

Structural and Reactivity Effects in the Copper-Catalyzed Hydrogenolysis of Aliphatic Esters

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Received November 15, 1983; revised February 14, 1984

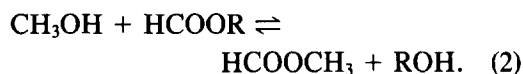
The hydrogenolysis of a series of alkyl esters to their corresponding alcohols has been studied over a Raney copper catalyst in the temperature range 210–280°C. Generally, the rate of hydrogenolysis was found to increase with molecular weight while the selectivity to alcohol, derived from the acyl part of the ester, decreased due to transesterification reactions. The rate data correlated well to a Taft equation in which inductive effects were more important than steric effects, provided the equation included a term to account for the hydrogens on the α -carbon atoms. Reaction kinetics for ethyl acetate hydrogenolysis were found to be first order in hydrogen and -0.5 order in ethyl acetate.

INTRODUCTION

In a previous paper (1) the structure–reactivity dependence has been discussed for the hydrogenolysis of a range of alkyl formates over a copper chromite catalyst.



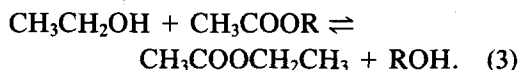
It was found that the rate of hydrogenolysis of alkyl formates decreased with increasing molecular weight and that the selectivity to methanol was significantly decreased by a transesterification reaction with the original formate.



This reaction exhibited a rapid equilibrium, the position of which was only slightly influenced by temperature over the range studied.

Like the formates, the hydrogenolysis of aliphatic acetates has been very little studied. Indeed, mention of acetate hydrogenol-

ysis to ethanol can generally only be found in the patent literature. Lazier (2), in describing a process for producing alcohols from esters of nonaromatic carboxylic acids, used ethyl acetate, *n*-butyl acetate, and ethyl *n*-butanoate as starting materials. The major components of the catalyst included copper oxide and zinc oxide, with temperatures of 320–400°C and pressures of 17–25 MPa being employed. Similar reactions were studied by Schmidt (3) using comparable temperatures, atmospheric pressure and a copper-, nickel-, or cobalt-based catalyst. More recently, Grey *et al.* (4) described a soluble ruthenium complex catalyst for the hydrogenation of carboxylic acid esters to their corresponding alcohols. Much milder conditions were employed (90°C, 720 kPa) and small amounts of ethyl acetate, together with methanol and ethanol, were observed when methyl acetate was used as the starting material. This was explained in terms of transesterification by reaction



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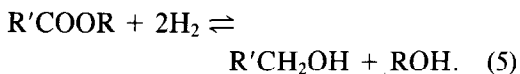
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Zdrzil (5, 6) has studied extensively the hydrogenolysis of aliphatic esters over a rhodium catalyst. In those studies, the products of hydrogenolysis were the corresponding alkane and acid according to



While this reaction involves splitting of a different bond in the molecule, the trends observed with a series of esters are noteworthy. It was found that the rate of hydrogenolysis increased with increasing molecular weight of the molecule for any given series of esters with the same acyl group. This was related primarily to electron directing effects and results were correlated to a Taft equation.

This paper extends the study of the hydrogenolysis of esters to alcohols by investigating a range of aliphatic acetates together with methyl propanoate and methyl butanoate over copper-based catalysts. The esters react according to the general equation



EXPERIMENTAL

The catalyst mainly used in this study was Raney copper, which was prepared from a commercial 50 wt% Cu, 50 wt% Al copper alloy (CuAl₂). The preparation involved leaching particles (350–500 μm) of the alloy with a 20 wt% sodium hydroxide solution at 50°C for 4 h as described by Marsden *et al.* (7). The resultant catalyst had a total surface area of 19.8 m²/g and a copper surface area of 17.3 m²/g based on nitrous oxide chemisorption as described by Evans *et al.* (8). The catalyst was stored under water at 3°C until used.

The esters used were obtained from the Ajax Chemical Company and Fluka Chemicals and were of purity greater than 99%. Impurities were mostly water and the parent alcohol.

Measurements of activity and selectivity were performed using a standard flow apparatus. The catalyst (0.5–5 cm³) was contained in a 9-mm-i.d. U-tube reactor immersed in a vigorously stirred molten salt bath, the temperature of which was controlled to ±1°C. High purity hydrogen and helium (Commonwealth Industrial Gases) were metered to a preheater maintained at the same temperature as the reactor and esters were introduced to the stream of H₂/He mixture by a metering pump (Eldex A-30-S-2). The gas streams leaving the preheater and reactor were sampled sequentially using a 10 port valve (Valco) and analyzed with a Gow-Mac Series 550 gas chromatograph equipped with thermal conductivity detectors. Chromatographic columns and operating conditions varied widely depending upon the ester used. A 2-m × 0.25-in. Porapak Q column and hydrogen carrier gas flow rates of 35–45 cm³ min⁻¹ were used at 130–200°C for all acetates except isobutyl. For isobutyl acetate, methyl propanoate, and methyl butanoate a 2-m × 0.25-in. Porapak PS column was used at temperatures between 140 and 240°C with 40–50 cm³ min⁻¹ of hydrogen carrier gas.

