

Gas phase reaction of hydrogen with carboxyl and carbonyl functions in aromatic systems over Ni/SiO₂

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Abstract

The hydrogen treatment of methanolic and 2-propanolic solutions of benzoic and *o*-toluic acid in the gas phase was studied over a Ni/SiO₂ catalyst. The reactions were conducted in the absence of diffusion limitations and reproducible turnover frequencies are presented. The products generated resulted from the hydrogenolysis and esterification (in the case of methanolic solutions) of the substituent –COOH group and from the hydrogenolytic cleavage of the aryl–carboxyl C–C bond where the aromatic ring remained intact. Esterification proceeded at a greater rate on the pure silica support but was not observed when 2-propanol was used as solvent; apparent activation energies for the esterification step are given. The temperature dependencies of the specific rates and product selectivities are shown and these reveal the increasing predominance of hydrogen cleavage as the reaction temperature was increased. The presence of the *ortho*-substituted methyl group served to lower the reactivity of the carboxyl function due to steric and electronic effects which are discussed in terms of reactant(s) adsorption/activation. The reaction of methylbenzoate and methyl 2-methylbenzoate over the same catalyst was investigated and the overall reaction pathway is identified. The reactivity of the carbonyl group in aromatic aldehydes under identical reaction conditions was found to be considerably higher where substituent hydrogenolysis rather than substituent cleavage was promoted to a greater degree. The response of both carbonyl and carboxyl groups in the transformation of 2-carboxybenzaldehyde is used to further illustrate the higher reactivity of the carbonyl group. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Ni/SiO₂; Aromatic acids; Hydrogenolysis; Esterification; Electronic effects; 2-Carboxybenzaldehyde

1. Introduction

The selective heterogeneous hydrogenation of organic compounds that possess more than one unsaturated function has become an increas-

ingly challenging area in catalysis research [1]. The hydrogenation of aromatic acids, for instance, is problematic in that either or both the aromatic ring or the carboxyl substituent may be attacked. Aromatic acids are however generally more facile in reduction than aliphatic acids [2]. Palladium is used industrially for the conversion of benzoic acid to hexahydrobenzoic acid, a nylon-6 intermediate [3,4]. Reduction of the benzene ring has been achieved catalytically by

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platinum oxide in alcoholic media [5] and electrochemically at a Pt electrode [6]. The hydrogenation of benzoic acid to benzaldehyde is also of commercial significance as aromatic aldehydes are important intermediates in the production of pharmaceuticals, agrochemicals and perfumes and this process has been the subject of a number of patents [7–11]. In addition, electrochemical reduction has also been shown to produce the aldehyde as well as the dimer and benzil [12,13]. Exclusive reduction to the aromatic aldehyde has proved very difficult but Yokoyama et al. [14] have recently developed a modified zirconia catalyst that hydrogenates benzoic acid to benzaldehyde with selectivities in excess of 95%. Benzaldehyde, in turn, has been selectively hydrogenated to benzyl alcohol in a number of liquid phase homogeneous [15,16] and heterogeneous [17–19] catalytic systems. In the case of the homogeneous reduction of benzaldehyde using nickel 2-ethylhexanoates– Et_3Al , hydrogenolysis to toluene and disproportionation to benzylbenzoate has been shown to occur in addition to benzyl alcohol formation [20].

To the best of the author's knowledge, the gas phase hydrogen treatment of benzoic acid over supported nickel catalysts has not been reported. The known hydrogenolysis activity of nickel systems [21] can however be expected to have a bearing on product selectivity. All functional groups, with the exception of acids, esters and amides are hydrogenated in preference to the benzene ring over Raney nickel in the temperature range $373 \text{ K} \leq T \leq 423 \text{ K}$ [22]. Alkyl substitution in the benzene ring can have an appreciable effect on reactivity [3,21,23–25] and the rate of the liquid phase hydrogenation of a range of methyl- and methoxybenzoic acids over Adams platinum was shown, in a very early paper [26], to decrease with an increasing number of substituents. As part of a programme of research dealing with the catalytic hydrogenation/hydrogenolysis action of Ni/SiO_2 , the effect of temperature ($413 \text{ K} \leq T \leq 603 \text{ K}$) on the product distribution resulting from the hydrogen

treatment of benzoic acid was examined and reproducible specific activities and selectivities are reported in this paper. The effect of *ortho*-methyl substitution on overall reactivity and selectivity has also been considered and the reaction of the respective aromatic aldehydes and 2-carboxybenzaldehyde (which bears both a carbonyl and carboxyl group in the *ortho* position) under identical experimental conditions are presented.

2. Experimental

A nickel-dilute (1.5% w/w) silica catalyst was prepared by homogeneous precipitation/deposition and characterised as described in some detail elsewhere [25,27]. The hydrated catalyst precursor was reduced, without a precalcination step, by heating in a $150 \text{ cm}^3 \text{ min}^{-1}$ stream of dry hydrogen (99.9%) at a fixed rate of 5 K min^{-1} to a final temperature of $723 \pm 1 \text{ K}$ which was maintained for 18 h. The nickel metal dispersion, reproducible to better than $\pm 3\%$, expressed as $(\text{Ni}_{\text{surface}}/\text{Ni}_{\text{total}}) \times 100\%$, equals 73% which represents a surface weighted average crystallite diameter of 1.4 nm. All the catalytic reactions were carried out under atmospheric pressure in a fixed bed glass reactor (i.d. = 15 mm) over the temperature range $413 \text{ K} \leq T \leq 603 \text{ K}$. The catalyst was supported between a glass frit and a layer of glass beads, thereby ensuring that the aromatic reactant was vapourised and reached the reaction temperature before contacting the catalyst bed. The reactor temperature was monitored by a thermocouple inserted in a thermowell within the catalyst bed; reactor temperature was constant to within $\pm 1 \text{ K}$. A KDS 100 Single Channel Infusion pump was carefully calibrated and used to deliver the aromatic feed via a syringe at fixed rates and the aromatic vapour was carried through the catalyst bed in a stream of purified hydrogen; the reactor effluent was frozen in a liquid nitrogen trap for subsequent analysis. Methanolic and 2-propanolic solutions of benzoic and *o*-

