# Liquid-Phase Hydrogenation of Citral over Pt/SiO<sub>2</sub> Catalysts

II. Hydrogenation of Reaction Intermediate Compounds

Utpal K. Singh, Matthew N. Sysak, and M. Albert Vannice<sup>1</sup>

Department of Chemical Engineering, Pennsylvania State University, 107 Fenske Laboratory, University Park, Pennsylvania 16802-4400

Received September 3, 1999; revised December 16, 1999; accepted December 22, 1999

Liquid-phase hydrogenation of the four principal reaction intermediates formed during citral hydrogenation, i.e., nerol, geraniol, citronellal, and citronellol, was studied at 298 and 373 K under 20 atm H<sub>2</sub> at concentrations of 0.5 to 1.0 M in hexane. A decrease in the initial reaction rate as temperature increased from 298 to 373 K was exhibited during the hydrogenation of all four compounds, just as reported earlier for citral; however, the decrease in rate at 373 K was only one-half for citronellal whereas it was orders of magnitude greater for nerol and geraniol. Furthermore, simultaneous hydrogenation of citronellal and geraniol at 298 K resulted in a continuous decrease in the rate of citronellal disappearance in contrast to the nearly constant rate of disappearance observed during hydrogenation of citronellal alone. Competitive hydrogenation of citral with either geraniol or citronellal showed that geraniol hydrogenation to citronellol is kinetically insignificant during citral hydrogenation at 373 K. The initial activity for hydrogenation of the intermediates at 298 K follows the following trend: geraniol  $(1.9 \text{ s}^{-1}) > \text{nerol}$  $(1.5 \text{ s}^{-1}) > \text{citronellol} (0.21 \text{ s}^{-1}) > E \text{-citral} (0.13 \text{ s}^{-1}), \text{ citronellal}$  $(0.13 \text{ s}^{-1}) > Z$ -citral (0.06 s<sup>-1</sup>). Based on the relative hydrogenation rates of the intermediate alone versus its hydrogenation in the presence of other reactants, the relative size of the adsorption equilibrium constants for the various organic compounds appears to be as follows:  $K_{citral} > K_{citronellal} > K_{geraniol}$ ,  $K_{nerol} > K_{citronellol} > K_{3,7-dimethyloctanol}$ . This study indicates that activation of the C=O bond should be performed at higher reaction temperatures to maximize selectivity to the unsaturated alcohols. © 2000 Academic Press

## **INTRODUCTION**

This is the second portion of a two-part series discussing liquid-phase hydrogenation of citral and its intermediate products over Pt/SiO<sub>2</sub> catalysts. Hydrogenation of  $\alpha$ , $\beta$ -unsaturated aldehydes represents a broad class of reactions relevant to the specialty and fine chemicals industry because of the importance of selectivity control in systems containing conjugated C=C and C=O bonds. For example, much work remains to be done to understand the influence of reaction parameters and metal-support interactions (MSIs)

<sup>1</sup> To whom correspondence should be addressed.

on the kinetics of citral hydrogenation. In the previous paper, an unusual effect of temperature on product distribution and reaction rate was reported and a model was developed to explain the observed behavior. The minimum in activity for citral hydrogenation that occurred between 298 and 423 K was attributed to Pt site blockage by adsorbed CO formed by decomposition of the unsaturated alcohols (geraniol and nerol) coupled with its subsequent desorption at higher temperatures (1). Literature regarding the kinetics of liquid-phase hydrogenation of the reaction intermediates that can be formed during the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes is extremely scarce (2). As with citral, the influence of reaction parameters on these kinetics remains to be studied in a systematic fashion under conditions shown to be free of transport limitations and poisoning effects. Figure 1 presents the reaction pathways that can occur to form intermediate compounds during citral hydrogenation. In the present paper, hydrogenation of the reaction intermediates both as a single component in the solvent and in a mixture of reactants was investigated using citronellal (partially saturated aldehyde), nerol and geraniol (unsaturated alcohol), and citronellol (partially saturated alcohol). In addition to measuring turnover frequencies (TOFs) to appropriately compare relative activities, emphasis was placed on examining temperature effects for hydrogenation of reaction intermediate compounds.

## **EXPERIMENTAL**

SiO<sub>2</sub> (Davison grade 57, 220 m<sup>2</sup>/g, 60–100 mesh) was dried and calcined at 773 K for 4 h prior to the dropwise addition of an aqueous solution of chloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>, Aldrich 99.995%) via an incipient wetness (2 cm<sup>3</sup>/g) method, then dried overnight in air at 393 K. Three SiO<sub>2</sub>-suupported catalysts with Pt loadings of 0.49, 1.44, and 3.8 wt% were prepared and characterized by hydrogen chemisorption as described previously (1), and respective dispersions of 0.45, 0.41, and 0.67 were measured.

