

XIV.—*The Relative Strengths of Bases in Non-aqueous Solutions. Part III.**

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THE reduction of availability of hydrogen chloride in alcoholic solution, as determined by its catalytic effect on the esterification of carboxylic acids (Goldschmidt and Udby, *Z. physikal. Chem.*, 1907, **60**, 728; Lapworth and Partington, *J.*, 1910, **97**, 19), may be attributed to combination of the water, or other weak base producing the effect, with hydrion as the effective catalyst, and this hypothesis has been adopted in the present communication, although such a specific assumption is not necessary (Lapworth, *Trans. Faraday Soc.*, 1928, **24**, 721).

Mitchell and Partington (*J.*, 1929, 1562) investigated the effects of other oxygen compounds which might be expected to exhibit the same type of anticatalytic activity as water. Ethyl ether had a slight accelerating effect, methyl ether no effect at all, and dimethylpyrone a retarding effect about double that caused by an equivalent amount of water. This was explained, tentatively, by the assumption that whereas water could combine with one molecule of hydrion, dimethylpyrone could combine with two, and (as had been suggested by Kendall, *J. Amer. Chem. Soc.*, 1914, **36**, 1722; 1915, **37**, 160; 1917, **39**, 2303; and by Knox and Richards, *J.*, 1919, **115**, 508) that the carbonyl oxygen atom could also combine with hydrion. This assumption, as will be seen in what follows, is not capable of explaining the results with other compounds and is no longer entertained.

The present investigations are the first of a series of experiments which have for their object the discovery of some relation between the particular type of linkage of oxygen in compounds which might be expected to act as weak bases and the strengths of the basic properties exhibited by such compounds as measured by the anticatalytic effect.

It has been found that di-*n*- and -*iso*-propyl ethers have no appreciable effect on the reaction, and this, taken in conjunction with the results of Mitchell and Partington with methyl and ethyl ethers, shows that the alkyl ethers do not exhibit any basic properties in the conditions of these experiments. In pursuance of the idea that some generalisations might be drawn from the effect of substances containing a heterocyclic oxygen atom, furan was used, but was found to produce no effect beyond a slight acceleration. The

* Part I, Lapworth and Partington, *J.*, 1910, **97**, 19; Part II, Mitchell and Partington, *J.*, 1929, 1562.

oxygen linkage in furan is, however, the same as that in γ -pyrone, which was found to possess marked anticatalytic activity. The carbonyl group as such does not appear to possess any marked basic function, since benzil produced no effect beyond a slight acceleration. From figures given by Lapworth (J., 1908, 93, 2199) it appears that acetone should have no anticatalytic effect.

It was thought probable that the capacity of a substance for combining with hydrion might run parallel with its capacity for molecular association. A substance which appears to be highly associated is glycerol (compare Young, "Stoicheimetry," 1908, p. 359), but this was found to have no effect on the reaction velocity.

Since pyrones appeared to be the most promising substances, other members of the series were tried, particular attention being paid to the influence of the groups attached to the two carbon atoms adjacent to the oxygen atom in the ring. With diphenylpyrone a retarding effect was produced which, although greater than that produced by an equimolecular amount of water, was not so great as that produced by an equimolecular amount of dimethylpyrone. Phenylmethylpyrone had an effect intermediate between those of dimethyl- and diphenyl-pyrene. Unsubstituted γ -pyrone was found to have an effect about half as great as that produced by an equimolecular amount of water, and considerably less than that of diphenylpyrone.

Lapworth's theory (J., 1908, 93, 2187) was then applied to calculate the ratios of the equilibrium constants for the formation, by each pyrone and by water respectively, of complex ions with hydrion, the assumption being made that each molecule of hydrion combines with one of base. In this way a quantitative measure of the relative strengths of the bases as compared with water could be obtained. If we denote by K_2, K_2' , and K_2'' the equilibrium constants for water, alcohol, and another weak base, in the reaction $B + H^+ = B \cdot H^+$, where $K_2 = [H^+][B]/[B \cdot H^+]$, we find the following values of K_2/K_2'' :

Series.	Water value.	Kc.	Base.	K_2/K_2'' .
A	0.18	1.85	Diphenylpyrone	1.19
B	0.14	2.27	Diphenylpyrone	1.31
			Phenylmethylpyrone	1.83
			Dimethylpyrone	2.81
C	0.135	1.85	γ -Pyrone	0.55
			Dimethylpyrone	2.67

(The meanings of the water value and of K_c are explained below.)

EXPERIMENTAL.

