Some similar measurements[29] using neutrons of higher energy from the D^2 $(d,n)He^3$ reaction have been performed. These indicate qualitative agreement with the polarizations calculated assuming a spin-orbit interaction of the type in equation (9). As yet however, the data are so sparse and the experimental uncertainties so large that little can be said about the spin-orbit forces in the average neutron-nucleus scattering interaction.

Zusammenfassung

Die Untersuchung der Atomkerne mit Neutronen wird diskutiert. Bei den leichten Kernen geben die Experimente Auskunft über die Energieniveaux des betreffenden Kerns. Die Experimente an schweren Kernen lassen sich am einfachsten an Hand einer gemittelten Kern-Neutron-Wechselwirkung interpretieren.

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[29] A. E. REMUND, Helv. phys. Acta, *29*, 545 (1956).

Brèves communications - Kurze Mitteilungen
Brevi comunicazioni - Brief Reports

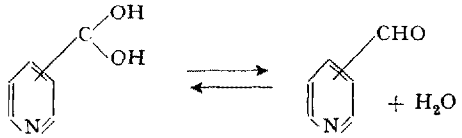
Polarographic Reduction of Isomeric Pyridine-Aldehydes at the Dropping Mercury Electrode

In acidic supporting electrolytes, e.g. solutions of strong acids (0·1 N H_2SO_4, 0·1 N HCl) or buffer solutions of pH 1–2, all three isomeric pyridine-monoaldehydes give polarographic waves which are much lower than the full diffusion current corresponding to the reduction of aldehydes according to the Ilkovič equation. With pyridine-3-aldehyde at pH 1·9, the height of the wave is about 19% of the current due to a two-electron process. The limiting current in this region does not depend on the height of the mercury column (Fig. 1). With increasing pH, the height of the waves grows until it reaches a limiting value for all three aldehydes at the pH of about 6.

The wave of pyridine-3-aldehyde is simple, while the waves of pyridine-2-aldehyde and pyridine-4-aldehyde are composed of two parts of approximately equal height. Simultaneously with the growth of the waves with pH, the waves gradually attain the characteristics of a diffusion current. In the alkaline range of pH, the diffusion current remains nearly constant and decreases only at pH greater than 10 (Fig. 2).

The reduction proceeds in the case of pyridine-4-aldehyde (pH 4) at – 0·35 V and – 0·49 V vs. N.C.E., of pyridine-2-aldehyde at – 0·56 V and of pyridine-3-aldehyde at – 0·79 V. The half-wave potentials of all three compounds are shifted to more negative values with increasing pH, the slope being 60 mV/pH for pyridine-3-aldehyde and 75 mV/pH for the other two.

From the variation of the height of the waves with the concentration of hydrogen ions, which is similar to that of formaldehyde[1], it can be assumed that in aqueous medium the three compounds are present mainly in their hydrated form, the concentration of the free aldehyde being low. Only the latter is polarographically reducible. The limiting currents are controlled by the rate of dehydration of the hydrated form as the two forms are in a reversible equilibrium:



This reaction is subject to general base catalysis, hence the height of the waves varies with the concentration of

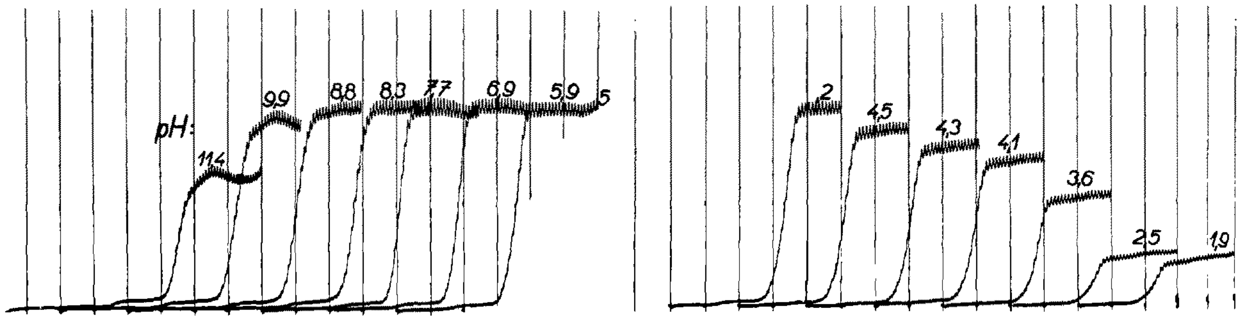


Fig. 1.—Dependence of the wave of pyridine-3-aldehyde on the pH of the supporting electrolyte.
Electrolyte: buffer solution according to BRITTON and ROBINSON; 1·12 × 10^{-3} M pyridine-3-aldehyde; from – 0·2 V (satd. cal. elect.); 196 mV/absc.; nitrogen atm.; s = 1:30.

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[1] K. VESELÝ and R. BRDIČKA, Coll. Trav. chim. Tchécosl. *12*, 313 (1947). – R. BIEBER and G. TRÜMPLER, Helv. chim. Acta *30*, 706 (1947). – R. BRDIČKA, Chem. Listy *48*, 1458 (1954).

hydrogen ions in a manner which is similar to that of formaldehyde[2]. This furnishes the first example of hydration of aromatic aldehydes found polarographically.

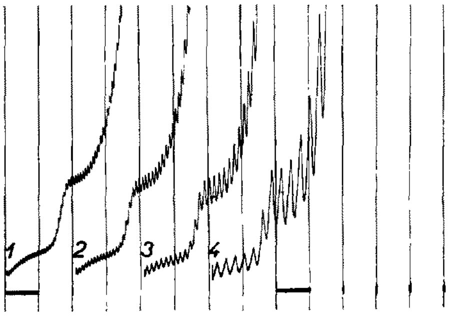

Fig. 2.—Dependence of the height of wave of pyridine-2-aldehyde on the height of the mercury column.

