

## DECARBONYLATION OF AROMATIC ALDEHYDES ON PLATINUM METAL CATALYSTS

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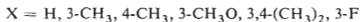
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Received May 19th, 1971

Decarbonylation of benzaldehyde and substituted benzaldehydes on palladium, platinum, rhodium or ruthenium on charcoal at 180°C in gaseous phase was studied in a flow apparatus. Only with platinum catalyst reaction rate depended, and that only slightly, on the kind of substituent. Deuterium exchange in simultaneous reaction of the benzaldehyde deuterated in the formyl group and the undeuterated derivative was further studied and kinetic isotope effects in the decarbonylation of  $C_6H_5CDO$  were measured. The course of the reaction is discussed and reaction mechanism is suggested.

Within the framework of the study of mechanisms of heterogeneous catalysed reactions of organic compounds, in the present work decarbonylation of substituted benzaldehydes on platinum metals was subjected to analysis. This reaction has been chosen on the basis of following considerations. One of the means for elucidation of reaction mechanism, used both in our and in other laboratories, is to examine the effect of the structure of reacting substances on their reactivity; while in the reactions catalysed by substances having acidic character good correlations of rate data with structural parameters have been achieved<sup>1</sup>, in the case of metal-catalysed reactions the dependences of little significance<sup>2</sup> or showing unexplainable deviations, have frequently been observed<sup>3,4</sup>. It seemed to us that accumulation of further experimental data is necessary. Because of simple kinetics, we have preferred a monomolecular reaction over a bimolecular one and, as we wished to compare also several catalysts, we sought for a reaction catalysed by platinum group metals, which are very similar in their properties. The search of literature showed that decarbonylation of aldehydes could be the suitable reaction, which in fact was proved by preliminary experiments. During those we have also found that the decarbonylation is catalysed not only by palladium<sup>5-13</sup>, rhodium<sup>13</sup> and platinum<sup>14</sup>, but also by ruthenium and iridium. The activity of iridium was however very low. We have therefore limited ourselves to the first four metals; as substrates, we have used substituted benzaldehydes (Eq. (A)). Along with the kinetics and the effect of substituents attached to the aromatic ring, we have studied also the kinetic isotope effect and deuterium exchange in this reaction.

Decarbonylation of aldehydes may be induced by acids, bases, metal complexes and various metals<sup>1,5</sup>. In literature, decarbonylation on palladium, both of aliphatic and of aromatic aldehydes, is most frequently reported<sup>5-13</sup>. Mechanism of the reaction was studied by Tsuji and Ohno<sup>13</sup> who assumed in the first step oxidative addition of the aldehyde to palladium atom to form acyl-palladium species, which in the second step is transformed to alkylpalladium compound with the splitting-off of CO, and finally in the third step the cleavage of the alkyl to palladium bond to form olefin and hydrogen, eventually alkane. This mechanism has been suggested for decarbonylation (and in the opposite direction for hydrocarbonylation) of olefins catalysed both by palladium complexes in solution and by palladium metal. The effect of the structure of aldehydes on the rate of their cleavage was studied by Hoffman and Puthenpurackal<sup>7</sup> in the decarbonylation of *trans*- $\alpha$ -cinnamaldehydes on palladium: their data could be correlated<sup>1</sup> by Taft equation.



## EXPERIMENTAL

### Catalysts

To a suspension of charcoal (Supersorbon) of 0.25 to 0.5 mm particle size in seven- to tenfold weight amount of water was added dropwise with stirring c. 1% solution of palladium dichloride or hexachloroplatinic acid, rhodium trichloride, ruthenium trichloride. On the basis of preliminary experiments the amount of the metal was chosen so that the catalysts prepared would be of approximatively the same activity. After 2 h of stirring, the charcoal was filtered off and dried at 100°C. The preparations containing 0.52% Pd, 1.60% Rh, 1.36% Pt, and 3.8% Ru were activated by reduction with a mixture of 3% hydrogen in nitrogen at 200°C for 2 h, which was carried out directly in the catalytic reactor prior to experiment. It was verified that the support itself does not catalyse the decarbonylation and that at the particle size used internal diffusion does not exert any significant effect, and that also external diffusion does not retard the reaction.

