

INVESTIGATION OF HYDROGENATION IN LIQUID PHASE. XXXI.*
 EFFECT OF SOLVENTS ON THE RATE
 OF THE CATALYTIC HYDROGENATION OF 2-METHYL-3-BUTEN-2-OL

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A contribution is presented to the efforts to express quantitatively the effect of solvents on the rate of the catalytic hydrogenation of the double bond. Hydrogenations of 2-methyl-3-buten-2-ol over the 5% Pt on silica gel and 5% Pt on active charcoal catalysts have been studied in 19 solvents at usual conditions. In correlations, τ' was used as the solvent-characteristic parameter (defined in the preceding paper on the basis of kinetics of the hydrogenation of cyclohexene over the 5% Pt on silica gel catalyst under the same conditions). The influence of the substrate and the catalyst carrier on the validity of correlations has been studied on the basis of linear relations of free enthalpies.

It has been shown¹ that it is hardly possible to generalize the results of investigations on correlations between the observed kinetic data and a special property of the solvent since when another system is used, the correlation is invalid. The effect of the solvent obviously depends on the whole set of the solvent properties from which some property may predominate. Such correlations might be valid within homologous series of solvents only. The attempted¹ correlation of hydrogenation rates of cyclohexene over the 5% Pt on silica gel catalyst in 19 solvents with the τ constants of the Drougard-Decrooq equation² failed. Analogous constants τ' were therefore proposed which should be valid in favourable cases for catalytic hydrogenations of double bonds over platinum catalysts¹:

$$\tau' = \log (r_{Cn}^0 / r_{Co}^0), \quad (1)$$

wherein r^0 is the initial (o) hydrogenation rate (r) of cyclohexene (C) in the solvent n (r_{Cn}^0) or in a standard solvent o (r_{Co}^0). The correlation was based on methanol which is frequently used as solvent for hydrogenations in liquid phase; for the hydrogenation of cyclohexene under the conditions stated, $\lambda' = 1$. A successful correlation was then performed of the observed initial hydrogenation rates of 1-hexene with the thus-defined τ' constants in the same solvents and on the same catalyst. The λ' value of 1-hexene was 0.96.

The object of the present paper consists in an extension of the earlier results¹ on another substrate (thus, instead of 1-hexene, 2-methyl-3-buten-2-ol was used, carrying an additional hydroxylic function and a methyl group on the carbon atom

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at the α -position in respect to the double bond) and on another catalyst carrier (silica gel was replaced by active charcoal) as an approach to a general theory of the effect of solvents on the rate of catalytic hydrogenations.

EXPERIMENTAL

Catalysts. The 5% Pt on silica gel catalyst³ was prepared in the same way as in the preceding paper¹; the particle size below 0.063 mm was used. The 5% Pt on active charcoal catalyst was prepared as follows. Active charcoal (Supersorbon Degussa, German Federal Republic, HB-3, specific surface 1200 m²/g, particle size below 0.063 mm) was treated with aqueous chloroplatinic acid, the mixture evaporated to dryness, the residue reduced with a mixture of hydrogen and nitrogen at 200°C for 3 h, and then kept under nitrogen for 10 h. For the solvents and purification of hydrogen see the preceding paper¹. *2-Methyl-3-buten-2-ol* (Koch-Light, Great Britain) was purified by distillation (b.p. 97°C).

Hydrogenations were carried out at 20°C and the atmospheric pressure of hydrogen. For the apparatus and methods see the preceding paper¹. Depending on the absolute hydrogenation rates in particular solvents, the amount of the catalyst varied from 0.02 g to 0.3 g. For the elimination of the influence of both the internal and external mass transport on the reaction rate see the preceding paper¹.