The alcohol used throughout was prepared from 96% spirit which was refluxed for 6 hours with half its volume of well-burnt lime and

two sticks of caustic soda per litre. It was then distilled into a flask containing another charge of lime and soda mixture, the refluxing being repeated and followed by distillation into a clean dry flask, the exit of which was guarded with a calcium chloride tube. Clean, fresh calcium turnings were dropped in, and the whole left to stand for a day. It was then refluxed for 6 hours and distilled off through a 12-bulb fractionating column. The middle fraction was collected. The product, which was free from aldehyde, ketone, and ammonia, was stored in a vessel with a siphon attachment and a guard tube of phosphoric oxide.

Di-*n*-propyl ether was prepared by the method of Norton and Prescott (*Amer. Chem. J.*, 1884, **6**, 243). On redistillation from fresh sodium, the fraction of b. p. 88—90° was collected and used.

Diisopropyl ether, prepared by the method of Erlenmeyer (*Annalen*, 1863, **126**, 306), had b. p. 68°.

Attempts were made to prepare furan by the method of Freundler (*Compt. rend.*, 1897, **124**, 1157). Pyromucic acid was heated in portions of 5 g. in sealed tubes for 2 hours at 270°. In all, six tubes were used, four of which burst on heating. The other two were opened in the usual way. Nothing was found in them except a little pyromucic acid. The furan was therefore made by another method described by Freundler in the same paper. Barium pyromucate was heated alone, and the distillate collected and purified. The product was a colourless liquid, b. p. 32°, which had no action on sodium.

Benzil was purified by recrystallising it twice from absolute alcohol and drying it in a vacuum over phosphoric oxide; m. p. 95°.

Pure commercial glycerol was distilled twice in a vacuum, the first and last fractions being rejected.

Diphenylpyrone was made from distyryl ketone (Vorländer and Meyer, *Ber.*, 1912, **45**, 3355; Claisen and Claparède, *Ber.*, 1881, **14**, 2461). The product consisted of white needles, m. p. 139—140°, and gave a violet fluorescence in concentrated sulphuric acid.

Phenylmethylpyrone was made by a modification of the method of Ruhemann (*J.*, 1908, **93**, 431), recommended by Gibson and Simonsen (*J.*, 1928, 2307). The product on recrystallising from ligroin and drying over wax in a vacuum was obtained as small white needles, m. p. 86—87°.

Unsubstituted γ -pyrone was prepared by the method of Willstätter and Pummerer (*Ber.*, 1904, **37**, 3704, 3734). The crude product was purified by distillation under reduced pressure, the fraction boiling at 105°/16 mm. being collected; m. p. 31.5°.

Dimethylpyrone (British Drug Houses) was used direct; m. p. 132°.

In other respects the materials used and the experimental procedure adopted were the same as those of Mitchell and Partington (*loc. cit.*). Alcoholic solutions of phenylacetic acid and hydrogen chloride were made up and their concentrations determined. When the solutions attained the temperature of the thermostat (25° ± 0.05°), 25 c.c.-portions of each solution were mixed. 5 C.c. of the mixture were withdrawn from time to time and titrated with *N*/10-sodium hydroxide. The water value of the alcohol, *R*, was calculated from the formula

$$Kc = \frac{(R + W + Y_0)(\log_e Y_1 - \log_e Y) - (Y_1 - Y)}{t - t_1} \quad (1)$$

Kc in the tables is based on the value of *K* referring to one litre of solution, and *c* is expressed in mols. per litre. In equation (1), *c* is in *N*/10 c.c. units per litre and *K* refers to 10 c.c. of solution, since *R*, *W*, and *Y* are in these units. Therefore *Kc* (proper) = *Kc* (equation 1) × (1/10,000) × 100 = *Kc* × 10⁻². Thus, in Series A, Flask 1, the values of *Kc* from equation (1), taking *R* = 18 (*i.e.*, *r* = 0.18), *W* = 0, *Y*₀ = 10.56, give a mean result of 0.185. *Kc* is, therefore, entered in the table as 0.00185. In the calculation of *Kc*, the value of *Y*₁ was taken as that of the first titre of 10 c.c., *i.e.*, 15 minutes after the commencement of the reaction, and the correct value of *r* was taken as that which made the mean values of *Kc* for the normal and the retarded reaction coincide. In substituting *W* or *M*'' in equations (1) and (2), the weight in grams in 40 c.c., *g*, was converted into *N*/10 c.c. units in 10 c.c. by the relation

$$M'' = g \times 10,000 / (\text{mol. wt. of subst.}) \times 4.$$

The equation for the case in which a second weak base in addition to water is present in the solution in concentration *M*'' is readily found from the equations given by Lapworth (*J.*, 1908, **93**, 2187) to be

$$Kc = \frac{(R + W + K_2 M'' / K_2'' + Y_0)(\log_e Y_1 - \log_e Y) - (Y_1 - Y)}{t - t_1} \quad (2)$$

