Indian Journal of Chemistry
Vol. 23A, October 1984, p. 883

Kinetic Evidence for Steric Enhancement of Resonance in Ti(III) Reduction of Substituted Methyl Phenyl Sulphoxides

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Received 1 *February* 1984; *accepted* 23 *April* 1984

The rates of Ti(III) reduction of some substituted methyl phenyl sulphoxides provide, yet another evidence for the phenomenon of steric enhancement of resonance. The rate of reduction of 3-chloro-4-methoxyphenyl methyl sulphoxide (**7**) is significantly higher than the value predicted on the basis of the additivity of group effects, indicating enhanced resonance interaction of methoxy and sulphinyl groups in **7** compared to that in 4-methoxyphenyl methyl sulphoxide (**2**). The enhancement of resonance interaction is still higher in 3-bromo-4-methoxyphenyl methyl sulphoxide (**8**) than that in **7**.

In this note further evidence is presented for the steric enhancement of resonance[1-13] from the data obtained on Ti(III) reduction of substituted methyl phenyl sulphoxides.

All the sulphoxides were prepared by known methods. The experimental details for the Ti(III) reduction of sulphoxides are given elsewhere[14].

p-Methoxyphenyl methyl sulphoxide (**2**) undergoes reduction about 2.7 times faster than methyl phenyl sulphoxide (**1**) (Table 1). This may be due to greater electron density at the sulphur in case of **2** caused by the resonance interaction of methoxy and sulphinyl groups. The observed rate constant for the reduction of 3-chloro-4-methoxyphenyl methyl sulphoxide (**7**) is significantly higher than the value calculated on the basis of the additivity of group effects, indicating that there is greater conjugative interaction of methoxy and sulphinyl groups in **7** than that in **2**. This enhancement of resonance is due to the steric effect of 3-chloro group (*ortho* to $-OCH_3$) which restricts the free rotation of the methoxy group, thereby increasing the probability of the latter to attain planarity with the benzene ring. It is also of interest to note that 3,5-dichloro-4-methoxyphenyl methyl sulphoxide (**6**) undergoes reduction at a rate slower than **2** (Table 1). In fact, the ratio of k_{obs}/k_{calc} in the case of **6** is far less than unity (Table 1) indicating that there is expected steric inhibition of resonance in **6**. It is further interesting to note that the ratio of k_{obs}/k_{calc} in 3,5-dichlorophenyl methyl sulphoxide (**5**) is almost unity indicating that the effect of groups is additive.

Table 1—Rate Constants for Reduction of Sulphoxides (**1-8**) by Ti(III)

Sulphoxide	$k_2 \times 10^2$ litre mol^{-1} sec^{-1}		k_{obs}
	Obs	Calc	k_{calc}
Methyl phenyl (**1**)	3.63	—	—
p-Methoxyphenyl methyl (**2**)	9.69	—	—
3-Chlorophenyl methyl (**3**)	1.56	—	—
3-Bromophenyl methyl (**4**)	1.55	—	—
3,5-Dichlorophenyl methyl (**5**)	0.73	0.67	1.08
3,5-Dichloro-4-methoxyphenyl methyl (**6**)	1.13	1.95	0.58
3-Chloro-4-methoxyphenyl methyl (**7**)	5.80	4.16	1.39
3-Bromo-4-methoxyphenyl methyl (**8**)	6.07	4.14	1.47

The steric enhancement of resonance is still higher in 3-bromo-4-methoxyphenyl methyl sulphoxide (**8**) presumably due to the greater steric effect of 3-bromo group as compared to that of 3-chloro group in **7**.

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