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Electronic Substituent Effects on the Adsorption and Hydrogenation of the Olefinic Bond on Palladium

A. P. G. KIEBOOM AND H. VAN BEKKUM

Laboratory of Organic Chemistry, Delft University of Technology, Julianalaan 136, Delft, The Netherlands

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A kinetic study of substituent effects in the liquid-phase hydrogenation of the olefinic bond has been made using palladium on carbon as the catalyst. Individual and competitive hydrogenations have been carried out with 2-aryl-3-methyl-2-butenes (**1**) and substituted 3,4-dihydro-1,2-dimethylnaphthalenes (**2**) in basic, neutral, and acid media.

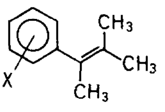
Electronic substituent effects on the rate of hydrogenation are found to be rather small. The adsorbed state in the basic medium is not seriously influenced by the substituents. More substantial substituent effects on the strength of adsorption are observed in neutral and acid media. Coadsorption of the dimethylamino and ethoxycarbonyl group on palladium takes place.

It is concluded that the electronic nature of the transition state of hydrogenation on palladium is quite similar to that of the initial state. Higher π-electron density at the olefinic bond favors the strength of adsorption; this is consistent with a π-bonded adsorbed olefin.

INTRODUCTION

The mechanism of the heterogeneously catalyzed hydrogenation of the olefinic bond has been studied very intensively during the last forty years (*1*). However, the influence of electronic substituent effects on the rate of hydrogenation has been studied (*2-4*) only recently with a series of 1-substituted propenes and 2-methylpropenes. No clear picture was obtained from this work because the rate data could not be correlated by means of Taft's polar free energy equation.

In order to diminish the serious interference of the substituents with the reaction center, which was a troublesome factor in the above-mentioned series, we have studied the palladium-catalyzed hydrogenation of substituted 2-aryl-3-methyl-2-butenes (**1**) and 3,4-dihydro-1,2-dimethylnaphthalenes (**2**).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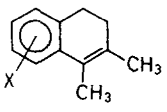
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The aromatic ring, which is not reduced, serves (i) to separate the substituent from the reaction center, *i.e.*, to avoid the influence of direct steric effects, and (ii) to pass on, via its π-electrons, the polar effects of the substituents to the reaction center.

The influence of substituents on both the rate of reaction and the strength of adsorption of **1** and **2** has been studied over palladium on carbon in basic (0.5 *M* potassium hydroxide in ethanol), neutral (*n*-heptane), and acid media (acetic and trifluoroacetic acid) at 30°C and atmospheric hydrogen pressure.

EXPERIMENTAL

The mass spectra were measured with a Varian MAT SM-1 and the PMR spectra with a Varian A-60 and T-60 spectrometer. Gas-chromatographic analyses were performed with SE-30 or PEG-1000 as the stationary phase. Structures of new compounds were confirmed by elemental analysis and PMR spectra.

Materials

Ethanol (99.5%), acetic acid (99.8%), and trifluoroacetic acid (99.5%) were Baker Analyzed Reagents. *n*-Heptane, treated with concentrated sulfuric acid and water, was distilled and dried with molecular sieves. Palladium (10% on carbon) was purchased from Drijfhout N.V., Amsterdam.

2-(3-*t*-Butylphenyl)-3-methyl-2-butanol (bp 125–130°C/8 mm, n_D^{25} 1.5028), 2-(4-bromophenyl)-3-methyl-2-butanol (bp 140°C/10 mm, n_D^{25} 1.5473), and 2-(3-*N*,*N*-dimethylaminophenyl)-3-methyl-2-butanol (bp 96–97°C/0.2 mm; methiodide, mp 201.5–202°C) were prepared as described earlier for a number of other 2-aryl-3-methyl-2-butanols (*5*, *6*).

2-Aryl-3-methyl-2-butenes (1). The 2-aryl-3-methyl-2-butanols were dehydrated with sulfuric acid in acetic acid (*5*). The crude alkenes were purified by chromatography on silica gel impregnated with silver nitrate (30%) using hexane, carbon tetrachloride, or benzene/ether (9:1) as the eluent. Compounds **1**, X = 3- and 4-hydroxy were obtained in a one-step procedure from the corresponding acetophenones and a large excess of isopropylmagnesium bromide; **1**, X = 3- and 4-carboxy were prepared from **1**, X = 3- and 4-bromo through the Grignard compound and carbon dioxide. The ethyl esters were prepared in the usual way.