RESULTS AND DISCUSSION

The observed data were evaluated similarly to the preceding paper. In respect to the concentration of hydrogen, the reaction was assumed to be of the first order; in respect to the partial pressure of the solvent, the reaction rate values were corrected to the partial pressure of hydrogen (760 Torr). By the use of initial reaction rates in correlations according to the equation (1) instead of reaction rates, an assumption was introduced of the equal reaction order of the unsaturated compound to be hydrogenated (substrate) and cyclohexene in respect to their initial concentrations in the particular solvent. Only experiments could confirm correctness of this assumption. In Table I, there are summarised initial hydrogenation rates of 2-methyl-3-buten-2-ol at equal v/v concentrations (1 ml of the substrate per 25 ml of the solvent) along with formal reaction orders in respect to the instant substrate concentration, as determined by the use of the reduced kinetic equation¹. Similarly to the preceding paper¹, a high reaction order was observed in the hydrogenation over the 5% Pt on active charcoal catalyst with the use of diethyl malonate as solvent. On the other hand, the order was zero when the hydrogenation was performed in the same solvent but over the 5% Pt on silica gel catalyst. This effect can be hardly explained without a direct measurement of the reaction order in respect to the initial concentrations of the substrate.

The comparison is again based on the hydrogenation rate in methanol. The relative hydrogenation rates in other solvents were correlated according to the equation (1) with the use of τ' values given in the preceding paper¹. The results of correlations

are shown in Figs 1 and 2. The data obtained for hydrogenations over the 5% platinum catalyst on the two carriers are rather different. In the case of the silica gel carrier (the same carrier was used in the preceding paper¹ to determine the τ' values; another batch of this catalyst has been used in the present experiments), the correlation is considerably better than with the active charcoal carrier (the correlation coefficients for 19 values are 0.90 and 0.69, resp.). Another significant difference was observed with the parameter λ' value: 0.86 in the case of the 5% Pt catalyst on silica gel and 0.54 with the Pt catalyst on active charcoal (in the hydrogenation of 1-hexene over 5% Pt on silica gel, the λ' value was¹ equal to 0.96). Finally, the hydrogenations over the catalyst on the silica gel carrier were in most solvents of zero order in respect to the instant substrate concentration while with the catalyst on active charcoal carrier, the formal order in the exponential kinetic equation was fractional at the given concentration range.

The correlation obtained on the first catalyst may be regarded as successful. When the most deviating solvent, namely, ethyl benzoate, is not taken into account,

TABLE I
Correlation Data in Hydrogenations of 2-Methyl-3-buten-2-ol

No	Solvent	Reaction order		r^0 , ml H ₂ /min g		τ'
		5% Pt on SiO ₂	5% Pt on C	5% Pt on SiO ₂	5% Pt on C	
1	Hexane	0.3	0	97.3	236.2	-0.697
2	Cyclohexane	0.4	0.2	304.9	427.3	-0.158
3	Dibutyl ether	0	0.4	150.0	248.4	-0.468
4	Diethyl ether	0	0	403.2	1 079.8	-0.012
5	Cumene	0	0.3	150.6	127.9	-0.074
6	1-Butanol	0	0.6	243.8	329.0	-0.069
7	Ethylbenzene	0	0.3	103.8	181.7	-0.232
8	1-Propanol	0	0.4	273.3	411.1	+0.021
9	Ethanol	0	0.4	235.8	754.4	-0.155
10	Toluene	0	0.2	69.8	149.5	-0.596
11	Methanol	0.4	0.3	223.3	779.2	0.000
12	Benzene	0.2	0	36.1	136.9	-0.772
13	Ethyl acetate	0	0.3	166.3	523.1	+0.030
14	Tetrahydrofuran	0	0.5	199.3	487.6	-0.291
15	Dioxane	0	0.2	74.6	94.7	-0.338
16	Benzyl alcohol	0	0.4	82.2	80.5	-0.485
17	Diethyl malonate	0	10.7	5.1	48.9	-1.760
18	Ethyl benzoate	0	0.1	82.2	74.3	-1.072
19	1,1,2,2-Tetrachloroethane	0	0	159.6	113.9	-0.232

the correlation coefficient value is increased to 0.94; this is characteristic of a good linear dependence (dashed line on Fig. 1). The cause of the highest deviation is difficult to explain.

