VISIBLE ABSORPTION SPECTRUM OF BENZOPHENONE RADICAL ANION IN DIPOLAR APROTIC SOLVENTS

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Two-parameter regression including the acceptor number (AN) and permittivity (ε) of the solvent explains to some extent the solvatochromic shift of the absorption band of benzophenone radical anion ($Ph_2\dot{C}–O^-$) in the visible region. In 11 dipolar aprotic solvents characterized by $\varepsilon > 10$, in which the $Ph_2\dot{C}–O^-$ anions are not associated with $(C_2H_5)_4N^+$ cations (the radicals were prepared by cathodic reduction of benzophenone in the presence of $(C_2H_5)_4N^+ClO_4^-$ as electrolyte) a correlation equation has the form ν_{max} (in cm^{-1}) = $86.2(AN) - 19.7 \cdot 10^3[(\varepsilon - 1)/(2\varepsilon + 1)] + 21.32 \cdot 10^3$. It reflects the relative stabilization of the ground state in a medium with a high acceptor number and an increase in the dipole moment of $Ph_2\dot{C}–O^-$ during excitation.

Key words: Benzophenone radical anion; Electronic absorption spectroscopy; Solvent effects; Ketyl radicals; Ketones; Solvatochromism; Electroreductions.

Ketyl radicals, both in neutral and anionic forms, are known as intermediates in the electrochemical and photochemical reduction of aromatic ketones. Their physicochemical properties and reactivity are strongly solvent-dependent, which provokes considerable research. We are interested in the role of solvent to modify the electronic absorption spectra.

It is well established that the visible absorption spectrum of $Ph_2\dot{C}–O^-$, the benzophenone radical anion, is strongly shifted upon the nature of a solvent, but the decisive solvent parameters were not recognized. The spectrum exhibits a single distinct band of the $D_0 \rightarrow D_1$ transition characterized by the λ_{max} values of 690, 720, 740 and 740 nm in 1,2-dichloroethane[1] (DCE), *N*,*N*-dimethylformamide[2] (DMF), acetonitrile[2] (ACN) and dimethyl sulfoxide[1] (DMSO), respectively. As can be seen, the λ_{max} values differ by 20 nm in ACN and DMF, *i.e.*, in nearly isodielectric media, and by 60 nm in DCE and DMF, *i.e.*, in solvents with quite similar Lewis acidities, as expressed by the corresponding acceptor numbers. In a 2-methyltetrahydrofuran matrix at 77 K, which is characterized by a relatively small interaction between the solute anion and the matrix molecules, the spectrum is considerably red-shifted[3] (λ_{max} 800 nm). Thus, neither the changes in solvent polarity nor the changes in acid properties of solvent alone are sufficient to describe the observed variation of λ_{max}. This induced us to undertake a more detailed investigation of solvent effects on the spectrum of $Ph_2\dot{C}–O^-$.

In this work, we report on the measurements performed in 10 aprotic media which were selected so as to give a respectable range of acceptor properties and rather high static permittivities. Protic liquids were omitted in our study because of considerable differences between the solvation behaviour of the $Ph_2\dot{C}–O^-$ anion in protic[4,5] and in aprotic solvents. It is also noticeable that ion pairs between $Ph_2\dot{C}–O^-$ and corresponding counter-ions are formed in media of low dielectric properties and in these cases additional spectral shifts arising from ion pairing are observed[6,7]. Therefore, in order to minimize the effects of ion pairing we have restricted our study to the solvents with static permittivities above 10.

EXPERIMENTAL

Benzophenone radical anions were prepared by cathodic reduction of the parent compound in a cell placed in the cavity of a Philips PU 8370 spectrophotometer with data station based on an IBM PC 486 computer. A potentiostat OH-404 Radelkis was employed to maintain a constant potential between a Hg pool cathode and a reference electrode. The measurements were carried out at 25 ± 1 °C. The solvents ACN, DMF, acetone and pyridine were purchased as Fluka-certified chemicals for UV spectroscopy and used without purification. The remaining solvents DMSO, *N*,*N*-dimethylacetamide, tetramethylurea, *N*-methyl-2-pyrrolidone, propylene carbonate (4-methyl-1,3-dioxolan-2-one) – all from Merck – and γ-butyrolactone (butano-4-lactone) from Fluka were dried and purified using the methods described in the literature[8]. Benzophenone (Merck) was twice recrystallized from ethanol and dried under reduced pressure at room temperature. All details of the experiments were the same as those reported previously[9].

