POLAROGRAPHIC INVESTIGATION OF THE HYDROGENATION PROCESS

II. HYDROGENATION OF MALEIC AND FUMARIC ACID MIXTURES

A. L. Markman

The behavior of cis- and trans-ethylenes is an individual problem in catalytic hydrogenation of ethylene compounds. Paal and Schiedewitz [1], Ott [2], and Golendeev and Plisov [3], who hydrogenated, individually, various geometric isomers, have found that the saturation rate for cis-isomers is always higher than for trans-isomers.

The author has not found in the literature information on the behavior of cis- and trans-isomers when they are hydrogenated as combined mixtures; nor any general description on combined hydrogenation experiments. The author, therefore, undertook a study of the behavior of maleic and fumaric acids during their separate and their combined hydrogenation.

Maleic acid was prepared from chemically-pure maleic anhydride and purified by three recrystallizations from aqueous solution. After drying, the m.p. was 130°. The fumaric acid was chemically-pure when used.

The author carried out a number of experiments on separate hydrogenations of the acids named with platinum and with palladium catalysts which were precipitated onto aluminum and nickel supports, as the result of which the hydrogenation rate constants were determined, which are given in Table 1. The experimental procedure was the same as described earlier [4].

It can be seen from Table 1 data that the relationship of the saturation rate constants for maleic and fumaric acids to the nature of the catalyst, and its amount, varies over quite a wide range – from 0.92 to 9.29, and in the majority of cases, maleic acid saturates more rapidly than fumaric acid.

In the hydrogenation of maleic-fumaric acid mixtures, the author has developed a method for their combined polarography. The author has established that these acids give two different waves upon reduction at the dropping mercury cathode, in absolute ethyl alcohol acidified with 0.1 N hydrochloric acid, and which differ in the half-wave potential values by 0.2 V, the difference amounting to 0.17-0.18 V in 95-96% alcohol. This circumstance was utilized by the author to analyze mixtures of maleic and fumaric acids during the course of their hydrogenation.

TABLE 1

Expt. No.	Acid hydrogenated (0.005 mole)	Catalyst	Amount of catalyst (in mg)	Metal support	Amount of metal support (in mg)	Hydrogenation rate constants	Ratio of the constants, $k_{maleic}/k_{fumaric}$
157	Maleic	Pd	32	Ni	105	0.088	0.92
153	Fumaric					0.960	
45	Maleic	Pd	64	Ni	105	0.188	2.29
152	Fumaric					0.082	
103	Maleic	Pd	32	Al	105	0.0468	6.59
154	Fumaric					0.0071	
107	Maleic	Pd	64	Al	210	0.0613	9.29
155	Fumaric					0.0066	
19	Maleic	Pt	58	Ni	105	0.0190	2.00
16	Fumaric					0.0095	

The sequence of carrying out experiments on combined hydrogenation of the two geometrically isomeric acids is given.

1. Hydrogenation of Maleic-Fumaric Acid Mixture with Palladium Catalyst

Experiment 104. 0.58 g of maleic and 0.58 g of fumaric acids (in 1/200 mole portions), 210 mg of Al and 64 mg of Pd, 30 ml of alcohol in 10 ml water. Bath temperature was 25°, air temperature 14°, pressure 717.5 mm, theoretical volume of hydrogen absorbed, H_0, was 252.8 ml. For the polarography, 1 ml of each sample was dissolved in 25 ml of the medium (0.1 N HCl in 96% alcohol). $\pi_{1/2}$ for maleic acid) 0.72 V, and for fumaric acid, 0.89 V. The concentration of each acid in the polarographed solution for sample No. 1, as sampled before hydrogenation, was equal to $0.005 = 500 \cdot 10^{-5}$ moles/liter. For convenience and for unity of concentration of the polarographed solutions, the concentration $1 \cdot 10^{-5}$ moles/liter was adopted. Then for the case investigated, the concentration of each acid, C, in relative units, was equal to 500.

During the course of hydrogenation, 12 samples were taken and polarographed. By measurement of the polarographic wave heights for both acids, their concentrations in each sample were determined, after which the reaction mixture composition following each consecutive state of hydrogenation, was calculated. The resulting data are given in Table 2.