Hydrogenation experiments were conducted in a 100-ml EZ-seal autoclave with automated data acquisition. The





FIG. 1. Reaction network for citral hydrogenation.

pretreatment procedure is identical to that used during the study of citral hydrogenation and has been described before (1). Briefly, the catalyst was reduced *in situ* at 673 K for 75 min prior to cooling to room temperature and storing overnight under a static  $H_2$  pressure of 20 atm.

Geraniol (trans-3,7-dimethyl-2,6-octadienol), nerol (cis-3,7-dimethyl-2,6-octadienol), citronellal (3,7-dimethyl-6octenal), and citronellol (3,7-dimethyl-6-octenol) were used as received from Sigma with respective purities of 98, 98, 85, and 95%. Both the reactants and the hexane solvent were degassed by sparging with high flow rates of nitrogen for 30 min prior to injection into the reactor. Competitive hydrogenation reactions of geraniol and citronellal were performed by mixing equal volumes of each reactant and sparging the mixture for 30 min with nitrogen prior to addition into the reactor. Experiments were also performed in which an intermediate was introduced into the reaction system during the course of citral hydrogenation. As with citral, extra precautions were taken to remove trace quantities of oxygen dissolved in any reactant introduced into the reactor. The standard reaction conditions in the present study consisted of conducting the reaction using 10 ml of reactant (5 ml of each reactant during competitive hydrogenation) dissolved in 50 ml of hexane under a constant  $H_2$ pressure of 20 atm. n-Hexane (Fisher, 99.9% saturated C<sub>6</sub> hydrocarbons) was fed into the reactor from an enclosed environment to prevent any exposure to air at the reaction temperature and pressure using a high-pressure syringe

pump (ISCO 500D). The hexane/catalyst slurry was stirred and allowed to equilibrate for 30 min prior to the introduction of the reactant at reaction temperature and pressure to obtain a total reaction volume of 60 ml. The reactor pressure was continuously maintained to within 5% of the set point (20 atm) using a Brooks 5860 pressure controller. A liquid sample (ca. 0.5 ml) was periodically withdrawn through a dip tube inside the reactor, collected in a closed, N<sub>2</sub>-purged vessel, then analyzed in a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector and a 10% Carbowax 20 M on Supelcoport column. Initial rates of citral disappearance were evaluated using the slope of the linear portion of the temporal citral conversion profile (for citral conversions below 20%). The selectivity to each product was calculated based on the following equation:

$$S_i = \frac{\text{molar concentration of species } i}{\sum_{\text{products molar concentration of species } i}.$$

## RESULTS

Figure 2a displays the temporal concentration profiles of reactants and products during geraniol hydrogenation at 298 K. All results are under standard conditions unless otherwise noted. Citronellol and 3,7-dimethyloctanol were the principal products. Trace quantities of *trans*-3,7-dimethyl-2-octenol from hydrogenation of the isolated C=C bond



**FIG. 2.** (a) Temporal concentration profile during hydrogenation of geraniol in hexane at 298 K over 1.44% Pt/SiO<sub>2</sub> (20 atm H<sub>2</sub> pressure, 1 M geraniol, 98% pure). (b) Differential treatment of the rate of geraniol disappearance.

in geraniol were detected, but this product could not be quantitatively resolved from citronellol. During nerol hydrogenation, the GC peak for the cis isomer of the unsaturated alcohol (cis-3,7-dimethyl-2-octenol) could be separated from that for citronellol, and the results revealed that the solvent-free composition of this product was less than 5% of the total reaction mixture; also, it was rapidly hydrogenated to the final saturated product after the initial stages of the reaction to give nondetectable concentrations. The initial TOF for geraniol hydrogenation was 1.8 s<sup>-1</sup>. Such a large value for the TOF raises a concern about possible mass transfer limitations; however, the Weisz-Prater criterion for minimal mass transport limitations was satisfied for geraniol hydrogenation as a value of  $2.4 \times 10^{-4}$  was obtained for this dimensionless parameter at 298 K (3, 4). Therefore, the kinetics displayed in Fig. 2a should be free of any mass transport control. The results indicate that geraniol hydrogenation occurs rapidly to yield primarily citronellol. At higher conversions, citronellol was further hydrogenated to yield 3,7-dimethyloctanol. A reaction order of 0.5 in geraniol concentration was obtained from a differential treatment of the rate of geraniol disappearance as shown in Fig. 2b.

