
INFLUENCE OF THE SOLVENT ON THE TRANSMISSION OF POLAR EFFECTS IN FREE RADICAL REACTIONS. A THEORETICAL STUDY

Robert PONEC and Milan HÁJEK

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, Prague 6-Suchbát*

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Dedicated to the memory of Dr Karel Bláha.

The influence of the solvents on the transmission of polar effects in free radical reactions has been analysed theoretically by using the combined approach based on the incorporation of delocalizabilities as static indices of chemical reactivity into the framework of virtual charge model. The possibility of using this theoretical description as a general methodology of characterizing solvent effects is discussed.

Because of small differences in the charge separation between the initial and transition state, the free radical reactions were frequently assumed to be little sensitive to the variation of solvent polarity. The convincing experimental indications accumulated from the late fifties by Russell¹⁻⁵, Walling⁶⁻⁹, Huyser^{10,11} and others¹²⁻¹⁶ demonstrated, however, that the validity of this widespread opinion was not so universal as originally believed. The solvents have been shown to influence not only the reactivity and selectivity of free radical reactions but also their sensitivity to the transmission of polar effects. This sensitivity is quantitatively characterized by the value of the Hammett reaction constant ρ .

In contrast to "normal" heterolytic reactions where the solvent-induced dependence of ρ constants is documented and understood relatively well¹⁷⁻²⁰, our knowledge of the factors determining in this respect the behaviour of free radical reactions is much more fragmentary. The most restrictive feature manifesting itself in this respect is the lack of studies dealing with the solvent dependence of polar effects in a systematic way. Although there are exceptions confirming the above general situation²¹⁻²³ they are still very scarce so that their conclusions, being moreover based on very restricted range of solvents and systems, can still be regarded as only preliminary.

In order to overcome this limitation and to obtain a deeper insight into the nature of the studied problem, we have attempted to complement the existing fragmentary experimental data^{21,22} by simulating the solvent dependence of ρ constants theoretically in terms of quantum chemical calculations.

THEORETICAL

The philosophy of our approach arises from recent theoretical study dealing with more general problem of solvent effect on free radical reactivity²⁴. In that study a simple formalism was proposed the principal idea of which is based on incorporation of usual quantum chemical treatment of free radical reactivity in terms of delocalizabilities D_r (ref.²⁵) into the framework of the so-called virtual charge model of solvent effect²⁶. In terms of this combined approach the study of solvent dependence of polar effects was performed by analyzing the variation of "theoretical ρ constants" represented by the slopes of Hammett-like correlations D_r vs σ in a series of substituted derivatives for various solvents.

Before presenting the result of such analysis it is, however, fair to mention some possible limitations arising from the approximate nature of the approach.

The first what should be realized is, that because of simplicity of the model, the above slopes are not of course, equal to numerical values of experimental ρ constants but only a proportionality can be expected. This, however, is not too restrictive since our primary aim is the investigation of changes in ρ rather than reproduction of ρ values themselves.

Another source of potential limitations concerns the use of delocalizabilities as static indices of reactivity. This restricts the applicability of the model only to the rationalization of relative reactivities in a series of structurally related compounds. Since, however, in studying the polar effects this is just the case, this restriction can be expected to have no important impact. Such a belief is supported not only by the frequently reported successful application of delocalizabilities to the elucidation of various aspects of free radical reactivity²⁷⁻²⁹ but also by the results of our previous study dealing with the theoretical characterization of polar effects in free radical additions to substituted styrenes³⁰. Much more important are thus the limitations arising from the inherent nature of the virtual charge model (VCM). The specific feature of this model is that the solvent is treated as structureless dielectric continuum. The effect of the solvent thus manifests itself only in the modification of the effective hamiltonian of the solute molecule where the terms reflecting the polarity of the medium appear³¹. As a consequence of this specific feature, the general formula (1) for calculating the delocalizabilities remains unchanged and the only

