

**177.** *Mechanism of Substitution at a Saturated Carbon Atom. Part XII.*  
*Hydrolysis of Benzhydryl Chloride in Acidic Moist Acetone.*

By MERVYN G. CHURCH and EDWARD D. HUGHES.

A criticism and revision are recorded of another paper by Taylor, in which he reports data held to support a bimolecular mechanism for the hydrolysis of benzhydryl chloride in moist acetone.

Again Taylor claims to observe compositions at equilibrium, and sets forth a calculation which assumes a bimolecular mechanism and reproduces the figures with great precision (cf. p. 913). The equilibrium is, once more, shown not to exist under Taylor's conditions. His "observation" is the axial intercept given by back-production of the "straight" part of a reaction-time curve. Actually the "extrapolation" is made in the most sharply bent region of his curve. Even the curves themselves could not be experimentally reproduced. Similarly the "calculation" of equilibrium compositions is based on inaccurate rate data, and is incorrect in method.

In an earlier paper Taylor claimed the proportionality to water concentration of the specific rate of decomposition of *tert.*-butyl bromide in acetone containing 1 and 2 vols. % of water as direct evidence for the bimolecular mechanism. This argument is not applied to benzhydryl chloride: it would have given an inconsistent answer. Instead, the variation of rate with water content is treated by Taylor from a different point of view, which, however, is directly contrary to thermodynamics. The actual facts in this field are readily explained on the lines already indicated (*loc. cit.*).

SOON after the appearance of the paper just criticised (5; references, this vol., p. 900), Taylor published another (paper 9) describing a similar treatment of the hydrolysis of

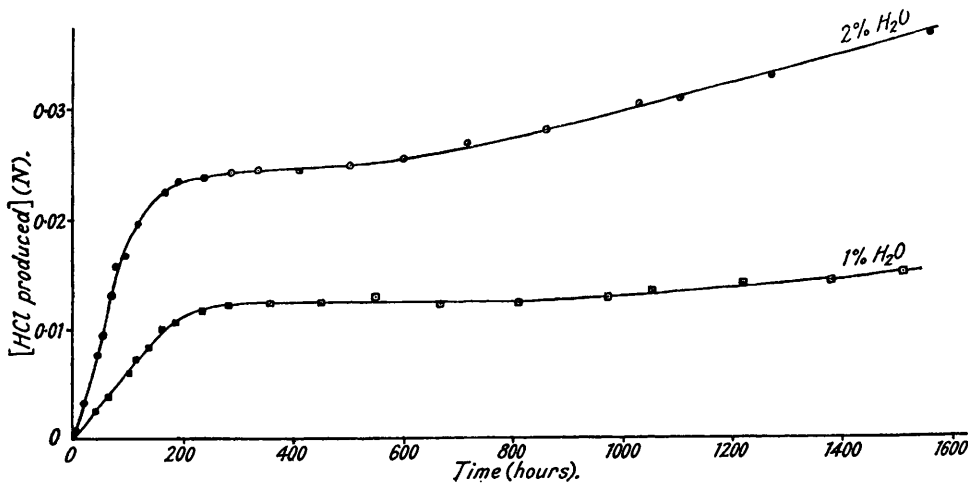
benzhydryl chloride in a set of solvents alleged to be the same as before (although actually they were not—see below), *viz.*, acetone containing 1, 2, etc., vols. % of water. Of the two methods which he might have used, following the lines of paper 5, he actually employed only the first (the second would have given the wrong answer). We shall, however, consider both methods, especially as a method essentially identical with his second has been again employed by him in yet another paper (10), which appeared while the present papers were being written.

(1) *Taylor's First Method.*

The description of this is in the preceding paper. Broadly speaking, the same criticisms apply, but the paper by Taylor now considered contains certain points which necessitate special comment.

In the present case there is no complication due to olefin formation. However, Taylor still assumes that the halide is involved only in the reversible process  $\text{CHPh}_2\text{Cl} + \text{H}_2\text{O} \rightleftharpoons \text{CHPh}_2\text{OH} + \text{HCl}$ , and therefore that the entities  $\text{H}_2\text{O}$  and  $\text{HCl}$  do not interact variably to give  $\text{H}_3\text{O}^+$  and  $\text{Cl}^-$  according to the conditions of acidity and hydration. The effect of the self-condensation of the solvent again produces serious disturbances; nevertheless

FIG. 1.



he continues to determine supposed equilibrium positions (in good agreement with calculated values) by rectilinear extrapolation of selected portions of the reaction-time curves (cf. Fig. 2, p. 922). We have again shown that the solvent decomposition is accompanied by a loss, which he disregards, of ionised or hydrolysable halogen.