3,4-Dihydro-1,2-dimethylnaphthalenes (2). Compounds **2**, X = 5- and 6-methoxy, 7-*t*-butyl, and 6-acetamido were obtained from the corresponding 2-methyl-1-tetralones (*7*) and methylmagnesium chloride, followed by dehydration of the crude alcohols with formic acid as described for 3,4-dihydro-1,2-dimethylnaphthalene (*8*).

The physical constants of **1** and **2** are summarized in Table 1.

TABLE 1

2-Aryl-3-methyl-2-butenes (**1**) and 3,4-Dihydro-1,2-dimethylnaphthalenes (**2**)

Compound	bp (°C/mm)	n_D^{25}
1		
H[a]	84–85/17	1.5203
3-CH_3	97–98/15	1.5189
4-CH_3	99–100/15	1.5198
4-C_2H_5	112–113/15	1.5173
4-isoC_3H_7	121/15	1.5134
3-*t*-C_4H_9	70/1.2	1.5092
4-*t*-C_4H_9	131/15	1.5140
3-OH	86–92/0.8	1.5474
4-OH[b]	86–87/0.6	1.5486
3-OCH_3	121–122/16	1.5280
4-OCH_3[c]	116–117/14	1.5298
3-$N(CH_3)_2$	74/0.3	1.5507
4-$N(CH_3)_2$	76–77/0.4	1.5590
3-CF_3	86–87/16	1.4645
3-COOH	mp 100–102	
4-COOH[d]	mp 101–103	
3-$COOC_2H_5$	85/0.6	1.5203
4-$COOC_2H_5$	89–90/0.6	1.5261
2		
H[e]	123/15	1.5747
5-OCH_3	96/1	1.5786
6-OCH_3	102/0.7	1.5780
6-$NHCOCH_3$	mp 108–110	
7-*t*-C_4H_9	101–103/0.9	1.5421

[a] Lit. (*9*), bp 191–192°C, n_D^{25} 1.5202. [b] Lit. (*9*), bp 81–84°C/0.5 mm. [c] Lit. (*9*), bp 234°C, n_D^{16} 1.5304. [d] Lit. (*9*), mp 101.5–102.5°C. [e] Lit. (*8*), bp 101°C/1.5 mm.

Apparatus and Procedure

The kinetic experiments were carried out as described earlier (*6*, *10*). The reactant (1 mmol) in the solvent (5 ml) was hydrogenated over 10% palladium on carbon (10–500 mg) at 30.0 ± 0.1°C and atmospheric pressure (760 ± 20 mm). Formulations were chosen to prevent diffusion limitation.

Competitive hydrogenations were carried out with mixtures of two alkenes (0.5 mmole of each) in the solvent (5 ml) under the same conditions. Samples were withdrawn from the reaction mixture and analyzed by glc. The percentage of conversion of **2**, X = 6-acetamido, which could not be determined by glc, was calculated from the conversion of the other reactant and the total hydrogen uptake.

Reduction of the aromatic ring was not observed. No hydrolysis of the ethoxycarbonyl group occurred in 0.5 *M* potassium hydroxide in ethanol. Trifluoroacetylation of the alkenes was observed in trifluoroacetic acid, *e.g.*, the formation of 2-methyl-2-trifluoroacetyl-3-(3-trifluoromethylphenyl)butane (bp 80–82°C/9 mm) from 3-methyl-2-(3-trifluoromethylphenyl)-2-butene. This reaction was found to be very fast for alkenes with electron-donating substituents on the aromatic ring. Therefore only a few 2-aryl-3-methyl-2-butenes with electron-withdrawing substituents could be measured in this medium.

KINETICS

Individual Hydrogenations

Hydrogenations were found to be first order with respect to catalyst and were assumed to be first order with respect to the hydrogen pressure in order to correct the reaction rate for deviations from atmospheric pressure. So we may write for a compound A, using Langmuir kinetics,

$$-\frac{dn_{\mathrm{A}}}{dt} = k_{\mathrm{A}}\Theta_{\mathrm{A}}wp = \frac{k_{\mathrm{A}}b_{\mathrm{A}}C_{\mathrm{A}}wp}{1 + b_{\mathrm{A}}C_{\mathrm{A}} + \Sigma bC} \qquad (1)$$

in which n_{A} is the number of moles of A, C_{A} is the concentration of A in solution, k_{A} is the reaction rate constant, Θ_{A} is the fraction of the active catalyst surface covered by A, w is the amount of catalyst, p is the hydrogen pressure (corrected for the vapor pressure of the solvent), and ΣbC is the sum of the contributions of the solvent, the hydrogenated product, and the hydrogen to the denominator of the Langmuir expression.