### Aldehydes

Benzaldehyde, 3-methylbenzaldehyde, 4-methylbenzaldehyde, 3-methoxybenzaldehyde (Fluka, Buchs), and 3-fluorobenzaldehyde (Koch-Light, Colnbrook) were distilled through a 30 TP column at reduced pressure; their purity was checked by gas chromatography and by refractive index determination. All manipulations with these substances were carried out in nitrogen atmosphere and the aldehydes were stored in sealed ampoules. 3,4-Dimethylbenzaldehyde was synthesized according to ref.<sup>16</sup>, b.p. 101.5°C/11 Torr (lit.<sup>17</sup> records 101°C/11 Torr), purified through semicarbazone (m.p. 228°C in agreement with literature) and distilled through a 30 TP column. Deuteriated benzaldehyde (C<sub>6</sub>H<sub>5</sub>CDO) was obtained by the reduction of benzoyl chloride with deuterium on a palladium catalyst at 200°C in a flow apparatus, with benzoyl chloride feeding rate 0.05 mol/h per 5 g catalyst (0.52% Pd on charcoal). The condensate contained c. 70% aldehyde, the rest being benzene and chlorobenzene; traces of the chloride were removed by washing the condensate with heavy water. Distillation on a 30 TP column yielded deuteriobenzaldehyde which had b.p. 74°C/21 Torr and was deuteriated exclusively in the formyl group, as shown by mass spectrometry.

## Apparatus and Procedure

A glass flow apparatus of the common type was used. The aldehydes were stored in black containers connected with a feeder. The containers and the apparatus were flushed with nitrogen containing less than 40 p.p.m. of oxygen. The same gas was used to dilute the vapours of aldehyde in experiments. The products were condensed at the temperature of solid carbon dioxide and analysed by gas chromatography. As single samples of the reduced catalysts differed in activity, we made use of the procedure suggested by Hájek and coworkers<sup>18</sup> and, from the point of view of accuracy of the measurements, favourably evaluated by Šlemrová and Kraus<sup>19</sup>. First, the catalyst was reduced under the conditions specified above, its activity was tested with the use of benzaldehyde at standard conditions, three samples of the product being taken in 15 min intervals and the second and the third one analysed, and tested further in proper measurements at the required conditions, here also by taking three samples. When changing conditions, the activity of the catalyst was again tested. The conditions were chosen so that conversions would not exceed 10 mol %. The temperature was always  $180 \pm 0.5^\circ\text{C}$ , the partial pressure of the aldehyde in the feed was 0.03–0.40 atm. With each catalyst one space velocity was used, being with Pd 390, with Rh 234, with Pt 156 and with Ru 39 mol/h kg catalyst. Initial reaction rates  $r^0$  were calculated as the ratio of the corrected conversion to reciprocal space velocity.

## Analysis and Errors

Condensed reaction products were analysed gas chromatographically on an instrument equipped with heat-conductivity detector. The columns were filled with 20% Apiczon L on Celite, the column temperature was 125 or 150°C in dependence on volatility of the mixtures. The content of the substances formed by decarbonylation was determined from the heights of peaks on the basis of preceding calibrations. The error of the determination did not exceed 2 rel. %. The other errors were estimated<sup>19</sup> as follows: the relative error in determination of benzaldehyde conversion was 3.8%, that in substituted benzaldehyde conversion was 5.0%, the error in reaction rate for benzaldehyde was 8.1% and for substituted benzaldehyde 9.3%.

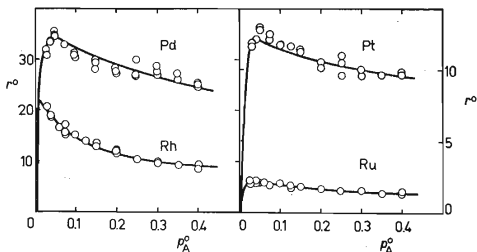


FIG. 1

Dependence of Initial Reaction Rates of Decarbonylation of Benzaldehyde on Pd, Rh, Pt and Ru Catalysts

Points experimental data; curves were calculated according to Eq. (3) using the constants presented in Table II.

