

can select  $10 - 6 = 4$  independent components of  $g_{ij}$ , say,  $g_{12}$ ,  $g_{22}$ ,  $g_{24}$  and  $g_{44}$ . The other components of  $g_{ij}$  can then be expressed in terms of  $g_{12}$ ,  $g_{22}$ ,  $g_{24}$ ,  $g_{44}$ . Interestingly this is not the situation in the polar coordinate system<sup>1</sup> or the cylindrical coordinate system<sup>2</sup>.

In the case of a polar coordinate system<sup>1</sup>  $g_{12} = g_{13} = g_{23} = g_{24} = g_{34} = 0$  and  $g_{11}$ ,  $g_{22}$ ,  $g_{44}$ ,  $g_{14}$  are functions of  $r$  and  $t$ ,  $g_{33} = g_{22} \sin^2 \theta$ .

For the cylindrical coordinate system  $g_{12} = g_{23} = g_{24} = 0$  and assume  $g_{13} = 0 \Rightarrow g_{11} = g_{33} = g_{22} r^2 = A$  and  $g_{44} = B$ ,  $g_{14} = C$ .

We then obtain (2) with

$$\begin{aligned} g_{24} &= (y/z)C, \quad g_{14} = (x/z)C, \quad g_{23} = (z/x)B, \\ g_{13} &= (z/y)B, \quad g_{11} = [(x/y) - (y/x)]B + A, \\ g_{33} &= [(z^2 - y^2)/xy]B + A, \end{aligned}$$

where  $g_{22} = A$ ,  $g_{12} = B$ ,  $g_{34} = C$  and  $g_{44} = D$ . After some adjustment the line element assumes the form

$$\begin{aligned} ds^2 &= [A - (y/x)B] (dx^2 + dy^2 + dz^2) + Ddt^2 \\ &+ 2C/z (xdx + ydy + zdz) dt \\ &+ [(B/xy)(xdx + ydy + zdz)^2], \end{aligned}$$

which is the form of Takeno<sup>1</sup> with

$$h_1 = [A - (y/x)B], \quad h_2 = B/xy, \quad h_3 = D, \quad h_4 = C/z.$$

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## STUDIES IN NUCLEOPHILIC SUBSTITUTIONS : II. REACTIONS BETWEEN ARYL ALKYL ETHERS AND HYDROBROMIC ACID

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THE acid cleavage of alkyl ethers is a reaction that can proceed by a  $A_2$  or  $A_1$  pathway depending on the nature of the alkyl substituent<sup>1,2</sup>. While there have been a number of kinetic studies on acid-catalysed

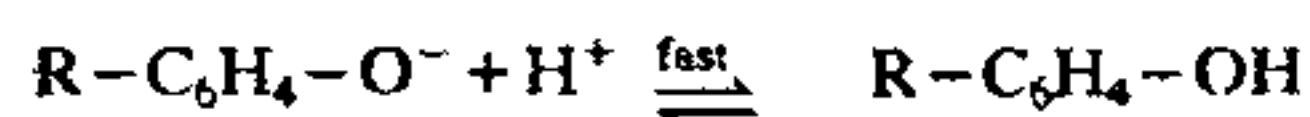
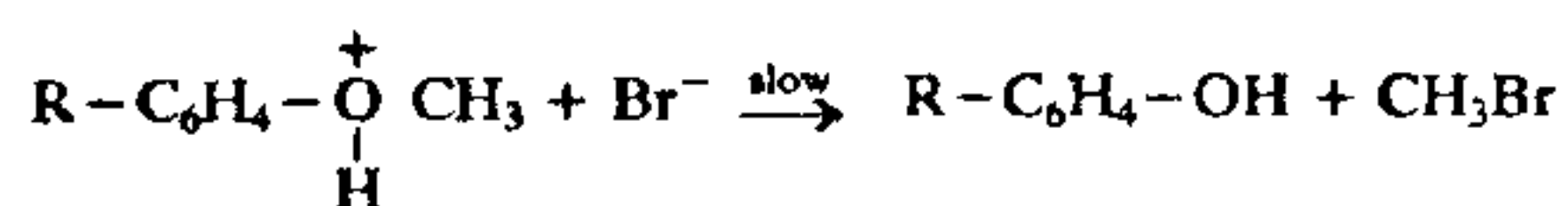
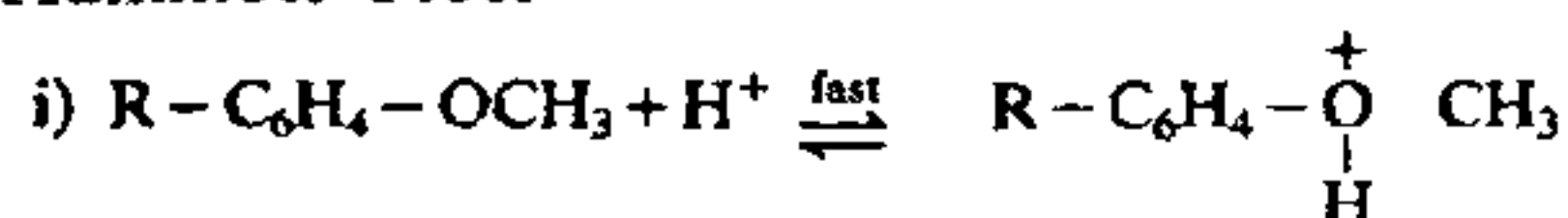
hydrolysis of dialkyl ethers, only a few investigations exist on aryl alkyl ethers. This system, with suitable modifications of the aryl system is eminently suited to study the structure-reactivity relationship in a displacement reaction. The results of such a kinetic study of the reaction between a number of substituted phenyl methyl ethers (anisoles) and HBr are now reported.

