Experimental and theoretical study of the association of radical anions with alkali metal cations. III. Spectral study of the effect of medium on the formation of associates of fluorenone radical with cations

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Fluorenone radical anion prepared by electrolysis has been studied by quantum chemical methods and experimentally by u.v. spectroscopy. The quality and concentration effects of supporting electrolyte as well as the effect of solvent polarity, addition of proton-donor agent, and temperature on the formation of fluorenone associates with cations of supporting electrolyte have been investigated.

Методами квантовой химии и экспериментально по УФ спектрам были изучены анион-радикалы флуоренона, приготовленные электролизом. Было изучено влияние типа и концентрации поддерживающего электролита и также полярности растворителя, добавок протоно-донорного агента и температуры на образование ассоциатов флуоренона с катионами поддерживающего электролита.

In preceding papers of this series [1, 2] we investigated ion pair formation of radical anions of nitrobenzene and 4-nitrobenzophenone prepared by electrolysis with cations of supporting electrolyte (Li^+, Na^+, K^+, Cs^+). The association of these cations with radical anions also in polar medium of dimethylformamide (DMF) was shown. The concentration of supporting electrolyte was considerably higher than the concentration of radical anions. The present paper deals with the fluorenone anion and the effect of supporting electrolyte concentration and solvent polarity on ion pair formation. So far, the associates of fluorenone with cations formed by chemical reduction of fluorenone by alkali metals or alkaline earth metals in medium polar solvents (tetrahydrofuran, dioxan, *etc.*) with cation concentration always equimolar to radical anions [3—5] have been studied. The existence of several forms of aggregates, ion pairs with various structures, triple ions, quadruplets, clusters, *etc.* has been confirmed under the mentioned conditions.

Experimental

The fluorenone anion was prepared by electrolytic reduction at Hg cathode in the presence of supporting electrolyte, perchlorates ($NaClO_4$, tetra-*n*-butylammonium perchlorate — TBAPC) in an inert atmosphere (N_2). A Radelkis OH 404 potentiostat was employed to keep the reduction potential constant at −1.6 V against SCE. Part I of this series contains details on the preparation and experimental equipment [1]. DMF (Merck, spectral grade) was deprived of H_2O by additional purification as described earlier [1]. The electronic spectra were measured with a UV VIS Specord spectrometer.

Calculations

The electronic structure of fluorenone anion was calculated by the LHP-π (PPP-like) method [6]. The limited configuration interaction was used for calculation of electron transitions. Ion pairs were examined in the same way using the modified LHP-π (PPP-like) method including an alkali method into computation [7]. All details on parametrization as well as geometry of fluorenone are given in publications [7, 8]. The energy of solvation stabilization for the system studied was expressed according to eqn [9]

$$-E_{\text{solv}} = \frac{1}{2}\left(1 - \frac{1}{\varepsilon}\right) \sum_{\mu} \sum_{\nu} Q^i_\mu Q^i_\nu \gamma_{\mu\nu} \qquad (1)$$

where Q^i_μ and Q^i_ν are the net charges at μ-th and ν-th atoms in the i-th state (either ground or excited as long as we are interested in sólvent energy in the excited state), $\gamma_{\mu\nu}$ is the bicentric electron repulsion integral, and ε the dielectric constant of medium.

Results and discussion

Interpretation of electronic spectra of fluorenone anion

Fig. 1 shows the electronic spectrum of the fluorenone anion in the presence of the equimolar amount of $NaClO_4$ and TBAPC. There are three groups of bands in the measured region consistent with the recently published spectrum of the fluorenone anion prepared by γ irradiation [10]. A qualitatively good agreement with the calculated theoretical transitions (denoted by vertical lines) is evident. A band of low intensity at 12 000 cm^{-1} is better identifiable by an increase in radical anion concentration. The band corresponds to a transition from singly occupied MO (φ_8) to the first unoccupied MO (φ_9)*. At 27 000 cm^{-1}, there are two bands not suitable for a study of the medium (or temperature) effect because in this region a neutral substance absorbs and thus an eventual reverse conversion to neutral substance has here an undesirable effect. For this reason, attention is paid

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* The numbering of molecular π orbitals is in the direction of the energy increase.

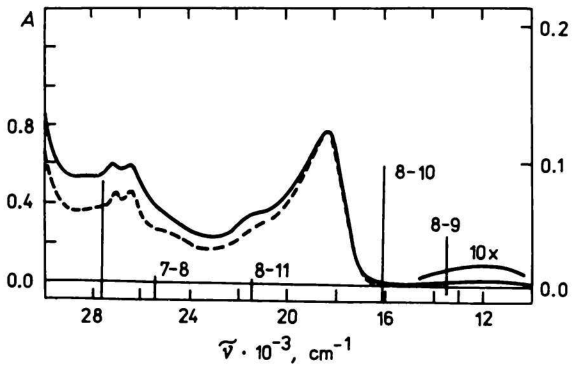

Fig. 1. Experimental and calculated spectrum of 9-fluorenone.
Experimental conditions: 5×10^{-4} M in DMF; (—) 5×10^{-4} M-$NaClO_4$; (– – –) 5×10^{-4} M-TBAPC.

to the absorption between 17 000 and 23 000 cm^{-1} The same range was investigated also for the fluorenone anion prepared by reduction with alkali metals [3—5].

