ASSOCIATION OF RADICAL ANIONS ALKALI METAL CATIONS. III. EXPERIMENTAL AND THEORETICAL STUDY OF THE ASSOCIATES OF NITROBENZENE RADICAL ANIONS WITH Li^+, Na^+, K^+, Cs^+ AND $(n\text{-}C_4H_9)_4N^+$ CATIONS

Stanislav MIERTUŠ, Ondrej KYSEĽ and Juraj DANCIGER

Polymer Institute,
Slovak Academy of Sciences, 809 34 Bratislava

Received March 2nd, 1979

The nitrobenzene radical anion prepared by electrolysis was studied by UV spectroscopy. Formation of associates with Li^+, Na^+, K^+, Cs^+ and $n(C_4H_9)_4N^+$ cations was examined. It has been found that associates are also formed in a polar medium such as dimethylformamide. The enthalpy of the associate-free ion equilibrium was estimated as being equal to 6 ± 4 kJ/mol^{-1}. The quantum-chemical LHP method (in the π-approximation) was employed to study a simple ion pair model used for calculation of the most stable geometrical structure.

In recent years, a considerable amount of attention has been paid to radical anions, as they take part in numerous important processes (initiation of anion polymerization, *etc.*)[1-4]. Most of the studies have so far dealt with radical anions prepared by chemical reduction with alkali metals[1-4] in nonaqueous moderately polar solvents (tetrahydrofuran, dioxan). It has been found that ion pairs of radical anions with alkali metal cations are formed, which can influence the reactivity of the radical anions. During generation of radical anions by electrolytic cathodic reduction[5], a strongly polar nonaqueous medium is used, *e.g.* dimethylformamide, in the presence of supporting electrolytes (alkali metal salts). Here the reduction potential can be kept constant and thus prevent reduction to dianions, which is not always possible during reduction with an alkali metal.

So far it has been assumed[1] that electrolytic preparation leads neither to ion pair formation (because of the strongly polar medium) nor to any change in the properties and the reactivity of the free radical anions. The present study was carried out to examined these assumptions on the nitrobenzene radical anion system prepared by electrolytic reduction in dimethylformamide in the presence of salts of supporting electrolytes (perchlorates Li, Na, Cs and $(n\text{-}C_4H_9)_4N^+$).

EXPERIMENTAL

Preparation of Radical Anions

Radical anions were prepared in an electrolytic cell (Fig. 1) (ref.[6]) representing the three-electrode system: a working Hg cathode 1, a Pt anode separated by sintered glass 2 and a reference electrode (standard calomel electrode with KCl bridge) 3 separated from the working space by sealed graphite. A potentiostat (Radelkis OH-404) is employed to maintain a constant reduction potential on the cathode *vs* S.C.E. The system is kept in an inert atmosphere, purified nitrogen is introduced through a capillary 4 and the system is stirred with a magnetic stirrer. On generating the radical anion, solution is poured through a ground glass joint 5 into the cells.

Very unstable radical anions must be generated directly in the cell (1 cm length) of the spectrometer. Therefore, a vessel was constructed for generating the radical anion directly in the cell of the UV-VIS Specord spectrometer (Fig. 2). Here A is the anode, K is the Hg cathode, B is the S.C.E. and C is a teflon capillary for nitrogen introduction. At the same time, a Pt wire placed inside the capillary was connected to the mercury cathode. The spectrophotometric cell was thermostatted and the temperature measured with a thermocouple.

Purification of Solvent and Inert Gas

Dimethylformamide was purified by the method proposed by Thomas and Rochov[7]. The method was modified in order to lower the water concentration more.

From a mixture of dimethylformamide, 10% benzene and BaO, an azeotropic mixture (water, benzene) and excess benzene were separated by distillation on a column under atmospheric pressure. The residue was distilled at 1·3 kPa (10 mm Hg) in a nitrogen atmosphere. The purified dimethylformamide was dried by distillation with CaH_2 under the same conditions. The middle fraction was distilled directly into a storage vessel.