Figure 3 displays the temporal concentration profile during hydrogenation of geraniol at 373 K. These results indicate that there is rapid hydrogenation of geraniol during the first few minutes of reaction to yield citronellol and give a conversion near 20%; however, activity is subsequently suppressed by orders of magnitude and a TOF of only  $0.005 \text{ s}^{-1}$  was obtained after this early period. An initial TOF of 0.20  $s^{-1}$  was observed with negligible deactivation during hydrogenation of pure citronellol at 298 K; however, reaction at 373 K resulted in rapid conversion of 15% after 2 min followed by deactivation and a TOF of only 0.0004  $s^{-1}$  during the latter period as shown in Fig. 4. Figures 5a and 5b show the temporal concentration profiles during citronellal hydrogenation at 298 and 373 K. The initial TOFs for citronellal disappearance were  $0.13 \text{ s}^{-1}$  at 298 K and 0.07 s<sup>-1</sup> at 373 K. In stark contrast to the kinetic behavior of geraniol, hydrogenation of citronellal at 298 and 373 K exhibited zero-order kinetics as shown in Figs. 6a and 6b, respectively. The results in Figs. 5a and 6a indicate that citronellal hydrogenation at 298 K exhibits zero-order kinetics up to 50% conversion and a twofold lower rate is observed for conversions greater than 50%; however, zero-order kinetics are maintained at this lower rate. It should be noted that the *v* intercepts for citronellal concentration profile in Figs. 5a and 5b are at 85% due to the presence of isopulegol in the feed. It was necessary to correct for the feed impurity to properly evaluate selectivities since isopulegol is a product of citronellal hydrogenation. This was especially true at 298 K where the temporal isopulegol concentration profile exhibits a continuous decrease with time. Therefore, an approximate correction was made by assuming that no isopulegol was formed under reaction



FIG. 3. Hydrogenation of geraniol in hexane at 373 K over 1.44% Pt/SiO<sub>2</sub> (20 atm H<sub>2</sub> pressure, 1 M geraniol, 98% pure).



FIG. 4. Hydrogenation of citronellol in hexane at 373 K over 1.44% Pt/SiO<sub>2</sub> (20 atm H<sub>2</sub> pressure, 1 M citronellol, 95% pure).

conditions and the isopulegol present in the feed reacted to form the menthol isomers. The selectivity at 373 K was evaluated by subtracting the isopulegol feed concentration from that evaluated at each point in time. Figures 7a and 7b display the selectivity-versus-conversion profile for citronellal hydrogenation at 298 and 373 K, respectively, and dramatic differences can be seen between the two product distributions. Reaction at 298 K yielded dihydrocitronellal,



FIG. 5. Hydrogenation of citronellal in hexane at (a) 298 K and (b) 373 K over 1.44% Pt/SiO<sub>2</sub> (20 atm H<sub>2</sub> pressure, 1 M citronellal). Citronellal was obtained with a purity of 85% and used as is.



FIG. 6. Differential treatment of the rate of citronellal disappearance for reaction at (a) 298 K and (b) 373 K over over 1.44% Pt/SiO<sub>2</sub> (20 atm  $H_2$  pressure, 1 M citronellal). Citronellal was obtained with a purity of 85% and used as is.



FIG. 7. Product distributions during hydrogenation of citral in hexane at (a) 298 K and (b) 373 K over 1.44% Pt/SiO<sub>2</sub> catalyst (20 atm H<sub>2</sub> pressure, 1 M citral).

citronellol, and 3,7-dimethyloctanol while reaction at 373 K yielded only isopulegol and citronellol. The selectivity to dihydrocitronellal at 298 K decreased from 58 to 33% as the citronellal conversion increased from 17 to 70% while the selectivity to 3,7-dimethyloctanol increased from 19 to 33% over the same conversion range. No dihydrocitronellal or 3,7-dimethyloctanol was observed during reaction at 373 K, and the selectivities to citronellol and isopulegol were 60 and 40%, respectively, and essentially constant with respect to conversion.

