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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

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### LACK OF ENHANCED REACTIVITY OF $\alpha$ -NUCLEOPHILES IN THE $S_N2$ REACTIONS OF BENZYL BROMIDES AND SMALL $\alpha$ -EFFECT IN THE MICHAEL ADDITION REACTION OF AMIDES TO P-TOLYL VINYL SULFONE

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**To cite this Article** Oae, Shigeru and Kadoma, Yoshito(1997) 'LACK OF ENHANCED REACTIVITY OF  $\alpha$ -NUCLEOPHILES IN THE  $S_N2$  REACTIONS OF BENZYL BROMIDES AND SMALL  $\alpha$ -EFFECT IN THE MICHAEL ADDITION REACTION OF AMIDES TO P-TOLYL VINYL SULFONE', Phosphorus, Sulfur, and Silicon and the Related Elements, 123: 1, 293 – 300

**To link to this Article:** DOI: 10.1080/10426509708044217

**URL:** <http://dx.doi.org/10.1080/10426509708044217>

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## LACK OF ENHANCED REACTIVITY OF $\alpha$ -NUCLEOPHILES IN THE $S_N2$ REACTIONS OF BENZYL BROMIDES AND SMALL $\alpha$ -EFFECT IN THE MICHAEL ADDITION REACTION OF AMIDES TO P-TOLYL VINYL SULFONE

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(Received 21 January, 1997; In final form 24 April, 1997)

Both second-order rate constants of  $S_N2$  reactions on benzyl bromide and *p*-nitrobenzyl bromide with hydroxy nucleophiles and those of the Michael addition reactions of a few amines to *p*-tolyl vinyl sulfone have been determined. The values of  $k_{HOO^-}/k_{HO^-}$  for benzyl and *p*-nitrobenzyl bromide were very small, i.e., 1.3 and 1.2 respectively; in the  $S_N2$  reaction on  $sp^3$  carbon this may be due to the lack of tight  $\sigma$ -bond formation at the transition state. A very small positive deviation from the Brønsted plots was observed in the Michael addition of hydrazine and other amines to *p*-tolyl vinyl sulfone. This may be due to the small  $\beta$ -value associated with the reaction.

**Keywords:** Vinyl sulfone; Michael addition; hydrazine; Brønsted plots

Certain nucleophiles react faster than what would be expected from their proton basicities. These nucleophiles include hydroperoxide ion, hydroxylamine, oxime anions, hydrazine, hypohalite ions and hydroxamic acids. All of these nucleophiles have in common the presence of an atom with unshared electron pairs adjacent to the nucleophilic center. Because of this structural feature, the enhanced reactivity of these nucleophiles has been called the alpha effect.<sup>2</sup>

The origin of this effect has been discussed extensively<sup>3,4</sup> and believed to be due to one or more of the following factors.

- (1) Ground state destabilization by repulsion between the adjacent pairs of electrons.<sup>5</sup>
- (2) Stabilization of the transition state.<sup>6</sup>
- (3) Stabilization of the product.
- (4) Reduced solvation of  $\alpha$ -nucleophiles.<sup>4,7,8,9</sup>

A literature survey reveals that the alpha effect appears to be most prominent with compounds in which the reaction center is sp hybridized carbon and diminishes somewhat with those having sp<sup>2</sup> carbon while the reaction on sp<sup>3</sup> carbon do not seem to produce a sizable  $\alpha$ -effect,<sup>10,11</sup> at most ca. 10 fold increase in the reaction of methyl phenyl sulfates with ion,<sup>6d</sup> with possibly one exception,<sup>12</sup> namely the reaction of benzyl bromide with hydroperoxide ion. The alpha effect is also known to be substantial on the nucleophilic attack on the tetracoordinate phosphorus<sup>4b,13</sup> and sulfur atom.<sup>14</sup>

Although we could not detect any rate enhancement in the reactions of methyl, isopropyl, allyl and benzyl iodides in acetonitrile with hydrazine, relative to other amines,<sup>10</sup> another report claimed that hydroperoxides ion reacted 34 times faster than hydroxide ion with benzyl bromide in 50% aqueous acetone. Thus, we have reexamined the reactions of hydroperoxide ion with benzyl and *p*-nitrobenzyl bromides. Since the latter compound has a more electropositive reaction center than the unsubstituted one and this will allow to form a strong  $\sigma$ -bonding interaction with nucleophiles at the transition state, while the repulsion between the adjacent lone pairs on hydroperoxide ion would be substantially reduced, a larger alpha effect would be expected. However, again no significant rate enhancement was observed by the  $\alpha$ -nucleophile in this S<sub>N</sub>2 reaction on benzylic carbon atom.