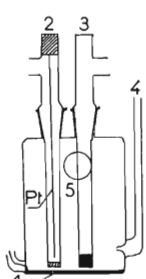

FIG. 1
Electrolytic Vessel for Preparation of Radical Anions

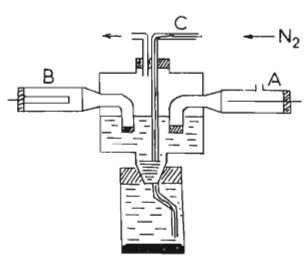

FIG. 2
Apparatus for Electrolytic Preparation of Radical Anions in a Cuvette of a UV Spectrometer

A Cu_2O — containing catalyst was used to remove oxygen from nitrogen. The column with a catalyst was heated to 220°C. To dry the gas, H_2SO_4, KOH, P_2O_5 and silica gel were used. All driers were located in separated columns. Nitrobenzene was distilled several times.

Preparation of the radical anion: 10 ml of solution of neutral substance and supporting electrolyte of exact concentration in dimethylformamide was bubbled through nitrogen and electrolysis was begun. The potential of the cathode against S.C.E. was usually chosen according to the polarographic half-wave potentials of the reduced compounds and was always 0·1—0·2 V higher than this value if no further polarographic waves occurred in this region.

The concentration of the radical anion was only approximate. The course of current decreasing with time was followed and the reduction proceeded till the current decreased below 5% of the initial value. Assuming that no consecutive reactions take place, the concentration of radical anion formed can be regarded as being 90% of the initial concentration of neutral substance. As this assumption is not always exactly satisfied, graphical representation of UV spectra gives only absorbance and not extinction on the y axis.

CALCULATIONS

The modified Longuet-Higgins–Pople method with the π-approximation (PPP-like) was used for calculations[8]. The modification consists in incorporation of both the π system of radical anions and the alkali metal[9] in the calculation. Details of the modification of this method as well as of the parameters employed are given in[9], where also calculations of electronic transitions are described thoroughly.

The anion radical with the cation was considered as one system ("supersystem" model). The cation approached the radical anion in the chosen Y or XY direction (Fig. 3) until the most stable energy position was reached. As in the studied systems the solvent effect is important, it was considered so that, for each configuration of the system, the solvation energy was calculated according to the relation[10]

$$-E_{\mathrm{solv}} = \tfrac{1}{2} \sum_{\mu,\nu} Q_\mu Q_\nu \gamma_{\mu\nu}(1 - 1/\varepsilon), \qquad (1)$$

where Q_μ and Q_ν are the net atomic charges, $\gamma_{\mu\nu}$ the repulsion electron integrals and ε is the dielectric constant of the medium.

RESULTS AND DISCUSSION

The system of nitrobenzene radical anion with alkali metal cation was studied in two directions. In our calculations we tried to find the most stable geometrical structure of the model ion pair for the nitrobenzene radical anion–Li^+ system. Simultaneously, we followed the changes in electronic transitions during association. The changes in the UV spectra of nitrobenzene radical anion taking place during variations in the cation of the supporting electrolyte and temperature were studied experimentally. Possibilities of ionic association were deduced from these changes.

*Calculation of the Model Nitrobenzene Radical Anion–*Li *System*

In the search for the most stable position of the Li cation with respect to nitrobenzene radical anion, two directions of cation approach were considered (Fig. 3). The total energy of the system has a minimum in both directions (Fig. 4), the minimum in the *Y* direction ($2{\cdot}25 \cdot 10^{-10}$ m from the oxygen atom) being 0·219 eV (21·4 kJ mol^{-1}) more stable than the minimum in the *XY* direction ($1{\cdot}7 \cdot 10^{-10}$ m from the oxygen atom). This does not disagree with experimental findings, as in the ESR spectrum of the ion pair[11] splittings of two pairs of equivalent protons (*ortho-* and *meta-*protons) were measured.

By the solvation energy the minima are shifted to greater distances (in the *Y* direction to $2{\cdot}9 \cdot 10^{-10}$ m and in the *XY* direction to $2{\cdot}6 \cdot 10^{-10}$ m) without significant change in their mutual energy ratios. The energy difference in the minima of *XY* and *Y* will increase by the solvent effect by 0·03 eV (2·9 kJ mol^{-1}). The shift in the energy minima to greater distances as a result of solvation is of a more general character[9] and is caused especially by the fact that the term

$$-1/2 \sum_{\nu} Q_{\mathrm{Me}} Q_{\nu} \gamma_{\mathrm{Me}\nu}(1 - 1/\varepsilon), \quad \nu \neq \mathrm{Me} \tag{2}$$

in expression (*1*) in the radical anion-cation system is repulsive and decreases with decreasing value of $\gamma_{\mathrm{Me}\nu}$, *i.e.* with increasing distance between the cation and radical

