CCCXLII.—*The Chemistry of the Three-carbon System. Part XIV. The Effect of Conditions on Isomeric Change in Unsaturated Acids.*

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IN previous papers of this series the terms " mobility " and " position of equilibrium " were used somewhat freely, but their expression in quantitative terms was not possible. The position of equilibrium was assumed to be constant for a definite pair of isomerides, and subsequent experimental evidence has supported this view (Linstead, this vol., p. 362; Johnson and Kon, J., 1926, 2748). The work of the latter on the β-alkylcinnamic acids, however, was based on a salt-separation method, whilst that of the present author on the *cyclo*hexane acids was limited in scope. Further work has now been carried out on this important point and on the quantitative expression of mobility. The technique of the equilibration experiments has been improved and the convenient iodine method of analysis (Linstead and May, preceding paper) has been used in place of the bromine method.

The value now found for the equilibrium is 88·2% Δ^1-*cyclo*hexenylacetic acid (βγ) $\rightleftharpoons$ 11·8% *cyclo*hexylideneacetic acid (αβ), which confirms that (88 $\rightleftharpoons$ 12) previously reported. The probable accuracy of both analytical methods is shown by the agreement between the results. In addition, it has now been found that this position of equilibrium is, within the limits of experimental error, independent of temperature, concentration of the unsaturated acid and of the catalytic alkali, the nature of the alkali, and the presence of alcohol. It may therefore be regarded with some certainty as a structural constant. The independence of the equilibrium point of temperature indicates that the reaction between the acids, whilst requiring considerable energy for its inception, takes place with scarcely any heat change. In view of the work of Derick (*J. Amer. Chem. Soc.*, 1910, **32**, 1333), it is of interest to note that the ionisation constants of the two acids are very similar, 0·00260 for the αβ- and 0·00249 for the βγ-acid (Zelinski and Izgaryschev, *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1379).

The *mobility* of systems such as these, tautomeric in the presence of a powerful catalyst, can only be expressed rationally in terms of the velocity of the interconversion reaction. As previously pointed out (this vol., p. 368), a definite set of conditions has to be standardised before the mobilities of different series can be compared. From a survey of the results so far obtained, the following have been selected as the most convenient conditions : The equilibration is carried out at 100°, the unsaturated acid being treated with 25% aqueous potassium hydroxide (ten times the quantity required for exact neutralisation).* The velocity coefficient of interconversion is given by $k_1 + k_2 = \log_e \{\xi/(\xi - x)\}/t$ (this vol., p. 367). It is proposed to take the expression 100 $(k_1 + k_2)$, when t is expressed

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* If 0·01 g.-mol. of unsaturated acid is used, this quantity is 18·12 c.c. of a solution containing 25 g. of potassium hydroxide in 100 g. of solution (30·96 g. in 100 c.c.), $d_{4^\circ}^{15^\circ}$ 1·239. Solutions between 24 and 26%, if used in equivalent amounts, may be taken as satisfactory.

in hours and ξ and x in g. of potassium salt per c.c. of water, as a convenient numerical figure for the *degree of mobility* of the system. For the acids here dealt with, this figure becomes 10·0 ± 1·3 units (see p. 2584). Previous work was not carried out under these standard conditions, but various acids, including the simplest straight-chain olefinic acids, are now being examined with a view to obtain definite values for their mobility and position of equilibrium.

EXPERIMENTAL.

Equilibration.—Δ^1-*cyclo*Hexenylacetic acid and *cyclo*hexylideneacetic acid were prepared and purified by the standard methods. The acid under investigation (1·40 g.; 0·01 g.-mol.) was sealed up in a thick-walled tube of resistance glass with the appropriate amount of alkali. The concentrations and the excess of the alkali solutions were varied to suit the particular conditions required. The concentrations, allowing for neutralisation, of the potassium salt of the acid and the excess alkali in the various solutions are given in Table I.

TABLE I.

Concentrations of Reactants.

	Amount present (g.).			Concentration (g./c.c.).	
Sol.	K salt.	KOH.	Water.	K salt.	KOH.
A	1·78	5·04	15·74	0·114	0·321
B	,,	,,	17·53	0·102	0·287
C	,,	0·56	3·29	0·541	0·170
D	,,	,,	22·63	0·079	0·025
E	,,	,,	13·93	0·128	0·041

Solutions A and B are approximately "standard," the theoretical concentrations conforming with the conditions given on p. 2580 being 0·105 g. K salt and 0·297 g. KOH per c.c.

The reaction tube was heated at the desired temperature in a bath of boiling liquid (chloroform, 61·2°; trichloroethylene, 87°; water, 100°; saturated solution of potassium nitrate, 115°). At the end of the required interval of time the product was freed from a trace of lactone in the usual way and the acid was dried, carefully freed from solvent, and weighed. The loss was of the order of 5%.