Our reaction-time curves for acetone with approximately 1 and 2 vols. % of water (the exact concentrations are recorded in the experimental section) at Taylor's temperature are shown in Fig. 1. Their complexity precludes any significant extrapolation procedure for determining the positions of the assumed equilibria.

In Fig. 2 we give an illustrative curve showing Taylor's data for a medium stated to contain 1 vol. % of water. The discrepancy between his results and ours is considered below. The point to be made now is that his linear extrapolation, also reproduced, which gives the very close agreement with the "equilibrium composition" calculated from rate values could scarcely have been made more inappropriately, having regard to the shape of his reaction-time curve.

Turning now to the rate measurements, which form part of the basis of the second stage of Taylor's three-stage argument, we find a marked discrepancy between his results and ours: Taylor's data for his medium with 1% of water compare more closely with our data for a medium with about 2% of water than with those for 1% of water, and our results for acetone with 2% and 5% of water show similar disagreements with Taylor's results. The comparatively slight differences between his recorded compositions and ours would not

explain discrepancies of this magnitude; however, in order to obtain a stricter comparison, and to confirm our own results, we instituted experiments in two media (1% and 2% of water) of the precise compositions recorded by Taylor. The results substantiated our previous findings, and a consideration of all the differences strongly suggests that the "dry" acetone used by Taylor to make up his solvent mixtures already contained about 0.5% of water. A comparison of our initial rates, quoted formally as second-order rate constants, with Taylor's rates, which he expresses in this form ( $k_2'$  in l./g.-mol.-hour), is given in Table I, and the reaction-time curves for acetone with 1% of water are compared in Fig. 2.

FIG. 2.

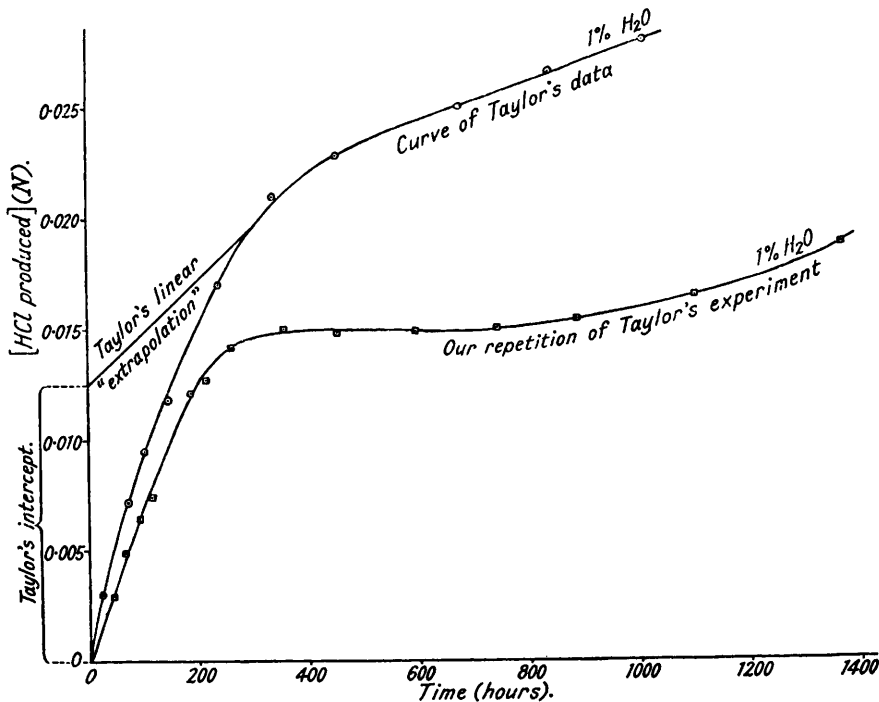


TABLE I.

	Taylor.			This paper.		
$[H_2O]$ .....	0.5556*	1.1111*	2.7778*	0.551	1.111	2.632
$10^3 k_2'$ .....	2.30	4.15	17.1	1.19	1.99	8.31

\* We do not know whether all these significant figures were intended, because the water is stated to have been measured by volume.

The unnoticed extra water in Taylor's experiments has a serious effect on the rate constants from which he calculated the "equilibrium" compositions. Although the water concentrations in all his experiments were so strongly buffered that the data cannot justify the assumption of a second-order rate law, Taylor expressed his initial rates as second-order constants, which, naturally, contained the supposed water concentrations as factors.

There are clearly other errors in the rate constants employed in the calculation of the proportion of reactants at "equilibrium." Thus one constant given as 0.127 is a mean of two values 0.140 and 0.114, the first of which depends on a titre difference of either 0.2 or 0.1 c.c. (cf. preceding paper). Other constants, besides depending on very small titre differences, are affected by a large and doubtful correction for the removal of acidity by the secondary reactions of the acetone solvent. Having regard to the method of observation (cf. Fig. 2), we again conclude that the claimed significance of the precise

agreement of calculated and "observed" compositions is not justified by the methods used in order to obtain the agreement.