Meanwhile, the alpha effect is usually substantial when the attacking center of  $\alpha$ -nucleophiles is sp<sup>2</sup> carbon and hence a substantial rate enhancement would be observed in the Michael type addition reaction to  $\alpha,\beta$ -unsaturated olefins. Thus, we have studied the addition of a few selected amines, including hydrazine, to *p*-tolyl vinyl sulfone; however, an unexpectedly small positive deviation in this addition reaction.

## RESULTS AND DISCUSSION

### A. Reactions of Benzyl and *p*-Nitrobenzyl Bromides with Hydroperoxide Ions

The reaction of benzyl and *p*-nitrobenzyl bromide with 0.04215 mol/l sodium hydroxide in a buffer solution containing 0.1N sodium carbonate and with hydrogen peroxide in the same buffer solution was carried out. Since hydrogen peroxide is unstable at pH higher than 12, the sodium carbonate buffer solution was used. The rate constants are listed in Table I.

The rate constant, ( $k_2 = 9.1 \times 10^{-3}$ ) for the reaction of *p*-nitrobenzyl bromide with 0.04215 mol/l of sodium hydroxide ( $1.1 \times 10^{-2}$ ) is in good accord with that in the

TABLE I Second Order Rate Constants for Benzyl and *p*-Nitro-benzyl Bromides in 50% Aqueous Acetone (by volume) Containing  $\text{OOH}^-$  and  $\text{OH}^-$  Ions at 30°C

Substrate <sup>a</sup>	$k_{\text{OH}^-}$ ( $\text{l.mol}^{-1}, \text{sec}^{-1}$ ) with $\text{NaOH}^b$	$k_{\text{OH}^-}$ ( $\text{l.mol}^{-1}, \text{sec}^{-1}$ ) in buffer soln.	$k_{\text{OOH}^-}$ ( $\text{l.mol}^{-1}, \text{sec}^{-1}$ ) in buffer soln.	$k_{\text{OOH}^-}/k_{\text{OH}^-}$
Benzyl bromide	$1.8 \times 10^{-3}$	$9.1 \times 10^{-3}$	$2.4 \times 10^{-3}$	1.3
<i>p</i> -Nitrobenzyl bromide	$1.1 \times 10^{-2}$	$9.4 \times 10^{-3}$	$1.3 \times 10^{-2}$	1.2
pH of the buffer solution		11.6, 11.3 <sup>c</sup>	11.5	

a) 0.0300 mol/l. b) 0.04215 mol/l

c) The pH value of the buffer solution changes gradually as the reaction proceeds, since  $\text{Br}^-$  ion is liberated

buffer solution ( $k_2 = 9.4 \times 10^{-3}$ ) within experimental error. On the other hand, those for benzyl bromide differ widely due to side reactions, mainly spontaneous hydrolysis which predominates in the less basic buffer solution. Therefore, the rate constant for the reaction of benzyl bromide with 0.04215 mol/l NaOH ( $1.8 \times 10^{-3}$ ) which was used as  $k_{\text{OH}^-}$  for estimation of  $k_{\text{HOO}^-}/k_{\text{HO}^-}$  value. The value in the buffer solution ( $k = 9.1 \times 10^{-3}$ ) was not used, due mainly to the occurrence of side reactions in less basic buffer solution. Thus, contrary to the observation of Pearson *et al.*,<sup>12</sup> we could not observe a large  $\alpha$ -effect; the value of  $k_{\text{HOO}^-}/k_{\text{HO}^-}$  being only 1.2 even with *p*-nitrobenzyl bromide and 1.3 for unsubstituted one.

Earlier, Dixon and Bruice reported a substantially large  $\alpha$ -effect in the reaction of methyl *p*-tosylate with amines and hydroperoxide ion in aqueous media.<sup>16</sup> Recently, Buncel *et al.* have also found a sizable  $\alpha$ -effect in the  $\text{S}_{\text{N}}2$  reactions of methyl phenylsulfates with  $\alpha$ -nucleophiles.<sup>6a,b</sup> Apparently, methyl derivatives are specially suitable substrates fitted to show the  $\alpha$ -effect, due mainly to formation of a tight transition state as compared to other alkyl derivatives, since the normal  $\text{S}_{\text{N}}2$  reaction would proceed with simultaneous Nu-R bond formation and R-X bond cleavage, i.e., increased Nu-R and decreased R-X bond order. This may be especially notable for the nucleophilic substitution of benzylic halides or related derivatives in which a sizable  $\alpha$ -effect was observed. Even so, the negligibly small rate enhancement observed for the  $\text{S}_{\text{N}}2$  reaction of *p*-nitrophenyl bromide with hydroperoxide ion is rather intriguing, since in the  $\text{S}_{\text{N}}2$  reaction of *p*-nitrobenzyl bromide, bond orders of both R-X and Nu-R bondings would be increased more than those in the same reaction of unsubstituted benzyl bromide.