In *n*-heptane and in acetic acid the rate of reaction was found to be independent of the concentration of the reactant A, *i.e.*, $b_{\mathrm{A}}C_{\mathrm{A}} \gg 1 + \Sigma bC$. Hence, we may write

$$-\frac{dn_{\mathrm{A}}}{dt} = k_{\mathrm{A}}wp. \qquad (2)$$

The reaction rate was determined by measuring the amount of hydrogen dV (ml at p' atm and T °K) consumed during time dt (min), in which p' denotes the pressure of the hydrogen—free from solvent vapor—in the gas cylinder. Since

$$-dn_{\mathrm{A}} = 1.013 \times 10^5 \times p' \times 10^{-6} \times dV/RT \qquad (3)$$

and $R = 8.31\ J\ \mathrm{mol}^{-1}\ K^{-1}$, Eq. (2) becomes

$$\frac{1.013 \times 10^5 \times p' \times 10^{-6} \times dV}{8.31 \times T \times 60 \times dt} = k_{\mathrm{A}}wp \qquad (4)$$

or, in the integrated form,

$$k_{\mathrm{A}} = 203 \times 10^{-6} \times \frac{p'V}{pTwt}, \qquad (5)$$

in which k_{A} is the pseudo-zero order reaction rate constant (mol s^{-1} g catalyst^{-1}) at atmospheric pressure.

In 0.5 M potassium hydroxide in ethanol the order with respect to the reactant varied from 0.2–0.7, *i.e.*, $b_{\mathrm{A}}C_{\mathrm{A}} \geqslant 1 + \Sigma bC$. The decreasing rate of hydrogenation is not caused by coadsorption on the catalyst of the product formed, because addition of toluene did not affect the reaction rate. Therefore, we conclude that the basic medium is responsible for the relatively weak adsorption of the organic reactant. Since the order in reactant is rather low (~ 0.2–0.3) for most of the reactants in the (initial) concentration region used and the initial concentration was taken constant (0.2 mol/l) for all the experiments, the k values in the basic medium were derived from Eq. (5) in which V/t has been replaced by $(dV/dt)_{t=0}$, *i.e.*, the rate of the hydrogen uptake at time zero. It may be noted, that these k values will be affected in a measure by the Langmuir adsorption term and are not quite the true reaction rate constants.

Competitive Hydrogenations

For a competitive reaction of A and B we may write Eq. (1) for both A and B, in which the denominator has been enlarged by the term $b_{\mathrm{B}}C_{\mathrm{B}}$. Dividing the two equations gives (*11*)

$$\frac{dn_{\mathrm{A}}}{dn_{\mathrm{B}}} = \frac{dC_{\mathrm{A}}}{dC_{\mathrm{B}}} = \frac{k_{\mathrm{A}}b_{\mathrm{A}}C_{\mathrm{A}}}{k_{\mathrm{B}}b_{\mathrm{B}}C_{\mathrm{B}}} \qquad (6)$$

or, in the integrated form,

$$\log\frac{C_{\mathrm{A}}}{C_{\mathrm{A}}^0} = K_{\mathrm{A,B}}\frac{k_{\mathrm{A}}}{k_{\mathrm{B}}}\log\frac{C_{\mathrm{B}}}{C_{\mathrm{B}}^0}, \qquad (7)$$

in which C_{A}^0 and C_{B}^0 are the concentrations of A and B in solution at time zero and $K_{\mathrm{A,B}}$ is the adsorption equilibrium constant of A with respect to B, *i.e.*, b_A/b_B. Thus, $K_{A,B}$ can be calculated from the slope of the plot of $\log(C_A/C_A^0)$ vs. $\log(C_B/C_B^0)$, and the reaction rate constants k_A and k_B as derived from the individual hydrogenations of A and B. The results for a number of competitive experiments between some 2-aryl-3-methyl-2-butenes and 2-(4-ethylphenyl)-3-methyl-2-butene are shown in Fig. 1.

