

STUDIES ON THE KINETICS OF THE DECOMPOSITION OF MUREXIDE IN ACID SOLUTIONS

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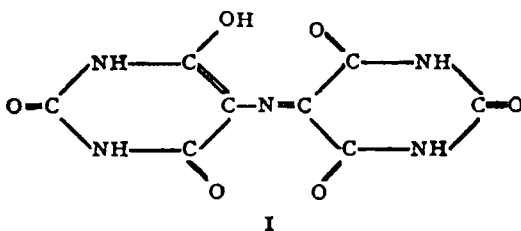
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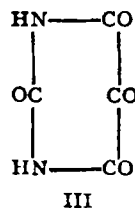
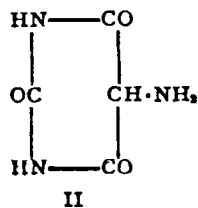
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INTRODUCTION

IN recent years, murexide or ammonium salt of purpuric acid (I) is being extensively used as an analytical reagent for many metallic ions, especially



of Ca^{++} . Beck¹ employed murexide for the detection of Sc, Zn, Th and other rare earth and rare metals; Leonid Kul'berg² used the same as reagent for heavy metals. Schwarzenbach and Gysling³ described in detail the use of murexide for quantitative estimation of Ca^{++} . Since then it proved to be an efficient reagent for determination of calcium-content in pharmaceutical products,⁴ milk ultra filtrate,⁴ etc.⁵ Estimation with ease of Ca^{++} in sugarcane juices is problematical in sugar technological laboratories. During a series of experiments on this investigation employing murexide, a few interesting results on the decomposition of murexide in acid solutions were obtained. It is known^{7, 8} that murexide in solutions of low pH undergoes decomposition leading chiefly to the production of uramil (II) and alloxan (III). No data



exist in the literature on the kinetics of this reaction. The present communication reports for the first time the kinetics of the decomposition of murexide

investigated by employing the characteristic absorption spectra of the substance in the visible region.

EXPERIMENTAL

The commercial (B.D.H.) sample of murexide was purified by the method described by Davidson.⁸ One gram of the crude substance was dissolved in 900 c.c. of pure distilled water. The filtrate was salted out with 60 gm. of ammonium chloride. The precipitated substance was washed with absolute methyl alcohol, to be free from chloride and later dried at 120° C., when fine reddish brown crystals possessing a green reflex were obtained.

Absorption spectra of a solution of known concentration of murexide with an equal volume of a buffer solution of desired pH, were studied with Unicam S.P. 350 D.G. spectrophotometer; this last had one cm. effective light path.

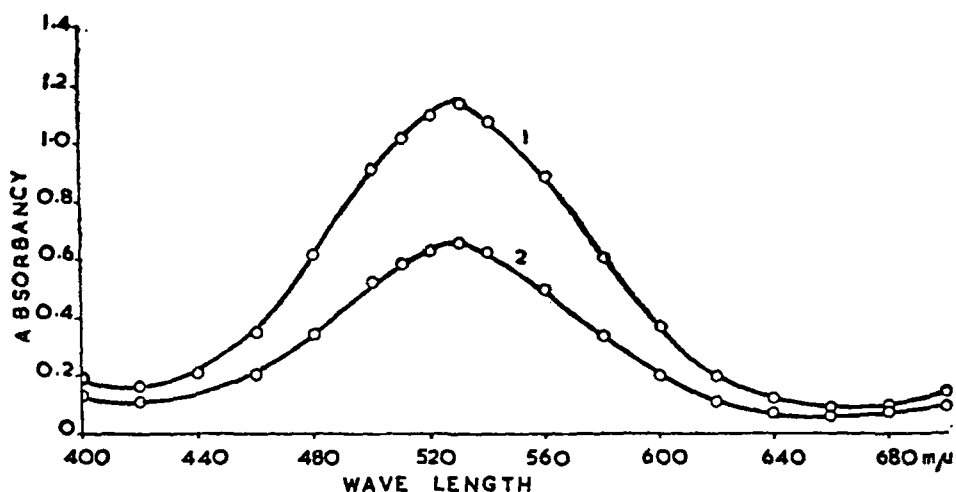


FIG. 1. Absorption Spectra of murexide in the visible region.
(Curve 1 refers to the concentration of 0.125 and Curve 2, to 0.0625 mM of Murexide; pH = 6.0.)