The kinetics of these reactions were followed by argentometric determination of unreacted HBr. The reaction between HBr and anisole is essentially one that follows the rate law

$$\frac{-d[\text{HBr}]}{dt} = k_2 [\text{anisole}] [\text{HBr}].$$

All the other substituted anisoles also obey a similar rate law. However, it is interesting to note that whatever be the substituent in the phenyl ring, each of the substituted anisoles reacts faster than the parent compound (table 1). The kinetic data, when subjected to a Hammett LFER analysis, yield a concave-up type of curve (figure 1). To our knowledge, this is the first instance of such a behaviour in the cleavage of aryl alkyl ethers. The splitting of halogen-substituted phenoxyacetic acid with hydriodic acid showed only a small substituent effect<sup>3</sup>, but certainly not such a dichotomy.

The biphasic plot is clearly indicative of competing mechanisms for the cleavage of these aryl methyl ethers. Although ethers cleavage can take place either by an  $A_1$  or  $A_2$  mechanism, the observed rate law and the nature of the alkyl ethers (primary) would rule out the unimolecular pathway. Therefore, the incidence of the biphasic plot has to be explained on the basis of subtle variations in one and the same mechanism. The following explanations are offered to explain the observed trend in the Hammett Plot.



The first of these two pathways would account for the left part of the plot (where the conjugate acid formation is facilitated by the electron-releasing substituents in the phenyl ring) and the second