The measured spectrum has a band at 18 300 cm^{-1} (Fig. 1) corresponding to the $\varphi_8 \rightarrow \varphi_{10}$ transition in free radical anion and another not well resolved band at 21 300 cm^{-1} By changing the electrolyte ($NaClO_4$ instead of TBAPC) and maintaining equimolar concentration with radical anion, no energy shift and no change in the band intensity at 18 300 cm^{-1} are observed. Moreover, the maximum of the band is very close to the maximum of radical anion prepared by γ irradiation [10] which should be very little affected by medium. This indicates that the band belongs to free radical anion. Determination of the form to which the absorption band at 21 300 cm^{-1} belongs is questionable. This band occurs also in other solvents (medium polar solvents, reduction with alkali metals), assuming that this absorption corresponds either to diamagnetic dimer of radical anion or to dianion formed by disproportionation reaction from radical anion [3, 4]. The interpretation is complicated by the fact that the $\varphi_8 \rightarrow \varphi_{11}$ transition corresponding to free radical anion lies in this region. We shall assume that this band belongs to the absorption of diamagnetic dimer or dianion.

Quantity and quality effects of supporting electrolyte

As the concentration of supporting electrolyte increases the band at 18 300 cm^{-1} shifts hypsochromically and intensity of the band at 21 300 cm^{-1} increases (Fig. 2). At higher concentrations of supporting electrolyte, associates of the ion pair type are formed to a higher degree; absorption bands of ion pairs are shifted hypsochromically with respect to the bands of free ions. The magnitude of hypsochromic shift of the band considered depends on the interaction of radical anion and cation. The shifts of the absorption band measured indicate that at higher concentrations the magnitude of the effect depends on the size of cation (Fig. 2). Here the change of supporting electrolyte (concentration 10^{-1} M) from TBAPC (curve *B*) to $NaClO_4$ (curve *C*) causes a slight hypsochromic shift of the first band accompanied by a decrease in its intensity and an increase in the intensity of the second band at 21 400 cm^{-1} In the presence of 10^{-1} M ethanol (curve *D*), the first band is again hypsochromically shifted (to 19 200 cm^{-1}) and its intensity lowered and the intensity of the second band (at 21 600 cm^{-1}) with a distinct maximum considerably increases.

The hypsochromic shift of the first band indicates the effect of hydrogen bond formation between ethanol and carbonyl group of 9-fluorenone radical anion. The changes can be evaluated by calculation of electron transitions in the ion pair. The shifts of the first three transitions for the alkali metal—fluorenone ion pairs have been calculated in [8] where the qualitative agreement between calculated and measured shifts was confirmed. The calculated $\varphi_8 \rightarrow \varphi_{10}$ transition in free radical anion is at 16 100 cm^{-1} and in solvated ion pair at 17 800 cm^{-1} (in the calculated ion pair Li^+ it lies 3×10^{-10} m from the carbonyl oxygen in the plane of the molecule in the direction of the C=O bond). This shift (1700 cm^{-1}) is comparable with the experimental shift (600—1200 cm^{-1}).

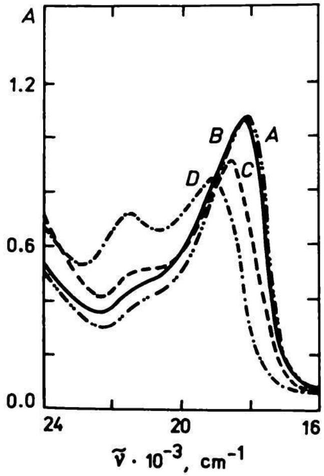

Fig. 2. Electronic spectrum of 9-fluorenone ($c = 5 \times 10^{-4}$ M) in DMF.
A. TBAPC (5×10^{-4} M); *B*. TBAPC (10^{-1} M); *C*. $NaClO_4$ (10^{-1} M); *D*. TBAPC (5×10^{-4} M) + C_2H_5OH (10^{-1} M).

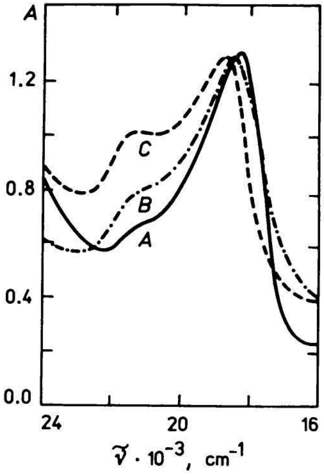

Fig. 3. Electronic spectrum of 9-fluorenone 5×10^{-4} M, 2×10^{-2} M-$NaClO_4$.
A. In dimethyl sulfoxide; *B*. 80% DMF + 20% dioxan; *C*. 50% DMF + 50% dioxan.

