BEHAVIOUR OF BENZYL TRIMETHYL AMMONIUM IODIDE AND BENZAL ACETONE AT DME

R. Sivakumar, N. Satyamurthy and T.K. Venkatachalam

Department of Chemistry, PSG Arts College, Coimbatore-14

(Received Jan. 31, 1977: accepted March 5, 1977)

A polarographic study using benzyl trimethyl ammonium iodide unfolds its usefulness as an indifferent electrolyte at high negative potentials (-2.4V). The polarographic behaviour of benzalacetone shows the formation of benzaldehyde and acetone in alkaline medium through ketol formation. In general, the behaviour of benzalacetone is comparable with that of many other unsaturated ketones at DME.

The use of tetramethyl, ethyl and butyl quaternary ammonium iodides, hydroxides, bromides and chlorides is well known in polarographic works. The tetra methyl ammonium compounds, however, are much better than the tetraethyl compounds, since, the former gets reduced at a higher negative potential than the latter by 0.2 V[1,2]. Polarographic reduction potentials of quaternary ammonium ions have been widely studied [3-10]. But there has been no report on the polarographic studies using benzyl trimethyl ammonium iodide as supporting electrolyte, though Supin[11] reports benzyl triethyl ammonium chloride as a supporting electrolyte for polarographic studies. Benzal acetone at DME has been studied by many workers[12-23], but a comparative study in different media reveals striking results and these are correlated with structure in this communication.

EXPERIMENTAL

Benzyl trimethyl ammonium iodide was prepared by usual methods purified by crystallization and then dissolved in double distilled conductivity water to a concentration of 0.05 M. For the neutral medium studies 25 ml of the Solution has been taken in a polarographic cell. The polarograms were taken in an automatic Sargent-Welch polarograph with voltage range selector at O to -3V (vs SCE) and sensitivity at 0.400 μA/mm. The droptime was maintained at 10 seconds.

For acid medium studies, 10 ml of 0.2 M acetic acid was added to 25 ml of the Solution. For alkaline medium 10 ml of 0.4 M NaOH was added. All the polarograms were recorded at 27±1°C.

For benzalacetone studies, the compound was prepared[24] using benzaldehyde and acetone. Exactly 10^{-4} M solution of the above compound was prepared in 20% EtOH. For basic medium studies 25 ml of 1.6 M NaOH and 10 ml of 10^{-4}M benzalacetone in 20% EtOH was used[20]. The sensitivity was kept at 0.010 μ A/mm and for acid medium studies (using 25 ml of 0.2 M ACOH + 10 ml of 10^{-4}M benzalacetone), at 0.060 μA/mm. The neutral medium studies were conducted using 0.05 M tetraethyl ammonium iodide as supporting electrolyte at 0.040 μA/mm sensitivity. Nitrogen gas was bubbled and all the polarograms were taken in an inert atmosphere.

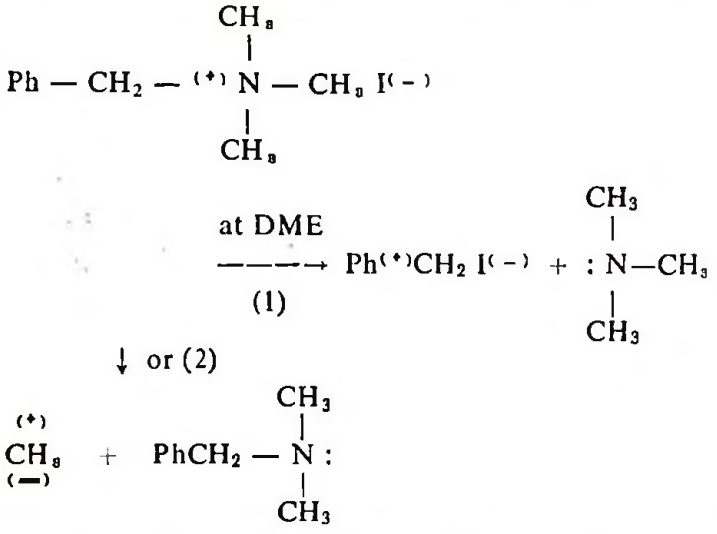
RESULTS AND DISCUSSIONS

Table I presents the $E_{\frac{1}{2}}$ values of several quaternary ammonium compounds and their structure. It also gives the values obtained for benzyl trimethyl ammonium iodide when used as an indifferent electrolyte in all the three media. It has been found that in acidic and neutral media it gives a reduction wave with an $E_{\frac{1}{2}}$ value of -2.3 V (Vs SCE). The curve commences at about -1.9 V and proceeds for the complete reduction. In basic medium, the $E_{\frac{1}{2}}$ for the compound has been found to be more negative, around - 2.46 V. In acid medium two waves are observed with $E_{\frac{1}{2}}$ value of -1.575 V and -2.30 V respectively. But in neutral and basic medium, only one wave was spotted.

