INTERPRETATION OF HYDROXYLIC SOLVENT EFFECTS BASED ON CORRELATIONS WITH SOLVENT PARAMETERS. REACTION OF Et_3N WITH EtI

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Received May 24, 1993
Accepted September 20, 1993

Hydroxylic solvent effects on 20 rate constants, *k*, of the Menschutkin reaction of Et_3N with EtI are unravelled and rationalized by means of multiple linear regression equations. To perform this analysis new *k* values in 2 mono- and 9 dialcohols are obtained. New values are also presented for the Kamlet and Taft solvatochromic parameters π^*, α and β of 1-hexanol. The results show that the solvent dipolarity, polarizability and cohesive energy density are the main properties influencing the reactivity, for the set of studied solvents.

The study of the effect of medium in Menschutkin reactions started many years ago. However, experimental and theoretical studies of solvent effects on these reactions still attract a large popularity due to the fact that these reactions exhibits a high sensitivity to solvent effects and that its quantitative description by empirical parameters was largely improved during the last decades. Reviews of this matter were recently published[1,2].

Accepting the basic principle that solvent effects on chemical reactivity are essentially similar in their nature and that only a few mechanisms of interaction take place between solvent and solute molecules, a general way of treating data in order to express these interactions is the method of linear solvation energy relationships (LSER), using a suitable model to connect the macroscopic solvent parameters and the microscopic details of the physico-chemical interaction processes. In practice, multiparameter correlations of the logarithm of the rate constants, log *k*, or the Gibbs energy of activation, $\Delta G^{\neq}$, with empirical solvent parameters have been successfully applied to several reactions[1 – 11].

We started our studies of LSER presenting work on the solvolysis of *tert*-butyl halides in hydroxylic solvents, a classic example of a unimolecular reaction[9 – 11]. We continue our studies of LSER, investigating the Menschutkin reaction of triethylamine

(Et_3N) with ethyl iodide (EtI) in water, 10 monoalcohols and 9 dialcohols. From the kinetic point of view, a conductometric technique was chosen to construct concentration–time plots, taking account of the actual ionic reaction product, the tetraalkylammonium salt ($Et_4N^+I^-$), as described before[12]. Rate constants of Et_3N/EtI reactions in mono- and dialcohols were then experimentally determined at 25 °C. Between the most suitable empirical equations for evaluation of the medium effects, we chose Eqs (*1*) (refs[9 – 11]) and (*2*) (refs[5,6]):

$$\log k = a_0 + a_1 f(\varepsilon) + a_2 g(\eta) + a_3 E_T^{\mathrm{N}} + a_4 C \qquad (1)$$

$$\log k = a_0' + a_1' \pi^* + a_2' \alpha + a_3' \beta + a_4' C \,. \qquad (2)$$

Data for the solvent parameters are from literature[2,9,13], except the values for the Kamlet and Taft solvatochromic parameters π^*, α, and β of 1-hexanol. Both multiparameter approaches take into consideration the three dominant types of interactions: non-specific and specific solvent–solute interactions and solvent–solvent interactions from the cavity effect. In Eqs (*1*) and (*2*), $f(\varepsilon)$ is a measure of the dipolarity effect, $g(\eta)$ a measure of the polarizability effect, E_T^{N} is the normalized Dimroth and Reichardt parameter which consists of a blend of dipolarity and solvent HBD acidity, C is the solvent contribution to the cavity term, π^* a measure of solvent dipolarity/polarizability, α is a scale of hydrogen bond donor – HBD acidities and β a scale of hydrogen bond acceptor – HBA basicities.

The results are discussed in terms of the fundamental solute–solvent–solvent interactions mechanisms and compared with previous results.

EXPERIMENTAL

Apparatus. A Wayne–Kerr B905 conductometric bridge and a modified version of the Shedlovsky cells were used to obtain the conductometric data in order to calculate the kinetic rate constants. A Beckman DU-7 spectrophotometer, with a 10 mm cells, was used for acquisition of the absorbance data of the solvatochromic indicators.