Although the linear correlations obtained are consistent with the Langmuir picture of adsorption for these compounds, any errors incidental in the use of this model may not be excluded *a priori*. However, both the application of exactly the same reaction conditions for all compounds and the use of the relative rather than the absolute k and b values for the elucidation of substituent effects will eliminate these possible errors in some degree. In particular, since a great variety of substituents is employed, it is unlikely that the general picture of steric and electronic substituent effects will be affected to a large extent by some error in the use of Langmuir kinetics.

RESULTS AND DISCUSSION

The results of the hydrogenation of 2-aryl-3-methyl-2-butenes (**1**) and substituted 3,4-dihydro-1,2-dimethylnaphthalenes (**2**) over palladium are presented in Table 2. The adsorption equilibrium constants $K_{X,H}$ and the selectivity factors $S_{X,H}$ of these compounds with respect to 3-methyl-2-phenyl-2-butene (**1**, X = H) are given by

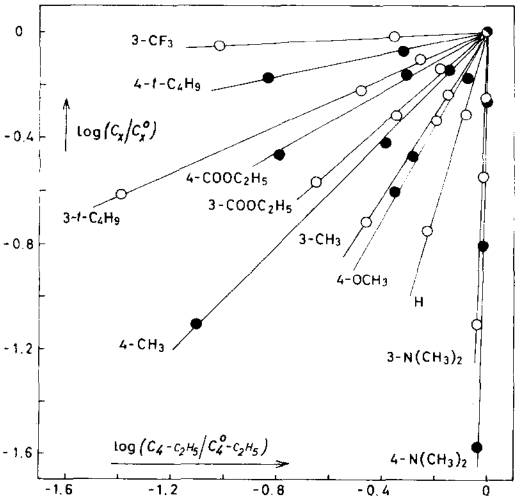
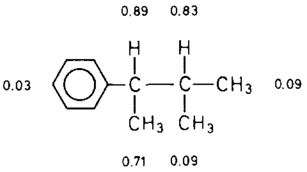


FIG. 1. Plots for the competitive hydrogenations of some 2-aryl-3-methyl-2-butenes (**1**, X) and 2-(4-ethylphenyl)-3-methyl-2-butene (**1**,4-C_2H_5) over palladium in *n*-heptane at 30.0°C and 1 atm.

$$K_{X,H} = \frac{b_X}{b_H} \text{ and } S_{X,H} = \frac{b_X k}{b_H k_H}, \qquad (8)$$

respectively, in which X refers to X-substituted **1** or **2**, and H to **1**, X = H. The selectivity factors $S_{X,H}$ were obtained from competitive hydrogenation experiments using Eq. (7). Subsequently, the adsorption equilibrium constants $K_{X,H}$ were calculated from Eq. (8) using the reaction rate constants k_X and k_H obtained from individual hydrogenations with the aid of Eq. (5). The polar character of the substituents is expressed by their Hammett σ^n values (*12–14*).

Deuteration of 3-methyl-2-phenyl-2-butene over palladium in ethanol-*d* at 30°C and 1 atm gave 3-methyl-2-phenylbutane with the following isotopic content (MS and PMR):



Substituent Effects on the Adsorbed State

Steric effects. In order to get a clear picture of the influence of electronic effects on the strength of adsorption, one has to rule out any steric factors. The series with H, CH_3 (or C_2H_5), and t-C_4H_9 as the substituents would seem useful to estimate the influence of the steric factors in the case of the other substituents.

In the basic medium the influence of steric factors in the series **1**, X = alkyl on the adsorption proves to be moderate, so that hardly any correction has to be made. In *n*-heptane and acetic acid, however, steric factors are much more pronounced. Substitution at the 3-position has less effect than at the 4-position. It may be

TABLE 2

Hydrogenation of **1** and **2** over Palladium[a]