TABLE — I Polarographic Half Wave potentials of Quaternary ammonium compounds

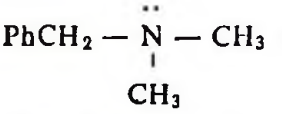
(+) ion	(—) ion	$-E_{\frac{1}{2}}$ (SCE)	
NH_4^+	Cl^-	2.21	
$H\overset{(+)}{N}(CH_3)_3$	Cl^-	2.23	
$\overset{(+)}{N}(C_2H_4OH)_3\,C_2H_5$	Br^-	2.38	
$\overset{(+)}{N}C(C_6H_7)_4$	I^-	2.52	
$\overset{(+)}{N}(C_4H_9)_4$	I^-	2.57	
$\overset{(+)}{N}(CH_3)_3C_2H_4OCOCH_3$	Cl^-	2.64	
$\overset{(+)}{N}(C_2H_5)_4$	Br^-	2.67	
$\overset{(+)}{N}(CH_3)_3C_2H_4OH$	Cl^-	2.72	
$\overset{(+)}{N}(C_3H)_4$	Br^-	2.93	
$\overset{(+)}{N}(CH_3)_3CH_2Ph$	I^-	2.30	(Neutral & Acidic)
,,	,,	2.46	(Basic)

The change in the reduction potential for the same compound in different media may be attributed to the pH variation. In acid medium probably the reaction path may be different compared with basic and neutral medium. During the process of reduction at DME it is likely that tetraalkyl ammonium ions yield an amine and hydrocarbon according to the following scheme.



Formation of $PhCH_3$ and $:N(CH_3)_3$ or $PhCH_2-\underset{\cdot\cdot}{N}(CH_3)_2$

and CH_4 may take place at DME during the process of reduction. But it is very difficult to decide which one of the two pairs will be formed in the system under study. A similar ambiguity was experienced[3] where a compound of the type $(C_6H_5)(C_2H_5)N^{(+)}(CH_3)_2\ Y^{(-)}$ was taken and it was impossible to decide whether the single reduction observed was that of ethyl or that of the phenyl radical. If we consider the stability aspect, $PhCH_2^{(+)}$ (which will be more stable) has to be formed preferentially. It was also observed during the course of this investigation that as time progressed the solution became coloured, maybe due to the formation of



or : $N(C_3H)_3$ or iodine itself.

Since in basic medium, it has a higher negative potential range it can be safely used as an indifferent electrolyte during polarographic investigations. The $E_{\frac{1}{2}}$ value was also lying in the same region as that for other quaternary ammonium compounds reported by earlier workers.

Polarographic studies conducted on benzalacetone in different media resulted in a number of striking observations. Table II projects the information concerning the $E_{\frac{1}{2}}$ values obtained for benezalacetone when studied at different intervals of time and the i_d values obtained each time. In neutural, acid and basic media two waves were observed. As time progressed the $E_{\frac{1}{2}}$ value of the second wave was found to increase in basic medium and decrease in acid medium and almost remain constant in the neutral medium. In McI lavine buffer the $E_{\frac{1}{2}}$ values for benzal acetone was found to be -1.33 V at neutral pH range ($\cong 7.2$) and the value obtained in the present study, using tetraethylammonium iodide as supporting electrolyte, was around -1.32V. Kolthoff and Lingane[26] have likewise reported that benzalacetone gave two waves at neutral pH ranges. The pH for our study was around 6.9.

