148. *The Chemistry of the Glutaconic Acids. Part XXIII. The Catalytic Effect of Acids on the Rate of Racemisation of* l-trans-αγ-*Dimethylglutaconic Acid.*

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MEASUREMENTS on the rate of racemisation of *l-trans*-αγ-dimethylglutaconic acid under the influence of certain reagents have been recorded by McCombs, Packer, and Thorpe (J., 1931, 547), who have shown that they support the view (see also Packer and Thorpe, J., 1926, 1199; Thorpe, J., 1931, 1014) that the racemisation is brought about by tautomeric mobility in the three-carbon system of the glutaconic acid, so these rates may be taken as a direct measure of this mobility under the conditions employed.

The results are now given of a much more detailed study of the catalytic action of various concentrations of hydrochloric and sulphuric acids on this prototropic system at 100°. The rate of racemisation was measured polarimetrically, essentially the same methods as before being used. The results are in Table I.

TABLE I.

M.	100 k (hr.$^{-1}$).	100 k/M.	γ.	$a\pm$.	100 $k/a\pm$.	p_H.
(Water)	3·0	—	—	—	—	2·7
Hydrochloric acid.						
0·0005	2·75	5500	0·991	0·00049	5550	2·66
0·001	2·6	2600	0·984	0·00098	2640	2·65
0·0025	2·6	1040	0·965	0·0024	1080	2·58
0·005	2·5	500	0·947	0·0047	528	2·46
0·0075	2·3	307	0·932	0·0070	329	2·33
0·008	2·1	263	0·931	0·0075	283	—
0·01	2·1	210	0·924	0·0092	227	2·26
0·05	1·9	38	0·860	0·043	44·2	1·65
0·1	1·8	18	0·814	0·082	22·1	1·37
0·25	1·9	7·6	0·770	0·193	9·87	0·99
0·5	2·0	4·0	0·762	0·381	5·25	0·73
1·0	2·5	2·5	0·823	0·823	3·03	0·44
1·5	3·1	2·07	0·920	1·38	2·25	0·30
2·5	4·9	1·96	1·18	2·95	1·66	0·09
3·0	5·9	1·97	1·35	4·05	1·46	−0·05
3·5	6·6	1·9	1·58	5·53	1·20	−0·10
4·0	8·7	2·18	1·84	7·36	1·18	−0·12
4·5	12·0	2·7	2·17	9·77	1·24	−0·25
5·0	12·1	2·42	2·51	12·6	0·964	−0·25
6·0	15·4	2·57	3·4	20·4	0·755	−0·35
Sulphuric acid.						
0·0005	2·85	5700	0·871	0·00044	6550	—
0·001	2·7	2700	0·831	0·00083	3250	—
0·005	2·4	480	0·696	0·0035	690	—
0·01	1·9	190	0·617	0·0062	308	1·98
0·025	2·0	80	0·48	0·012	167	1·62
0·05	1·8	37	0·397	0·020	93·3	1·37
0·1	1·75	17·5	0·313	0·031	55·9	1·16
0·25	1·8	7·2	0·230	0·058	31·3	0·84
0·5	2·4	4·8	0·178	0·089	27·0	0·59
1·0	3·1	3·1	0·150	0·150	20·7	0·37
2·0	5·8	2·9	0·147	0·294	19·7	0·12
3·0	8·5	2·8	0·166	0·498	16·9	−0·05
Potassium hydroxide (0·0395 mol. per mol. of glutaconic acid).						
(0·005)	4·6	—	—	—	—	2·89

M is the molarity of the catalyst (hydrochloric or sulphuric acid), k the unimolecular velocity constant at 100°, γ the activity coefficient, $a \pm$ the mean ionic activity of the mineral acid in pure aqueous solution at 25° (taken from Lewis and Randall's "Thermodynamics"), and p_H relates to the glutaconic–mineral acid mixtures (measured at 25° with a quinhydrone electrode). The concentration of the glutaconic acid was 2 g. per 100 c.c. of solution except in the most concentrated hydrochloric acid solutions, in which 1 g. per 100 c.c. was used.

