

Polarographic studies on the quantitative treatments of substituent effects of some aromatic isothiocyanates

WAHID U MALIK, R N GOYAL and SUDHA TYAGI
Department of Chemistry, University of Roorkee, Roorkee 247 672

MS received 19 August 1978; revised 20 November 1978

Abstract. The polarographic reduction of aromatic isothiocyanates takes place in a single 4e reduction wave in the B.R. buffers of pH 4·6–10·0. The limiting current is diffusion controlled and the waves are irreversible in nature. The half wave potential and limiting current are independent of pH. The reduction in these compounds occurs at -N = C = S group and the effect of substituents has been interpreted in the terms of Hammett equation. The value of specific reaction constant (ρ) is found to be 0·12 V and the positive sign of ρ indicates the nucleophilic nature of the reduction.

Keywords. Polarography ; reduction ; aromatic isothiocyanates ; Hammett equation.

1. Introduction

The study of aromatic isothiocyanates, the esters of iso or pseudothiocyanic acids, is quite interesting due to their presence as glucosides of amino thiocarbonic acid in various plants (Senning 1972). They have been proved invaluable as the flavor constituent of condiments such as mustard and horseradish. Isothiocyanates possess antibiotic and antifungal properties (Virtanen 1962) are cytotoxic and cancerostatic (Horokova *et al* 1976) and protect plants against parasites (Robinson 1963). Literature survey revealed that most of the studies made so far deal with aliphatic isothiocyanate (Zahradnik 1955, 1959) and systematic polarographic studies on aromatic isothiocyanates have attracted little attention.

The aim of the present work was to investigate the mechanism to determine the reduction of these compounds at d.m.e. and the effect of substituents on $E_{1/2}$. For this purpose, only *m*- and *p*-substituents are chosen in these studies; ortho derivatives are excluded as they offer steric hindrance to coplanarity.

2. Experimental

The synthesis of aromatic isothiocyanates (I–VIII) was carried out in the laboratory by the standard methods (Antos 1960; Kristian 1961a, b) and the products were checked for their purity by melting point determination and by T.L.C.

For polarographic analysis the stock solutions (3×10^{-3} M) of all these compounds were prepared in dimethylformamide. The B.R. buffer solutions used for polarography in the pH region 2–10 were prepared by adding suitable amounts of 0.2M NaOH solution in a stock B.R. buffer solution (pH 1.8) composed of A.R. boric acid, phosphoric acid and glacial acetic acid.

3. Apparatus and procedure

A cambridge pen recording polarograph was used for recording the polarograms at $30^\circ \pm 0.1^\circ$ C. The capillary characteristic was $2.040 \text{ mg}^{2/3} \text{ S}^{-1/2}$. 1M solution of potassium chloride (A.R.) was used as supporting electrolyte. The value of pH of the buffer solutions were measured with a ELICO LI 10 pH meter using glass electrodes. The polarographic measurements were carried out in the solution composed of 9.0 ml buffer, 2.0 ml compound and 1.0 ml KCl solution after removing oxygen of the solution by purified nitrogen. The value of n , number of electrons involved in the reduction were determined by millicoulometric method of De Vries and Kroon (1953) using a mercury pool cathode and methanolic azobenzene as a reference. The equation used was

$$n_2 = n_1 \left(\frac{\Delta i_d(\text{cad})}{i_d(\text{cad})} \right) \left(\frac{i_d(\text{sub})}{\Delta i_d(\text{sub})} \right) \frac{V_1 C_1}{V_2 C_2}$$

where the symbols have their usual significance. The temperature coefficient was determined by Nejedly's (1922) method.

4. Results and discussion

It is found that all these compounds reduce in a single $4e$ transfer wave besides the hydrogen wave at -1.6 V. Typical polarograms are depicted in figure 1. The nature of the wave is found to be diffusion-controlled as the wave heights are proportional to the square root of the mercury reservoir height (figure 2) as well as

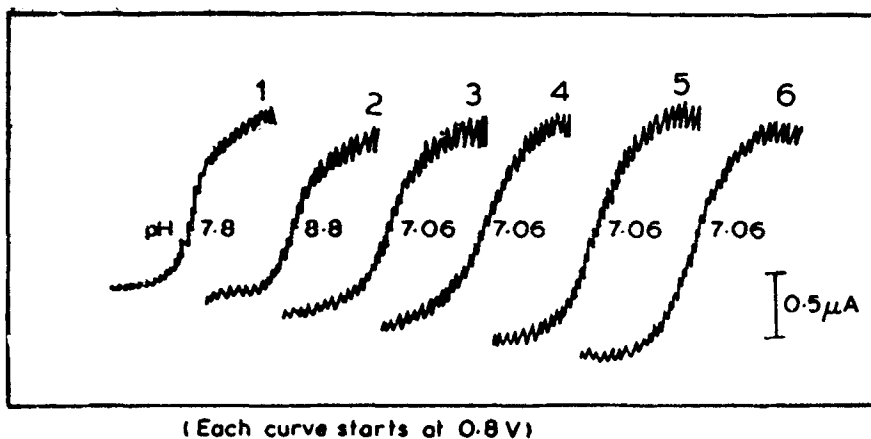


Figure 1. Typical polarograms of aromatic isothiocyanates.

