Solvent Effects on the Unimolecular Dissociation of Radical Anions Studied by Pulse Radiolysis

Norio KIMURA* and Setsuo TAKAMUKU
The Institute of Scientific and Industrial Research, Osaka University,
8-1 Mihogaoka, Ibaraki, Osaka 567

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Synopsis. The rate constants of the unimolecular dissociation of radical anions formed by one-electron reduction of chloroacetophenone isomers in dipolar aprotic solvents were measured by a pulse radiolysis technique. The reactivities of these isomers were affected by the polarity of the solvent used.

Solvent effects on chemical reactivity are commonly found in a wide variety of reactions involving electron-transfer reactions which are currently attracting the interest of chemists.[1,2] However, only a few investigations have been reported about solvent effects on the further reactions of radical anions formed by one-electron reduction.[3] For example, radical anions of aromatic halides are well-known to undergo unimolecular dissociation producing an aryl radical and halide ion,[3-7] but the rate constants reported spread over a wide range, probably due to the effect of the solvent used.[4,7] Therefore, the present purpose is to clarify the solvent effects on the unimolecular dissociation of radical anions of chloroacetophenone isomers (*o*-, *m*-, and *p*-CAP) and also to elucidate the reaction mechanism by use of a pulse radiolysis technique.

Experimental

Chemicals. Chloroacetophenone isomers (Wako Pure Chemical and Aldrich) and *o*-chlorobenzaldehyde (Wako Pure Chemical) were purified by distillation. *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidone (NMePy), and hexamethylphosphoric triamide (HMPA) used as solvents were distilled over calcium hydride. Solutions were prepared freshly before irradiation and were degassed under high vacuum.

Apparatus. The electron pulse from Osaka Univ. linear accelerator was used. The energy was 28-MeV and the pulse width was 8-ns. The dose was 1 kGy per pulse. A 450W xenon pulse lamp (OPG-450, Osram), a monochromator (Nikon G-250), and a photomultiplier (R-928) were used. The output of the photomultiplier was monitored by a programable transient digitizer (Tektronix 7912AD) with 7A29 plug-in and stored for display in a Melcom 70/25 computer (Mitsubishi Electric Co.).

Results and Discussion

Transient absorption spectra obtained by the pulse radiolysis of *o*-CAP in HMPA are shown in Fig. 1. The spectra with λ_{max} at 330 and 490 nm are assigned to the radical anion of *o*-CAP on the basis of the similarity to that of acetophenone which was measured in this work under the same reaction conditions (λ_{max} 330 and 490 nm).[8] The decay of the 330-nm band followed first order kinetics and the rate, 5.3×10^6 s^{-1}, was independent of the concentration of *o*-CAP (1×10^{-2}—1×10^{-3} mol dm^{-3}). This fact is consistent with the unimolecular dissociation of the radical anion. Similar spectra were observed with *m*- and *p*-CAP. The decay rate of 330-nm bonds of *m*- and *p*-CAP were 9.6×10^4 and 2.8×10^5 s^{-1}, respectively. These rates are much slower than that of *o*-CAP.

The chemical reactivities of radical anions of these CAP isomers were also examined in other dipolar aprotic solvents such as DMA, DMF, DMSO, and NMePy. The spectral features of the radical anions formed in these solvents were not different from that in HMPA. However, the rate constants were dependent on the nature of solvents used. A good correlation between the rate constants (log *k*) and an acceptor number (AN) of the solvent[9] which is an empirical parameter reflecting the electrophilic properties of solvent was obtained as shown in Fig. 2.

In the cases of *m*- and *p*-CAP, an increase of solvent polarity resulted in an increase in the rate. In general, an acceleration of the rate is induced in such a case where the solvation is stronger in the transition state than in the initial state. In the present reactions, therefore, the negative charge of the radical anion must be localized in a molecule at the transition state which makes the solvation more tight. Indeed, the negative charge may be present initially at the delocalized π-orbital of an acetophenone moiety since the absorption spectra of the CAP radical anions are

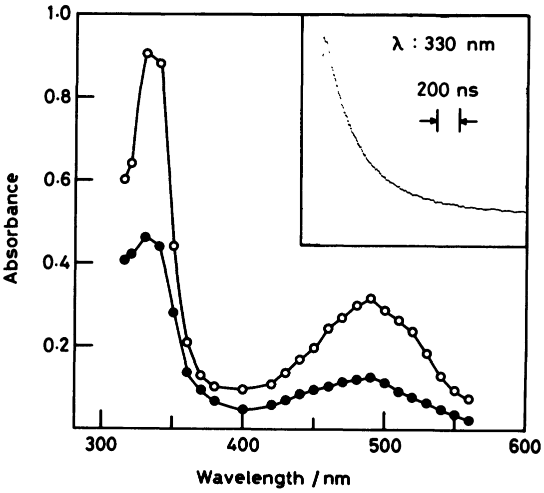


Fig. 1. Transient absorption spectra observed at immediately (○) and 200 ns (●) after an 8-ns pulse irradiation of a degassed HMPA solution of *o*-CAP (1×10^{-2} mol dm^{-3}) at room temperature. Absorption dose was 1 kGy/pulse. Insert: Decay curve of the 330-nm band.

