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Pitfalls in Assessing the α-Effect: Reactions of Substituted Phenyl Methanesulfonates with HOO^-, OH^-, and Substituted Phenoxides in H_2O

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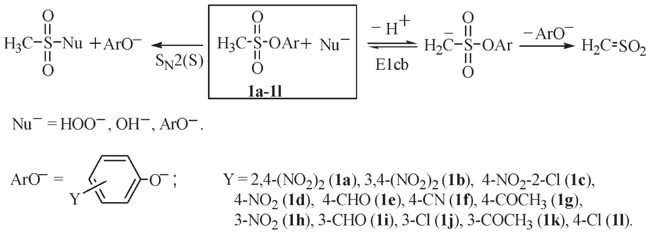

Toward resolving the current controversy regarding the validity of the α-effect, we have examined the reactions of Y-substituted phenyl methanesulfonates **1a−1l** with HOO^-, OH^-, and Z-substituted phenoxides in the gas phase versus solution (H_2O). Criteria examined in this work are the following: (1) Brønsted-type and Hammett plots for reactions with $HOO^-$and OH^-, (2) comparison of β_{lg} values reported previously for the reactions of Y-substituted phenyl benzenesulfonates **2a−2k** with HOO^- ($\beta_{lg} = -0.73$) and OH^- ($\beta_{lg} = -0.55$), and for those of **1a−1l** with HOO^- ($\beta_{lg} = -0.69$) and OH^- ($\beta_{lg} = -1.35$), and (3) Brønsted-type plot showing extreme deviation of OH^- for reactions of 2,4-dintrophenyl methanesulfonate **1a** with aryloxides, HOO^-, and OH^-, signifying extreme solvation vs different mechanisms. The results reveal significant pitfalls in assessing the validity of current interpretations of the α-effect. The extreme negative deviation by OH^- must be due, in part, to the difference in their reaction mechanisms. Thus, the apparent dependence of the α-effect on leaving-group basicity found in this study has no significant meaning due to the difference in operating mechanisms. The current results argue in favor of a further criterion, i.e., a consistency in mechanism for the α-nucleophiles and normal nucleophiles.

Introduction

The origin of the enhanced reactivity that is generally observed for nucleophiles possessing an atom with an unshared electron pair adjacent to the nucleophilic center, described originally by Edwards and Pearson as the α-effect,[1] continues to be controversial.[2−19] Prevalent theories on the α-effect phenomenon include ground-state (GS) destabilization, transition-state (TS) stabilization, thermodynamic stabilization of products. and solvent effects.[2−19] Impetus for these studies has recently come from two fronts: (1) development of new mass spectrometric techniques, which have provided insight into gas-phase reactivity, and (2) rapid advances in calculational methods.[3−6]

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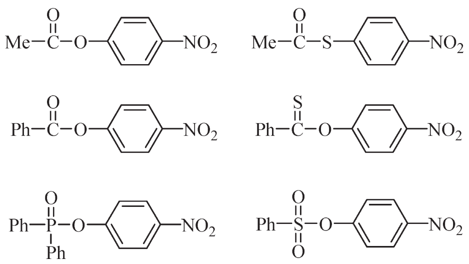
Because of the absence of solvent, the mass spectrometric studies are deemed to address experimentally the fundamental question of whether, in the absence of solvents, α-nucleophiles intrinsically display greater reactivity than normal nucleophiles.[3,4] Of course, this conundrum is also addressed through calculational studies.[4−6] Thus, interestingly, in a recent gas-phase study of the reactions of α-nucleophiles with alkyl chlorides, using a tandem flowing afterglow-selected ion flow tube instrument, Bierbaum et al. concluded that "the α-effect is not due to an intrinsic property of the anion but instead due to a solvent effect".[3a] This is in contradiction to a study of hydroperoxide anion with dimethyl methylphosphonate in a modified quadrupole ion trap mass spectrometer, combined with a DFT calculational study, which concluded that HOO^- reacts with lower activation energy (7.8 kJ mol^{-1}) compared to CH_3O^-, in accord with a gas-phase α-effect.[4]

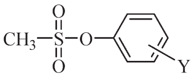
CHART 1



A further development of the Hoz SET model for the α-effect has been reported by computing barrier heights at the HF/6-311++G (2df, 2p) level of theory.[5] In methyl transfer from methyl formate to HOO^- and EtO^- (gas-phase acidity-matched), a 3.6 kcal/mol lowering of TS was found, i.e., more single electron transfer character with HOO^- than with HO^- or EtO^-.[5] This bolstered our earlier suggestion of TS stabilization derived in the earlier solution studies of methyl transfer from aryl methyl sulfates to hydrazine and glycine ethyl ester.[7]