The relief of repulsion of the  $\alpha$ -nucleophile in going from the ground state to the transition state of tight bonding formation seems to be quite important for the occurrence of rate enhancement by  $\alpha$ -nucleophile.<sup>17</sup> In the  $\text{S}_{\text{N}}2$  reactions on  $\text{sp}^3$  carbon atom, a tight  $\sigma$ -bonding at the transition state is impossible, and hence

relief of repulsion would not be significant, especially in the reaction on resonance-stabilized benzylic carbon atom, since our early SCF MO calculation<sup>18</sup> revealed that both oxygen atom of  $\text{HOO}^-$  ion are involved in forming a tight  $\sigma$ -bonding at the transition state of nucleophilic substitution in the ester hydrolysis. In the nucleophilic ester hydrolysis, a tightly bound discrete addition intermediate is formed and hence the relief of repulsion would be substantial. This may be part of the reason why allyl and benzyl iodides which have Brønsted  $\beta$ -values (0.60 and 0.55, respectively), similar to *p*-nitrophenyl acetate (0.54) did not show any sizable  $\alpha$ -effect in our earlier aminolyses reactions,<sup>10</sup> nor in the alkaline hydrolyses of benzylic bromides, while in the hydrolysis of *p*-nitrophenyl acetate a distinct  $\alpha$ -effect ( $10\text{--}10^2$ ) was observed.<sup>19</sup>

## B. The Michael Type Addition of Amines to *p*-Tolyl Vinyl Sulfone

If a sizable  $\alpha$ -effect can be observed in nucleophilic substitution reactions, in which bond formation is more important than bond cleavage a large  $\alpha$ -effect would be observed similarly in the Michael type nucleophilic addition of  $\alpha$ -nucleophilic amines to electrophilic olefines, provided that attack of  $\alpha$ -nucleophile takes place on olefinic carbon at the transition state. The reaction between *p*-tolyl vinyl sulfone and amines is known to give only the corresponding amino-sulfones, identical to those of the addition reactions. Thus, the reactions of *p*-tolyl vinyl sulfone with a few selected amines have been carried out and the results obtained are tabulated in Table II and III.

TABLE II Second-order Rate Constants for Michael Addition of Primary and Secondary Amines to *p*-Tolyl Vinyl Sulfone <sup>a</sup> in Absolute Ethanol at 25°C

Nucleophile <sup>b</sup>	$k_2$ ( $\text{l.mol}^{-1}\text{, sec}^{-1}$ )	$\log k_{\text{rel}}$	$\text{pK}_a^{\text{d}}$ in water
Amonia	$1.37 \times 10^{-4}$	0	9.21
Hydrazine	$2.41 \times 10^{-1}$	2.94 <sup>c</sup>	7.96
Hydroxylamine	$4.63 \times 10^{-2}$	2.53	6.05
Benzylamine	$1.22 \times 10^{-2}$	1.95	9.34
Monoethanolamine	$5.52 \times 10^{-3}$	1.61	9.50
n-Butylamine	$2.43 \times 10^{-2}$	2.53	10.6

a)  $2.0 \times 10^{-3}$ ,  $2.0 \times 10^{-4}$  mol/l.

b)  $2.0 \times 10^{-1}$ ,  $2.0 \times 10^{-2}$  mol/l.

c)  $k_{\text{rel}}$  value was divided by 2 because of two nucleophilic centers on hydrazine.