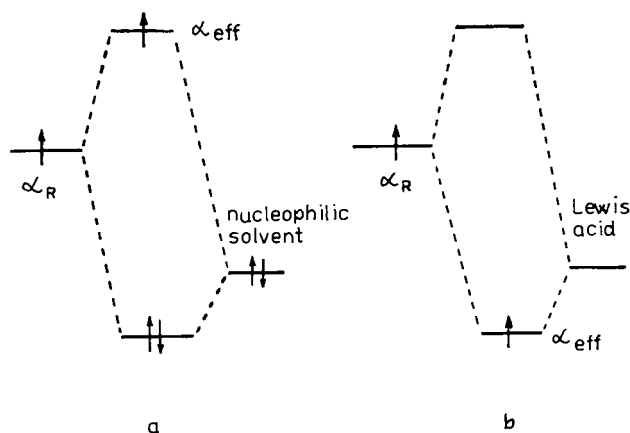
$$D_r = \sum_i^{\text{occ}} \frac{C_{ri}^2}{\alpha - \epsilon_i} + \sum_j^{\text{virt}} \frac{C_{rj}^2}{\epsilon_j - \alpha} \quad (1)$$

modification consists in that the necessary quantities (LCAO expansion coefficients, orbital energies) become solvent dependent. Such a modification can be formally respected by rewriting the Eq. (1) in the form (2) in which the argument (s) explicitly denotes the solvent dependence of corresponding quantities.

$$D_r(s) = \sum_i^{\text{occ}} \frac{C_{ri}^2(s)}{\alpha - \varepsilon_i(s)} + \sum_j^{\text{virt}} \frac{C_{rj}^2(s)}{\varepsilon_j(s) - \alpha} \quad (2)$$

Since the only quantity characterizing the solvent within the framework of VCM is the dielectric permittivity ε , the "solvent corrected" delocalizabilities defined by Eq. (2) primarily reflect the isolated effect of solvent polarity. This, however, is rather crude simplification since from the whole complexity of inter and intra-molecular interactions contributing to what is known as solvent effect only the non-specific electrostatic effects of solvent polarity are included. On the other hand any specific intermolecular solute... solvent interactions are completely ignored.

Such an idealization is, however, rather restrictive since especially in the field of free radical reactivity a majority of reactions was studied in aromatic solvents where the formation of specific solute... solvent complexes was frequently reported¹⁻¹¹. Fortunately the negative impact of this restriction is not so important as it might seem to be. This is due to the fact that the combined nature of our model makes it possible to compensate the above limitations of VCM and to include the specific intermolecular interactions indirectly. Such inclusion is based on the fact that in addition to affecting primarily the solute molecule, the solvent alters also the reacting radical. Since in our approach the radical is modelled by the parameter α the specific radical ... solvent interactions can be qualitatively respected by the appropriate variation in α values. Even if the detailed quantitative determination of the extent of corresponding changes in α can be in each particular case rather difficult, the qualitative estimation of general trends is quite simple and can be easily rationalized on the basis of simple orbital Scheme 1. Thus as can be seen from the scheme Ia, the interactions with nucleophilic solvents, like aromates, can be expected to increase the α value so that the "complexed radical" effectively behaves as being

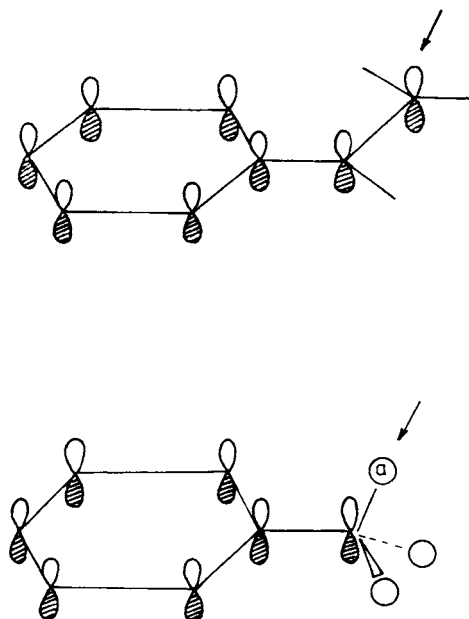


SCHEME 1

less electrophilic. On the other hand, the reverse is true for interactions with solvents or other complexing agents of electrophilic nature, where the decrease of the effective α value (Scheme 1b) suggests the increase in the electrophilicity of the radical. The effect of specific radical ... solvent complexation is thus in our model analogous to the effect of structural variation in the radical. This analogy serves then as a basis for the qualitative estimation of the effect of specific radical ... solvent interactions on the transmission of polar effects which is simply based on comparison of changes in "theoretical q constants" for several selected model α values.

