

## STRUCTURE-REACTIVITY DEPENDENCE IN HYDROGENOLYSIS OF ESTERS ON RHODIUM

M.ZDRAŽIL and M.KRAUS

*Institute of Chemical Process Fundamentals,  
Czechoslovak Academy of Sciences, 165 02 Prague - Suchbát*

Received September 19th, 1973

Hydrogenolysis of 24 aliphatic esters of primary alcohols on rhodium was studied by the method of competitive reactions at 300°C with reactants in gaseous phase. Reaction products were corresponding carboxylic acid and hydrocarbon. For each ester relative reactivity with respect to methyl butyrate was determined. Structure effects observed were found to correlate with boiling points, heats of evaporation, and with  $\nu(\text{C}=\text{O})$  frequencies. The Taft equation correlates data after its extension by the term expressing the number of hydrogens on  $\alpha$  carbon atoms. A mechanism is suggested which involves coordination of the acyl oxygen of an ester to electrophilic center on catalyst surface, which results in formation of the electrophilic center on the alkoxy carbon. This center is then attacked by a nucleophilic species, likely by hydride anion formed on the surface, which brings about cleavage of the C—O bond.

In connection with the study of structure-reactivity dependences (*e.g.*<sup>1-3</sup>) and in continuation of the study of kinetics of hydrogenolysis of esters on rhodium<sup>4,5</sup> in this work we were concerned with effects of the structure of alkyl groups  $\text{R}^1$  and  $\text{R}^2$  on the reaction of esters with hydrogen (Equation (A)) carried out on a Rh/C catalyst at 300°C with reactants in gaseous phase. As we wished to include as many compounds as possible to the set of substrates studied, we chose the method of competitive reactions for determining the relative reactivities.



### EXPERIMENTAL AND RESULTS

Apparatus, experimental procedure and analysis were described in the previous work<sup>4</sup>. Boiling points of the compounds used agreed with reported data and their purity was confirmed by gas chromatography.

Relative reactivities of the ester  $i$  with respect to the ester  $j$ ,  $R_{ij}$ , were calculated from the earlier derived and confirmed<sup>5</sup> relation

$$R_{ij} = \log(1 - x_i) / \log(1 - x_j), \quad (\text{I})$$

where  $x_i$  and  $x_j$  denote conversions of the esters. For selected pairs of esters several pairs of conversions, usually from 3–6, were obtained at the total pressure of esters in the feed 0.4 atm, hydrogen pressure 0.6 atm, and at the molar ratio of esters in the feed equal to one. By series of more detailed experiments the independence of  $R_{ij}$  on these parameters as well as on total conversion was confirmed. The values of  $R_{ij}$  calculated from individual couples of conversions were averaged. Esters were arranged to pairs considering both possibilities of chromatographic analysis, *i.e.* ensuring good separation of peaks, and relative reactivities of esters, since at great difference in conversions the result is less accurate. Methyl butyrate was chosen as a standard substrate. Reactivity of several esters was evaluated by competitive experiments with this standard. Relative reactivities (with respect to methyl butyrate) of the other esters were calculated from 28 relative reactivities for different pairs of esters, using Eq. (2). The validity of this relation was verified in several cases by comparing  $R_{ij}$  values obtained by experiment with the values calculated from Eq. (2), or by comparing the values of  $R_{ij}$  calculated from Eq. (2) with the use of different  $R_{ik}$  and  $R_{jk}$ .

$$R_{ij} = R_{ik}/R_{jk} \quad (2)$$

A good agreement was always found, which proves that the set of data obtained is consistent. Relative reactivities with respect to methyl butyrate are given in Table I. In composing Table I from a set of experimental reactivities, *i.e.* the reactivities determined directly by experiments with corresponding pairs of esters, several rules were followed. Experimental reactivities were preferred to the reactivities calculated according to Eq. (2). Of calculated reactivities, those calculated from the least number of experimental reactivities, *i.e.* from two or three, were preferred. In calculations the reactivities determined from the greater number of couples of conversions were used preferentially.

Reactivity of neopentyl esters of acetic and butyric acids was evaluated by non-competitive experiments. As these compounds did not react, it was verified that they do not poison the catalyst, this being made by their intermittent feeding with pentyl acetate or with butyl butyrate.