All measurements were made with the reactor operating at essentially atmospheric pressure.

Relative molar response factors for all reactants and products were measured experimentally using accurately prepared liquid standards and were found to agree with those published by Messner *et al.* (9). The accuracy of the analytical method was checked using a mass balance; agreement was always within ±5%.

Conversion has been defined as moles of ester converted per mole of ester introduced. In order to account for the change in number of moles in reaction (5), selectivity has been defined so that total selectivity of all carbon containing products equals 100%. Thus, for the reaction of ethyl acetate, selectivity is defined as (here 2 mol of ethanol are initially produced)

$$S_{\text{Ethanol}} = \frac{\frac{1}{2} (\text{moles ethanol produced})}{(\text{moles CH}_3\text{COOCH}_2\text{CH}_3 \text{ reacted})} \times 100$$

$$S_{\text{Acetaldehyde}} = \frac{\frac{1}{2} (\text{moles acetaldehyde produced})}{(\text{moles CH}_3\text{COOCH}_2\text{CH}_3 \text{ reacted})} \times 100$$

$$S_{\text{CO+CH}_4} = \frac{\frac{1}{4} (\text{moles CO and CH}_4 \text{ produced})}{(\text{moles CH}_3\text{COOCH}_2\text{CH}_3 \text{ reacted})} \times 100.$$

For the other acetates, the selectivity to ethanol is decreased due to the transesterification reaction (3). In this case:

$$S_{\text{Ethanol}} = \frac{\frac{1}{2} \left(\frac{\text{moles EtOH produced by reaction (5)}}{\text{reaction (5)}} \right) - \left(\frac{\text{moles EtOH reacted by reaction (3)}}{\text{reaction (3)}} \right)}{(\text{moles R}'\text{COOR reacted})} \times 100$$

$$S_{\text{Alcohol}} = \frac{\frac{1}{2} \left(\frac{\text{moles EtOH produced by reaction (5)}}{\text{reaction (5)}} \right) + \left(\frac{\text{moles EtOH reacted by reaction (3)}}{\text{reaction (3)}} \right)}{(\text{moles R}'\text{COOR reacted})} \times 100$$

$$S_{\text{Ethyl acetate}} = \frac{\text{moles EtOH reacted by reaction (3)}}{(\text{moles R}'\text{COOR reacted})} \times 100.$$

The moles of ethanol consumed by reaction (3) was obtained from the moles of ethyl acetate produced by this reaction.

RESULTS AND DISCUSSION

1. Product Distribution for Ethyl Acetate Hydrogenolysis

In initial screening tests the activity and selectivity range of hydrogenation catalysts for ester hydrogenolysis were determined. Raney copper and two copper chromites (Harshaw 1808:43% CuO balance Cr₂O₃ and Harshaw 0203:80% CuO balance Cr₂O₃) exhibited high activity and selectivity. A 9.5% Cu-0.5% Ni/Al₂O₃ catalyst (Dow K) and 1% Pd/Al₂O₃ exhibited some initial activity at 260°C but this declined to zero over 30 min. Raney cobalt, Raney nickel, and 3.4% NiO-19.8% MoO/Al₂O₃ had considerable activity but low selectivity for ethanol production. It would appear that metallic copper is a necessary catalytic component to accomplish the desired ester hydrogenolysis.

On a mass basis the activity of the Raney copper was much greater than that of either copper chromite, so that the former was chosen for detailed investigation. Conver-

sion and product distribution as a function of temperature, hydrogen/ester ratio and residence time are shown in Figs. 1, 2, and 3. Under all conditions ethanol was the dominant product with some acetaldehyde and small amounts of CH₄ and CO being

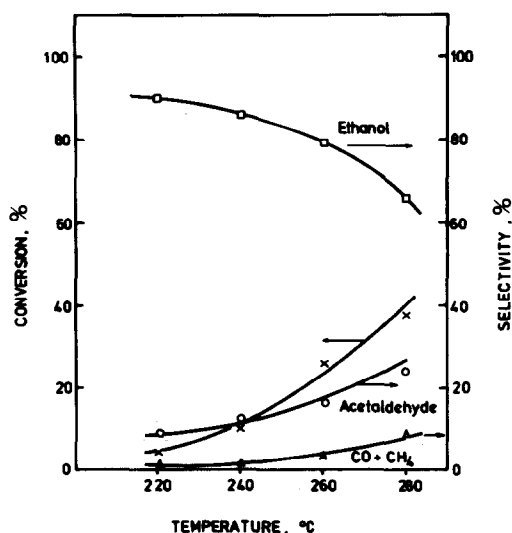


FIG. 1. Conversion of ethyl acetate and selectivity as a function of temperature. Conditions: 1 cm³ Raney copper, 0.1 cm³ min⁻¹ CH₃COOC₂H₅, ratio H₂:CH₃COOC₂H₅ = 20.