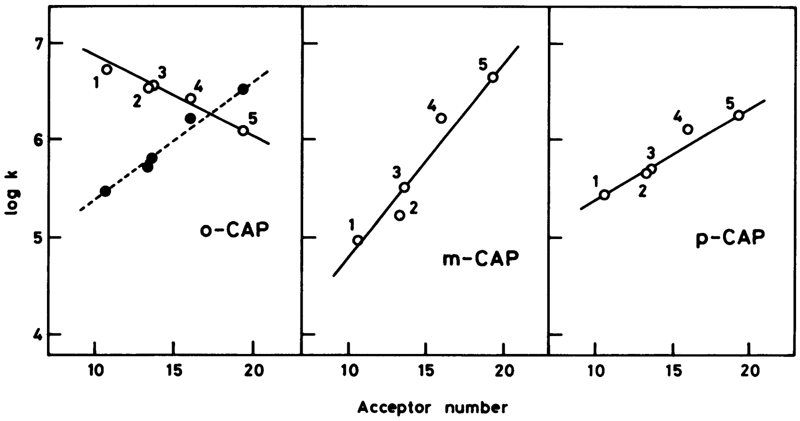


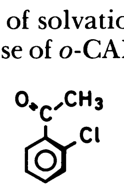
Fig. 2. Plot of log k(s^{-1}) vs. the acceptor number of the following solvents: 1, HMPA, 2, NMePy; 3, DMA; 4, DMF; 5, DMSO. The dotted line (--●--) indicates the result for *o*-chlorobenzaldehyde.

similar to that of acetophenone itself. The negative charge migrates to a C–Cl σ^* orbital at the transition state and finally localizes at a dissociated chlorine atom. Such an intramolecular electron-transfer mechanism has been proposed for the dissociation of aromatic halides by Neta and Behar[5] as shown in Eq. 1. The present observation is compatible with this mechanism.

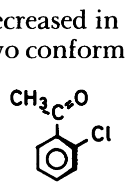
$$\begin{array}{lll} \overline{\mathrm{CH_3COC_6H_4}}^{\,\overline{\cdot}}\text{-Cl} \rightleftarrows & \mathrm{CH_3COC_6H_4}\overset{\overline{\cdot}}{\text{-}}\mathrm{Cl} \longrightarrow & \\ \quad(\mathrm{I}) & \quad(\mathrm{II}) & \\ \mathrm{CH_3COC_6H_4}\cdot + \mathrm{Cl}^- & & (1) \\ \quad(\mathrm{III}) & & \end{array}$$

The slope of the straight line for the plot of log k vs. AN reflects the relative extent of solvation to the initial state and the transition state. The larger slope for *m*-CAP than for *p*-CAP as shown in Fig. 2 is explained by the fact that the negative charge at the C–Cl σ^* orbital in the transition state is more delocalized in *p*-CAP than in *m*-CAP simply due to the presence of an electron-withdrawing group at the para position. This delocalization of the negative charge at the transition state decreases the solvation and reduces the rate.

On the other hand, a negative slope was obtained in the case of *o*-CAP, that is, an increase of solvent polarity resulted in a decrease in the rate. This means that the extent of solvation decreased in the transition state. In the case of *o*-CAP, two conformers (IV and V)



(IV)



(V)

exist and the C–CO–C plane is rotated from that of the phenyl ring on the basis of the strong steric interaction between the chlorine atom and oxygen atoms or methyl groups.[10] Consideration of steric and electrostatic factors indicated that an antiperiplanar-conformation, IV, is more favored than V. This argument concerning the stable conformation is also applicable to the radical anion. Therefore, the solvation of the negative-charged C–Cl bond at the transition state of the radical anion will be subject to steric hindrance by the proximately faced methyl group which leads to the abnormal solvent effect. The validity of such an explanation is supported by the findings that a normal behavior is observed for *o*-chlorobenzaldehyde in which such an intense steric effect as *o*-CAP cannot be expected as shown in Fig. 2 (dotted line).

In conclusion, we have demonstrated that the unimolecular dissociation of radical anions is subject to a remarkable solvent effect; normally an increase of solvent polarity results in an increase in the rate in consistent with the dissociation mechanism. Works along these lines are currently in progress.

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