The validity of the correlation obtained on the second catalyst is problematic. When the deviating points are not taken into account (*e.g.*, those of cumene, dioxane, benzyl alcohol, and 1,1,2,2-tetrachloroethane; dotted line on Fig. 2), the correlation coefficient is increased to the value of 0.84. The most deviating points lie again on a straight line of practically the same slope. On Fig. 2, there may be observed some other several-membered series of solvents forming a straight line the slope of which differs more or less from that of the straight line of the whole set of solvents. We did not find any relation between the particular members of these series or any relation to the order with respect to the instant concentration of the substrate. Since the analogous¹ correlation was successful in spite of the unequal reaction orders in respect to the instant substrate concentration, the higher variance observed on the 5% Pt on charcoal catalyst must be due to some other effects.

Of interest is also the sensitivity of hydrogenations (expressed by the parameter λ') in respect to the parameter τ' , characteristic of the particular solvent. In the case of the same type of the catalyst, λ' depends on the structure of the substrate (1-hexene,

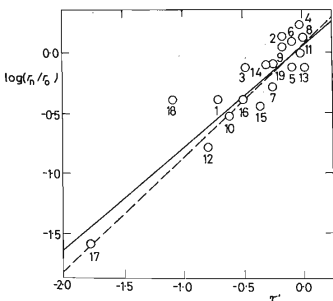


FIG. 1

Correlation of Relative Rates in Hydrogenations of 2-Methyl-3-buten-2-ol over the 5% Pt on Silica Gel Catalyst with τ' Constants

For the numbering of solvents see Table I. Full line: all points were taken into consideration. Dotted line: except for the point No 18.

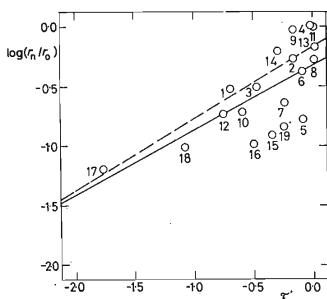


FIG. 2

Correlation of Relative Rates in Hydrogenations of 2-Methyl-3-buten-2-ol over the 5% Pt on Active Charcoal Catalyst with τ' Constants

For the numbering of solvents see Table I. Full line: all points were taken into consideration. Dotted line: points No 5, 15, 16, and 19 were not taken into consideration.

$\lambda' = 0.96$; 2-methyl-3-buten-2-ol, $\lambda' = 0.86$). When the same substrate is used, λ' depends on the type of the catalyst (5% Pt on silica gel, $\lambda' = 0.86$; 5% Pt on active charcoal, $\lambda' = 0.54$). The latter value was calculated from a set of data of a considerable wide variance but, notwithstanding, this observation appears of a great importance. As shown by correlations of the influence of the olefinic structure on the reactivity in hydrogenations over platinum catalysts in ethanol by means of the Taft equation^{4,5}, there is no appreciable dependence of the carrier character on the sensitivity of the particular series of substrates towards polar or sterical effects of substituents at the double bond. On the other hand, the sensitivity of hydrogenations of aromatic nitro compounds towards polar effects has been observed by Růžička and Šantrochová⁶ to increase with the increasing surface of the catalyst; this finding was ascribed to the distribution of platinum over the surface of the carrier. Because of the lack of some additional data, there is hardly possible to draw conclusions from the present results.

It has been shown in the present paper that the τ' constants are valid not only in hydrogenations of the alkyl-substituted double bonds but also in hydrogenations of olefins, the α -carbon atom (in respect to the double bond) of which is substituted by a hydroxylic function. Moreover, the τ' constants are valid in hydrogenations on the same type of the catalyst as in the standardizing measurements. On the other hand, when another type of the catalyst carrier is used, the applicability of the τ' constants is somewhat limited. The nature of the catalyst or of the catalyst carrier is thus more important than the character of the double bond substituents. Investigations on generalisations of the present results are in progress.

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