CALCULATIONS

The above technique was applied to two model free radical reactions – the addition to substituted styrenes and H-abstraction from substituted toluenes. The calculations were performed by simple CNDO/2 method^{32,33} modified y incorporating the formalism of virtual charge model²⁶. On calculating the necessary delocalizabilities, the p_z orbital of terminal C atom in styrenes and s orbital of H_a atom in toluenes (Scheme 2) were assumed to play the role of the center of primary attack. Because of simplicity of our model no optimization of geometry was performed and the corresponding molecules have been considered in idealized geometries with standard bond lengths²⁶. The H, p -F, p -Cl and m -NO₂ groups have been used as substituents throughout.



SCHEME 2

In characterizing the effect of solvent polarity the delocalizabilities were calculated for the values of ϵ systematically varying within the range $\epsilon = 1$ to $\epsilon = 80$. To investigate the effect of radical polarity and of specific radical ... solvent interactions, all the calculations were performed for three model α values equal to -10 eV, -5 eV and 0 eV.

RESULTS AND DISCUSSION

In order to analyse the solvent effect on the transmission of polar effects, the primary delocalizabilities calculated by the above procedure were converted into "theoretical ρ constants" represented by the slopes of D_r vs σ correlations. These values are summarized in Table I. The calculated data suggest that the general trends governing the "solvent induced" variation in are completely analogous both in the effect of solvent polarity and the specific radical ... solvent interactions.

Let us start by the discussion of the effect of solvent polarity first. The general trend that can be extracted in this respect from Table I is that the absolute value of both negative ρ constants for electrophilic radicals ($\alpha = -10$ eV) and positive ρ constants for nucleophilic radicals ($\alpha = 0$ eV) decrease on increasing the dielectric permittivity ϵ . This decrease is so strong that at the limit of high solvent polarities both reactions can be expected to become independent of substitution. Let us attempt now to compare this theoretical prediction with experiment. The situation here is, however, somewhat complex since in spite of relative abundance of experimental

TABLE I

Values of "theoretical ρ constants" represented by the slopes of D_r vs σ correlations in a series of substituted toluenes and styrenes for various values of solvent dielectric permittivity ϵ and radical polarity α (Because of the fact that delocalizabilities as a measure of reactivity are negative, the signs of D_r vs σ slopes and of experimental ρ constants are reversed i.e. negative D_r vs σ slopes correspond to positive ρ constants and vice versa.)

Series	α , eV	$\epsilon = 1$	$\epsilon = 2$	$\epsilon = 5$	$\epsilon = 10$	$\epsilon = 50$	$\epsilon = 80$
Styrenes	-10	0.011	0.090	0.007	0.005	0.002	0
	-5	0	0	0	0	0	0
	0	-0.008	-0.006	-0.003	-0.002	0	0
Toluenes	-10	0.133	0.114	0.089	0.068	0.028	0.022
	-5	0	0	0	0	0	0
	0	-0.314	-0.206	-0.070	+0.018 ^a	-0.035	-0.017

^a This value is slightly anomalous; because of being close to zero we do not consider it to alter the general trend of the decreasing sensitivity to polar effects.

data on solvent dependence of polar effects, (Tables II and III) the restricted range of solvents used makes it difficult to trace any systematic trends concerning the effect of solvent polarity. To our best knowledge the only study attempting to discuss the role of solvent polarity systematically is the study by Howard and Ingold²¹ who predicted the increase of absolute value of ρ with increasing dielectric permittivity, This conclusion is, however, completely opposite to what follows from our calculations. Even if we are aware of the simplicity of our approach, there are, however,

TABLE II

Selected experimental values of ρ constants for the hydrogen abstraction from substituted toluenes by various radicals