Electrolyte: 2 *N* sulphuric acid; $1{\cdot}12 \times 10^{-3}$ *M* pyridine-2-aldehyde; from $-0{\cdot}2$ V (satd. cal. elect.); 210 mV/absc.; nitrogen atm.; $s = 1:7$. Curve *1* height of the mercury column 80 cm; *2* 60 cm; *3* 40 cm; *4* 20 cm.

As yet hydration has been observed polarographically only in the case of formaldehyde[1], glycerinaldehyde[3], glyoxal[4], and glyoxalic acid[5], i.e. of aliphatic aldehydes. Nevertheless the explanation conforms also with the behaviour of a compound closely related to the pyridinealdehydes, viz. 5-desoxy-pyridoxal[6], where hydration was supposed from the study of ultraviolet spectra.

The results of this communication will be published in detail elsewhere.

J. Volke

Polarographic Institute, Czechoslovak Academy of Sciences, Prague, November 12, 1956.

Zusammenfassung

Aus polarographischen Messungen an den isomeren Pyridinaldehyden ergibt sich, dass diese in wässerigen Lösungen in zwei Formen vorliegen, von denen nur eine polarographisch reduzierbar ist. Der Reduktion unterliegt das freie Aldehyd, während die hydratisierte Form inaktiv ist.

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[2] K. Veselý and R. Brdička, Coll. Trav. chim. Tchécosl. *12*, 313 (1947). – R. Bieber and G. Trümpler, Helv. chim. Acta *30*, 706 (1947).

[3] J. Trnka, Proc. I. Int. Pol. Congr. Prague *3*, 512 (1952).

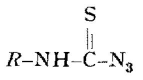
[4] J. Kuta, Private communication.

[5] P. J. Elving and C. E. Bennett, J. Amer. chem. Soc. *76*, 1412 (1954).

[6] D. E. Metzler and E. E. Snell, J. Amer. chem. Soc. *77*, 2431 (1955).

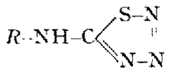
Some Observations on Substituted 5-Aminothiatriazoles

In a recent communication[1], we commented on the anomalous infrared spectra of 'thiocarbamyl azide' (I*A*) and its phenyl derivative (I*B*). We now report some spectroscopic data (see table) on 3 other 'thiocarbamyl azides' (*sic*) and some related substances. Again it is evident that the spectra of these 'thiocarbamyl azides' are conspicuous by the absence of any azide stretching absorption in the 2180–2160 cm^{-1} region[2]. This spectroscopic anomaly we now suggest can best be rationalized by ascribing to the so-called 'thiocarbamyl azides' a cyclic structure of the thiatriazole (II) type[3].

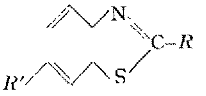


$R{-}NH{-}C({=}S){-}N_3$

I



II

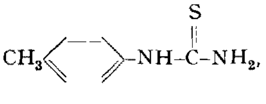


III

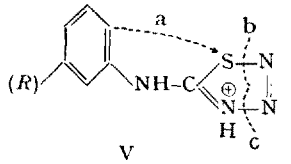
I: *A*, $R = H$;
B, $R = C_6H_5$;
C, R = alkyl.

II: *A*, $R = H$;
B, $R = C_6H_5$;
C, $R = p\text{-}CH_3\text{-}C_6H_4$.
D, R = alkyl.

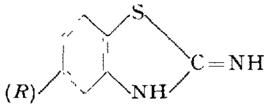
III: *A*, $R = NH_2$, $R' = H$;
B, $E = NH_2$, $R' = CH_3$;
C, $R = N_3$, $R' = H$;
D, $R = NH_2$, $R' = Cl$.



IV



V



VI

Despite their cyclic formulation, the thiatriazoles readily desulphurize in the presence of base[1], the alkyl derivatives (II*D*), as well as II*A*, being roughly five times more prone to loss of sulphur than the aryl compounds. The latter compounds, however, are far more sensitive to phototropism. They are also reactive towards acids. Thus, when 5-phenylaminothiatriazole (II*B*) is refluxed in concentrated hydrochloric acid it yields 2-amino-benzothiazole (III*A*), in addition to elimination products. We have now confirmed analogous thiazole formation with 5-*p*-tolylaminothiatriazole (II*C*). This in the presence of boiling concentrated hydrochloric acid affords a 36% yield of 2-amino-6-methylbenzothiazole (III*B*), identified both by its spectroscopic identity with an authentic sample as well as by mixed m.p. therewith, together with *p*-tolylthiourea (IV) in 4% yield, sulphur (ca. 5%) and a so far unidentified substance of formula $C_{16}H_{19}N_4SO$, m.p. 136–137°, which depresses the m.p. of III*B*, in ca. 3% yield.

Some observations have also been made with regard to the conversion of II*B* into III*A*. It appeared likely previously[1] that this rearrangement involved 2-benzothiazolyl azide (III*C*) as an intermediate. When III*C* was then prepared, its behaviour in acid, viz. a 20% recovery of III*C* after 20 min refluxing in concentrated hydrochloric acid together with its extensive decomposition to a black tar, eliminated this possibility. This

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[1] F. L. Scott, Chem. and Ind. *1956*, 1350.

[2] L. J. Bellamy, *Infra-red Spectra of Complex Molecules* (Methuen and Co. Ltd., London 1954), chap. 15.

[3] This same conclusion was reached independently and almost simultaneously by the author and as informed in private communications by Professors P. A. S. Smith of the University of Michigan and E. Lieber of De Paul University.