CCIV.—*The Influence of Ethyl Ether and of Dimethylpyrone on the Availability of Hydrogen Chloride in Alcoholic Solution.*

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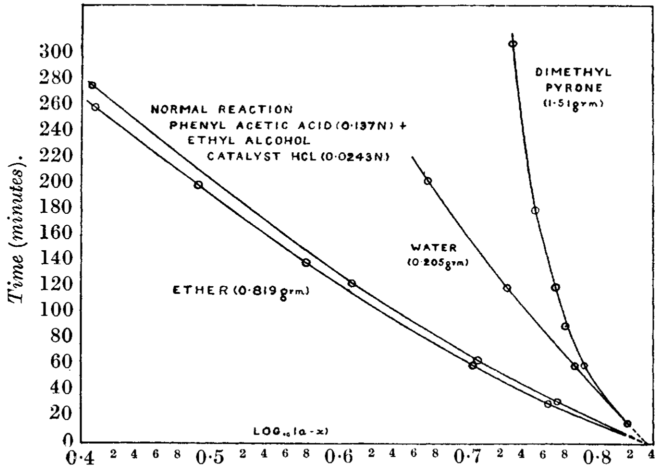
GOLDSCHMIDT and UDBY (*Z. physikal. Chem.*, 1907, **60**, 728) and Lapworth and Partington (J., 1910, **97**, 19) have shown that small amounts of water exert a retarding effect on the esterification of carboxylic acids in alcoholic solution under the catalytic influence of hydrogen chloride. This effect is attributed to a change in the availability of the catalyst, which is greatly altered by small changes in water content. These changes in availability cannot be explained by Arrhenius's theory of salt hydrolysis, but were interpreted on the assumption that the water acts as a base by uniting with hydrion to form a complex ion.

Lapworth and Partington (*loc. cit.*) define the availability of an acid as a function proportional to its capacity for forming complexes of hydrion with any monoacid base, and at any moment the concentration of complex ion is given by $\xi = KBP$, where K is a constant for the base in the medium used, B is the concentration of free base, and P is the availability of the acid. The definition of a base here employed is that it is a substance capable of uniting with hydrion.

Goldschmidt and Udby found that with a given concentration of mineral acid and carboxylic acid, the velocity of esterification is nearly proportional to $1/(r + w)$, where r is a constant which depends only on the alcohol, and w is the concentration of water.

Fig. 1.



The constant r is called the " water value " of the sample of alcohol used.

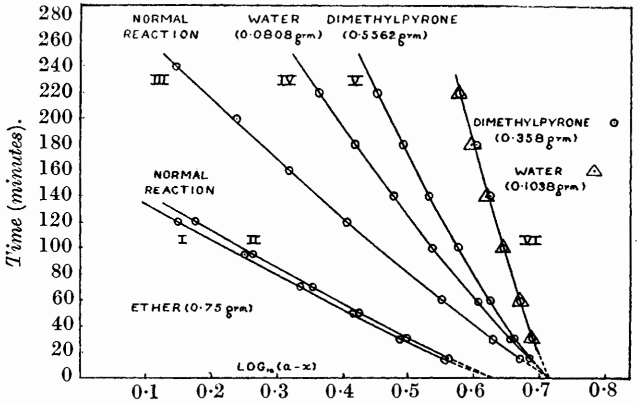
Since it is assumed that water retards the reaction by union with hydrion, the present work was undertaken with the view of determining the effect of other compounds, containing oxygen atoms which might be thought capable of similarly uniting with hydrion, on the rate of esterification of phenylacetic acid under the catalytic influence of hydrogen chloride.

The compounds investigated were ethyl ether and dimethylpyrone. Preliminary investigations indicated that, whereas dimethylpyrone retarded the rate of esterification, a small amount of ether actually accelerated it. This is illustrated graphically in Fig. 1. In every case $(a - x)$ is the equivalent of unchanged phenylacetic acid at the end of time t, in 5 c.c. of the mixture, expressed in c.c. of $N/10$-sodium hydroxide. The weights of water, ether, and dimethylpyrone represent, in every case, the amount added to 40 c.c.

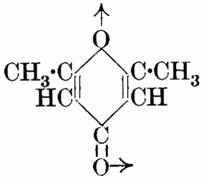
The accelerating effect of ether was confirmed (Fig. 2). This acceleration might be due solely to the solvent effect of this small amount of ether, or to the predominance of the solvent effect over retardation due to union with hydrion.

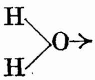
The effects of equimolecular amounts of dimethylpyrone and water did not at first appear comparable (Figs. 1 and 2). Dimethylpyrone has, however, two oxygen atoms each of which might be capable of uniting with hydrion ("co-ordinating protons," hypothetically), whereas water has only one :

FIG. 2.



