

[1]. This maximum would proceed from the decrease of the water activity when the concentration of acid increases. In fact, our study of the hydrolysis of thioamides in aqueous sulphuric solutions, reveals that the origin is only the difference of the variations of solvation energies between the protonated form (XH^+) and the transition state (CT^*). This difference is evaluated by acidity functions. Thioamides were chosen because solvent effects do not exist with aliphatic compounds.

a) *Protonation*. The 2H ($= -\log h_2$) acidity function [2] governs the protonation of thioamides. This calculated function is almost identical to the experimental functions H_o'' and H_T relative to tertiary amines and thioamides respectively [1, 3]. For a given thioamide, the same pK value is obtained whatever the wavelength in UV spectroscopy and the technical method (UV, 1H NMR) may be, (pK (thioacetamide) = -2.51 ; pK (thiobenzamide) = -3.20). The value, $\tau = 2$, of the apparent solvation ratio [2] means that the protonated form gets a solvation energy lower than the one of the oxonium cation ($\text{C}=\text{OH}^+$, $\tau = 5$) [4], result confirmed by the corresponding values of entropy variations.

b) *Hydrolysis*. By calling H_* ($= -\log h_*$), the acidity function governing the formation equilibrium of the transition state from the neutral form, we demonstrate that the rate law can be written:

$$v = k_o \frac{h_*}{K_*} \frac{|X_o|}{1 + \frac{h_{XH^+}}{K_{XH^+}}} \quad (1)$$

We find that the H_* function is identical to the 4H function (${}^4H \cong H_A$ [1]) and so, the solvation energy of the transition state ($\tau = 4$) is stronger than the one of the protonated form ($\tau = 2$); in effect, we get:

$$H_{XH^+} (= {}^2H) < H_* (= {}^4H) \text{ or } h_{XH^+} > h_* \quad (2)$$

From the definition of the acidity function and the one of the transfer activity coefficient, this result means:

$$\Delta G_t^\circ(XH^+) < \Delta G_t^\circ(CT^*)$$

where ΔG_t° is the variation of transfer free enthalpy linked to the variation of solvation energy.

In the acidity range, where the inequality $h_{XH^+} \gg K_{XH^+}$ is verified, relation (1) gives:

$$\log k_{\text{exp}} = \log \frac{k_o K_{XH^+}}{K_*} + \log \frac{h_*}{h_{XH^+}} \quad (3)$$

This relation is verified by the experimental values. The rate is decreasing whatever the water activity

may be. The rate maximum occurs when the concentration of acid corresponds to the half-neutralization of X. The decrease of the reaction rate proceeds only from the different natures of acidity functions H_* and H_{XH^+} ; when the concentration of acid increases the variation of solvation energy of the protonated form is lower than the one of the transition state (inequality (2)).

References

- 1 M. Liler, 'Reaction Mechanism in Sulphuric Acid', (1971), Academic Press.
- 2 J. M. Carpentier and M. B. Fleury, *Bull. Soc. Chim.*, 11, 2941, 2946, 2952 (1973).
- 3 J. T. Edward, G. D. Derald and S. C. Wong, *Canad. J. Chem.*, 55, 2331 (1977).
- 4 P. Lemetals and J. M. Carpentier, *Tetrahedron Lett.*, 6, 569 (1979).

Solvation and Reactivity of 2-Adamantyl Tosylate in Fluorinated Alcohol–Water Systems

B. ALLARD, E. CASADEVALL, A. CASADEVALL and C. LARGEAU

Laboratoire de Chimie Organique Physique, ERA CNRS 685, E.N.S.C.P., 11 rue Pierre et Marie Curie, 75231 Paris Cédex 05, France

Fluorinated alcohols exhibit solvating properties contrary to those of aprotic dipolar solvents. Thus they show a strong solvating ability towards anions (high ionizing power Y) and a weak solvating ability towards cations (low nucleophilicity N). A systematic study of commercial fluorinated alcohols has shown [1] that these properties are particularly pronounced in the case of hexafluoroisopropyl alcohol (HFP) which exhibits *both* the highest ionizing power and the lowest nucleophilicity. The binary mixtures HFP– H_2O possess also peculiar solvating properties; moreover, such media should promote various reactions of synthetic interest and especially cyclization-solvolysis [2].

The above considerations prompted us to examine the effect of water fraction on the ionizing power of HFP– H_2O mixtures, *i.e.* on their ability to promote the heterolytic cleavage of C-leaving group bond during solvolysis. The results will be compared to those observed in EtOH– H_2O and trifluoroethanol (TFE)– H_2O systems (since, as a result of its characteristics [1], TFE is representative of R_fCH_2-OH and $R_fCHOHCH_3$ fluorinated alcohols).