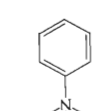

FIG. 3

Directions of the Approach of Li^+ to Nitrobenzene Radical Anion Considered in the Calculations

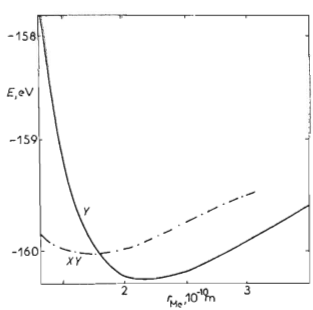

FIG. 4

A Plot of the Total Energy of the Nitrobenzene Radical Anion–Li^+ System *vs* Distance r_{Li} in Directions Y and *XY* (Fig. 3)

anion. Then, as ε increases, the value of term (2) increases, leading to an increase of the equilibrium distance in the real system.

The total energy of isolated free ions ($E_{NB^-} + E_{Li^+}$) can be calculated in a similar way. If the total energy of these free ions is compared with the energy of ion pairs, it will be found that, in the system with $\varepsilon = 1$, the ion pairs are more stable by 3·68 eV (355·7 kJ mol^{-1}). The solvation energy decreases this difference considerably but ion pairs are also more stable for $\varepsilon \to \infty$ than free ions (by 0·36 eV. *i.e.* 35·2 kJ mol^{-1}), and thus the ΔH value of the dissociation of ion pairs should be positive.

Experimental Study of Electronic Spectra of the Nitrobenzene Radical Anion

The electronic spectrum of nitrobenzene radical anion prepared by γ-irradiation is affected little by the medium[12]. An intense band was observed at 21200 cm^{-1}, corresponding to the excitation $\varphi_6 \to \varphi_8$ (from a singly occupied MO to the second lowest unoccupied MO). Molecular orbitals φ (π-type) were numbered according to increasing energy. Spectrum of nitrobenzene radical anion prepared by electrolysis in dimethylformamide with 0·1M tetrabutylammonium perchlorate as supporting electrolyte exhibits a maximum at 21700 cm^{-1} or two maxima at 21200 and 23000 cm^{-1} if 0·1M-$NaNO_3$ is used[13]. The authors[13] assumed formation of an ion pair with Na, to which the band at 23000 cm^{-1} should correspond. This system was examined in more detail, so that perchlorates with various sizes of the respective cation increasing in the series Li^+, Na^+, K^+, Cs^+, $(C_4H_9)_4N^+$ were used as supporting electrolytes. The spectra measured are shown in Fig. 5. It is evident that the two bands gradually separate with decreasing cation radius. The first band at 21500 cm^{-1} is not shifted with varying cation size, while the second band exhibits a relatively marked hypsochromic shift. If the dependence of the maximum of the second absorption band is plotted as a function of $(1/r_c + \text{const})$, a linear dependence is obtained (Fig. 6). A similar relationship was found for radical anions prepared chemically, where ion pair formation was demonstrated.

The formation of the second absorption band is interpreted as a hypsochromic shift of the first band (corresponding to the free radical anion) as a result of the association with the cation. Calculations on the nitrobenzene radical anion–Li^+ model system yielded a hypsochromic shift of the first band.

The $\varphi_6 \to \varphi_8$ transition of the free radical anion assigned to the band at 21500 cm^{-1} is calculated for the free radical anion at 16100 cm^{-1}. Under the experimental conditions, however, the radical anion occurs in a polar medium which stabilizes the ground state more than the respective excited state ($\varphi_6 \to \varphi_8$). From charge distribution in these states, the solvation stabilization for both states can be calculated according to relationship (1). The mentioned transition will be shifted hypsochromically under the solvent effect by 6100 cm^{-1}, *i.e.* to the value of 22200 cm^{-1} (for a completely solvated radical anion).