A glance at the values at different intervals of time reveal a change in some media. It is known that in neutral medium bimolecular reduction with accompaniment of formation of the saturated compound in varying amount has been observed. Hence the reaction sequence can be stated as follows which is in good agreement with results of previous workers[26].

$$R-CH=CH-CO-R + 2e^- + 2H^+ \rightarrow RCH_2CH_2COR$$

In the case of benzalacetone in neutral medium,

$$C_6H_5CH=CHCOCH_3 + 2C^- + 2H^+ \rightarrow C_6H_5CH_2CH_2COCH_3$$

In acid medium studies (pH 4 – 5) two waves were observed with $E_{\frac{1}{2}}$ values at -0.45 V and -1.29 V respectively. But the $E_{\frac{1}{2}}$ values of both waves decreased slowly as time progressed. In acid medium it is possible that the reduction proceeds by a 1,4 bimolecular mechanism to give a dimeric ketone as per the following mechanism :

$$2\ Ph\ CH=CHCOCH_3 \xrightarrow[2H^+]{2e^-} \begin{matrix} Ph-CH-CH_2-COCH_3 \\ | \\ Ph-CH-CH_2-COCH_3 \end{matrix}$$

The amount of dimeric ketone varies as time progresses and hence slowly the reduction wave of original compound may be shifted to some other $E_{\frac{1}{2}}$ values. The above argument of formation of dimeric ketone in the acid medium is akin to the observation that benzalacetophenone at pH 1.3 produces only bimolecular ketone[26].

In basic medium studies (pH = 12), formation of saturated ketone similar to neutral medium is contemplated. In basic medium the $E_{\frac{1}{2}}$ values were found to be – 0.48 V and – 1.29 V respectively. As time progressed, the $E_{\frac{1}{2}}$ was found to shift to more negative values. This is exactly the reverse of what has been observed in acid medium, In basic medium, the ketol formation has to be accounted for, as time progressed It is likely that the ketol formed in the case of benzalacetone is unstable and is converted into benzaldehyde and acetone in the medium. For the reaction of benzalacetone with hydroxyl ions, deviations from simple first order kinetics were observed[27] at higher conversions. Nevertheless, these deviations might be affected by consequtive reactions. Hence the second wave produced in the basic medium may be due to benzaldehyde produced as follows :

$$H^+ + PhCH = CHCOCH_3 + OH^{(-)} \rightleftharpoons Ph-\underset{\underset{OH}{|}}{CH}-CH_2COCH_3$$

$$PhCH(OH)-CH_2COCH_3 \rightleftharpoons Ph-\underset{\underset{O}{\|}}{C}-H + CH_3COCH_3$$

The acetone formed in the above reaction may not be getting reduced in basic medium for want of supporting electrolyte (Supporting electrolyte used for acetone is usually tetraethyl ammonium iodide and the $E_{\frac{1}{2}}$ is —2.4 V). Hence the overall reaction in the case of basic medium using benzalacetone at DME can be represented as follows :

$$PhCH=CHCOCH_3 + OH^{(-)} \rightleftharpoons CH_3COCH^{(-)}CH-\underset{\underset{OH}{|}}{CH}-Ph \quad (1)$$

$$Ph-\overset{OH}{\underset{|}{CH}}-\overset{(-)}{CH}\,COCH_3 + H_2O \rightleftharpoons CH_3COCH_2\,\underset{\underset{OH}{|}}{CH}-Ph + OH^{(-)} \quad (2)$$

$$CH_3COCH_2-\underset{\underset{OH}{|}}{CH}-Ph + OH^{(-)} \rightleftharpoons CH_3COCH_2-\underset{\underset{O^{(-)}}{|}}{CH}-Ph + H_2O \quad (3)$$

$$CH_3\overset{\downarrow}{C}OCH_2-\underset{\underset{O^{(-)}}{|\uparrow}}{CH}-Ph \rightleftharpoons CH_3\overset{-}{C}OCH_2 + Ph-\underset{\underset{O}{\|}}{C}-H \quad (4)$$

$$CH_3\overset{(-)}{C}OCH_2 + H_2O \rightleftharpoons CH_3COCH_3 + OH^{(-)} \quad (5)$$

The structure of the starting compound may also be playing a role during reduction and $E_{\frac{1}{2}}$ value is also dependent on the structure. To relate inductive, resonance and steric contributions to the change in reaction rates during reduction process at DME, a more detailed study has to be undertaken using various substituted α, β unsaturated ketones.