As before, the mutarotation followed a unimolecular course, but the values of k were not calculated by the usual formula $k = 1/t \,.\, \log_e a/(a - x)$, where a = initial rotation and x = change in rotation in time t; this method gives undue weight to the earlier readings and particularly to the initial one, so a modification was used. The equation may be written in the form $\log_e (a - x) = \log_e a - kt$, which is of the general form $y = a + bx$. The constants in this equation may therefore be found by dividing the data into two equal (or nearly equal) parts; then for each part $\Sigma \log_e (a - x) = n \log_e a - k\Sigma t$, where $n =$

number of data in the division. The initial value at $t = 0$ being included in $\log_e (a - x)$, the equations can be solved for k and $\log_e a$ by the "method of zero sum" (Campbell, *Phil. Mag.*, 1920, **39**, 177; 1924, **47**, 816; cf. Roseveare, *J. Amer. Chem. Soc.*, 1931, **53**, 1651).

In Fig. 1, k is plotted against the concentration (M) of the mineral acid; the curves show very clearly the depressing effect of low concentrations of acid on the rate of racemisation, and the existence of a definite minimum in this rate at acid concentrations of 0·1—0·2M. The value of k at the minimum is the same for both acids within the probable limits of error of the measurements. Greater concentrations of acid bring about an increasingly strong positive catalysis and ultimately this effect is nearly proportional to the concentration of the acid.

FIG. 1.

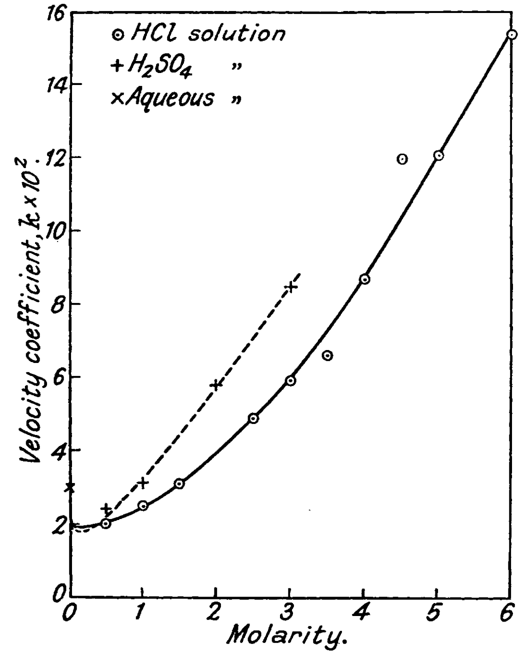
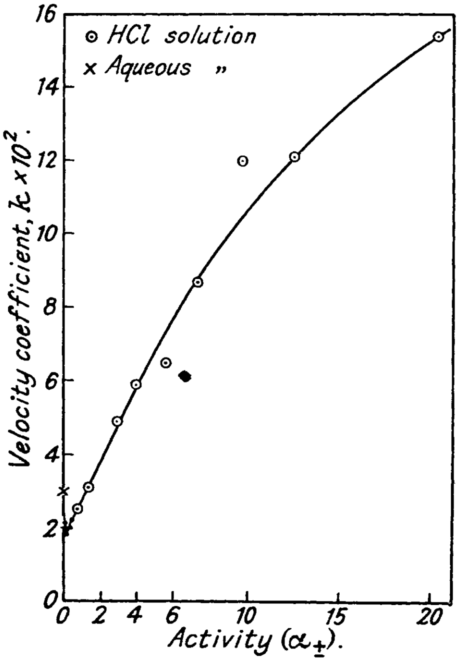


FIG. 2.



In Figs. 2 and 3, k is plotted against $\alpha \pm$, but there is no direct proportionality even at the higher concentrations. This is further evident from the values of $k/\alpha \pm$ in col. 6 of Table I. The departure from constancy is so great, especially in the case of hydrochloric acid, that it seems hardly likely that it can be due to the use of activities measured at 25° instead of at 100° (for which temperature no values are available) or to the influence of the glutaconic acid on the activity of the mineral acid.