toluic acid and, for comparative purposes, undiluted benzaldehyde, *o*-tolualdehyde, methylbenzoate and methyl 2-methyl benzoate and methanolic/2-propanolic solutions of 2-carboxybenzaldehyde were used as feedstock where the aromatic reactant concentration was in the range 1.5×10^{-3} – 7.3×10^{-3} mol h⁻¹. The reactions were conducted at a space velocity of 2×10^3 h⁻¹ and in the overall *W/F* range 40–250 g mol⁻¹ h where *W* is the weight of activated catalyst and *F* is the flow rate of aromatic. Reaction rates measured over this *W/F* range, where both *W* and *F* were independently varied, were constant to $\pm 7\%$ at a particular *W/F* value. Steady state conversions were kept below 25 mol% by varying *W* in order to minimize heat and transfer effects. Conversions were within $\pm 4\%$ using three separate sets of catalysts sieved in the mesh ranges 75–125, 125–150 and 150–300 μm . The intermediate catalyst particle size range 125–150 μm was adopted for all catalytic measurements wherein intraparticle diffusion contributions can be considered negligible. The catalytic reactor system and product analysis procedure is fully described elsewhere [28]. Mol% conversion of the aromatic is defined as $(m_i - m_o)/(m_i) \times 100$ where m_i is the initial concentration or number of moles of reactant entering the reactor per unit time and m_o is the number of moles of reactant exiting the reactor per unit time. Molar selectivity in terms of product *x* is defined by $m_x/m_{\text{tot}} \times 100$ where m_{tot} is the total number of moles of product. All the catalytic data presented in this paper were obtained at steady state and represent the average of at least five separate test samples where the overall reproducibility was better than $\pm 5\%$. Each reactant (benzoic acid/benzaldehyde/*o*-toluic acid 99 + %, methylbenzoate/methyl 2-methylbenzoate 99%, *o*-tolualdehyde 98%, 2-carboxybenzaldehyde 97%, Aldrich) and both alcohol solvents (Aldrich, A.C.S. spectrophotometric grade) were thoroughly degassed by purging with purified helium and stored over activated molecular sieve type 5 A.

3. Results and discussion

3.1. Effect of reaction temperature

3.1.1. Catalytic activity

The gas phase hydrogen treatment of benzoic acid in methanol over Ni/SiO₂ in the temperature range $413 \text{ K} \leq T \leq 603 \text{ K}$ generated products resulting from substituent esterification (methylbenzoate), hydrogenolysis of the substituent C–OH and C=O bonds (toluene) and hydrogenolysis of the aryl carbon-substituent carbon bond (benzene). The conversion of *o*-toluic acid yielded the corresponding products, namely methyl 2-methylbenzoate, *o*-xylene and toluene as well as secondary products, methylbenzoate and benzene, which were formed at temperatures in excess of 558 K. In every instance the aromatic ring remained intact. The effect of temperature on the turnover frequency (TOF), the number of benzoic acid molecules converted per metal site per second, to the three identified products is illustrated in Fig. 1a. Maintenance of activity was verified by ascending and subsequent descending temperature sequences over the entire temperature interval. At $T \leq 458 \text{ K}$, methylbenzoate was the only detected product and its rate of formation was observed to increase with increasing temperature. Hydrogenolysis of benzoic acid to toluene was initiated at $T \geq 460 \text{ K}$ and also increased upon elevating the reaction temperature while benzene formation, which was only appreciable at temperatures in excess of 483 K, was the major product at $T > 553 \text{ K}$. The variation of the TOF of *o*-toluic acid with temperature, illustrated in Fig. 1b, exhibits markedly different trends. Esterification with methanol produced methyl 2-methylbenzoate which, in this instance, passed through a maximum (T_{max}) at 573 K. Hydrogenolysis of the carboxyl function to form *o*-xylene likewise attained a maximum but at a lower temperature ($T_{\text{max}} = 538 \text{ K}$). Benzene and methylbenzoate were detected in the product mixtures at $T > 558 \text{ K}$ and representative turnover frequencies are given in Table 1.

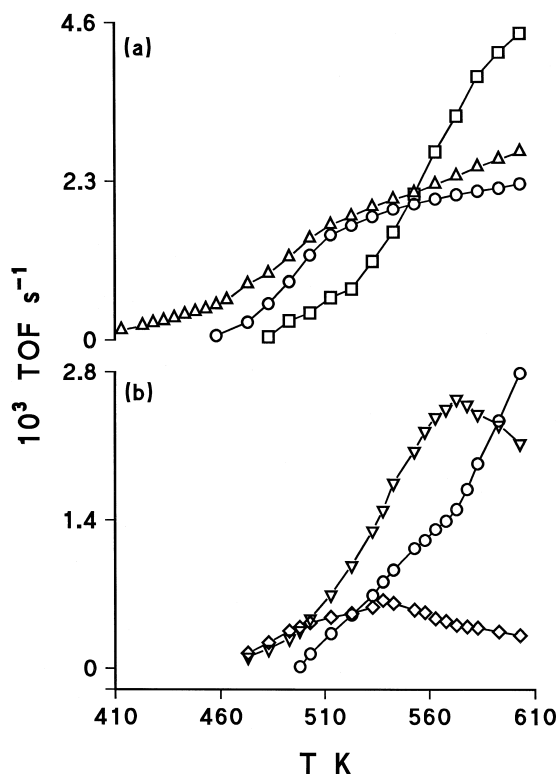


Fig. 1. The temperature dependence of the turnover frequency of (a) benzoic acid to methylbenzoate (Δ), toluene (\circ) and benzene (\square) and of (b) *o*-toluic acid to methyl 2-methylbenzoate (∇), *o*-xylene (\diamond) and toluene (\circ).