The reactivity of isopropyl and tert-butyl acetates was estimated from preliminary experiments. While the former ester is not liable to thermal decomposition under conditions used, the ester of the tertiary alcohol undergoes elimination followed by hydrogenation of the olefin and this process competes with hydrogenolysis. However, though considering this phenomenon isopropyl acetate reacts at a rate which is as fast as or only little faster than the rate of hydrogenolysis of propyl acetate, and the reactivity of tert-butyl acetate is comparable within one order of magnitude with that of butyl acetate. Reactivity of butyrolactone is low; under conditions where butyl acetate gives conversion 0.5, the conversion of  $\gamma$ -butyrolactone is 0.1.

Exchange experiments were carried out with the couples methyl butyrate–butyl acetate and methyl propionate–ethyl acetate. These experiments were aimed at finding whether assumed equilibrium adsorption of esters is dissociative; in such a case the esters with exchanged alkyl groups could be found among reaction products. Such substances were not, however, detected.

## DISCUSSION

As established by a detailed kinetic analysis for four esters in the previous paper<sup>4</sup> and demonstrated by the data in Table I, the reactivity of esters increases with their molecular weight. At the same time, a decrease in reactivity is observed for esters with branched  $R^1$  or  $R^2$  groups. The rate increases with the size of the alkyl group attached to both the acyl and alkoxy part of the molecule. Literature search revealed

TABLE I  
Relative Reactivities  $R_{ij}$  of Esters  $R^1\text{COOCH}_2\text{R}^2$  with Respect to Methyl Butyrate at 300°C on 3% Rh on Activated Carbon

$R^2$	$R^1$					
	$\text{CH}_3$	$\text{C}_2\text{H}_5$	$\text{C}_3\text{H}_7$	$i\text{-C}_3\text{H}_7$	$i\text{-C}_4\text{H}_9$	$t\text{-C}_4\text{H}_9$
H	0.12	0.36	1.00	0.88	1.31	1.65
$\text{CH}_3$	0.35	0.68	1.51	1.03	—	—
$\text{C}_2\text{H}_5$	1.42	2.58	4.39	2.77	6.21	4.67
$\text{C}_3\text{H}_7$	4.65	10.4	13.6	—	—	—
$i\text{-C}_3\text{H}_7$	1.94	3.02	6.97	—	—	—
$\text{C}_4\text{H}_9$	7.46	—	—	—	—	—
$i\text{-C}_4\text{H}_9$	5.88	—	—	—	—	—

that this behaviour is unique. In so far known reactions their rate decreases with increasing size of the acyl group and usually decreases with increasing size of the alkoxy group, in olefin-forming eliminations it sometimes slightly increases. This rules out the possibility to seek for mechanistic similarities between hydrogenolysis and solvolytic or elimination reactions. The structure of esters exerts, however, a similar effect on their boiling points. Fig. 1 shows that reactivities in hydrogenolysis correlate well with normal boiling points of esters,  $t_b$  ( $\log R_{ij} = 0.0176 t_b - 1.80$ , correlation coefficient  $r = 0.966$ ) as well as with their heat of evaporation at boiling point of esters  $\Delta H_b$  ( $\log R_{ij} = 0.852 \Delta H_b - 6.96$ ,  $r = 0.946$ , four esters for which the heat of evaporation was not found in literature are not included in this correlation). Simultaneous validity of these correlations follows from the well-known Trouton rule  $\Delta H_b = \text{konst.} \times t_b$ . These correlations indicate that intermolecular forces playing an important role in the liquid are similar to the forces affecting reactivity. As the reactivity obtained include both the ratio of rate constants and that of adsorption coefficients<sup>5</sup>, one can believe that this forces influence adsorptivity. This assumption is in harmony with kinetic analysis<sup>4</sup> which on the basis of Langmuir-Hinshelwood model made it possible to separate the rate and adsorption coefficients; the adsorption coefficients increased with molecular weight. In view of the fact that the rate constants also increased with increasing molecular weight, this explanation does not seems to be exhaustive.

The attempt to correlate obtained relative reactivities with the Taft equation by means of inductive  $\sigma^*$  and steric  $E_s$  constants<sup>9</sup> has not met with success. When using the sum of inductive constants of  $R^1$  and  $\text{CH}_2\text{R}^2$  groups in the ester  $R^1\text{COOCH}_2\text{R}^2$  i.e.  $\sum\sigma^* = \sigma^*(R^1) + \sigma^*(\text{CH}_2\text{R}^2)$ , we observed that data are grouped

to the lines according to the sum of the number of  $\alpha$  hydrogen atoms in groups  $R^1$  and  $-\text{CH}_2R^2$ . After introducing the corresponding term to the Taft equation

