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

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THE rate of racemisation of *l-trans-αγ*-dimethylglutaconic acid under the influence of various concentrations of hydrochloric and sulphuric acids has been studied by Fitzgerald and Packer (J., 1933, 595), who showed that it may be expressed as the sum of the partial rates due to the different catalytic entities present. The following equation most nearly fits their experimental values :

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

The constant term includes the catalytic effect of the water and glutaconic acid molecules, the concentration of which may be considered to be constant in acid solutions. The rate of racemisation is here represented by v, instead of k as in the above paper, because, although numerically equal to the pseudo-unimolecular velocity constant (k) for the change at each fixed concentration of the catalyst, and therefore independent of the concentration of the glutaconic acid, it is, obviously, a function of the concentration of the catalyst.

The work has now been extended to a study of catalytic effect of various concentrations of potassium and ammonium hydroxides on the same system. The methods of measuring and calculating the rate of racemisation were exactly as described in the previous paper. The results are given in Table I, in which M is the concentration of catalyst (mols./l.), r gives the ratio of M to the molarity of glutaconic acid, which was approx. 0·125M (2 g. per 100 c.c.), and k is the unimolecular velocity constant at 100°; p_{H} relates to the glutaconic–alkali mixtures, and was measured colorimetrically, several of the lower concentrations being checked by measurements with a hydrogen electrode.

TABLE I.

M.	*r.*	100*k* (hr.$^{-1}$).	p_H.	*M.*	*r.*	100*k* (hr.$^{-1}$).	p_H.	*M.*	*r.*	100*k* (hr.$^{-1}$).	p_H.
				(Water)		2·92	2·48				
				Potassium hydroxide.							
0·0005	0·004	3·02	2·6	0·10	0·8	14·28	4·4	0·30	2·4	4·63	8·6
0·001	0·008	3·13	2·7	0·125	1·0	8·95	4·6	0·40	3·2	17·44	9·6
0·005	0·04	4·59	2·9	0·15	1·2	6·98	5·0	0·50	4·0	33·01	10·2
0·01	0·08	5·97	3·0	0·20	1·6	2·43	5·8	0·60	4·8	42·15	—
0·05	0·4	12·96	4·0	0·225	1·8	0·995	6·0	0·75	6·0	90·46	—
0·075	0·6	14·50	4·2	0·25	2·0	0·644	7·4	1·00	8·0	135·3	—
				Ammonium hydroxide.							
0·0005	0·004	3·44	2·6	0·10	0·8	14·98	4·4	0·30	2·4	0·597	8·0
0·002	0·016	4·32	2·7	0·125	1·0	11·31	4·6	0·40	3·2	1·19	8·6
0·01	0·08	8·38	3·4	0·15	1·2	10·21	4·95	0·50	4·0	0·43	9·0
0·05	0·4	13·19	3·8	0·20	1·6	3·35	5·4	1·00	8·0	1·27	9·5
0·075	0·6	15·86	4·1	0·25	2·0	0·669	6·0	5·09	40	1·17	—

The value for the p_H of the aqueous solution of the glutaconic acid (2·48) is somewhat lower than that given in the previous paper (2·7), obtained with a quinhydrone electrode, for it has now been found that, both in the aqueous solutions and in those containing added hydrochloric acid or potassium hydroxide, this electrode gives a somewhat higher value than the hydrogen electrode. This difference is negligible for the present work, and is probably due to a " salt effect " of glutaconic acid on the former electrode.

FIG. 1.