## Treatment of Kinetic Data

Experimental dependences of initial reaction rates  $r^0$  on partial pressure  $p^0$  (Fig. 1) were treated by combining the methods of linear and nonlinear regression<sup>20</sup> for 27 rate equations of Hougen-Watson type and for power-law equation. On deriving these equations, it was successively assumed that rate determining step is adsorption, surface reaction and desorption. Further, different views on the mode of adsorption (on one or two centres, with or without dissociation) and on total number of the centres needed for the reaction were applied. The suitability of individual rate equations was estimated on the basis of the sums of squared deviations of the calculated from the experimental reaction rates. In the course of the calculations the worst expressions were stage by stage eliminated. So all equations assuming adsorption or desorption as rate determining step gave worse results already on using linear regression. On its basis also the power law equation and the three expressions for surface reaction as rate determining step were excluded. The other relations were further compared by nonlinear regression. On its basis the best equations turned out to be relations (1)–(3) (Table I) which will be discussed later.

## Kinetic Isotope Effects

As separate kinetic measurements with benzaldehyde deuteriated in the formyl group did not yield sufficiently accurate results, isotope effects were determined by competition method. The equimolar mixture of  $C_6H_5CHO$  and  $C_6H_5CDO$  was injected into a stream of nitrogen to achieve overall partial pressure of aldehydes 0.1 atm. Their space velocity was chosen so that in four experiments with each of the catalysts the conversion would be from 7 to 90%. The products were analysed by gas chromatography to determine overall conversion and by infrared spectroscopy

TABLE I  
Best Rate Equations and Corresponding Reaction Schemes

A Aldehyde, R benzene, S carbon monoxide; B, C hypothetical particles on the surface, n active site.

Scheme	Equation
$A + 2n \rightleftharpoons B \cdot n + C \cdot n$ $B \cdot n + C \cdot n + n \rightarrow R \cdot 2n + S \cdot n$ $R \cdot 2n \rightleftharpoons R + 2n$ $S \cdot n \rightleftharpoons S + n$	$r^0 = \frac{kK_A p_A^0}{[1 + 2\sqrt{(K_A p_A^0)}]^3} \quad (1)$
$A + 2n \rightleftharpoons B \cdot n + C \cdot n$ $B \cdot n + C \cdot n + 2n \rightarrow R \cdot 2n + S \cdot 2n$ $R \cdot 2n \rightleftharpoons R + 2n$ $S \cdot 2n \rightleftharpoons S + 2n$	$r^0 = \frac{kK_A p_A^0}{[1 + 2\sqrt{(K_A p_A^0)}]^4} \quad (2)$
$A + 2n \rightleftharpoons A \cdot 2n$ $A \cdot 2n + n \rightarrow R \cdot 2n + S \cdot n$ $R \cdot 2n \rightleftharpoons R + 2n$ $S \cdot n \rightleftharpoons S + n$	$r^0 = \frac{k[\sqrt{(1 + 8K_A p_A^0)} - 1]^3}{64 (K_A p_A^0)^2} \quad (3)$

to determine the degree of the transformation of the individual aldehydes. From ratios of absorbancies of the bands at  $2115\text{ cm}^{-1}$  (C—D stretch) and  $2825\text{ cm}^{-1}$  (C—H stretch) and on the basis of the preceding calibration, the ratio of unreacted aldehydes was determined. It was checked that the deuteriated benzenes formed do not show significant absorption at the given wavenumbers. From the found total conversion  $x$  and the ratio of the deuteriobenzaldehyde to benzaldehyde concentration  $C$ , the conversions  $x_H$  and  $x_D$  were calculated according to the relations

$$x = x_H + x_D, \quad C = (0.5 - x_D)/(0.5 - x_H). \quad (4), (5)$$

Under the assumption that the adsorption coefficients of the deuteriated and nondeuteriated benzaldehydes are the same, it follows from relations (1)–(3) for the ratio of reaction rates

$$r_H/r_D = k_H p_{A,H} / k_D p_{A,D}, \quad (6)$$

where  $p_{A,H}$  and  $p_{A,D}$  are partial pressures of the nondeuteriated and deuteriated benzaldehydes. After the introduction of conversion in place of partial pressures, the inclusion of the condition on the equality of partial pressures in the feed  $p_{A,H}^0 = p_{A,D}^0$  and the integration, the following relation for the calculation of isotope effect was obtained

$$\frac{k_H}{k_D} = \frac{\log [0.5/(0.5 - x_H)]}{\log [0.5/(0.5 - x_D)]}. \quad (7)$$

