THE HYDROLYSIS OF THE AMIDES OF αβ-UNSATURATED ACIDS AND OF THEIR SATURATED ANALOGUES.

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It has been shown previously that αβ-unsaturated mono-basic acids are esterified by the catalytic process much more slowly than the corresponding saturated acids.[1] The ratio of the esterification constants of the two varies from 1 : 20 to 1 : 60. Similarly it has been shown that the ethyl esters of αβ-unsaturated acids are hydrolysed by dilute hydrochloric acid or dilute barium hydroxide less readily than their saturated analogues under similar conditions. With hydrochloric acid the velocities are frequently as 1 : 30, but with barium hydroxide as 1 : 4 and the ratio varies with the relative strengths of the two acids; in the case of ethyl acrylate and ethyl propionate it is 1 : 1·1.[2]

The object of the present investigation has been to ascertain whether the presence of an αβ-olefine linking in the molecule of an acid amide produces any appreciable retardation in the hydrolysis of the amide, either with dilute mineral acids or dilute alkalis. The amides studied are *n*-butyramide, crotonamide, β-phenylpropionamide and cinnamamide, and the results of the hydrolytic experiments at 100° are given in Table I.

The results show that in the two cases examined the unsaturated amide is hydrolysed more slowly than its saturated analogue, but that the difference is more marked with a mineral acid than with an alkali as hydrolysing agent; there is thus a certain parallelism between the esters and the acid amides, but the inhibiting effect of the olefine linking appears to be more pronounced in the case of the esters than in the case of the acid amides.

[1] *J. Chem. Soc.*, 1905, **87**, 1840; 1907, **91**, 1033; 1909, **95**, 313; 1911, **99**, 2307; This vol. 89.
[2] *J. Chem. Soc.*, 1912, **101**, 412. With hydrochloric acid at 20° the ratio ethyl butyrate : ethyl crotonate is 30 : 1, whereas Bürki (*Helv. Chim. Acta*, 1918, **1**, 250) gives the ratio for the methyl esters of the same acids at 40° as 16 : 1.

TABLE I.

Hydrolysis of Acid Amides at 100°.

Amide.	Formula.	Constant.	Ratio.
With Sodium Hydroxide—			
n-Butyramide	$CH_3 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$	0·111	1·6 : 1
Crotonamide	$CH_3 \cdot CH : CH \cdot CO \cdot NH_2$	0·0697	
β-Phenylpropionamide	$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO \cdot NH_2$	0·172	3·4 : 1
Cinnamamide	$C_6H_5 \cdot CH : CH \cdot CO \cdot NH_2$	0·0511	
With Sulphuric Acid—			
n-Butyramide	...	0·0888	9 : 1
Crotonamide	...	0·00980	
β-Phenylpropionamide	...	0·0837	11 : 1
Cinnamamide	...	0·00748	

It will be observed that, in the case of the saturated amides, the one with the β-phenyl group is hydrolysed more readily with sodium hydroxide but less readily with sulphuric acid than the corresponding methyl compound, and with the unsaturated amides the phenyl compound is hydrolysed more slowly than the methyl compound with both acid and alkali.

EXPERIMENTAL.

I. Preparation of Amides.

n-Butyramide.—Several methods [1] have been described for the preparation of this compound, but we have found that given by Hofmann, in which ammonium butyrate is heated to 230–250°, the most convenient.

The ammonium salt was prepared by passing dry ammonia into a solution of *n*-butyric acid in dry benzene, and the precipitated salt filtered as quickly as possible at the pump and transferred rapidly, without drying, to a sealed tube as it is extremely hygroscopic. After

[1] Hemilian, *Annalen*, 1875, **176**, 7; Hofmann, *Ber.*, 1882, **15**, 982; Aschan, *ibid.*, 1898, **31**, 2348; H. Meyer, *Monatsh.*, 1906, **27**, 43.

being heated for five hours at 250° and allowed to cool, the contents were pressed on a porous plate and a yield of 70 per cent. of the crude amide obtained in the form of shining plates. After crystallisation from a mixture of chloroform and light petroleum it was obtained as glistening flat needles melting at 115·5–116·0°.[1]