Solvatochromic dyes. We use four solvatochromic indicators sensitive to the solvent polarity π^* – 4-nitroanisole (**1**), 2-nitroanisole (**2**), 4-ethylnitrobenzene (**3**) and *N*,*N*-diethyl-4-nitroaniline (**4**), two sensitive to π^* and hydrogen bond acceptor capability β – 4-nitroaniline (**5**) and 4-nitrophenol (**6**), and one particularly sensitive to π^* and hydrogen bond donor capability α – 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)phenolate or Reichardt's Dye (**7**) to obtain the π^*, α and β values of 1-hexanol*. Dyes (**1**) and (**5**) were from Merck; (**2**), (**3**), (**4**) and (**7**) were from Aldrich; (**7**) was from Scharlau.

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* π^*, α and β values for 1-hexanol have been already published[6]. However, we repeat the procedure in order to obtain a coherent list of data.

Substrats and solvents. The triethylamine and ethyl iodide were from Fluka (≥99.5%) and they were used without further purification. Alcohols were from Merck (≥99%). The water content was kept lower than 0.02%.

Procedure. The mole fraction–time plots for the ionic reaction product, the tetraalkylammonium salt, were based on standard curves relating mole fractions to experimental conductances. The calibration method has been exemplified before[12]. At least five different standard solutions of tetraethylammonium iodide were used to obtain the relationships. The cells, filled fully with the standard solutions or the reactant solutions were placed within the thermostat (25.00 ± 0.01 °C). After the thermal equilibrium had been reached, we started conductance readings for both types of solutions at regular intervals of time, chosen according to the systems. All the solutions were prepared by weight after dry oxygen-free nitrogen has been passed through. All the observed kinetics show an experimental error < 1% in k (mole fraction^{-1} s^{-1}).

The absorbance data for each indicator were recorded as previously described[13]. The spectrophotometer cell was externally thermostatted at 25.0 ± 0.2 °C with a water jacket. The maximum wavelength of each indicator was obtained after numerical smoothing of the absorbance data. The parameter π^* was obtained from indicators (**1**) to (**4**), β from indicators (**5**) and (**6**) and the π^* previously computed, and α from indicator (**7**) and the π^* and β values.

RESULTS AND DISCUSSION

In Table I we summarized the available second-order rate constants for the Menschutkin reaction Et_3N with EtI in water and alcohols. Most of the data in this table are new; those which are cited from the literature are suitable footnoted. A compilation of the values of the empirical solvent parameters, $f(\varepsilon)$, $g(\eta)$, E_T^N, π^*, α, β and C for the set of studied solvents is also shown in Table I.

The non-collinearity assumption between any two of the chosen parameters, with respect to Eqs (*1*) and (*2*), was tested. As before[9], a strong collinearity was observed between $f(\varepsilon)$ and E_T^N. Some influence of solvent dipolarity in E_T^N is most probably the reasonable explanation, as stated by several authors using different sets of solvents[16 – 18]. We also observed collinearities between E_T^N and C, π^* and β and α and C. In these cases, however, we believe, as Glikberg and Marcus pointed out[19], that there are no relevant relationships from a physico-chemical point of view, since much smaller correlation coefficient values can be found for other sets of solvents.

Although both complete versions of Eqs (*1*) and (*2*) accommodate successfully the rate constant values of the reaction under study ($r \cong 0.95$; $s \cong 0.2$), the decision about the best fits was achieved by reference to a suitable criterion. We decided to use the Ehrenson's criterion[20]. The f function was then calculated for the complete and truncated versions of Eqs (*1*) and (*2*) showing the lower standard deviations, s, and from the ratio f_j/f_{j+1}, where j represents the number of estimated coefficients a in the simple and multiple linear regressions, we were able to conclude about the confidence levels and, consequently, about the statistically preferred correlations.