	0.5 M KOH in ethanol		n-Heptane		$S_{X,H}$				
Reactant	10^6k[b]	$K_{X,H}$	10^6k[b]	$K_{X,H}$	0.5 M KOH in ethanol	n-heptane	AcOH[d]	CF_3COOH[d]	σ^n[c]
1									
H	11.0	1.0	635	1.0	1.0	1.0	1.0	(1.0)[e]	0.00
3-CH_3	9.6		560	0.52		0.46			−0.07
4-CH_3	9.7		570	0.34		0.30			−0.12
4-C_2H_5	9.6	0.68	510	0.37	0.59	0.30	0.25		−0.13
4-isoC_3H_7	9.3		450	0.30		0.21			−0.16
3-t-C_4H_9	2.7	0.61	460	0.18	0.15	0.13	0.09		−0.07
4-t-C_4H_9	2.4		350	0.12		0.067			−0.17
3-OCH_3	14		635	0.58		0.58			0.08
4-OCH_3	18	0.86	830	0.40	1.4	0.52	0.23		−0.10
3-$O^{\ominus}$	7.1								−0.47
4-$O^{\ominus}$	11.5	0.56			0.59				−0.81
3-$N(CH_3)_2$	6		620	8.7		8.5			−0.05
4-$N(CH_3)_2$	13.5	3.5	800	10.8	4.3	13.6	1.3[f]	0.003[f]	−0.3[g]
3-$COOC_2H_5$	3.3		570	0.30		0.27			0.37
4-$COOC_2H_5$	5.5	2.2	700	0.16	1.12	0.18	0.05	0.02	0.46
3-$COO^{\ominus}$	3.6								0.02
4-$COO^{\ominus}$	4.1								0.11
3-CF_3	4.7	0.52	760	0.016	0.22	0.019	0.006	0.01	0.47
2									
H	21	2.0							0.00
5-OCH_3	25	1.9	2100	2.7	4.3	8.8	2.7		0.08
6-OCH_3	29	3.3	2200	3.9	8.5	13.6	4.2		−0.10
7-t-C_4H_9	4								−0.07
6-$NHCOCH_3$	17	2.6			4				0.1
Acetophenone	7.9	68	300	100	49	46			

[a] Temperature 30.0 C; atmospheric H_2 pressure; Pd, 10% on carbon.

[b] Mol s^{-1} g $catalyst^{-1}$.

[c] From refs. (*12–14*).

[d] Reaction rate independent of the substituent.

[e] Estimated value with respect to **1**, X = 4-$COOC_2H_5$.

[f] X = 4-$N^+(CH_3)_2H$ with σ^n = 0.55 (*5*).

[g] Mean value from refs. (*12, 13*).

noted that similar differences in strength of adsorption have been observed for toluene and the xylenes on platinum and rhodium (*15*) and for substituted acetophenones on palladium (*16*). Disturbance of optimal flat adsorption of the π-system by steric repulsion of the substituent with the catalyst surface is clearly a quite general phenomenon.

Electronic effects. The electronic character of a substituent will influence the π-electron density of both the aromatic nucleus and the olefinic bond. Since the contribution of the π-electrons of the aromatic nucleus as such to the adsorption is small—as appears from the weak adsorption of toluene with respect to 2,3-dimethyl-2-butene—we may interpret differences in strength of adsorption by electronic factors in terms of adsorption of the olefinic bond.

We define the trifluoromethyl group as a standard for the interpretation of electronic effects, *i.e.*, being a strongly electron-withdrawing substituent *without* any contribution of its own to the adsorption. Furthermore, the size of the trifluoromethyl group is well defined (Van der Waals radius 2.8 Å) because of its symmetry. Correction for steric factors may be easily achieved by comparison with the methyl (2.1 Å) and *t*-butyl (3.8 Å) groups, providing a minimum and maximum correction factor, respectively.

In 0.5 *M* potassium hydroxide in ethanol the electronic nature of the substituent scarcely influences the adsorption constant of **1**. This follows from the small effect of the trifluoromethyl group. The higher values in this series for the 4-dimethylamino and 4-ethoxycarbonyl groups—which possess opposite electronic effects—will be due to coadsorption of the substituents through their free electron pair and π-electrons, respectively. No significant contribution of this type is observed for both the methoxy group and the phenolate anion.