RESULTS AND DISCUSSION

A typical series of results on the characteristic absorption spectra of murexide in the range 400 to 700 mμ are given in Fig. 1; in this, curve 1 refers to a concentration of 0.125 mM while curve 2, to 0.0625 mM of murexide at pH = 6.0. It was interesting to note that the absorbance of murexide increased progressively to a maximum followed by a decrease with increase in the wave-length. Thus, *e.g.*, it was 0.35, 1.13 and 0.2 at $\lambda = 460$,

620 $m\mu$ respectively. Murexide has maximum absorption at $\lambda = 530 m\mu$ in accordance with the data obtained by other workers.⁵ Further, this wavelength λ_m was unaffected by a change in the concentration or/and the pH value of the solution.

At a fixed pH, increase of the concentration of the murexide solution especially in the range 10^{-3} to 10^{-6} M enhanced the maximum absorbancy. Thus, *e.g.*, the absorbancy at $\lambda = 530 m\mu$ was 0.17, 0.65 and 1.13 at 0.016, 0.063 and 0.125 mM of murexide. Further, it was interesting to note that the absorbancy increased sensibly linearly with the concentration (see Fig. 2) in accordance with Beer's law; the corresponding constant had a value of 1.04×10^4 at 25° C. (Table I).

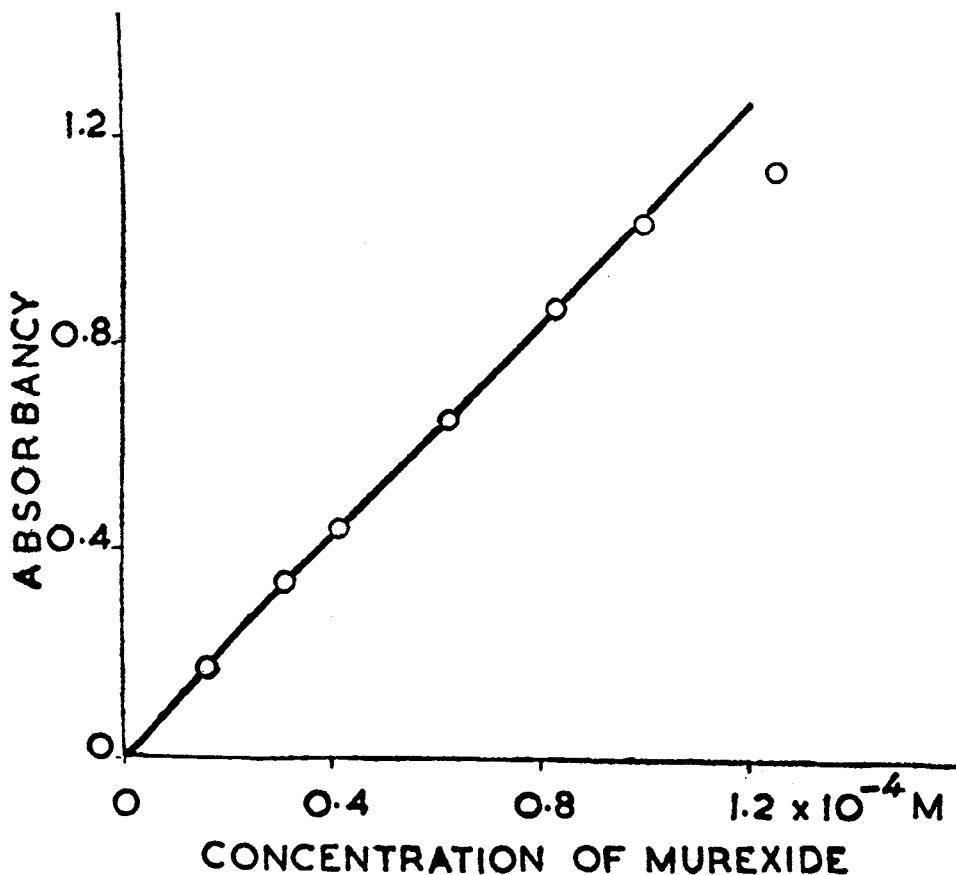


FIG. 2. Variation of absorbancy with the concentration of murexide.
($\lambda = 530 m\mu$; pH = 6.0)

TABLE I
Variation of maximum absorbancy at $\lambda = 530 m\mu$ with concentration of Murexide

Concentration $M \times 10^3$	Optical density	Beer's Constant (10^{-4})
0.125	1.135	0.91
0.10	1.03	1.03
0.0833	0.87	1.04
0.0625	0.655	1.05
