

CATALYTIC HYDROGENATION OF UNSATURATED ORGANIC ACIDS AND THEIR SODIUM SALTS

Libor ČERVENÝ, Eva FIALOVÁ and Vlastimil RŮŽIČKA

*Department of Organic Technology,
Prague Institute of Chemical Technology, 166 28 Prague 6*

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Catalytic hydrogenation of unsaturated organic acids in methanol and their sodium salts in water was studied at 20°C and atmospheric pressure of hydrogen using a catalyst of 3% Pd on activated carbon. The effect of the structure of the acids and salts on the hydrogenation rates is discussed.

The effect of structure of organic substances on their hydrogenation kinetics has been studied extensively and the results obtained have been reviewed by Kraus^{1,2} and by Červený and Růžička^{3,4}. Some conclusions of general validity, even of quantitative nature, have been arrived at. Still, much remains to be investigated. Among topics that have not yet been examined in detail, there is the catalytic hydrogenation of unsaturated acids and their salts. Only hydrogenations of individual acids or their derivatives have been examined⁵⁻⁹, usually with a view to establishing the optimum hydrogenation conditions, but a comparison of reactivity in a wider acid series has not yet been made. This may be due, among other things, to the *a priori* lack of structure parameters of substituents (Taft constants) in such series, where the carboxy group is only a substituent rather than the reaction centre; here the relations between the structure and reactivity are very difficult to evaluate. The aim of the present work was to obtain basic data for characterizing these relations in a series of acids and their sodium salts.

EXPERIMENTAL

Substances. Commercial acids (Koch-Light, Fluka, Lachema) were purified by distillation or crystallization from water; their boiling or melting temperatures agreed well with tabulated data. Methanol of reagent grade purity (Lachema, Brno) was used as the medium for the hydrogenation of the acids, water was used for the sodium salts. The catalyst was Cherox 41-00 (3% Pd/activated carbon; Chemical Works, Litvínov), grain size below 0.063 mm.

Apparatus and procedure. A standard apparatus⁵ with a magnetically stirred reactor was used for the liquid phase hydrogenation kinetics study. The experiments were performed at 20°C and atmospheric pressure of hydrogen. The reaction rate was measured by monitoring the rate of hydrogen loss in volumetric burettes. To the reactor were invariably added 1.15 mmol of acid and 10 ml of methanol, the system was homogenized, and 0.01–0.1 g of catalyst was added.

The sodium salts were prepared in the hydrogenation reactor immediately before the hydrogenation by neutralizing the acid with the stoichiometric amount of sodium hydroxide in aqueous solution. In this case the homogenization was performed for 30–60 min and the final pH was 7–7.5. The molar concentrations of the sodium salts in water were equal to those of the acids in methanol. The amount of catalyst added was 0.2–0.35 g.

RESULTS AND DISCUSSION

Under the conditions used, the effect of external mass transport on the reaction rate was eliminated by stirring, and the potential effect of internal diffusion was limited by using the catalyst in dust form. The hydrogenation rates were constant up to high degrees of conversion for all the acids. For 2,4-hexadienoic acid, the time dependence of the hydrogen take-up during the hydrogenation exhibited a knee at the consumption of 1 mol of hydrogen per mol of acid, dividing the plot into two straight line segments, the first of which possessed a higher slope; owing to this, the hydrogenation rates for the two double bonds could be determined from a single measurement. The reaction rates were determined as the slopes of the straight lines in the coordinates of amount of consumed hydrogen *vs* time, per unit amount of catalyst. In the hydrogenations of the sodium salts, the reaction order with respect to the actual concentration of substrate was nonzero; the reaction rate decreased with time. For sodium 2,4-hexadienoate, a break again appeared in the time dependence of the hydrogen take-up during the hydrogenation, in the point corresponding to the consumption of 1 mol of hydrogen per mol of salt. The initial hydrogenation rates for the sodium salts were determined as the curve tangents in the origin (or in the break point for 2,4-hexadienoate).

The initial rates of hydrogenation of the free acids in methanol and their sodium salts in water are given in Table I. The hydrogenation rates of the unsaturated acids are appreciably affected by their structure; for the sodium salts the effect of structure is much less pronounced. This can be well seen in Fig. 1, where the relative values with respect to *cis*-2-butenedioic acid or its sodium salt are plotted. A nonlinear relationship exists between them; the only acids that do not obey this relationship are 3-phenylpropenoic acid (the only acid involving an aromatic ring system) and 2,4-hexanedioic acid (the only dienoic acid; the relation is obeyed for neither of the bonds). Except for 3-phenylpropenoic acid, the acids in methanol were hydrogenated appreciably more rapidly than their sodium salts in water.

Several semiquantitative conclusions can be derived from these results. For the first four acids in Table I, which differ in the R¹ substituent only, the reactivity order is CH₃ > CH₃(CH₂)₄ > COOH > C₆H₅. In the salt series, this order is disturbed by the relatively high reactivity of the 3-phenylpropenoate. As to the two dicarboxylic acids (No 4 and 5), the reaction rate is somewhat increased for the latter where the distance between the carboxy group and the reaction centre is extended and the carboxy group oxygen is no more in conjugation with the double

bond. A comparison of acids No 5 and 6 demonstrates that the reaction rate drops appreciably if the hydrogen atom is replaced by a CH_2COOH group, and the values for acids No 6 and 7 show that the reactivity decreases as the distance between the double bond and the carboxy group is extended. For 2,4-hexadienoic acid, where two different values of reaction rates are obtained, the lower value was attributed to the hydrogenation of the α,β -double bond because this value is between those for 2-butenoic and 2-octenoic acids with the same position of the carboxy group with respect to the double bond. The higher value, on the other hand, corresponds better with the reactivities of acids where the carboxy group is more remote from the reaction centre, such as 3-butenoic or 10-undecenoic acids. For sodium 2,4-hexadienoate, although the kinetic dependence also exhibits a break in the point of consumption of 1 mol of hydrogen per mol of salt, the assignment of the two experimental "initial reaction rates" is not straightforward because of the low curve tangent in the break point ($r = 0.12 \text{ mmol/min g}_{\text{cat}}$); the low reaction rate of the consecutive step is likely to be due to catalyst poisoning.

