REDUCTION OF VINYL—QUINOLONES AT DROPPING MERCURY ELECTRODE

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The vinylquinolones showed three reduction waves and the difference in their $E_{\frac{1}{2}}$ values is attributed to the structural effects on the reduction mechanism. At neutral pH ranges the reduction was found to be very distinct in comparison with that observed in acidic and alkaline ranges. It may be reasonably assumed that the three stage reduction involves the 'Quinoline-,' the 'Oxo–' and the 'Vinyl–' moieties.

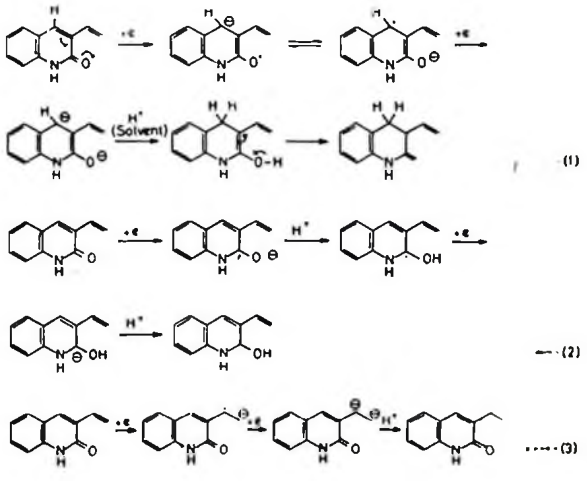
In connection with the synthesis of Furo–, Thieno and other similarly fused ring systems, Shanmugam et al[1] prepared several 3-vinyl-2-quinolones. Quinoline was reported[2] to produce three waves at DME in weakly acidic solution and two waves of equal height in neutral and alkaline media. A report by Stone[3] on the reduction of 2-quinolone (2-hydroxyquinoline) in borate buffer and in potassium chloride solutions indicated a single reduction wave at-1.9V. The reduction of quinoline and its derivatives has been studied at DME by several workers.[4–18] There are no previous reports on the electrochemical behaviour of quinolones possessing a vinyl group proximal to the oxo group. This communication presents the observations made on these vinylquinolones at DME and the probable mechanism of the reduction process.

Experimental

All the substituted quinolones were synthesised and purified according to the proce ure of Shanmugam et al[1] The quinolones were dissolved in twice-distilled methanol and the concentration was adjusted to 10^{-3} M. The reductions were carried out in solutions buffered with (i) 0.2M acetic acid and 0.2M sodium acetate, and (ii) 0.2M ammonium chloride and 0.2M ammonium hydroxide and in an unbuffered solution of 0.4M sodium hydroxide. Tetraethyl-ammonium iodide (0.05M) and Benzyltrimethyl-ammonium iodide (0.05M) were used as supporting electrolytes in all the cases. Dry oxygen-free nitrogen was bubbled through the solution prior to the experimentation Poloragrams were first run for the base electrolytes and then the reductions were carried out with vinylquinolones in methanol solution. Gelatin was added (1%) as 'maxima' suppressor. In order to attest that the solvent viz., methanol does not interfere in the reduction process, a trial polarogram of the solvent with the electrolyte was run. The droptime was maintained to be 5 seconds. The voltage range was fixed at 0 to-3V. The sensitivity was fixed at 0.06 A mm for all the polarograms. The experiments were counducted at room temperature of 27±1°C.

Results and Discussion

The half wave potential values in unbuffered as well as in buffered solutions using 0.05M tetraethyl-ammonium iodide and 0.05M benzyltrimethyl ammonium iodide as supporting electrolytes are summarised in the Table. In unbuffered solution three waves are obtained for most of the quinolones, the first wave being around-1.4V, second wave around -1. 9V and the third wave around-2.2V. The halfwave potential for the first wave corresponds to the value reported by Stonehill[5] for quinoline in 0.02N tetra-methylammonium chloride. The reduction occurring at-1.4V may be mechanistically viewed as in Reaction 1.



The second wave at 1-9V is assumed as being due to the reduction of the carbonyl group. 2-Quinolone has been reported[3] to be reducible polarographically and a reasonable wave was obtained in a borate buffer of pH 8 and in potassium chloride solution. In both the solutions the halfwave potential was the same viz., -1.9V. The reduction of the carbonyl group may be visualised as in Reaction 2.

The third wave obtained at -2.2 to -2.3V for the vinylquinolones is attributed to the reduction of the vinyl group which is similar to the situation obtained in styrene. The reduction potential of the double bond in styrene was reported[19] to be around –2.3V in 0.175M tetraethylammonium iodide and 75% dioxane and this halfwave potential is independent of pH. Based on the mehanisms suggested for the reduction of styrene[20] a possible one for the reduction of the vinyl group in vinylquinolones may be visualised as in Reaction 3.

The slight variation in the halfwave potentials of individual quinolones in the unbuffered solution may be due to the structural effects as were experienced by earlier workers[18], who studied the electrochemical behaviour of substituted quinoline carboxylic acid isomers.