The strength of adsorption of the trifluoromethyl compound in *n*-heptane is much smaller than that of the corresponding methyl and *t*-butyl compounds. After correction for the small electron-donating character of the 3-alkyl group a Hammett ρ value of about -2 is obtained. According to this picture we would expect about the same strength of adsorption in the case of the equally strong electron-withdrawing ethoxycarbonyl group as the substituent. The much stronger adsorption found (10–20 times stronger than trifluoromethyl) implies weak adsorption of the ethoxycarbonyl group itself, as shown before in the basic medium. In *n*-heptane, the decrease in strength of adsorption of the ethoxycarbonyl compound by the electron-withdrawing effect of the substituent is almost compensated by coadsorption of the ethoxycarbonyl group on the catalyst. The strong adsorption of the dimethylamino compounds in *n*-heptane is caused by coadsorption of the nitrogen. In a strong acid medium like trifluoroacetic acid this coadsorption is completely inhibited by protonation of the dimethylamino group. It may be noted that in *n*-heptane the 4-substituted olefin is more strongly adsorbed than the 3-substituted one, in contrast with other substituents like methyl, *t*-butyl, methoxy, and ethoxycarbonyl. The difference in adsorption of at least 2.1 units is in accordance with the much greater electron-donating power of the dimethylamino group from the 4- than from the 3-position. The result is a higher electron density and a stronger adsorption of the olefinic bond, in accordance with the negative ρ value.

The fact that **2** adsorbs more strongly than **1** will be due to the more favorable flat conformation of the former. About 1 kcal/mole is required for **1** to acquire this conformation, because of steric repulsion of the methyl group and the *ortho* hydrogen atoms of the aromatic nucleus (*5*). The effects of the methoxy substituents in **2** further support the influence of electronic effects on the strength of adsorption. This is in contrast to **1**, X = 3- and 4-methoxy, where the electronic effects are probably obscured by steric interactions of the substituents with the catalyst surface as found for the alkyl groups.

Altogether, the observed substituent effects support the occurrence of a π-complexed olefin species, in which the olefin–palladium donor bond (π-*spd* overlap) is more important than the backbond (π^*-*d* overlap) between palladium and the olefin (*17*). For an eclipsed 1,2-diadsorbed species (σ-bonded) the substituent effects are expected to be just the reverse (*18*, *19*).

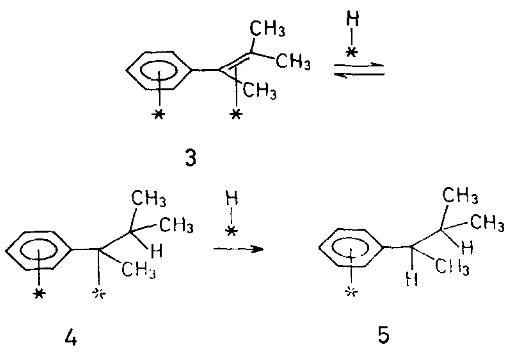
Substituent Effects on the Rate of Hydrogenation

In *n*-heptane, acetic acid, and trifluoroacetic acid the rate of hydrogenation of **1** proves to be independent of the electronic nature of the substituents. Thus, in *n*-heptane, the ρ value of the Hammett relation (*20*) is 0.0 ± 0.1, *i.e.*, the electronic nature of the transition state is quite similar to that of the initial state. The same picture applies to **2**, in which the different electronic character of the methoxy group at the 5- and 6-position with respect to the reaction center has no influence on the reaction rate.

In 0.5 M potassium hydroxide in ethanol somewhat more pronounced effects are observed. However, the rate of reaction is also more governed by retarding steric factors than in n-heptane, which is demonstrated by comparison of 3-, 4-, and 7-t-butyl with the unsubstituted compound. The total picture remains rather irregular, even after correction for steric influences. Since a highly scattered Hammett relation ($\rho \approx -0.3$) is obtained, we may tentatively infer a slightly positive transition state with respect to the initial state in this medium. A similar trend is observed for **2** in the basic medium. Finally, the data exclude a serious contribution of the adsorption constants to the experimental reaction rate constants in the basic medium because the experimental k values and selectivity factors could not be correlated by

$$\frac{(k_{\mathrm{X}})_{\mathrm{exp}}}{(k_{\mathrm{H}})_{\mathrm{exp}}} \approx S_{\mathrm{X,H}},$$

derived from Eq. (1) with $C_{\mathrm{X}} = C_{\mathrm{H}}$ and $b_{\mathrm{X}}C_{\mathrm{X}}$, $b_{\mathrm{H}}C_{\mathrm{H}} < 1 + \Sigma bC$. In conclusion we may state that the difference in electronic character of the initial state and the transition state for the hydrogenation of the olefinic bond over palladium is negligible.