Due to the drastic differences in the kinetic behavior of citronellal and geraniol, the competitive hydrogenation of citronellal and geraniol was examined, and the initial hydrogenation rates for each intermediate alone and that during competitive hydrogenation of an approximately equimolar mixture of the two intermediates are presented in Table 1. As mentioned previously, the initial hydrogenation rates for citral, citronellal, and geraniol decrease as the temperature increases from 298 to 373 K. The temporal concentration profiles for simultaneous hydrogenation of 0.5 M geraniol and 0.4 M citronellal over the 1.44% Pt/SiO<sub>2</sub> catalyst are shown in Fig. 8a. The profiles during the first 3 h of reaction are shown in the inset to Fig. 8a and these were used to calculate the initial TOFs for disappearance of geraniol and citronellal, which were 0.18 and  $0.08 \text{ s}^{-1}$ , respectively. There is a sustained decrease in the total rate of hydrogenation and negligible activity exists after 40 h of reaction as seen from the H<sub>2</sub> uptake profiles in Fig. 8b which show that the rate of H<sub>2</sub> uptake during competitive hydrogenation of geraniol and citronellal is near  $0.5 \text{ s}^{-1}$  initially but eventually decreases to near zero after 40 h of reaction time. Figure 9 displays the concentration profiles during hydrogenation of a similar mixture at 373 K. A 20% conversion of geraniol is observed during the first 5 min of reaction, and after this high initial reaction rate, the concentration profile levels out, yielding a much lower TOF of  $0.005 \text{ s}^{-1}$ . The initial rate of disappearance of citronellal in the mixture was  $0.03 \text{ s}^{-1}$ , which represented a twofold drop compared with reaction with citronellal alone.

TABLE 1
---------

TOF at 298 K TOF at 373 K Activity at 298 K Activity at 373 K ( $\mu$ mol/g cat/min)  $(s^{-1})$ ( $\mu$ mol/g cat/min)  $(s^{-1})$ Citral E-isomer: 0.13 *E*-isomer: 0.0098 236 18 112 Z-isomer: 0.06 9 Z-isomer: 0.0050 3330 (852)<sup>a,b</sup>  $1.9(1.2)^{a,b}$ Geraniol 9 0.005<sup>c</sup> Nerol 2688 4 0.007<sup>c</sup> 1.5 Citronellal 251 (196)<sup>a</sup>  $0.13 (0.11)^a$ 131 0.07 Citronellol 140 0.21 0.7 0.0004<sup>c</sup> Geraniol/nerol 829 Geraniol: 0.46 (50 mol%) 862 Nerol: 0.48 7 Geraniol/citronellal 331 Geraniol: 0.18 Geraniol: 0.004. 30 (50 mol%) 138 Citronellal: 0.08 Citronellal: 0.02

Initial Turnover Frequencies for Hydrogenation of Reaction Intermediates at 298 and 373 K over 1.44% Pt/SiO<sub>2</sub> Catalyst (20 atm H<sub>2</sub>, 1 M in Hexane)

<sup>a</sup> Values in parentheses obtained with 0.5 M citral in hexane.

<sup>b</sup>Reaction conducted over 0.49% Pt/SiO<sub>2</sub>.

<sup>c</sup>Rapid initial deactivation.



FIG. 8. (a) Temporal citral concentration profile and (b) temporal  $H_2$  uptake during competitive hydrogenation of citronellal and geraniol in hexane over 1.44% Pt/SiO<sub>2</sub> at 298 K (20 atm  $H_2$ , 0.4 M citronellal, 0.5 M geraniol).



**FIG. 9.** (a) Temporal citral concentration profile and (b) temporal  $H_2$  uptake during competitive hydrogenation of citronellal and geraniol in hexane over 1.44% Pt/SiO<sub>2</sub> at 373 K (20 atm  $H_2$ , 0.4 M citronellal, 0.5 M geraniol).

Figures 10a and 10b show the TOFs for  $H_2$  uptake during reaction at 298 K before and after addition of geraniol or citronellal. Citronellal addition after 40 min of reaction had essentially no influence on the rate of  $H_2$  uptake and the TOF for  $H_2$  uptake. Addition of geraniol, on the other hand, resulted in a twofold increase in the total rate of  $H_2$ consumption which was due primarily to an increase in the rate of conversion of geraniol to citronellol; however, the TOF for  $H_2$  uptake eventually decreased to that observed without the addition of geraniol.