#### Decarbonylation of a Mixture of 4-Methylbenzaldehyde and Deuteriated Benzaldehyde

A mixture of  $\text{CH}_3\text{C}_6\text{H}_4\text{CHO}$  and  $\text{C}_6\text{H}_5\text{CDO}$  was decarbonylated on the palladium catalyst. As found by mass spectrometry the product did not contain 4-methylbenzaldehyde deuteriated in its formyl group, although formed hydrocarbons were both deuteriated and nondeuteriated.  $d_0$ -Toluene and  $d_1$ -toluene were present in the 4 : 1 ratio, and  $d_2$ -toluene appeared in trace amounts.

### RESULTS AND DISCUSSION

The three rate equations (Table I) which turned out to be best in correlation of experimental dependence of initial reaction rates on partial pressures of reactants for all the catalysts and all the substrates corresponded to the schemes given also in Table I. These equations could not be distinguished on the basis of statistical criteria. The three models have some features in common: all assume that the rate is controlled by surface reaction of the adsorbed aldehyde, this being adsorbed on two centres, and further that at least one more centre assists in the surface reaction. Models (1) and (2) differ from model (3) in that they assume adsorption with dissociation, whereas model (3) assumes molecular adsorption. Models (1) and (3) differ from model (2) in the number of active centres assisting in the surface reaction (one or two). As to the form, equations (1) and (2) are similar and differ from each other only by the exponent in the denominator; equation (3) is however quite different. Notwithstanding, the agreement between the calculated and the experimental values is very good. The constants of equations (1)–(3) are presented in Table II and the agreement of equation (3) with experiments is evident from examples in Fig. 1. The

other aldehydes yielded similar curves. On the whole, this result confirms the already stated fact<sup>18,20,21</sup> that at the given accuracy of measurements an unambiguously best equation cannot be selected. One can be thus inclined to consider selected equations of Langmuir-Hinshelwood type as empirical relationships. On the other hand, it is striking that the set of the best relations is based as a rule on very closely related schemes, which indicates a certain soundness of basic assumptions. A partial

TABLE II

Values of Rate Constants  $k$  (mol h/kg) and of Adsorption Coefficients  $K_A$  (atm<sup>-1</sup>) Calculated by Method of Nonlinear Regression for Benzaldehydes X-C<sub>6</sub>H<sub>4</sub>CHO

X	$k$			$K_A$		
	(1)	(2)	(3)	(1)	(2)	(3)
Palladium catalyst						
H	895	2 143	271	19	3.5	18
3-CH <sub>3</sub>	842	2 050	255	11	2.9	12
4-CH <sub>3</sub>	893	2 129	266	29	5.2	26
3,4-(CH <sub>3</sub> ) <sub>2</sub>	547	1 318	166	9	2.5	10
3-CH <sub>3</sub> O	957	2 265	283	27	5.0	23
Rhodium catalyst						
H	628	1 192	173	140	9.4	86
3-CH <sub>3</sub>	607	1 175	170	140	10.4	92
4-CH <sub>3</sub>	707	1 346	210	224	16.1	176
3,4-(CH <sub>3</sub> ) <sub>2</sub>	572	1 141	164	154	12.9	110
3-CH <sub>3</sub> O	805	1 480	223	231	14.9	150
Platinum catalyst						
H	332	783	98.5	30	4.9	25
3-CH <sub>3</sub>	316	761	95.2	20	4.2	19
4-CH <sub>3</sub>	261	613	78.3	21	4.4	19
3-CH <sub>3</sub> O	291	701	86.8	24	4.9	21
3-F	417	1 002	125.4	19	4.0	18
Ruthenium catalyst						
H	57.1	136	17.0	29	4.7	25
3-CH <sub>3</sub>	69.7	151	20.5	79	8.7	64
4-CH <sub>3</sub>	52.3	126	15.5	27	5.1	26
3,4-(CH <sub>3</sub> ) <sub>2</sub>	71.4	172	21.3	21	4.4	19
3-CH <sub>3</sub> O	66.8	159	19.8	24	4.7	21
3-F	51.6	114	14.9	47	6.0	34

answer to this problem we attempted to get by confrontation of the result of kinetic analysis with the knowledge provided by other independent procedures.