0.0417	0.44	1.06
0.0313	0.342	1.09
0.0157	0.171	1.09

Mean Value = 1.04

The data given in Figs. 3 and 4 represent the variation of the absorbancy at $\lambda = 530 m\mu$ of murexide solution with time, at pH = 2.2 and 2.6 respectively. In these curves 1 and 2 refer respectively to the above data with initial concentrations of 0.125 and 0.0625 mM of murexide. These data were obtained as follows: A known volume of the murexide solution was mixed with equal volume of a buffer and the absorbancy was recorded at different intervals of time at $\lambda = 530 m\mu$. It was interesting to observe that the absorbancy at $\lambda = 530 m\mu$ characteristic of the substance decreased progressively with time. Thus for an initial concentration of 0.125 mM and at pH = 2.2, the optical density was 0.72, 0.42 and 0.22 at 1, 5 and 9 min. after the solution was mixed with the buffer. With further increase in time, it decreased to a negligibly small value (see Fig. 3). Essentially similar data were recorded at other pH values (Fig. 4). The decrease with time of the absorbancy was accompanied by the gradual disappearance of the characteristic pink-red colour of the murexide. Furthermore, the above change in the absorption or the colour, appeared permanent and irreversible in the sense that when the acid-reacted solution was made alkaline, the characteristic colour was not restored, and the absorption at $\lambda = 530 m\mu$ was not exhibited. This is illustrated clearly by the data given in Figs. 5 and 6; these refer to the experiments in which during the progress of the reaction, the