TABLE 2

Sample No.	H_2 absorbed (in %)	Maleic acid		Fumaric acid		Composition of mixture (in %)		
		C	saturation (in %)	C	saturation (in %)	maleic acid	fumaric acid	succinic acid
1	0	500	0	500	0	50.0	50.0	0
2	8.3	420	16.0	500	0	42.0	50.0	8.0
3	17.0	338	32.4	500	0	33.8	50.0	16.2
4	25.7	250	50.0	500	0	25.0	50.0	25.0
5	34.7	198	60.4	456	8.8	19.8	45.6	34.6
6	43.8	134	73.2	428	14.4	13.4	42.8	43.8
7	53.3	58	88.4	410	18.0	5.8	41.0	53.2
8	63.1	47	90.6	323	35.4	4.7	32.3	63.0
9	73.3	0	100	267	46.6	0	26.7	73.3
10	83.6	0	100	164	67.2	0	16.4	83.6
11	98.2	0	100	58	88.4	0	5.8	94.2
12	100.0	0	100	0	100	0	0	100

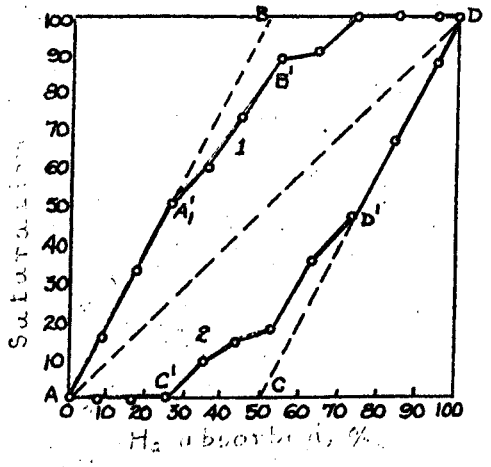

Fig. 1. Characteristics of selectivity of the hydrogenation process for a mixture of unsaturated compounds, using Pd and 25°. 1) Maleic acid; 2) fumaric acid. Explanations in the text.

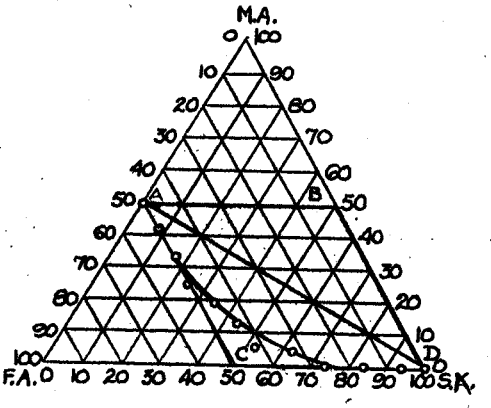

Fig. 2. Change in composition of the reaction mixture upon hydrogenation of the acids. M.A. = Maleic Acid; F.A. = Fumaric Acid; S.A. = Succinic Acid.

On the basis of the data in this Table, the curve (Fig. 1) was constructed. If the saturation process were completely unselective, then the saturation curve for each component of the mixture should coincide with the diagonal, AD. With completely selective saturation, for example of maleic acid, its saturation should proceed along the broken

line, ABD, and fumaric along the line ACD. Actually, the saturation curves showed certain deviations from the absolute selectivity.

Of special interest in connection with this fact is the nature of the degree of selectivity of the process.

A method for relating the content of saturated fatty acids in a fat with the iodine number [5] is well known, or a similar method for combining the iodine and thiocyanogen numbers for a fat, which have been applied to fats.

The A. A. Zinovyev method is of considerable interest, according to which the degree of selectivity is characterized by the ratio of the constants for the rate of saturation of both components of the mixture: $K=\frac{K_1}{K_2}$ [6]. However, it would have been more convenient, in the author's opinion to select the value, 1−K, to characterize the process. This value for a completely selective process is equal to 1, if completely unselective, 0, and for any other it acquires a value lying between 0 and 1, and therefore, is closer to 1 the more selective the process.

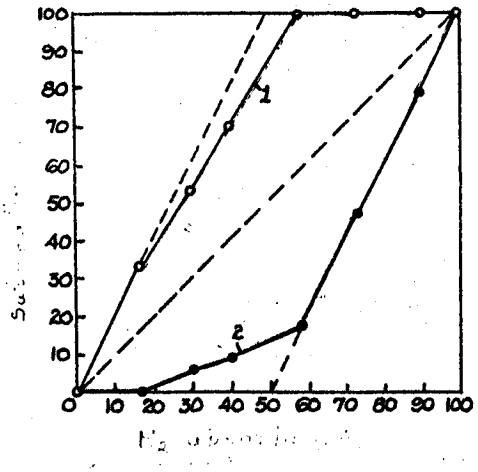

Fig. 3. Characterization of the degree of selectivity of the hydrogenation process for unsaturated acids, using Pd and at 40°. 1) Maleic acid; 2) fumaric acid. Explanation in the text.