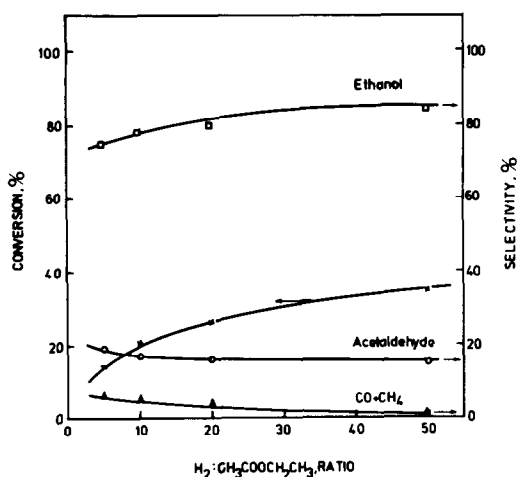
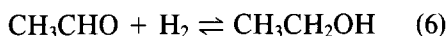


FIG. 2. Conversion of ethyl acetate and selectivity as a function of $H_2 : CH_3COOC_2H_5$ ratio. Conditions: 1 cm^3 Raney copper, $0.1 \text{ cm}^3 \text{ min}^{-1}$ $CH_3COOC_2H_5$, 260°C .

produced at high conversions. In each case, the ratio CH_3CH_2OH/CH_3CHO varied with temperature and hydrogen pressure in the direction expected if the reaction



was at equilibrium. This can be clearly seen from the comparison in Table 1 of the $\log K_t$,

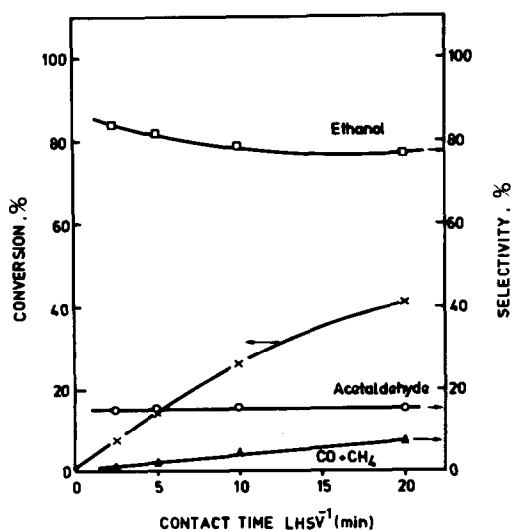


FIG. 3. Conversion of ethyl acetate and selectivity as a function of residence time. Conditions: 1 cm^3 Raney copper, $H_2 : CH_3COOC_2H_5 = 20$, 260°C .

TABLE 1

Comparison of $\log K_t$ and $\log Q_p$ for Reaction (6) during Ethyl Acetate Hydrogenolysis

Conditions	Temperature ($^\circ\text{C}$)	Ethyl acetate conversion (%)	$\log K_t$	$\log Q_p$
As per Fig. 1	220	5	2.8	2.3
	240	10	2.1	2.0
	260	23	1.6	1.6
	280	38	0.9	1.1
As per Fig. 2	260	14	1.6	1.5
	260	21	1.6	1.6
	260	28	1.6	1.7
	260	44	1.6	1.9
As per Fig. 3	260	7	1.6	1.8
	260	16	1.6	1.7
	260	26	1.6	1.7
	260	41	1.6	1.7

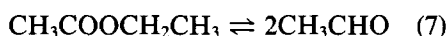
(derived from thermodynamic data taking heat capacities into account) and the quantity $\log Q_p = \log[P_{CH_3CH_2OH}/P_{CH_3CHO}P_{H_2}]$ calculated from the product distribution for reaction (6). Unfortunately $\log K_t$ values are subject to systematic errors of ± 1 (arising from the limited accuracy of available thermodynamic data) so that firm conclusions regarding equilibration cannot be drawn by direct comparison. Nonetheless, the parallel dependence of each quantity on temperature and the constancy of the experimentally derived quantities for all data at 260°C strongly favors complete equilibration. Similar calculations for the ethyl acetate hydrogenolysis reaction showed that equilibrium was never achieved.

Further support for equilibration was obtained by the experiments detailed in Table 2 in which ethanol was fed with varying hydrogen pressures and temperatures. The calculated values for $\log Q_p$ were identical to those obtained when ethyl acetate was the starting compound indicating that reaction (-6) was rapid. Similarly, measurements of the rate of hydrogenation of acetaldehyde (reaction (+6)) at 220°C showed it to be 500–1000 times as fast as ethyl acetate hydrogenolysis under similar conditions. Since both reactions (+6) and (-6) were rapid, equilibrium is expected to be attained.

