EXPERIENTIA

Vol. 28 – Fasc. 8 Pag. 873–992 15. 8. 1972

SPECIALIA

Polarographic Kinetics of Reactions which Proceed via Carbonium Ion Intermediates

We wish to describe further work on the polarography of the carbonium ion II[1] and on its use in the kinetics of reactions proceeding via this intermediate.

To achieve a rigorous assignment of the observed polarographic waves to the carbonium ion II we have first of all determined the NMR-spectrum of this species and correlated it with its UV-absorption maximum.

The NMR-spectrum of a solution of dimethyl-*p*-methoxyphenyl carbinol I in absolute fluorosulphonic acid at $-10°$ clearly demonstrates the presence of only one species i.e. the carbonium ion II. [Sharp singlet (6H) $\tau = 7.54$ ppm $(-\underset{+}{C}=(CH_3)_2)$, sharp singlet (3H) $\tau = 6.27$ ppm $(-O-CH_3)$, quadruplet (4H) $\tau = 2.19, 2.29, 3.41, 3.51$ ppm (aromatic H)]. This spectrum is consistent with the NMR of the *p*-methoxyphenyl methyl carbonium ion determined by OLAH[2].

The UV-spectrum of a solution of the alcohol I in absolute fluorosulphonic acid at $-10°$ displays an absorption maximum at 357 nm ($\varepsilon = 2.6 \times 10^4$). In view of the preceeding we must assign this absorption maximum to the carbonium ion II.

In mixtures of sulphuric acid and water containing the alcohol I a UV-absorption maximum at 361 nm ($\varepsilon = 2.6 \times 10^4$) and a one electron polarographic reduction wave [$E_{1/2} = -0.49$ V vs S.C.E.] may be simply shown to belong to the same species which consequently must be the carbonium ion II[3].

In acetic acid-chloroform mixtures containing a small amount of sulphuric acid *p*-methoxy 2-phenyl propylene III gave a well defined polarographic wave ($E_{1/2} = -0.4$ V vs S.C.E.) which decreased with time to a limiting value. This wave resembled closely the polarographic reduction wave of the carbonium ion II and the agreement of halfwave potential if we consider the different solvent system is satisfactory.

The wave was independent of mercury pressure[4–6] and surfactants, linearly dependent on the concentration of III and gave smooth 'i–t' parabolas with an exponent $k = 0.65$–0.68[7,4,5]. Consequently we are dealing with a fully rate controlled volume reaction in which the rate of production and the rate of disappearance of the carbonium ion II controls the wave height.

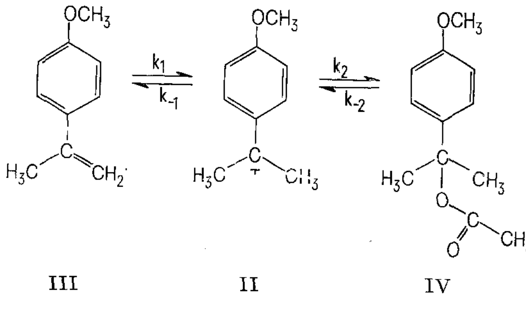
For solutions of (III) in acetic acid, 15% chloroform (v/v), 6% sulphuric acid (v/v) and 0.0005% gelatin, the initial wave height was 4.03×10^{-2} of the theoretical diffusion current $(\bar{i}_{k0}/\bar{i}_d)$. The wave decreased as a first order reaction with a rate constant $k_{exp} = 9.65 \times 10^{-4}\ s^{-1}$, until it reached a constant height of 2.56×10^{-2} of the theoretical diffusion current $(i_{k\infty}/i_d)$. The curves were recorded at 25° with capillary characteristics: m (outflow velocity) $= 2.95$ mg s^{-1}, t (drop time) $= 2.87$ s. The theoretical diffusion current values were estimated from the known diffusion-controlled waves of acetophenone.

In the same system a UV-absorption maximum was observed at 368 nm which decreased at the same rate as the polarographic wave. We again ascribe this absorption maximum to the species II. The absorbance at time zero obtained by extrapolation was 2.28×10^{-3} of that determined for the carbonium ion II (vide supra).