The relationship between the rate of racemisation and the p_H is shown *by the points* in Fig. 4; those for hydrochloric and sulphuric acids fall on the same curve, which shows a fairly flat minimum in the rate of racemisation at values of p_H between 1 and 2. The general form of the curve is that of the catalytic catenary, indicating that the rate of racemisation is mainly controlled by the hydrogen- and hydroxyl-ion concentration.

Following Dawson, we express the actual rate of racemisation, k, as the sum of the partial rates due to the different catalytic entities present. Thus, neglecting the effects due to the chloride and sulphate ions, which are strong anions and would be expected on current theories of acid–base catalysis to have very little if any catalytic activity, we write

$$k = k_{OH'}[OH'] + k_{H^\cdot}[H_3O^\cdot] + k_W[H_2O] + k_M[C_7H_{10}O_4] + k_{A'}[C_7H_9O_4'] + k_{A''}[C_7H_8O_4''] \quad (1)$$

Since the concentration of the water and glutaconic acid molecules may be considered constant, their catalytic effect can be represented by a constant term k'. Further, the expression may, as a first approximation, be simplified by neglecting the variations in the concentrations of the glutaconate ions and including the factors due to them in the constant k'. So long as the partial velocity coefficients or the concentrations of these ions are sufficiently small compared with the corresponding quantities for the hydrogen and hydroxyl ions, this will not lead to any serious error. In any case, the influence of these factors will be greatest at or near the minimum point and will become relatively negligible at greater hydrogen- or hydroxyl-ion concentrations. The expression (1) is therefore reduced to the form

$$k = k' + k_{OH}[OH'] + k_{H^{\cdot}}[H_3O^{\cdot}] \quad . \; . \; . \; . \; . \; . \; . \quad (2)$$

Since the hydrogen- and the hydroxyl-ion concentration are inversely proportional to one another, the plot of k against $[H_3O^{\cdot}]$ for such an equation is a catenary curve with a definite minimum, called by Dawson the isocatalytic point. It can be shown that at this point $[H_3O^{\cdot}]_i = \sqrt{K_W k_{OH'}/k_{H^{\cdot}}}$, where $[H_3O^{\cdot}]_i$ is the hydrogen-ion concentration at this point and $K_W = [H_3O^{\cdot}][OH']$. Hence $k_{OH'}/k_{H^{\cdot}} = [H_3O^{\cdot}]_i/[OH']_i$, *i.e.*, the ratio of the partial velocity coefficients for the hydroxyl and the hydrogen ion is inversely proportional to the respective ionic concentrations at the isocatalytic point.

FIG. 3.

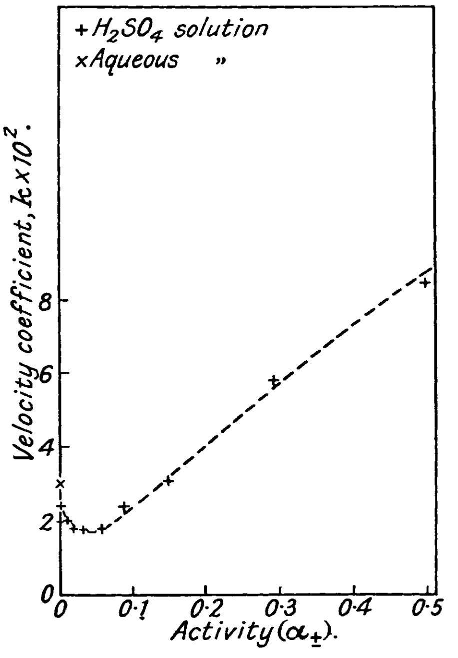
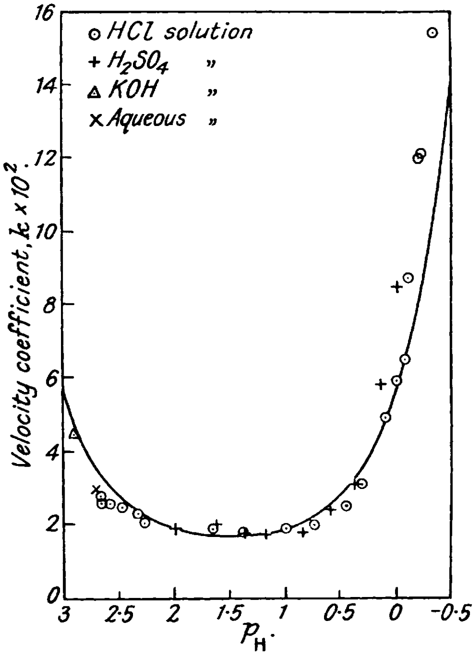