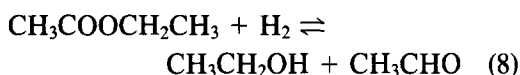
TABLE 2
Comparison of $\log K_r$ and $\log Q_p$ for Reaction (6) Using Ethanol at Varying Hydrogen Pressures and Temperatures

Temperature (°C)	Outlet pressures (atm)				$\log K_r$	$\log Q_p$
	H ₂	CH ₃ CH ₂ OH	CH ₃ CHO	CH ₃ COOCH ₂ CH ₃		
260	0.31	0.39	0.26	0.028	1.6	1.57
260	0.83	0.121	0.03	0.0088	1.6	1.58
260	0.92	0.057	0.011	0.0051	1.6	1.73
260	0.97	0.026	0.0046	0.0009	1.6	1.76
260	0.92	0.062	0.012	0.0055	1.6	1.73
260	0.92	0.067	0.012	0.0030	1.6	1.82
260	0.92	0.971	0.012	0.0016	1.6	1.99
220	0.92	0.0721	0.003	0.0011	2.8	3.2
240	0.92	0.068	0.0072	0.0015	2.1	2.3
260	0.92	0.062	0.012	0.0051	1.6	1.7
280	0.92	0.0169	0.0169	0.0055	0.9	1.0

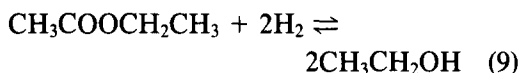
Given that equilibrium did hold for reaction (6) then, in the absence of isotopic tracer experiments, it was not possible to decide if the primary cleavage reaction involved



or



or



Similarly it is not possible to decide the origin of the minor products CH₄ and CO. The process



assumed by other workers to account for by-product formation during ethanol dehydrogenation (10, 11) would seem the most likely given the simplicity of the internal rearrangement required. However, experiments at 200°C in which acetaldehyde was fed in the absence of hydrogen yielded only minor amounts of ethyl acetate with virtu-

ally no CH₄ or CO. This result tends to suggest the latter are derived from the ester or alcohol.

2. Kinetics of Ethyl Acetate Hydrogenolysis

It is clear from Fig. 2 that conversion increases with H₂/ester ratio so the reaction order in hydrogen must be greater than that in ester. Actual kinetic orders in each reactant were determined at 210, 220, and 230°C under differential conditions. At the temperatures employed, experimental rates showed that effectiveness factors were greater than 0.99. Since conversion was kept low (<10%), the formation of byproducts (carbon monoxide and methane) was negligible and the amount of acetaldehyde was small. Product inhibition was assumed to be negligible.

Experiments were performed by fixing the partial pressure of one reactant and measuring the rate of ethyl acetate hydrogenolysis at varying partial pressures of the other reactant. Where a diluent was required, helium was used. From the slope of the resultant log rate vs log partial pressure plot, a first-order dependency with respect to hydrogen and a -0.5-order dependency

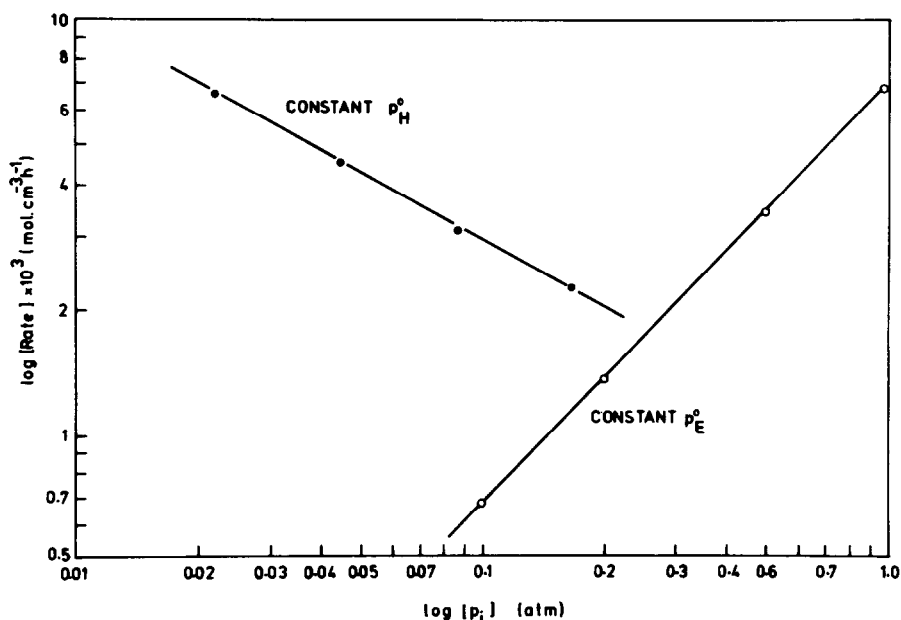


FIG. 4. Rate of hydrogenolysis of ethyl acetate versus partial pressure of reactants at constant initial ethyl acetate pressure (p_E^0) and constant initial hydrogen pressure (p_H^0). Conditions: 1 cm³ Raney copper, 0.1 cm³ min⁻¹ CH₃COOC₂H₅, 220°C.

with respect to ethyl acetate was found (Fig. 4). Reaction orders obtained at the three temperatures studied differed by less than 5% from the values of 1 and -0.5.

