

# THE EFFECT OF SOLVENTS ON THE CATALYTIC HYDROGENATION OF *p*-SUBSTITUTED NITROBENZENES

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Using platinum coated (5%) silica gel as catalyst, hydrogenation of *p*-substituted nitrobenzenes in seven solvents under the normal conditions has been studied. The effects of the solvents on the rate constants and on the relative adsorption constants of the hydrogenated substrates were investigated.

The present paper is a sequel to the preceding papers<sup>1-7</sup> on the effect of solvents on the courses of catalytic hydrogenations. These have shown that the effects of a solvent on the rate constant and on the adsorption constant of a substituted ethylene can be characterized by two parameters,  $\tau'$  and  $\varphi$ . However, the linear correlations

$$\log k_n/k_o = \lambda' \tau', \quad (1)$$

$$\log (K_i/K_j)_n / (K_i/K_j)_o = \gamma \varphi \quad (2)$$

gave satisfactory results only with structurally similar compounds, *e.g.* unsaturated alcohols. In an attempt to draw some general rules from our findings we now studied hydrogenation of *p*-substituted nitrobenzenes, *i.e.* compounds having a different functional group.

Although hydrogenation of aromatic nitro compounds has been the subject of a number of papers, the effects of solvents on its course were never quantitated even with structurally similar solvents, such as a series of aliphatic alcohols<sup>8</sup>, which testifies to the complexity of the problem. On the other hand it was found<sup>9</sup> that the effect of structure of substituted nitrobenzenes on the rate of their catalytic hydrogenation in certain solvents could be described by the Hammett equation.

The objective of the present paper was to ascertain whether the effects of solvents on the rate constants and on the relative adsorption coefficients of aromatic nitro-compounds can be described by equations analogous to those used earlier<sup>1-5</sup> with the olefinic substrates.

## EXPERIMENTAL

*Chemicals.* The catalyst, Pt (5%) on silica gel<sup>10</sup>, was prepared as previously described<sup>1</sup>. The fraction used had a grain size  $< 0.063$  mm. The solvents employed were cyclohexane, di-

ethyl ether, toluene, methanol, benzene, ethyl acetate and 1,4-dioxan; they were purified as described in the preceding paper<sup>1</sup>. All the solvents, distilled before use, appeared chromatographically pure. Commercial electrolytic hydrogen (Technoplyn, Pardubice) was used directly. The substrates were *p*-nitroacetophenone, *p*-nitroaniline (laboratory stores), *p*-nitrochlorobenzene, *p*-nitrotoluene (Spolek pro chemickou a hutní výrobu, Ústí nad Labem), nitrobenzene (VCHZ, Pardubice) and *p*-nitroanisole (Farbwerke Meister Lucius and Brüning, Hoechst a.M.). The nitrobenzene was purified by vacuum distillation, the other substrates were crystallized three times with an addition of activated carbon. *p*-Nitrotoluene, *p*-nitrochlorobenzene and *p*-nitroaniline were crystallized from ethanol, *p*-nitroacetophenone from acetone, and *p*-nitroanisole from diethyl ether. All the compounds had the tabulated melting points and were chromatographically pure.

*Apparatus and methods.* The apparatus and methodology were described previously<sup>1-3</sup>. Hydrogenation experiments were carried out in a stirred reactor at 20°C and an atmospheric pressure of hydrogen. The reactor was charged with the catalyst (0.08–0.5 g) and a solvent (5–20 ml). Following activation of the catalyst under stirring in the hydrogen atmosphere the remaining 20–5 ml of the solvent, containing as solute an adequate quantity of the substrate ( $5 \cdot 10^{-3}$  to  $10^{-2}$  mol), was added. Nitrobenzene, being a liquid substrate, was brought in directly, without a solvent<sup>1</sup>. Using a gasometric burette the uptake of hydrogen with time was measured and after every consumption of 150 ml of hydrogen 0.1 ml samples were withdrawn to be analysed chromatographically.