The decrease of the kinetically controlled polarographic wave of the carbonium ion II with time to a constant limiting value means clearly that an equilibrium is being established and that the carbonium ion II participates in this equilibrium.

The only scheme which is acceptable from the point of view of mechanistic organic chemistry and which at the same time accounts for all the facts is the conversion of III into an equilibrium mixture of III and IV via a rapid equilibrium with the carbonium ion II.

Such a scheme formally closely resembles the scheme for the mutarotation of D-glucose with consideration of



III II IV

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[1] D. BARNES and K. WIESNER, Experientia *27*, 1379 (1971).

[2] G. A. OLAH, M. B. COMISAROW, E. NAMANWORTH and B. RAMSAY, J. Am. chem. Soc. *89*, 5259 (1967).

[3] This section has been abbreviated.

[4] J. HEYROVSKÝ and J. KŮTA, *Principles of Polarography* (Publishing House of the Czechoslovak Academy of Sciences, Prague 1965).

[5] S. G. MAIRANOVSKIJ, *Catalytic and Kinetic Waves in Polarography* (Plenum Press, New York 1968).

[6] K. WIESNER, Z. Electrochemistry *49*, 164 (1943).

[7] K. WIESNER, Colln. Czech. chem. Commun. *12*, 64 (1947).

the intermediate aldehyde[8,9] and by a similar set of arguments it is possible to derive the kinetic current of the carbonium ion at time zero ($\bar{i}_{ko}$) and time inifinity ($\bar{i}_{k\infty}$) as functions of the theoretical diffusion current ($\bar{i}_d$) and the 4 rate constants k_1, k_{-1}, k_2, k_{-2}(1,2.)

$$\bar{i}_{ko}/\bar{i}_d = 0.886\, t^{1/2} k_1/(k_{-1}+k_2)^{1/2} = 4.03\times10^{-2} \quad (1)$$

$$\bar{i}_{k\infty}/\bar{i}_d = 0.886\, t^{1/2} k_1 k_{-2}(k_{-1}+k_2)^{1/2}/(k_{-1}k_{-2}+k_1k_{-2}+k_1k_2) = 2.56\times10^{-2} \quad (2)$$

The overall reaction rate can be simplified to

$$k_{exp} = (k_1k_2+k_{-1}k_{-2})/(k_{-1}+k_2) = 9.65\times10^{-4}s^{-1} \quad (3)$$

The fourth equation needed to calculate all the 4 unknown rate constants is provided by the extrapolated extinction at 268 nm to time zero. This value yields the concentration of II at time zero and consequently it yields the equilibrium constant of the rapidly established equilibrium between II and III.

$$k_1/k_{-1} = 2.28\times10^{-3} \quad (4)$$

From equations (1), (2), (3) and (4) the 4 rate constants are as follows: $k_1 = 0.32\ s^{-1}$, $k_{-1} = 140\ s^{-1}$, $k_2 = 0.15\ s^{-1}$, $k_{-2} = 6.2\times10^{-4}\ s^{-1}$.

The value k_1 is in agreement with the rates of protonation of substituted styrenes in acetic acid sulphuric acid mixtures[10].

Polarographic kinetic currents prove to be a novel tool for the study of chemical reactions proceeding via carbonium ion intermediates.

Zusammenfassung. Mit Hilfe der Polarographie wird die Kinetik der Solvolyse von *p*-Methoxy-isopropalakohol bestimmt.

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[8] J. M. Los and K. WIESNER, J. Am. chem. Soc. *75*, 6346 (1953).