ACKNOWLEDGEMENT : We are thankful to Principal Varadarajan. Prof. Sethu Rao, all colleagues and the Management of PSG Arts College for help and facilities provided. One of us (NS) is thankful to UGC for award of a fellowship.

TABLE –II Observed i_d and $E_{\frac{1}{2}}$ values for Benzal acetone at different times

	Neutral Medium (TEAI)				Acid Medium				Basic Medium			
	$\mu A/i_d$ Observed		$-E_{\frac{1}{2}}$		i_d Observed		$-E_{\frac{1}{2}}$		i_d Observed A		$-E_{\frac{1}{2}}$	
Time Min	Ist Wave	IInd Wave	Ist Wave	IInd Wave	Ist Wave	IInd Wave	Ist Wave	IInd Wave	Ist Wave	IInd Wave	Ist Wave	IInd Wave
0	1.88	3.32	0.51	1.32	1.72	3.30	0.45	1.29	1.53	1.45	0.48	1.29
15	1.88	3.40	0.30	1.35	1.76	3.44	0.39	1.11	1.60	1.62	1.24	1.74
30	1.80	3.44	0.33	1.39	1.88	3.36	0.36	1.06	1.55	1.59	1.14	1.65
45	1 88	3.41	0.30	1.32	1.82	3.56	0.33	1.05	1.45	1.70	1.14	1.65
60	1.88	3.48	0.30	1.29	—	—	—	—	1.50	1.68	1.14	1.64
75	1.88	3.40	0.29	1.29	1.80	3.56	0.24	0.93	—	—	—	—
105	1.92	3.36	0.28	1.30	1.72	3.51	0.18	0.81	—	—	—	—

REFERENCES

1 I. Zlotowski and I.M. Kolthoff, Ind Eng Chem Anal Edn 14, (1942) 473

2 M Von Stackelberg and W Stracke Z Electro chem 53, (1949) 118

3 Van Rysselberghe and JM Mcchee J Amer Chem Soc 67, (1945) 1039

4 F.L. Lambert Anal Chem 30, (1958) 1018

5 RJ Meakins J Appl Chem (London) 17 (6), (1967) 157

6 BC Southworth CA 55, (1961) 1267

7 BC Southworth, KD Fleischer et al Anal Chem 33, (1961) 208

8 B Jaselskis and H Diehl J Amer Chem Soc 80, (1958) 4197

9 F Cappehlina Ann Chem 50, (1960) 744

10 W Kemula and D Sybilska Roczniki Chem 26, (1952) 460

11 GS Supin Zh Analit Khim 17, (1962) 258

12 DM Coulson and WR Crowell J Amer Chem Soc 74, (1952) 1290

13 DM Coulson and WR Crowell J Amer Chem Soc 74, (1952) 1294

14 A Kolusheva and N Nino CA 66, 34243 j (1967)

15 IA Korshunov and Yu V Vodzinskii Zhur Fiz Khim 27, (1953) 1152

16 AH Cropp and H Letaw J Phys Chem 57, (1953) 964

17 R Pasternak Helv Chem Acta 31, (1948) 753

18 H Sato CA 52, (1958) 16089

19 H Sato CA 59, (1963) 3546

20 L Smith and F Takazawa Proc Iowa Acad Sci 51, (1944) 301

21 S Wawzonek and A Gundersen J Electro Chem Soc 111 (3), (1964) 324

22 S Wavzonek and HA Laitinen J Amer Chem Soc 63, (1941) 2341

23 H Adkins and FW Cox J Amer Chem Soc 60, (1938) 115

24 NL Drake and P Allen. Organic Synthesis (Second Ed) Coll Vol I, p 77, John Wiley, New York (1947)

25 "IM Kolthoff and J Lingane " Polarography " Vol II p 688 – Inter Science Publishers (1965)

26 IM Kolthoff and J Lingane "Polarography" Vol. II p 686 Inter-Science Publishers (1965)

27 P Zuman "Topics in Organic polarography" p 202 Plenum Press New York (1970)

WITH BEST COMPLIMENTS
FROM :

Duro Metochem Private Limited

Manufacturers of
'DUROFLEX' Adhesives, Stopping off Lacquer
Special Thinner & Metallic Stearates

'Nirlon House'
254-B, Dr. A. Besant Road, Worli,
Bombay-400025

Cable : 'DUROMET' Telephone : 457373