

## Excited-State Proton Transfer in Chiral Environments. 1. Chiral Solvents.

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### Supporting Information

#### 1. Measurement of dielectric parameters.

The dielectric properties of optical isomers of 2-butanol were determined by a commercial time-domain dielectric spectrometer (TDS), manufactured by Dipole TDS, Jerusalem. This spectrometer determines dielectric properties of materials by measuring the response of a sample to an applied rapidly increasing pulse of electric field.<sup>1</sup>

In the framework of lumped capacitance approximation the complex dielectric permittivity is written as follows:

$$\epsilon^*(\omega) = \frac{1}{i\omega C_0} \frac{L\{I(t)\}}{L\{V(t)\}} \quad (\text{S1})$$

where  $I(t)$  is the current flow through the sample,  $V(t)$  is the voltage applied to the sample,  $L$  is the operator of the Laplace transform and  $C_0$  is the capacitance of the empty sample cell which terminates the end of the coaxial line.

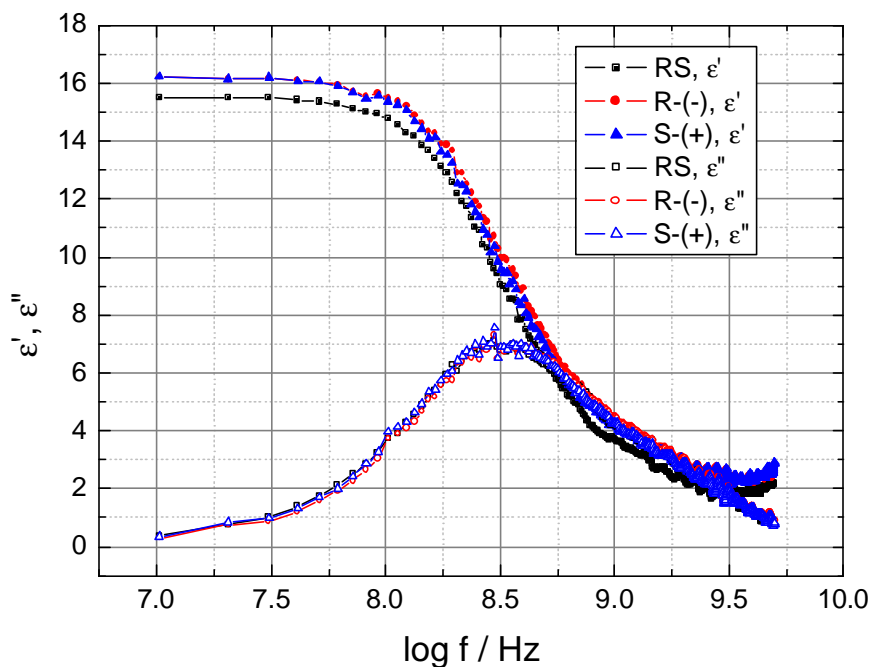
A small sample (150  $\mu\text{L}$ ) of each alcohol was injected into the sample cell (the capacitance of the empty cell is 0.17 pF), and the time domain response of the sample was determined from the accumulation of 25600 individual scans. Non-uniform sampling of the time window (2.6  $\mu\text{s}$ ) of each pulse enables the generation of spectra in the frequency range from 400 kHz up to 10 GHz. Measurements were taken at 25  $^\circ\text{C}$ .

Typical spectra are presented in Fig. (S1). Analysis of all spectra has shown that they can be well described by a function viz. a Cole-Davidson process:

<sup>1</sup> Yu. Feldman, A. Andrianov, E. Polygalov, G. Romanychev, I. Ermolina, Yu. Zuev, and B. Milgotin "Time Domain Dielectric Spectroscopy: An Advanced Measuring System." *Rev. Sci. Instrum.* **1996**, 67, 3208-3216.

$$\mathbf{e}^*(\mathbf{w}) - \mathbf{e}_\infty = \frac{\Delta \mathbf{e}}{(1 + i\mathbf{w}t)^b} \quad (\text{S2})$$

where  $t$  and  $\Delta \mathbf{e}$  are the relaxation time and relaxation strength of the processes,  $\mathbf{w}$  is angular frequency,  $\mathbf{e}_\infty$  is the high frequency limit of the dielectric permittivity, and  $b$  is the Cole-Davidson parameter.



**Figure S1.** Dielectric dispersion and absorption curves for optical isomers of 2-butanol at 25 °C.

The experimental values of static dielectric permittivity  $\epsilon$  are 15.8 for racemic 2-BuOH and 16.4 for both  $R(-)$  and  $S(+)$  isomers. It is worth noting that slight increase of  $\epsilon$  for chiral 2-BuOH corresponds to the higher stability of homo-dimers and higher oligomers. However, this difference in dielectric permittivities is too small to explain the observed difference in the PTTS rates.

## 2. Kinetic analysis of Scheme 1.

According to Scheme 1 the excited state populations of naphthol and its anion can be represented by two coupled differential equations. The spherically symmetric Smoluchowski

equation (eq S3) describes the probability density,  $p(r,t)$ , of CIP to separate to a distance  $r$  at time  $t$  after excitation in its bound excited-state ( $R^*OH$ ), whereas the simple kinetic equation (S4) denotes the probability  $P(t)$  of observing  $R^*OH$ .

$$\frac{\partial}{\partial t} p(r,t) = \left[ r^{-2} \frac{\partial}{\partial r} D r^2 e^{-V(r)} \frac{\partial}{\partial r} e^{V(r)} - k_0' \right] p(r,t) + [k_d P(t) - (k_a + k_q) p(r,t)] \frac{d(r-a)}{4\pi a^2} \quad (S3)$$

$$\frac{\partial}{\partial t} P(t) = k_a p(a,t) - (k_d + k_0) P(t) \quad (S4)$$

Here  $D = D_{H^+} + D_{R^*O^-}$  is the mutual diffusion coefficient of the proton and its conjugate base. The Coulomb attraction potential is  $V(r) = -R_D/r$  where the Debye radius,  $R_D$ , at the temperature  $T$  is given by

$$R_D \equiv |z_1 z_2| e^2 / (k_B T \epsilon) \quad (S5)$$

$z_1$  and  $z_2$  are the charges of the proton and the base and  $\epsilon$  is the static dielectric constant.

In practice we solve *numerically* the system of the coupled partial differential equations (S3) and (S4) and compare the time-dependent  $R^*OH$  signal with  $P(t)$ , and  $R^*O^-$  with

$$S(t) = 4\pi \int_a^\infty p(r,t) r^2 dr \quad (S6)$$

Usually, diffusion coefficients, Debye radius, and contact radius are estimated from literature, while excited-state lifetimes  $\tau_0$  and  $\tau_0'$  are determined from the independent measurements at the conditions when ESPT is suppressed. As a result, only three kinetic parameters,  $k_d$ ,  $k_a$  and  $k_q$ , are varied. A detailed procedure of fitting and parameters estimation is described in our previous publications (See Refs. 1(b-h) in the Communication).

In both  $R^*OH$  and  $R^*O^-$  kinetics, a long-lived kinetic component with a lifetime of about 5 ns and relative amplitude less than 1% was observed in all solutions. As in previous works, we attribute this minor compound to fluorescence from aggregates or impurities.

In addition to major PTTS non-exponential component all  $R^*OH$  kinetics show an initial ultrafast decay with the lifetime 70 ps and relative amplitude ~20%. Such component is due to slow solvation of DCN2 by 2-BuOH. For related systems see: Laitinen, E.; Salonen, K.; Harju, T. *J. Chem. Phys.* **1996**, *105*, 9711.