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A NOTE ON THE EFFECT OF CONCENTRATION OF HYDROCHLORIC ACID ON THE DECOMPOSITION OF MUREXIDE

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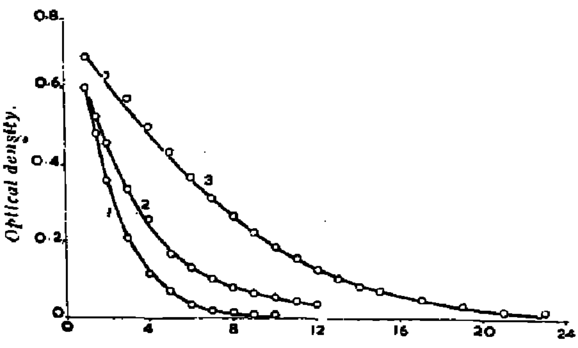
It is known (Davidson and Epstein, *J. Org., Chem.* 1936, **1**, 305) that murexide undergoes decomposition in acidic solutions to furnish uramil and alloxan. No data exist in the literature on the kinetics of this reaction which appears primarily to be an acid hydrolysis. During a series of experiments undertaken in this laboratory to investigate the calcium content in sugarcane juices with the help of murexide, specially using its characteristic absorption spectra, the rate of decomposition of murexide in acid solutions was examined. The present communication reports the effect of the concentration of a strong acid like HCl on the kinetics of the above reaction.

Murexide of B.D.H. quality was used; this was purified by the method of Davidson (*J. Amer. Chem. Soc.*, 1936, **58**, 1821) yielding 99-100% purity (cf. Moser and Williams, *Anal. Chem.*, 1954, **26**, 1167). Hydrochloric acid of B.D.H.- Analar quality was used. Absorption spectra of murexide were recorded with Unicam 350 D.G. Spectrophotometer, using 10 mm. cells.

Murexide exhibits characteristic absorption maximum at $\lambda = 530\ m\mu$. The optical density at this wave-length increased sensibly linearly with the concentration of murexide, providing a value of 1.04×10^4 mole/litre^{-1} cm^{-1}for the Beer's constant.

The data in Fig. 1 show the variation with time of the optical density of murexide of a fixed concentration (0 10 mM) at the optimum wave-length $\lambda = 530\ m\mu$; here, curves 1, 2 and 3 refer to different concentrations of HCl, viz., 10, 6.25 and 2.5mM respectively. These data were obtained as follows:

Fig. 1



(Conc of murexide = 1 10 mM

Equal volumes of murexide solution and HCl of desired strength were mixed, and the absorption of the mixture at $\lambda = 530\ m\mu$ was recorded at different intervals of time. It was interesting to note that the absorption decreased progressively and permanently with time (Fig. 1); this was accompanied by gradual disappearance of the reddish pink colour, characteristic of murexide. The data in Fig. 1 further show that smaller the concentration of HCl, the slower is the decrease in the absorption. Thus e.g., the time necessary for a decrease to half of the initial value of the optical density was 2.9, 3.4 and 7 mins. with 10, 6.25 and 2.5 mM of HCl.

The results obtained for the decomposition of half of the initial amounts of murexide with a fixed acid concentration showed that the reaction was essentially of first order (Table I).

TABLE I

p_H.	Molar conc. of murexide $C_1 \times 10^3$.	$C_2 \times 10^3$.	$t^1_{\frac{1}{2}}$	$t^2_{\frac{1}{2}}$	n.
2.2	0.125	0.0625	4.25	3.825	0.96
2.4	0.125	0.0625	6.625	5.125	0.93
2.6	0.125	0.0625	8.25	7.00	0.96
2.6	0.100	0.0500	4.30	3.20	0.93
2.6	0.075	0.0375	3.60	3.05	0.96
2.6	0.050	0.0250	3.20	3.00	0.98
2.8	0.125	0.0625	17.00	12.00	0.91
				Mean	0.95

TABLE II

Variation of the first order rate constant with the concentration of the hydrochloric acid.

Murexide concentration = 0.10 mM.

Molar conc. of HCl ($C \times 10^3$).	Approx. p_H of the mixed soln.	$k_1 \times 10^5$.	Molar conc. of HCl ($C \times 10^3$).	Approx. p_H of the mixed soln.	$k_1 \times 10^5$.
10.0	2.15	22.7	5.0	2.45	13.2
8.75	2.20	22.4	4.25	2.55	10.8
8.25	2.25	21.2	3.75	2.60	8.8
7.50	2.30	18.9	2.50	2.70	6.3
6.25	2.35	12.3	1.00	3.15	1.3

The first order rate constant, k_1, can be calculated from the following equation relating the readings (r) of optical density with time t

$$\log (r' - r) = a - k_1 t$$

when is the reading at time $t + T$, where T is a suitably chosen constant interval of time. Plots of log $(r' - r)$ against t gave straight lines. The values of k_1, computed from the slope of these lines, are shown in Table II. k_1 increased sensibly linearly with the concentration (C) of HCl; it appeared to obey the following relationship up to a concentration of 0.01 M of HCl (temperature 25°):

$$k_1/\text{min}^{-1} = 2.56 \times 10^{-3} C.$$

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