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LETTER TO THE EDITOR

More on the Reversible Transfer of Hydrons to Carbonyl Groups

My previous note (1) sought to correct some representations which might have confused an uninformed reader in papers by Biaglow *et al.* (2):

—That in an acid solution of the strength of trifluoroacetic acid (TFA) the state of a base-like acetone is represented by a hydrogen-bonded complex "but *not* by any exchange processes involving chemical equilibria" ((2a, p. 780), emphasis in the original).

—That in stronger acids the change in the acid–base interaction consists of an increase in the strength of a hydrogen bond in a static complex, rather than the change in the position of a hydron transfer equilibrium, of mesityl oxide (2b, p. 376, second column, lines 34–36) and of imines (2b, pp. 382–383 and Schemes 6 and 9) contradicting the description of imines in (2b, second column, lines 14–16).

—That the model of static complex for acid–base interaction in zeolites follows from the similar mechanism of interaction in solution and that the strength of hydrogen bonds is a good measure for acid strength ranking in both (2a, p. 780, first column, lines 10–22).

—That a special nature of the interaction of mesityl oxide with a zeolite acid site is evidenced by peculiar changes in ^{13}C (isotropic) chemical shifts, claiming that the $C{=}O$ signal moves downfield *less* in zeolite than in superacid, whereas the $C\beta$ signal shifts downfield *more* in zeolite than in superacid (2b, p. 383).

—That reactions such as enolization, aldol condensation, and halogenation do not involve separate proton (hydron) transfer steps, but are accomplished in one collision between neutrals (2b, Schemes 1, 3, 5, and 8 and comments on p. 382, fifth paragraph).

To clarify the matter, I presented the theory of intrinsically fast hydron exchange, seen normally but not exclusively when the transfer occurs between electronegative atoms such as O or N and discussed particular features which I expected for such transfers in nonpolar media and in solids (1). I also pointed out that one of the conclusions (2b) was based on an error which had already been corrected in the literature. Some of my observations are criticized in the letter by Gorte *et al.* (3). I take it that they agree with the rest of my observations (1). Those on which they still disagree will be discussed below:

1. (a) "Fărcaşiu's statement. . . seem[s] to suggest that we question the principle of microscopic reversibility. . ." (3). I quote from their previous paper: "proton displacements here should only be thought of as small fluctuations. . . rather than proton exchange reactions satisfying microscopic reversibility" (2b, p. 373). The quote is necessarily out of context, because I cannot quote the entire papers, but the statement and those noted above are categorical; to see the whole context the reader is urged to read the original papers (2, 3).

(b) "Interpretations which describe NMR spectra of the 1 : 1 adsorption complex for acetone. . . in H–ZSM-5 as being the result of some chemical equilibrium process cannot explain our results" (3). The existing data indicated to me that (i) hydronated acetone in a hydrogen-bonded ion pair with the site anion should be at least as rigid as neutral acetone hydrogen-bonded with the site and (ii) the extent of hydronation might be around 1% (1). For a fast exchange, the resulting averaged powder pattern could not be distinguished from that of the major species, which *does* explain their results (2). (In addition, the position of the equilibrium for an intrinsically fast hydron transfer changes normally very little with temperature.) The point of my comments was that such nonobservable species are mechanistically significant ((1) and Refs. (1) and (28) therein).

2. (a) "We did not include charged species in our reaction diagrams because. . .they are not spectroscopically observable. . . . We do not question the existence of charged species along the reaction coordinate. . ." (3). There could be no objection to the second sentence. As concerns the first, however, the reaction mechanism must give an account of all intermediates. *The unstable intermediates are normally the essential ones.* Thus, I evaluated that in TFA the fraction of acetone which is hydronated is 10^{-8} (1). Nonetheless, even in the much weaker acetic acid solvent isotope effect measurements indicated that the enolization of acetone includes substrate hydronation as a reversible first step (4). As I stated before, a "full description of a reaction mechanism has to address several questions. Thus, it must establish the reaction steps and intermediates. Then, it needs to determine the energy barriers (both heights and shapes), that is, the reaction kinetics. Next, the mechanistic picture has to give an account of the movement of atoms in each reaction step. Ultimately, the mechanistic representation

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should give a description of the flow of electrons in all reaction steps, experimentally or by calculation and inferences" (5). In other words, at the *lowest* level of mechanistic representation the full description of steps and intermediates is required; whether the authors accept ionic mechanisms in zeolites in general is immaterial. Also, when opinions expressed in a subsequent paper contradict those presented earlier, it is understood that the authors stand by their latest report (for example, compare (6) with (7) and (8) with (9)).

Gorte *et al.* criticize my work for not showing formation of a hydrogen-bonded complex first in the equation for hydron transfer in a paper on acidity measurements of strong acids in aqueous solutions (3). As stated before, in polar hydroxylic solvents the encounter of acid and base molecules is not necessary for reaction, because the hydron in relayed by the solvent (1).

(b) "The energetics of protonation and the relative stability of carbocations are *very* different in the zeolite compared to acid solutions" (3). Far from contradicting my position, this statement is in full agreement with it. What I wrote was: "The present author has been arguing for years that isolation of sites preventing anion stabilization. . . makes solids, zeolites included, significantly weaker acids than structurally related analogs in liquid phase" (1).

3. "Adsorption complexes result from both proton transfer and local bonding interactions" (3). Yes, indeed, the acid–base interaction outside of polar hydroxylic media is an equilibrium of a complex of hydrogen-bonded neutrals and a hydrogen-bonded ion pair, rather than either one or the other; this was the essential point of my previous note (1). Even when the equilibrium is very much displaced in one direction, the inherently fast nature of hydron transfers between electronegative atoms and the very low barrier for the transfer in the exothermic direction make the minor species mechanistically significant. An analogy between solid acids and acids in solution, *which Gorte et al. employed* (2a), cannot justify any conclusions when the representation of acid–base interaction in solution is flawed, as theirs was. On the other hand, I fully agree with the viewpoint that correlation of gas phase acidities/basicities and the same properties in zeolites is limited to molecules very similar in structure (3) (and, I add, in size), as is the correlation of these properties in gas phase and in solution.

At the end of their letter (3), Gorte *et al.* cite inaccurately the findings of a neutron diffraction study of water hydronation in zeolites. A discussion of the literature on water as a base in zeolites is available elsewhere (10).

In closing, I should re-emphasize not only that hydrogen bond strength is a poor measure of acid strength, but that use of the chemical shift for one atom in the molecule of a base is unsatisfactory as a measure of acid strength, because of medium effects (10). To correct for medium effects we applied the $\Delta\delta$ parameter, which behaved properly even in media such as solutions with large amounts of corrosion products (magnetic) and other impurities, where the chemical shifts for individual signals could by no means be correlated with the values in standard media (10). Successful extension of the use of $\Delta\delta$ for the measurement of acidities of liquid composite acids and solids was reported from other laboratories (11).

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