The hydrogen cleavage of the aryl/carboxyl C–C bond, to form toluene, was again the predominant process at the highest temperature that was studied.

The differences in the temperature dependence of the TOF of both aromatic acids for the three identified processes (–COOH esterification, –COOH hydrogenolysis and C–C hy-

Table 1

Turnover frequencies and percentage selectivities of the secondary reaction products resulting from the hydrogen treatment of *o*-toluic acid in methanol at representative temperatures

T (K)	Benzene		Methylbenzoate	
	10^4 TOF (s^{-1})	S (%)	10^4 TOF (s^{-1})	S (%)
563	1.4	3	0.6	1
578	2.6	5	2.1	4
593	5.7	10	3.0	5
603	8.7	13	3.7	6

drogenolysis) is better illustrated in Fig. 2. The rate of ester formation was higher for the benzoic acid feed at every temperature that was considered. The silica support alone promoted the esterification step and the variation of the esterification rate constants for both Ni/SiO₂ and SiO₂ yields the apparent Arrhenius plots (correlation coefficient > 0.997) shown in Fig. 3, giving computed E_{app} values of 45 and 57 kJ mol⁻¹ with 95% confidence limits of ± 2 and ± 3 kJ mol⁻¹ for the conversion of benzoic acid and *o*-toluic acid, respectively, over Ni/SiO₂. The corresponding rate constants for SiO₂ are consistently higher but the apparent activation energies are essentially equivalent when the error of the fit and the reproducibility

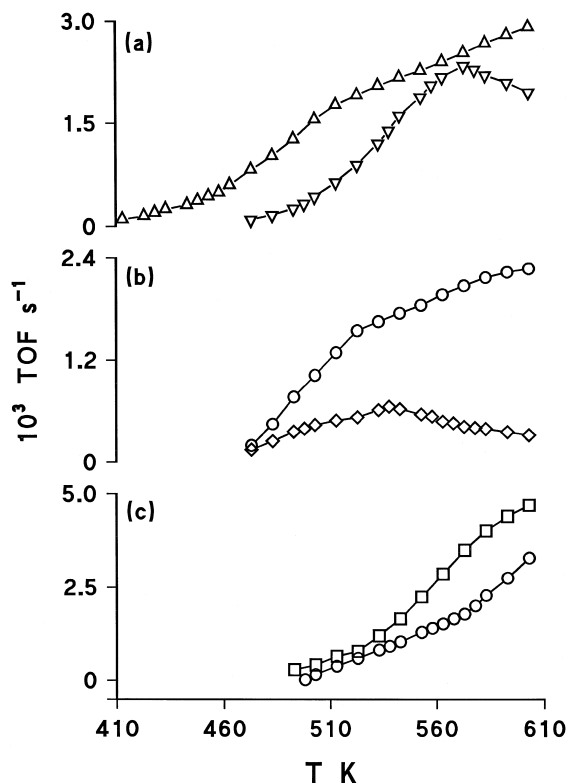


Fig. 2. The variation of TOF with temperature for: (a) the esterification of benzoic acid to methylbenzoate (Δ) and *o*-toluic acid to methyl 2-methylbenzoate (∇); (b) the hydrogenolysis of benzoic acid to toluene (\circ) and *o*-toluic acid to *o*-xylene (\diamond); (c) the hydrogenolysis of benzaldehyde to benzene (\square) and *o*-toluic acid to toluene (\circ).

of k ($\pm 4\%$) are taken into account, i.e., $E_{\text{app}} = 41 \pm 1$ and 52 ± 3 kJ mol⁻¹. Indeed, the esterification rate constant at a particular temperature over Ni/SiO₂ was 0.5–0.6 that measured for SiO₂ which roughly corresponds to the drop in exposed silica due to the presence of surface nickel [27]. Aromatic acid esterification must then proceed virtually exclusively on the silica support. It is instructive to note that these activation energies are lower than the corresponding values of 49 ± 2 and 64 ± 3 kJ mol⁻¹ recorded for the hydrogenation of benzene and toluene over the same catalyst [28]. The carboxyl function of the aromatic acid must then react with the methanol solvent in preference to the hydrogen reduction of the benzene ring because of the lower energy barrier for the former reaction on both the support alone (SiO₂) and Ni/SiO₂. The degree of hydrogenolysis (Fig. 2b) and hydrogen cleavage (Fig. 2c) of the carboxyl function are both appreciably higher for the benzoic acid feed. At elevated temperatures, the conversion of *o*-toluic acid to methylbenzoate and benzene may account, at least in part, for the lower turnover of the feed to toluene. The effect of temperature on the overall rate constant for the conversion of both aromatic acids is illustrated in Fig. 4. Reactivity is clearly modified due to the presence of the *o*-CH₃ substituent in that the temperature at

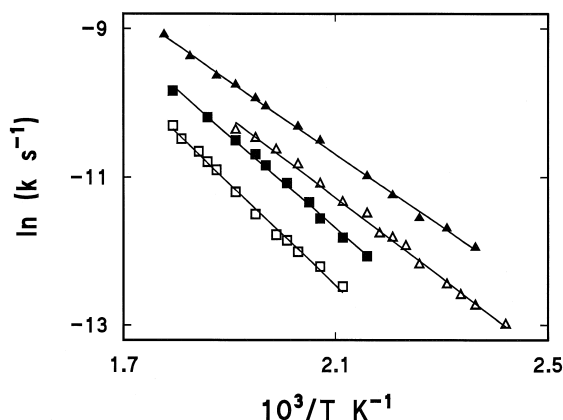


Fig. 3. Apparent Arrhenius plots for the esterification of benzoic acid (Δ , \blacktriangle) and *o*-toluic acid (\square , \blacksquare) over SiO₂ (closed symbols) and Ni/SiO₂ (open symbols).