Additional rate data were obtained at varying ethyl acetate and hydrogen pressures so that the range of pressures covered was 2.2 to 33.7 kPa for ethyl acetate and 10.1 to 99.1 kPa for hydrogen. In all cases a stoichiometric or excess ratio of hydrogen to ethyl acetate ($R > 2$) was maintained.

All data were then correlated by a power

rate law expression of the form

$$r = Ae^{-E/RT}P_{\text{EtOAc}}^x P_{\text{H}_2}^y \quad (11)$$

where r is the rate of ethyl acetate disappearance (mole cm⁻³ h⁻¹) and p_i is the partial pressure (atm) of reactant i (1 atm = 101.3 kPa). These data were fitted to a linearized form of Eq. (11) using least-square multiple regression analysis. The resulting values of the model parameters were obtained

Order with respect to ethyl acetate
Order with respect to hydrogen
Activation energy
Preexponential factor

$$\begin{aligned} x &= -0.505 \\ y &= 1.03 \\ E &= 88.0 \text{ kJ mol}^{-1} \\ A &= 2.73 \times 10^6 \text{ mol cm}^{-3} \text{ h}^{-1} \text{ atm}^{-0.52} \end{aligned}$$

The regression coefficient r obtained from the analysis was 0.993 and results predicted on the basis of Eq. (11) were in good agreement with experimental rates of reaction (Fig. 5).

Attempts were then made to fit these ki-

netic results to a Langmuir-Hinshelwood model. After consideration of many alternatives only three basic models could be conceived to be correct, due to the limitation of the -0.5 order with respect to ethyl acetate, which implies dissociative adsorp-

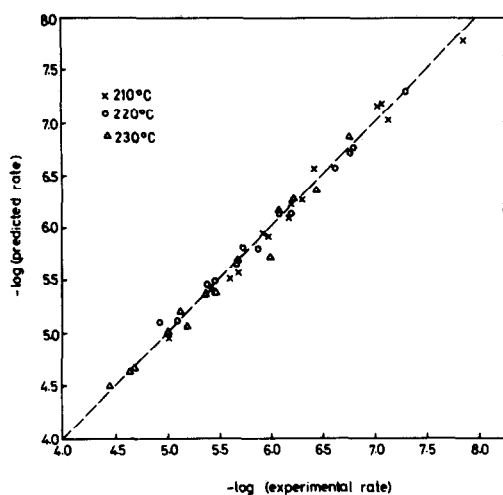
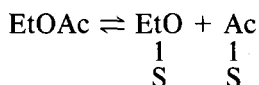


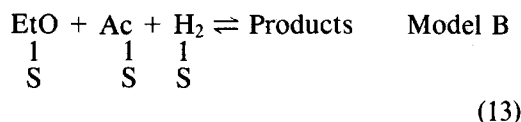
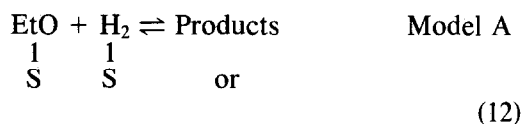
FIG. 5. Predicted versus experimental rate for ethyl acetate hydrogenolysis. Conditions: Raney copper, $0.1 \text{ cm}^3 \text{ min}^{-1} \text{ CH}_3\text{COOC}_2\text{H}_5$, 210, 220, and 230°C.

tion. If ethyl acetate dissociates as

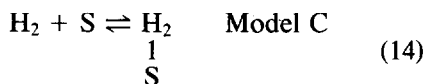


where 1 represents an adsorbed site, then

reaction of adsorbed molecular hydrogen via



will result in mathematically correct rate expressions. Alternatively, if the rate of hydrogen adsorption is the slow step, i.e.,

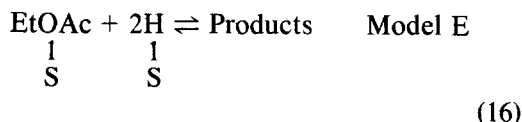


then first-order and -0.5 -order kinetics can also be predicted.

The Langmuir-Hinshelwood expressions obtained from the above three models were linearized and fitted by least-square multiple regression. While the data could

be well-fitted to all the models with correlation coefficients >0.99 , the parameter estimates in most cases led to negative values for the hydrogen adsorption coefficient, K_H . Attempts to obtain better parameter estimates by using restrained regression, limited data or deletion of the $K_H P_H$ term in the denominator of the model were not successful. However, in all cases, the value of K_H was always very much smaller than the adsorption coefficient value for ethyl acetate, K_E . This is to be expected as copper is known to be a poor chemisorber of hydrogen (13). To test which model is correct would involve the measurement of rate data in a region where $K_H P_H > \sqrt{K_E P_E}$. Given the relative magnitudes of K_E and K_H , this would present severe experimental difficulties.