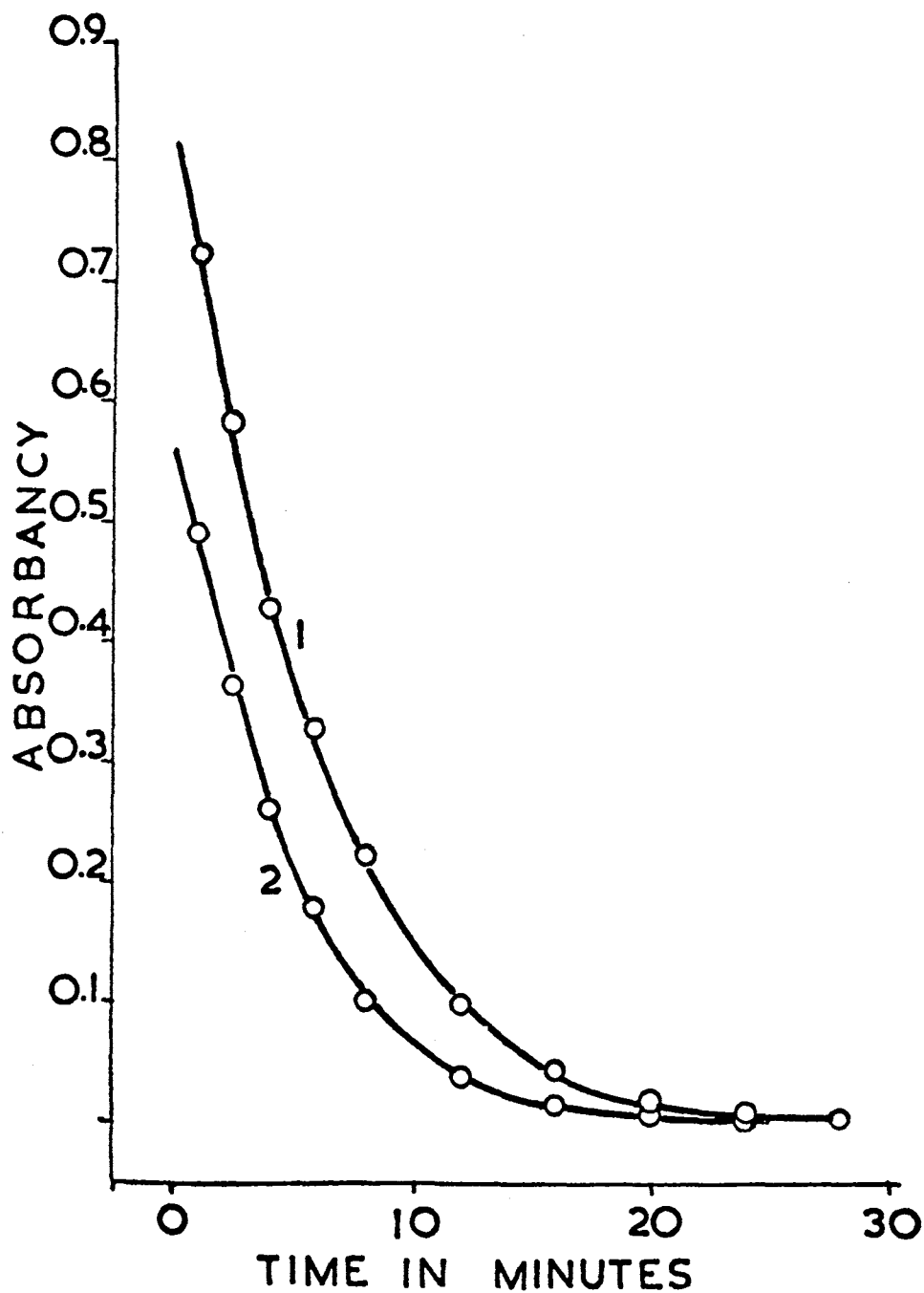


FIG. 3. Decomposition of murexide with time at pH = 2.2.
(Curve 1 = 0.125 and Curve 2 = 0.0625 mM of murexide ; $\lambda = 530 \text{ m}\mu$)