Studies of solvent effects on the α-effect have produced a wealth of information.[17−19] The remarkable discovery of bell-shaped solvent effect plots suggested a differential solvent effect when kinetic studies aided by ΔH of solution of the substrates in Chart 1, possessing C=O, P=O, SO_2, and C=S centers, with butane-2,3-dione monoximate and *p*-chlorophenoxide were performed in $DMSO-H_2O$ mixtures.[17−19] The two-phase plots indicated differential TS stabilization in DMSO-rich media and differential GS destabilization in H_2O-rich media.[17−19] The above results amply illustrate the complexity of solvent effects on the α-effect.

In the present study we have examined the relative reactivities of HOO^- and OH^- as bases and as nucleophiles in their reaction with Y-substituted phenyl methanesulfonates **1a**−**1l**. OH^- is a strong enough base in deprotonation, enabling an E1cb pathway; however, because of its lower basicity and enhanced nucleophilicity (α-effect), reaction of HOO^- proceeds via an $S_N2(S)$ mechanism. On the other hand, in the reaction of substituted phenoxides with 2,4-dinitrophenyl methanesulfonate **1a**, OH^- is slightly more reactive than HOO^-, i.e., lack of an α-effect (Table 1).



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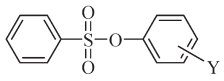

2

Y = 2,4-$(NO_2)_2$ (**a**), 3,4-$(NO_2)_2$ (**b**), 4-NO_2-2-Cl (**c**),
4-NO_2 (**d**), 4-CHO (**e**), 4-CN (**f**), 4-$COCH_3$ (**g**),
3-NO_2 (**h**), 3-CHO (**i**), 3-Cl (**j**), 3-$COCH_3$ (**k**), 4-Cl (**l**).

Results

Reactions were performed under pseudo-first-order conditions with the concentration of nucleophiles in excess over the substrate concentration. All reactions obeyed first-order kinetics with quantitative liberation of Y-substituted phenoxide ion. Pseudo-first-order rate constants (k_{obsd}) were calculated from the equation $\ln(A_\infty - A_t) = -k_{obsd}t + C$.

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TABLE 1. Summary of Second-Order Rate Constants for Reactions of Y-Substituted Phenyl Methanesulfonates 1a−1l with HOO^- and HO^- in H_2O at 25.0 ± 0.1 °C

Y	pK_a	$10^3 k_{HOO^-}$/M^{-1} s^{-1}	$10^3 k_{HO^-}$/M^{-1} s^{-1}
2,4-$(NO_2)_2$ (**1a**)	4.11	101 000	309 000
3,4-$(NO_2)_2$ (**1b**)	5.42	7 730	40 100
4-NO_2-2-Cl (**1c**)	5.45	4 640	19 500
4-NO_2 (**1d**)	7.14	315	67.6
4-CHO (**1e**)	7.66	232	6.90
4-CN (**1f**)	7.95	*a*	4.26
4-$COCH_3$ (**1g**)	8.05	71.1	1.54
3-NO_2 (**1h**)	8.35	96.4	1.93
3-CHO (**1i**)	8.98	39.6	0.246
3-Cl (**1j**)	9.02	*a*	0.168
3-$COCH_3$ (**1k**)	9.19	21.3	0.137
4-Cl (**1l**)	9.38	*a*	0.0697

[a] Rate constants could not be measured due to the interference by HOO^-.

TABLE 2. Summary of Second-Order Rate Constants for Reactions of 2,4-Dinitrophenyl Methanesulfonate 1a with Substituted Phenoxides, HOO^-, and OH^- in H_2O at 25.0 ± 0.1 °C

entry	Z	pK_a	10^3 k_{ArO^-}/M^{-1} s^{-1}
1	4-$CNPhO^-$	7.95	4.23
2	3-$ClPhO^-$	9.02	116
3	4-$ClPhO^-$	9.38	193
4	PhO^-	9.95	626
5	4-$MePhO^-$	10.19	2 090
6	HOO^-	11.62	101 000 [a]
7	HO^-	15.7	309 000 [b]

[a] k_{HOO^-}. [b] k_{OH^-}.