One of the problems with the above models is that they all involve adsorption of molecular hydrogen whereas atomic hydrogen would normally be expected. As a result approximately 20 further Langmuir-Hinshelwood models were evaluated. Of these only 2 gave positive coefficients



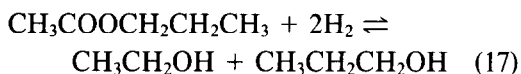
However, the Arrhenius dependency of the rate constant, k , was very poor in both cases, while the value of K_E remained essentially constant over the three temperatures used. As was observed for models A, B, and C, the values of K_H obtained for models D and E were a factor of 500–1000 smaller than the corresponding K_E values.

Overall therefore, it appears that the rate determining step in the hydrogenolysis of ethyl acetate involves the surface reaction of adsorbed ethyl acetate or a dissociated fragment with adsorbed hydrogen. The surface coverage of the ester or its adsorbed

fragment is very high compared to the hydrogen coverage.

3. Hydrogenolysis of Other Esters

The hydrogenolysis of a series of aliphatic acetates and of methyl propanoate and methyl butanoate was studied at 220°C over the Raney copper catalyst. Unfortunately *sec*-butyl acetate and *tert*-butyl acetate could not be used as they decomposed thermally (14). For each ester a product spectrum was obtained at varying conversions by varying the space velocity. The resultant selectivity versus conversion plots were essentially the same for all esters. An example is shown in Fig. 6 for the hydrogenolysis of *n*-propyl acetate. For this acetate the desired reaction is



and as expected, the selectivity to propanol and ethanol is 50% at low conversion. At higher conversions, the selectivity to ethanol is decreased due to the transesterification of the *n*-propyl acetate and ethanol

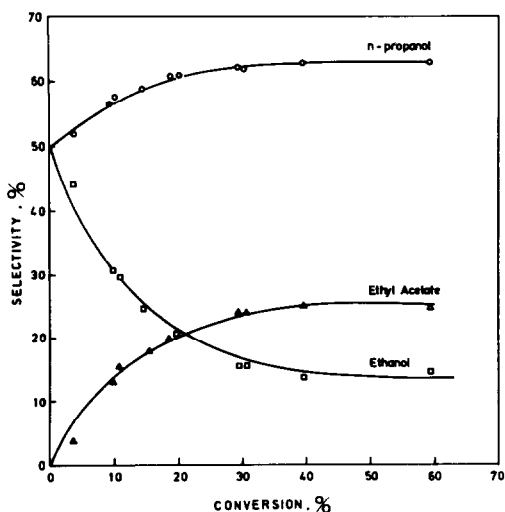
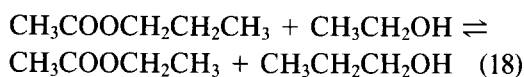


Fig. 6. Selectivity versus conversion for *n*-propyl acetate hydrogenolysis. Conditions: Raney copper, $\text{H}_2 : \text{CH}_3\text{COOC}_3\text{H}_7 = 20$, 220°C.



and the selectivity to *n*-propanol increases. Similar effects were seen with all acetates except, of course, ethyl acetate which does not undergo a detectable transesterification reaction.

Experiments performed with equimolar mixtures of methyl acetate and ethanol in a reactor packed with glass beads in place of the catalyst proved the transesterification reaction to be uncatalyzed, at least in part. The extent of the reaction was 0.04% of equilibrium conversion at 220°C and 0.17% at 260°C, respectively. When the glass beads were replaced by 6.5 g of high surface area (300 m² g⁻¹) silica gel the conversion rose to 6.1% at 220°C and 9.4% at 260°C. In this case the increased activity may be due to the weak acidic nature of the silica but more likely due to the increased surface area for the uncatalyzed reaction to take place.

Copper catalysts were found to promote the transesterification reaction beyond that observed over inert material but attempts to measure quantitatively the extent of promotion failed. Equimolar mixtures of ethanol and alkyl acetates were passed over Raney copper at 260°C (reaction (3)) to yield ca. 12–15% of equilibrium conversion. However, both the ethanol and the product alcohol were dehydrogenated to the corresponding aldehyde.

Transesterification was also found to reduce selectivity in the hydrogenolysis of alkyl formates (1), but the reaction is less important in the case of the acetates. The transesterification of alkyl formates with methanol has been found to be sufficiently rapid at 120°C to reach equilibrium regardless of the concentration or residence time used (1). In the hydrogenolysis of the acetates the transesterification reaction was never greater than 50% of the expected equilibrium value (15). High levels of transesterification were only observed at very high conversions of the acetates. The fact

that the transesterification for the acetates was much slower than for the formates can be seen from Fig. 7. The transesterification quotient for ethyl formate was always at its equilibrium value, while the quotient for the acetates only reached ca. 0.6 at 70% conversion.