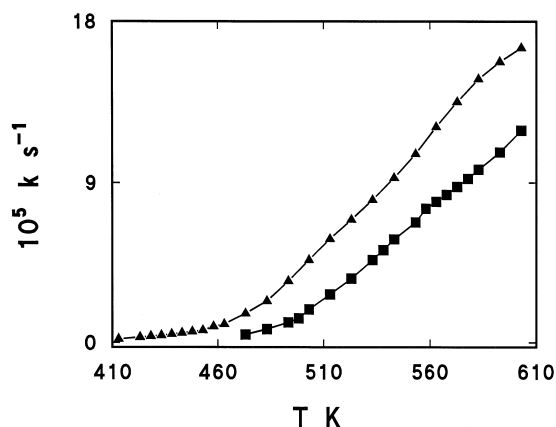


Fig. 4. The variation of the overall rate constant, k , with temperature for the conversion of benzoic acid (\blacktriangle) and *o*-toluic acid (\blacksquare).

which the conversion of *o*-toluic acid was initiated is ca. 60 K higher than that observed for benzoic acid while the rate constant for the former is markedly lower over the entire temperature interval.

3.1.2. Catalytic selectivity

The variation of product selectivity with temperature is demonstrated in Fig. 5. The benzoic acid feed exhibits a decrease in selective esterification with increasing temperature (Fig. 5a) and a temperature related maximum ($T_{\text{max}} = 513$ K, Fig. 5b) with regard to carboxyl hydrogenolysis. In contrast, the selective esterification of *o*-toluic acid passes through a maximum ($T_{\text{max}} = 558$ K) while selectivity in terms of hydrogenolysis to *o*-xylene decreases continuously over the same temperature interval. The carboxyl function in benzoic acid undergoes esterification in preference to hydrogenolysis at every temperature that was studied whereas hydrogenolysis of *o*-toluic acid was favoured over esterification at $T \leq 498$ K. Molar selectivity in terms of aryl/substituent C–C hydrogenolysis (Fig. 5c) increases with temperature for both aromatic feeds and exceeds 40% at the highest temperature studied. Residual selectivity in the case of *o*-toluic acid conversion is accounted for by the secondary conversion to methylbenzoate and benzene; the molar selectivity with

which these products were formed is given in Table 1. Under identical reaction conditions, methylbenzoate and methyl 2-methylbenzoate, as the reaction feedstock, yielded toluene/benzene and *o*-xylene/toluene mixtures, again as a result of the hydrogenolysis of the substituent and the hydrogen cleavage of the substituent from the ring. The silica support alone did not generate any hydrogenolysis products in the hydrogen treatment of either ester. The specific aromatic ester hydrogenolysis ratios over Ni/SiO₂ at representative temperatures are given in Table 2 and compared with the corre-

Table 2

The relative specific rate of substituent hydrogenolysis to substituent/aryl hydrogen cleavage resulting from the hydrogen treatment of benzoic acid, *o*-toluic acid, methylbenzoate and methyl 2-methylbenzoate at representative temperatures

T (K)	TOF _{tol} /TOF _{benz}		TOF _{<i>o-x</i>} /TOF _{tol}	
	Benzoic acid	Methylbenzoate	<i>o</i> -Toluic acid	Methyl 2, methylbenzoate
513	2.5	1.1	1.5	0.9
533	1.6	0.7	0.8	0.5
553	1.0	0.5	0.5	0.3
573	0.7	0.4	0.3	0.2
593	0.5	0.3	0.2	0.1

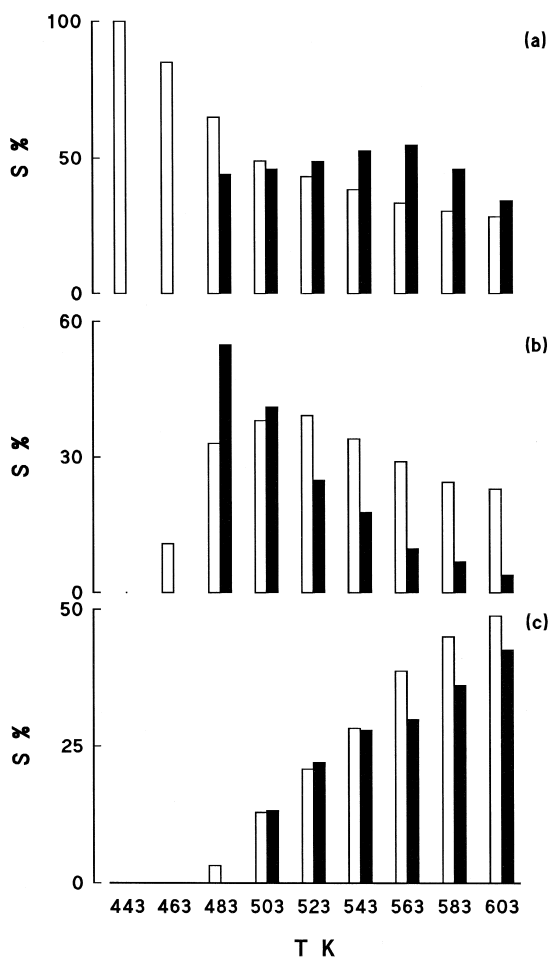


Fig. 5. Percentage molar selectivity in the conversion of benzoic acid (open bar) and *o*-toluic acid (solid bar) in terms of (a) carboxyl esterification, (b) carboxyl hydrogenolysis and (c) aryl/carboxyl C–C hydrogenolysis at representative temperatures.

sponding aromatic acid. It is immediately evident that the product distribution generated by the aromatic ester differs from that generated by the acid. The degree of hydrogen scission of the substituent ester group is markedly greater and this may be ascribed to the electron donating properties of the –OCH₃ function which weakens the aryl/substituent bond in the adsorbed benzoate and better facilitates hydrogen cleavage. In view of the different hydrogenolytic behaviour of the ester, the formation of toluene/benzene and *o*-xylene/toluene must result from the direct attack of the adsorbed acid and not as a result of the further conversion of the esterification product, i.e., methylbenzoate or methyl 2-methylbenzoate do not serve as intermediates for the hydrogenolysis steps. In the case of the *o*-toluic acid feed, the secondary products (methylbenzoate and benzene) first appeared in the product mixture at the same temperature (563 K) and must result from the hydrogen cleavage of the *ortho*-methyl substituent prior to the desorption of the esterification or hydrogenolysis product.