*Analytical methods.* The analyses were performed in a gas chromatograph Chrom-2 with a flame-ionization detector in a range of 150–220°C. Two glass columns of I.D. 2.5 mm and length 2.5 m were used. One was filled, by loose pouring, with Chromaton N-AW coated with silicon elastomer SE-31 (10%), the other was packed in the same way with Chromaton NAW-HMDS coated with Apiezon L (15%) + NaOH (3%).

In evaluating the chromatograms from competitive hydrogenations of *p*-derivatives of nitrobenzene the sum of areas of triangles approximating the peaks of a nitro compound and the corresponding amino compound was regarded as 100%. From the ratio of these areas, corresponding to a nitro compound and an amino compound with the same substituent, the percentual contents of the two components were calculated. This way of evaluating competitive hydrogenation of two nitro compounds can be considered satisfactory since with either pair of derivatives (nitro and amino) the difference between the response of a nitro derivative and that of the amino derivative can be expected to be the same.

## RESULTS AND DISCUSSION

The kinetic measurements refer to conditions under which the reaction rate was not affected by transport of mass<sup>1,3</sup>. With a catalyst amount of 0.08 g–0.1 g, in the starting concentration range  $5 \cdot 10^{-3}$  to  $10^{-2}$  mol of nitrobenzene in 25 ml of a solvent, the initial hydrogenation rate was independent of the substrate concentration. With substrates hydrogenated at a rate of 1 ml of hydrogen per min in the presence of 0.1 g of the catalyst the quantity of the catalyst was raised to 0.5 g.

In the course of the reaction the activity of the catalyst decreased. This decrease, evidently due to the reaction water, was especially marked in non-polar solvents, where even agglutination of the catalyst particles occurred. A similar phenomenon had been observed before<sup>7</sup>. Attempts to adsorb the reaction water by additions

of a molecular sieve to the reaction medium were not successful. To compare the reactivities we therefore used the initial reaction rates, determined as slopes of the tangents to the time courses.

Hydrogenation of *p*-nitroaniline and *p*-nitroacetophenone in cyclohexane was not studied since the solubilities of these substrates in this solvent are very low.

*The effect of solvents on the rate constants.* The measured reaction rates, which in the case of zero order to the reacting substrate equal the rate constants, are given in Table I. The rate constants are recalculated<sup>1-3</sup> to a hydrogen pressure of 98.07 kPa (1 at) by taking corrections for the barometric pressure and solvent vapour tension, assuming the reaction is first order in respect to the partial pressure of hydrogen.

TABLE I  
Survey of Parameters Determined from Rate Data

Substrate or parameter	Cyclo- hexane 2 <sup>a</sup>	Diethyl ether 4	Toluene 10	Methanol 11	Benzene 12	Ethyl acetate 13	1,4- Dioxan 15
Rate constants							
<i>p</i> -Nitroacetophenone	—	147.5	124.0	191.0	166.0	55.5	36.2
<i>p</i> -Nitrochloro- benzene	90.0	49.0	51.5	170.0	62.0	18.5	12.5
Nitrobenzene	157.0	120.0	80.1	155.0	110.0	26.8	35.4
<i>p</i> -Nitrotoluene	90.0	49.2	40.1	75.6	55.5	10.5	6.2
<i>p</i> -Nitroanisole	52.6	19.8	30.0	58.0	53.0	9.0	3.1
<i>p</i> -Nitroaniline	—	12.3	26.1	26.2	20.0	5.7	2.6
Correlation of rate constants by the Hammett equation							
$\rho$	0.49	0.94	0.59	0.84	0.74	0.86	11.09
$h$	-0.22	-0.34	-0.16	-0.17	-0.19	-0.18	-0.48
$r_{x,y}$	0.52 <sup>b</sup>	0.86	0.88	0.96	0.90	0.92	0.84
Parameters $\tau'_N$ and $\bar{\tau}'_N$							
$\tau'_N$	0.01	-0.11	-0.26	0.00	-0.15	-0.77	-0.65
$\bar{\tau}'_N$	-0.08	-0.35	-0.25	0.00	-0.16	-0.77	-1.04

<sup>a</sup> Numbering of solvents as in the preceding papers<sup>1-7</sup>. <sup>b</sup> Critical value of the correlation coefficient on a 95% significance level  $r_{x,y}^{\text{crit}} = 0.95$ , in other cases 0.81.