The amounts of acetaldehyde from the dehydrogenation of ethanol and other aldehydes from the dehydrogenation of methanol, propanol, etc. formed under reaction conditions (220°C) were always very small. Typically, at conversions of ca. 40%, they accounted for no more than 0.5 mol% of the product.

4. Kinetic Effects in the Hydrogenolysis of All Esters

The rates of hydrogenolysis of alkyl acetates, methyl propanoate, and methyl butanoate were determined over the Raney copper catalyst at 220°C. Measurements were based on differential conversions which were less than 10%. Results are shown in Table 3, where column 1 lists the overall

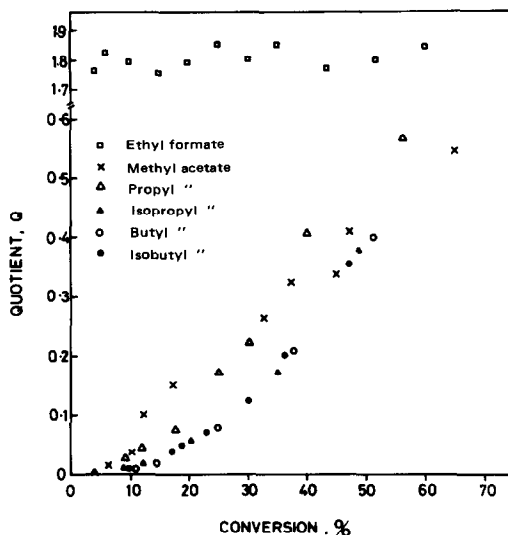


FIG. 7. Transesterification reaction quotient versus conversion for alkyl acetates and ethyl formate. Alkyl acetates: $Q = (\text{ROH})(\text{CH}_3\text{COOC}_2\text{H}_5)/(\text{CH}_3\text{COOR})(\text{C}_2\text{H}_5\text{OH})$, Raney copper, $\text{H}_2:\text{CH}_3\text{COOR} = 20$, 220°C. Ethyl formate: $Q = (\text{C}_2\text{H}_5\text{OH})(\text{HCOOCH}_3)/(\text{HCOOC}_2\text{H}_5)(\text{CH}_3\text{OH})$, Raney copper, $\text{H}_2:\text{HCOOC}_2\text{H}_5 = 10$, 160°C.

TABLE 3

Ester Hydrogenolysis Rates at 220°C over Raney Copper Catalyst with H_2 : Ester = 20

Acetate	Total rate $\times 10^3$ (mol h ⁻¹ cm ⁻³)	Estimated hydrogenolysis rate $\times 10^3$ (mol h ⁻¹ cm ⁻³)
Methyl	7.9	6.0
Ethyl	6.7	6.7
<i>n</i> -Propyl	11.6	9.9
Isopropyl	6.2	5.6
<i>n</i> -Butyl	12.6	11.2
Isobutyl	15.7	13.6
Methyl propanoate	4.1	3.2
Methyl butanoate	7.1	5.0

rate of ester disappearance. Since some ester is also lost in the transesterification reaction, the data has also been recalculated taking into account the amount of ethyl acetate and alcohol formed by this reaction. This is shown in column 2 and is termed the estimated rate of hydrogenolysis.

For the series of *n*-alkyl acetates, the rate of hydrogenolysis increases as the size of the alkyl group increases. Furthermore, the addition of a methyl group on the alkoxy carbon (isopropyl) hinders the hydrogenolysis rate while branching on the second alkoxy carbon (isobutyl) increases the rate.

The rate data were then fitted to the Taft equation in an attempt to correlate relative reactivities with inductive (σ^*), steric (E_s), and hyperconjugative (Δn) constants (16). Correlation was poor when only the inductive and/or the steric parameters were included. However, when the term $\Delta n = 6 - \Sigma n$ was introduced to account for the α hydrogens in the molecule, a reasonable fit was obtained for the equation

$$\log R_i = p^*\Sigma\sigma^* + h\Delta n + C \quad (19)$$

where R_i = rate of hydrogenolysis of acetate relative to methyl acetate, $\Delta n = 6 - \Sigma n$ where n = number of α hydrogens on alkoxy and acyl carbons, and $\Sigma\sigma^*$ = sum of inductive constants of R' and R groups in the ester R'COOR, i.e., $\Sigma\sigma^* = \sigma^*(\text{R}') + \sigma^*(\text{R})$.