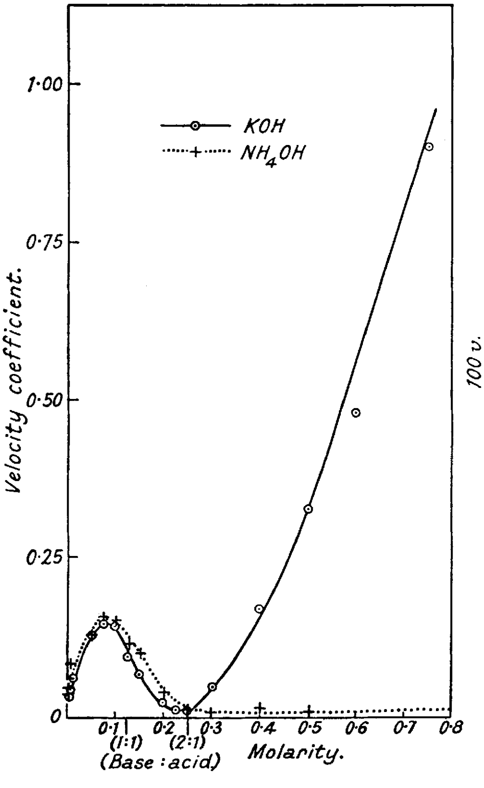
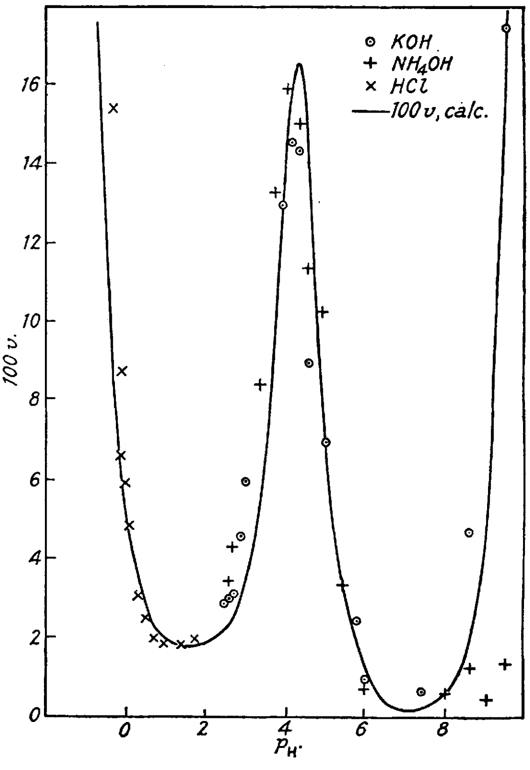


FIG. 2.



In Fig. 1 *k* is plotted against *M*. With increasing concentration of potassium hydroxide the rate of racemisation first increases, as would be expected from Fitzgerald and Packer's equation, to a maximum at 0·075*M*, then falls to a minimum at 0·25*M*, and finally increases again rapidly. With ammonium hydroxide, the curve is similar up to 0·25*M*, but above that the rate altered very little, although experimental difficulties made its determination less accurate in this region. For this difference between the two alkalis no explanation has been found; no chemical interaction between the ammonia and glutaconic acid could be detected. The slightly stronger catalytic effect of ammonium hydroxide up to concentrations of 0·25*M* may be due to the catalytic activity of ammonia molecules, but is of minor importance and has been neglected in the discussion.

The maximum in k occurs when r is just less than unity, whereas at the minimum $r = 2$, corresponding to formation of the normal salt. The racemisation is brought about by tautomeric mobility in the three-carbon system of the glutaconic acid, and the effect of adding alkali to this system is not only to increase the hydroxyl-ion concentration, but also to bring about ionisation of the terminal carboxyl groups by salt formation. According to modern theories of prototropic change, the presence of a negative charge produced by such ionisation would be expected to bring about decreased mobility in the prototropic system. In order to test this view and obtain a quantitative measure of the effect of replacing a CO_2H by a CO_2' group, it is necessary to know the concentrations of the undissociated glutaconic acid molecules ($C_7H_{10}O_4$), and of the partially dissociated ($C_7H_9O_4'$) and completely dissociated ($C_7H_8O_4''$) ions at each concentration of added alkali. These values have been calculated from the measured dissociation constants of the glutaconic acid (see p. 1657) and are recorded in Table III. The three species are denoted in the following by HCH, HC′, and C″ respectively.

It may be shown that above p_H 2·8 the catalytic effect of the hydrogen ions is negligible in comparison with that of the hydroxyl ions; and also that at p_H less than 3·3 the system HCH is the only one present in appreciable concentrations, whereas above p_H 8·4, C″ alone is present. Hence the relative rates of change of the undissociated glutaconic acid and doubly ionised normal salt can be obtained by comparing the hydroxyl-ion concentrations of the two systems at equal values of k. Practically constant values are obtained over a considerable range as is shown in Table II, from which it appears that the rate of change of the undissociated glutaconic acid (HCH) is $4·5 \times 10^5$ times that of the doubly-ionised normal salt ions (C″).