In all the schemes considered it is assumed that also the products, aromatic substance and carbon monoxide, may be adsorbed on metal surface. The corresponding terms do not appear, of course, in the equations for initial reaction rates. If  $r^0$  is measured in such a way that the feed contains besides an aldehyde also one of the products, from the ratio of the conversions of the aldehyde obtained without ( $x$ ) and with ( $x'$ ) the addition of the product, the adsorption coefficient can be calculated after appropriate modification of the rate equation (conversion should be low, within the limits of the validity of approximation of initial rates). So *e.g.* from equation (3) it follows

$$K_i = \left\{ \frac{8K_A p_A^0 - \left\{ \sqrt[3]{(x/x')} [\sqrt{(1 + 8K_A p_A^0)} - 1] \right\}^2}{2 \sqrt[3]{(x/x')} [\sqrt{(1 + 8K_A p_A^0)} - 1]} - 1 \right\} \frac{1}{p_i^0} \quad (8)$$

From the measurements with different partial pressures  $p_i^0$  of benzene and carbon oxide added to benzaldehyde, the values of adsorption coefficients for both products were obtained in this way for models (1)–(3), for benzene being alternatively assumed that it is adsorbed with dissociation. From the average values summarized in Table III it follows that both products are adsorbed relatively strongly, comparably with benzaldehyde. Although somewhat lesser scattering of the data was obtained with the use of the coefficients assuming dissociation of benzene, it cannot be said that this assumption is to be preferred. From the values presented in Table II it follows that the substituents affect the reactivity of benzaldehyde only very little. This, in fact, was also obvious from comparison of reaction rates at equal partial pressures, so that the small effect cannot be the consequence of the work-up of rate data to rate equations. On the contrary, it is obvious that relative values of the constants do not depend on the type of equation. More distinct differences exist between single catalysts; it seems likely that they would be even greater, if the content of the metal on the support were the same. For the purpose of the easier measurement we have tried, on the other hand, by using different content of the active component to equalize activities of the catalysts. When the reaction rates related to weight unit of the metal are compared, the following relative values of the activity are obtained: Pd 100, Rh 16, Pt 13, Ru 1.

With the exception of platinum catalyst, already qualitative comparison of  $k$  and  $K_A$  shows that reactivity of individual benzaldehydes does not parallel the electronegativity of the substituents and that observed differences are rather fortuitous. This was proved also in an attempt to correlate both series of constants  $k$  and  $K_A$  and initial reaction rates  $r^0$  by Hammett equation<sup>22</sup>. Only rate constants  $k$  from all three equations and  $r^0$  for platinum catalyst gave correlation which was ensured, however, only on 80% level of reliability. The constant  $\rho$  equaled to 0.5.

These findings indicating nonexisting or weak effect of substituents lead to the conclusion that in the rate determining step the bond between the aromatic nucleus and the formyl group is already strongly weakened or completely broken. This could be accounted for by assumption that the rate determining step is preceded by equilibrium dissociative adsorption of the aldehydes to the species  $\text{XC}_6\text{H}_4\text{—}$  and  $\text{—CHO}$ . We have therefore decarbonylated simultaneously benzaldehyde deuteriated in the formyl group and nondeuteriated *p*-methylbenzaldehyde. If equilibrium dissociation on the surface did proceed then the exchange between the labelled and the nonlabelled formyl group would inevitably be observed. As we have not found among the products any deuteriated *p*-methylbenzaldehyde this alternative can be excluded. This experiment further showed that also equilibrium dissociative adsorption to the species  $\text{XC}_6\text{H}_4\text{CO—}$  and  $\text{—H}$ , suggested by Tsuji and Oho<sup>7,13</sup>, is improbable, since in such a case extensive deuterium-hydrogen exchange between the two aldehydes would have been proceeding. The observed presence of deuterium in the formed toluene indicates on the contrary that isolated hydrogen atoms appear on the surface simultaneously with the species  $\text{XC}_6\text{H}_4\text{—}$ .