FIG. 4.



From Fig. 4 it is seen that the minimum lies near p_H 1·5, whence $k_{OH'}/k_{H^{\cdot}} = 10^{11}$, which is extremely large but not impossible. From this value for the ratio, we may write $k_{OH'} = a \times 10^9$ and $k_{H^{\cdot}} = a \times 10^{-2}$, where a = constant. Substitution of these values in (2) gives

$$k = k' + a \times 10^9[OH'] + a \times 10^{-2}[H_3O^{\cdot}].$$

The values of k' and a which most nearly fit the experimental values are $k' = 1{\cdot}5 \times 10^{-2}$ and $a = 4$, whence (2) becomes

$$k = 1{\cdot}5 \times 10^{-2} + 4 \times 10^9[OH'] + 4 \times 10^{-2}[H_3O^{\cdot}].$$

The curve shown in Fig. 4 is the graph of k against $[H_3O^{\cdot}]$ for this equation. It is clear that the experimental points do not fit this (or any other) catenary exactly, but this may be due to the factors which have been explicitly neglected in the above treatment or to the neglect of the undissociated molecules of strong acids possibly present in the more concentrated solutions.

The very flat minimum may be explained, in part at least, if we assume that the partial velocity coefficients of the glutaconate ions are of the same order as that of the hydrogen ions, since in dilute acid solutions the concentration of the former will be inversely proportional to the latter and there will be a balancing out due to the two factors. As the concentration of the hydrogen ions is increased, however, the effect due to the glutaconate ions will rapidly become negligible. In any case exact agreement can hardly be expected between experimental results and a theoretical equation involving two constants of such very different orders as 10^9 and 10^{-2}, especially where the quantities to which they refer are present in more or less equivalent concentrations, the values of which cannot be measured with certainty.

The results obtained for the catalytic influence of aqueous acids on the rate of racemisation of *l-trans-αγ*-dimethylglutaconic acid are in agreement with current theories of acid–base catalysis, as developed by Dawson and others (see *Ann. Reports*, 1926, **37**; 1927, **33**). In particular, the very much greater efficiency of the hydroxyl as compared with the hydrogen ion (10^{11} : 1) supports the view that racemisation of this acid is brought about by prototropic change in the three-carbon system, and is in agreement with what would be expected from the now generally accepted theories of the mechanism of prototropic change (see *ibid.*, 1926, **38**; 1927, **106**; 1928, **123**; 1929, **116**).

In a further communication it is hoped to record the rates of racemisation of this acid in more alkaline solutions.

EXPERIMENTAL.

l-trans-*αγ-Dimethylglutaconic Acid.*—The inactive form of this acid (Thole and Thorpe, J., 1911, **99**, 2187) was converted into the *l*-form as follows (cf. J., 1931, 554): 2 Equivs. of the inactive acid in acetone were added to a hot solution of 1 equiv. of strychnine in $CHCl_3$, and the mixture refluxed for 4 hr. The pptd. strychnine hydrogen αγ-dimethylglutaconate was filtered off, and the active acid separated from this salt as before. The acid (recovery 90%) obtained generally gave $[M]_D^{25°}$ *ca.* — 89° in aq. solution and, although still containing some 11% of the inactive form, was used in the racemisation expts. without further purification.