The plots of k_{obsd} vs nucleophile concentration for the reactions with HOO^- and Z-substituted phenoxide anions were linear with positive intercepts due to the contribution of H_2O and/or OH^- from hydrolysis of the anionic nucleophiles (see Figures S1−S14 in the Supporting Information). The second-order rate constants (k_N) were calculated from the slope of linear plots of k_{obsd} vs [nucleophile] and are summarized in Table 1 for the reactions of **1a**−**1l** with HOO^- and OH^- and in Table 2 for those of **1a** with Z-substituted phenoxide anions. It is estimated from replicate runs that the uncertainty in the rate constants is less than ±3%.

Discussion

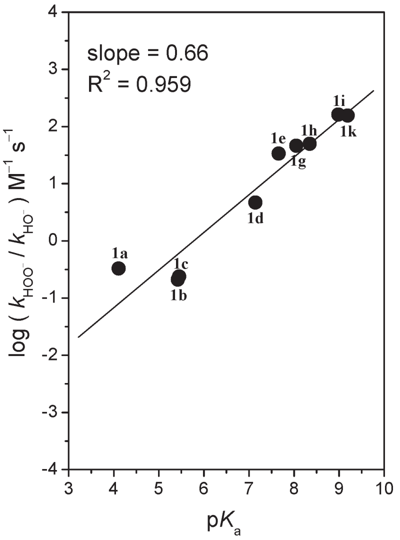

FIGURE 1. Dependence of the α-effect on leaving-group basicity for reactions of Y-substituted phenyl methanesulfonates **1a**−**1l** with HOO^- and HO^- in H_2O at 25.0 ± 0.1 °C.

a. Unusual Reversal in Reactivity of Hydroperoxide vs Hydroxide. Table 1 shows that the second-order rate constant for the reaction with HOO^- decreases as leaving-group basicity increases, e.g., k_{HOO^-} decreases from 101 M^{-1} s^{-1} to 0.315 and 0.0213 M^{-1} s^{-1} as the pK_a of the conjugate acid of the leaving group increases from 4.11 to 7.14 and 9.19, in turn. Similar results are shown for the corresponding reactions with OH^-, e.g., k_{OH^-} decreases from 309 M^{-1} s^{-1} to 6.76×10^{-2} and 6.97×10^{-5} M^{-1} s^{-1} as the pK_a of the conjugate acid of the leaving group increases from 4.11 to 7.14 and 9.38, in turn. It is important to note that HOO^- is more reactive than OH^- for the reactions of substrates possessing a poor leaving group (e.g., **1d**−**1k**). However, the former is less reactive than the latter for the reactions of substrates bearing a good leaving group (e.g., **1a**−**1c**). This is quite an unexpected result since HOO^- has often been reported to exhibit significantly enhanced reactivity compared to OH^- for various nucleophilic reactions performed in H_2O, e.g., rate enhancement of ca. 10^2 in reactions of C=O- and SO_2-centered electrophiles[20,21] or even up to 10^4 in reactions of benzonitriles, with an sp-hybridized electrophilic center.[22]

Figure 1 illustrates the magnitude of the α-effect assessed by a traditional method (i.e., the k_{HOO^-}/k_{OH^-} ratio) as a function of the leaving-group basicity. The plot of log(k_{HOO^-}/k_{OH^-}) vs the pK_a of the conjugated acids of the leaving aryloxides is linear with a slope of 0.66, although some scattered points are present. The current result appears to be similar to the reports that the magnitude of the α-effect increases linearly as the leaving-group basicity increases for methyl transfer reactions of Y-substituted phenyl methyl sulfates with hydrazine and glycine ethyl ester (i.e., an S_N2 mechanism)[7] as well as nucleophilic substitution reactions of Y-substituted phenyl benzoates with hydrazine and glycylglycine.[23] The reactions of aryl benzoates with hydrazine and glycylglycine have been shown to proceed through the same mechanism, i.e., a stepwise mechanism in which breakdown of a zwitterionic tetrahedral intermediate is the rate-determining step (RDS).[23] In contrast, the current reactions of **1a**−**1l** with HOO^- and HO^- are not considered to proceed through the same mechanism on the basis of the significant difference in β_{lg} values between the two reaction series, as shown in Figure 2.

