

13. Work done by Prof. C. T. Ahn, Hankuk Univ. of Foreign Studies, Seoul, Korea.
14. ^1H NMR(CDCl_3) 1.04(t, $J=7.3$ Hz, 3H, H-1), 1.15(t, $J=7.3$ Hz, 3H, H-6), 2.24(q, $J=7.3$ Hz, 2H, H-5), 2.36(s, 3H, methyl), 2.89(q, $J=7.3$ Hz, 2H, H-2), 7.15(d, $J=7.8$ Hz, 2H), 7.26(d, $J=7.8$ Hz, 2H); IR 1501, 1313 cm^{-1} ; MS, m/z (relative intensity), 251(84, M^+), 221(80),

- 177(35), 163(100), 123(32), 119(43), 79(64).
15. ^1H NMR(CDCl_3) for E-2-*p*-toluenethio-3-nitro-2-butene, 2.04(s, 3H, methyl) 2.30(s, 3H, methyl), 2.39(s, 3H, methyl), 7.20(d, $J=8$ Hz, 2H), 7.36(d, $J=8$ Hz, 2H); for Z-2-*p*-toluenethio-3-nitro-2-butene, 1.91(s, 3H, methyl), 2.32(s, 3H, methyl), 2.39(s, 3H, methyl), 7.18(d, $J=8$ Hz, 2H), 7.42(d, $J=8$ Hz, 2H).

The Effect of Polarizability on Reactivity

Dong-Sook Kwon, Kyung-Eun Choi, and Ik-Hwan Um*

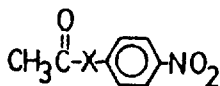
Department of Chemistry, Ewha Womans University, Seoul 120-750. Received July 18, 1989

As many as 17 factors have been suggested to be important in influencing nucleophilic reactivity,¹ and numerous relationships have been established to correlate nucleophilicity with one or more properties of the nucleophiles.² Polarizability has also been recognized as an important factor in determining nucleophilicity.³ The best known description based on polarizability is Pearson's concept of hard and soft acids and bases, the so-called HSAB principle.⁴

The discovery that acylated coenzyme A, an intermediate in many biochemical reactions, is a thiol ester has accelerated the kinetic and spectroscopic investigations of thiol esters.⁵ However, thionesters have not been studied intensively yet, largely due to their inaccessibility.⁶ Recently the development of synthetic methods for the thiocarbonyl compounds has encouraged their systematic investigation.⁷

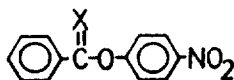
The replacement of oxygen atom by sulfur either in the carbonyl oxygen or in the ether-like oxygen in carboxylic esters has been reported to cause a significant increase in polarizability of the reaction center, and consequently to cause great differences in reactivity.⁸ Although scattered information on the effect of polarizability on reactivity is available,^{9,10} systematic studies have been lacking.

Thus we have prepared the following 4 esters (I, II, III, and IV) and performed kinetic studies of these esters with various nucleophiles of different nucleophilic atoms. Such a systematic change in the structure has been suggested to cause a significant difference in polarizability of the reaction center.⁸ Thus any reactivity change upon the systematic structural change would be interpreted as an effect of polarizability on reactivity.



I: X=O, PNPA (*p*-nitrophenyl acetate)

II: X=S, PNTPA (*p*-nitrothiophenyl acetate)



III: X=O, PNPB (*p*-nitrophenyl benzoate)

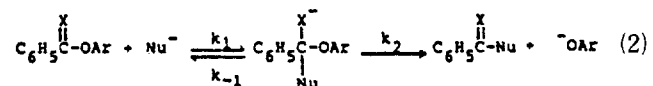
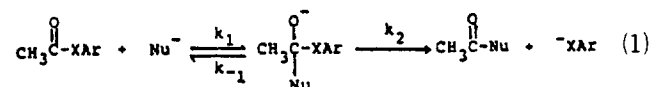
IV: X=S, PNPTB (*p*-nitrophenyl thionbenzoate)