Taylor's final conclusion is that, as his observed and calculated equilibrium compositions show "practical identity," and since his calculation employs the mass-law, assuming reactions of the second order in both directions, the forward reaction, *i.e.*, the hydrolysis, is thereby shown to be a reaction of the second order. We quote his figures in Table II, and show also the values of the equilibrium compositions when calculated from the mass-law on the basis of first-order hydrolysis. The reason why the particular formula used is not critical has been explained (preceding paper), and we must again deny that any conclusions are to be drawn from our own calculation except that the whole method is worthless as a criterion of mechanism.

TABLE II.

Vol. % H <sub>2</sub> O.	From Taylor's Table.						Eqn. (3), p. 916.
	[H <sub>2</sub> O].	[CHPh <sub>2</sub> Cl].	$k_2'$ .	$k_2''$ .	$x_\infty$ (obs.).	$x_\infty$ (calc.).	$x_\infty$ (calc.).
1	0.5556	0.0974	0.00230	0.658	0.0125	0.0127	0.0128
2	1.1111	0.1052	0.00415	0.556	0.0270	0.0255	0.0257
5	2.7778	0.1064	0.0171	0.127	0.0842	0.0860	0.0864
10	5.5556	0.1170	0.0636	0.0186	0.1140	0.1157	0.1165

(2) *Taylor's Second Method.*

In paper 5 (*cf.* preceding paper), Taylor claimed the approximate identity of the second-order constants,  $k_2'$ , for the hydrolysis of *tert.*-butyl bromide in acetone containing 1 and 2 vols. % of water as direct evidence of the bimolecular character of the hydrolysis: he added that this could happen only "by coincidence" on Hughes and Ingold's theory. In paper 9 he records the corresponding, but now widely different second-order constants, 0.00230 and 0.00415, for benzhydryl chloride, and does not refer to them specifically in this connection. Neither does he mention the previous argument based on the approximate identity of the constants for *tert.*-butyl bromide, nor the previous contention that the effects of 1% and 2% of water on the solvent properties of acetone should be similar (preceding paper).

He does make a statement, covering the whole set of  $k_2'$  values shown in Table II, that the rise with increasing water content is due to the depolymerising action of water on itself, the monomeric water molecule being regarded as more reactive than associated forms. That an *increase* in the concentration of a substance should tend to *depolymerise* it is an idea new to us. In any case it is not clear why these considerations do not apply in Taylor's paper 5, where the identity of the second-order constants is claimed as evidence for, not a "coincidence" on, Taylor's theory.

The matter is really very simple. Initial constancy in the second-order coefficient means proportionality between the specific rate of disappearance of the alkyl halide and the water content. If there is *no* stoichiometric intervention of water in the rate-measured process, the relationship between these variables must start linearly; and if the main solvent is inactive whilst the added solvent is highly active, initial linearity means initial proportionality. At some stage, which cannot theoretically be specified, and will evidently differ from case to case, the linear relation will begin to fail. Hence the only conclusion to be drawn is that the failure begins to be appreciable at concentrations above (and only just above) 2% of water in the case of *tert.*-butyl bromide, and at concentrations somewhat below 2% in the example of benzhydryl chloride. We now know that Taylor's results for benzhydryl chloride do not refer to 1% and 2% of water and a correction for this would increase the deviation from the linear law. On the other hand, according to our results, the difference of behaviour between the two halides is not so great as would appear from his data; for whereas the ratio of his two second-order constants for benzhydryl chloride is 1.80, our ratio of initial rates, calculated for comparison as second-order constants also, is nearer unity, *viz.*, about 1.63.

In paper 10 Taylor again takes the initial constancy of second-order  $k_2'$  values as "unambiguous evidence" for the bimolecular mechanism, this time for the hydrolysis of

triphenylmethyl chloride in dioxan with small additions of water; he denies the obvious truth that initial proportionality is the relation to be expected for the unimolecular mechanism.

In both papers 9 and 10 Taylor cites Olson and Halford's work (*J. Amer. Chem. Soc.*, 1937, **59**, 2644) on the fugacity formula for the curve of rate against solvent composition as supporting his contention that the hydrolysis of tertiary and other halides in aqueous solvents is bimolecular, having evidently overlooked the circumstance (cf. Bateman, Hughes, and Ingold, *J.*, 1938, 881) that a more complete application of Olson and Halford's method reverses this conclusion.

## EXPERIMENTAL.

*Materials.*—Benzhydriyl chloride, prepared from pure benzhydrol, had b. p. 141°/4 mm. Acetone was again purified by the method due to Conant and Kirner.