As shown in Figure 2, the Brønsted-type plots exhibit excellent linear correlation. However, the slope of the Brønsted-type plots (β_{lg}) is significantly different, i.e., $\beta_{lg} = -0.69$ for reactions with HOO^- and $\beta_{lg} = -1.35$ for the corresponding reactions with OH^-. The β_{lg} value for the reactions of **1a**−**1k** with HOO^- ($\beta_{lg} = -0.69$) is practically the same as that reported previously for the reactions of **2a**−**2k** with HOO^- ($\beta_{lg} = -0.73$).[21] Thus, one can suggest that the reactions of **1a**−**1k** with HOO^- proceed through the same mechanism as those of Y-substituted phenyl benzenesulfonates **2a**−**2k** with HOO^-. In contrast, a β_{lg} value of −1.35 implies that the reactions of **1a**−**1l**

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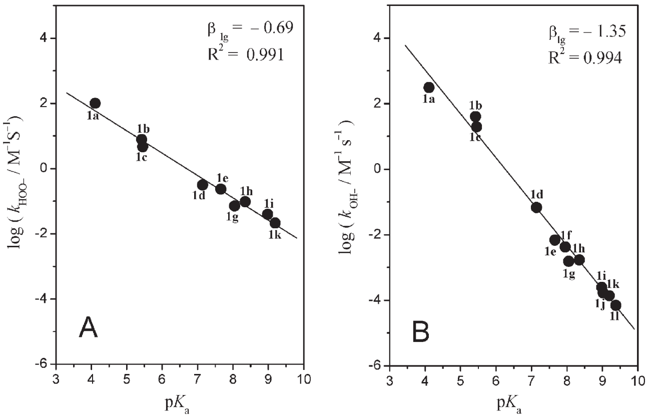


FIGURE 2. Brønsted-type plots for reactions of Y-substituted phenyl methanesulfonates **1a−1l** with HOO^- (A) and HO^- (B) in H_2O at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

with OH^- proceed through a different mechanism from the corresponding reactions with HOO^- ($\beta_{lg} = -0.69$).

Many different pathways are possible for the reactions of **1a−1l** as shown in Scheme 1, e.g., (a) a two-step addition/elimination mechanism, (b) an $S_N2(S)$ mechanism (a concerted bimolecular nucleophilic displacement at sulfur, following the first suggestion of $S_N2(P)$ nomenclature in the related organophosphate system),[24] (c) an E2 mechanism, and (d) an E1cb reversible or E1cb irreversible mechanism.

b. Hydroperoxide Reaction Pathways: One-Step $S_N2(S)$ vs Two-Step Addition/Elimination, E2, E1cb (irrev.), or E1cb (rev.). It is evident that the reactions of Y-substituted phenyl benzenesulfonates **2a−2k** would proceed either through a two-step addition/elimination mechanism (e.g., Scheme 1, path a) or through an $S_N2(S)$ pathway (e.g., path b) but cannot proceed through an E2 (e.g., path c) or E1cb mechanism (e.g., path d) due to the absence of acidic protons. Thus, one can suggest that the reactions of **1a−1k** would proceed also through a two-step addition/elimination mechanism or through an $S_N2(S)$ pathway on the basis of the similarity in their β_{lg} values, as mentioned above.

If the reactions proceed through a stepwise mechanism with an addition intermediate, the RDS should be formation of the intermediate. This is because HOO^- is more basic and a poorer nucleofuge than the leaving aryloxides. Thus, if the reactions proceed through a stepwise mechanism, no negative charge would develop on the O atom of the leaving aryloxide at the transition state of the RDS. In this case, one might expect that σ° constants would result in a better Hammett correlation than σ^- constants.