By least-square multiple regression it was found that $p^* = -22.4$, $h = -2.2$, $C = 0.0251$, and correlation coefficient, $r = 0.96$

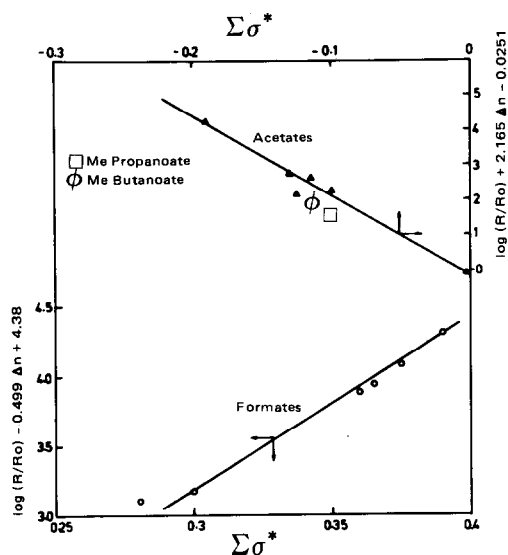


Fig. 8. Correlation of relative reactivities of acetates according to Eq. (19) and of formates according to Eq. (20).

(Fig. 8). While the value of p^* is high when compared with values obtained in liquid-phase homogeneous reactions, it is nevertheless in agreement with the value of $p^* = -25.7$ observed by Zdrzil (6) for the hydrogenolysis of acetates over a rhodium catalyst. Zdrzil suggests that the high value is due to the fact that the constant is the sum of the slopes of two consecutive steps; equilibrium adsorption followed by surface reaction.

Introduction of the steric constants into the Eq. (19) did not improve the fit of the data and so it would appear that the hydrogenolysis of acetates to alcohols, as the hydrogenolysis of acetates to acetic acid and alkanes (6), is mostly influenced by the inductive and mesomeric effects of the acetates. Further, since both constants (p^* and h) in Eq. (19) are of the same sign, then an increase in electron density is favorable for hydrogenolysis.

The rates in Table 3 for methyl propanoate and methyl butanoate were used to tabulate their relative reaction rates (16) according to Eq. (19) and these also appear in Fig. 8. While the two points do not fit the line very well, they still exhibit the same

trend as the acetates. This infers that the addition of methyl (CH_3) groups to the ester on either the acyl or alkoxy carbon does not appear to have any effect on the mechanism of reaction but merely influences its relative rate of hydrogenolysis depending upon its inductive and hyperconjugative effects.

As a result of these observations, the applicability of the Taft plot to the hydrogenolysis of alkyl formates to methanol was considered. Formates have only one hydrogen attached to the acyl carbon atom and so present a completely different situation to that of the acetates, propanoates, etc. Methyl formate has been excluded from the reaction series as its reactivity appears to be completely different. This may be due to the fact that it does not enter into any detectable transesterification reaction but more likely due to deactivation problems associated with methyl formate hydrogenolysis (17) as compared to other formates.

The hydrogenolysis rate data at 130°C previously presented for alkyl formates (1) were fitted to the Taft equation using the appropriate constants (16). Like the acetates, the formate activities do not correlate well with the inductive or steric constants alone. However, a good fit was obtained with the equation

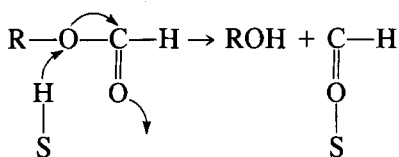
$$\log R_j = p^* \Sigma \sigma^* + h \Delta n' + K \quad (20)$$

where R_j = hydrogenolysis of formate j relative to methyl formate, $\Delta n' = 3 - \Sigma n$ where n = number of α hydrogens on the alkoxy carbon, and $p^* = 10.88$, $h = 0.499$, and $K = -4.38$ with regression coefficient $r = 0.96$ (Fig. 8).

A slight improvement was noted when the steric constants were added to Eq. (20), although the values of p^* , h , and K were not changed markedly (<8%).

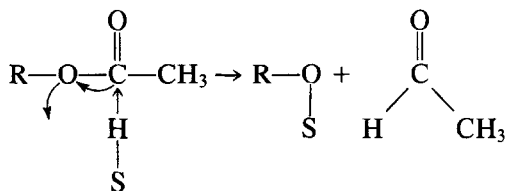
Even allowing for the fact that the Taft equation is not necessarily applicable to gas phase heterogeneous reactions, the large difference in p^* (both in magnitude and sign)

between the acetates and formates implies that a totally different mechanism is involved in each case. Generally, a negative p^* is associated with a positively charged intermediate and vice versa. While it is not the purpose of this paper to propose definitive mechanisms for ester hydrogenolysis, schemes can be written which are consistent with the observed results. These include, for example, for formates



SCHEME I

and for acetates



SCHEME II

While there is no absolute proof for either of the above schemes, Scheme II involves the production of acetaldehyde which is detected among the reaction products, while Scheme I does not involve the equivalent production formaldehyde; formaldehyde has not been detected in formate hydrogenolysis experiments. Experiments designed to explore reaction mechanisms are currently in progress.

ACKNOWLEDGMENTS

Funding of the project under the Australian Research Grants Scheme is gratefully acknowledged.

Support was provided under the National Energy, Research, Development, and Demonstration Programme administered by the Commonwealth Department of National Development.

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