1a**, even less hindered than **1b**, the interconversion of the hydrogen-bonded acid–base pair and hydrogen-bonded ion pair (Eq. [1]) should be at least as fast as for **1b**.

To examine an even more hydrophobic nonhydroxylic solvent, we investigated the interaction of *p*-toluenesulfonic acid (TsOH), an acid of medium strength (8c, 20) with methanol (MeOH) and MTBE in toluene (18b). Upon mixing one equivalent of TsOH (δOH 11.25) with 0.5 equivalent of MeOH (δOH 4.54) at room temperature one sharp signal resulted. Had the interaction been merely by hydrogen bonding, two signals would have been seen. The chemical shift of the combined signal, 11.78 ppm

(greater than that of TsOH) demonstrates that hydronated methanol was formed (2g, h, 21) and predominated at equilibrium. Likewise, upon addition of 1 equivalent of MTBE to the solution of TsOH in toluene, the OH signal moved downfield, to 12.51 ppm, proving that hydronation had occurred in that case as well.

The inability of hydronated bases of forming hydrogen bonds with the anion was seen when the site which should form the hydrogen bond is hindered, like in MTBE (18b) and 2,6-di-(*t*-butyl)pyridine (18a), or the positive charge is spread over several atoms in an otherwise nonpolar structure, like in hydronated hexamethylbenzene (22a–c). In such cases hydrogen bonding between the unreacted acid and the nonhydronated base is also absent. This is not the case for an unhindered polar molecule like **1a**.

(c) Hydron transfers in the solid state. It has been established that for generation of organic cations, either at equilibrium or as unstable intermediates, hydrogen bonding, rather than dielectric constant, is the most important property of the medium (16). Likewise, the inherently fast hydron transfers are slowed down if an unfavorable hydrogen bond structure has to be altered before the reaction can take place (13). If the locations of the acid and base in a solid establish a favorable hydrogen bond interaction, however, the reaction is faster than in solution, to the extent that no diffusion step is necessary. Thus, hydron transfer in ice is 60 times faster than in water (13) and other solids with OH and NH bonds also undergo extremely fast hydron transfer (13, 23). An interesting example is that of the monoanion of salicylic acid (solid) (23a). The carboxylate and phenol groups are held in a position favorable for hydrogen bonding. The reversible exchange of Eq. [2] is very fast, showing that the left-to-right process is fast, even though the equilibrium is very much to the left ($K < 10^{-4}$). Such is precisely the situation for **1**/HZSM-5, where NMR data (10) indicate that adsorption locks the acid–base pair in the geometry required for hydron transfer. Thus, even if the acid strength of sites in HZSM-5 were only the same as that of CF_3COOH, conversion $3 \to 4$ should be rather fast on chemical time scale. Note that hydron transfer between partners locked in by hydrogen bonding also leads to rigidity of the adsorbate. For ketones, hydronation leads to structural rigidity even in solution (2i).

$$C_6H_4 \begin{array}{c} OH \\ COO^- \end{array} \rightleftharpoons C_6H_4 \begin{array}{c} O^- \\ COOH \end{array} \qquad [2]$$
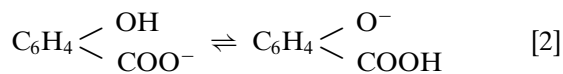
(d) Existence or lack of special (unique) properties of zeolites as acids. The present author has been arguing for years that isolation of sites preventing anion stabilization by hydrogen bonding with excess acid (cooperative effect) makes solids, zeolites included, significantly weaker acids than structurally related analogs in liquid phase (7b, 8a, 22). Reduction of the strength of the acid–base interaction, however, does not have to change it from a two-minima to

a one-minimum energy surface. Even interactions as weak as between thioglycol and imidazole, or between glucose and ammonia, are reversible hydron transfers, albeit very much displaced toward the neutrals (13). Therefore, it would be a special case, requiring thorough proof, if the reactions of **1a–d** with zeolite acids were represented by a one-minimum energy surface.