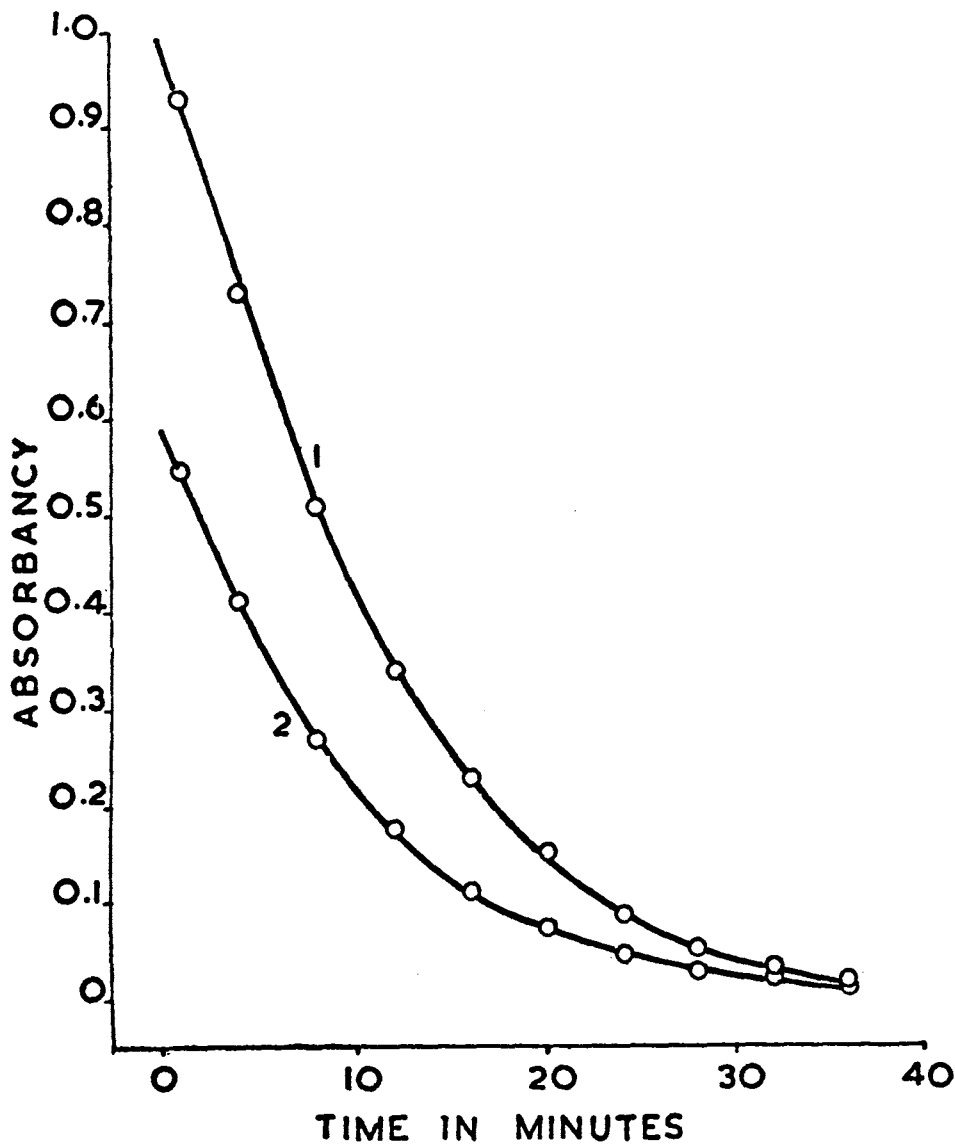


FIG. 4. Decomposition of murexide with time at pH = 2.6.
(Curve 1 = 0.125 and Curve 2 = 0.0625 mM of Murexide; $\lambda = 530 \text{ m}\mu$)

pH of the solution has been increased to 8 by addition of 0.2 c.c. of 4 N sodium hydroxide solution, which caused negligible dilution of the murexide solution. It was interesting to note that as soon as the pH was raised, the reaction leading to the decrease in the absorbancy of murexide was quenched as evidenced by the observation that the absorbancy of the solution recorded

just before addition of alkali remained later sensibly constant (see Figs. 5 and 6). These data not only demonstrate the irreversible nature of the decomposition, but also reveal the marked dependence of the reaction on the hydrogen-ion concentration of the solution.