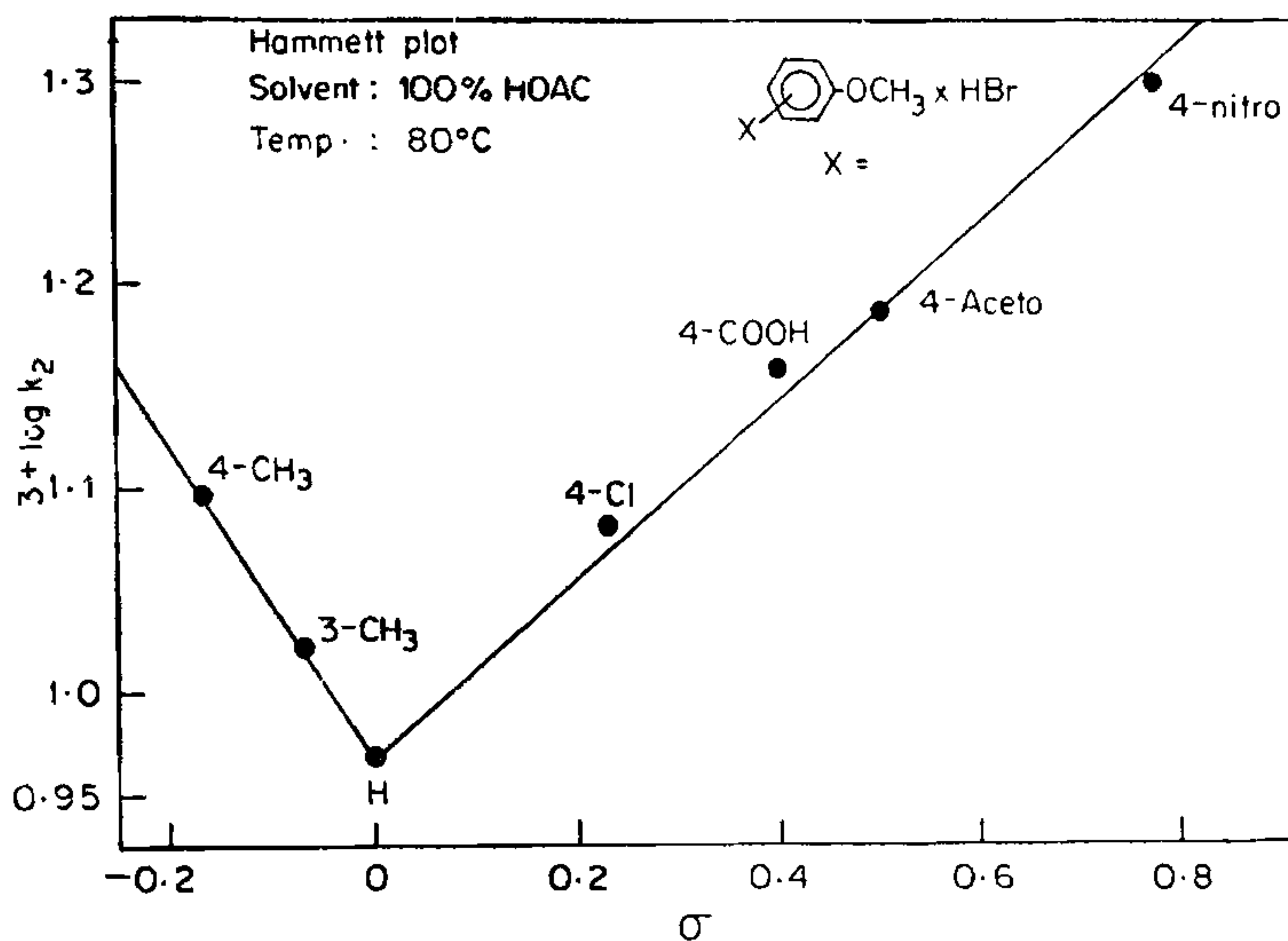


Figure 1.

Table 1 Second order rate constants for the reaction between substituted anisoles and HBr at 80°C in 100% HOAc

R-	$10^2 k_2$ lit mol <sup>-1</sup> min <sup>-1</sup>
H-	0.912
2-CH <sub>3</sub>	2.43
3-CH <sub>3</sub>	1.05
4-CH <sub>3</sub>	1.25
4-COOH	1.45
4-Cl	1.21
4-NO <sub>2</sub>	2.03
4-COCH <sub>3</sub>	1.51

[HBr] =  $9.49 \times 10^{-2}$ M, [Anisole] =  $5.51 \times 10^{-2}$ M

variation of the mechanism would explain the right side of the plot (where electron-withdrawing substituents like a -NO<sub>2</sub> group also accelerate the reaction because the *p*-NO<sub>2</sub>-phenoxide ion being a good leaving group gets displaced in a S<sub>N</sub>2 process quite easily).

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### HIGH-RESOLUTION SOLID-STATE CARBON-13 NUCLEAR MAGNETIC RESONANCE STUDY OF ACETAMINOPHEN: A COMMON ANALGESIC DRUG\*

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A variety of analytical techniques such as, infra-red (IR) spectroscopy, differential scanning calorimetry (DSC), X-ray powder diffraction, and other such methods are available for the study of solid state chemistry of drugs. However, only a few of them allow direct analysis in the tablet form. For example, among the IR and DSC methods which have been used to characterize crystalline forms, some forms known to be different show identical IR spectra and DSC properties. While, X-ray diffrac-

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