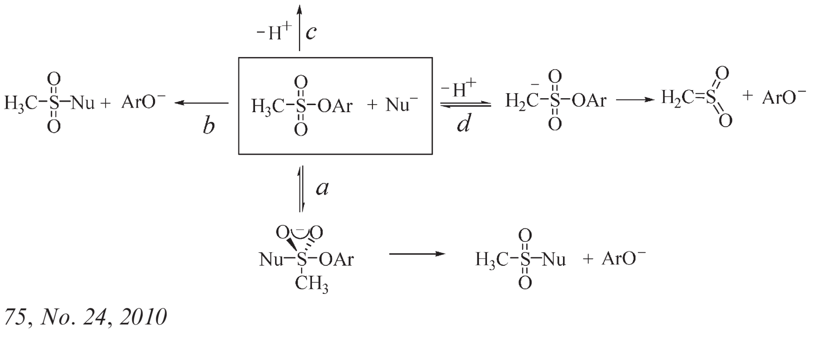
To investigate the nature of RDS, Hammett plots have been constructed with σ° and σ^- constants. As shown in Figure 3, σ° constants (A) result in significantly poorer correlation with scattered points than σ^- constants (B), indicating that leaving-group departure is advanced in the transition state of RDS. This result excludes a stepwise mechanism (path a). Thus, one can conclude that the reactions of **1a−1k** with HOO^- proceed through an $S_N2(S)$ mechanism, in which departure of the leaving group and attack of the nucleophile occur simultaneously. This mechanism can be further supported by the fact that $\beta_{lg} = -0.69$, which is typical for reactions reported to proceed through a concerted mechanism (e.g., aminolysis, alkaline hydrolysis, and ethanolysis of Y-substituted phenyl diphenylphosphinates and phosphinothioates).[25]

c. Hydroxide Reaction Pathways: E1cb (rev.) vs E1cb (irrev.), E2, $S_N2(S)$, or Two-Step Addition/Elimination. The large negative β_{lg} value (i.e., −1.35) found for the reactions of **1a−1l** with OH^- implies that departure of the leaving group is significantly advanced in the transition state of RDS. To examine this idea, Hammett plots have been constructed using σ° and σ^- constants. As shown in Figure 4, the Hammett plot correlated with σ° constants exhibits highly scattered points (A), while that correlated with σ^- constants results in better correlation (B). This supports the above idea that departure of the leaving group is significantly advanced in the transition state of RDS.

The fact that σ^- constants exhibits better correlation than σ° constants excludes a two-step addition/elimination mechanism (i.e., path a in Scheme 1). This is because, if the reactions proceed through an addition/elimination mechanism, expulsion of the leaving group should occur after the RDS on the basis of the fact that OH^- is much more basic and a poorer nucleofuge than aryloxides. One can also rule out an E1cb irreversible mechanism, in which departure of the leaving group occurs after the RDS.

Therefore, three different pathways remain for the reactions of **1a−1l** with OH^-, e.g., an $S_N2(S)$, an E2, or an E1cb reversible mechanism. The reactions of Y-substituted phenyl benzenesulfonates **2a−2k** with OH^- have been reported to proceed through an $S_N2(S)$ mechanism on the basis of the

SCHEME 1. **Plausible Pathways for Reactions of 1a−1l with Anionic Nucleophiles: (a) Two-Step Addition/Elimination, (b) $S_N2(S)$, (c) E2, and (d) E1cb Reversible or E1cb Irreversible Mechanisms**



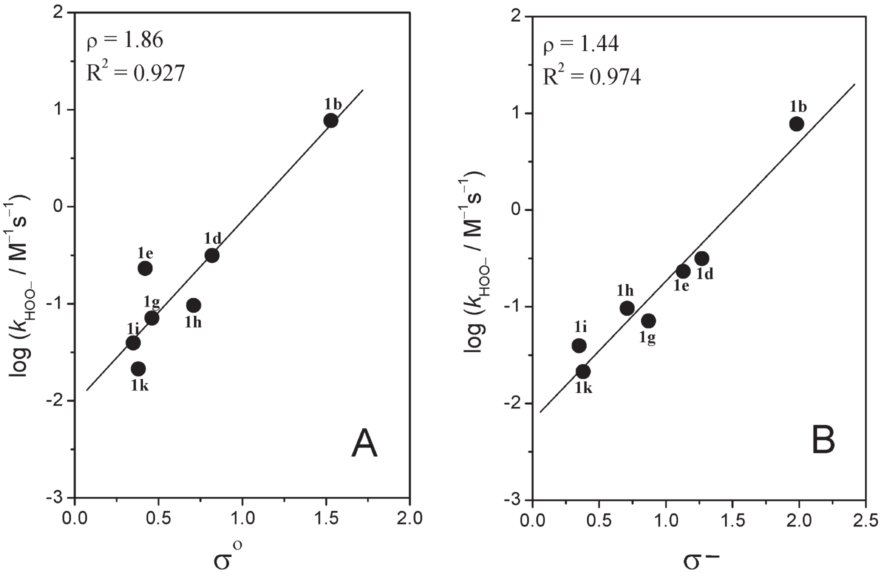


FIGURE 3. Hammett plots correlated with σ° (A) and σ^- constants (B) for reactions of Y-substituted phenyl methanesulfonates **1b**−**1k** with HOO^- in H_2O at 25.0 ± 0.1 °C. The identity of points is given in Table 1.