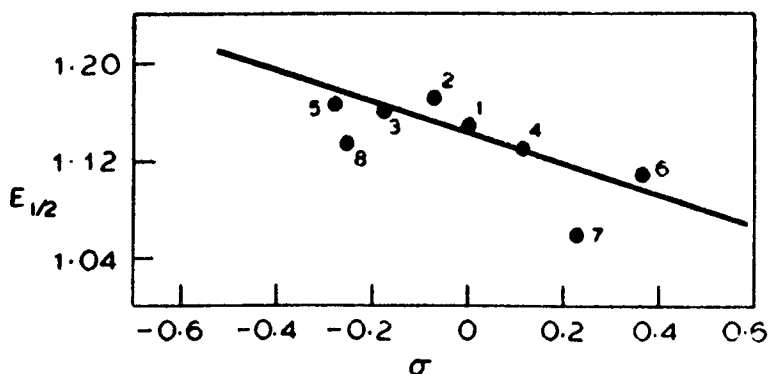


Figure 2. Dependence of half wave potential of aromatic isothiocyanates in BR buffer pH 7.06 on Hammett substituent constant.

Table 1. Polarographic characteristics of phenyl isothiocyanates at pH 7.06, $C = 2.0 \times 10^{-4} M$

Sl. No.	R	$-E_{1/2}$ (V)	i_d , μA	$\Delta E_{1/2}$ (V)	an	I	σ
1.	H	1.15	1.30	0.00	0.66	3.18	0.00
2.	3-CH ₃	1.18	1.40	0.06	0.67	3.43	-0.07
3.	4-CH ₃	1.16	1.05	0.01	0.66	2.57	-0.17
4.	3-OCH ₃	1.13	1.50	-0.02	0.66	4.41	+0.11
5.	4-OCH ₃	1.16	1.42	0.01	0.66	3.48	-0.27
6.	3-Cl	1.12	1.25	-0.03	0.66	3.06	+0.37
7.	4-Br	1.06	1.00	-0.11	0.66	2.45	+0.23
8.	4-OC ₂ H ₅	1.13	1.30	-0.04	0.66	3.18	-0.25

$$I = \frac{i_d}{C_m^{2/3} t^{1/6}}$$

to the concentration of the depolarizer (1.0×10^{-4} to be $2.5 \times 10^{-4} M$) in the pH range 4.6–10.0. Studies below pH 4.60 were not possible due to mixing of the reduction wave with hydrogen wave. The characteristics of the waves are shown in table 1.

The half wave potential of all these compounds is shifted to negative potential with increase in concentration of depolariser suggesting thereby the irreversible nature of the waves. The irreversibility of the waves was further confirmed by log plots (Meites 1967). Contrary to the result of Vlachova *et al* (1962) for all the compounds studied, the wave height and half wave potentials are practically independent of pH (table 2). Such a pH independence of half wave potential for irreversible reduction suggests that no proton transfer in these processes occurs before the slow electron transfer step. The general sequence of electrons and protons involved, therefore, may be (e, H^+ ; e, H^+) or (e, e ; H^+, H^+). Similar behaviour of pH on $E_{1/2}$ at values higher than the corresponding pK values (~ 5.0) has been reported by other workers (Vlachova *et al* 1962) in alkyl and aryl isothiocyanates. Vlachova *et al* (1962) have suggested that reduction of

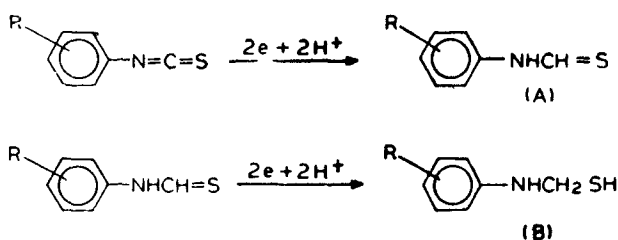
Table 2. Polarographic characteristics of phenyl isothiocyanates at different pH and at concentration $2.0 \times 10^{-4} M$.