With respect to Eq. (*1*), $f_2 = 0.003883$, $f_3 = 0.002894$ and $f_4 = 0.002185$ (and, consequently, $f_2/f_3 = 1.341$ and $f_3/f_4 = 1.325$), which means that the hypothesis that a parameter set provides as a good fit as another set obtained by the removal of one parameter from the previous one must be rejected at a confidence level ≅ 99.9%, going from two to one parameter, and at a confidence level ≅ 99.6%, going from three to two parameters. In conclusion, the statistically preferred correlation is:

$$\log k = -(26.4 \pm 2.6) + (41.4 \pm 6.2)\, f(\varepsilon) + (10.9 \pm 3.1)\, g(\eta) + \\ + (0.48 \pm 0.21) \,.\, 10^{-3}\, C \\ (N = 20;\ r = 0.953;\ s = 0.22)\,. \qquad (3)$$

TABLE I

Rate constants k (mole fraction^{-1} s^{-1})[a] of the Menschutkin reaction of triethylamine with ethyl iodide in hydroxylic solvents, at 25 °C and selected properties of the solvents[b]

n	Solvent	$-\log k$	$f(\varepsilon)$	$g(\eta)$	E_T^{N}	π^*	α	β	$C/10^3$ MPa
1	Water	2.718[c]	0.49048	0.20569	1.000	1.13	1.16	0.50	2.307
2	Methanol	3.999[d]	0.47738	0.20311	0.762	0.60	1.09	0.73	0.887
3	Ethanol	4.288[d]	0.47006	0.22147	0.654	0.55	0.88	0.80	0.703
4	1-Propanol	4.571[d]	0.46420	0.23467	0.617	0.53	0.79	0.85	0.590
5	2-Propanol	4.389[d]	0.46327	0.23011	0.546	0.48	0.68	0.93	0.552
6	1-Butanol	4.706[d]	0.45836	0.24210	0.602	0.54	0.74	0.84	0.485
7	2-Butanol	4.491[d]	0.45604	0.24087	0.506	0.54	0.54	0.91	0.488
8	1-Pentanol	4.897[d]	0.44792	0.24776	0.568	0.50	0.73	0.88	0.497
9	2-Methyl-1-butanol	4.980	0.45350	0.24712	0.534	0.51	0.64	0.93	0.482
10	3-Methyl-1-butanol	4.845	0.45220	0.24627	0.565	0.48	0.74	0.91	0.497
11	1-Hexanol	5.087[d]	0.44565	0.25190	0.554[e]	0.52[e]	0.68[e]	0.86[e]	0.471[f]
12	1,2-Ethanediol	3.725	0.48037	0.25927	0.790	0.89	0.88	0.72	0.887
13	1,2-Propanediol	3.670	0.47422	0.25958	0.722	0.76	0.83	0.78	0.881
14	1,3-Propanediol	3.304	0.47886	0.26345	0.747	0.84	0.80	0.77	0.847
15	1,2-Butanediol	3.952	0.46718	0.26240	0.676	0.71	0.80	0.71	0.60
16	1,3-Butanediol	3.777	0.47420	0.26407	0.682	0.75	0.76	0.74	0.562
17	2,3-Butanediol	3.977	0.46614	0.25885	0.651	0.75	0.68	0.88	0.602
18	1,5-Pentanediol	3.912	0.47289	0.26843	0.654	0.76	0.70	0.82	0.603
19	Diethylene glycol	3.257	0.47670	0.26745	0.713	0.92	0.72	0.67	0.615
20	Triethylene glycol	3.342	0.46900	0.27173	0.704	0.88	0.66	0.69	0.480

[a] Standard deviation of $k < 1\%$, except for 1-hexanol (≅ 3%). [b] Values listed in refs[2,9,13], except otherwise indicated. [c] Value calculated from data in ref.[14]. [d] Values from ref.[12]. [e] This work. [f] Value calculated from data in ref.[15].