β-Phenylpropionamide was prepared in exactly the same manner from hydrocinnamic acid, with the exception that light petroleum (b.p. 70–90°) was used for crystallisation. The yield of crude amide was 73·5 per cent. of the theoretical and of the pure amide 62 per cent. After several crystallisations the melting point was 101·5–102·0° as compared with the value 105° given in the literature.[2]

Crotonamide.—After several attempts to prepare this by heating the ammonium salt or by the action of aqueous ammonia on the chloride, the method described by Stoermer and Stockmann[3] was used, with slight modifications, for example, liquid air was used instead of solid carbon dioxide and ether as the cooling medium; in this way solid ammonia was obtained and the solution of crotonyl chloride in ether was added gradually to the ammonia contained in a beaker and kept stirred; from time to time the beaker was removed from the bath in order to allow the temperature slowly to rise, and after about 0·5 hour the beaker was placed in a fume-cupboard until the ether and excess of ammonia had evaporated. The crude product so obtained was extracted with dry acetone, and a 50 per cent. yield of product melting at 156–158° obtained; after crystallisation from benzene it melted at 159–160°.

Cinnamamide was prepared by von Rossum's method.[4] The yield of crude product melting at 140–144° was 66 per cent. of the theoretical and after three crystallisations from dry benzene the amide was obtained as glistening needles melting at 147–148°.[5]

II. Hydrolysis of the Amides.

Three methods for determining the velocity of hydrolysis of acid amides have been used by earlier workers.

1. By estimating the amount of ammonia or ammonium salt formed during hydrolysis by decomposing with hypobromite solution and measuring the volume of nitrogen evolved. This was used by

[1] Meyer gives 115–116°.
[2] Hofmann, *Ber.*, 1885, 18, 2740, whereas Hughes *Proc. Chem. Soc.*, 1891, 7, 70 gives 82°.
[3] *Ber.*, 1914, 47, 1786.
[4] *Zeitsch.*, 1886, 362.
[5] Remfry, *J. Chem. Soc.*, 1911, 99, 623 gives 148–148·5°.

Ostwald[1] for determining the velocity of hydrolysis of acetamide by mineral and organic acids and later by Peskoff and Meyer,[2] who measured the velocity constants of the reactions between dilute hydrochloric acid or potassium hydroxide solution and the following amides :—acetamide, propionamide, butyramide, valeramide, capronamide and *iso*butyramide.

2. When a mineral acid is used as the hydrolysing agent, by boiling the reaction mixture with magnesium hydroxide and collecting the evolved ammonia in a known volume of standard acid, and subsequently boiling with sodium hydroxide solution and estimating the undecomposed amide from the amount of ammonia evolved.

This method was used by Remsen and Reid [3] for studying the hydrolysis of numerous aromatic amides at 100°. At this temperature the difficulty of measuring accurately the volume of the reacting mixture taken for analysis presents difficulties. In the experiments with hydrochloric acid the volume was not measured, but the total amide originally present in the volume of solution used was given by the sum of the two ammonia estimations and the quantity hydrolysed at the given time by the first ammonia titration. The method of procedure was as follows. About 75 cc. of the reaction mixture at 100° were forced over into a 250 cc. cylinder containing about 150 cc. of cold water. The temperature was thus immediately reduced to 40° at which the rate of hydrolysis is very slow. The solution was transferred to a 750 cc. flask, the cylinder washed out twice and the washings added to the flask, then 10 cc. of a solution containing 0·5 gram of magnesium sulphate per cc. were run in and a solution of sodium hydroxide added until a slight precipitate of magnesium hydroxide remained even after shaking and then sufficient sodium hydroxide solution to precipitate as hydroxide about two-thirds of the total magnesium present (viz., 2·0 to 2·5 cc. of a solution of sodium hydroxide containing 0·25 grams per cc.). After removal of the ammonia and absorption in standard acid, 20 cc. of sodium hydroxide solution (0·5 gram per cc.) were added to the large flask and the distillation continued.