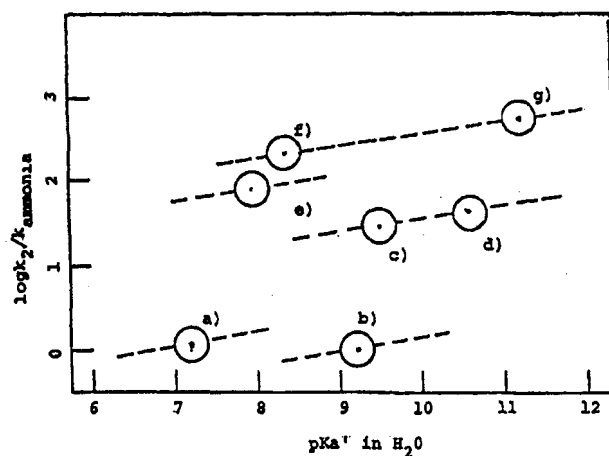
d) Values of  $\text{pK}_a$ 's in Table 2 are taken from Perrin<sup>21</sup>, since  $\text{pK}_a$ 's in ethanol are well correlated with  $\text{pK}_a$ 's in water

TABLE III Second-order Rate Constants for Michael Addition of Amines to *p*-Tolyl Vinyl Sulfone<sup>a</sup> in Acetonitrile at 40°C

Nucleophile <sup>b</sup>	$k_2$ ( $\text{l.mol}^{-1}\text{s}^{-1}$ )	$\log k_{\text{rel}}$	$pK_a'$ in MeCN <sup>d</sup>
Hydrazine	$2.00 \times 10^{-3}$	0.0903 <sup>c</sup>	16.61
Morpholine	$8.12 \times 10^{-4}$	0.000	16.61
n-Butylamine	$2.14 \times 10^{-3}$	0.421	18.26
Ethylenediamine	$2.94 \times 10^{-3}$	0.559 <sup>c</sup>	18.46
Piperidine	$2.93 \times 10^{-2}$	1.558	18.92

a)  $1.667 \times 10^{-3}$  mol/l.b)  $2.0 \times 10^{-3}$ ,  $4.0 \times 10^{-2}$  mol/l.c)  $k_{\text{rel}}$  value was divided by 2 because of two nucleophilic centers on hydrazine.d) These values are taken from Coetzee and Padmanabhan.<sup>24</sup>

Since it is known that relative basicities are little affected by changing solvent from aqueous media to ethanol, the data in ethanol are plotted against  $pK_a$ 's of amines in water as shown in Fig. 1 which does not refer to the Michael addition data given in Table II. According to McDowell and Stirling,<sup>20</sup> this difference is caused by the change of solvation; namely primary amines are considered to be more hydrogen-bonded in ethanol and hence become bulkier than cyclic secondary amines which are hence more reactive than primary amines. The transition state of the Michael addition of amines is carbanionic character in such a rather polar solvent as ethanol, as shown below.



a) Imidazole b) Ammonia c) Monoethanolamine d) *n*-Butylamine  
e) Hydrazine f) Morpholine g) Piperidine

FIGURE 1 Brønsted Plot for the Reactions of Primary and Secondary Amines to *p*-Toluenesulfonyl Chlorides in Ethanol

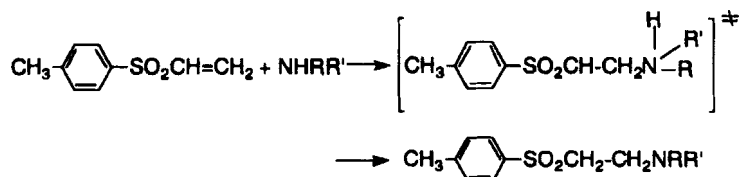


FIGURE 1 (continued)

Hydroxylamine and hydrazine obviously deviate from the line for normal primary amines and are more reactive than cyclic secondary amines.

Since the rates of addition of amines to *p*-tolyl vinyl sulfone in ethanol are mainly controlled by the number of branching on nitrogen atoms of amines, esters<sup>23</sup> while the aminolysis of *p*-toluenesulfonyl chloride was carried out in the same solvent,<sup>15</sup> it is difficult to claim the deviation of the plots of the rates of  $\alpha$ -nucleophiles from the line is large enough to be ascribed to the  $\alpha$ -effect.

However, if one assumes the solvation around primary amines can be nearly equal, then one may claim these deviations which line in Fig. 1 to be due to the  $\alpha$ -effect.

Meanwhile, the same reaction was carried out in acetonitrile to avoid unfavorable solvation. The rates obtained are listed in Table III. In Fig. 2, the second rate constants in acetonitrile are plotted against  $\text{pK}_a'$  values of amines in acetonitrile<sup>24</sup> as a Brønsted plot.