The reduction of the vinylquinolones was tried in buffered solution containing sodium acetate and acetic acid at pH 3.7 and no characteristic reduction waves were observed.

From the table it is seen that the parent vinylquinolone gives only one wave with $E_{\frac{1}{2}}$ –1.88V at pH 8.0 whereas it has given three waves in unbuffered solution, thus indicating that the reduction is pH-dependent. This is similar to the observation of Given[4] who had pointed out that the reductions of Pyridine and Quinoline ring systems are pH - dependent.

Two well-defined waves are observed for vinylquinolones in buffered and unbuffered solutions using benzyltrimethylammonium iodide as supporting electrolyte and the $E_{\frac{1}{2}}$ values are listed in the table. In unbuffered solution, methoxy substituted vinylquinolone (III) has given three waves whereas other vinyl-quinolones studied gave only two waves. In buffered solution at pH 8 all the quinolones studied have given three reduction waves.

The reduction waves of vinylquinolones in acidic medium using benzyltrimethylammonium iodide as supporting electrolyte are not clear. Stock et al[16] did not get any reduction wave for quinoline derivatives in acidic medium. Hydrogen overvoltage during reduction of quinoline derivatives has been reported[16], but we did not observe hydrogen overvoltage in ourwork. Attempts are being made to separate and confirm the identity of the reduction products.

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REFERENCES

1. P. Shanmugam, R. Palaniappan, N. Soundararajan, T. K. Thiruvengadam and K. Kanagarajan, Monatsh Che. 107, 259 (1976) and references cited therein.
2. I. Tachi and H. Kabai J. Electrochem. Assoc. Japan 3, (1935) 250.
3. K. G. Stone, J. Am. Chem. Soc., 69, (1947) 1832.
4. P. H. Given, J. Chem. Soc., (1958) 2684.
5. R. C. Kaye and H. I. Stonehill, J. Chem., Soc., (1952) 3240
6. B. Lovrecek and D. Cipris, J. Electroanal. Chem. 11, (1966)44
7. M. Maturova, V. Preininger and F. Santavy CA, 62, (1965) 7620.
8. D. R. Norton, CA, 49, (1955) 11470.
9. C. Parkanyi and R. Zahradrik, Bull. Soc. Chem. Belges 73, (1964) 57.
10. J. Pech Collection – Czech. Chem. Commons, 6, (1934) 126.
11. A. G. Stromberg and T. M. Markacheva Zhur. Fiz. Khim. 28, (1954) 671.
12. J. T. Stock and F. J Pinchin, Chemistry and Industry, (1953) 1204.

13. J. T. Stock and F. J. Pinchin, Chemistry and Industry, (1954) 347.

14. E. Fornasari, G. Giacometti and G. Rigatti CA, 58, (1963) 1125.

15. A. Heyndrickx and R. Boven, J. of Pharm. Belg. 11, (1956) 13.

16. J. T. Stock, T. R. Williams and F. J. Pinchin, J. Chem. Soc., (1960) 3221.

17. M. K. Shchennikova and I. A. Kovschunov J. Phys. Chem. USSR 22, (1948) 503

18. J. T. Stock, T. R. Williams and F. J. Pinchin, J. Chem Soc. (1 60) 3221.

19. I. M. Kolthoff and J. J. Lingane, 'Polarography' Vol. 1, Interscience Publishers P 635.

20. a) S. Wawzonak and D. Wearring, J. Am. Chem. Soc. 81, (1959) 2067

b) M. Fleichmann and D. Pletcher in "Reactions of Molecules at lectrodes' Ed by N. S. Hush, Wiley-Interscience (London) 1971, p. 395.

Table 1. **Halfwave Potentials (Negative Volts) for Vinylquinolones**
Concentration of the Compound 10^{-3} M

Compound	Tetraethylammonium iodide as supporting electrolyte									Benzyltrimethyl ammonium iodide as supporting electrolyte					
	Unbuffered solution			ammonium chloride + amm. hydroxide, pH 8.			0.4M NaOH			Unbuffered Solution			Ammonium chloride + Amm. hydroxide, pH8		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
I*	1.34	1.91	2.3	1.88	–	–	1.54	1.84	–	1.46	1.94	–	1.32	1.87	2.35
II	1.41	1.91	2.27	1.49	1.95	2.17	1.48	1.74	–	1.37	2.01	–	1.40	1.92	2.30
III	1.41	2.12	–	1.38	2.01	–	1.66	–	–	1.46	1.76	2.1	1.33	2.02	2.40
IV	1.31	1.75	2.1	1.43	1.82	2.14	1.4	1.85	–	1.49	1.8	–	1.32	1.79	2.25

I*. 3—Vinyl—2—quinolone; II. 4—Methyl—3—vinyl—2 quinolone; III. 4—Methyl—7—methoxy—3—vinyl—2—quinolone; IV. 6, 7—Methylenedioxy—3—vinyl—2—quinolone

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