Table 1. The second order rate constants (k , $\text{M}^{-1}\text{s}^{-1}$) for the reactions of the esters (I, II, III, and IV) with various types of nucleophiles at 25.0 °C

| Nu ⁻ | pKa (NuH) ^a | k, M ⁻¹ s ⁻¹ | | | |
|------------------------------|------------------------|------------------------------------|-------------------|------------------------|--------------------|
| | | I | II | III ^d | IV ^d |
| N ₃ ⁻ | 4.0 | 0.0342 | 0.853 | 0.00288 | 10.1 |
| CN ⁻ | 9.3 | 0.164 | 0.174 | 0.0698 | 0.0852 |
| <i>p</i> -ClPhO ⁻ | 9.38 | 0.683 ^b | 3.27 ^b | 0.144 | 2.20 |
| PhO ⁻ | 9.95 | 0.967 ^b | 3.77 ^b | 0.303 | 2.30 |
| OH ⁻ | 15.7 | 12.0 | 6.01 | 6.3 | 0.71 |
| | | | | 1.45 ^c | 0.172 ^c |
| <i>p</i> -ClPhS ⁻ | 7.50 | 0.143 | 42.7 | 0.02-0.03 ^e | 342 |
| PhS ⁻ | 7.80 | 0.36 ^b | 36 ^b | | |

^areference 13. ^breference 9. ^creference 10(a). ^dThe reactions for III and IV were performed in 10 mole % DMSO-H₂O mixture due to a solubility problem. ^eA large error might be expected due to a long reaction time which caused the oxidation of thiophenoxide to disulfide.

In Table 1 is presented a summary of the second-order rate constants for the nucleophilic substitution reactions, as shown in the following equation 1 and 2. The reaction mechanism of the present system has generally been suggested as a two-step reaction, *i.e.* the formation of a tetrahedral intermediate followed by the breakdown of it.^{2b-c,9,10}



It is clearly demonstrated in Table 1 that the effect of polarizability on the substrate reactivity is strongly dependent on the polarizability of nucleophiles. The reactivity of the sulfur containing substrates toward HO⁻ ion is decreased by two to ten folds when the substrate changes from I to II and from III to IV, respectively. On the contrary, the thiol

and thione esters show remarkable increases in reactivity toward sulfur centered nucleophile (*p*-ClPhS⁻), *i.e.* 300 to about 17,000 folds rate enhancements compared to the corresponding oxygen esters.

It is also interesting to note that the nucleophilicity decreases in the order of HO⁻ > PhO⁻ > CN⁻ > *p*-ClPhS⁻ > N₃⁻ for the oxygen esters (I & III), as expected from their pK_a values. However the nucleophilic reactivity order toward the thionester increases in order of CN⁻ < OH⁻ < *p*-ClPhO⁻ < PhO⁻ < N₃⁻ < *p*-ClPhS⁻, which is quite unexpected based on the Bronsted correlation. Although the basicity of *p*-ClPhS⁻ is over 8 pK_a unit lower than that of HO⁻, *p*-ClPhS⁻ is 45.6 folds more nucleophilic than HO⁻ toward the thionester.

Thus the present results seem to be consistent with the so-called HSAB principle, *i.e.* very polarizable *p*-ClPhS⁻ is highly reactive toward the polarizable substrate while relatively nonpolarizable HO⁻ shows an extremely low reactivity. The small reactivity change for N₃⁻ and aryloxy ions upon the substrate change is well understandable if one admits that their polarizability is not so great as that of the sulfur centered nucleophile.