The rate constants in each solvent were correlated by the Hammett equation<sup>11</sup>:

$$\log(k/k_0) = \rho\sigma + h. \quad (3)$$

The values of the parameter  $\sigma$  were taken from Exner's paper<sup>12</sup>. Regression analysis of the measured data gave the values of  $\rho$  and the absolute term  $h$ . These values along with those of the correlation coefficients are listed in a lower part of Table I.

The measured rate constants proved correlable by the Hammett equation, except the values for cyclohexane, where the correlation coefficient lay below its critical value. In cyclohexane, however, hydrogenation of *p*-nitroaniline and *p*-nitroacetophenone have not been performed, owing to low solubilities, which circumstance considerably narrows the scale of  $\sigma$  parameters. Linear regression for all solvents gave graphs with non-zero values of the absolute term  $h$ . The values of the absolute term for the individual solvents are different, which suggests that the error in measurement is not the only factor affecting the absolute term. A non-zero value of the absolute term might be due to substituent-catalyst interactions, which would naturally depend on the solvent used. However, the experimental evidence hitherto gathered does not allow of any interpretation of the absolute term.

Correlation of the effects of solvents on the rate constants by equation (1), using the parameter  $\tau'$ , defined<sup>1</sup> in hydrogenation of cyclohexene, was not successful, which proves that these parameters are not valid for hydrogenation of a different functional group. For this reason the parameters  $\tau'_N$  in hydrogenation of nitrobenzene, as the definition substrate, were defined analogously<sup>1</sup>. The correlation was based on methanol again<sup>1</sup>. There was further introduced a parameter  $\bar{\tau}'_N$ , defined as arithmetic average of similarly defined parameters  $\tau'_{Ni}$ , where the subscript  $i$  designates the  $i$ -th substrate from the series employed excepting nitrobenzene. The parameter  $\bar{\tau}'_N$  involves the effects of all the compounds used and might, therefore, be more satisfactory in the correlation of other compounds, not tried as yet, than the parameter  $\tau'_N$ . From Table I it is seen that with the exception of 1,4-dioxan there are no great differences between the values of  $\tau'_N$  and  $\bar{\tau}'_N$ .

The regression analysis was performed using the parameter  $\tau'_N$  and equation (1). The data for nitrobenzene also show the interdependence of  $\tau'_N$  and  $\bar{\tau}'_N$ . The results are given in Table II. The value of  $b$  represents the value of the absolute term on the right-hand side of equation (1). It appears that the quantity  $\bar{\tau}'_N$  as defined is a solvent parameter that is in a very good agreement with the measured values of the rate constants.

The interdependence of  $\tau'$  and  $\bar{\tau}'_N$  has been found to be a non-linear one, which proves again that these parameters are not applicable to substrates that are structurally different, so that they are not independent of their structures. Their utility consists mainly in their applicability to hydrogenation of structurally similar substances, but their generalization is not possible.

The effect of solvent on selectivity and on the relative adsorption coefficients. Using the method of concurrent (competitive) reactions<sup>13</sup> we determined the values of hydrogenation selectivity in a number of solvents and from these and the rate constants calculated the relative adsorption coefficients. The values of selectivity were determined as slopes of lines in coordinates  $\log C_A$  and  $\log C_B$ .

Nitroacetophenone was not used for a competitive hydrogenation since it had been found to form Schiff bases with the arising amino compounds. In the hydrogenation of *p*-nitrochlorobenzene chlorine was released in the form of hydrogen chloride from the nitro compounds. The reaction mixture contained aniline as the hydrogenation product of the formed nitrobenzene. The amount of aniline at the end of the reaction did not exceed a 5% conversion of *p*-nitrochlorobenzene to nitrobenzene and was, therefore, neglected in the competitive hydrogenation with *p*-nitrochlorobenzene. Pairs of substrates for competitive hydrogenation were so selected, taking into account the facility of analysis, that the hydrogenation did not proceed selectively. The pairs hydrogenated in all solvents were: nitrobenzen-*p*-nitrochlorobenzene, *p*-nitrochlorobenzene-*p*-nitrotoluene, *p*-nitrotoluene-*p*-nitroanisole, *p*-nitroanisole-*p*-nitroaniline and nitrobenzene-*p*-nitroanisole. From the measured data we calculated the values of selectivity related to nitrobenzene (Table III).