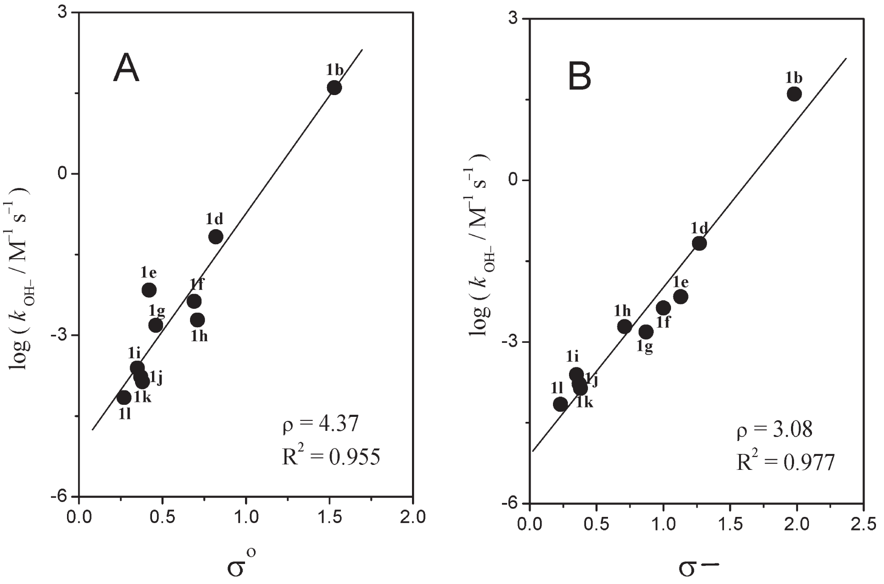


FIGURE 4. Hammett plots correlated with σ° (A) and σ^- constants (B) for reactions of Y-substituted phenyl methanesulfonates **1b**−**1l** with HO^- in H_2O at 25.0 ± 0.1 °C. The identity of the points is given in Table 1.

linear Brønsted-type plot with $\beta_{lg} = -0.55$.[26] The β_{lg} value of −1.35 suggests that the reactions of **1a**−**1l** with OH^- do not proceed through an $S_N2(S)$ mechanism. Such a large β_{lg} value excludes also an E2 mechanism, since β_{lg} values have been reported to be -0.5 ± 0.1 for reactions proceeding through an E2 mechanism.[27a−c] Thus, the large β_{lg} suggests that the reactions of **1a**−**1l** with OH^- proceed through an E1cb reversible mechanism, in which expulsion of the leaving group occurs in the RDS. This can be supported by the report that hydrolysis of aryl 3,5-dimethyl-4-hydroxybenzenesulfonates proceeds through an E1cb mechanism on the basis of $\beta_{lg} = -1.55$.[27d]

To examine the above argument that the reactions of **1a**−**1l** with OH^- proceed through an E1cb reversible mechanism, deuterium exchange experiments have been performed by allowing substrate **1d** to react with NaOD in 80 mol % D_2O/20 mol % CD_3CN. The ^1H NMR spectrum of the methyl moiety of **1d** taken from the reaction mixture (Figure 5) shows overlapping spectra of undeuterated, monodeuterated,

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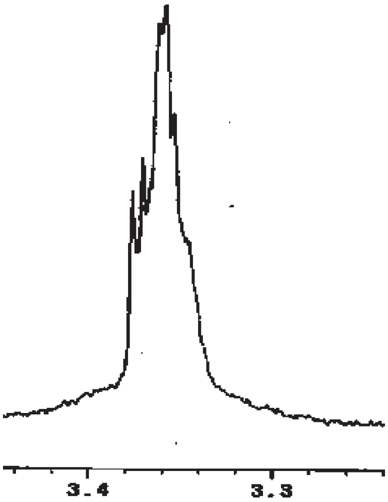

FIGURE 5. ^{1}H NMR spectrum of the methyl group of **1d** after partial reaction with NaOD in 80 mol % D_2O/20 mol % CD_3CN.