As Li^+ approaches nitrobenzene radical anion, the $\varphi_6 \rightarrow \varphi_9$ transition shifts hypsochromically, the transition being of the same character as the $\varphi_6 \rightarrow \varphi_8$ transition in the free radical anion, *i.e.* φ_8 and φ_9 have practically the same distribution. For $r_{Li} = 2{\cdot}9 \cdot 10^{-10}$ m (the energy minimum for the ion pair in the Y direction incorporating the solvation), the $\varphi_6 \rightarrow \varphi_9$ transition has an energy equal to 20300 cm^{-1}. If the solvation energy is calculated according to Eq. (*1*), it will be found that the ground state is stabilized more than the excited state, but only by 0·29 eV (2300 cm^{-1}), and thus the transition will be shifted hypsochromically to 22600 cm^{-1}. This leads to a hypsochromic shift of the $\varphi_6 \rightarrow \varphi_9$ transition of the ion pair, compared to the corresponding transition ($\varphi_6 \rightarrow \varphi_8$) in the free radical anion in a nonsolvating medium ($\varepsilon = 1$) by 4200 cm^{-1}, only by 400 cm^{-1} in a completely solvating medium ($\varepsilon \rightarrow \infty$). The hypsochromic shifts measured vary between 1000 and 2000 cm^{-1}. This is in qualitative agreement with the described theoretical interpretation but possible formation of higher associates, which might also be responsible for the spectral changes discussed, cannot be excluded.

If the first band in the measured spectra (Fig. 5) corresponds to the free radical anion and the second to the associate (which can be approximately represented

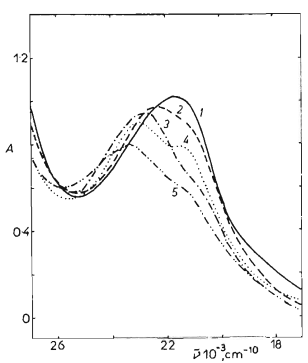

FIG. 5

The Electronic Spectrum of Nitrobenzene Radical Anion in Dimethylformamide in the Presence of Various Perchlorates
1 $(C_4H_9)_4NClO_4$; *2* $CsClO_4$; *3* $KClO_4$; *4* $NaClO_4$; *5* $LiClO_4$.

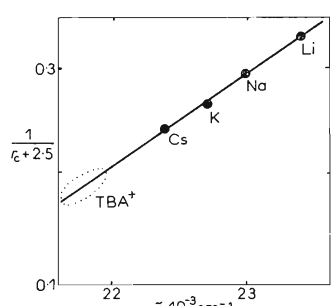

FIG. 6

A Plot of the Maximum of the Absorption of Ion Pairs of Nitrobenzene Radical Anion with Various Cations *vs* Radius of Cations

by the ion pair), their equilibrium can be expressed by the temperature-dependent equilibrium constant,

$$K = \frac{[NB^{\mp}][Me^{+}]}{[NB^{\mp}\ Me^{+}]} . \qquad (3)$$

We studied the effect of temperature on the spectra of the given systems of nitrobenzene radical anion ($5 . 10^{-4}$) with supporting electrolytes (10^{-2}M) in dimethylformamide. For illustration, the spectra are shown with $NaClO_4$ (Fig. 7*a*) and tetrabutylammonium perchlorate (Fig. 7*b*) supporting electrolytes. For $NaClO_4$ at lower temperatures, the intensity of the first band decreases (at 21 500 cm^{-1}), the intensity of the second band increases and, simultaneously, the second band is shifted hypsochromically from 22 800 to 23 200 cm^{-1}. In the presence of tetrabutylammonium perchlorate (Fig. 7*b*), a hypsochromic shift of the band from 21 700 to 22 200 cm^{-1} is observed on a temperature decrease. Similar temperature dependences were found using $KClO_4$ and $CsClO_4$.

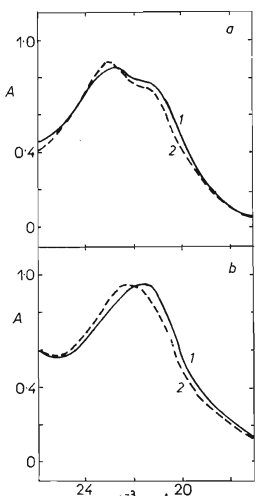

FIG. 7

The Electronic Spectrum of Nitrobenzene Radical Anion ($c = 5 . 10^{-4}$M) in Dimethylformamide in the presence of 10^{-2}M-$NaClO_4$ (*a*); $(C_4H_9)_4NClO_4$ (*b*)
t: *1* 40°C; *2* —10°C.