RESULTS AND DISCUSSION

Benzophenone, when studied in the above-mentioned solvents containing 0.1 M $(C_2H_5)_4N^+ClO_4^-$ as a supporting electrolyte, is reduced at a dropping mercury electrode forming two one-electron waves[10,11]. The first reversible step, which is the object of our interest, yields the radical anion $Ph_2\dot{C}–O^-$ in its free form unassociated with $(C_2H_5)_4N^+$ (ref.[10]).

$$Ph_2C{=}O + e \rightleftharpoons Ph_2\dot{C}–O^- \qquad (1)$$

Therefore, we prepared the $Ph_2\dot{C}–O^-$ anions by cathodic reduction of the parent compound at the controlled potential corresponding to the beginning of the limiting current appropriate for the process (*1*). The electrolysis gave a blue solution of $Ph_2\dot{C}–O^-$. The resulting values of λ_{max} (in nm) are shown in Table I. The radical was quite stable in deoxygenated solutions, having a half-life of more than 1 h in all the solvents studied. The accuracy of the wavelengths of maximum absorption and reproducibility of the values determined in different measurements were in the range of ±2 nm. The values already published in DMSO (ref.[1]), DMF (ref.[2]) and ACN (ref.[2]) solutions agree satisfactorily with our λ_{max} values, therefore Table I also contains the corresponding quantity reported in DCE (ref.[1]), *i.e.*, in the solvent with a smaller permittivity.

The data in Table I allow to analyse spectral characteristics in terms of solvent effects. However, there is no single solvent parameter that correlates our data. This means that more than one solvent parameter is important and, hence, the application of multiple linear regressions with various explanatory variables should be considered. We have reported that in the case of fluorenone radical anion, a two-parameter regression including sol-

TABLE I
λ_{max} Values of benzophenone radical anion in solvents of different acceptor numbers and static dielectric permittivities

No.	Solvent	λ_{max}, nm	AN[a]	D[b]
1	Acetonitrile	720	18.9	37.5
2	Dimethyl sulfoxide	738	19.3	46.68
3	*N*,*N*-Dimethylformamide	742	16.0	36.71
4	*N*,*N*-Dimethylacetamide	752	13.6	37.78
5	Butano-4-lactone	734	17.3	39
6	Acetone	740	12.5	20.70
7	*N*-Methyl-2-pyrrolidone	749	13.3	32.0
8	4-Methyl-1,3-dioxolan-2-one	739	18.3	66.1
9	Tetramethylurea	756	10.7[c]	23.06
10	Pyridine	710	14.2	12.3
11	1,2-Dichloroethane	690[d]	16.7	10.36

[a] Acceptor number[12]. [b] Permittivity[13]. [c] Estimated[11]. [d] From ref.[1].

vent acceptor numbers (AN) and static permittivities (ε) fits the solvent-dependent wavenumber values, ν_{max}, quite well[9]. Therefore, the ν_{max} values of $Ph_2\dot{C}–O^-$ (in cm^{-1}) were now subjected to a regression analysis as shown in Eq. (*2*)

$$\nu_{max} = \alpha(AN) + \beta[(\varepsilon - 1)/(2\varepsilon + 1)] + \gamma \qquad (2)$$

As a consequence, we have found for the ten solvents investigated (Nos 1–10 in Table I) a regression of the form

$$\nu_{max} = (87.2 \pm 19.5)(AN) - (19.51 \pm 5.77) \cdot 10^3 \, [(\varepsilon - 1)/(2\varepsilon + 1)] + \\ + (21.47 \pm 2.54) \cdot 10^3 \qquad (3)$$

with a correlation coefficient of $r = 0.959$, a mean square standard deviation of ν_{max} from regression of $s = 70$ and a Fisher and Snedecor test of $F = 40.4$ (errors were determined on the basis of Student's distribution with a confidence level of 0.95). A difficulty in regression (*3*) is that for the solvents examined is non-negligible correlation between $[(\varepsilon - 1)/(2\varepsilon + 1)]$ and AN (r = 0.540). It should be noted, however, that simple linear regressions of ν_{max} with AN and $(\varepsilon - 1)/(2\varepsilon + 1)$ hold with $r = 0.439$ and 0.480, respectively. In that situation, an introduction of the second explaining parameter is statistically justified at the 0.95 level; this follows clearly from the procedure based on calculations of corresponding *F*-tests as proposed by Shorter[14]. Moreover, an application of Eq. (*2*) to an extended solvent set (the literature value for DCE solutions was included) resolved completely the problem of colinearity. For all the eleven solvents listed in Table I, AN and $(\varepsilon - 1)/(2\varepsilon + 1)$ are not colinear and have a mutual correlation coefficient of 0.278. Now, statistical analysis leads to

$$\nu_{max} = (86.2 \pm 21.0)(AN) - (19.17 \pm 3.24) \cdot 10^3 \, [(\varepsilon - 1)/(2\varepsilon + 1)] + \\ + (21.32 \pm 1.47) \cdot 10^3 \qquad (4)$$

$r = 0.982$, $s = 67$ and $F = 110.3$ (Fig. 1).

Although the correlations given by Eqs (*3*) and (*4*) can be assumed to be satisfactory, some comments are needed before further discussion. The first of these is associated with a chosen solvent series; their electrophilic and dielectric properties may be of critical importance for resulting correlations. Among the solvents discussed, the AN values lie between 10.7 in tetramethylurea and 19.3 in dimethyl sulfoxide, whereas ε changes from 12.3 in pyridine (and 10.36 in 1,2-dichloroethane) to 66.1 in 4-methyl-1,3-dioxolan-2-one. These ranges of the variability of AN and ε are considerably wider than those in our previous work[9] and their further enlargement is simply impossible. As it was pointed out above, the ion pairs formation between the radical anion and electrolyte cations may be anticipated in media of low permittivities and low electrophilic properties, and this influences additionally the electronic spectrum of $Ph_2\dot{C}–O^-$. That is why that such solvents as, *e.g.*, ethers and aromatic hydrocarbons were useless in our study. On the other hand, most of the solvents characterized by high AN show protic character.