The calculation, based on the assumption that the substrates interact in no way either in adsorption or in the reaction, has been justified by comparing the measured value of  $S_{NAS,NB}$  (Table III) designated  $(S_{NAS,NB})_m$  with the value obtained by the calculation. With the given solvents the only significant aberration between the measured values and the calculated ones (*i.e.* those related to nitrobenzene) was observed in the case of methanol.

From the selectivities in Table III and the rate constants in Table I we calculated

TABLE II  
Correlation of Rate Constants with Parameters  $\bar{r}'_N$  of the Solvents

Substrate	$\lambda'$	$b$	$r_{x,y}$
<i>p</i> -Nitroacetophenone	0.65	0.03	0.98 <sup>a</sup>
<i>p</i> -Nitrochlorobenzene	0.82	-0.20	0.95
Nitrobenzene	0.75	0.002	0.91
<i>p</i> -Nitrotoluene	1.10	0.08	0.98
<i>p</i> -Nitroanisole	1.23	0.05	0.98
<i>p</i> -Nitroaniline	0.97	0.07	0.97 <sup>a</sup>

<sup>a</sup> Critical value of the correlation coefficient on a 95% significance level  $r_{x,y}^{crit} = 0.75$ , in other cases 0.71.

the adsorption coefficients of the *p*-derivatives of nitrobenzene related to nitrobenzene. These are given in a lower part of Table III, along with the results of correlation of selectivities and the relative adsorption coefficients by the Hammett equation (analogue to Eq. (3)). It appears that these correlations were satisfactory in the polar solvents only. The correlation of the rate constant was successful in all solvents except cyclohexane. As there is no apparent reason why correlability of the selectivities and of the relative adsorption coefficients should be possible in polar solvents only we believe that selectivity, as well as the relative adsorption coefficients,

TABLE III  
Survey of Parameters Determined from Rate and Adsorption Data

Parameter	Cyclohexane 2	Diethyl ether 4	Toluene 10	Methanol 11	Benzene 12	Ethyl acetate 13	1,4-Dioxan 15 <sup>a</sup>
Selectivities							
$S_{NCB,NB}$	0.67	1.05	0.53	2.50	0.53	1.10	0.95
$S_{NTO,NB}$	0.16	0.15	0.13	0.40	0.10	0.19	0.15
$S_{NAN,NB}$	—	0.04	0.32	0.10	0.35	0.05	0.04
$S_{NAS,NB}$	0.16	0.10	0.13	0.25	0.07	0.11	0.07
$(S_{NAS,NB})_m$	0.15	0.10	0.09	0.13	0.07	0.10	0.08
Relative adsorption coefficients							
$K_{NCB,NB}$	1.16	3.40	0.83	2.28	0.94	1.56	2.76
$K_{NTO,NB}$	0.27	0.48	0.26	0.82	0.21	0.47	0.88
$K_{NAN,NB}$	—	0.43	0.90	0.60	2.00	0.21	0.54
$K_{NAS,NB}$	0.46	0.57	0.34	0.76	0.17	0.31	0.81
Correlation of selectivities by the Hammett equation							
$\rho_1$	1.64	1.73	0.44	1.61	0.43	1.71	1.77
$h_1$	-0.37	-0.35	-0.44	-0.06	-0.50	-0.31	-0.39
$r_{x,y^1}$	0.68 <sup>b</sup>	0.91	0.36	0.97	0.29	0.93	0.90
Correlation of relative adsorption coefficient by the Hammett equation							
$\rho_2$	1.13	0.94	0.04	0.60	-0.24	1.04	0.72
$h_2$	0.16	0.08	-0.23	0.09	-0.27	-0.09	0.12
$r_{x,y^2}$	0.78 <sup>b</sup>	0.83	0.06	0.88	0.17	0.95	0.90
$\rho + \rho_2$	1.62	1.88	0.63	1.44	0.50	1.90	1.81