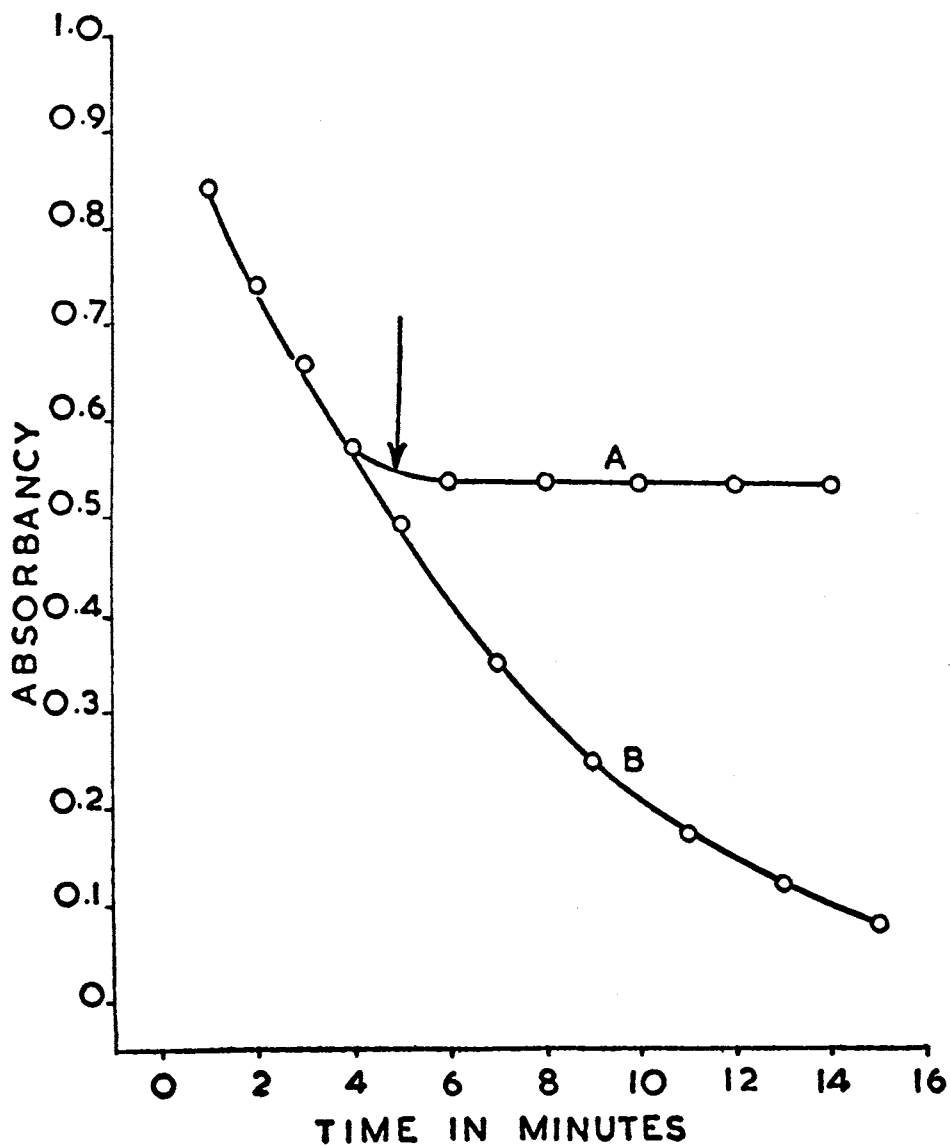


FIG. 5. Effect of addition of alkali to the acid reacted murexide solution. [Initial pH of the solution = 2.2 (Curve B), pH after addition (at the instant indicated by the arrow) of the alkali = 8.0 (Curve A). $\lambda = 530 \text{ m}\mu$.]