The competition of determination of relative reactivities of the nondeuteriated and in the formyl group deuteriated benzaldehyde, in spite of lesser accuracy of spectroscopic analysis, has turned out to be more reliable than separate measurements of rate constants. The average values of the  $k_{\text{H}}/k_{\text{D}}$  ratio were as follows:

Catalyst	Pd	Rh	Pt	Ru
$k_{\text{H}}/k_{\text{D}}$	$2.14 \pm 0.24$	$1.94 \pm 0.32$	$1.30 \pm 0.10$	$1.43 \pm 0.24$

For the purpose of comparison the maximum effect<sup>23</sup> was calculated from the wave-numbers of C—H and C—D stretching vibrations in the formyl group of benzaldehyde ( $\nu_{\text{H}} = 2745$  and  $2825 \text{ cm}^{-1}$  and  $\nu_{\text{D}} = 2060$  and  $2115 \text{ cm}^{-1}$ ) according to the relation

$$(k_{\text{H}}/k_{\text{D}})_{\text{max}} = \exp \left[ \frac{hc}{2kT} (\nu_{\text{H}} - \nu_{\text{D}}) \right], \quad (9)$$

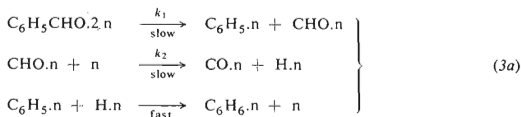
where  $h$  is Planck constant,  $k$  Boltzman constant,  $c$  light velocity and  $T$  temperature. In the calculation the average of both wave-numbers for C—H and C—D bonds were used and the resultant value was 2.92.

These results show that hydrogen transfer takes place in the rate determining step. As distinct isotope effects on the palladium and on the rhodium catalysts are within experimental error the same, we can assume that also transition states are similar; the effects of substituents were very small as well. In the case of the platinum and ruthenium catalysts low isotope effects were observed, which indicates that here somewhat different mechanism has to be taken into account. At the same time platinum differs also in the sensitivity to substituent effects.



## Mechanism of Reaction

Observed substituent effects, the attempted deuterium exchange as well as isotope effects are not fully compatible with any of the schemes given in Table I. Models (1) and (2) are highly improbable since they assume dissociative adsorption. Model (3) with benzaldehyde adsorbed without dissociation can be further improved, however. It is possible to modify its second step, *i.e.* the step of surface reaction determining reaction rate, by assuming that it consists of two consecutive processes. Of numerous schemes, most could be rejected, since they either require a greater effect of the structure (*i.e.* those which involved the species  $\text{XC}_6\text{H}_4$  in the slow step) or should manifest themselves by parallel occurrence of significant isotope and structure effects and *vice versa*, whereas in the series Pd, Rh, Pt opposite combinations have been observed. The analysis left the only alternative (3a), which, as to the number of active centres, is written here with respect to equation (3). This is quite a formal matter, however, and the participation of active sites in these steps could be assumed to proceed also otherwise.



The model of surface reaction (3a) is to illustrate the fact that in the rate determining step adsorbed aldehyde molecule is split to three species ( $\text{C}_6\text{H}_5$ , CO and H), cleavage of both bonds being not strictly simultaneous; either of the bonds may be cleaved little earlier than the other. It is understandable that  $k_1$  and  $k_2$  do not differ by an order of magnitude. We suppose that in the case of Pd and Rh  $k_1 > k_2$ , since on these catalysts substituents effects were very small and isotope effect was significant. For platinum catalyst, where isotope effect was small but the effect of structure was significant, we assume that  $k_1 \approx k_2$  or even  $k_1 < k_2$ . In the light of this interpretation

TABLE III

Adsorption Coefficients of Products for Models (1)–(3)