$$\log R_{ij} = \rho^* \sum \sigma^* + h \Delta n + C, \quad (3)$$

where  $\Delta n = 6 - \sum n$  ( $n$  is the number of  $\alpha$  hydrogens) we obtained a good correlation which is shown in Fig. 2, with parameters  $\rho^* = -25.7$ ,  $h = -2.28$ ,  $C = -0.67$ , and  $r = 0.956$ . A similar modification of the Taft equation (for review see<sup>10</sup>) was used for hydrogenation of aldehydes and ketones<sup>11</sup>. The value of  $\rho^*$  obtained by us is unusually high. This may be due to the fact that this constant is the sum of the slopes for two consecutive steps (equilibrium adsorption followed by surface reaction) which are of the same sign. Correlations of structure and properties in which the numbers of  $\alpha$  hydrogen atoms play a role are usually interpreted as being indicative of occurrence of hyperconjugation. This effect can also be expected to take place in our case. The same direction of inductive and mesomeric effects is evident from the same signs of the constants of Eq. (3). Due to both effects electron density on the ester group is changed, and its increase obviously facilitates the reaction.

Before entering into discussion of mechanism of hydrogenolysis, it seems useful to give a brief account of the knowledge concerning the structure of esters. In aliphatic

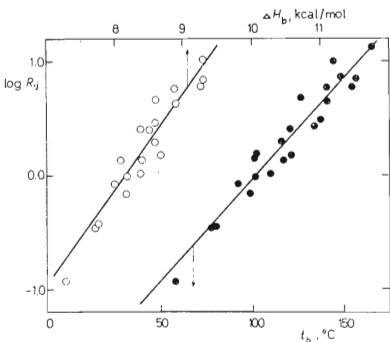


FIG. 1  
Correlation of Relative Reactivity  $R_{ij}$  for Hydrogenolysis of Esters from Table I with Boiling Point<sup>6</sup>  $t_b$  and with  $\Delta H_b$  at Boiling Point<sup>7,8</sup>

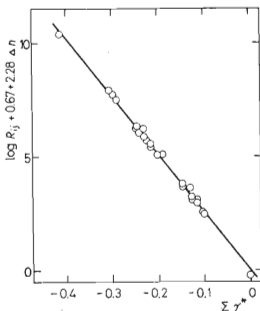
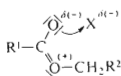


FIG. 2  
Correlation of Relative Reactivities According to Eq. (3)

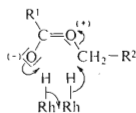
esters planar *Z*-conformation of the ester group is preferred<sup>12,13</sup>; the *E*-conformation is encountered only with lower lactones. Rotation around the ester C—O bond is then strongly restricted. Dipole moment measurements show that this occurs also at elevated temperatures<sup>13</sup>. In the ester group there is mesomerism between structures *I* and *II* which causes that the C—OCH<sub>2</sub> bond acquires some double bond character, this being the reason of restricted rotation around this bond. From interpretation



of changes of the stretching<sup>14</sup>  $\nu(\text{C}=\text{O})$  and deformation<sup>15</sup>  $\delta_1, \delta_2(\text{C}-\text{O})$  vibrations in dependence on structure it follows that structure *II* for the ester  $\text{R}^1\text{COOR}^2$  becomes increasingly more important as the size of alkyl groups  $\text{R}^1$  and  $\text{R}^2$  increases. On increasing size of the acyl and alkoxy groups the wavenumber of the stretching  $\text{C}=\text{O}$  vibration decreases, this being indicative of decreasing double bond character in the sense of the structure *II*. Morgan and Unwin<sup>14</sup> found a good linear correlation between  $\tilde{\nu}(\text{C}=\text{O})$  and  $\sum\sigma^*$  for 16 esters (seven of which are included also in our set). (This correlation cannot be interpreted as being solely due to inductive effect, since for the set of esters studied by the above mentioned authors the relation  $\Delta n = 6 + 10 \sum\sigma^*$  is practically accurately fulfilled, so that to speak about hyperconjugation effect seems to be at least similarly justified.) When discussing the effect of structure on reactivity we concluded that the increase of electron density on the ester group brought about by the inductive and hyperconjugation effect of alkyl, *i.e.* the shift to structure *II*, is favourable for the course of hydrogenolysis. This may be expected if one of reaction steps will involve interaction of the ester with electrophilic species or with electrophilic center on catalyst surface. In similar interactions the carboxylic oxygen acts as nucleophilic center, which was confirmed for proton<sup>16,17</sup> and Lewis acids<sup>18,19</sup>. By this way the importance of the structure *II* increases, as depicted in scheme *III* in which X stands for the acid. In hydrogenolysis either