In our treatment the acceptor number was chosen as a measure of the Lewis acidity. There is, however, no obvious reason why other electrophilicity parameters should have a radically different influence on the ν_{max} value compared with that for AN. By way of example, the regression of ν_{max} against the Dimroth and Reichardt parameter expressed in normalized scale, E_N^T, and $(\varepsilon - 1)/(2\varepsilon + 1)$ yields $r = 0.964$ and $F = 51.9$ for 11 solvents

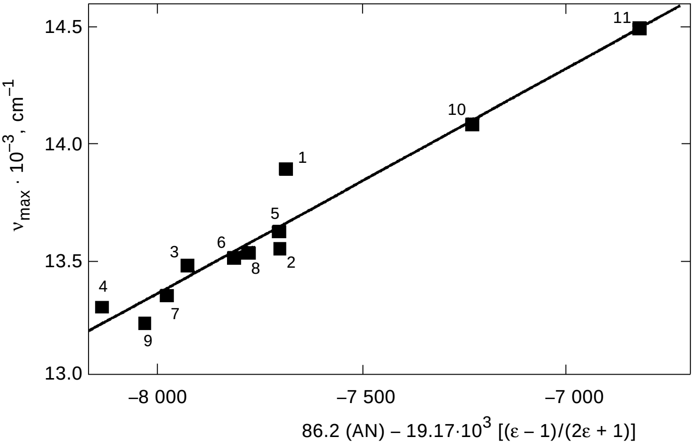

FIG. 1
Correlation of the ν_{max} value for benzophenone radical anion with acceptor numbers and static permittivities of solvents (Eq. (*4*)) (for solvents 1–11, see Table I)

collected in Table I. This is not surprising, since AN and E_T^N are quite well mutually correlated, similarly as many other quantities that have been proposed for the description of the Lewis acidity. Note that a linear regression of ν_{max} *vs* E_T^N holds with $r = 0.183$.

The problem of solvent effects on ν_{max} was also attacked from another direction: taking into account the formalism proposed by Koppel and Palm[15], the refractive index function in the form of $(n^2 - 1)/(2n^2 + 1)$ was used as an explaining parameter instead of $(\varepsilon - 1)/(2\varepsilon + 1)$. In that case, however, two-parameter treatment with AN and $(n^2 - 1)/(2n^2 + 1)$ gave $r = 0.400$, indicating that the spectral shift observed in this study is not susceptible on the changes of solvent polarisability. Thus, it can be safely concluded that the solvent shift of the ν_{max} values of $Ph_2\dot{C}–O^-$ can be considered indeed in terms of the changes of electrophilicity and permittivity, at least in dipolar aprotic media.

Return, therefore, to Eqs (*3*) and (*4*). The regression coefficients α and β of these equations characterise the sensitivity of ν_{max} towards electrophilic and dielectric solvent effect, respectively. The partial regression coefficients[16] of Eq. (*4*) are equal to 0.696 and 1.599, which indicates that the percentage contributions to the observed solvent shift are 30 and 70% for AN and $(\varepsilon - 1)/2\varepsilon + 1)$, respectively. Moreover, as can be seen, the α and β values show opposite signs. This means that, at the same time, an increase in the Lewis solvent acidity is responsible for a hypsochromic shift and an increase in the polarity makes a bathochromic contribution to the total solvent shift of ν_{max}. One may suggest that the positive value of α is due to relative stabilization of the ground state in a solvent with a high acceptor number; it was established earlier that the formal potential corresponding to the $Ph_2C=O/Ph_2\dot{C}–O^-$ redox pair becomes more positive with an increase in AN (refs[10,11]). Next, the negative sign of β can be attributed to the fact that the dipole moment of $Ph_2\dot{C}–O^-$ increases during the excitation (*cf., e.g.*, Chap. 6 in ref.[17]), and we assume that these suggestions explain the chemical meaning of Eq. (*4*).

An interesting aspect of the present study is that the solvent effect on the visible spectrum of $Ph_2\dot{C}–O^-$ is qualitatively similar to that observed for the spectrum of fluorenone radical anion[9] ($FN^{-\bullet}$). Thus, if comparing the present data with those reported in ref.[9], one finds that the β coefficient of Eq. (*4*) for $Ph_2\dot{C}–O^-$ is considerably smaller than the value obtained from the analysis for the spectrum of $FN^{-\bullet}$. The above-mentioned observation can be attributed to weak solvent effect on the changes of the dipole moment of $Ph_2\dot{C}–O^-$ during the excitation, but a more precise discussion of this problem is still impossible. The situation is particularly complex in the case of $Ph_2\dot{C}–O^-$, in which the hindered rotation of the benzene rings occurs[18], and is most probably variable depending on the solvent nature, but this phenomenon is not confirmed quantitatively.

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