In studying the decomposition of an acid amide by alkali at 100° the same method cannot be adopted, as ammonia escapes from the solution during the reaction: no attempt is made to estimate the ammonia produced during the hydrolysis, this is driven off in the presence of magnesium hydroxide, and the undecomposed amide in a given volume of solution determined as before. Remsen and Reid

[1] *J. pr. Chem.*, 1883, [11], 27, 1.
[2] *Z. Physikal. Chem.*, 1913, 82, 129.
[3] *Amer. Chem. J.*, 1899, 21, 281.

carried out the operation as follows. At the end of the given interval of time a sample of the reacting mixture was blown over into a 100 cc. flask containing 10 cc. of a solution of magnesium sulphate (0·5 gram per cc.), the hydrolysis was thus stopped, and, after cooling, the volume of water (*b* cc.) required to bring the volume to 100 cc. noted. The flask used was standardised by adding 10 cc. of the magnesium sulphate solution and noting the volume (*a* cc.) of alkali solution required to make the volume 100 cc. In this way any error due to the volume of the precipitated magnesium hydroxide was overcome. The volume of reaction mixture taken was thus $(a-b)$ cc.

3. The determination of the electrical conductivity of the solution as a means of ascertaining the diminution of the acid or alkali concentration during hydrolysis. This method was used by Crocker [1] for studying the hydrolysis of certain aliphatic amides with hydrochloric acid at 63·2° and by Crocker and Lowe [2] for studying the hydrolysis of the same amides with sodium hydroxide at 40·06°.

In our earlier experiments we attempted to use the sodium hypobromite method for determining the amount of ammonia or ammonium salt formed during hydrolysis, and working at 25° obtained values for the hydrolysis of *n*-butyramide with potassium hydroxide solution agreeing fairly well with those obtained by Peskoff and Meyer.

Experiments made with crotonamide showed that reliable results could not be obtained, as the volume of gas obtained from a given volume of the reaction mixture and excess of hypobromite solution gradually increased with the time and amount of shaking: the method used by Remsen and Reid was therefore adopted. A temperature of 100° was selected, as most of the amides used are somewhat sparingly soluble in water at 25° or 30°. An experiment was made with *n*-butyramide at 25° using potassium hydroxide, as this amide is more soluble than the others. A few experiments were made with hydrocinnamide in a mixture of equal parts by weight of alcohol and water, but no constant values could be obtained.

A constant temperature of 100° was attained by means of a boiling 18 per cent. solution of common salt,[3] and the reaction flasks were immersed in the boiling solution. The bath used was a stout rectangular copper vessel with a capacity of sixteen litres and measuring 8″ × 13″ × 12″. This was provided with a well-fitting lid which was

[1] *J. Chem. Soc.*, 1907, **91**, 593.
[2] *Ibid.*, 952.
[3] With a mean barometric pressure of 685 mm. it is impossible to attain a temperature of 100° with water alone.

practically steam-proof and which carried four outlets provided with collars. Two of these were two inches in diameter and through these the necks of the two reaction flasks (1,000 cc. capacity) protruded, the remaining two were one inch in diameter and carried the thermometer and condenser; all four were made steamtight by means of corks.

The estimations were carried out as recommended by Remsen and Reid with the following deviations :—

(*a*) Sodium hydroxide was used for titrating the excess of acid after the absorption of the ammonia; and methyl-red was used as indicator.

(*b*) Sulphuric was used in place of hydrochloric acid as the hydrolytic agent as it reacts more slowly.

(*c*) In the experiments with *n*-butyramide and hydrocinnamide both by sulphuric acid and sodium hydroxide the concentrations of amide and of acid or alkali were the same, so that the equation used for calculating k was

$$k = \frac{1}{t} \frac{x}{(a-x)\,a}$$

(*d*) With the unsaturated amides, on the other hand, an excess of acid or alkali was used as the reactions are slower, and hence the equation used for calculating k was

$$k = \frac{2{\cdot}3025}{t\,(b-a)} \log_{10} \frac{b\,(a-x)}{a\,(b-x)}.$$

As no comparisons appear to have been made of the constants obtained by the hypobromite and magnesium hydroxide methods, we have determined the constant for *n*-butyramide with potassium hydroxide at 25° by using the magnesium hydroxide method (cf. Table X). The mean value obtained is $k = 0{\cdot}0529$ as compared with the value 0·0515 obtained by Peskoff and Meyer and the value 0·0506 obtained by us by the hypobromite method. The magnesium hydroxide value is rather higher, e.g., about 3 per cent., than Peskoff and Meyer's hypobromite value and this may be due to the error inherent in the hypobromite method of estimating ammonia.