Examination of the Mixed Acids.—In the earlier work little or no addition of water to the double bond occurred when the unsaturated acids were boiled with 60% alkali. The absence of such addition products was shown in the present work by the normal iodine addition values of all the products and by the fact that no hydroxy-acid could be isolated by Fittig's method (separation by steam distillation), although in control experiments a quantity of 2% could readily be isolated under the conditions used.

The mixed unsaturated acids were then examined by the iodine addition method (First method, Linstead and May, *loc. cit.*) and the proportion of the isomerides was determined by reference to the standard curves.

Tabulation and Examination of Results.

I. *Point of Equilibrium.*—

TABLE II.

Concentrations of Reagents—A (Table I).

				Product.	
Expt.	Initial material.	Temp.	Time (hrs.).	% Addition of iodine.	% αβ-Acid.
1	αβ-Acid	100°	21	61·8; 62·8; 62·8; 63·0	12·0 ± 1·0
2	,,	,,	23	63·8; 62·8; 63·2; 62·5	10·8 ± 1·0
3	,,	,,	49	63·7; 62·7; 62·7	10·8 ± 1·1
4	,,	B. p.	7·5	62·6	12·2
5	βγ-Acid	100	8·8	62·6; 62·5; 61·0	13·3 ± 1·7
6	,,	,,	24	62·9	11·0
7	,,	115	17·5	63·2	10·5

The effect of less vigorous conditions was most conveniently tested by starting with the equilibrium mixture. A quantity of this (addition value, 62·6%; αβ-acid content, 12·2%) was prepared from the αβ-acid and treated under the following conditions:

(8) Concentrations, A; temperature, 61°; time, 24 hrs. The product had addition value, 62·5%; αβ-acid content, 12·3%.

(9) 1·40 G. of the equilibrium mixture were treated with 18·62 c.c. of 24·4% KOH solution (B) and an additional 18·62 c.c. of ethyl alcohol were added. Temperature, 100°; time, 24 hrs. The product had addition value, 63·1%; αβ-acid content, 10·5%.

(10) 1·40 G. of the equilibrium mixture were treated with ten times the amount required for neutralisation of a 25% solution of sodium hydroxide. The product had addition value, 61·3%; αβ-acid content, 15·0%.

The mean of these results corresponds to an αβ-acid content at equilibrium of 11·8% ± 1·1%. The corresponding mean value for the equilibrium in boiling 40, 50, and 60% potassium hydroxide solutions is 12% ± 0·8% (Linstead, *loc. cit.*). The equilibrium is therefore constant over a wide range of conditions.

II. *Effect of Temperature on Mobility.*—These experiments were carried out with the "standard" solutions, namely, at concentrations (A). In experiments 18 and 22 the slightly weaker solution (B) was used. The initial material was αβ-acid throughout, except in experiment 28 where βγ-acid was used.

TABLE III.

Interconversion under Standard Conditions.

			Product.		
Expt.	Temp.	Time (hrs.).	% Yield.	% Addition of iodine.	% $\alpha\beta$-Acid.
11	61°	2·0	97	—	100 *
12	,,	5·0	97	—	100 *
13	87	5·5	96	16·3; 16·3	90·4
14	,,	17·25	90	25·6; 25·2; 25·6	78·7 ± 0·2
15	,,	21·0	91	26·5; 24·7; 23·2; 25·0	79·6 ± 1·3
16	,,	47·0	97	44·2; 43·5; 43·6	49·7 ± 0·5
17	100	2·0	—	25·1; 23·5	80·3 ± 1·0
18	,,	3·92	86	26·8; 26·0	77·5 ± 0·5
19	,,	6·0	—	37·8; 37·5; 36·9	60·5 ± 0·5
20	,,	6·0	90	34·6; 34·4; 34·9	65·1 ± 0·2
21	,,	8·0	94	40·2; 38·8; 38·8; 37·6	58·1 ± 1·2
22	,,	8·75	91	43·8; 44·2	49·5 ± 0·5
23	,,	10·0	94	47·4; 45·9; 45·5	45·2 ± 1·2
24	,,	15·0	89	56·8; 56·3; 54·4	27·4 ± 2·0
25	115	3·08	93	38·9	58·0
26	,,	4·5	87	49·5	39·6
27	,,	5·5	64	57·3	24·6
28	87	47·0	98	65·3; 64·6; 64·7	5·2 ± 1·1

* From melting point and crystalline form.

The results indicate that there is no interconversion at 61° and that at the higher temperatures the reaction follows fairly closely a reversible unimolecular course. The figures for the velocity coefficient calculated from the equation (p. 2580) are in Table IV.

TABLE IV.

Initial concentration, $\alpha\beta$-K salt 0·114 g./c.c. (except in Expts. 18 and 22); equilibrium concentration of $\beta\gamma$-K salt (ξ) 0·1006 g./c.c.; x = change in concentration of $\alpha\beta$-K salt; t in hours.