The precision of the data measured was high (the individual rate values did not differ more than $\pm 5\%$ from the average of triplicate measurements). The observations do not disagree with any of the general rules concerning the effect of structure on reactivity¹⁻⁴. Attempts at quantification of the dependences of the reaction rates on the substrate structure were made by employing the Taft-Pavelich equation^{10,11},

TABLE I

Hydrogenation kinetics parameters for unsaturated acids and their sodium salts on a palladium catalyst

No	Acid	Substituents in $\text{R}^1\text{---CH=CH---R}^2$		Initial hydrogenation rate, mmol/min g_{cat}	
		R^1	R^2	acid	sodium salt
1	2-Butenoic	$\text{CH}_3\text{---}$	---COOH	8.44	0.94
2	2-Octenoic	$\text{CH}_3(\text{CH}_2)_4\text{---}$	---COOH	3.40	0.71
3	3-Phenylpropenoic	$\text{C}_6\text{H}_5\text{---}$	---COOH	0.95	0.91
4	<i>cis</i> -2-Butenedioic	HOOC---	---COOH	1.91	0.51
5	3-Hexenedioic	$\text{HOOC---CH}_2\text{---}$	$\text{---CH}_2\text{---COOH}$	2.30	0.59
6	3-Butenoic	H---	$\text{---CH}_2\text{---COOH}$	14.41	1.04
7	10-Undecenoic	H---	$\text{---(CH}_2)_8\text{COOH}$	5.73	0.92
8	2,4-Hexadienoic	$\text{CH}_3\text{---}$	---CH=CH---COOH	18.11	0.80
9	2-Hexenoic ^a	$\text{CH}_3(\text{CH}_2)_2\text{---}$	---COOH	3.96	0.12

^a Assumed product of hydrogenation of 2,4-hexadienoic acid in the first step.

estimating the unknown E_s constants for some substituents based on the isostericity principle¹²; thus, the E_s values for the $-\text{COOH}$, $-\text{CH}_2\text{COOH}$, $-\text{CH}=\text{CH}-\text{CH}_3$, $-\text{CH}=\text{CH}-\text{COOH}$, and $-\text{C}_6\text{H}_5$ groups were approximated by those of the $-\text{C}_3\text{H}_7$, $-\text{C}_4\text{H}_9$, $-\text{C}_3\text{H}_7$, $-\text{C}_5\text{H}_{11}$, and cyclo- C_6H_{11} groups, respectively. The other σ^* and E_s constants were taken from refs^{11,13}. The isolated $\text{C}=\text{C}$ double bond was regarded as the reaction centre and the sums of the constants for the four substituents were used. 10-Undecenoic acid (No 7) was not included in the correlation because the estimates of the σ^* and E_s constants for the $-(\text{CH}_2)_8-\text{COOH}$ substituent are rather uncertain. The Taft-Pavelich equation parameters were determined by double linear regression. 3-Butenoic acid was found not to obey the dependence obtained. When omitting this compound, a very tight correlation was obtained in the form

$$\log r = -0.07 \sum \sigma^* + 1.78 \sum E_s - 2.39. \quad (1)$$

The correlation coefficient for this relation was 0.957 (for 7 compounds), which is higher than the critical value at the 0.1% significance level (0.898). The dependence is plotted in Fig. 2.

Taking into account the fact that of the two unsaturated acids with their double bonds at the ends of the chains, 10-undecenoic acid could not be evaluated and 3-butenoic acid did not obey the relation obtained, it can be concluded that the correlation found is applicable to unsaturated acids other than those having their double bonds at the ends of the chains opposite to those carrying the carboxy

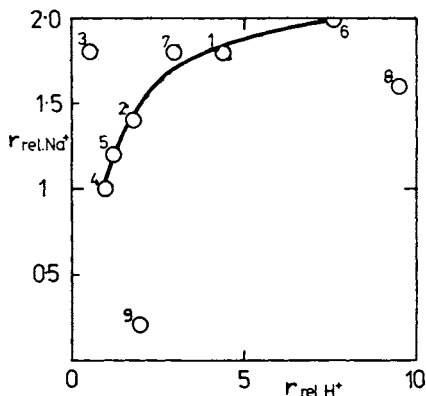


FIG. 1

Relation between the relative hydrogenation rates of sodium salts and the respective acids. Compound numbering as in Table I

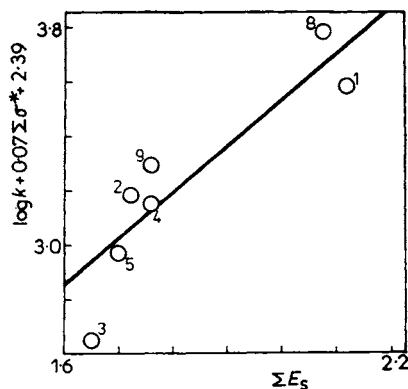


FIG. 2

Dependence of the hydrogenation rates of unsaturated acids on the substituent structure parameters (Taft-Pavelich equation). Compound numbering as in Table I

group. The parameters of the correlation equation demonstrate that the reactivity of unsaturated acids in their hydrogenation is determined mainly by the steric effects whereas the electronic effects of the substituents at the double bonds play a minor role.

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