Tetrahedron. Vol. 26, pp. 1109 to 1114. Pergamon Press 1970. Printed in Great Britain

OXIDATIONS INVOLVING SILVER—VII

THE OXIDATION OF ALIPHATIC SECONDARY AMINES AT SILVER ELECTRODES IN ALKALI

N. A. HAMPSON,* J. B. LEE, J. R. MORLEY,† K. I. MACDONALD,
and B. SCANLON‡

Department of Chemistry, The University of Technology, Loughborough, Leicestershire.

(*Received in the UK* 18 *October* 1969; *Accepted for publication* 7 *November* 1969.)

Abstract—The results of experiments on the anodic oxidation of secondary amines at silver oxide electrodes are presented. The reaction differs significantly from the analogous reactions of primary amines. A reaction mechanism is proposed which involves the participation of a carbonium ion intermediate.

INTRODUCTION

THE use of silver in its higher valence states in the oxidation of organic functional groups is well founded.[1] In previous papers we have shown that high valent silver either as the picolinate,[2] or the oxide,[3] may act as a specific oxidising agent. Electrochemical and chemical studies show that primary amines are readily oxidized by 'AgO' in aqueous electrolytes.[4]

This paper describes a study of the oxidation of secondary amines at a silver electrode in alkali.

RESULTS AND DISCUSSION

(a) *Constant potential experiments.* The rate of oxidation of secondary amines at silver electrodes was found to be very slow. Typically currents of ~ 1 mAcm^{-2} were observed at the relatively high positive potential 0·75 V NHE.

The reaction rate appears to be dependent upon the branching of the alkyl substituents. For example, the rate of oxidation of $(n\ Bu)_2$ NH is 2–3 times greater than that of n-Bu-NH-t-Bu. It is not clear whether this difference reflects a difference in availability of reactant at the electrode interphase or an intrinsic difference in reaction rate constant. In this connection it must be emphasised that a certain lack of control always exists over conditions at the immediate electrode–electrolyte boundary due primarily to variation in electrode surface conditions and to a lesser extent to complex patterns of mass transport in soln. In the present experiments this is manifested as a certain lack of reproducibility in the relative amounts of products formed. In view of this a detailed kinetic analysis of results is not possible and the nature of the intermediate mechanisms must be deduced from the type of products obtained.

The products of oxidation are shown in Table 1. In addition to aldehydes and nitriles being formed we find products derived from carbonium ions. Thus for example $(n\text{-}Bu)_2$ NH yields in addition to n-PrCN and n-PrCHO the alcohol

---

* To whom communications should be sent.

† Present Addresses: Dupont Co. Ltd. (U.K.), Maydown Works, Londonderry, Ulster.

‡ Distillers Co. Ltd. (Research), Menstrie, Clackmannanshire, Scotland.

n-BuOH. Previous work[4] showed that the oxidation of corresponding primary amines followed the reaction path:

$$\underset{\text{I}}{RCH_2{-}NH_2} \xrightarrow{-2e,\ -2H^+} \underset{\text{II}}{RCH{=}NH} \xrightarrow{-2e,\ -2H^+} \underset{\text{III}}{RC{\equiv}N}$$

in which case the alcohol should not be formed, although hydrolysis of II may yield the aldehyde in certain circumstances.[4]

The oxidation mechanism in the case of secondary amines is clearly not analogous to that of primary amines. Specifically, in no case were Schiff bases (the analogue of II) found among the products of the oxidation, nor did the oxidation of Schiff base yield products (viz. alcohols) produced in the oxidation of secondary amines. These results are shown in detail in Table 2.

It is suggested that the mechanism of the oxidation of secondary amines is as follows:

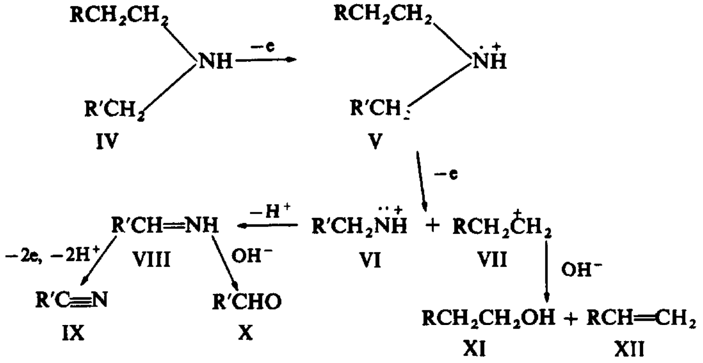


TABLE 1. PRODUCTS FROM THE ELECTROCHEMICAL OXIDATION OF SECONDARY ALIPHATIC AMINES AT SILVER ELECTRODES.
Supporting Electrolyte: 1·0 M NaOH; 23°; 0·75 V NHE.