	Time.	% $\beta\gamma$-Acid.	x.	$\xi - x$.	$(k_1 + k_2)$.
87°	5·5	9·6	0·0109	0·0897	0·021
	17·25	21·3	0·0243	0·0763	0·016
	21·0	20·4	0·0232	0·0773	0·012
	47·0	50·3	0·0574	0·0433	0·018
					Mean 0·017 ± 0·004
100°	2·0	19·7	0·0225	0·0781	0·126
	3·92	22·5	0·0256	0·0750	0·088
	6·0	39·5	0·0450	0·0556	0·099
	6·0	34·9	0·0398	0·0608	0·083
	8·0	41·9	0·0477	0·0528	0·080
	8·75	50·5	0·0576	0·0430	0·103
	10·0	54·8	0·0625	0·0381	0·097
	15·0	72·6	0·0847	0·0159	0·126
					Mean 0·100 ± 0·013
115°	3·08	42·0	0·0479	0·0527	0·209
	4·50	60·4	0·0689	0·0318	0·256
	5·50	75·4	0·0860	0·0146	0·350
					Mean 0·272 ± 0·051

The reaction velocity is approximately doubled for a 10° rise above 100°, and the low value at 87° is to be expected from the zero reaction at 61°. From the figures found for the reaction at 100°, the degree of mobility of the series is 10·0 ± 1·3. An inspection of the above figures and others previously obtained indicates that for rapid determinations of the degree of mobility of a series it is best to carry out three or four estimations of the amount of interconversion over periods ranging from $\frac{1}{4}$ to $\frac{1}{2}$ the time required for complete equilibration. On this basis the mobility in the present series would be 9·3 ± 0·8.

III. *Effect of Concentration on Mobility.*—The velocity of the reaction diminishes with dilution and is particularly sensitive to decrease in alkali concentration. The mathematical relationship between these factors has not been obtained, but several points of interest arise from the results given below.

TABLE V.

Initial material, *αβ*-acid; temperature, 100°.

Expt.	Conc. (see Table I).	Time (hrs.).	Product.		
			% Yield.	% Addition of iodine.	% *αβ*-Acid.
29	D	21·0	90	21·8; 21·1; 22·0; 19·4	84·4 ± 1·1
30	D	47·5	94	20·2; 18·4	86·7 ± 1·2
31	C	21·0	54	48·1; 48·7; 45·9; 45·6	43·8 ± 2·3
32	E	6·0	94	10·8; 11·8	95·3 ± 0·4
33	E	17·0	97	13·3; 11·9; 15·5	93·1 ± 1·1
34	E	24·0	89	18·2; 15·6; 16·0	89·8 ± 1·2
35	E	41·5	97	20·9; 20·1; 20·9	84·9 ± 0·5

Experiments 29 and 30 show that the αβ-acid is essentially unchanged by 5% alkali just below its boiling point even over long periods of time. In experiment 31, the concentration of potassium salt is very high (five times that under the standard conditions), and the catalyst concentration is about half its standard value. As a result the reaction velocity decreases considerably, there being only 56% change instead of complete equilibration in 21 hours. In the last four experiments (Series E) the concentration of the potassium salt is approximately standard, while that of the catalyst is much lower. The velocity coefficients compare as follows :

	Conc. of K salt.	Conc. of KOH.	Mean ($k_1 + k_2$).
Standard (Series A)	0·114	0·321	0·100
Series E	0·128	0·041	0·0048

The effect of catalyst concentration is clearly marked. General theoretical considerations indicate that the catalytic agent is the hydroxyl ion and are supported by the fact that sodium hydroxide does not affect the equilibrium attained in potash solution. An obvious analogy exists between this effect and that of the hydrogen ion in hydrolyses, when the velocity of reaction is proportional to the concentration of the catalyst.

The Hydrolysis of Esters of Mobile Acids.

The results obtained are of value in that they indicate the conditions under which the ester of a comparatively unstable, unsaturated acid can be hydrolysed with alkali without movement of the double bond. The alcohol liberated from the ester does not affect the equilibrium (Experiment 9) and the following results show that, if anything, it has a slight *retarding* influence on the velocity of interconversion.

Concentrations, (A); solvent, 70% water + 30% ethyl alcohol; temperature, 100°.

		Product.	
Time (hrs.).	% Yield.	% Addition of iodine.	% $\alpha\beta$-Acid.
6	96	37·8; 36·4	61·1 ± 1·2
25	94	58·5; 59·3; 57·9; 58·5	21·8 ± 0·9

It may therefore be predicted that in this series hydrolysis of either ester with cold aqueous or alcoholic alkali of any strength will yield the corresponding acid in a state of purity. Hydrolysis with boiling solutions of 10% alkali for periods of 8 hours or so will yield substantially pure products. The latter conditions should prove more convenient than those used at present, which involve 50% alkali and often lead to considerable fission.

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