Pergamon

Tetrahedron Letters 40 (1999) 5771–5772

TETRAHEDRON
LETTERS

Solvent Effect on Cleavage Rate Constants of Radical Anions. Contribution from Non-equilibrium Solvent Polarization

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Received 25 March 1999; accepted 3 June 1999

Abstract: Solvent effects on the bond cleavage in three aromatic radical anions are described in an uniform way applying the Savéant model: the intrinsic rate constants, obtained from experimental data measured recently by Jensen and Daasbjerg after the substraction of a thermodynamic contribution to the activation barrier, depend linearly on the solvent Pekar factor. Calculations of the solvent reorganization energy support the correlations found.

Solvent effects on the kinetics of bond cleavage in aromatic radical anions have attracted considerable attention.[1-5] Earlier results[1-2] have been discussed in terms of a specific solvation of a transition state but later a dominant role of leaving anion solvation (through a thermodynamic free-energy contribution ΔG° to the activation barrier[6]) has been emphasized.[3,4] Very recently the solvent effect on the intrinsic activation barrier $\Delta G^{\ddagger}_{o}$ (i.e. a barrier for $\Delta G^\circ = 0$) has been experimentally found[7] for the cleavage of 4-chlorobenzophenone radical anion. The last effect was proposed by Savéant in the theoretical model[6] describing the bond cleavage of a radical anion as a concerted process with intramolecular electron transfer of the unpaired electron from the π^* orbital of an aromatic ring into the C-Cl σ^* orbital. This new approach allows the description of solvent effects on the cleavage rate constants k_{cl} of different anion radicals in an uniform way as is shown in this letter for data recently reported by Jensen and Daasbjerg. They proposed[5] separate correlations of k_{cl} values for radical anions of 9-chloroanthracene **1**, 3-nitrobenzyl chloride **2** and 3-chloroacetophenone **3** with the solvent acceptor number AN, donor number DN and Kamlet and Taft π^* parameter, respectively. However, no physical meaning for the use of π^* parameter is offered and the explanation for the use of DN based on the counterbalance of a solvation of a nitro group and the developing chloride ion is not cogent.

The Savéant model predicts[6] the relationship[8] between the activation barrier and the reaction driving force $\Delta G^{\ddagger} = \Delta G^{\ddagger}_{o} + 0.5\Delta G^\circ$ and a solvent affects both terms. The main solvent effect on ΔG° is described[6,7] by the difference in standard potentials $\Delta E^\circ = E^\circ(Cl/Cl^-) - E^\circ(ArCl/ArCl^{\cdot-})$ for the halogen couple and for the formation of a radical anion from the parent halide ArCl, respectively. The solvent effect on $\Delta G^{\ddagger}_{o}$ is given by the solvent reorganization energy $0.25\lambda_o$, describing a non-equilibrium solvent polarization in the transition state as in the Marcus theory: $\lambda_o = e_o^2(1/2a_1 + 1/2a_2 - 1/d)\gamma$, where e_o is the electron charge, a_1 and a_2 are the radii of spheres approximating the region where the charge is initially located in the radical anion and on the leaving anion, respectively, d is the distance between the centres of charge at the transition state and $\gamma = (1/\varepsilon_{op} - 1/\varepsilon_s)$ is the Pekar factor, described by the optical ε_{op} and static ε_s electric permittivity of a solvent.

For **1** $E^\circ(ArCl/ArCl^{\cdot-})$ is solvent independent because of a spin delocalization; for other reactants they correlate linearly with the solvent AN, but a dependence of $E^\circ(Cl/Cl^-)$[9] against AN is three times stronger. Substracting $0.5\Delta E^\circ$ values from experimental $RT\ln k_{cl}$ gives $RT\ln k_o - 0.5\Delta G_{BD}$, the solvent dependent

0040-4039/99/$ - see front matter © 1999 Elsevier Science Ltd. All rights reserved.
PII: S0040-4039(99)01109-0

contribution to the intrinsic rate constant k_o, which should be a linear function of the Pekar factor if solvent variations of ΔG_{BD} (which is the Gibbs energy change for the homolytic bond dissociation of ArCl) is small, as pointed out by Savéant.[6b] Reasonable correlations are indeed observed for all three reactants as is shown in Fig. 1. The lowest slope found for **1** is in line with the charge delocalization at this big radical anion. Thus, for **1** the solvent effect on ΔG^o is dominant originating the observed correlation of $\log k_{cl}$ vs. AN.[1,4,5]

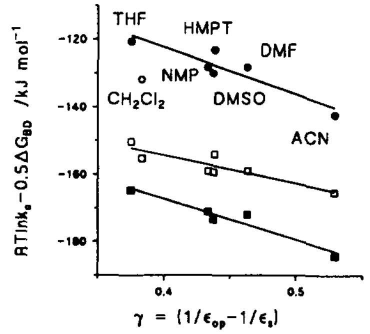

Fig. 1. Variation of the intrinsic rate constants with the Pekar factor.