I *and* II. *Phenylacetic acid,* 0·0857N ; *hydrochloric acid,* 0·0524N.
III, IV, *and* V. *Phenylacetic acid,* 0·104N ; *hydrochloric acid,* 0·0321N.
VI. *Phenylacetic acid,* 0·104N ; *hydrochloric acid,* 0·0163N.





On this assumption, dimethylpyrone is regarded as dibasic, and if equivalent amounts of dimethylpyrone and water are compared the results are similar (Fig. 2).

This similarity of effect between equivalent amounts of dimethylpyrone (dibasic) and water is further supported by the calculation of *Kc* from a modification of Goldschmidt and Udby's equation, as is shown below. A comparison of *Kc* for a normal solution with *Kc* for a solution to which water had been added indicates a value $r = 0{\cdot}18$ for the alcohol used.

As the availability of very dilute hydrogen chloride in moist alcohol is nearly an inverse linear function of the amount of water present, for quantities of water not exceeding a concentration of $N/2$, no further treatment of the alcohol with calcium was considered necessary.

If, in Goldschmidt and Udby's equation, for W, the equivalent of initially added water, we substitute the value in mols. of dimethylpyrone, the results are not comparable. If, however, dimethylpyrone is regarded as dibasic, as suggested above, the calculated results are comparable with those obtained with water when equivalent amounts are used, and give $r = 0{\cdot}18$.

EXPERIMENTAL.

The alcohol employed in these determinations was prepared from 99% alcohol, which was refluxed with sodium hydroxide to resinify the small traces of aldehyde present, distilled, refluxed over fresh calcium turnings, and finally redistilled. 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.

Phenylacetic acid (Kahlbaum), m. p. 75—77°, dried over sulphuric acid in a vacuum, was employed in all cases.

The ether was treated with sodium hydroxide for some days, distilled, treated with calcium chloride, decanted off, redistilled, and treated with sodium wire until this remained unchanged. It was left for several weeks, then again distilled and placed over fresh sodium, from which it could be distilled as required.

Dimethylpyrone (British Drug Houses), m. p. 132—135°, was used directly. The amounts of phenylacetic acid were roughly weighed, but the amounts of water, ether, and dimethylpyrone were accurately weighed in each case.

The alcoholic hydrogen chloride was prepared by passing the dry gas into about 120 c.c. of the alcohol.

The strengths of the hydrochloric and phenylacetic acids were determined by titration with $N/10$-sodium hydroxide, phenolphthalein being used as indicator. The flasks employed were carefully cleaned and dried in hot air before each experiment.

In each case, the alcoholic solutions were first heated to the temperature of the thermostat, $25{\cdot}0° \pm 0{\cdot}05°$, then 20 c.c. of each were mixed and the time noted. One or two titrations were always made near the commencement of the reaction, for the purpose of obtaining the true initial titre by extrapolation in order that this value might confirm the previous determinations.

The intermediate values of the coefficients being the most trustworthy, the approximate water value of the alcohol is best gauged by comparing the intermediate values for the normal reaction and the corresponding one with water present. This method was adopted by Lapworth and Partington (*loc. cit.*) in calculating their results, since the more trustworthy values for the velocity are those calculated from the time when the change has become steady at a point not far from half-way towards the end.

$R(= 100\ r)$ was calculated throughout from the formula corresponding to that used by Goldschmidt and Udby as

$$-\,dY/dt = KcY/(R + W + Y_0 - Y)$$

when the concentration of catalyst is constant, whence

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

where Y_0 = initial titre of phenylacetic acid in 10 c.c. of the solution against $N/10$-NaOH;
Y_1 = first such titre after reaction has commenced, made at time t_1;
Y = similar titre of 10 c.c. of solution at time t, *i.e.*, $Y = 2(a - x)$;
R = water equivalent of 10 c.c. of the alcohol in terms of c.c. of $N/10$;
W = equivalent of initially added water;
c = concentration of hydrogen chloride;
K = a constant (Lapworth, J., 1908, **93**, 2195);
t = time in minutes.

Series A. Phenylacetic acid, 0·104N; hydrochloric acid, 0·0321N.

Flask 1. *No water.*

		$Kc \times 10^3$, assuming			
t.	$Y = 2(a - x)$.	$r = 0{\cdot}17$.	$r = 0{\cdot}18$.	$r = 0{\cdot}19$.	$r = 0{\cdot}20$.
0	10·40	—	—	—	—
15	9·40	—	—	—	—
30	8·56	1·15	1·21	1·27	1·33
60	7·23	1·12	1·17	1·23	1·29
120	5·11	1·18	1·24	1·30	1·36
160	4·17	1·17	1·23	1·29	1·34
200	3·45	1·19	1·25	1·30	1·36
240	2·79	1·16	1·24	1·29	1·35
	Mean	1·16	1·22	1·28	1·34

Flask 2. *Water*, 0·0808 *g*.