Measurement of Rate of Racemisation of l-trans-*αγ-Dimethylglutaconic Acid at* 100°.—*Method of heating.* The calc. quantity of the glutaconic acid to give a solution of 2 g. per 100 c.c. was dissolved in a measured vol. of the reagent solution and then filtered into the reaction flask, usually a 30-c.c. thin-walled Pyrex flask. After the initial rotation of the solution had been measured at 25° (see below), the flask was placed in a boiling water-bath and at measured time intervals was removed and rapidly cooled in running water, the rotation of the solution being measured at 25°. This procedure was continued until colour or loss of material made further readings impossible. The time error introduced by this repeated heating and cooling of the solution was negligible: portions of a solution which was kept in a large boiling-tube in a boiling water-bath were withdrawn by a pipette, rapidly cooled, and the rotation determined; this method avoided cumulative heating and cooling errors, and a thermometer immersed in the solution showed that the temp. never varied by more than 0·3° from 100°, but both methods of heating gave the same results. The first and simpler method was generally adopted.

Measurement of Optical Rotation.—The polarimeter used was a Laurent's half-shadow instrument (Schmidt and Haensch) taking tubes up to 24 cm. long. The light source used was either a Na flame, or an electric lamp, the light being filtered respectively through dil. aq. $K_2Cr_2O_7$ or through dil. solutions of $CuSO_4$ and $K_2Cr_2O_7$, which reduce the range of wave-lengths to a band in the yellow (Schoorl, *Chem. Weekblad*, 1926, **23**, 21, 113). Since abs. rotation of one definite wave-length was not required and the rotations measured were small ($< 2·5°$), no appreciable error was introduced by the latter method, which was much more convenient.

The polarimeter tube was surrounded by a jacket through which H_2O at 25° was circulated from a thermostat by means of a special circulator. The value taken for a reading was the average of at least 20 observations, which were reproducible to 0·015°.

Results.—The results are in Table II; after the first three cases, only the initial and the final observation are recorded; *a* is the rotation observed after the number of hours recorded in parentheses. The values of *k* for each set were calculated as described on p. 596, the values of log a being plotted against t and the straight-line graph corresponding to the calc. value of k drawn. Only those sets of results have been retained for which the obs. points fall reasonably close to and symmetrically about this straight line.

TABLE II.

Water:
a 2·48° (0 hr.), 2·30° (3 hrs.), 2·10° (6), 2·00° (7·5), 1·87° (9), 1·73° (12), 1·75° (13·5), 1·63° (15). $k = 2·89 \times 10^{-2}$.
a 2·31° (0), 2·16° (3), 1·92° (6), 1·80° (9), 1·65° (12), 1·46° (15), 1·35° (18), 1·21° (21), 1·04° (24). $k = 3·19 \times 10^{-2}$.
Mean of two sets: $k = 3·04 \times 10^{-2}$.

0·0005M-HCl:
a 2·50° (0), 2·28° (2), 2·17° (4), 2·03° (6), 1·93° (8), 1·78° (11), 1·71° (13), 1·61° (15·5). $k = 2·75 \times 10^{-2}$.
0·001M-HCl: a 2·40° (0), 1·32° (24). $k = 2·57 \times 10^{-2}$.
a 2·48° (0), 1·48° (20). $k = 2·58 \times 10^{-2}$. } Mean of two sets: $k = 2·58 \times 10^{-2}$.

0·0025M-HCl: a 2·36° (0), 1·57° (16). $k = 2·63 \times 10^{-2}$.
0·005M-HCl: a 2·33° (0), 1·38° (21). $k = 2·52 \times 10^{-2}$.
0·0075M-HCl: a 2·40° (0), 1·33° (27). $k = 2·27 \times 10^{-2}$.
0·008M-HCl: a 2·33° (0), 1·53° (21). $k = 2·06 \times 10^{-2}$.
0·01M-HCl: a 2·71° (0), 2·02° (14). $k = 2·08 \times 10^{-2}$.
a 2·33° (0), 1·61° (18). $k = 2·18 \times 10^{-2}$. } Mean of two sets: $k = 2·13 \times 10^{-2}$.