Trial experiments with the different amides and magnesium hydroxide showed that the amount of hydrolysis is very small and varied from 0·14 per cent. for crotonamide to 0·43 per cent. for *n*-butyramide after boiling for 1·25 hours.

The values for k at 25° are calculated on the basis of unit time one hour and for comparison with the values at 100° must be divided by sixty.

SERIES A.

Hydrolysis by means of Sulphuric Acid.

The experimental data for the hydrolysis of the four amides by means of dilute sulphuric acid are given in Tables II–V.

The times are all given in minutes and the concentrations a, b, x are expressed in terms of normal in all cases.

SERIES B.

Hydrolysis by means of Sodium Hydroxide.

The experimental data for the four amides are given in Tables VI–IX.

The times are given in minutes and the concentrations a, b, x are expressed in terms of normal in all cases.

SUMMARY.

1. The four amides, *n*-butyramide, crotonamide, β-phenylpropionamide, cinnamamide, have been prepared and the velocity constants of hydrolysis determined with sodium hydroxide and with sulphuric acid at 100°. The method of estimating the amount of amide hydrolysed was similar to that used by Remsen and Reid in the case of aromatic amides.

2. The results show that the αβ-unsaturated amides are hydrolysed somewhat less readily than their saturated analogues.

With sodium hydroxide the ratio of saturated to unsaturated is 1·6 : 1 for the methyl and 3·4 : 1 for the phenyl compounds.

With sulphuric acid the corresponding ratios are 9 : 1 and 11 : 1.

3. The two methods of estimating the percentage hydrolysis, viz., heating with magnesium hydroxide and shaking with hypobromite give much the same values. On the whole the latter method gives slightly lower values.

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TABLE II.

Hydrolysis of Butyramide with Sulphuric Acid.

In Tables II and III 50 cc. of 0·1297N. acid was used in each estimation for absorbing ammonia, either from the hydrolysed or unhydrolysed amide.

$a = b = 0{\cdot}04942.$

	Time in minutes	cc. of 0·08798N. alkali used for titrating excess of acid	cc. of 0·1297N. alkali	cc. of 0·1295N. acid used up by the ammonia	Percentage of amide hydrolysed	x	$a-x$	$\frac{1}{t}\frac{k}{a}\frac{x}{(a-x)}$
(A)	30	67·60[1]	46·91	3·09	11·64	0·00575	0·04367	0·0888
		39·10[2]	26·53	23·47				
	60	64·10	43·48	6·52	23·71	0·01171	0·03771	[0·1072]
		42·80	29·02	20·98				
	90	62·55	42·42	7·58	29·08	0·01437	0·03505	0·0922
		46·45	31·51	18·49				
	120	59·60	40·42	9·58	34·42	0·01701	0·03241	0·0885
		46·80	31·74	18·26				
	150	57·45	38·96	11·04	39·60	0·01957	0·02985	0·0884
		48·90	33·16	16·84				
	180	55·40	37·58	12·42	43·04	0·02127	0·02815	0·0869
		49·50	33·57	16·43				
(B)	30	67·60	46·91	3·09	11·75	0·00581	0·04361	0·0898
		39·50	26·79	23·21				
	90	61·55	41·76	8·24	28·51	0·01409	0·03533	0·0896
		43·25	29·34	20·66				
	150	56·40	38·25	11·75	39·45	0·01949	0·02993	0·0879
		47·80	32·42	17·58				
	210	53·05	35·98	14·02	47·57	0·02351	0·02589	0·0875
		50·95	34·55	15·45				
	280	49·25	33·40	16·60	54·95	0·02716	0·02226	0·0881
		53·65	36·39	13·61				
	360	47·35	32·12	17·88	61·35	0·03032	0·01910	0·0892
		57·10	38·73	11·27				

Mean value of k. (A) = 0·0889. (B) = 0·0887. (A + B) = 0·0888.