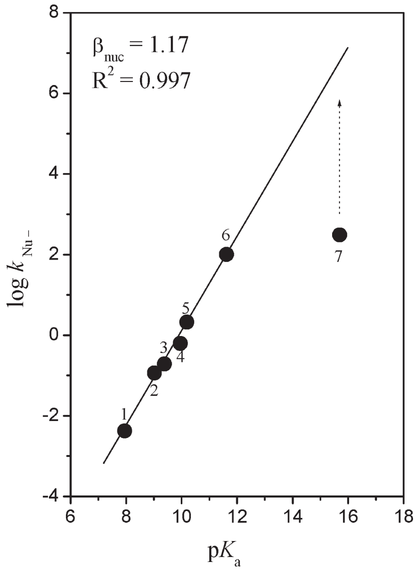

FIGURE 6. Brønsted-type plot for reactions of 2,4-dinitrophenyl methanesulfonate **1a** with Z-substituted phenoxides (1−5), HOO^- (6), and OH^- (7) in H_2O at 25.0 ± 0.1 °C. The identity of points is given in Table 2. Point 7 (i.e., OH^-) is excluded in calculations of the slope and correlation coefficient.

and dideuterated methyl groups, indicating that deprotonation and reprotonation of the methyl group occur. The observation of deuterium exchange is consistent with an E1cb reversible mechanism.

d. Pitfalls in Assessing the α-Effect. The α-effect was defined as a positive deviation from a Brønsted-type nucleophilicity plot.[2c] Thus, the reference (or normal) nucleophile should have the same basicity as the α-nucleophile in order to assess the α-effect. However, HOO^- and OH^- have traditionally been employed as the α-nucleophile and normal nucleophile, respectively, although their basicities are significantly different.[3,22,28] Our current study shows that assessment of the α-effect in a traditional way (e.g., comparison of rate constants for reactions with HOO^- and OH^-) can be misleading. For example, the α-effect for the reactions of **1a**−**1k** with HOO^- and OH^- illustrated in Figure 1 has no significant meaning since the two series of reactions proceed through different mechanisms, as mentioned in the preceding section, e.g., an $S_N2(S)$ mechanism for the reactions with HOO^- but an E1cb reversible pathway for those with OH^-.

We have performed reactions of **1a** with a series of Z-substituted phenoxides and constructed a Brønsted-type plot in Figure 6, including the data for the reactions with HOO^- and OH^-. Aryloxides have been chosen as a series of normal nucleophiles in this study, since they would behave as a nucleophile rather than as a base due to their weak basicity. The second-order rate constants (k_{ArO^-}) are summarized in Table 2, together with k_{HOO^-} and k_{OH^-} values for comparison.

e. Solvation Effects. As shown in Figure 6, reactions of **1a** with the aryloxides and HOO^- result in an excellent linear Brønsted-type plot, while OH^- deviates negatively from linearity. The fact that the aryloxides and HOO^- result in excellent linear correlation, with $\beta_{nuc} = 1.17$, suggests that the reactions of **1a** with the aryloxides and HOO^- proceed through a common mechanism, i.e., an $S_N2(S)$ mechanism. This is reasonable since aryloxides are not basic enough to proceed through an E2 or E1cb mechanism. One can also exclude an addition/elimination mechanism. This is because, if the reactions proceed through an addition/elimination mechanism, leaving-group departure would occur after the RDS, as mentioned above. One then might expect a β_{nuc} value of 0.3 ± 0.1, as reported previously for nucleophilic substitution reactions of esters which proceed through a stepwise mechanism, with formation of an intermediate being the RDS (e.g., aminolysis and pyridinolysis of esters possessing a good leaving group).[29−31] Clearly, the β_{nuc} value of 1.17 is too large for a stepwise mechanism, in which leaving-group departure occurs after the RDS. Thus, one can suggest that reactions of **1a** with aryloxides also proceed through an $S_N2(S)$ mechanism.

It is important to note that OH^- deviates negatively from the linear Brønsted-type plot, as shown in Figure 6. Such negative deviation has often been reported for reactions with OH^- performed in H_2O.[20] Solvation effect has been suggested to be responsible for the deviation since OH^- is known to be 12 kcal/mol more strongly solvated than HOO^- in H_2O.[32] However, it is apparent that the negative deviation shown by OH^- in the current study is not solely due to the

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differential solvation effect but is also due to the difference in reaction mechanisms, as discussed in the preceding section.