With respect to Eq. (*2*), using the same criterion, we consider that the following two coefficients correlation is the best statistical fit:

$$\log k \ = \ -(6.37 \pm 0.20) \ + \ (3.33 \pm 0.29)\,\pi^* \qquad (N = 20;\ r = 0.939;\ s = 0.23)\,. \qquad (4)$$

The statistical quantities a_0 and a_0' correspond to the value of the solvent dependent property log *k*, in the gas phase or in an inert solvent. We may note that hexane shows the smallest experimentally determined *k* value, log *k* = –6.990 (ref.[14]). In this context, Eq. (*4*) seems to present a more direct logical connection between the statistical approach and the physico-chemical interpretation. Unfortunately, log *k* value in gas phase is not available and it is difficult to assign an “inert” solvent for the Menschutkin reactions.

Concentrating our attention in Eq. (*3*), we may observe, for the set of studied solvents, that: (i) the non-specific solvent–solute interactions, represented by $f(\varepsilon)$ and $g(\eta)$, are both relevant, i.e., rate constants of Et_3N with EtI reaction show a marked dependence on solvent dipolarity and polarizability; (ii) the specific solvation, represented by E_T^N, is unrelevant, i.e., the solvent–solute interaction on account of the solvent HBD acidity does not influence the Menschutkin reaction to a relative significant extent; (iii) solvent–solvent interactions, measured by the *C* parameter, are important, i.e. disruption and reorganization of solvent molecules in order to create a suitable cavity to accommodate the substrate molecule contributes to the overall solvent effect on the reaction under study.

If we extended our analysis to the results obtained by Eq. (*4*) for the hydroxylic solvents, we may conclude that: the solvent dipolarity-polarizability (π^* term) is the main factor influencing the rate constants and, conversely, the acidity and basicity of the solvent (α and β terms) are not significant. These two conclusions are in good agreement with those taken from Eq. (*3*). A different interpretation, however, can be drawn from the relative importance of the cavity term. Nevertheless, it is interesting to note that, according to Eq. (*1*), the best two parameters correlation does not include the *C* term and that, according to Eq. (*2*), the best three parameters correlation contains the *C* (and the α) term.

The reaction between Et_3N and EtI has been examined before by Abraham et al.[3,6], Pytela[1], and Bekárek and Nevecna[8] who found, for a set of solvents including aprotic and protic solvents (hydrocarbons, aromatics, alcohols)*, that solvent dipolarity was the

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* Although within the hypothesis of LSER nothing is stated about the mechanism of the reactions under study and, consequently, about the possible configurations of the activated complexes, it seems desirable to apply LSER to a set of solvents for which we may postulate a certain type of transition state. This way, solvent effects can be descriminated, compared and interpreted in a more solid basis. This is why we prefer to consider the influence of hydroxylic solvents (water and alcohols – class 3)[21] separated from the influence of other classes of solvents.

over-riding factor influencing the reaction rate, with solvent hydrogen-bond acidity and basicity being statistically much less significant. Although our set of studied solvents differs considerably from those used before, our conclusions agree in the fundamental points. Within the set of hydroxylic solvents used in this work proton-donor ability of medium did not strongly affect the reaction; however, this was not the case described by other authors[1,8], using several classes of solvents simultaneously.

CONCLUSIONS

In the present work, we focussed our attention on the solvent effects on the bimolecular reaction of Et_3N with EtI in water and alcohols. Dipolarity and polarizability influence the Menschutkin reaction, most probably stabilising the ion-pair like transition state and, consequently, increasing the rate constant and, conversely, the effectiveness of the solvents as hydrogen bond donors seems to be irrelevant in this case. Presumably, as Abraham et al.[6] pointed out, the stabilisation of the leaving iodide ion in the transition state by electrophilic assistance is counterbalanced by stabilisation of triethylamine in the initial state. Finally, the nucleophilic solvent assistance is not significant for the studied Menschutkin reaction in the hydroxylic solvents water, mono- and dialcohols.

We are grateful to the Instituto Nacional de Investigacao Científica of Portugal (project 1C and 3C-CECUL) and to the Direccion General de Investigacion Cientifica y Tecnica of Spain (project PB91-0262) for financial support.

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