Inasmuch as each pair of curves for unsaturated compounds is constructed analogously to the one presented in Fig. 1, for purposes of clarity, it is possible, therefore, to characterize the degree of selectivity by the area defined by the closed curve, AA'B'DD'C', and the area of the parallelogram, ABDC. Apparently, in a strictly selective process, when saturation of one of the components of the mixture takes place along the broken line, ABD, and the second component along the broken line, ACD, this ratio becomes equal to 1; in a completely unselective process, where both compounds become saturated along the straight line AD, the ratio and the degree of selectivity are equal to 0; in the remainder of cases the degree of selectivity lies between 0 and 1. In the particular case of fumaric and maleic acids, according to experimental data from the 104th experiment, the degree of selectivity was found to be equal to $S=\frac{41.05}{50}=0.821$, where 41.05 and 50 are the areas for the figure (in cm^2).

Measurement of the areas of the figures with their irregular shape, is accomplished by means of a planimeter. Without a planimeter, this problem can be solved by gravimetric procedure.

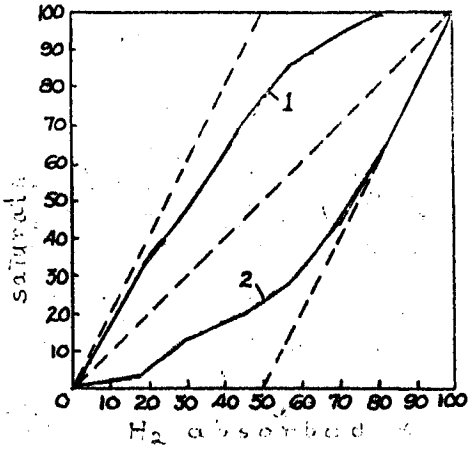

Fig. 4. Characterization of the degree of selectivity of the hydrogenation process for a mixture of unsaturated compounds, using Pt at 24°. 1) Maleic acid; 2) fumaric acid. Explanations in text.

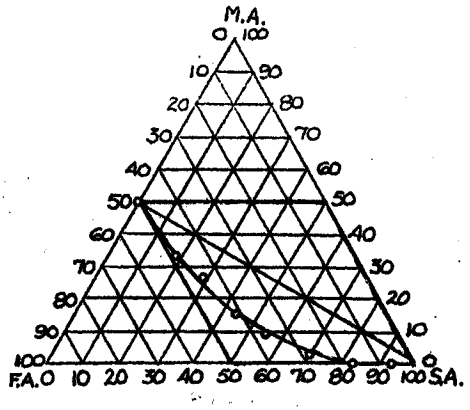

Fig. 5. Change in composition of the reaction mixture upon hydrogenation of the acids. F.A. = fumaric acid; M.A. = maleic acid; S.A. = succinic acid.

The change in composition of the reaction mixture, in agreement with the values in the last three columns of Table 2, is presented in a triangular coordinate system in Fig. 2. Point A corresponds to initial composition of the mixture; point D = the product from complete saturation. The transition from point A to point D can be realized by various routes: along the broken line, ABD, under the conditions of selective steric saturation, first with fumaric and then with maleic acid; along the broken line ACD with a strictly selective hydrogenation, first of maleic and then of fumaric; and along the straight line, AD, under conditions of completely unselective hydrogenation.

In the author's experiment, the points corresponding to composition of mixtures in a number of consecutive hydrogenation stages are distributed most closely to the broken line, ACD, on the AD curve. This indicates that the process proceeds with almost complete selectivity, maleic acid being saturated first, and then fumaric.

Similar experiments at 40° indicated a higher degree of selectivity, S = 0.874 (Fig. 3).

2. Hydrogenation of a Mixture of Maleic and Fumaric Acids with Platinum Catalyst

Experiment 158. A mixture of maleic and fumaric acids (in 1/200 mole portions), 210 mg of Al and 232 mg of Pt, 30 ml of alcohol in 10 ml of water. Bath temperature was 24°, air 11°, pressure 726.5 mm, theoretical hydrogen absorption, H_0, 243.8 ml. Results of the hydrogenation are given in the Figs. 4 and 5 curves. In this case, again maleic acid saturates predominately; however, the degree of selectivity was less than with hydrogenation in the presence of palladium catalyst (S = 0.686).

SUMMARY

1. The method of polarographic analysis has been used for the first time to investigate the hydrogenation process for mixtures of unsaturated organic compounds, which makes it possible to follow the course of the hydrogenation, and in particular the distribution of hydrogen between components in the mixture.

2. A method for quantitatively expressing selectivity of the hydrogenation process for binary mixtures by determining the ratio of figure area circumscribed by saturation curves for components of the mixture to the area corresponding to absolute selectivity of the process (S index) has been used.

3. It has been determined that for mixtures of geometrically-isomeric acids (maleic and fumaric) the first hydrogenates selectively for the most part, and selectivity is more pronounced when working with palladium catalyst than with platinum; however, in none of these cases does it bear an absolute character.

LITERATURE CITED

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Central Asian Polytechnical Institute

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