[1] For the ammonia from the hydrolysed amide.
[2] For the ammonia from the unhydrolysed amide.

TABLE III.

Hydrolysis of Hydrocinnamamide with Sulphuric Acid.

$a = b = 0{\cdot}05116.$

	Time in minutes	cc. of 0·08798N. alkali used for titrating excess of acid	cc. of 0·1297N. alkali	cc. of 0·1297 N. acid used up by the ammonia	Percentage of amide hydrolysed	x	$a-x$	$= \frac{1}{t} \cdot \frac{x}{a(a-x)}$
(A)	30	67·45	45·75	4·25	14·41	0·00737	0·04379	0·1097
		36·50	24·76	25·24				
	90	61·30	41·59	8·41	29·30	0·01499	0·03617	0·0900
		43·80	29·71	20·29				
	150	56·40	38·25	11·75	38·35	0·01962	0·03154	0·0812
		45·85	31·11	18·89				
	210	52·90	35·88	14·12	44·64	0·02283	0·02833	0·0750
		47·80	32·48	17·52				
	280	52·50	35·61	14·39	49·52	0·02534	0·02582	0·0685
		52·10	35·33	14·67				
	360	41·10	27·87	22·13	57·02	0·02917	0·02199	0·0720
		49·10	33·31	16·69				
(B)	30	63·60	45·73	4·27	14·35	0·00734	0·04382	0·1091
		34·10	24·52	25·48				
	90	58·25	41·88	8·12	29·22	0·01495	0·03621	0·0897
		42·20	30·34	19·66				
	150	54·00	38·83	11·17	39·04	0·01997	0·03119	0·0834
		45·30	32·57	17·43				
	210	51·60	37·10	12·90	46·50	0·02379	0·02737	0·0809
		48·90	35·16	14·84				
	280	50·85	36·56	13·44	51·37	0·02628	0·02488	0·0737
		51·95	37·27	12·73				
	360	47·60	34·22	15·78	57·81	0·02890	0·02226	0·0721
		52·65	37·85	12·15				

Mean value of k. (A) = 0·0827. (B) = 0·0848. (A + B) = 0·0837.

TABLE IV.

Hydrolysis of Crotonamide with Sulphuric Acid.

In Tables IV and V 50 cc. of 0·08622 N. acid were used for absorbing the ammonia.

$a = 0{\cdot}05$. $b = 0{\cdot}4818$.

Time in minutes	cc. of 0·08798 N. alkali used for titrating excess of acid	cc. of 0·08622 N. alkali	cc. of 0·08622 N. acid used up by ammonia	Percentage of amide hydrolysed	x	$a - x$	$b - x$	$\log \frac{b(a-x)}{a(b-x)}$	$k = \frac{2{\cdot}302}{t(b-a)} \times \log \frac{b(a-x)}{a(b-x)}$
(A) 30	43·95	44·85	5·15	13·26	0·00663	0·04337	0·4752	0·0559	0·00993
	16·00	16·33	33·67						
90	36·15	36.89	13·11	34·08	0·01704	0·03296	0·4648	0·1654	0·00980
	24·15	24·64	25·36						
150	28·95	...	...	50·00	0·02500	0·02500	0·4568	0·2781	0·00988
	28·95	...	...						
210	23·70	24·18	25·82	61·49	0·03075	0·01925	0·4510	0·3860	0·00980
	33·15	33·83	16·17						
280	21·55	21·99	28·01	71·14	0·03557	0·01443	0·4462	0·5064	0·00964
	37·85	38·63	11·37						
360	17·50	17·85	32·15	79·87	0·03994	0·01006	0·4419	0·6590	0·00976
	41·05	41·89	8·11						
(B) 30	55·50	45·96	4·04	13·53	0·006766	0·04323	0·4750	0·0571	0·01014
	29·20	24·18	25·82						
90	47·25	39·13	10·87	34·85	0·01743	0·03257	0·4644	0·1703	0·00975
	35·85	29·68	20·32						
150	41·35	34·27	15·73	49·94	0·02497	0·02503	0·4568	0·2776	0·00987
	41·30	34·21	15·77						
210	37·10	30·73	19·27	61·62	0·03081	0·01919	0·4510	0·3874	0·00984
	45·90	38·00	12·00						
280	35·30	29·23	20·77	71·17	0·03558	0·01442	0·4462	0·5067	0·00965
	50·20	41·58	8·42						
360	31·35	25·96	24·04	79·52	0·03977	0·01023	0·4420	0·6518	0·00965
	52·90	43·81	6·19						

