

temperatures below 350°. Alexander and Pidgeon² obtained a logarithmic growth law in their study throughout the range 25 to 330°. However, above 460° both investigations established that oxidation was controlled by diffusion. The latter investigators state that the parabolic growth law was not applicable to their data.

According to Gulbransen and Andrew the energy of activation for temperatures above 350° is 26.0 kcal./g. mole of activated complex. The author's calculation from the slope at lower temperatures leads to 12.4 kcal./g. mole for this energy of activation. In a study of the oxidation of tantalum, the authors³ observed a similar change in the energy of activation from 12.57 kcal./g. mole for the logarithmic growth law to 27.2 kcal./g. mole for the parabolic rate.

The present study was undertaken to determine whether the break in the Arrhenius plot of Gulbransen and Andrew's data is due to a change in the rate law. It was found that a logarithmic growth law represents the data up to 316°

$$\lambda = k_L \log(t + 1)$$

where λ is the wave length corresponding to maximum absorption after t hours of exposure. At this temperature, one run was observed to follow a cubic growth law.

Experimental Procedures.—Iodide titanium analyzing 500 p.p.m. of aluminum and 10 p.p.m. each of iron, silicon and magnesium was cold rolled without intervening anneals to 28 mil sheet specimens at Battelle Memorial Institute. These specimens were hand polished through 4/0 aloxite metallographic paper and then finished on dry gamal cloth without added abrasive.

The course of oxidation was followed spectrophotometrically as well as gravimetrically. The details of the two methods and evidence of the reliability of the former method have been presented elsewhere.^{3,4}

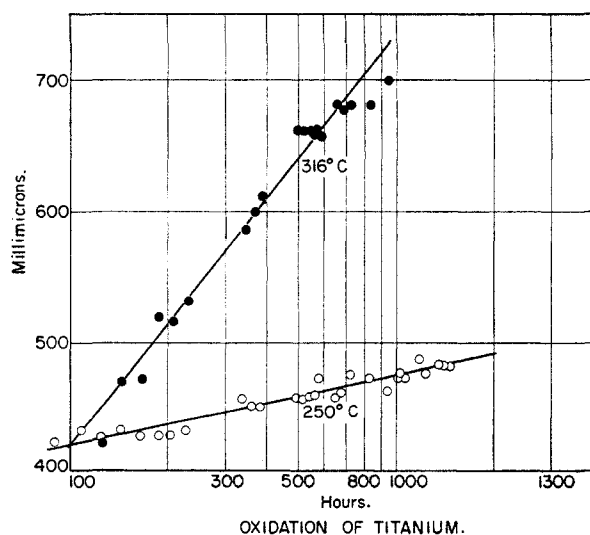


Fig. 1.—A logarithmic plot of the spectrophotometric data obtained in the study of the oxidation of iodine titanium.

(2) W. A. Alexander and L. M. Pidgeon, *Can. J. Research*, **28B**, (1949).

(3) J. T. Waber, E. N. Wise, G. E. Sturdy and C. R. Tipton, *J. Electrochem. Soc.*, **99**, 121 (1952).

(4) It should be pointed out that small thicknesses of lower oxides may increase the phase shift in terms of equivalent oxide thickness although the fundamental equations of the spectrophotometric method are not changed. It has been assumed that lower oxides of titanium were not present in significant amounts.

The specimens lost weight for about 50 hours, although the interference colors due to the oxide were present. These colors progressed smoothly, changing to those characteristic of greater oxide thicknesses with ensuing time. Repeated heating, followed by polishing to remove the oxide coating, reduced the magnitude and duration of the weight loss.

Alexander and Pidgeon² mention that their titanium, made by the Kroll-Dean method, contained about 0.05% hydrogen, which could only be partially removed by outgassing at 311°. The authors believe that the large weight decrease was probably a result of the escape of hydrogen.

Dr. Gulbransen kindly tested one of these samples in his vacuum microbalance. After the sample was outgassed in a high vacuum at 600°, there was a slight decrease in weight prior to oxidation but the behavior of this sample was then no different from that of outgassed specimens which he had discussed earlier in his paper with Andrew.

Experimental Results.—The spectrophotometric data are summarized in Fig. 1. Fairly consistent data were obtained both at 250 and 316°. The ordinate plotted is the wave length of the light which at each time corresponded to the minimum on the reflectance curve. The present data are too few to permit accurate determination of the activation energy, ΔE , in the lower temperature range. However, a preliminary estimate of this quantity based upon the rate constant, k_L , indicates that it is of the order of 13 kcal./g. mole. The values from which it was estimated are given in terms of ångströms in Table I.

TABLE I
VALUES OF THE LOGARITHMIC RATE CONSTANT FROM THE SPECTROPHOTOMETRIC DATA

Temp., °C.	k_L in Å.	
250	507	520
316	3350	5700

Conclusions.—The oxidation of titanium below 350° has been reinvestigated and found to follow the logarithmic growth law, confirming the work of Alexander and Pidgeon. The break in the Arrhenius plot of Gulbransen and Andrew is due to the change from the logarithmic to the parabolic rate law at temperatures increasing above 350°.

Acknowledgments.—The assistance of C. R. Tipton in procuring the cold-rolled specimens is acknowledged. Discussions with F. W. Schonfeld, A. S. Coffinberry and E. R. Jette were helpful and the kind counsel of E. A. Gulbransen was greatly appreciated.