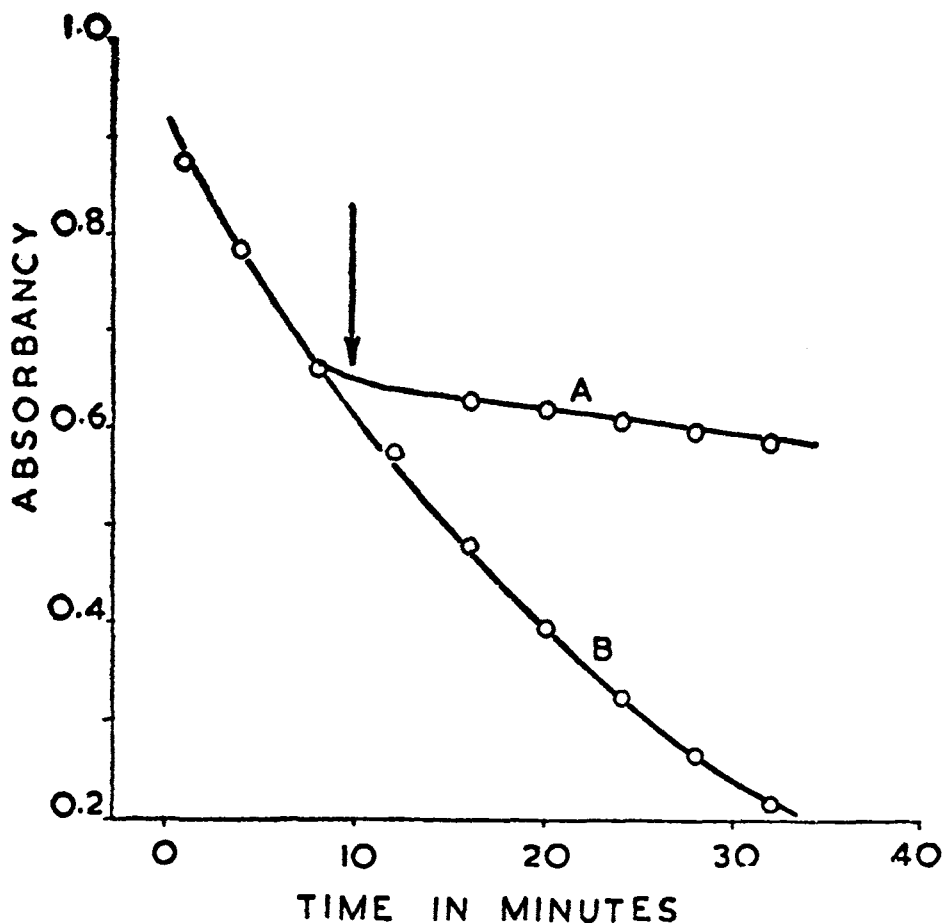


FIG. 6. Effect of addition of alkali to the acid reacted murexide solution. [Initial pH of the solution = 2.8 (Curve B), pH after addition (at the instant indicated by the arrow) of the alkali = 8.0 (Curve A). $\lambda = 530 \text{ m}\mu$.]

The data in Figs. 3 and 4 further show that larger the pH of the solution, the greater is the time necessary for complete decomposition of a known concentration of murexide. Thus the absorbance at $\lambda = 530 \text{ m}\mu$ decreased to undetectably small value within 25 min. at pH = 2.2 (curve 1, Fig. 3), while the same at pH = 2.6 decreased to zero value by about 40 min.

Table II gives the results on the time necessary for half decomposition of a known initial concentration of murexide, recorded at different pH values. These were employed for the determination of the order (n) of the reaction under investigation. The figures in the last column gave an average value of 0.93 or ~ 1 for n . It is for this reason that the authors considered the

reaction to be roughly first order in nature and presumably similar to the acid hydrolysis, inversion of cane sugar, etc.

TABLE II
Determination of the order of reaction
 $C_1 = 0.125 \text{ mM}$ and $C_2 = 0.0625 \text{ mM}$ of Murexide

pH	Time for half decomposition of C_1 ($t_{\frac{1}{2}}$)	Time for half decomposition of C_2 ($t_{\frac{2}{2}}$)	Order of reaction (n)
2.2	4.25	3.625	0.96
2.4	6.625	5.125	0.93
2.6	8.25	7.0	0.96
2.8	17.0	12.0	0.91

There are several methods employed for calculating the first order rate constant k_1 from the readings r at time t of some physical property characteristic of the substance undergoing reaction, and proportional to the concentration thereof. Since the variation of the absorbancy of murexide solution obeys roughly Beer's law (Table I, Fig. 2), it has been felt that the same could be satisfactorily utilised for obtaining the value of k_1 . For this purpose, the authors employed the following equation due to Guggenheim.⁹

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

where r' is a reading at time $t + \tau$, where τ is a chosen constant interval; and a , a constant. The remarkable simplicity of this equation is that it is only necessary to plot $\log (r' - r)$ against t and measure the slope of the line thus obtained, which gives directly the value of the first order rate constant. Fig. 7 shows one of the typical lines thus obtained by the application of the above formula to the data given in Fig. 3 (Curve 1). This gave a value of $7.98 \times 10^{-6} \text{ min.}^{-1}$ (25° C.) for k_1 for an initial concentration of 0.125 mM of murexide at $\text{pH} = 2.2$.