Mean value of k. (A) = 0·00980. (B) = 0·00981. (A + B) = 0·00980.

TABLE V.

Hydrolysis of Cinnamamide with Sulphuric Acid.

$a = 0{\cdot}05.$ $b = 0{\cdot}4818.$

Time in minutes	cc. N. alkali used for titrating excess of acid	cc. of 0·08798 N. alkali	cc. of 0·08622N acid used up by the ammonia.	Percentage of amide hydrolysed	x	$a - x$	$b - x$	$\log \frac{b(a-x)}{a(b-x)}$	$k = \frac{2{\cdot}302}{t(b-a)} \times \log \frac{b(a-x)}{a(b-x)}$
(A) 90	37·95	38·73	11·27	27·68	0·01384	0·03616	0·4680	0·1284	0·00761
	20·15	20·56	29·44						
150	32·55	33·21	16·79	41·24	0·02062	0·02938	0·4612	0·2120	0·00753
	25·55	26·07	23·93						
210	28·95	29·54	20·46	51·61	0·02581	0·02419	0·4560	0·2916	0·00740
	30·20	30·82	19·18						
280	22·05	22·50	27·50	61·31	0·03066	0·01934	0·4511	0·3840	0·00731
	32·00	32·65	17·35						
360	18·80	19·19	30·81	70 57	0·03529	0·01471	0·4461	0·4980	0·00739
	36·40	37·15	12·85						
(B) 30	45·00	45·92	4·08	10·28	0·00514	0·04486	0·4767	0·0425	0·00755
	14·10	14·39	35·61						
90	38·35	39·13	10·87	27·43	0·01371	0·03629	0·4681	0·1267	0·00751
	20·80	21·22	28·78						
150	32·80	33·47	16·53	41·46	0·02073	0·02927	0·4611	0·2136	0·00759
	26·15	26·68	23·32						
210	26·85	27·39	22·61	52·43	0·02622	0·02378	0·4556	0·2986	0·00758
	28·90	29·49	20·51						
280	24·20	24·69	25·31	61·78	0·03089	0·01911	0·4509	0·3991	0 00760
	33·65	34·34	15·66						
360	15·80	16·13	33·87	70·23	0·03510	0·01490	0·4467	0·4930	0 00730
	34·90	35·61	14·39						

Mean value of k. (A) = 0·00745. (B) = 0·00752. (A + B) = 0·00748.

TABLE VI.

Hydrolysis of Butyramide with Sodium Hydroxide.

In each estimation in Tables VII–X 50 cc. of 0·0922 N. acid was used for absorbing the ammonia derived from the unhydrolysed amide.

$a=b=0{\cdot}0513.$

Time in minutes.	cc. of Solution taken.	cc. of 0·08726 N. Alkali used for titrating excess of acid.	cc. of 0·09221 N. Alkali.	cc. of 0·09221 N. acid used up by the ammonia from undecomposed amide.	Percentage of amide hydrolysed.	x	$a-x$	$k=\frac{1}{t}\cdot\frac{x}{a(a-x)}$
(A)30	64·00	20·75	19·64	30·36	14·75	0·00757	0·04373	0·113
60	72·10	21·40	20·25	29·75	25·83	0·01325	0·03805	0·113
90	68·90	25·90	24·51	25·49	34·56	0·01773	0·03457	0·111
120	74·95	26·95	25·51	24·49	41·23	0·02118	0·03012	0·114
180	59·20	35·25	33·36	16·64	49·48	0·02538	0·02592	0·106
240	76·70	33·50	31·71	18·29	57·14	0·02931	0·02199	0·108
(B)30	73·15	16·40	15·52	34·48	15·29	0·00784	0-04346	0·117
60	71·25	21·75	20·59	29·41	26·02	0·01325	0·03805	0·114
90	74·10	23·85	22·57	27·43	33·45	0·01716	0·03414	0·109
120	74·65	26·85	25·41	24·59	40·78	0·02092	0·03038	0·112
180	68·00	33·00	31·23	18·77	50·40	0·02585	0·02545	0·110
270	77·35	34·45	32·60	17·40	59·60	0·03057	0·02073	0·106

