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IONIZING POWER, NUCLEOPHILICITY AND BASICITY OF TRIFLUOROETHANOL. A NEW MECHANISTIC PROBE

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The Winstein-Grunwald mY relationship (eq. 1), based on the solvolysis rates of _t_-butyl chloride has provided an effective, empirical means for the evaluation of solvent ionizing power and for the prediction of rates of other solvolysis reactions.[1,2] However, recent studies have suggested that this relationship may break down in the case of aqueous

$$\log (k/k_o) = mY \qquad (1)$$

trifluoroethanol,[3,4] a solvent which has been much used in the last several years as a result of its combination of high ionizing power[3,5,6] and low nucleophilicity.[7,8] We have examined the solvolysis rates of a series of substrates in both aqueous ethanol and aqueous trifluoroethanol, and we conclude that the breakdown of the mY relationship in trifluoroethanol is a consequence of a change in rate determining step of the model substrate, _t_-butyl chloride.

Equation (1) actually represents a restricted form of a more general relationship (eq. 2) which explicitly considers both the ionizing power (Y) and the nucleophilicity (N) of the solvent.[1,9] In a large number of cases the more easily evaluated equation (1) provides a satisfactory correlation of solvolysis rates because the kinetic influences of solvent nucleophilicity are either minimal or vary inversely with ionizing power. Similar arguments

$$\log (k/k_o) = mY + \ell N \qquad (2)$$

apply to solvent basicity (that is, nucleophilic attack on β-hydrogen).

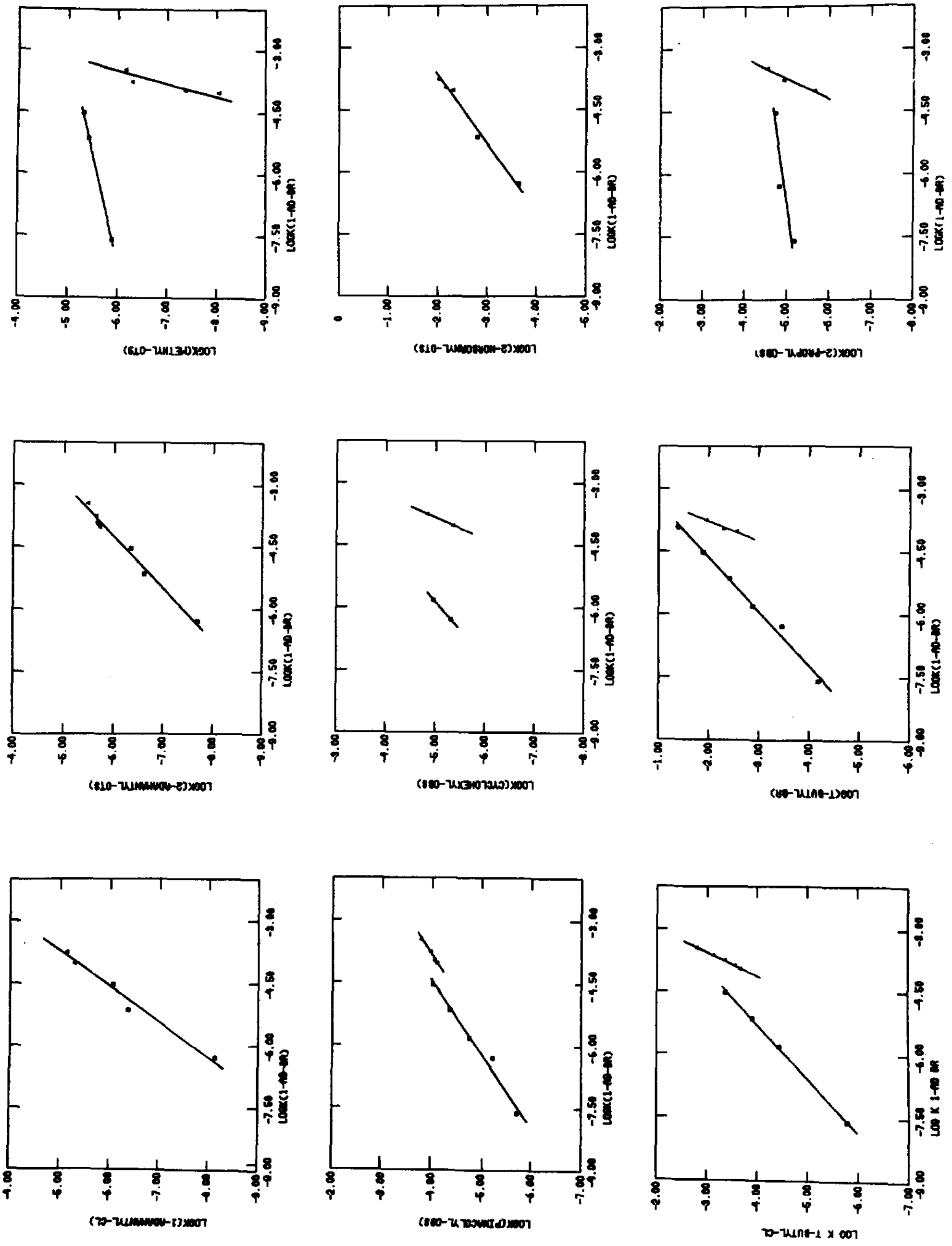
We reported earlier that with the exception of aqueous trifluoroethanol equation (1) correlates the solvolysis rates of 1-adamantyl bromide in a wide variety of solvents.[3] Since 1-adamantyl bromide can undergo neither elimination nor backside displacement,[10] we conclude that _t_-butyl chloride and not 1-adamantyl bromide behaves abnormally in trifluoroethanol. Shiner[6] has suggested that trifluoroethanolysis of _t_-butyl chloride involves competition between substitution and rate-limiting elimination at the stage of an ion pair. Thus the mechanistic assumption of no bimolecular contribution to the rate, implicit in equation (1), does not appear to be valid for the reference substrate (_t_-butyl chloride) in aqueous trifluoroethanol.