For each solvent mixture the ionizing power has been determined from $Y = \log k/k_0$ where k is the rate constant for solvolysis of 2-adamantyl tosylate in the solvent under examination and k_0 that in a reference medium: 80% v/v, ethanol/water. Hence, owing to its peculiar structure 2-adOTs is a suitable substrate for a meaningful determination of ionizing power: 1), the rate determining step is the cleavage of C-OTs bond for an extensive range of solvents including fluorinated alcohols 2), the internal ion pair return is negligible.

In the light of experimental data it can be noted that HFP-H₂O systems appear, at first sight, to exhibit an unexpected behaviour. Although H₂O is considerably more ionizing than HFP, a decrease in the ionizing power of these mixtures is observed as water content increases. Consequently HFP-H₂O systems show a lower ionizing power than each component taken alone.

In sharp contrast, aqueous EtOH mixtures exhibit a 'normal' behaviour, since the ionizing power of the medium increases along with the proportion of water (which is more ionizing than EtOH). However Y always remains below the statistical value according to which $Y_{\text{EtOH-H}_2\text{O}} = Y_{\text{H}_2\text{O}}X_{\text{H}_2\text{O}} + Y_{\text{EtOH}}(1 - X_{\text{H}_2\text{O}})$.

The binary TFE-H₂O mixtures show similar qualitative trend. However, increase in Y with respect to the proportion of water is much less pronounced than in the case of EtOH-H₂O mixtures (though the difference $Y_{\text{H}_2\text{O}} - Y_{\text{TFE}}$ is large). Consequently the ionizing power of the mixture is much lower than the statistical value.

The solvent effects upon the rate of ionization of a substrate such as 2-adOTs mainly depend on the ability of the solvent to interact with the leaving group (OTs) via hydrogen bonding [1]. The hydrogen bonding ability of binary alcohol-water systems arises not only from specific properties of each component, but also from the interactions which appear between their hydrogen bond donor and acceptor sites. We will discuss how the peculiar structure of water ('polymeric' structure involving few donor and acceptor sites) and the structure of alcohols (increase of the donor ability and decrease of the acceptor ability in the following order EtOH, TFE, HFP) account for the whole range of Y variations observed.

References

- 1 B. Allard, E. Casadevall, A. Casadevall and C. Largeau, *Nouv. J. Chim.*, **3**, 335 (1979).
- 2 W. S. Johnson, *Accounts Chem. Res.*, **1**, 1 (1968); E. E. Van Tamelen, *Accounts Chem. Res.*, **1**, 111 (1968).

The Role of Solvents on the Behaviour of some Azo Compounds

MAMDOUH S. MASOUD

Chemistry Department, Faculty of Science, Alexandria, Egypt

The azo containing groups may behave as +R as well as -R groups, depending on the electronic requirements of the reaction. The aryl azo group is sufficiently polar for proximity effects to become significant in the *ortho* position, where its inherent behaviour may be masked by field effects and by even more interaction with side chain [1]. The β -diketoaryl azo compounds were taken as an example (I). The azo group can act as a proton acceptor in hydrogen bonds and the carbonyl oxygen acts as a proton acceptor with protonic solvents. The sole interaction with acetone will be the hydrogen bonding between the hydrogen of the OH-group and the oxygen of the solvent molecules to decrease the electron density on the oxygen atoms; similar behaviour is apparent in chloroform with slight increase in the strength of the *intra*-molecular hydrogen bonding. The (¹L_a - ¹A) transition of the phenyl ring was solvent independent. The donor *p*-OCH₃ substituent with mesomeric and inductive effects properties, where the electron density on the oxygen atoms of the carbonyl groups assists the electron migration from the highest occupied orbitals of the methoxy group to the vacant orbital on the carbonyl group [2]. The *intra*-molecular hydrogen bonding of the *p*-NO₂ compounds, mainly with π - π^* transition of the chromophoric groups is influenced by charge migration from the O-H group, not affected by non polar solvents. The *o*-NO₂ compounds are affected by increasing the volumes of R¹ and R². The polar solvent molecules are oriented to the polar sites of the solute in the ground state and on excitation, the solvent molecules are in a position to solvate the more stabilized polar excited states. The non-protonated ligands were the counter part for complexation with divalent transition metals in water-alcohol medium. The stability constants of the traced 1:1 chelates proved that the metals behave as π -electron acceptor depending on the nature of the substituents (σ), the dissociation constants of the ligands (pK) and the nature of the solvent (mainly its dielectric constant) [3].