Mean value of k. (A) = 0·111. (B) = 0·111. (A+B)=0·111.

TABLE VII.

Hydrolysis of Hydrocinnamamide with Sodium Hydroxide.

$a=b=0{\cdot}0513.$

(A)30	57·80	26·00	24·61	25·39	21·06	0·0108	0·0405	0·173
65	70·45	26·60	25·18	24·82	36·69	0·01882	0·03248	0·173
90	67·30	30·65	29·00	21·00	43·92	0·02253	0·02877	0·170
120	80·15	30·00	28·39	21·61	51·53	0·02644	0·02486	0·173
180	68·40	37·35	35·35	14·65	61·52	0·03156	0·01974	0·173
240	73·75	38·80	36·72	13·28	67·64	0·03470	0·01660	0·170
(B)30	70·55	20·10	19·02	30·98	20·07	0·01081	0·04049	0·173
60	67·15	26·95	25·51	24·49	34·46	0·01768	0·03362	0·171
90	64·15	31·85	30·14	19·86	44·33	0·02274	0·02856	0·173
120	73·15	31·90	30·19	19·81	51·34	0·02633	0·02497	0·171
180	72·00	36·35	34·41	15·59	61·09	0·03134	0·01996	0·170

Mean value of k. (A) = 0·172. (B) = 0·172. (A + B) = 0·172.

TABLE VIII.

Hydrolysis of Crotonamide with Sodium Hydroxide.

a=0·05, b=0·2955.

Time in minutes.	cc. of Solution taken.	cc. of 0·08726 N. Alkali used for titrating excess of acid.	cc. of 0·09221 N. Alkali.	cc. of 0·09221 N. Acid used up by ammonia from unde-composed amide.	Percentage of amide hydrolysed.	x	$a-x$	$b-x$	$\log \frac{b(a-x)}{a(b-x)}$	$k = \frac{2\cdot302}{t(b-a)} \times \log \frac{b(a-x)}{a(b-x)}$
(A) 30	74·35	28·85	27·31	22·69	43·74	0·02187	0·02813	0·2736	0·2164	0·06764
60	73·80	39·90	37·77	12·23	69·44	0·03472	0·01528	0·2608	0·4608	0·07199
90	72·80	45·95	43·49	6·51	83·92	0·04175	0·008245	0·2538	0·7168	0·07467
120	72·60	49·00	46·37	3·63	90·78	0·04538	0·00462	0·2501	0·9629	0·07510
(B) 15	73·75	19·25	18·22	31·78	20·53	0·01027	0·03973	0·2852	0·0845	0·05282
30	76·40	27·30	25·84	24·16	41·68	0·02084	0·02916	0·2747	0·2027	0·06336
45	74·90	34·20	32·36	17·64	56·57	0·02829	0·02171	0·2672	0·3186	0·06637
60	73·75	39·75	37·61	12·39	69·04	0·03452	0·01548	0·2610	0·4552	0·07112
90	75·50	45·50	42·96	7·04	82·79	0·04140	0·00860	0·2541	0·6991	0·07285
120	79·80	48·70	46·09	3·91	90·97	0·04548	0·00452	0·2500	0·9715	0·07590

Mean value of k. (A) = 0·07235. (B) = 0·06707. (A + B) = 0·06971

TABLE IX.

Hydrolysis of Cinnamamide with Sodium Hydroxide.

a=0·05, b=0·2955.