*Rate Measurements.*—These were carried out essentially as described in the preceding paper. The reaction mixtures were made up either at 0° (expts. 1, 3, and 5) or at 20° (expts. 2 and 4). The results are in Table III, where  $t$  is the time in hours, and  $x$  and  $y$  the concentrations of hydrogen chloride and unchanged benzhydriyl chloride respectively (in g.-mols./l.). These concentrations are not corrected for the expansion of the solvent, but the water concentrations refer to the temperature of the experiments, *viz.*, 50·10° ± 0·05°. The recorded first-order

TABLE III.

Expt. 1; [CHPh <sub>2</sub> Cl] = 0·1014, [H <sub>2</sub> O] = 0·518 (cf. Fig. 1).										
$t$ .....	41	65	101	113	137	160	185	233	281	356·5
$x$ .....	0·0025	0·0038	0·0060	0·0072	0·0082	0·0099	0·0105	0·0115	0·0120	0·0122
$10^3 k_1'$ .....	6·07	5·88	6·04	6·50	6·15	6·42	5·90	(5·16)	(4·48)	—
$t$ .....	449·5	548	665	809	973	1053	1220	1381	1511	
$x$ .....	0·0123	0·0127	0·0121	0·0122	0·0127	0·0133	0·0140	0·0142	0·0149	
Expt. 2; [CHPh <sub>2</sub> Cl] = 0·1032, [H <sub>2</sub> O] = 0·551 (cf. Fig. 2).										
$t$ .....	0	44	68	92	116	188	212	260	356	451
$x$ .....	0	0·0029	0·0049	0·0064	0·0074	0·0121	0·0127	0·0142	0·0150	0·0148
$10^3 k_1'$ .....	—	6·49	7·15	6·96	6·41	6·64	(6·20)	(5·70)	—	—
$x + y$ .....	0·1032	0·1025	—	0·1020	0·1005	0·0995	—	—	—	—
$t$ .....	596	740	884	1100	1364					
$x$ .....	0·0149	0·0150	0·0154	0·0165	0·0188					
$x + y$ .....	0·0810	0·0766	0·0723	0·0675	0·0646					
Expt. 3; [CHPh <sub>2</sub> Cl] = 0·1011, [H <sub>2</sub> O] = 1·050 (cf. Fig. 1).										
$t$ .....	4·5	19·5	44	53	68	76·75	93	116	165	189
$x$ .....	0·0008	0·0032	0·0076	0·0094	0·0130	0·0156	0·0166	0·0196	0·0224	0·0234
$10^3 k_1'$ .....	1·79	1·65	1·78	1·84	2·02	2·18	1·93	1·86	(1·52)	(1·39)
$t$ .....	237	285	333	408·5	501	600	717	861	1029	1105
$x$ .....	0·0237	0·0241	0·0243	0·0243	0·0248	0·0254	0·0267	0·0280	0·0302	0·0307
$10^3 k_1'$ .....	(1·13)									
$t$ .....	1272	1563								
$x$ .....	0·0328	0·0366								
Expt. 4; [CHPh <sub>2</sub> Cl] = 0·1030, [H <sub>2</sub> O] = 1·111.										
$t$ .....	0	18	42	66	90	114	162	186	234	330
$x$ .....	0	0·0035	0·0084	0·0155	0·0210	0·0247	0·0275	0·0279	0·0286	0·0291
$10^3 k_1'$ .....	—	1·92	2·02	2·47	2·53	2·40	1·92	(1·69)	—	—
$x + y$ .....	0·1030	0·1029	—	0·1012	0·1002	0·0999	0·0943	—	—	—
$t$ .....	377	449	547	666	786	953	1193	1385		
$x$ .....	0·0293	0·0301	0·0305	0·0322	0·0337	0·0358	0·0383	0·0414		
$x + y$ .....	—	—	0·0766	—	0·0719	0·0710	0·0698	0·0687		
Expt. 5; [CHPh <sub>2</sub> Cl] = 0·0980, [H <sub>2</sub> O] = 2·632.										
$t$ .....	3	5	7·5	12	16	20	25	32	40·25	50
$x$ .....	0·0056	0·0092	0·0139	0·0222	0·0298	0·0360	0·0442	0·0527	0·0586	0·0641
$10^3 k_1'$ .....	1·96	1·97	2·04	2·14	2·27	2·29	2·40	2·41	2·27	2·12
$t$ .....	74	100·5	150·25	240						
$x$ .....	0·0690	0·0704	0·0708	0·0705						
$10^3 k_1'$ .....	(1·65)	—	—	—						

rate constants ( $k_1'$ , hrs.<sup>-1</sup>) are calculated from the formula  $k_1' = (1/t) \log_e \{a/(a - x)\}$ , where  $a$  is the initial concentration of benzhydryl chloride; no attempt is made to correct for solvent decomposition.

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THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,  
UNIVERSITY COLLEGE, LONDON, W.C. 1.

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