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Studies in the Furan Series. Reaction of Some Substituted 2-Furamides with Phenyl Isocyanate

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In conjunction with other studies in the furan series, some 5-substituted-2-furamides were treated with phenyl isocyanate according to the procedure of Wiley¹ to give the corresponding 1-(5-substituted-2-furoyl)-3-phenylureas. To show that normal addition had occurred, 1-(2-furoyl)- and 1-(5-bromo-2-furoyl)-3-phenylurea were prepared by reaction of phenylurea with the corresponding furoyl chloride according to the method of Stoughton.² In accord with the observations of Wiley,^{1b}

(1) (a) P. F. Wiley, *THIS JOURNAL*, **71**, 1310 (1949); (b) **71**, 3746 (1949).

(2) R. W. Stoughton, *J. Org. Chem.*, **2**, 514 (1938).

TABLE I

R-	M. p., °C.	Solvent	Color	Yield, %	Carbon, %		Hydrogen, %		Nitrogen, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
2-Furyl	186-188	EtOH	White	50	62.60	62.75	4.38	4.55	12.27	12.18
5-Bromo-2-furyl-	198-200	HOAc	White	98	46.59	46.91	2.93	2.95	9.06	9.35
5-Methyl-2-furyl-	162-163	EtOH	White	45	63.91	63.98	4.95	4.99	11.47	11.58
5- <i>t</i> -Butyl-2-furyl	186-188	EtOH	White	64	67.49	67.66	6.34	6.32	9.79	9.96
5-Nitro-2-furyl-	249-251	HOAc	Yellow	79	52.37	52.57	3.30	3.53	15.27	15.27
β -(2-Furyl)-vinyl-	198-201	EtOH	Tan	73	65.61	65.64	4.77	4.99	10.94	11.03

N-substituted furamides did not add normally to phenyl isocyanate and no characterizable product could be isolated from the reaction mixture.

Experimental

Starting Materials.—Details of the preparation of the substituted 2-furamides will appear in a later paper in this series.

Addition of Amides to Phenyl Isocyanate.—A mixture of the amide with a slight excess of phenyl isocyanate was heated under gentle reflux until entirely liquid (5-10 minutes). Ten milliliters of absolute ethanol was added cautiously to react with excess phenyl isocyanate and the solution was chilled. The solid which separated was isolated on a filter, washed with cold ethanol and recrystallized to constant melting point. The properties of the resulting 1-acyl-3-phenylureas are given in Table I.

Acylation of Phenylurea.—A solution of 6.75 g. (0.05 mole) of phenylurea in 20 ml. of benzene was heated to the reflux temperature and to the hot mixture was added slowly a solution of 6.5 g. (0.05 mole) of 2-furoyl chloride in 10 ml. of dry benzene. The mixture was heated under reflux while stirring vigorously for 6 hours.

The solution was cooled to room temperature and the solid which separated was isolated and recrystallized from hot ethanol to give 0.8 g. (7%) of 1-(2-furoyl)-3-phenylurea which melted at 187-188°. Mixing with the product from addition of 2-furamide to phenyl isocyanate did not depress the melting point of this product.

1-(5-Bromo-2-furoyl)-3-phenylurea was prepared similarly in 1% yield by acylation of a toluene solution of phenylurea with 5-bromo-2-furoyl chloride.

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COMMUNICATIONS TO THE EDITOR

ENZYMATIC PHOSPHORYLATION OF *l*-ASPARTATE

Sir:

The biological incorporation of amino acids into more complex compounds is known in certain instances¹ to utilize energy from ATP.² However, phosphorylated intermediates have not been demonstrated in these processes, and the mechanisms of energy transfer are obscure. The enzymatic formation of an "energy-rich" amino acid-phosphate compound, β -aspartyl phosphate, is described here. Suggestive evidence that this substance is a precursor of asparagine is the presence in the enzyme preparation of a very active asparagine "transferase" similar to the enzymes found by Waelsch and co-workers³ in certain bacteria.

The enzyme was obtained from an extract of baker's yeast and purified about 10-fold with weak acid and ammonium sulfate. It appears to catalyze the reaction



Though its equilibrium is unfavorable to accumulation of the new compound, the reaction may be

(1) P. P. Cohen in W. D. McElroy and B. Glass, "Phosphorus Metabolism," The Johns Hopkins Press, Baltimore, Md., 1951, Vol. I, p. 630.

(2) Abbreviations used are ATP (adenosine triphosphate), ADP (adenosine diphosphate), AMP (adenosine-5-phosphate), and tris-[tris-(hydroxymethyl)-methylamine].

(3) H. Waelsch, *Advances in Enzymol.*, **13**, 237 (1952).

followed readily if hydroxylamine is used to trap the aspartyl phosphate, forming a hydroxamic acid, as has been done with acetyl phosphate.⁴ In Table I are shown the essential components of the system and the effect on hydroxamate formation of omitting each. Substitution of *d*-aspartate or *l*-glutamate reduced hydroxamic acid formation to 2 and 6%, respectively, of the value with *l*-aspartate.

TABLE I

All tubes contained 0.4 μ M. hydroxylamine hydrochloride brought to pH 8.0 with tris. The incubation was at 30° for 30 minutes in a total volume of 1.0 ml.

Component omitted	Hydroxamic acid formed, μ M.
None	3.2
25 μ M. <i>l</i> -aspartate (potassium salt)	0.09
10 μ M. ATP (sodium salt)	0.00
10 μ M. MgCl ₂	0.14
Enzyme, 0.1 ml.	0.00

High concentrations of aspartate and ATP favor synthesis of aspartyl phosphate, as shown in Table II. In this experiment hydroxylamine at pH 4.0 was added to stop the enzymatic activity after samples had been taken for phosphate analyses. Acyl phosphate was determined as hydroxamic acid,⁵ and as the difference between inorganic

(4) F. Lipmann, *ibid.*, **6**, 231 (1946).

(5) F. Lipmann and L. C. Tuttle, *J. Biol. Chem.*, **159**, 21 (1945).