method previously reported in the literature.[2]

The following procedure for preparing compound 6 is representative. To a precooled (-30 °C) stirred solution of 1 (20 mmol)[4] was added 20 mmol of 2 slowly, the mixture was maintained at -30 °C for 6 hrs with stirring. The reaction mixture was allowed to reach to room temperature. It was then flash distilled and the usual workup afforded product 6, purified by distillation.

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8. Spectral data of 6: ^{19}F-NMR spectrum was measured in $CDCl_3$. Chemical Shifts are reported in ppm with referenced to $CFCl_3$. -100.8(s, 2F), -106.9(s, 2F), -113.5(s, 2F), -129.6(m, 2F, J = 4Hz); IR(neat film) 1795 cm^{-1} ($\nu_{C=C}$ of cyclopropene), 1615 cm^{-1} ($\nu_{C=C}$ of cyclopentene); MS (m/z) 318 (M$^+$, 12.3%), 283(M-Cl, 100%).

The Effect of Medium on the α-Effect

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The rationalization of nucleophilic reactivity has intrigued chemists since the monumental work of Ingold.[1] Basicity has been most commonly used to correlate nucleophilicity, although recently the vertical ionization energy has also showed good correlations with the nucleophilicity of various types of anionic nucleophiles.[2] However, abnormally higher nucleophilicity than predicted from the basicity has often observed in the reactions of nucleophiles containing an atom with one or more nonbonding electron pairs adjacent to the reaction center (the α-position). Thus such a type of nucleophiles was termed α-nucleophiles and the enhanced nucleophilic reactivity of the α-nucleophiles was therefore termed the α-effect.[3]

Many theories have been advanced to explain the cause of the α-effect.[4] The suggested origins of the α-effect are 1) ground-state destabilization of the α-nucleophile,[5] 2) transition-state stabilization,[6] 3) polarizability,[7] and 4) solvent effects.[8-9] However any one of these effects alone does not fully account for the cause of the α-effect. Especially the solvent effect has been the subject of controversy. It has been claimed that in some studies the solvation effect is unimportant as the origin of the α-effect[8a-d] but other studies,[9a-b] including theoretical molecular orbital calculations, indicate that solvation should be an important factor.

Recently a systematic study has revealed that the solvent effect on the α-effect is very important for the reaction of p-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (1) as the α-nucleophile, in comparison with p-chlorophenoxide (2) as the corresponding normal nucleophile in dimethyl sulfoxide (DMSO)-H_2O mixtures of varying compositions.[10] We have now studied the same reactions in

Table 1. Kinetic Data for Reactions of p-nitrophenyl acetate (PNPA) with butane-2,3-dione monoximate (1) and p-chlorophenoxide (2) in CH_3CN-H_2O mixtures at 25.0 °C

mol.% CH_3CN	$k(2)$, $M^{-1}s^{-1}$	$k(1)$, $M^{-1}s^{-1}$	$k(1)/k(2)$
0	.685 (.685)	65.8 (65.8)	96 (96)
10.0	.385 (-)	37.2 (-)	97 (-)
20.0	.255 (.760)	29.5 (139)	116 (183)
30.0	.197 (-)	29.2 (-)	148 (-)
40.0	.198 (2.80)	35.6 (740)	180 (264)
50.0	.217 (5.90)	45.6 (1,680)	210 (285)
60.0	.266 (13.6)	67.5 (3,850)	254 (283)
70.0	.391 (34.7)	122 (8,200)	312 (236)
80.0	.712 (94.8)	263 (17,200)	369 (181)
90.0	2.12 (334)	943 (40,500)	445 (121)

^{a}The data in parentheses are obtained from ref. 10 for the reactions run in DMSO-H_2O mixtures.

various compositions of CH_3CN-H_2O mixtures to examine whether the previous result is a limited phenomenon only in the DMSO-H_2O system.