3.2. The nature of catalyst/reactant interaction(s)

3.2.1. Benzoic acid

As all the products of the hydrogen treatment of both aromatic acids resulted from the exclusive attack of the COOH group, benzene ring

interactions must play little part in the ‘catalytically significant’ activation of the aromatic acid when adsorbed on Ni/SiO₂. While the author could find no spectroscopic study of either benzoic or *o*-toluic acid adsorption on nickel or silica, the mechanisms of benzoic acid adsorption on alumina [29], on silver [30], platinum [31] and gold [32] electrodes and on silver sol [30,33] have been considered in a number of publications. It is recognized that the carboxylic acid can bind to a metal via the oxygen lone pair electrons or the carboxylate π -system where the orientation of the adsorbed carboxylic acid on the surface depends on the binding mechanism [34,35]. Benzoic acid adsorption on a silver electrode is believed to occur via the oxygen lone pair electrons where the benzene ring assumes a perpendicular orientation [30] whereas adsorption on silver sol occurs via the carboxyl π -system [30,33] with a substantial deviation from a perpendicular arrangement [33]. Moreover, benzoic acid has been reported [31] to preferentially adsorb as a carboxylate on a platinum electrode while the interaction with a gold surface, proceeds only through the benzene ring π -orbitals with the carboxylic group pendant to the surface [32]. The surface catalysed hydrogenolysis of –COOH to –CH₃ can readily proceed where the acid is adsorbed through the carboxylate π -system as a benzoate-like structure rather than the single point oxygen lone pair interaction. Indeed, tartaric acid is known to adsorb from aqueous solution on Ni/SiO₂ as a carboxylate [27,36]. The distance between the two oxygen atoms in the carboxylate group is ca. 0.2 nm [37] and, as the average diameter of the supported nickel particles is taken to be 1.4 nm it is reasonable to assume that the aromatic acid binds to the metal as a bidentate. The presence of surface nickel is essential as it is the source of dissociated hydrogen and the silica support alone did not exhibit any hydrogenolysis activity. However, the bulk of the acid esterification may be considered to proceed on the silica support where the –OH of the carboxyl is activated via oxygen lone pair interactions. Ben-

zene is known to adsorb on nickel catalysts via π -bond interactions in which the ring lies parallel to the active surface [38,39]. In the absence of steric hindrance this orientation of the aromatic nucleus would be expected to remain and the adsorbed benzoate species may be assumed to take a flat or somewhat tilted orientation on the catalyst surface. However, the orientation may depend on surface coverage and it has been shown in other systems that a perpendicular orientation of the adsorbed aromatic acid is favoured at high fractional or monolayer coverages [31,40].

3.2.2. *o*-Toluic acid

In the case of *o*-toluic acid, the neighbouring methyl group can influence the product composition through electronic contributions and/or steric constraints. Functional group reactivity depends on the relative accessibility and binding strength to the catalyst. It is known that the presence of methyl substituents on the benzene ring strengthens the adsorbed π -complex with the resultant introduction of a higher energy barrier for aromatic ring hydrogenation [24,41–43]. Alkyl groups exhibit a greater tendency than hydrogen atoms to donate electrons [44] and the *ortho*-substituted methyl group must act to release electrons to the aromatic ring which are distributed to the carboxyl function, stabilizing the adsorbed carboxylate and lowering the turnover rate of the reactant. The author could find no spectroscopic study of *o*-toluic acid adsorption in heterogeneous systems. The repulsive potential due to the neighbouring methyl group must cause this function to bend away from the plane of the carboxyl/catalyst interaction in order to relieve the steric repulsion. The consequent distortion of the aromatic ring suggests that *o*-toluic acid has to overcome a larger barrier than benzoic acid at the adsorption step. A higher energy of interaction with the surface may be accompanied by a decrease in reactivity with the result that steric hindrance may also serve to lower reactivity of *o*-toluic acid. Moreover, in the esterification reaction the approach

of methanol from the gas phase must be hindered on one side due the presence of the *ortho*-methyl substituent which may account, at least in part, for the reduced rate of esterification of *o*-toluic acid, as is shown in Fig. 2.

The ratios of the specific rates of hydrogenolysis of $-\text{COOH}$ to the hydrogenolytic cleavage of the carboxyl group are presented as a function of reaction temperature in Fig. 6. It can be seen that both systems exhibit a decrease in the ratio with increasing temperature as the hydrogen scission of the carboxyl substituent becomes the dominant process. The specific ratios are greater for benzoic acid at each temperature. The inductive effect of the *o*- CH_3 group must weaken the aryl C–carboxyl C bond with the result that the temperature at which the ratio of specific rates falls below unity occurs ca. 30 K lower in the case of *o*-toluic acid. The degree of substituent cleavage may be quantified in terms of yield (Y) which is a combination of selectivity and reactivity, defined as $Y = \alpha S/W$ where S represents selectivity (%), α the overall fractional conversion of reactant and W the weight of catalyst. The effect of temperature on the yield of benzene and toluene from benzoic acid and *o*-toluic acid, respectively, is illustrated in