Radical	Solvent	Temperature °C	ρ	Ref.
Cl [•]	toluene	70	-0.76	8
	CCl ₄	40	-0.76	5
Br [•]	benzene	80	-1.36	15
	CCl ₄	80	-1.38	16
	freon 113	45	-0.35	22
t-BuO [•]	chlorobenzene	45	-0.32	22
	acetonitrile	45	-0.39	22
	CCl ₄	50	-0.41	35
	benzene	40	-0.75	14
	acetonitrile	0	-0.96	9
	CCl ₄	40	-0.86	13

TABLE III

Selected experimental values of ρ constants for the addition of various radicals to substituted styrenes

Radical	Solvent	Temperature °C	ρ	Ref.
CCl ₃ [•]	styrenes	80	-0.42	36
CCl ₃ [•]	CCl ₄	76	-0.40	37
NMe ₃ [•]	- ^a	- ^a	+0.69 ^b	38
NMe ₃ ...ZnCl ₂	- ^a	- ^a	-0.98 ^b	39

^a Conditions not reported; ^b values of ρ determined for α -methylstyrenes.

some indications that the above discrepancy need not be necessarily due to the failure of the theoretical model. First of all it is necessary to realize that the study is already more than 20 years old and that the amount of experimental data from which the mentioned conclusions were derived was at that time even much more restricted than now. This argument, even if certainly nonnegligible, is not, however, the only one. Another, probably more important support in favour of our conclusions is that they are completely analogous to what is known from the much better documented effect of solvent polarity on ρ constants of heterolytic reactions¹⁷⁻²⁰. As a typical example, the dissociation of substituted benzoic acids can be mentioned where the dramatic decrease in ρ is observed on going from the gas phase ($\epsilon = 1$, $\rho \sim 10$) to water ($\epsilon = 80$, $\rho = 1$) (ref.³⁴). The predicted behaviour of free radical reactions thus appears in this respect quite "normal" and reflects the fact that the difference between the free radical and heterolytic reactions is probably only quantitative one, consisting in the lower polarity of the transition state in the former case.

After having discussed the influence of the solvent polarity, let us proceed now to the analysis of the role of specific radical ... solvent interactions. Since the effect of this complexation was the most frequently observed in aromatic solvents, we confine ourselves to the discussion of this particular case only. In harmony with the qualitative MO model (Scheme 1a), the effect of the complexation can be in this case expected to decrease the effective polarity of the radicals. Since the above qualitative model is too simple to allow the estimate of the values of corresponding changes $\Delta\alpha$, the effect of specific complexation can be characterized only qualitatively by comparing the "theoretical ρ constants" for several selected values of α . In our case the values $\alpha = -10$ eV, -5 eV and 0 eV were used. The values presented in Table I demonstrate that the effect of alteration of the radical polarity is again completely analogous for both reactions. Thus, on going from $\alpha = -10$ eV to $\alpha = -5$ eV (which corresponds to the complexation of the electrophilic radicals) one can expect the decrease in the absolute value of ρ (the effect is stronger in solvents of low polarity). In another words, the aromatic solvents can be in this case expected to reduce the sensitivity to the transmission of polar effects so that on comparing the ρ values for several solvents of like (low) polarity, the values for aromatic solvents should be lower. This general tendency qualitatively predicted already by Howard and Ingold²¹ is completely reproduced. Thus for example Walling and Miller reported the decrease of sensitivity to polar effects for chlorine atom complexed by benzene⁸. Analogous, but probably even better example is provided by data on H-abstraction from substituted toluenes by t-BuO radicals. The results by Kennedy and Ingold¹³ and by Gilliom and Ward¹⁴ confirm the expected decrease of corresponding ρ values on going from CCl₄ to benzene ($\rho = -0.75$ (benzene) vs $\rho = -0.86$ (CCl₄)).

Unfortunately the lack of relevant experimental data prevents us again to verify the surprising effect of aromates on nucleophilic radicals predicting the increase in ρ .

This problem, as well as the verification of the effect of solvent polarity thus still waits for systematic experimental investigation. The present work aims at being the stimulation for such a study.

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