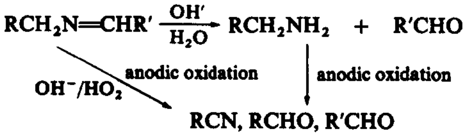
Amine	Products
$(Et)_2NH$	EtOH, MeCN, C_2H_4
(iso-Pr)$_2$NH	iso-PrOH
(n-Bu)$_2$ NH	n-PrCHO, n-PrCN, n-BuOH
n-Bu-NH-iso-Bu	n-PrCHO, iso-PrCHO, iso-PrCN, n-BuOH, iso-BuOH
n-Bu-NH-sec-Bu	n-PrCN, sec-BuOH, Butanone
n-Bu-NH-t-Bu	t-BuOH, n-PrCN

Thus the formation of products which can be attributed to the participation of carbonium ions can be explained if the intermediate V undergoes oxidative fission to produce VI and VII of which the latter is responsible for the appearance of alcohols (XI) and olefins (XII) in the reaction products. If such a mechanism operates V should *or* (would be expected to) be oxidised in such a manner that the most susceptible C—N bond undergoes fission (i.e. t-C-N sec-C-N n-C-N). This is reflected in the results shown in Table 1, for example the oxidation of n-Bu-NH-sec-Bu yields sec-BuOH and not n-BuOH, and similarly no n-BuOH is formed in the oxidation of n-Bu-NH-t-Bu.

TABLE 2. PRODUCTS FROM THE OXIDATION OF SCHIFF BASES AT SILVER ELECTRODES. Supporting Electrolyte 1·0 M NaOH; 23°; 0·75 V NHE.

Schiff base	Products
n-PrCH=N-n-Bu	n-PrCHO, n-PrCN
n-PrCH=N-iso-Bu	n-PrCHO, iso-PrCHO, iso-PrCN
n-PrCH=N-t-Bu	n-PrCHO, t-BuOH, t-$BuNO_2$
$\underset{Et}{\overset{Me}{>}}C{=}N\text{-}n\text{-}Bu$	Ethyl Methyl ketone, n-PrCHO, n-PrCN
n-PrCH=N-sec-Bu	n-PrCHO, Butanone

(b) *The oxidation of Schiff bases.* Attempts to oxidize Schiff bases, the results of which are shown in Table 2, were largely complicated by the rapid hydrolysis of the Schiff base by the alkaline electrolyte. As far as we have been able to ascertain the products of the oxidized Schiff base are identical with the oxidation products of the hydrolyzed Schiff base.



$$\begin{tikzcd} RCH_2N{=}CHR' \arrow[r, "OH'", "H_2O"'] \arrow[dr, "\text{anodic oxidation}", "OH^-/HO_2^-"'] & RCH_2NH_2 + R'CHO \arrow[d, "\text{anodic oxidation}"] \\ & RCN, RCHO, R'CHO \end{tikzcd}$$

(c) *Potential sweep experiments.* When a slow linear potential ramp is applied to a polished etched silver electrode, initially at equilibrium, a current-potential curve of the form shown in Fig. 1 (curve A) is obtained.[6] The current peaks represent the formation of thick layers of Ag_2O and AgO. Additions of an aliphatic secondary amine* to the electrolyte cause the magnitude of the peaks to increase (Fig. 1 curve B). The increase in peak "height" varies (to a first approximation) in direct proportion to the conc of amine present (Fig. 2). This effect is interesting. At $C_{amine} = 0$, the peaks corresponding to Ag_2O and to AgO are of approximately the same area (~100mC cm^{-2}) i.e. the AgO film results solely from the oxidation of Ag_2O. Additions of secondary amine to the electrolyte cause the AgO peak to increase at a greater rate than the Ag_2O peak (Fig. 2) and thus this effect cannot be caused by an amine "assisted" thickening of the film. When each oxide-formation reaction is complete all reaction ceases (the current drops to zero (within experimental accuracy) between peaks) and thus the effect does not involve dissolved or dissolving species. In this connection chemical studies do not indicate that any Ag^I (amine) complex such as was observed with primary amines[4] is formed with secondary amines.

We may explain these observations by the progressive blocking of the electrode surface by an oxidation product. The blocking of electrode surfaces is a well established phenomenon in electrochemistry. Frequently the surface concentration required to reduce an electrode reaction rate to an insignificant value is much less than a monolayer and is generally explained in terms of the deactivation of active sites. In the

---

* This effect was only appreciable with low molecular weight amines which had an appreciable solubility in the electrolyte.

present experiments it is suggested that a minor product of the electrode reaction becomes adsorbed at the electrode at lattice sites which become deactivated for the electrode oxidation reaction. The reaction occurs then only on the "clean" growing crystallites. The identity of the intruding species cannot be unequivocally stated but it is reasonable to suppose, since it must be formed more slowly at higher amine concentrations, that its production involves OH^-. Thus in accordance with step VII to XI it is most likely to be an alchol. At higher positive potentials it is to be expected that the adsorption of hydroxy compounds at an electrode would be facilitated. The oxidation of alcohols at silver oxide electrodes in this potential region is unexpectedly slow reinforcing this view.[7]

EXPERIMENTAL

All experiments were carried out under potentiostatic conditions. The cells, electrodes, apparatus and electrochemical techniques have been fully described in previous communications.[4, 5]

Secondary amines, obtained commercially (Fisons Ltd.) or prepared by reduction of Schiff bases with $NaBH_4$[6] were distilled and analysed by GLC before use. Schiff bases were prepared by the slow addition of the required carbonyl compound to a cooled dried soln of the required primary amine in ether. (Anhyd $MgSO_4$ was a satisfactory drying agent.)