Returning to our earlier suggestion[3] that 1-adamantyl bromide is a superior reference substrate, we have plotted log k for a series of substrates against log k of 1-adamantyl bromide for solvolysis in both aqueous ethanol and aqueous trifluoroethanol. Inspection of these plots shows that _t_-butyl chloride is not unique in showing a lack of correlation between rates in these two families of solvents. We suggest that this deviation is diagnostic for kinetically significant involvement of solvent as a base or nucleophile. In those cases where substantial nucleophilic solvent assistance[11] (methyl tosylate, 2-propyl brosylate, cyclohexyl brosylate) or facile elimination (_t_-butyl chloride, _t_-butyl bromide) is expected, the data for the different solvent systems are clearly represented by two distinct lines. On the other hand, for those cases in which elimination is prohibited (1-adamantyl chloride, 2-adamantyl tosylate) or in which rearrangement or ionization is indicated to be rate determining (_exo_-2-norbornyl tosylate, pinacolyl brosylate) the data for both solvent systems fall on (or very close to) a single line.

These plots clearly show that the m values (eq. 1) for aqueous trifluoroethanolysis of substrates such as 2-adamantyl tosylate, pinacolyl brosylate and 7-methyl-7-norbornyl tosylate are not abnormally low;[4] rather, the aqueous-trifluoroethanol m values of the _t_-butyl halides and the substrates reacting with nucleophilic solvent assistance are _abnormally high_. This

PLOT OF LOG K OF RX VS. LOG K OF 1-ADAMANTYL BROMIDE AT 25 DEG.

▲=AQUEOUS TRIFLUOROETHANOL; □=AQUEOUS ETHANOL



is almost certainly a consequence of the simplicity of equation (1) which includes no contribution for solvent nucleophilicity or basicity. In the case of aqueous ethanol mixtures, both components have high nucleophilicity and rate increases are largely a result of changes in ionizing power as the fraction of water is increased. In contrast, water and trifluoroethanol both have high ionizing power but differ greatly in nucleophilicity. Rate dependence on the fraction of water is minor for nucleophilicity-independent substrates such as 1-adamantyl bromide. However, when solvent nucleophilicity or basicity becomes kinetically significant, a large rate dependence upon the fraction of water is observed.[12] Consequently, the relative kinetic behavior of substrates in aqueous ethanol and aqueous trifluoroethanol should provide a valuable probe into the role of solvent in solvolysis reactions.

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