The ratio *K*₂/*K*₂'' can be found for the particular weak base by (i) finding the value of *R* from the normal reaction and the reaction in which water only has been added, by means of equation (1), and then (ii) substituting this value of *R* and the corresponding value of *Kc* in equation (2).

Series A.

Phenylacetic acid = 0.1055*N*; hydrogen chloride = 0.0505*N*.

<i>t.</i>	$Y = 2(a-x).$	$Kc \times 10^3, \text{ assuming}$			
		$r = 0.16.$	$r = 0.17.$	$r = 0.18.$	$r = 0.19.$
Flask 1. No water.					
0	10.56	—	—	—	—
15	8.97	—	—	—	—
30	7.85	1.61	1.70	1.79	1.88
50	6.59	1.66	1.75	1.84	1.92
70	5.63	1.64	1.73	1.81	1.90
90	4.75	1.69	1.77	1.86	1.94
120	3.71	1.73	1.82	1.90	1.98
150	2.98	1.72	1.80	1.89	1.97
	Mean	1.675	1.76	1.85	1.93
Flask 2. 0.1251 G. of water.					
0	10.56	—	—	—	—
15	9.69	—	—	—	—
30	8.97	1.78	1.83	1.88	1.93
50	8.16	1.72	1.77	1.82	1.87
70	7.42	1.72	1.77	1.82	1.87
90	6.67	1.79	1.83	1.88	1.93
120	5.83	1.76	1.81	1.85	1.90
150	5.06	1.77	1.82	1.87	1.92
	Mean	1.755	1.805	1.85	1.90

Therefore $r = 0.18$ and $Kc = 1.85$.

<i>t.</i>	$Y = 2(a-x).$	0.9306 G. of diphenylpyrone.		<i>t.</i>	$Y = 2(a-x).$	$K_2/K_3''.$
		$K_1/K_2''.$				
0	10.56	—		70	6.53	1.07
15	9.08	—		90	5.92	1.20
30	8.30	1.17		120	5.02	1.18
50	7.46	1.34		150	4.30	1.20
					Mean	1.19

Series B.

Phenylacetic acid = 0.1004*N*; hydrogen chloride = 0.05335*N*.

<i>t.</i>	$Y = 2(a-x).$	$Kc \times 10^3, \text{ assuming}$			
		$r = 0.13.$	$r = 0.14.$	$r = 0.15.$	$r = 0.16.$
Flask 1. No water.					
0	10.10	—	—	—	—
15	7.88	—	—	—	—
30	6.48	2.08	2.21	2.34	2.47
50	4.98	2.20	2.33	2.46	2.59
70	3.96	2.18	2.30	2.43	2.55
90	3.14	2.20	2.33	2.45	2.57
120	2.34	2.15	2.26	2.37	2.49
150	1.80	2.08	2.18	2.29	2.40
	Mean	2.15	2.27	2.39	2.51
Flask 2. 0.0915 G. of water.					
0	10.10	—	—	—	—
15	8.86	—	—	—	—
30	7.84	2.24	2.32	2.40	2.48
50	6.76	2.17	2.25	2.32	2.40
70	5.84	2.17	2.24	2.32	2.39
90	5.00	2.22	2.30	2.37	2.45
120	4.06	2.20	2.28	2.35	2.43
150	3.36	2.17	2.24	2.31	2.38
	Mean	2.20	2.27	2.34	2.42

Therefore $r = 0.14$ and $Kc = 2.27$.

Flask 3.

1.261 G. of diphenylpyrone.

<i>t.</i>	$Y=2(a-x).$	$K_2/K_2''.$
0	10.10	—
15	8.67	—
30	7.77	1.19
50	6.82	1.33
70	5.97	1.31
90	5.25	1.31
120	4.37	1.34
150	3.69	1.39

Mean 1.31

Flask 4.