Catalyst	CO			$\text{C}_6\text{H}_6$ , without diss.			$\text{C}_6\text{H}_6$ , with diss.		
	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
Pd	17.0	7.2	16.6	27.1	11.7	27.2	2.9	0.5	2.0
Rh	81.0	20.1	70.2	44.8	11.6	42.5	7.4	0.5	6.7
Pt	20.2	7.9	19.0	35.6	14.1	34.7	5.9	0.3	5.5
Ru	28.6	10.7	25.8	21.6	8.6	21.6	2.6	0.2	2.6

ruthenium is a special case; substituent effects are not observable and also isotope effect is small. This metal differs from the other three in some properties, especially by hexagonal lattice, while palladium, rhodium and platinum have cubic lattice. It is thus quite reasonable to assume that on this metal the reaction proceeds by somewhat different mechanism. These considerations can be confronted with the results of Hoffman and Puthenpurackal<sup>7</sup> who examined the effect of alkyl groups in the  $\alpha$ -position of cinnamaldehydes  $C_6H_5CH=CRCHO$  on the rate of decarbonylation on a palladium catalyst. Since in cinnamaldehydes significant resonance stabilization can be expected, the first step in the Scheme (3a) should be more difficult and thus  $k_1$  should be smaller than  $k_2$ . In such a case the action of substituents should be more important, which in fact has been observed<sup>7</sup>. Finally, we made an attempt to transform the Scheme (3a) to rate equation. We started from the assumption that in a stationary state the rates of both slow steps are the same, the other steps being in equilibrium. The resultant relations were however too complex to be verified. After further assumption has been made, e.g. on negligible surface concentration of some species, we have again obtained equation (3). It can be thus assumed that equation (3) is the first approximation of formal kinetic description of plausible mechanism.

## REFERENCES

1. Kraus M.: *Advan. Catal.* 17, 75 (1967).
2. Endryšová J., Kraus M.: *This Journal* 35, 62 (1970).
3. Hájek M., Kochloeff K.: *This Journal* 34, 2739 (1969).
4. Kubelka V., Kraus N.: *This Journal* 34, 2895 (1969).
5. Eshinazi H. E.: *Bull. Soc. Chim. France* 1952, 967.
6. Eshinazi H. E., Pines H.: *J. Org. Chem.* 24, 1369 (1969).
7. Hoffman N. E., Puthenpurackal T.: *J. Org. Chem.* 30, 420 (1965).
8. Hawthorne J. O., Wilt M. H.: *J. Org. Chem.* 25, 2215 (1960).
9. Newman M. S., Gill N.: *J. Org. Chem.* 31, 3860 (1966).
10. Conia J. M., Faget C.: *Bull. Soc. Chim. France* 1964, 1963.
11. Hemidy J. F., Gault F. C.: *Bull. Soc. Chim. France* 1965, 1710.
12. Wilt J. W., Abegg V. P.: *J. Org. Chem.* 33, 923 (1968).
13. Tsuji J., Ohno K.: *J. Am. Chem. Soc.* 90, 94 (1968).
14. Belskij I. F., Šujkin N. I., Šostakovskij V. M.: *Izv. Akad. Nauk SSSR, Ser. Chim.* 1962, 1821.
15. Kochloeff K., Kraus M.: *Preparativní reakce v organické chemii. IX. Isomerisace a degradace.* Academia, Prague 1967.
16. Shacklet C. D., Smith H. A.: *J. Am. Chem. Soc.* 75, 2654 (1953).
17. Sugawara S., Sugimoto N.: *J. Pharm. Soc. Japan* 61, 62 (1941); *Chem. Abstr.* 36, 92 (1942).
18. Hájek M., Duchet J. C., Kochloeff K.: *This Journal* 35, 2258 (1970).
19. Šlemrová J., Kraus M.: *J. Catal.* 20, 172 (1971).
20. Hančil V., Mitschka P., Beránek L.: *J. Catal.* 13, 435 (1969).
21. Davidova N., Penčev V., Beránek L.: *This Journal* 33, 1229 (1968).
22. Hammett L. P.: *J. Am. Chem. Soc.* 59, 96 (1937).
23. Melander L.: *Isotope Effects on Reaction Rates.* Ronald Press, New York 1960.

Translated by J. Hetflejš.