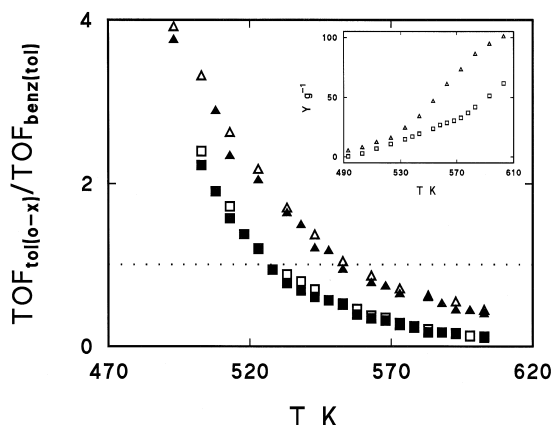


Fig. 6. The temperature dependence of the specific hydrogenolysis rate ratios for the conversion of benzoic acid (Δ/\blacktriangle , $\text{TOF}_{\text{tol}}/\text{TOF}_{\text{benz}}$) and *o*-toluic acid (\square/\blacksquare , $\text{TOF}_{\text{o-x}}/\text{TOF}_{\text{tol}}$) in methanolic (open symbols) and 2-propanolic (solid symbols) media. Inset: temperature dependence of the yield of benzene (Δ) and toluene (\square) from benzoic acid and *o*-toluic acid, respectively.

the inset to Fig. 6. Although the relative rates of substituent cleavage are higher for the *o*-toluic acid reactant, the yield of the decarboxylated aromatic is nevertheless greater from the benzoic acid feed due to the appreciably higher overall reaction rates. It is known [34] that the presence of bulky groups in the alcohol reactant slows down esterification. The use of 2-propanolic solutions of benzoic and *o*-toluic acid as feedstock did not generate any esterification products and the only detectable reactions were hydrogenolytic in nature where the aromatic nucleus again remained intact and reduction of the carboxyl function to the aldehyde or alcohol did not occur. The temperature dependence of the specific hydrogenolytic ratios in a 2-propanolic medium is included in Fig. 6. While it is evident that these rate ratios are essentially constant in both feed solvents, the data recorded for the 2-propanolic solutions are considered to best reflect the response of the carboxyl function to hydrogen attack in the presence of Ni/SiO₂.

3.3. Aromatic acids vs. aromatic aldehydes

The hydrogen treatment of benzaldehyde and *o*-tolualdehyde in the presence of Ni/SiO₂ under the same reaction conditions yielded benzyl alcohol and 2-methylbenzyl alcohol, respectively, as the only hydrogenated products while the hydrogenolysis of the C=O and C–C bonds generated toluene/*o*-xylene and benzene/toluene mixtures. Once again, the benzene nucleus was not reduced which suggests that the aromatic aldehyde interacts principally with the catalyst via the carbonyl function. Kuiper et al. [45] have provided spectroscopic evidence that benzaldehyde adsorbs on alumina as a benzoate species but the mechanisms of adsorption on nickel or silica have not been reported. The silica support alone did not induce any hydrogenation or hydrogenolysis of benzaldehyde or *o*-tolualdehyde under the same reaction conditions but ‘spillover’ hydrogen from the nickel metal may attack an analogous benzoate structure adsorbed on the silica carrier. The most

persuasive reaction mechanism invokes the interaction of the aromatic aldehyde with the catalyst through the oxygen lone pair electrons where the hydrogen dissociated on the metal attacks the carbonyl oxygen. It may also be assumed that in the adsorption of benzaldehyde the plane of the aromatic ring is essentially parallel to the catalyst surface and brings the substituent carbonyl group close enough to the active sites to allow for orbital interaction while the presence of the *o*-CH₃ group must again induce a Kekulé distortion in order to relieve the steric repulsion.

Representative overall turnover frequencies for the steady state conversion of both pairs of aromatic aldehydes and acids, are presented in Table 3. The TOF values increase in the order, *o*-toluic acid < benzoic acid < *o*-tolualdehyde < benzaldehyde which indicates that the carbonyl function is more reactive than the carboxyl function in this particular catalytic system. Indeed, it has been shown in a number of catalytic processes [3,46] that much more vigorous reaction conditions are required to hydrogenate acids. Appreciable hydrogen attack of the carbonyl substituent was observed at temperatures up to 60 K lower than that recorded for the carboxyl group. The presence of a methyl substituent in the *ortho* position also lowers the reactivity of the carbonyl function. In the case of the carbonyl double bond the mobile π -cloud is pulled strongly toward the more electronegative oxygen atom with the result that the car-

Table 3

Overall turnover frequencies resulting from the hydrogen treatment of benzoic acid, *o*-toluic acid, benzaldehyde and *o*-tolualdehyde at representative temperatures

T (K)	10 ³ TOF (s ⁻¹)			
	Benzaldehyde	<i>o</i> -Tolualdehyde	Benzoic acid	<i>o</i> -Toluic acid
503	10.8	8.8	2.8	1.0
513	11.0	9.1	3.5	1.5
528	11.3	9.6	4.5	2.2
543	11.5	10.5	5.5	3.3
553	11.7	10.8	6.2	3.7
563	11.9	11.0	7.0	4.4