Sl. No.	R	pH = 4.60		pH = 7.06		pH = 7.86		pH = 8.80		pH = 10.0	
		$-E_{1/2}, V$	$i_d \mu A$	$-E_{1/2}, V$	$i_d \mu A$	$-E_{1/2}, V$	$i_d \mu A$	$-E_{1/2}, V$	$i_d \mu A$	$-E_{1/2}, V$	$i_d \mu A$
1.	H	1.17	1.27	1.15	1.30	1.17	1.35	1.16	1.35	1.18	1.27
2.	3-CH ₃	1.19	1.57	1.18	1.40	1.20	1.55	1.20	1.60	1.20	1.60
3.	4-CH ₃	1.17	1.20	1.16	1.05	1.15	1.05	1.17	1.00	1.18	1.00
4.	3-OCH ₃	1.14	1.42	1.13	1.50	1.14	1.38	1.15	1.35	1.15	1.42
5.	4-OCH ₃	1.12	1.42	1.16	1.42	1.15	1.30	1.16	1.50	1.16	1.50
6.	3-Cl	1.10	1.30	1.12	1.25	1.12	1.35	1.14	1.30	1.14	1.05
7.	4-Br	1.03	1.00	1.06	1.00	1.05	1.00	1.06	1.10	1.05	1.05
8.	4-OC ₂ H ₅	1.10	1.30	1.13	1.30	1.12	1.30	1.12	1.30	1.11	1.25

isothiocyanates in acidic medium occurs in two $2e$ steps and in alkaline medium in a single $4e$ step. However, in our case a single $4e$ step was observed in the acidic as well as in the alkaline range.

5. Mechanism of reduction

The reduction in these compounds is possible either at $N=C$, $C=S$ or at both the sites. As the reduction of either of the two sites will require only $2e$, it can be assumed that reduction takes place at both the sites. The following general mechanism in which thioformanilide (A) is an intermediate compound, which on subsequent uptake of two electrons gives the final product, mercapto-N-methylaniline (B), can be proposed for these compounds



A similar mechanism has also been suggested by Lund (1959) and other workers (Vlachova *et al* 1962) for the reduction of isothiocyanates.

The quantitative effect of substituents on the $E_{1/2}$ for this series of compounds is expressed by the application of Hammett equation. As the general conditions (Zuman 1967) for the applicability of Hammett equation are fulfilled, the $E_{1/2}$ of the compounds are plotted against Hammett substituent constant. The values of the constants are selected from the collective review of Jaffe (1953). A linear relationship (figure 3) was observed when $E_{1/2}$ for different substituents were plotted against Hammett substituent constant (σ). It was observed that except 4-Br all other derivatives *m*- and *p*-fit in the straight line. In contrast to earlier

work (cf. Vlachova *et al* 1962) the higher value of specific reaction constant ($\rho = 0.12$ V) in alkaline media suggested that the substituents appreciably affect the reduction probably due to inductive effect of substituents. The positive-value of specific reaction constant (ρ) 0.12 V provides support to the nucleophilic mechanism of the reaction (electron uptake as potential determining step).

References

- Antos K 1960 *Chem. Zvesti* **14** 187
De Vries T and Kroon J L 1953 *J. Am. Chem. Soc.* **75** 2484
Horokova K, Drobnička L, Némec P, Antos A and Kristian P 1968 *Neoplasma* **15** 169
Jaffe H H 1953 *Chem. Rev.* **53** 1991
Kristian P 1961a *Chem. Zvesti* **15** 333
Kristian P 1961b *Chem. Zvesti* **15** 815
Lund H 1959 *Acta Chem. Scand.* **13** 249
Meites L 1967 *Polarographic technique* (New York : Interscience)
Nejedlý V 1922 *Coll. Czech. Chem. Commun.* **1** 319
Robinson T 1963 *The organic constituents of higher plants, their chemistry and inter-relationships* (Minneapolis : Burgess Pub. Co.)
Senning A 1972 *Sulfur in organic and inorganic chemistry* (New York : Marcel Dekker) Vol. 2
Vlachova D, Zahradník R, Antos K, Kristian P and Hulka A 1962 *Coll. Czech. Chem. Commun.* **27** 2826
Virtanen A I 1962 *Angew. Chem. Int. Engl. Ed.* **1** 299
Zahradník R 1955 *Chem. Listy* **49** 764
Zahradník R 1959 *Coll. Czech. Chem. Commun.* **24** 3407
Zuman P 1967 *Substituent effects in organic polarography* (New York : Plenum)