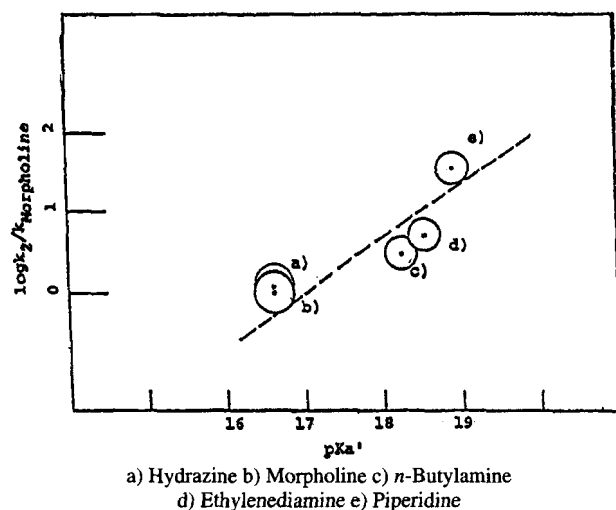
One finds in Fig. 2, that hydrazine shows a rather small rate enhancement. This unexpectedly small rate enhancement by hydrazine, as compared to the markedly large  $\alpha$ -effect observed in nucleophilic substitutions of esters, may be due to the small  $\beta$ value (the slope of the Brønsted plot) encountered in these reactions ( $\beta = 0.4$  in ethanol and  $\beta = 0.6$  in acetonitrile).

Generally, the  $\alpha$ -effect appears as a small rate enhancement in the bond forming step,  $\log k_{\text{rel}} \leq 10$ . For instance, in the addition of hydroperoxide  $\alpha$ -nucleophile to carbonyl bond of acetaldehyde and formaldehyde,  $k_{\text{HOO}}-/k_{\text{HO}}^-$  is  $\leq 10$ .<sup>25</sup> just as small  $\alpha$ -effect as in this Michael addition of hydrazine to *p*-tolyl vinyl sulfone. In contrast, in the alkaline hydrolyses of esters, the rate enhancement as observed by the ratio,  $k_{\text{HOO}}-/k_{\text{OH}}^- = 10^2$  is substantial.

## EXPERIMENTAL

### $\text{S}_{\text{N}}2$ Reaction of Benzyl Bromide

Benzyl bromide used for this reaction had bp 199 °C, while *p*-nitrobenzyl bromide (mp. 100 °C) was prepared by bromination of *p*-nitrotoluene.



$k_{rel}$  for hydrazine was divided by 2 because hydrazine has two nucleophilic centers.  
The  $pK_a'$  values are taken from Coetzee and Padmanabhan

FIGURE 2 Brønsted Plot for the Reactions of *p*-Tolyl Vinyl Sulfone with Amines in Acetonitrile at 40°C

Percent of ionization of hydrogen peroxide was calculated by the following formulae and the concentration of hydrogen peroxide was determined by iodometry.

$$\text{Percent of ionization} = 100/[1 + \text{antilog}(\text{pH} - \text{pK}_a)].$$

### Kinetic Measurement

All the kinetic measurements have been carried out in 50% acetone-water (by volume). The rate constant  $k_{HO^-}$  was obtained either with 0.0421 N sodium hydroxide or in the buffer solution, by monitoring eliminated bromide ion by the Volhard method. The reaction of benzyl bromides with hydroperoxide ion was carried out in 0.1N sodium carbonate solution, while pH of the solution in the reaction cell was also followed, and the mean value of hydrogen peroxide anion concentration from time initial to the desired time of kinetic measurement was used for calculation of  $k_{HOO^-}$ . Each run was repeated three times and  $k_{HOO^-}$  values were obtained according to the following equation,<sup>13a</sup> where  $k_1$  is the following pseudo-first order rate constant in the buffer solution and  $k_{HO^-}$  is second-order rate constant with sodium hydroxide.

$$k_{HOO^-} = [k_1 - k_{HO^-} \times [HO^-]/[HOO^-]]$$



### Michael Addition of Amines to *p*-Tolyl Sulfone

Materials used for this study were prepared according to the method applied by McDowell and Stirling,<sup>20</sup> or the method reported previously.<sup>10</sup> *p*-Tolyl vinyl sulfone used had mp. 66 °C (lit.,<sup>20</sup> 65-66 °C). The addition of the amine to *p*-tolyl vinyl sulfone to form the adduct was kinetically followed spectrophotometrically by monitoring the UV absorption of *p*-tolyl vinyl sulfone at 240m  $\mu$ . The rate are of first order dependence on the amine and of first order with respect to the concentration of the substrate, both in ethanol and in acetonitrile.

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