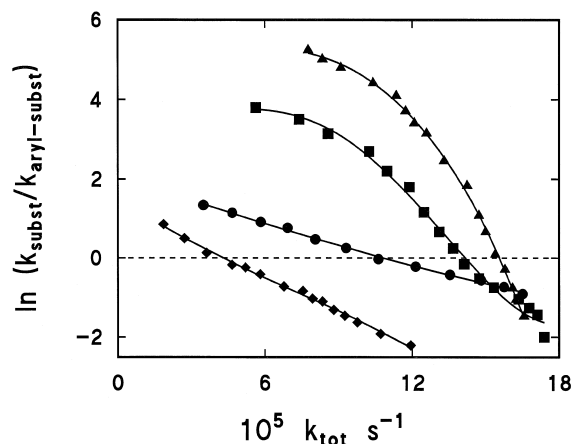


Fig. 7. The dependence on the overall rate constant (k_{tot}) of the ratio of the rate constants for hydrogenolysis of the substituent (k_{subst}) to substituent cleavage ($k_{\text{aryl-subst}}$) in the conversion of benzaldehyde (\blacktriangle), *o*-tolualdehyde (\blacksquare), benzoic acid (\bullet) and *o*-toluic acid (\blacklozenge) over Ni/SiO₂.

bonyl carbon is electron-deficient and the polarized group is therefore highly reactive. The dispersal of electrons due to the presence of the *ortho*-substituted methyl group reduces the positive charge on the carbonyl carbon with the result that *o*-tolualdehyde is more resistant than benzaldehyde to hydrogen attack. The lower reactivity may also be attributed to a steric effect where the adsorption of *o*-tolualdehyde is more energetically demanding and the energy requirements for hydrogenation/hydrogenolysis are greater. The ratios of the rate constant for hydrogen attack on the substituent function to that for hydrogen scission of the substituent/ring C–C linkage are graphically illustrated in Fig. 7 as a function of the overall rate constant. In common with the carboxyl systems, the ratios generated for both aldehydes decrease with increasing rate as hydrogen scission of the aromatic substituent predominates. In addition, the degree of carbonyl cleavage is greater in the presence of the *o*-CH₃ group again due to the inductive weakening of the aryl/carbonyl C–C bond. The relative rate of substituent cleavage is lower for both aromatic aldehydes. In the present catalytic system, carbonyl hydrogenolysis is therefore preferred to carbonyl cleavage to a

greater degree than is observed for the carboxyl function.

3.4. Hydrogen treatment of 2-carboxybenzaldehyde

Having examined the relative reactivities of the carboxyl and carbonyl functions in mono-substituted benzene and methyl-benzene, the catalytic behaviour of Ni/SiO₂ in the conversion of 2-carboxybenzaldehyde (CBA), which bears both functions, may now be considered. In the temperature range 413 K ≤ T ≤ 523 K, *o*-toluic acid and 3-hydroxyphthalide were the principal products (combined molar selectivity > 90%) generated from alcoholic solutions of CBA; product selectivities at representative temperatures in this range are illustrated in Fig. 8. As the reaction temperature is elevated further, toluene and benzene were formed via hydrogenolysis, while in methanolic solutions, methyl 2-methylbenzoate and methylbenzoate were also isolated in the product mixtures; representative selectivities at temperatures in excess of 523 K are provided in Table 4. In every instance the carbonyl substituent was attacked while *o*-toluic acid was formed as a principal product with the carboxyl group intact. At T < 503 K, *o*-toluic acid was the preferred product

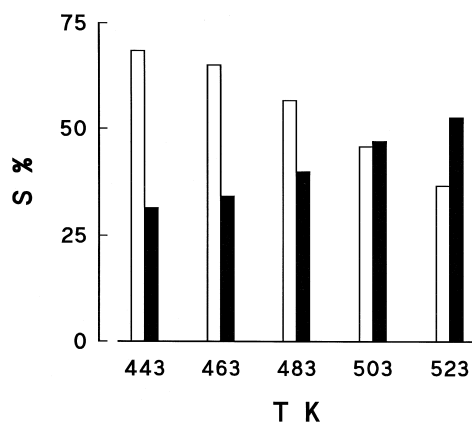


Fig. 8. Percentage molar selectivity for isomerization (solid bar) to 3-hydroxy-phthalide and hydrogenolysis (open bar) to *o*-toluic acid in the hydrogen treatment of 2-CBA over Ni/SiO₂ at representative temperatures.

Table 4

Product selectivity at T > 523 K for the hydrogen treatment of methanolic solutions of CBA in the presence of Ni/SiO₂

T (K)	3-Hydroxy phthalide	<i>o</i> -Toluic acid	Methyl 2-methylbenzoate	Methylbenzoate	Toluene	Benzene
533	56	32	3	5	4	–
548	58	25	4	7	6	1
563	54	17	7	12	8	2
578	48	11	9	16	10	4
593	36	8	15	21	12	7
603	30	8	17	23	14	9

and the selectivity with which it was produced decreased with increasing temperature. It should be noted that *o*-tolualdehyde was not formed which is in keeping with the lower rate of hydrogenolysis of the aromatic acid compared to the aldehyde. The selective formation of 3-hydroxyphthalide passed through a maximum at 553 K and was generated in preference to *o*-toluic acid at T ≥ 503 K. The degree of conversion to 3-hydroxyphthalide was the same in both alcoholic media and its formation can be viewed as an isomerization which involves ring closure where both functional groups must interact with the surface. Isomerization was also promoted by the silica support in the absence of nickel but the specific rate was less than a third of that obtained using the nickel catalyst. The difference in the reactivity of the carbonyl and carboxyl functions is also manifest in the isolation of toluene and methyl 2-methylbenzoate in the product (Table 4) where the carbonyl substituent is cleaved from the ring while the carboxyl concomitantly undergoes hydrogenolysis and esterification, respectively. Moreover, *o*-xylene formation was negligible (% S < 1) which clearly demonstrates the non-equivalency of the two functions with regard to the catalytic action of Ni/SiO₂. The proposed reaction mechanisms, for the three disubstituted aromatic systems (taking methanolic solutions of *o*-toluic acid and CBA) are illustrated in Fig. 9 and the temperature dependencies of each step are summarized.