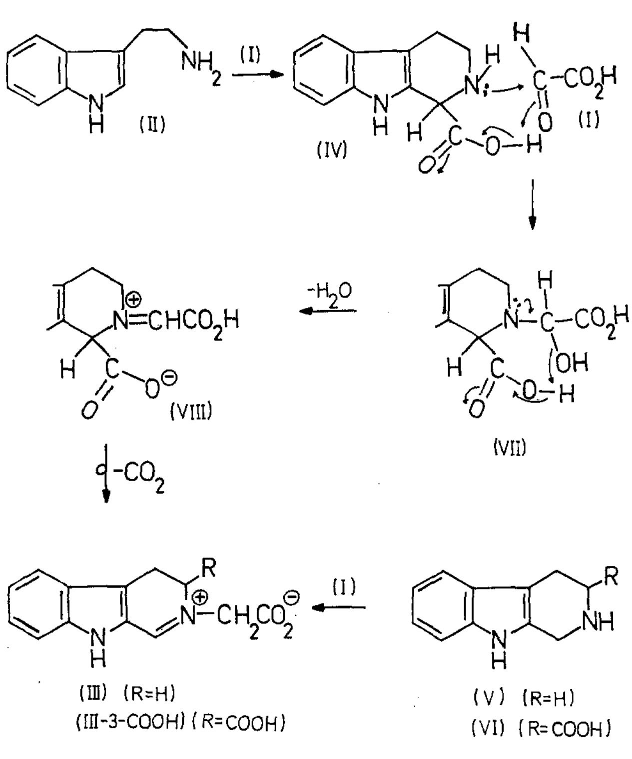
[9] J. M. Los, L. B. SIMPSON and K. WIESNER, J. Am. chem. Soc. *78*, 1564 (1956).

[10] R. CORRIU and J. GUENZET, Tetrahedron *26*, 671 (1970).

[11] We wish to thank the National Research Council of Canada for a grant in support of this study and the University of New Brunswick for a post doctoral fellowship for one of us (D.B.).

A New Reaction in Histochemistry: Structure and Mechanism of Formation of Fluorescent Compounds in the Reaction of Tryptamine and Carboxyl Substituted Tetrahydro-β-Carbolines with Glyoxylic Acid

Glyoxylic acid (I) has been found to react with biogenic amines (e.g. indoleamines, catecholamines), both in tissues and in solution, with the formation of highly fluorescent compounds. This reaction seems to offer a new very sensitive method for the histochemical demonstration of such amines in tissues[1].



Thus, the yellow, highly fluorescent compound formed after treatment of tryptamine hydrochloride (II) with a 4 molar excess of (I) (monohydrate) in *n*-BuOH at room temperature has been characterized and found to be the quaternary 2-carboxymethyl-3.4-dihydro-β-carbolinium chloride, III (Scheme); IR (KBr): 3100, 2750, 2500, 1720, 1630, 1540, 1340, 880 and 760 cm^{-1}; NMR (DMSO-d_6, 100 MHz): 3.32 (t, 2H, J = 9.0 Hz, $-CH_2-CH_2-$), 4.12 (t, 2H, J = 9.0 Hz, $-CH_2-CH_2-$), 4.96 (s, 2H, *pyr*-N$-CH_2-$), 7.5 (m, 5H, Ar-H and *ind*-NH), 9.21 (s, 1H, 1-H), 12.86 (broad s, 1H, –COOH); fluorescence: 375/500 nm; mass spectrum at 70 eV (*m/e* (relative intensity %) M+ 229 (0.3), 212 (3), 186 (13), 185 (6), 172 (6), 169 (6), 144 (17), 143 (100), 142 (10), 128 (6), and 115 (17); after $NaBH_4$-reduction: M+ 230 (5), 186 (10), 169 (3), 156 (5), 143 (100), 130 (7), 128 (7), 115 (23), 102 (7) and 89 (7).

Formation of III in the reaction of I with tetrahydro-β-carboline-1-carboxylic adic (IV) (intermediate in the formation of III form I and II), has been found to be more than 80 times as rapid as the analogous reaction of I with tetrahydro-β-carboline[2], (V) (Pseudo first-order conditions in *n*-BuOH at 84°C).

Owing to steric and inductive effects from the carboxyl group introduced in IV, the *pyr*-nitrogen in this compound ought to be less reactive against I than the *pyr*-nitrogen in V. However, since the molecular geometry in IV is so arranged that catalytic assistance from the carboxyl group may be possible, (both in the reaction of the *pyr*-nitrogen with the carbonyl carbon in I, as well as in the subsequent dehydration reaction of the carbinolamine, VII), this may be an explanation for the rapid formation of III from I

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[1] S. AXELSSON, A. BJÖRKLUND, B. FALCK, O. LINDVALL and L. Å. SVENSSON, Acta physiol. scand, in press.

[2] Z. J. VEJDĚLEK, V. TRČKA and M. PROTIVA, J. mednl pharm. Chem. *3*, 427 (1961).