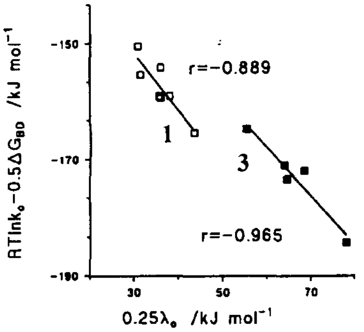

Fig. 2. Plots of the intrinsic rate constants against the solvent reorganization energy.

The quantitative support of the correlations shown in Fig. 1 can be obtained from calculations of the solvent reorganization energies. It was done using crystallographic data and Van der Waals radii[10] for system geometry and assuming the final charge localization lies at the Cl atom (a_2=175pm[10]) and is initially on the O atom in radical anion **3** (a_1=150pm,[10] d= 520pm from geometry of similar compounds[11]) and on the aromatic ring of **1** (a_1=345pm[12], d= 345+175pm). For **2** there are no crystallographic data. The correlations of the intrinsic rate constant $RT\ln k_o - 0.5\Delta G_{BD}$ against the calculated $0.25\lambda_o$ values[13] for **1** and **3** are shown in Fig. 2. Slopes of both correlations (-1.0 with the standard deviation 0.2 for **1** and -0.8±0.1 for **3**) are close to the theoretical value, supporting that the bond dissociation energy is not strongly solvent dependent.

REFERENCES AND NOTES

1. Wipf, D.O.; Wightmann, R.M. *Anal. Chem.* **1990**, 62, 98-102.
2. Kimura, N.; Takamuku, J. *Bull. Chem. Soc. Jpn.* **1992**, 65, 1668-1671; Kimura, N.; Takamuku, J. *J. Am. Chem. Soc.* **1995**, 117, 8023-8024.
3. Andrieux, C.P.; Robert, M.; Savéant, J.M. *J. Am. Chem. Soc.* **1995**, 117, 9340-9346.
4. Jaworski, J.S.; Leszczyński, P.; Tykarski, J. *Chem. Res. S* **1995**, 510-511.
5. Jensen, H,; Daasbjerg, K. *Acta Chem. Scand.* **1998**, 52, 1151-1164.
6. (a) Savéant, J.M. *J. Phys. Chem.* **1994**, 98, 3716-3724; (b) Savéant, J.M. *Tetrahedron* **1994**, 50, 10117-10165.
7. Jaworski, J.S.; Leszczyński, P, *J. Electroanal. Chem.* **1999**, 464, 259-262.
8. In general it is a quadratic dependence but the third term $(\Delta G^o)^2/16\Delta G^{\ddagger}_o$ can be neglected for a smaller range of ΔG^o and/or a big $\Delta G^{\ddagger}_o$.
9. (a) $E^o(Cl/Cl^-)$ values were calculated from the value in DMF[6] and the free energy of transfer ΔG_{tr} of Cl^- ion from water to a given solvent[9b]; for THF and CH_2Cl_2 ΔG_{tr}=68 and 56 kJ/mol, respectively, was calculated from the dependence of ΔG_{tr} for 12 aprotic solvents[9b] on Dimroth and Reichardt E_T parameter. (b) All solvent parameters are extracted from: Marcus, I. *Ion Solvation*; Wiley: Chichester, 1985, pp.136-138, 142-144 and 168-169.
10. Bondi, A. *J. Phys. Chem.* **1964**, 68, 441-451.
11. Engebretson, G.R.; Rundle, R.E. *J. Am. Chem. Soc.* **1964**, 86, 574-581; Evans, S.V.; Trotter, J. *Acta Crst., Sect.B* **1988**, 44, 63-72; Hashmi, A.S.K.; Ruppert, T.L.; Knöfel, T.; Bats, J.W. *J. Org. Chem.* **1997** 62, 7295-7304.
12. Calculated as a mean radius of an ellipsoid with semi-axes a=317, b=542, c=177pm, as evaluated from crystallographic data of d_{10}-anthracene: Lehman, M.S.; Pawley, G.S. *Acta Chem. Scand.* **1972**, 26, 199-211.
13. Pekar factor was calculated using values of $\varepsilon_{op}=n_D^2$ and ε_s taken from ref. 9b.