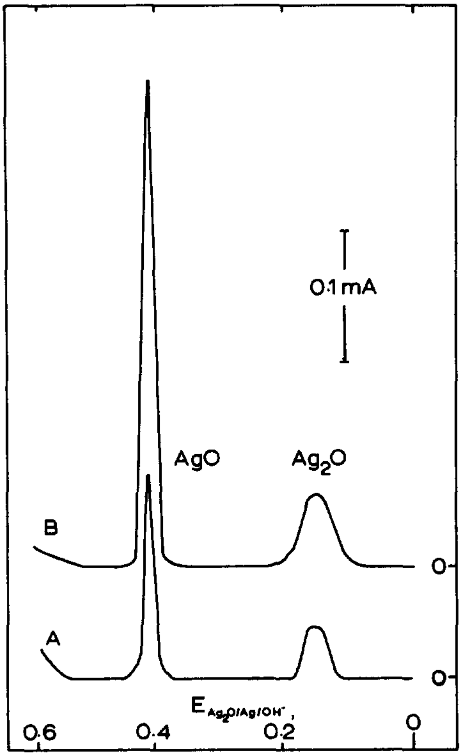


FIG. 1 Potentiodynamic current curves for Silver in alkaline electrolytes. 23°, electrode area $4{\cdot}45 \times 10^{-2}\,cm^2$, $6 \times 10^{-3}\,V\,sec^{-1}$. Curve A: 1·0M Na OH. Curve B: 1·0M NaOH + 7×10^{-2} M $(i\ Pr)_2NH$.

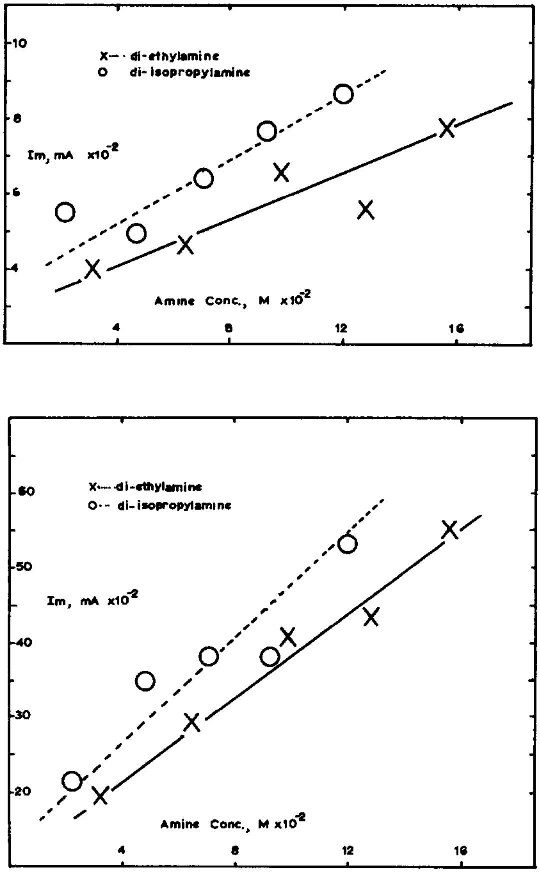


FIG. 2 Dependence of peak height on amine concentration (upper plot Ag_2O peak; lower plot AgO peak). Electrode area $4{\cdot}45 \times 10^{-2}$ cm^2, 23° 6×10^{-3}V sec^{-1}, 1·0M NaOH.

Preparative oxidations using amine saturated electrolytes were run for ~36 hr with a continuous slow N_2 purge exhausting through a Br_2/CCl_4 trap (to absorb any hydrocarbons). Organic products were extracted from the electrolyte (1·0M NaOH) into ether and analysed by GLC (Pye 104 chromatograph) using two or more of the following stationary phases: Silicone (S.E.30). P.E.A.G., Carbowax, D.N.P. and Fluorosilicone (Q.F.1.). Compounds were identified by comparison with authentic materials.

Acknowledgement—The Authors wish to acknowledge financial support from Loughborough University (JRM and KIM) and SRC (B.S.) Professor R. F. Phillips is thanked for continued interest and encouragement.

REFERENCES

[1] e.g. L. R. Subbaraman and L. Santappa, *Proc. Ind. Acad. Sci.* (A) **64**, 345 (1966).
[2] T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley and B. Scanlon, *Canad. J. Chem.* **47**, 1649 (1969).
[3] T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley and B. Scanlon, *Tetrahedron Letters* No. 54, 5685 (1968).
[4] Part V *Canad. J. Chem.* **47**, 3729 (1969).

[5] T. G. Clarke, N. A. Hampson, J. B. Lee, J. R. Morley and B. Scanlon, *Ber. Bunsenge. Phys. Chem.* 73, 279 (1969).

[6] J. H. Billman and A. C. Diesing, *J. Am. Chem. Soc.* 22, 1068 (1957).

[7] J. R. Morley, unpublished observations.