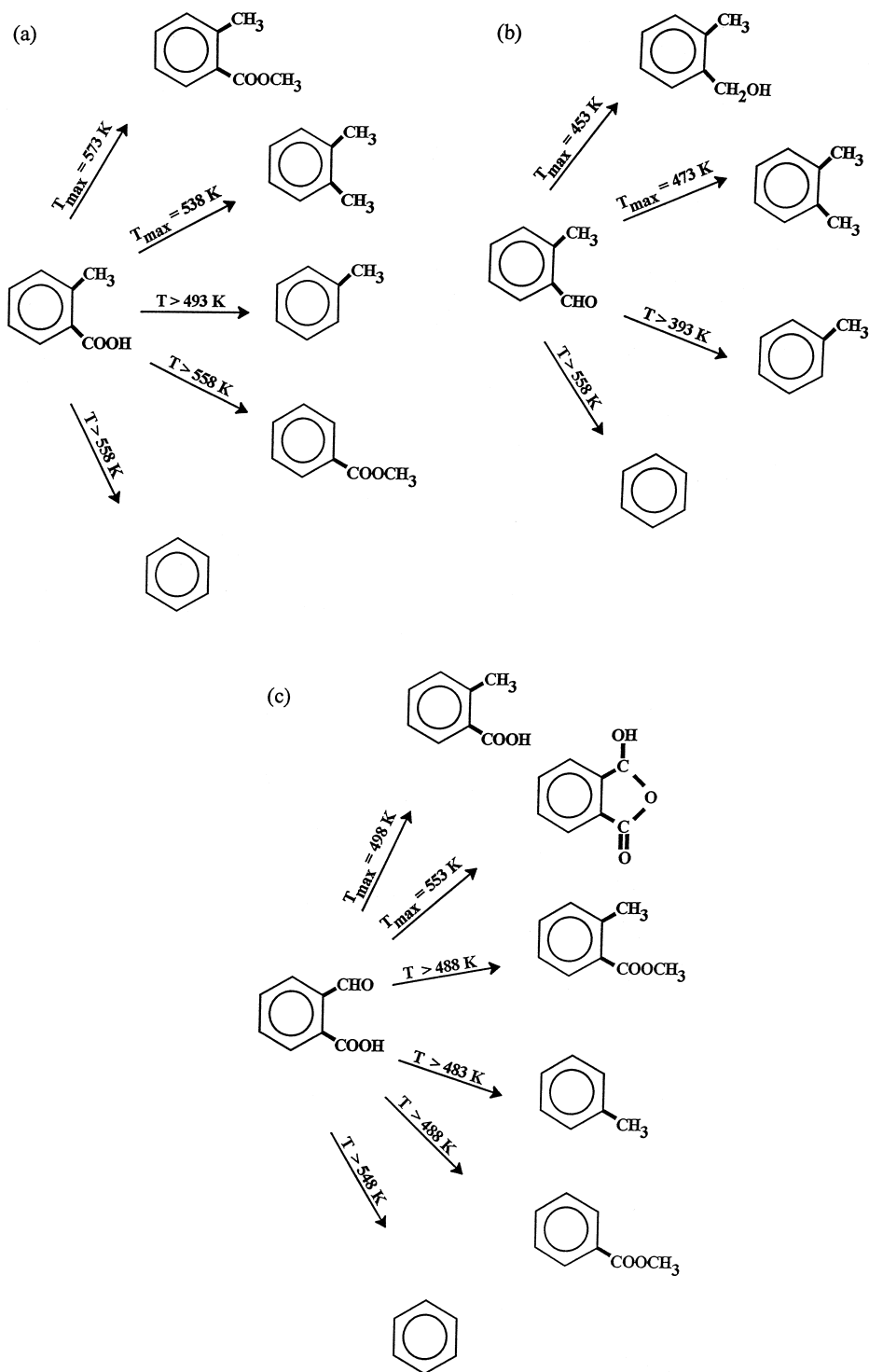


Fig. 9. Reaction scheme and TOF temperature dependencies (where $413 \text{ K} \leq T \leq 603 \text{ K}$) of each pathway in the hydrogen treatment of (a) *o*-toluic acid, (b) *o*-tolualdehyde and (c) 2-CBA over Ni/SiO_2 .

4. Conclusions

In the gas phase Ni/SiO₂ catalysed hydrogen treatment of a range of mono- and disubstituted oxygenated aromatics, the data presented in this paper support the following conclusions.

(i) The catalytically significant interaction of the aromatic acids, esters, aldehydes and carboxyaldehyde with Ni/SiO₂ occurs via the oxy-substituent(s) where the resonance energy of the benzene ring is not significantly lowered with the result that the aromatic nucleus remains intact in each case.

(ii) The presence of the *ortho*-substituted methyl group lowers the overall reactivity due to electronic and steric effects.

(iii) The aromatic acid is adsorbed via the carboxylate π -system as a benzoate and undergoes esterification (in methanol) and hydrogenolysis steps to –COOCH₃ and –CH₃, respectively. Esterification proceeds at a greater rate over the bare silica support but with an equivalent apparent activation energy and was not observed when 2-propanolic solutions were used as feedstock. The methyl ester also undergoes hydrogenolysis when treated under identical conditions but does not serve as a reactive intermediate in the hydrogen treatment of the acid in methanol. At higher temperatures, hydrogen cleavage of the carboxyl is the predominant process.

(iv) Hydrogen treatment of aromatic aldehydes yields the alcohol as the only hydrogenated product while hydrogenolysis to –CH₃ and hydrogenolytic cleavage of –CHO are in turn promoted with increasing temperature.

(v) The carbonyl function is considerably more reactive than the carboxyl group. The ratio of substituent hydrogenolysis to substituent cleavage is greater in the case of the aldehyde.

(vii) In the case of the carboxyaldehyde, the carbonyl function is attacked in preference to the carboxyl. Both substituents interact with the catalyst and the products result from isomerization (on both metal and support), hydrogenolysis and esterification reactions.

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