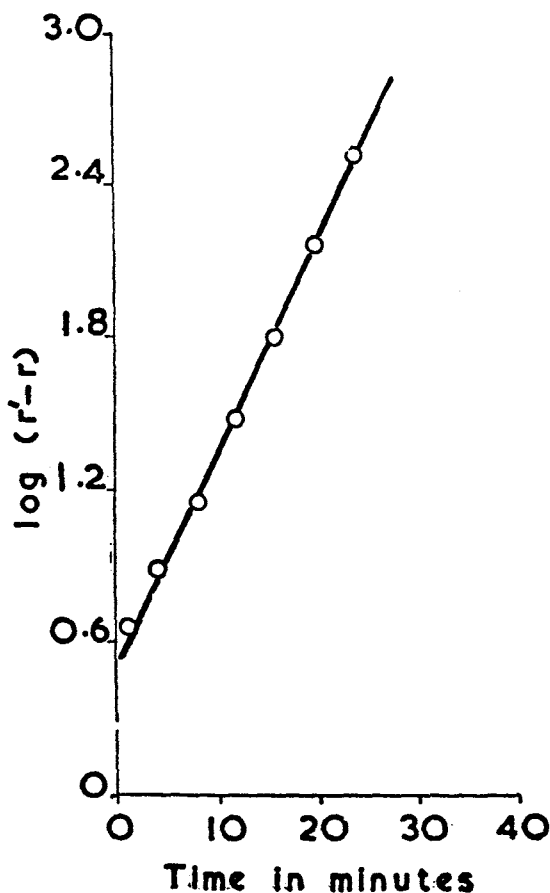


FIG. 7. Determination of the first order rate constant.
(pH = 2.2; concentration = 0.125 mM; $\lambda = 530 \text{ m}\mu$)

SUMMARY

Decomposition of murexide in solutions of low pH (2-6) has been investigated spectrophotometrically. At pH < 6, the characteristic absorption of murexide at $\lambda = 530 \text{ m}\mu$ decreased irreversibly with time, following first order law; the corresponding rate constant k_1 had a value of $7.98 \times 10^{-6} \text{ min.}^{-1}$ (25° C.) for an initial concentration of 0.125 mM of murexide at pH = 2.2.

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REFERENCES

1. Beck, G. .. *Anal. Chim. Acta*, 1947, 1, 69.
2. Leonid Kul'berg .. *J. Gen. Chem. U.S.S.R.*, 1947, 17, 1089.
3. Schwarzenbach, G. and Gysling, H. .. *Helv. Chim. Acta*, 1949, 32, 1314.
4. Flaschka, H. .. *Scientia Pharma*, 1953, 21, 126.
5. Smeets, W. Th. G. M. .. *Nature*, 1952, 169, 802.
6. Flaschka, H. .. *Textile Rundschau*, 1954, 9, 77; see also Parrish, J. R., *Proc. Internat. Soc. Sugarcane Tech.*, 1953, 742.
7. Heilbron, T. and Bunbury, H. *Dictionary of Organic Compounds*, Eyre & Spottiswoode, London, 1946, 3, 547.
8. Davidson, D. .. *J. Amer. Chem. Soc.*, 1936, 58, 1821.
9. Guggenheim, E. A. .. *Phil. Mag.*, 1926, 2, 538; cf., Bond, W. N., *Probability and Random Errors*, Longmans, Green & Co., London, 1935, 112. This method due to Bond is cumbersome and is not applied here.