TABLE II.

p_{H_1}	2·8	2·89	2·93	3·00	3·13	3·26
p_{H_2}	8·47	8·53	8·63	8·73	8·77	8·87
$[OH']_1 \times 10^{12}$	6·31	7·75	8·51	10·0	13·5	18·2
$[OH']_2 \times 10^6$	2·95	3·39	4·27	5·37	5·89	7·41
$([OH']_2/[OH']_1) \times 10^{-5}$	4·68	4·37	5·01	5·37	4·37	3·24
						Mean 4·5

In order to represent the velocity in the range in which rate of change of the uni- and bi-valent anions becomes important, it is necessary to expand Fitzgerald and Packer's equation by the addition of terms expressing the speeds of racemisation of these ions. Unless the relative catalytic efficiencies of the hydrogen and hydroxyl ions for the racemisation of the anions is very different from those for the undissociated acid molecules, it can be shown that, over the p_H range in which the anions HC′ and C″ are present, the effect of the former may be neglected in comparison with that of the latter. In support of this, it was found that the addition of only two terms, expressing the catalytic effect of the hydroxyl ions on the HC′ and C″ anions, sufficed to represent the results, notwithstanding that, owing to dissymmetry of the structure, two univalent ions ($'CO_2\cdot CHMe\cdot CH{:}CMe\cdot CO_2H$ and $CO_2H\cdot CHMe\cdot CH{:}CMe\cdot CO_2'$), in addition to the bivalent ion C″, might be expected to occur. The equation which best agrees with our results is

$$v = \{1·65 \times 10^{-2} + 4·06 \times 10^{-2}[H_3O^{\cdot}] + 2·03 \times 10^9[OH']\}m_{HOH} \\ + 7·62 \times 10^5[OH']m_{HO'} + 4·51 \times 10^3[OH']m_{O''}.$$

where m_{HOH}, $m_{HO'}$, and $m_{O''}$ represent the molar fractions of the total glutaconic acid present in the three states. The coefficients in this equation representing the catalytic activities of the undissociated glutaconic acid and of the hydrogen and hydroxyl ions on the undissociated acid molecules HCH are somewhat different from those in Fitzgerald and Packer's equation, but the change makes little difference to the agreement on the acid side previously studied.

The values of v calculated from this equation are shown in col. 5 of Table III, and are represented by the curve in Fig. 2. The points correspond to the experimentally determined values of k, those below p_H 2·5 being the values given by Fitzgerald and Packer, the p_H's of the solutions of very low hydrochloric acid concentration having been omitted.

TABLE III.

p_H.	[HCH].	[HC′].	[C″].	100v, calc.
2·48	0·124	0·003	—	2·2
2·6	0·124	0·003	—	2·4
2·7	0·124	0·003	—	2·61
2·9	0·121	0·006	—	3·08
3·0	0·116	0·011	—	3·45
3·2	0·114	0·013	—	4·37
3·4	0·108	0·019	—	5·74
3·6	0·097	0·0297	0·0008	7·43
3·8	0·088	0·037	0·0016	10·02
4·0	0·08	0·044	0·003	13·35
4·1	0·066	0·056	0·005	14·15
4·2	0·059	0·061	0·007	15·73
4·3	0·049	0·068	0·0096	16·28
4·4	0·040	0·074	0·013	16·58
4·5	0·029	0·080	0·018	15·08
4·6	0·022	0·085	0·020	14·30
4·8	0·008	0·087	0·032	8·22
5·0	0·0044	0·080	0·042	7·07
5·2	0·0016	0·069	0·056	4·15
5·4	0·0008	0·056	0·071	3·32
5·6	0·00041	0·046	0·081	2·74
5·8	0·00018	0·037	0·09	1·96
6·0	0·00008	0·022	0·105	1·41
6·2	0·000037	0·011	0·116	0·94
6·5	—	0·005	0·122	0·23
7·0	—	0·002	0·125	0·17
7·4	—	0·00074	0·1259	0·22
7·8	—	0·00029	0·1263	0·39
8·0	—	0·00017	0·1264	0·56
8·2	—	0·000114	0·1265	0·82
8·6	—	—	0·1266	1·79
9·0	—	—	0·1266	4·49
9·2	—	—	0·1266	7·12
9·6	—	—	0·1266	17·90

The results obtained give further support to Dawson's method of representing acid–base catalysis; a quantitative measure of the effect on the mobility of the three-carbon system, of altering the terminal activating groups from $-CO_2H$ to $-CO_2'$, has been obtained.

EXPERIMENTAL.

Measurement of Rate of Racemisation at 100°.—The acid was prepared and resolved, and the racemisation carried out, as described previously (Fitzgerald and Packer, *loc. cit.*). Except in the case of the more concentrated ammonia solutions, points on the graph obtained by plotting the logarithm of optical rotation against time fell close to, and symmetrically about, the straight line which was the calculated unimolecular velocity constant given in Table I. These observations are not recorded, but the values of k in the table represent the final mean calculated values.

Measurement of p_H.—The p_H of most of the solutions was measured after racemisation by means of a Hellige comparator with coloured glass standards. For the determination of the

TABLE IV.