<sup>a</sup> Numbering of solvents as in the preceding papers<sup>1-7</sup>. <sup>b</sup> Critical value of the correlation coefficient on a 95% significance level  $r_{x,y}^{crit} = 0.95$  in other cases 0.88.

may be affected by the reaction water. In studying a competitive reaction the conversion has to be allowed to reach a higher stage, when the quantity of water may be such as to influence considerably the ratio of the two reaction rates. The activity of a catalyst functioning in a non-polar medium may be changed also.

The similarity of the slopes  $\rho_1$  in Table III in the case of solvents where correlation of selectivities by the Hammett equation gave the highest correlation coefficient, leads to a noteworthy finding. Since

$$\rho_1 = \rho + \rho_2 \quad (4)$$

(Table III), a solvent sensitizing reactivity to a change in substituent must suppress sensitivity of adsorptivity to this change. This in another example of mutual compensation of the kinetic and the adsorption terms<sup>5,7,14</sup>.

Like in a previous paper<sup>3</sup>, the parameter  $\varphi_N$  for the solvent was defined by equation (2), choosing substitution  $\gamma = 1$  for the pair *p*-nitrochlorobenzene–nitrobenzene and  $\varphi_N = 0$  for methanol. Correlation of the relative adsorption coefficients with the parameter  $\varphi_N$  by equation (2) was not successful, with two exceptions ( $K_{NTO,NB}$ ,  $K_{NAS,NB}$ ). The reasons were probably similar to those mentioned in correlation of selectivities and the relative adsorption coefficients by the Hammett equation. This was good in polar solvents, but failed in non-polar solvents, which was evidently due to the effect of the reaction water. For this reason it is hardly possible to find an equation describing satisfactorily the dependence of the relative adsorption coefficients on a single parameter of the solvent in hydrogenation of aromatic nitro compounds in a series of solvents very different in character.

#### LIST OF SYMBOLS

$b$	absolute term in correlation of rate constants by equation (1)
$C_A$	instantaneous concentration of compound A (mol/l)
$h$	absolute term in correlation of rate constants by the Hammett equation (3)
$h_1$	absolute term in correlation of the selectivities by the Hammett equation (3)
$h_2$	absolute term in correlation of the relative adsorption coefficients by the Hammett equation (3)
NCB	<i>p</i> -nitrochlorobenzene
NB	nitrobenzene
NAS	<i>p</i> -nitroanisole
NAN	<i>p</i> -nitroaniline
NTO	<i>p</i> -nitrotoluene
N	general designation of a nitro compound
$k$	rate constant (ml of hydrogen/min g <sub>cat</sub> )
$K_i/K_j$	relative adsorption coefficient
$r_{x,y}$	correlation coefficient
$r_{x,y}^{crit.}$	critical value of the correlation coefficient
$S$	selectivity

$\gamma$	parameter characterizing sensitivity of relative adsorptivity to a change in solvent (Eq. (2))
$\lambda'$	parameter characterizing sensitivity of the rate constant to a change in solvent (Eq. (1))
$\varrho$	parameter characterizing sensitivity of the rate constant to a change in the polar effect of the substituent
$\varrho_1$	parameter characterizing sensitivity of selectivity to a change in the polar effect of the substituent
$\varrho_2$	parameter characterizing sensitivity of the relative adsorptivity to a change in the polar effect of the substituent
$\sigma$	parameter characterizing the polar effect of a substituent
$\tau'$	parameter characterizing the effect of solvent on the rate constant (Eq. (1))
$\bar{\tau}'_N$	the average value of $\tau'_N$
$\varphi$	parameter characterizing the effect of solvent on the relative adsorptivity (Eq. (2))

## Subscripts

i, j	general designation of substrates
m	measured value
n	general designation of a solvent
o	standard solvent (methanol) or standard substrate (nitrobenzene)

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