0	10·40	—	—	—	—
15	9·69	—	—	—	—
30	9·08	1·27	1·31	1·35	1·40
60	8·17	1·13	1·16	1·20	1·24
100	6·90	1·21	1·25	1·29	1·33
140	6·04	1·17	1·21	1·25	1·28
180	5·26	1·16	1·20	1·23	1·27
220	4·62	1·15	1·18	1·22	1·26
	Mean	1·18	1·22	1·26	1·30

Flask 3. *Dimethylpyrone*, 0·5562 *g*.

0	10·40	—	—	—	—
15	9·70	—	—	—	—
30	9·22	1·36	1·40	1·43	1·47
60	8·50	1·19	1·22	1·25	1·28
100	7·56	1·21	1·24	1·27	1·30
140	6·80	1·18	1·21	1·24	1·27
180	6·24	1·12	1·15	1·18	1·20
220	5·65	1·15	1·18	1·21	1·24
	Mean	1·20	1·23	1·26	1·29

In each case the value of r is 0·18.

Series B. Phenylacetic acid, 0·0987*N*; hydrochloric acid, 0·556*N*.

Flask 1. *No water*.

		Kc × 10³, assuming			
t.	*Y* = 2 (*a* − *x*).	r = 0·17.	r = 0·18.	r = 0·19.	r = 0·20.
0	9·87	—	—	—	—
15	8·44	—	—	—	—
30	7·19	2·04	2·14	2·25	2·36
50	6·11	1·81	1·90	2·00	2·09
70	5·09	1·86	1·95	2·05	2·14
90	4·31	1·86	1·95	2·04	2·13
120	3·35	1·88	1·97	2·06	2·14
	Mean	1·89	1·98	2·08	2·17

Flask 2. *Water*, 0·2002 *g*.

0	9·87	—	—	—	—
15	9·13	—	—	—	—
30	8·58	1·90	1·94	1·98	2·02
50	7·82	2·05	2·09	2·14	2·18
70	7·37	1·81	1·85	1·89	1·93
90	6·64	1·99	2·03	2·07	2·12
120	5·92	1·95	1·99	2·03	2·07
	Mean	1·94	1·98	2·02	2·06

Flask 3. *Dimethylpyrone*, 1·3778 *g*.

0	9·87	—	—	—	—
15	9·17	—	—	—	—
30	8·76	2·23	2·26	2·29	2·32
50	8·35	1·97	2·00	2·03	2·05
70	7·84	2·11	2·14	2·17	2·19
90	7·56	1·91	1·93	1·96	1·99
120	7·03	1·88	1·91	1·93	1·96
	Mean	2·02	2·05	2·08	2·10

By comparison of normal reaction (no water) with water = 0·2002 g., r = 0·18.

By comparison of normal reaction (no water) with dimethylpyrone, r = 0·19.

Series C. Phenylacetic acid, 0·104N; hydrochloric acid, 0·0163N.

(A comparison between 0·1038 g. of water and 0·358 g. of dimethylpyrone, these amounts being equivalent if dimethylpyrone is regarded as dibasic.)

	Flask 1. *Water*, 0·1038 *g.*					*Flask* 2. *Dimethylpyrone*, 0·358 *g.*				
		$Kc \times 10^3$, assuming r =					$Kc \times 10^3$, assuming r =			
t.	$Y = 2(a-x)$.	0·17.	0·18.	0·19.	0·20.	$Y = 2(a-x)$.	0·17.	0·18.	0·19.	0·20.
0	10·40	—	—	—	—	10·40	—	—	—	—
30	9·74	—	—	—	—	9·72	—	—	—	—
60	9·40	0·382	0·395	0·406	0·417	9·38	0·383	0·395	0·407	0·418
100	8·84	0·450	0·464	0·478	0·492	8·88	0·420	0·433	0·446	0·459
140	8·35	0·459	0·473	0·487	0·501	8·42	0·427	0·440	0·454	0·467
180	7·92	0·455	0·469	0·483	0·496	8·05	0·414	0·427	0·439	0·452
220	7·60	0·433	0·446	0·459	0·473	7·60	0·429	0·443	0·455	0·468
	Mean	0·436	0·449	0·463	0·486	Mean	0·415	0·428	0·440	0·453

Summary.

The rate of esterification of phenylacetic acid in dry alcoholic solution, under the influence of hydrogen chloride, is accelerated by the addition of small quantities of dry ethyl ether and retarded by the addition of small quantities of water or dimethylpyrone.

The effect with dimethylpyrone is analogous to that with water if the former is regarded as dibasic. Thus, on the assumption that the catalytic acceleration is due to hydrion, and retardation to combination with such ion, a molecule of water unites with one molecule of hydrion and a molecule of dimethylpyrone with two.

The slight accelerating influence of dry ether is possibly due to a solvent effect, and it is probable that ethyl ether does not, under these conditions, behave as a base.

Further investigations with other possibly basic substances, such as methyl ether and acetone, and in methyl-alcoholic solutions, are in progress.

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