Asian Journal of Chemistry Vol. 5, No. 3 (1993), 524–527

Kinetics of Reduction of Some Nitrobenzenes—Evidence for Steric Enhancement of Resonance

M. KRISHNA PILLAY* and C. RANGASAMY
Department of Chemistry
Bharathidasan University
Tiruchirapalli-620 023, India

The kinetics of HCl-catalyzed reduction of some substituted nitrobenzenes with tin(II) chloride in 90% (v/v) aqueous ethanol at 30° have been studied. The observed rate constant of 4-methoxy-3-methyl-nitrobenzene is lower than the calculated value indicating that the 3-substituent enhances the resonance interaction between the methoxyl and nitro groups. This is due to steric enhancement of resonance (SER).

INTRODUCTION

The exalted conjugation between methoxyl or thiomethyl group and an electron-accepting group in the *para*-position of anisoles or thioanisoles, when a substituent is present *ortho* to the methoxyl or thiomethyl group is termed steric enhancement of resonance (SER)[1,2]. Kamlet and his coworkers[3] observed a similar phenomenon while studying the ultraviolet absorption spectra of some 1-alkyl-2,4-dinitrobenzenes. In the present work, the rates of reduction of some substituted nitrobenzenes with tin(II) chloride by hydrochloric acid in 90% (v/v) aqueous ethanol at 30°C have been determined and analysed with a view to getting additional evidence for SER. This is the first kinetic study on the reactivity of nitro group which has been used to get support for SER.

EXPERIMENTAL

Commercial samples of nitrobenzene (BDH) and 3-methyl-nitrobenzene were purified by distillation till their boiling points agreed with the reported values. 4-Methoxynitrobenzene was obtained by the methylation of 4-nitrophenol using dimethyl sulphate in alkaline solution. 4-Methoxy-3-methylnitrobenzene was prepared by the methylation using methyl iodide of 2-methyl-4-nitrophenol which was got by the nitration of *o*-cresol. 4-Methoxy-3,5-dimethylnitrobenzene was obtained by the methylation of 2,6-dimethyl-4-nitrophenol. The latter was got by the nitration of 2,6-dimethylphenol. Absolute ethanol was prepared as per literature procedure[4]. Alcoholic hydrochloric acid was prepared by making up 156 ml of hydrochloric acid (35%) to exactly 1 litre with alcohol (99%). The concentration

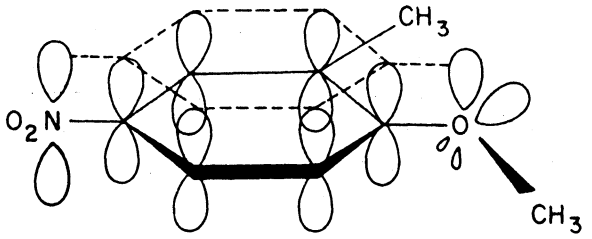
of the acid was confirmed by alkalimetry. The tin(II) chloride ($SnCl_2 \cdot 2H_2O$; BDH) solution was prepared by dissolving the crystals in ethanol (90%) containing 1.4512 M hydrochloric acid. The kinetics of the reaction was followed by determining the concentration of tin(II) chloride in the reaction mixture iodometrically. The details of the kinetics and mechanism are reported in the literature[5–8]. Duplication of our experimental runs revealed that the rate constant values were reproducible with an accuracy of ±3%.

RESULTS AND DISCUSSION

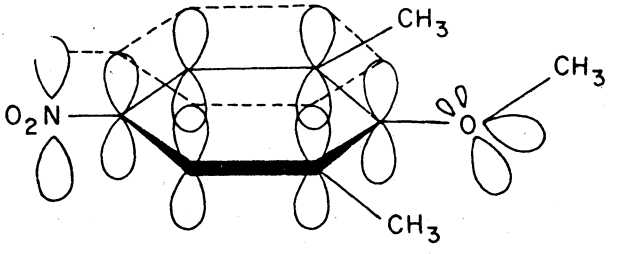
The rate constants at 30°C of some nitrobenzenes are given in Table 1. Nitrobenzene is reduced at a rate $1.28 \times 10^{-3}\ M^{-1}s^{-1}$. The rate is decreased by electron-donors in the benzene ring[5,6]. 3-Methylnitrobenzene has a rate constant of $1.14 \times 10^{-3}\ M^{-1}s^{-1}$. 4-Methoxynitrobenzene reacts almost 3.5 times ($k' = 0.38 \times 10^{-3}\ M^{-1}s^{-1}$) slower than nitrobenzene, the electron-releasing methoxyl group being responsible for this rate decrease. The rate of reduction of 4-methoxy-3-methyl-nitrobenzene is still lower ($k' = 0.30 \times 10^{-3}\ M^{-1}s^{-1}$) than that of 4-methoxynitrobenzene. This decrease in rate is not solely due to the 3-methyl group because the observed rate constant is about 12% lower than the value ($k' = 0.34 \times 10^{-3}\ M^{-1}s^{-1}$) calculated based on the principle of additivity of substituent effects[9]:

$$\log k'_{XY} = \log k'_X + \log k'_Y - \log k'_H$$

where k'_{XY} is the rate constant of disubstituted nitrobenzene, k'_X is that of 4-methoxynitrobenzene, k'_Y is that of 3-methylnitrobenzene and k'_H is that of nitrobenzene itself. This difference between the observed and calculated rate constants indicates that the 3-methyl group does not sterically inhibit the resonance interaction of the 4-methoxyl group with the aromatic ring but enhances it. the methyl of the methoxyl group seems to take an orientation *trans* to the 3-methyl group increasing the probability of its attaining planarity with the aromatic ring due to restricted rotation. In this conformation the lone pair orbital of oxygen is parallel to the *p*-orbitals of the aromatic carbons as shown in I. Compared to a free rotating $-OCH_3$ group, the coplanar $-OCH_3$ group utilizes its lone pair orbital for more effective overlap with the benzene orbital. In other words, there is enhanced conjugation between this coplanar $-OCH_3$ group and the nitro group. While a single substituent *ortho* to the methoxyl group enhances its resonance interaction with the *para*-substituent, the two *ortho*-substituents prevent the methoxyl group from attaining planarity with the benzene ring and diminish the conjugation with the ring as shown in II. In this geometry the $-OCH_3$ group lies in a plane which may be perpendicular to the plane of benzene ring. Neither of the two lone pair orbitals of oxygen is parallel to the *p*-orbital of aromatic carbons.



(I)



(II)

In this situation the conjugative ability of $-OCH_3$ group should be much less than that of free-rotation methoxyl group in 4-methoxynitrobenzene. Based on this reasoning it is expected that 4-methoxy-3,5-dimethylnitrobenzene should react at a faster rate than 4-methoxynitrobenzene. The rate constant of 4-methoxy-3,5-dimethylnitrobenzene is $0.72 \times 10^{-3}\ M^{-1}s^{-1}$ while the calculated value is $0.31 \times 10^{-3}\ M^{-1}s^{-1}$, which is 55% less than the observed value. The conventional phenomenon of steric inhibition of resonance operates in this compound.

The results from the present study are in complete conformity with the conclusion reached by the earlier workers[1,2], namely a single substituent *ortho* to methoxyl group enhances its resonance interaction whereas two substituents at both the o^{-}-positions inhibit the resonance interaction.

TABLE 1
RATE CONSTANTS FOR REDUCTION OF NITROBENZENES BY TIN(II) CHLORIDE IN 90% (V/V) EtOH AT 30°C

Substrate	$k' 10^3\ M^{-1}s^{-1}$
Nitrobenzene	1.28
3-Methylnitrobenzene	1.14
4-Methoxynitrobenzene	0.38
3-Methyl-4-methoxynitrobenzene	0.30(0.34)*
3,5-Dimethyl-4-methoxynitrobenzene	0.72(0.31)*

*Calculated values

REFERENCES

1. V. Baliah and M. Uma, *Tetrahedron Letters.*, **25**, 21 (1960).
2. V. Baliah, V. Premsagar, R. Krishnakumar and R. Jeyaraman, *Indian J. Chem.*, **B27**, 151 (1988).
3. M.J. Kamlet, J.C. Hoffsommer and H.G. Adolph, *J. Am. Chem. Soc.*, **84**, 3925 (1962).
4. A.I. Vogel, A Textbook of Practical Organic Chemistry, E.L.B.S. and Longman Group Ltd., p. 166 (1971).
5. W.K. Xing and Y. Ogata, *J. Org. Chem.*, **48**, 2515 (1983).
6. _____, *J. Org. Chem.*, **47**, 3577 (1982).
7. H. Goldschmidt and K. Ingebrechtsen, *Z. Phy. Chem.*, **48**, 435 (1904).
8. O. Manabe and H. Hiyma, Kongyo Kagatu Zasschi., **56**, 365 (1953).
9. H.P. Crocker and B. Jones, *J. Chem. Soc.*, 1808 (1959).

(*Received*: 19 October 1991; *Accepted*: 10 October 1992) AJC-480