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ELECTROLYTICALLY GENERATED RADICAL CATIONS OF 1,4-DIHYDROPYRIDINE DERIVATIVES IN SOLUTION [1]

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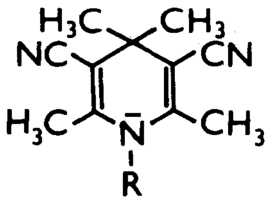
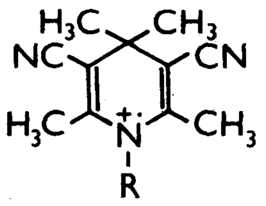
The reaction of 1,4-dihydropyridine derivatives (DHP) with reducible substrates (S) have been in the centre of interest because of analogy with the function of NADH in biological systems [2]. In the case of a one-electron oxidation of DHP- or of NADH- one may expect [3-6] the formation of radical ions $\mathrm{S}^{-\cdot}$ and $\mathrm{DHP}^{+\cdot}$ or $\mathrm{NADH}^{+\cdot}$ respectively. A proof of formation by EPR of the particle $\mathrm{HDP}^{+\cdot}$ or of its charge-transfer complex has been as yet only presented with several model reactions [3,7-9]. The only known formation of free radical cations $\mathrm{DHP}^{+\cdot}$ by electron impact in gaseous phase [10] bears no direct relation to the above processes which are interesting from the biochemical point of view. In this communicatios we demonstrate the first unambigous evidence for the formation of $\mathrm{DHP}^{+\cdot}$-type particles in solution during electrochemical generation from the corresponding DHP.



I.



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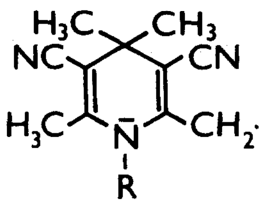

III.

3,5-dicyano-2,4,4,6-tetramethyl-1,4-dihydropyridines I were chosen as precursors; these substances were found to be subjected to one-electron oxidation [11] at a rotated platinum anode in aqueous solutions with 50 % (vol.) acetonitrile and therefore radical formation is most probable with them.

The radical cations were prepared <u>in situ</u> in the cavity of the EPR spectrometer [12] by controlled-potential oxidation at a stationary platinum anode in absolute acetonitrile with 0.05M tetrabutylammonium perchlorate as supporting electrolyte. At a temperature 24°C EPR spectra were obtained with a well resolved hyperfine structure (Fig.1):

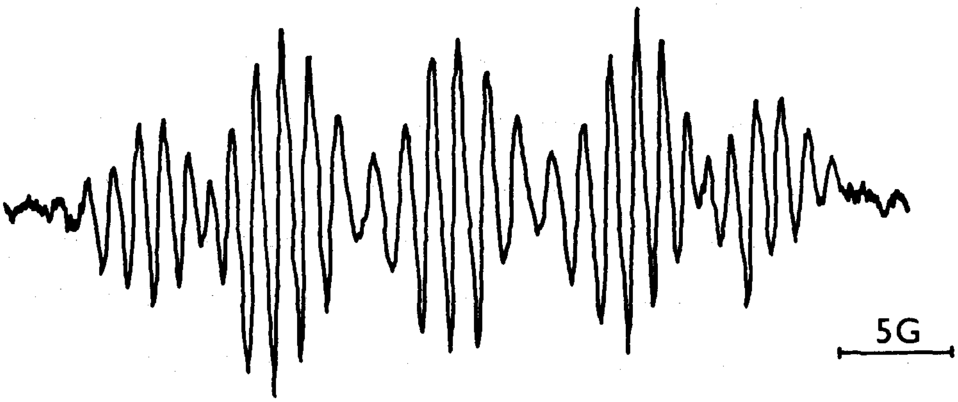

Fig.1 EPR spectrum of radicals generated electrochemically from I ($R = C_6H_5CH_2$).

The intensity of the signal strongly depends on the character of the substituent R which affects the radical stability and, consequently, also its concentration.

From the plot of the signal intensity versus time immediately after interrupting the electrolysis the value of half-times of the decomposition reactions of the radicals thus formed were assayed. For R = CH_3, $C_6H_5CH_2$, p-$ClC_6H_4CH_2$, p-$CH_3OC_6H_4CH_2$ and p-$NO_2C_6H_4CH_2$ the values of $t_{1/2}$ lie within 0.3 - 0.5s, for R = H $t_{1/2} \approx 0.05$s.

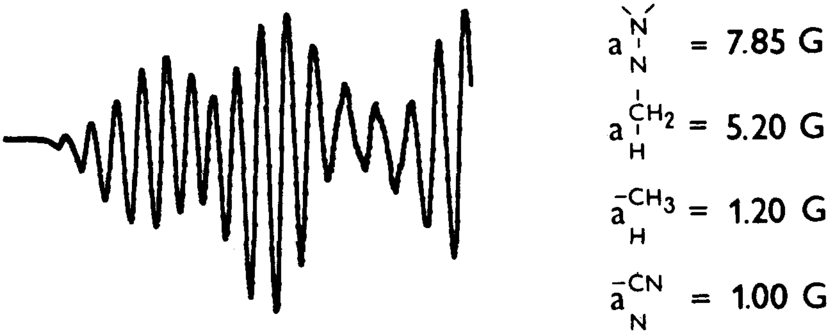

Fig.2 Simulated spectrum (one half) of radical II (R = $C_6H_5CH_2$).

By comparing the experimental spectra with those simulated [13] (Fig.2) the splitting constants of all generated radicals were determined except for R = H (here, the signal-to-noise ratio is to small). In addition to the splitting by the α-protons of the substituent R and by the nucleus of the nitrogen atom of the dihydropyridine nucleus all spectra also exhibit a splitting by two equivalent nitrogen nuclei of both nitrile groups and by the six equivalent protons of the methyl groups in positions 2 and 6. The findings confirm the existence of the radical cations II and simultaneously rule out that the observed signal is due to the deprotonated radicals III which are a possible intermediate in the reaction [14] of I with nitrous acid.

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