C.c.	p_H.	[A].	α.	$[C_7H_{10}O_4]$.	$[C_7H_9O_4']$.	$K_1 \times 10^4$.
0	2·48	0·1000	0·0331	0·0967	0·0033	1·13
1	2·82	0·0823	0·0184	0·0808	0·0101	1·89
2	3·10	0·0676	0·0118	0·0668	0·0166	1·97
3	3·36	0·0551	0·0079	0·0547	0·0222	1·77
4	3·62	0·0441	0·0054	0·0442	0·0272	1·48
6	3·85	0·0271	0·0052	0·0270	0·0355	1·86
8	4·16	0·0136	0·0051	0·0135	0·0421	2·14
10	4·40	0·00275	0·0145	0·0027	0·0473	(6·95)
					Average	1·75

C.c.	p_H.	$Na_2C_7H_8O_4$.	$NaC_7H_9O_4$.	$K_2 \times 10^6$.
12	4·62	0·134	0·866	(3·71)
14	4·82	0·323	0·677	7·06
15	4·93	0·418	0·582	8·44
16	5·10	0·512	0·488	8·24
17	5·41	0·607	0·393	6·01
17·5	5·59	0·654	0·346	4·86
18	6·22	0·701	0·299	(1·41)
20	11·22	0·890	0·110	—
			Average	6·92

dissociation constants, measurements were made at 25°, using a hydrogen electrode of the Hildebrand type, and a saturated calomel half-cell. *E.M.F.* measurements were checked against standard buffer solutions. A few measurements were made with a quinhydrone electrode (see p. **1654**).

Determination of the Dissociation Constants of the Acid.—This was done by electrometric titration with sodium hydroxide. The constants were calculated by Britton's method (J., **1925**, **127**, 1897). The results are given in Table IV, the concentration of the free acid being represented by [A]. Col. 1 gives the number of c.c. of $0{\cdot}0945M$-sodium hydroxide added to 10 c.c. of $0{\cdot}1M$-glutaconic acid; col. 2 the p_H measured by the hydrogen electrode. The remaining columns are calculated by Britton's method. The dissociation constants are calculated from the equations: $K_1 = [H^\bullet][HC']/[HCH]$, $K_2 = [H^\bullet][C'']/[HC']$. The values $K_1 = 1{\cdot}8 \times 10^{-4}$, $K_2 = 7 \times 10^{-6}$ are used in the sequel.

Constants were also calculated from Auerbach and Smolczyk's equation (*Z. physikal. Chem.*, **1924**, **110**, 83), but although results for K_1 were in good agreement with the above (average $K_1 = 1{\cdot}78 \times 10^{-4}$), yet those for K_2 varied according to the pairs of experimental values employed (cf. Britton, *loc. cit.*, p. 1908).

Calculation of Concentrations of [HCH], [HC′], *and* [C″] *at Different Concentrations of Potassium Hydroxide.*—The calculations are possible from a consideration of the above expressions for K_1 and K_2 together with the following expressions:

$$[K^\bullet] + [H^\bullet] = [OH'] + [HC'] + 2[C''] \quad \ldots\ldots \quad (1)$$

$$[HCH] + [HC'] + [C''] = [m] \quad \ldots\ldots \quad (2)$$

where $[m]$ is the original concentration of the acid.

It can be shown that:

(i) Up to p_H 2, only HCH is present in appreciable concentration.

(ii) Between p_H 2 and p_H 3·5, [OH′] and [C″] are negligible with respect to $[K^\bullet]$ and $[m]$, hence (1) and (2) reduce to

$$[K^\bullet] + [H^\bullet] = [HC']; \quad [m] = [HCH] + [HC'].$$

(iii) Between p_H 3·5 and p_H 6, [OH′] and $[H^\bullet]$ are negligible in comparison with $[K^\bullet]$, hence (1) reduces to $[K^\bullet] = [HC'] + 2[C'']$; and this combined with $K_2 = [H^\bullet][C'']/[HC']$ gives $[K^\bullet] = [C''](2 + [H^\bullet]/K_2)$.

Equation (2) holds up to p_H 5, above which [HCH] is very small, but not negligible in its effect; so this has been calculated from $K_1K_2 = [H^\bullet]^2[C'']/[HCH]$.

(iv) Above p_H 7. Values for $[K^\bullet]$ at any p_H below 7 were obtained by interpolation in the graph of molarity of added KOH plotted against the resultant p_H of the solution, but above p_H 7 this could not be done with accuracy. Equation (2) becomes $[m] = [HC'] + [C'']$, and combining this with $K_2 = [H^\bullet][C'']/[HC']$, we have $[m] = [C''](1 + [H^\bullet]/K_2)$.

The values for [HCH], [HC′], and [C″] have been tabulated in Table III.

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