Interestingly CN⁻ ion shows very little reactivity difference upon the structural change. Since CN⁻ has recently been suggested to be much softer than N₃⁻,¹¹ it would have been expected to be much more reactive than N₃⁻ toward the sulfur containing substrates on the basis of the HSAB principle. However experimental studies based on the data from free energy of transfer and solvent effect on rate have revealed that CN⁻ is not so polarizable¹² as was originally suggested based on calculation.^{4,11}

The present result seems to be consistent with the argument that CN⁻ is not so polarizable from the view point of the HSAB principle. However, one can not exclude the possibility that CN⁻ has showed an exceptional result in the present study. Also any changes in the rate limiting step, which have recently been a subject of controversy,^{2b-c,9,10,14,15} could be responsible for the present result. A more quantitative and mechanistic study is under way for a complete interpretation of the present work.

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References

1. J. F. Bunnett, *Annu. Rev. Phys. Chem.*, **14**, 271 (1963).
2. (a) M. J. Harris, S. P. McManus, Ed., *Nucleophilicity, Adv. Chem. Ser.*, American Chemical Society, Washington, D.C., 1986; (b) E. Buncl, S. S. Shaik, I. H. Um, and S. Wolfe, *J. Am. Chem. Soc.*, **110**, 1275 (1988); (c) E. Buncl, I. H. Um, and S. Hoz, *J. Am. Chem. Soc.*, **111**, 971 (1989).
3. (a) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962). (b) G. Bartoli and P. E. Todesco, *Acc. Chem. Res.*, **10**, 125 (1977). (c) T. L. Ho, "Hard and Soft Acids and Bases Principle in Organic Chemistry", Academic Press, New York, 1977.
4. R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
5. (a) J. Janssen, "The Chemistry of Carboxylic Acids and Esters", S. Patai Ed., Interscience Publishers, London, Chapt. 15 (1969). (b) D. J. Hupe and D. Wu, *J. Am. Chem. Soc.*, **99**, 7953 (1973).
6. For an example, CH₃C(S)Cl has not been synthesized yet even though its simple structure.
7. (a) A. B. Ghatas, E. A. El-Khirisy and S. O. Lowesson, *Sulfur Letter*, **1**, 69 (1982). (b) M. P. Cava and M. I. Levinson, *Tetrahedron*, **41**, 5061 (1985).
8. (a) S. Scheithauer and R. Mayer, *Chem. Ber.*, **98**, 838 (1965). (b) P. Y. Bruice and H. G. Mautner, *J. Am. Chem. Soc.*, **95**, 1582 (1973). (c) A. A. Neimysheva and I. L. Knunyants, *Dokl. Akad. Naur. USSR*, **181**, 888 (1968); Engl. Trans., p. 697.
9. D. J. Hupe and W. P. Jencks, *J. Am. Chem. Soc.*, **99**, 451 (1977).
10. (a) P. Campbell and B. A. Lapinskas, *J. A. Chem. Soc.*, **99**, 5378 (1977). (b) P. Campbell and N. T. Nashed, *Ibid.*, **104**, 5221 (1982).
11. R. G. Pearson, *J. Am. Chem. Soc.*, **110**, 7684 (1988).
12. A. J. Parker, *Chem. Rev.*, **69**, 1 (1969).
13. W. P. Jencks, F. Regenstein, In *Handbook of Biochemistry. Selected data for Molecular Biology*; H. A. Sober Ed., The Chemical Rubber Co., Cleveland, OH, 1968.
14. E. A. Castro and C. Ureta, *J. Org. Chem.*, **54**, 2153 (1989).
15. S. Ba-Saif, A. K. Luthra, and A. Williams, *J. Am. Chem. Soc.*, **109**, 6362 (1987).

Convenient Synthesis of Carboxylic Esters Using 2-Pyridyl Carbonates

Jae In Lee* and Sunggak Kim†

Department of Chemistry, Duksung Women's University, Seoul 132-031

†Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 130-012

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Carboxylic esters are usually prepared by the reaction of carboxylic acids or their derivatives with alcohols. However, only a few method have been reported on the derivation of

carboxylic esters from carboxylation of organic halides. Although reaction of Grignard reagents with methyl chloroformate,¹ diethyl carbonate,² and pentacarbonyl iron³ can af-