The reaction sequence may be considered as a stepwise addition of hydrogen through the α-adsorbed species **4** as the half-hydrogenated state. This is supported by both the much higher degree of H/D exchange at the α- than at the β-methyl group upon deuteration and the earlier observed "phenyl effect" (*21*). When the formation of **4** is rate determining, the transformation of the π-complexed species **3** into the σ-bonded species **4** should result in a greater sensitivity of the reaction rate constant towards the substituent constants, because of the opposite substituent effects on the stability of these species (*17–19*). Therefore, we may conclude that the rate-determining step is the reduction of the half-hydrogenated state **4**, in accordance with the suggestion of Smith *et al.* (*21*).

CONCLUSIONS

The influence of polar effects on the rate of hydrogenation of the olefinic bond over palladium is rather small or negligible, *i.e.*, the electronic nature of the transition state of hydrogenation is quite similar to that of the initial state. In the basic medium the adsorption of the olefinic bond is hardly influenced by the substituents. In neutral or acid media the strength of adsorption is decreased by electron withdrawal and enhanced by electron donation by substituents. A π-olefin complex is involved in the adsorption on palladium. Dimethylamino and ethoxycarbonyl groups show a significant contribution to the adsorption on palladium.

REFERENCES

1. SIEGEL, S., *Advan. Catal. Relat. Subj.* **16**, 123 (1966).
2. JARDINE, I., AND MCQUILLIN, F. J., *J. Chem. Soc. C* 458 (1966).
3. RUZICKA, V., CERVENY, L., AND PACHTA, J., *Collect. Czech. Chem. Commun.* **34**, 2074 (1969).
4. ENDRYSOVA, J., AND KRAUS, M., *Collect. Czech. Chem. Commun.* **35**, 62 (1970).
5. KIEBOOM, A. P. G., AND VAN BEKKUM, H., *Rec. Trav. Chim. Pays-Bas* **88**, 1424 (1969).
6. KIEBOOM, A. P. G., DE KREUK, J. F., AND VAN BEKKUM, H., *J. Catal.* **20**, 58 (1971).
7. KIEBOOM, A. P. G., AND VAN BEKKUM, H., *Synthesis* 476 (1970).
8. KLOETZEL, M. C., *J. Amer. Chem. Soc.* **62**, 1708 (1040).
9. NEWSOROFF, G. P., AND STERNHELL, S., *Aust. J. Chem.* **19**, 1667 (1966).

10. Mansveld, G. W. H. A., Kieboom, A. P. G., De Groot, W. Th. M., and Van Bekkum, H., *Anal. Chem.* **42,** 813 (1970).

11. *Cf.* Hussey, A. S., Baker, R. H., and Keulks, G. W., *J. Catal.* **10,** 258 (1968).

12. Van Bekkum, H., Verkade, P. E., and Wepster, B. M., *Rec. Trav. Chim. Pays-Bas* **78,** 815 (1959).

13. Yukawa, Y., Tsuno, Y., and Sawada, M., *Bull. Chem. Soc. Jap.* **39,** 2274 (1966).

14. Hine, J., *J. Amer. Chem. Soc.* **82,** 4879 (1960).

15. Smith, H. A., and Campbell, W. E., *Proc. Int. Congr. Catal. 3rd, 1964* **2,** 1383 (1965).

16. Van Bekkum, H., Kieboom, A. P. G., and Van De Putte, K. J. G., *Rec. Trav. Chim. Pays-Bas* **88,** 52 (1969).

17. *Cf.* Jones, R., *Chem. Rev.* **68,** 785 (1968); Hartley, F. R., *Chem. Rev.* **69,** 799 (1969).

18. Berngruber, O., Thesis, Technischen Hochschule, München, 1969; Simon, H., and Berngruber, O., *Tetrahedron* **26,** 1401 (1970), and references cited herein.

19. Treichel, P. M., and Stone, F. G. A., *Advan. Organometal. Chem.* **1,** 143 (1964).

20. Hammett, L. P., "Physical Organic Chemistry," 2nd ed. McGraw-Hill, New York, 1970.

21. Smith, G. V., and Roth, J. A., *J. Amer. Chem. Soc.* **88,** 3879 (1966).