0·05M-HCl: a 2·52° (0), 1·55° (24). $k = 1·91 \times 10^{-2}$.
0·1M-HCl: a 2·66° (0), 1·93° (17·5). $k = 1·84 \times 10^{-2}$.
0·25M-HCl: a 2·40° (0), 1·71° (17). $k = 1·89 \times 10^{-2}$.
0·5M-HCl: a 2·44° (0), 1·76° (15·25). $k = 2·19 \times 10^{-2}$.
a 1·99° (0), 1·43° (16·5). $k = 1·97 \times 10^{-2}$. } Weighted mean of two sets: $k = 2·0 \times 10^{-2}$.

1·0M-HCl: a 2·50° (0), 1·29° (25·75). $k = 2·46 \times 10^{-2}$.
1·5M-HCl: a 2·48° (0), 1·35° (22·5). $k = 3·11 \times 10^{-2}$.
2·5M-HCl: a 2·46° (0), 1·30° (14). $k = 4·93 \times 10^{-2}$.
3·0M-HCl: a 2·48° (0), 1·72° (6). $k = 5·91 \times 10^{-2}$.
3·5M-HCl: a 2·48° (0), 1·38° (9). $k = 6·45 \times 10^{-2}$.
a 2·46° (0), 0·74° (18). $k = 6·39 \times 10^{-2}$. } Mean of three sets: $k = 6·58 \times 10^{-2}$.
a 1·26° (0), 0·38° (16·5). $k = 6·89 \times 10^{-2}$.

4·0M-HCl: a 2·55° (0), 0·95° (10). $k = 8·71 \times 10^{-2}$.
a 1·23° (0), 0·51° (10). $k = 8·81 \times 10^{-2}$. } Weighted mean of two sets: $k = 8·7 \times 10^{-2}$.

4·5M-HCl: a 1·31° (0), 0·48° (9). $k = 12·0 \times 10^{-2}$.
5·0M-HCl: a 1·24° (0), 0·40° (9·5). $k = 12·1 \times 10^{-2}$.
6·0M-HCl: a 1·29° (0), 0·29° (10). $k = 15·4 \times 10^{-2}$.
0·0005M-H_2SO_4: a 2·40° (0), 1·18° (25). $k = 2·85 \times 10^{-2}$.
0·001M-H_2SO_4: a 2·41° (0), 1·22° (25·25). $k = 2·71 \times 10^{-2}$.
0·005M-H_2SO_4: a 2·43° (0), 1·46° (23). $k = 2·37 \times 10^{-2}$.
0·01M-H_2SO_4: a 2·45° (0), 1·56° (24). $k = 1·90 \times 10^{-2}$.
0·025M-H_2SO_4: a 2·42° (0), 1·53° (23). $k = 2·02 \times 10^{-2}$.
0·05M-H_2SO_4: a 2·22° (0), 1·67° (16). $k = 1·84 \times 10^{-2}$.
0·1M-H_2SO_4: a 2·01° (0), 1·46° (17·5). $k = 1·75 \times 10^{-2}$.
0·25M-H_2SO_4: a 1·47° (0), 1·10° (15). $k = 1·79 \times 10^{-2}$.
0·5M-H_2SO_4: a 1·22° (0), 0·88° (14). $k = 2·43 \times 10^{-2}$.
1·0M-H_2SO_4: a 2·11° (0), 1·41° (14·5). $k = 3·07 \times 10^{-2}$.
2·0M-H_2SO_4: a 1·25° (0), 0·74° (10). $k = 5·79 \times 10^{-2}$.
3·0M-H_2SO_4: a 2·04° (0), 1·21° (6). $k = 8·54 \times 10^{-2}$.
0·005M-KOH: a 2·23° (0), 1·22° (13·5). $k = 4·59 \times 10^{-2}$.

The Measurement of p_H.—As it was not possible to measure the [H$^\bullet$] under the conditions of racemisation (at 100°), these values were determined at 25° by using a quinhydrone electrode in the glutaconic–mineral acid mixture and measuring the *e.m.f.* against a satd. calomel half electrode in the usual way. Perfectly steady readings were readily obtained.

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