Conclusions

Our study has allowed us to conclude the following: (1) The reactions of **1a**−**1k** with HOO^- proceed through an $S_N2(S)$ mechanism, while the corresponding reactions with OH^- occur through an E1cb reversible pathway. (2) The dependence of the α-effect on leaving-group basicity found in this study has no significant meaning since the reactions of **1a**−**1l** with HOO^- and OH^- proceed through different reaction mechanisms, $S_N2(S)$ vs E1cb (rev.). (3) Reactions of **1a** with a series of aryloxides and HOO^- result in an excellent linear Brønsted-type plot, while OH^- exhibits extreme negative deviation from the linearity. The negative deviation is not solely due to solvation effect but is due, in part, to the difference in their reaction mechanisms. (4) The current results argue in favor of a further criterion, i.e., constancy in reaction of the α- and normal-nucleophiles. (5) Assessment of the α-effect by a traditional way based just on comparison of the rate constants of the α-nucleophiles and normal nucleophiles can be misleading. Controversial gas-phase results arise, in some cases, from different mechanisms for the chosen α-nucleophile compared to the normal nucleophile.

Experimental Section

Materials. Compounds **1a**−**1l** were prepared from the reaction of methanesulfonyl chloride with Y-substituted phenols in anhydrous ether in the presence of triethylamine as reported previously.[33] The crude products were purified through column chromatography. The purity of **1a**−**1l** was checked by means of the melting points and ^1H NMR characteristics. Other chemicals used, including H_2O_2 and phenols, were of the highest quality available. Doubly glass-distilled water was further boiled and cooled under nitrogen just before use.

Kinetics. The kinetic study was performed with a UV−vis spectrophotometer for slow reactions (e.g., $t_{1/2} \geq 10$ s) or with a stopped-flow spectrophotometer for fast reactions (e.g., $t_{1/2} < 10$ s), equipped with a constant-temperature circulating bath to maintain the temperature in the reaction cell at 25.0 ± 0.1 °C. The reaction was followed by monitoring the appearance of the leaving Y-substituted phenoxide ion. All the reactions were carried out under pseudo-first-order conditions in which nucleophile concentrations were at least 20 times greater than the substrate concentration. The ca. 0.2 M aryloxide stock solution was prepared by dissolving 2 equiv of Z-substituted phenol and 1 equiv of standardized NaOH solution to keep the pH constant in this self-buffered solution. All solutions were prepared freshly just before use under nitrogen and transferred by gastight syringes. It was found that HOOH does not react with the substrate in the absence of a base. Thus, the reaction of **1a**−**1k** with HOO^- was initiated by adding a calculated amount of ca. 0.5 M NaOH stock solution to a 10 mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent, the substrate, and an aliquot of the HOOH stock solution. This method could generate HOO^- ion in situ and minimize decomposition of HOO^- in the basic condition. The [HOOH]/[NaOH] ratio was kept at 5.0. The reaction with OH^- or aryloxide was initiated by adding 5 μL of a 0.02 M solution of the substrate in CH_3CN by a 10 μL syringe to a 10 mm quartz UV cell containing 2.50 mL of the thermostated reaction mixture made up of solvent and an aliquot of the NaOH or aryoxide stock solution.

Product Analysis. Y-substituted phenoxide was liberated quantitatively and identified as one of the products by comparison of the UV−vis spectrum at the end of reaction with that of the authentic sample under the experimental conditions.

Deuterium Exchange Experiments. The ^1H NMR spectra of substrate **1d** in 80 mol % D_2O/20 mol % CD_3CN were taken before and after addition of NaOD to check for deuterium exchange at the methyl group (Figures S15−S18, Supporting Information). The deuterated methyl signal resulted in upfield shifts of ca. 0.015 ppm with splitting due to H−D coupling (J = 2.5 Hz), which are characteristic of partial deuteration of methyl groups.[34]

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Supporting Information Available: Tables S1−S9, kinetic conditions and data for reactions of **1a**−**1l** with HOO^-; Tables S10−S21, kinetic data for reactions of **1a**−**1l** with OH^-; Tables S22−S26, kinetic data for reactions of **1a** with Z-substituted phenoxides; Figures S1−S9, plots of k_{obsd} vs $[HOO^-]$ for reactions of **1a**−**k**; Figures S10−S14, plots of k_{obsd} vs $[ArO^-]$ for the reactions of **1a** with Z-substituted phenoxides; Figures S15−S18, ^1H NMR spectra of the methyl group of **1d** in 80 mol % D_2O/20 mol % CD_3CN before and after addition of NaOD. This material is available free of charge via the Internet at http://pubs.acs.org.

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