None of the spectral or chemical data reported in Ref. (10) requires (as shown by the discussion above) that the interaction acid–base in zeolites be different in nature from other media, except for the claimed difference in response of signals for carbonyl (C-2) and $C\beta$ in mesityl oxide (**1c**). Thus, it was stated that interaction of **1c** with the acid site of HZSM-5 moves the signal for C-2 downfield with 6 ppm less than dissolution in the FSO_3H-SbF_5 superacid (magic acid), whereas the signal for C-β is shifted by 6 ppm more (farther downfield) in HZSM-5 than in magic acid (10b), where the species present is **2c**. It turns out that this is an unintended chemical consequence of a transcribing error: the original work in magic acid (24) used CS_2 (δ 194 ppm) as chemical shift standard and the $-$(minus) sign for the chemical shift for $C\beta$ was omitted in the published table. Correcting for that error leads to δ 205.5 for $C\beta$ in magic acid, such that the corresponding signal in HZSM-5 (δ 188) appears, quite normally, ca. 17 ppm upfield from magic acid. We pointed out the earlier report's (24) error in our publications (8c, 25). We then listed chemical shifts measured for at least 240 acid solutions of strength below the superacidic range, including materials such as phosphoric acid, for which $C\beta$ resonated at lower field than the purported (10) value for magic acid (7a, 8, 20); we also remeasured the spectrum of **1c** in magic acid (25). Our method was then applied for successful correlations of reaction mechanism with acid strength (26). Apparently, other investigators (9, 10) did not trust our results, but they could have run the spectrum of **1c** in magic acid (commercially available) themselves.

Examination of the ^{13}C chemical shifts for **1a** and **1c** in HZSM-5 indicates the normal behavior in a medium with the properties of a strong acid. For that purpose it is better to use as the measure of the degree of hydration the differences between chemical shifts for two carbons within the molecule than the chemical shift for any one carbon of the base (7, 8, 11, 20). As already observed by Haw and co-workers, for **1c** this difference ($\Delta\delta = \delta(C\beta) - \delta(C\alpha)$) is similar in HZSM-5 and 70% sulfuric acid (5). For **1a**, the results of Bosáček and co-workers allow a calculation of $\Delta\delta = \delta(C\text{-}2) - \delta(C\text{-}1)$ as 194–195 ppm (4). The same difference was found previously for **1a** in 70% sulfuric acid (2f). It is hard to ascribe this similarity for **1a** and **1c** to coincidence. It should also be noticed that in studies of persistent (16b) carbocations it was shown that chemical shifts in solution and in solid state are in agreement (27). Using the solution chemical shifts to evaluate the behavior of bases in zeolites (10a) one concludes that **1a** is very little

hydronated (ca. 1%), whereas **1c** is present mostly as **2c** on HZSM-5.

The subsequent reactions observed (5, 6, 10) also indicate normal acid–base behavior of acetone in HZSM-5. It is known that acid catalysis in enolization of ketones is specific acid catalyzed; a concerted mechanism was considered and found incompatible with the experimental results (28). Moreover, acetoneimine formation was observed from reaction of acetone with ZSM-5 and Y zeolites which had been fully neutralized with ammonia (29). As no one contests the existence of ammonium salts of zeolites, had the type of interaction with acetone been hydrogen bonding only, the sole nitrogen species present would be the ammonium ion, which cannot act as a nucleophile. The reaction observed requires reversible hydron transfer between the three bases, ammonia, acetone, and the zeolite anion, in a preliminary step.

Finally, we note an inconsistency: It was said that ability of bases of being hydronated by zeolites correlates with gas-phase hydron affinity (PA) (5). For H_2O, **1a**, and NH_3 PAs are 166.5, 196.7, and 204.0, respectively (30). H_2O and NH_3 are hydronated in HZSM-5. Why shouldn't **1a** be as well (31)?

We can conclude that all existing data are better explained by interaction between acid zeolites like HZSM-5 and oxygen bases, particularly ketones, being represented by a two-minima energy surface (Eq. [1]), rather than by a one-minimum energy surface (static hydrogen bonded complex). In the case of acetone the equilibrium favors heavily (ca. 2.6 kcal/mol) the neutral base; for mesityl oxide, the ion pair is even more heavily (3.6 kcal/mol) favored.

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31. Observation made by a reviewer of the manuscript.

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