The Polarographic Behavior of Hydroxylycoctonine

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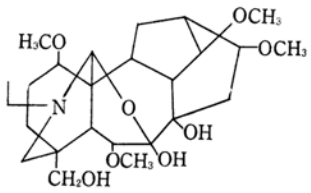
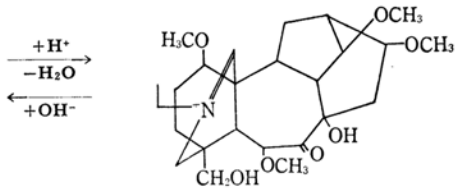
Hydroxylycoctonine[1,2] exhibited well-defined polarographic waves in an acidic medium. As is shown in Table I and in Fig. 1, the first wave was observed in the pH range of 2~8 and the second in the pH range of 5~8; the heights of both waves became smaller as the pH became greater, and the waves entirely disappeared at pH values greater than 8.

TABLE I. HALF-WAVE POTENTIAL AND WAVE HEIGHT OF HYDROXYLYCOCTONINE IN BRITTON-ROBINSON BUFFER SOLUTION
1.2 mmol./l; $m^{2/3}t^{1/6}=1.26$ mg$^{2/3}$ sec$^{-1/2}$

pH	$E_{1/2}$, −V. vs. SCE		i_d, μamp.	
	I	II	I	II
1.9	0.73		3.648	
3.9	0.75		3.648	
4.3	0.755		3.498	
4.85	0.76		3.318	
5.45	0.765		2.712	
5.9	0.77	1.725	1.464	3.0
6.9	0.775	1.725	0.240	1.56
7.75	unmeasurable			



I



II

A slope of 10 mV. per unit change of pH in the $E_{1/2}$~pH curve, a slope of 80 mV. in the log (i/i_d-i)~E curve at pH 1.9, and an $E_{1/4}-E_{3/4}$ value of 100 mV. at pH 1.9 were obtained, these values confirming the irreversibility of

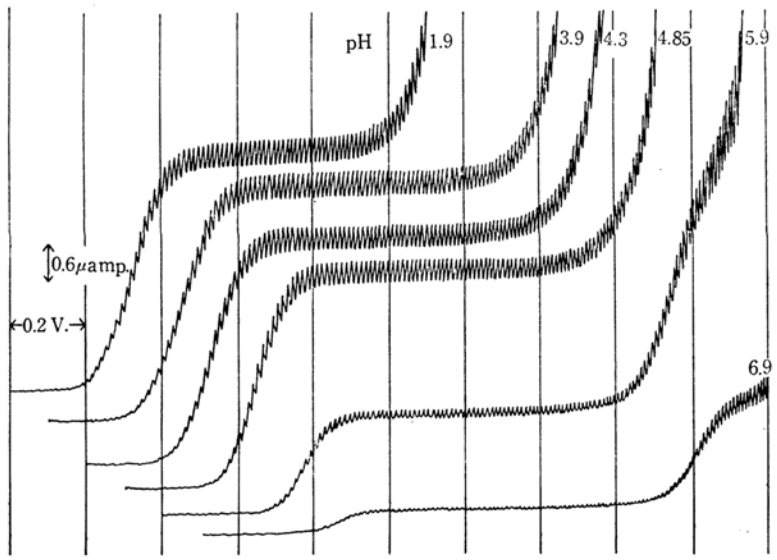


Fig. 1. Polarograms of hydroxylycoctonine in buffers at various pH values. (Curves start from −0.4 V.)

1) H. Suginome and K. Ohno, *J. Fac. Sci., Hokkaido Univ., Ser. III, Chem.*, 4, 36 (1950).

2) O. E. Edwards and L. Marion, *Can. J. Chem.*, 30, 627 (1952).

the electrode process. The irreversibility was observed also in the a. c. polarography of hydroxylycoctonine.

Applying Ilkovic equation with the D value estimated from the molecular weight, $n=2.0$ was obtained.

From the i_d~pH curve the apparent pK_a of hydroxylycoctonine was assumed to be 5.8; this value was concordant with the reported pK_a (5.8) in a 50% methanol solution.[3]

The limiting current of the wave was confirmed to be diffusion-controlled from the relationship between the height of the mercury column and the limiting current height; it was linearly proportional to the concentration between 0 and 0.27 mmol./l. at pH 1.9.

This polarographic behavior of hydroxylycoctonine can be readily interpreted from the defined structures[3,4] of hydroxylycoctonine (I) and its anhydronium salt (II). Therefore, it is considered that the first wave of the polarogram is due to the $>C=N^+<$ bond and the second to the ketone group in II,* which is formed in an acidic medium.

Similar behavior was observed also in the polarography of acetylanhydrolycoctonine** and of anhydrolycoctonine.***

Further details of the experiment will be published shortly.

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3) O. E. Edwards, M. Los and L. Marjon, ibid., **37**, 1996 (1959).
4) Z. Valenta, *Chem. & Ind.*, **1959**, 633; Z. Valenta and I. G. Wright, *Tetrahedron*, **9**, 284 (1960).

* The same immonium structure as that in hydroxylycoctonine has been reported in the case of diacetyldelcosine (T. Amiya and T. Shima. *J. Org. Chem.*, **26**, 2616 (1961)).

** Suginome's monoacetyl derivative, m. p. 132~133°C;[1] $C_{27}H_{41}O_7N$, $[\alpha]_D^{31}+11°$, ν_{max}^{Nujol} 1730, 1224 (ester), 1721 cm^{-1} (C=O).

*** Alkali hydrolysis product of acetylanhydrolycoctonine; $C_{25}H_{39}O_6N$, m. p. 158~160°C, $[\alpha]_D^{28}+21°$, ν_{max}^{Nujol} 3497 (OH), 1721 cm^{-1}(C=O).