Generally, as the temperature decreases, absorption in the first band decreases and that in the second band increases. On the basis of the Lambert–Beer law, concentration variations can be estimated from the changes in the band intensities, equilibrium constants K can be determined for various temperatures and from the temperature dependence of the equilibrium constant ΔH can be found. As the identification of the position of the maxima corresponding to the individual forms is rather imprecise, K and H are determined only qualitatively. It follows from the results that ΔH is positive and relatively low for all the systems studied. Its value varies between 2 and 8 kJ mol^{-1}. It is remarkable that, for the nitrobenzene radical anion–Na^+ system generated by chemical reduction in hexamethylphosphoramide[11], the value obtained for the enthalpy of the pair dissociation is negative, $\Delta H = -30{\cdot}2$ kJ mol^{-1}. As has already been mentioned, the theoretical calculation for nitrobenzene radical anion–Li^+ for $(\varepsilon \to \infty)$ yields $\Delta H = 35{\cdot}2$ kJ mol^{-1}, which is qualitatively closer to the experimental value obtained here. These contadictory experimental results may be due to the following facts: Hexamethylphosphoramide is among the solvents which solvate cations most strongly. This leads to a specific high stability for the free solvated ions and thus can be the main reason for fact that ion pair dissociation is exothermic in this solvent. It must also be considered that, in our experiment, the concentration of the cations of the supporting electrolyte is higher than the concentration of the radical anion. This might complicate matters and enable formation of several types of associates. From the sign and value of ΔH it can be predicted that these associates are probably strongly solvated.

CONCLUDING REMARKS

Quantum-chemical calculation based on a simple model provided us with some information on the structure and properties of the nitrobenzene radical anion–Li^+ ion pair. The most stable structure (in the Y direction) calculated is consistent with indirect experimental findings (*e.g.* ESR spectra). A simple description of the solvation energy pointed out the importance of the effect in the model system investigated.

The experimental study showed that, even in a strongly polar solvent such as dimethylformamide, the nitrobenzene radical anion forms associates with cations of the supporting electrolyte. The associates display characteristic absorption in the electronic spectrum. Despite considerable imprecision in the determination of the enthalpy of dissociation of these associates, it can be stated that the enthalpy of this process is positive, demonstrating strong solvation of the associate.

The authors wish to express their thanks to Dr M. Kalinowski, Warsaw University, Prof. Z. Grabowski, Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, and Dr V. Podaný, Institute of Experimental Oncology, Slovak Academy of Sciences, Bratislava, for valuable assistance applying the experimental methods for the preparation of radical anions.

REFERENCES

1. Szwarc M.: *Carbanions, Living Polymers and Electron Transfer Processes.* Wiley-Interscience, New York 1970.
2. Szwarc M. (Ed.): *Ions and Ion Pairs in Organic Reactions*, Vol. I.,Wiley-Interscience, New York 1972.
3. Szwarc M. (Ed.): *Ions and Ion Pairs in Organic Reactions*, Vol. II., Wiley-Interscience, New York 1974.
4. Gaylord N. G., Dixit S. S.: J. Polym. Sci. (Macromol. Rev.) *8*, 51 (1974).
5. Maki A. H., Geske D. H.: J. Amer. Chem. Soc. *83*, 1852 (1961).
6. Kalinowski M. K.: Rocz. Chem. *45*, 469 (1971).
7. Thomas A. B., Rochov E. G.: J. Amer. Chem. Soc. *79*, 1843 (1957).
8. Longuet-Higgins H. C., Pople J. A.: Proc. Roy. Soc., *68A*, 591 (1955).
9. Miertuš S., Kyseľ O., Mach P.: This Journal *55*, 351 (1980).
10. Jano I.: C. R. Acad. Sci. Paris *261*, 103 (1965).
11. Stevenson G. R., Echegoyen L., Lizardi L. R.: J. Phys. Chem. *76*, 2058 (1972).
12. Shida T., Iwata S.: J. Phys. Chem. *75*, 2591 (1971).
13. Sioda R. E., Kemula W.: J. Electroanal. Chem. Interfacial Electrochem. *31*, 113 (1971).