0.9454 G. of phenylmethylpyrone.

<i>t.</i>	$Y=2(a-x).$	$K_2/K_2''.$
0	10.10	—
15	9.08	—
30	8.28	1.69
50	7.40	1.89
70	6.60	1.79
90	5.94	1.77
120	5.12	1.92
150	4.40	1.94

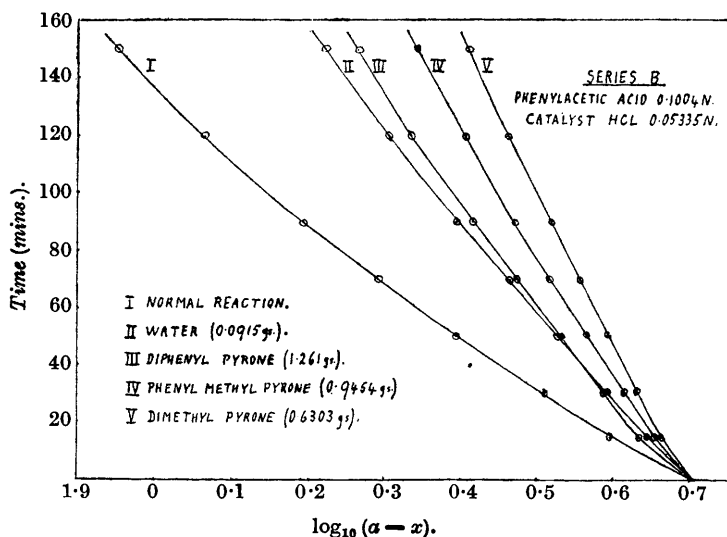
Mean 1.83

Flask 5. 0.6303 G. of dimethylpyrone.

<i>t.</i>	$Y=2(a-x).$	$K_2/K_2''.$	<i>t.</i>	$Y=2(a-x).$	$K_2/K_2''.$
0	10.10	—	70	7.21	2.79
15	9.19	—	90	6.63	2.82
30	8.59	2.77	120	5.81	2.78
50	7.89	2.87	150	5.17	2.84

Mean 2.81

In this series of reactions the water and pyrones were weighed out in exactly equimolecular quantities. The results are shown graphically in the accompanying figure.



Series C.

Phenylacetic acid = 0.1013*N*; hydrogen chloride = 0.0463*N*.

<i>t.</i>	$Y=2(a-x).$	$Kc \times 10^3$, assuming			
		$r=0.12.$	$r=0.13.$	$r=0.14.$	$r=0.15.$
Flask 1. No Water.					
0	10.08	—	—	—	—
15	8.30	—	—	—	—
30	6.98	1.67	1.78	1.89	2.02
50	5.64	1.67	1.78	1.89	2.01
70	4.61	1.69	1.79	1.90	2.01
90	3.76	1.73	1.82	1.92	2.03
120	2.88	1.71	1.80	1.91	2.01
150	2.26	1.68	1.77	1.87	1.98
	Mean	1.69	1.79	1.90	2.01
Flask 2. 0.0710 G. of water.					
0	10.08	—	—	—	—
15	8.97	—	—	—	—
30	8.03	1.73	1.80	1.88	1.95
50	6.98	1.72	1.79	1.86	1.94
70	6.07	1.74	1.81	1.88	1.95
90	5.33	1.73	1.80	1.87	1.94
120	4.38	1.74	1.81	1.88	1.95
150	3.60	1.76	1.83	1.90	1.95
	Mean	1.74	1.81	1.88	1.95

Therefore $r = 0.135$ and $Kc = 1.85$.

Flask 3. 0.4964 G. of γ -pyrone.			Flask 4. 0.4120 G. of dimethylpyrone.		
<i>t.</i>	$Y=2(a-x).$	$K_2/K_2''.$	<i>t.</i>	$Y=2(a-x).$	$K_2/K_2''.$
0	10.08	—	0	10.08	—
15	8.80	—	15	9.03	—
30	7.78	0.576	30	8.38	2.68
50	6.63	0.554	50	7.59	2.65
70	5.64	0.513	70	6.88	2.63
90	4.86	0.513	90	6.27	2.66
120	3.93	0.556	120	5.47	2.69
150	3.27	0.577	150	4.78	2.70
	Mean	0.548		Mean	2.67

Summary.

The rate of esterification of phenylacetic acid in dry alcoholic solution under the influence of hydrogen chloride is slightly accelerated by small quantities of benzil and furan, is not affected by small quantities of di-*n*- and -*iso*-propyl ethers and glycerol, and is retarded to various extents by diphenylpyrone, phenylmethylpyrone and unsubstituted γ -pyrone. None of these pyrones has as great a retarding effect as dimethylpyrone.

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[Received, November 26th, 1930.]