$$MeC(O)C(Me)=NO^- \qquad (1)$$

$$p-ClC_4H_4O^- \qquad (2)$$
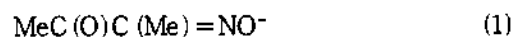
In Table 1 are presented the second order rate constants for the reactions of PNPA with (1) and (2). The rate constants decrease gradually as CH_3CN concentration increases
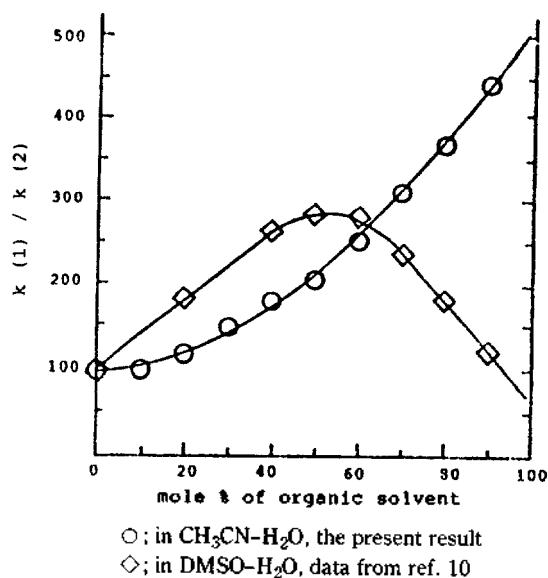
O ; in CH_3CN-H_2O, the present result
◇ ; in $DMSO-H_2O$, data from ref. 10

Figure 1. Plots of the magnitudes of the a-effect, $k(1)/k(2)$, vs. mole % CH_3CN (or DMSO) for reactions of p-nitrophenyl acetate with butane-2,3-dione monoximate (1) and p-chlorophenoxide (2) at 25.0 °C.

up to near 30–40 mole % CH_3CN, in which rate minima are observed. Furthermore the rate constants up to near 60–70 mole % CH_3CN are still smaller than the one in pure H_2O. The present result is therefore quite unexpected, since significant rate enhancements have generally been demonstrated upon the medium change from protic to aprotic dipolar solvents for the anionic nucleophilic reactions.[11] The a-nucleophile (1) shows smaller rate decrease in H_2O-rich region and much larger rate enhancement in the CH_3CN-rich region than the normal-nucleophile (2). Thus the magnitude of the a-effect is turned out to be associated with the medium composition significantly. Figure 1 shows that the magnitude of the a-effect is increasing with increasing CH_3CN concentration in the medium, i.e. from 96 in H_2O to 445 in 90% CH_3CN. Interestingly the present a-effect trend is quite different from the previous one which shows a maximum a-effect near 50 mole % DMSO, as shown in Figure 1 for a comparison purpose. Clearly the present result demonstrates that the previously observed medium dependent a-effects is not a confined phenomenon in the $DMSO-H_2O$ mixtures but a general one.

Recently it has been suggested that the solvent composition change does not cause any mechanism change for the reaction of PNPA with (1) and (2) in the $DMSO-H_2O$ mixtures.[12] Therefore it is unlikely that the present medium system would accompany any mechanism change. Also the pKa values of (1) and (2) have been suggested to vary in a similar manner as the solvent composition changes.[8-d,10] Thus the observed effect of medium on the alpha–effect would neither originate from a change in the mechanism nor from the differences in the basicities of the two nucleophiles as the solvent composition changes.

The rate decreases in the H_2O-rich region, in which hydrogen-bonding is most important,[11] seems to originate from more desolvation for the transition-state than for the ground-state. This is not unreasonable since the negative

charge on the transition-state is expected to be quite localized at the carbonyl oxygen atom, based on the Bronsted β value of 0.7–0.8 for the reaction of PNPA with aryloxides,[12-13] while the one on the nucleophiles (1) and (2) is considered to be widely delocalized on the whole molecule by resonance. On the other hand, the transition-state would be expected to get some stabilization in the CH_3CN-rich region, which is attributed to be responsible for the rate increases in this medium range, since the solvation of the transition-state is now mostly considered due to the charge dispersion interaction with CH_3CN.[11]

The medium dependent a-effect revealed by the present work is clearly significant. However more kinetic studies with thermodynamic work, such as measurements of solvation energy by a calorimetric technique, are necessary to dissect the medium effect into ground and transition-state contribution[14] for a complete interpretation of the present result.

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