Time in minutes.	cc. of solution taken.	cc. of 0·08726 N. alkali used for titrating excess of acid.	cc. of 0·09221 N. alkali.	cc. of 0·09221 N. acid used up by ammonia from undecomposed amide.	Percentage of amide hydrolysed.	x	$a-x$	$b-x$	$\log \frac{b(a-x)}{a(b-x)}$	$k=\frac{2\cdot302}{t(b-a)}\times \log \frac{b(a-x)}{a(b-x)}$
(A) 30	75·80	24·60	23·28	26·72	35·01	0·01751	0·03249	0·2780	0·1607	0·0502
60	75·65	34·35	32·51	17·49	57·38	0·02869	0·02131	0·2668	0·3261	0·0509
90	73·65	40·75	38·57	11·43	71·37	0·03569	0·01431	0·2598	0·4877	0·0508
120	72·95	45·00	42·59	7·41	81·27	0·040635	0·009365	0·2549	0·6633	0·0518
180	73·55	49·10	46·47	3·53	91·16	0.045575	0·004425	0·2499	0·9804	0·0511
(B) 15	73·00	19·45	18·41	31·59	20·21	0·01011	0·03989	0·2854	0·0830	0·0519
30	71·65	26·35	24·94	25·06	35·52	0·01776	0·03224	0·2777	0·1637	0·0512
60	76·10	34·30	32·50	17·50	57·62	0·02881	0·02119	0·2667	0·3282	0·0512
90	72·40	41·05	38·86	11·14	71·61	0·03581	0·01419	0·2597	0·4912	0·0512
120	77·50	44·40	42·03	7·97	81·04	0·04052	0·00948	0·2550	0·6581	0·0514
180	75·15	48·75	46·13	3·87	90·48	0·04525	0·00475	0·2502	0·9502	0·0500

Mean value of k. (A) = 0·0510. (B) = 0·0512. (A + B) = 0·0511.

TABLE X.

Hydrolysis of n-*Butyramide with Potassium Hydroxide at 25°.*

In each estimation 50 cc. of 0·1054N. acid was used for absorbing the ammonia.

$a = b = 0{\cdot}1221.$

Time in *hours*		cc. of solution taken	cc. of 0·09279 N. alkali for titrating excess of acid	cc. of 0·1054N. alkali	cc. of 0·1054N. acid used up by ammonia from un-decomposed amide	Percentage of amide hydrolysed	x	$a-x$	$\frac{k}{} = \frac{1}{t} \cdot \frac{x}{(a-x)\,a}$
(A)	14	25	26·6	23·42	26·58	8·845	0·01080	0·11130	0·05678
	26	25	28·3	24·92	25·08	13·26	0·01620	0·10590	0·04818
	38	25	30·3	26·74	23·26	19·69	0·02404	0·09806	0·05283
	50	25	32·3	28·44	21·56	25·58	0·03122	0·09088	0·05627
	62	25	33·1	29·14	20·86	27·97	0·03414	0·08796	0·05128

$b = 0{\cdot}4343.$ $a = 0{\cdot}09393.$

Time in *hours*		cc. of solution taken	cc. of 0·09279 N. alkali for titrating excess of acid	cc. of 0·1054N. alkali	cc. of 0·1054N. acid used up by ammonia from un-decomposed amide	Percentage of amide hydrolysed	x	$a-x$	$b-x$	$\log \frac{b}{a} \cdot \frac{a-x}{b-x}$	$\frac{k}{} = \frac{2{\cdot}302}{t(b-a)} \times \log \frac{b(a-x)}{a(b-x)}$
(B)	5	25	33·90	30·11	19·89	10·71	0·0101	0·08387	0·4243	0·0391	0·0529
	12	25	37·10	32·96	17·04	23·53	0·0221	0·07183	0·4122	0·0938	0·0529
	24	25	41·50	36·86	13·14	41·00	0·0385	0·0554	0·3958	0·1890	0·0533
	36	25	44·85	39·85	10·15	54·44	0·05114	0·04279	0·3832	0·2871	0·0539
	48	25	46·90	41·67	8·33	62·62	0·05881	0·03512	0·3755	0·3641	0·0513

Mean value of k. (A) = 0·0531. (B) = 0·0529. (A + B) = 0·0530.

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