Effect of solvent polarity

Fig. 3 shows the measured absorption spectrum of 5×10^{-4} M fluorenone + $+2\times10^{-2}$ M-$NaClO_4$ in dimethyl sulfoxide (curve *A*), a mixture of 80% DMF + 20% dioxan (curve *B*), and a mixture of 50% DMF + 50% dioxan (curve *C*). In dimethyl sulfoxide (DMSO), which is a strongly solvating solvent, the first band is at 18 400 cm^{-1} and in the region of the second absorption band only slight absorption has been measured. This absorption considerably increases with decreasing solvation ability of solvent (curves *B* and *C*) with respect to the intensity of the first absorption band. This band shows a hypsochromic shift which can be understood as a result of the increased formation of the associates of the ion pair type or diamagnetic dimers or dianions in less polar solvents. The hypsochromic shift caused by decreasing the polarity can be explained not only by the change in equilibrium in favour of free ions but also by the results of calculations of the most stable structure of the ion pair [8]. Here it was found that with increasing dielectric constant of solvent, the distance between cation and radical anion increases leading to a decrease in hypsochromic shift in the ion pair with respect to free radical anion.

Temperature effect

The energy ratios between individual forms can be evaluated on the basis of variations of the intensities of absorption bands caused by temperature. Fig. 4 presents the spectrum of 5×10^{-4} M fluorenone anion in DMF with 5×10^{-2} M-TBAPC of various temperatures. Apart from the hypsochromic shift of the first band and lowering of its intensity with a decrease in temperature, the band splits into two not well resolved maxima at 18 300 and 19 200 cm^{-1}. At the same time, the band at 21 500 cm^{-1} shifts slightly hypsochromically and its intensity

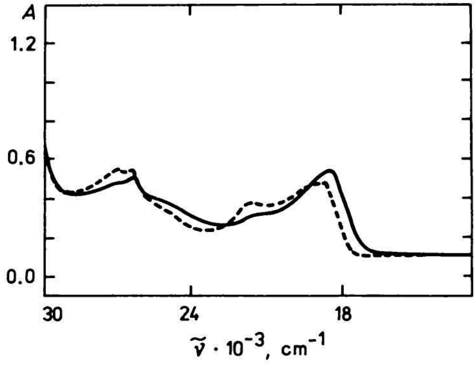

Fig. 4. Electronic spectrum of 9-fluorenone ($c = 5\times10^{-4}$ M) in DMF, 5×10^{-2} M-TBAPC, at $T = 25$°C (—), at $T = -25$°C (---).

increases. The enthalpy determination is in this case besides considerable imprecision in concentration determination of the individual forms complicated by the probable existence of three different forms. If for simplification we assume that the absorption over the region between 18 000 and 19 000 cm^{-1} corresponds to a solvated free radical anion (or ion pairs) and the absorption at 21 500 cm^{-1} to the diamagnetic form, *i.e.* either to diamagnetic dimer or dianion, then there exist two equilibria

$$\mathrm{R}^{2-} + \mathrm{R} \rightleftarrows 2\mathrm{R}^{\cdot-} \tag{2}$$

$$^{-}\mathrm{R{-}R}^{-} \rightleftarrows 2\mathrm{R}^{\cdot-} \tag{3}$$

From the changes in the respective intensities, ΔH of the total equilibrium between radical anion and diamagnetic form was determined to be 8—16 kJ mol^{-1} It is interesting that ΔH is positive. *De Boer* [11] found the negative value for ΔH for the equilibrium of naphthalene dianion with naphthalene radical anion $+\mathrm{Li}^+$ in 2-methyltetrahydrofuran.

The changes found support the fact that even in a polar medium, such as DMF, associates are formed between fluorenone anion and cations of supporting electrolyte. A scheme can be proposed for the description of the associate equilibria discussed

$$2\mathrm{R}^{\cdot-}_{\mathrm{solv}} + 2\mathrm{Na}^+ \rightleftarrows 2(\mathrm{R}^{\cdot-}\,\mathrm{Na}^+)_{\mathrm{solv}} \rightleftarrows \left(\mathrm{R}^- \frac{\mathrm{Na}^+}{\mathrm{Na}^+} \mathrm{R}^-\right)_{\mathrm{diamag}}$$

or

$$\mathrm{R}^{-2}(\mathrm{Na}^+)_2 + \mathrm{R}$$

Ethanol shifts the equilibrium to the right, while the polar aprotic solvent (DMSO, DMF), to the left.

However, it is evident that ion pairs or higher associates are formed only at considerably higher concentrations of supporting electrolyte compared with fluorenone radical anion. The experimental changes found agree qualitatively with the theoretical ones described in [8] where the system was modelled by the formation of a simple ion pair and simultaneously, the solvent effect was considered. The result indicates potential possibility of a successful use of simple semiempirical methods in the study of the associates between ions as well as solvent effect on these associates.

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