III



IV

surface metal atom, or positively polarised hydrogen atom  $H^{\delta+}$ , formed by dissociative adsorption of hydrogen molecule on rhodium, can be regarded as an electrophilic particle. Further reaction step should be then the attack of the nucleophilic particle on an electron-deficient centre in the adsorbed ester. This center is the alkoxy oxygen and adjacent carbon. Nucleophilic particle may be metal atom or, more likely, negatively polarised adsorbed hydrogen atom  $H^{\delta-}$ . It is also possible to assume a synchronous, or nearly synchronous, process involving two hydrogen atoms adsorbed on neighbouring sites of surface, oppositely polarised (IV). A similar heterolytic dissociative adsorption of hydrogen on metal was considered to take place in hydrogenolysis of chlorobenzenes on palladium<sup>3</sup> (compare<sup>20,21</sup>). An analogous cyclic mechanism was suggested also for hydrogenolysis of benzyl acetate on palladium on the basis of the study of the effect of substituents attached to aromatic ring<sup>22</sup>. A similar mechanism was also postulated for reactions of some sterically hindered esters with Grignard reagents<sup>23</sup>.

It remains to appreciate how this assumption agrees with further observation.  $\gamma$ -Butyrolactone, which is in the *E* conformation<sup>12</sup> and has high value of  $\nu(C=O)$  (ref.<sup>24</sup>), could be expected to react reluctantly, which is the case. The exchange of alkyl or alkoxy groups does not proceed, which indicates the absence of a dissociative step in the course of the reaction. Unreactivity of neopentyl esters can probably be attributed to steric hinderance which prevents the ester from acquiring a suitable position with respect to either hydrogen or adsorbed hydrogen atoms. This may be regarded as an indirect support of the cyclic mechanism which will be relatively strongly sterically demanding.

#### REFERENCES

1. Kraus M.: *Advan. Catalysis* 17, 75 (1967).
2. Kochloeff K., Kraus M., Bažant V.: *Proc. Fourth Int. Congr. Catal., Moscow 1968*, Vol. II, p. 490. Akadémiai Kiado, Budapest 1971.
3. Kraus M., Bažant V.: *Proc. Fifth Int. Congr. Catal., Miami Beach 1972*, p. 1073. North-Holland, Amsterdam 1973.
4. Zdražil M.: *This Journal* 39, 1488 (1974).
5. Zdražil M.: *J. Catal.* 31, 313 (1973).
6. West R. C. (Ed.): *Handbook of Chemistry and Physics*. 49th Edition 1968—1969. The Chemical Rubber Co., Cleveland, Ohio.
7. Polák J.: *Thesis*. Czechoslovak Academy of Sciences, Prague 1964.
8. Perry J. H.: *Chemical Engineers Handbook*. McGraw-Hill, New York 1963.
9. Taft R. W.: *J. Am. Chem. Soc.* 75, 4231 (1953).
10. Palm V. A.: *Grundlagen der Quantitativen Theorie Organischer Reaktionen*. Akademie Verlag, Berlin 1971.
11. Taft R. W., Kreevoy M. M.: *J. Am. Chem. Soc.* 79, 4011 (1957).
12. O'Gorman J. M., Shand W., Shomaker V.: *J. Am. Chem. Soc.* 72, 4222 (1950).
13. Marsden R. J., Sutton L. E.: *J. Chem. Soc.* 1936, 1383.
14. Morgan K. J., Unwin N.: *J. Chem. Soc. (B)* 1968, 880.

15. Tanaka S., Higuchi S., Kamata H.: J. Chem. Soc. Japan, Pure Chem. Sect. 87, 399 (1966).
16. Birchall T., Gillespie R. J.: Can. J. Chem. 43, 1045 (1965).
17. Siigur J., Haldna U.: Reakts. Sposobnost Org. Soedin. 7, 211 (1970).
18. Lappert M. F.: J. Chem. Soc. 1961, 817.
19. Lappert M. F.: J. Chem. Soc. 1962, 542.
20. Horiuti J., Toya T.: Solid State Surface Sci. 1, 1 (1969).
21. Bastl Z.: This Journal 38, 477 (1973).
22. Kieboom A. P. G., de Kreuk J. F., van Bekkum H.: J. Catal. 20, 52 (1971).
23. Hauser C. R., Saperstein P. O., Shivers J. C.: J. Am. Chem. Soc. 70, 606 (1948).
24. Welti D.: *Infrared Vapour Spectra*. Heyden, London 1970.

Translated by J. Hetflejš.