Table 2 displays the effect of geraniol or citronellal addition on the net rate of disappearance of reactants and formation of products for citral hydrogenation over 3.8% Pt/SiO<sub>2</sub> at 373 K. During citral hydrogenation, the TOF for citral disappearance was 0.006 s<sup>-1</sup>, while the TOFs for formation of geraniol and nerol, citronellal, citronellol, and



FIG. 10. Specific activity for  $H_2$  uptake before and after addition of (a) 8.5 ml of geraniol and (b) 8.5 ml of citronellal during hydrogenation of citral in hexane over 1.44% Pt/SiO<sub>2</sub> at 298 K (20 atm  $H_2$ , 1 M initial citral concentration).

isopulegol were 0.0039, 0.0002, 0.0008, and 0.0008 s<sup>-1</sup>, respectively. Addition of citronellal to a citral hydrogenation reaction mixture at 373 K yielded a TOF for citral disappearance of 0.0071 s<sup>-1</sup>, which was within experimental uncertainty of the value for the rate of citral disappearance

## TABLE 2

Effect of Addition of Geraniol or Citronellal on Hydrogenation Rates at 373 K in Hexane over 3.8% Pt/SiO<sub>2</sub> (20 atm H<sub>2</sub>, 1 M Citral)

Compound	TOF $(1000 * s^{-1})$		
	Prior to addition of intermediate	Addition of citronellal	Addition of geraniol
Citral	$(5.8)^{a}$	(7.1) <sup>a</sup>	(5.8) <sup>a</sup>
Geraniol and nerol	3.9	3.9	3.9
Citronellal	0.2	$(3.9)^{a}$	0.3
Citronellol	0.8	3.6	1.7
Isopulegol	0.8	3.9	0

<sup>a</sup>Values in parentheses represent net rate of disappearance.

exhibited prior to the addition of citronellal. A fivefold enhancement in the net rate of isopulegol and citronellol formation was observed after addition of citronellal as the TOF for isopulegol formation increased from 0.0008 to 0.004  $s^{-1}$ and that for citronellol formation increased from 0.0008 to  $0.0036 \text{ s}^{-1}$ . The net rate of formation of the unsaturated alcohol (geraniol and nerol) was unaffected, as seen by the constancy in the net rate of formation of the products before and after addition of citronellal. It should be noted that the TOF for citronellal disappearance, after the addition of citronellal to a citral hydrogenation reaction mixture, was 20fold lower than that during hydrogenation of 1 M citronellal alone. Addition of geraniol to a citral hydrogenation reaction mixture did not affect the rate of citral disappearance, and a more modest rise occurred from 0.0008 to 0.0017  $s^{-1}$ in the TOF for citronellol formation.

Table 1 also lists the specific activity (as TOF) at 298 K for hydrogenation of either 1 M geraniol or 1 M nerol separately as well as for simultaneous hydrogenation of 0.5 M geraniol and 0.5 M nerol. The initial TOFs for hydrogenation of 1 M geraniol and 1 M nerol were 1.9 and  $1.5 \text{ s}^{-1}$ , respectively. Simultaneous hydrogenation of 0.5 M geraniol and 0.5 M nerol gave an initial TOF of 0.94 s<sup>-1</sup> for the rate of disappearance of geraniol + nerol with a reactivity ratio of unity. This is contrasted with the TOF of 1.2 s<sup>-1</sup> obtained during hydrogenation of 0.5 M geraniol alone.

#### DISCUSSION

The results presented earlier for hydrogenation of citral (10 mol%) in hexane under reaction conditions similar to those used in the present study have shown the absence of transport limitations and poisoning effects (1). Because the TOFs for all intermediates, except geraniol and nerol, were similar to that for citral, the kinetic data from the present study are also free of transport limitations. The unsaturated alcohols (geraniol and nerol) exhibit very high TOFs; however, the Weisz–Prater criterion was satisfied and therefore even the results for geraniol hydrogenation at 298 K are free of transport limitations (3, 5). No evidence for the leaching of metals from the reactor walls was found (3); consequently, because similar compounds were used in the present case with the same solvent, no leaching is anticipated under reaction conditions.

The reaction network in Fig. 1 shows the *cis* and *trans* isomers of both 3,7-dimethyl-2-octenal (ENAL) and 3,7-dimethyl-2-octenol as products. These products have not been routinely reported in reaction networks for citral hydrogenation over Ru catalysts (6, 7). Although these products could not be unambiguously identified, indirect evidence for their presence was obtained based on GC–MS analysis and by the nerol hydrogenation kinetic data, which allowed the resolution of a peak for *cis*-3,7-dimethyl-2-octenol distinct from other product peaks (3).

The present study was conducted to understand the influence of the reaction intermediate on the kinetics of citral hydrogenation (1). Waghray and Blackmond have suggested that a saturated aldehyde (3-methyl-butanal) can undergo decarbonylation to yield a carbonaceous species similar to that obtained with 3-methyl-2-butenal in the presence of  $H_2$ , but which was not observed in the absence of  $H_2$  (8). Therefore, they concluded that the carbonaceous species and the adsorbed CO were due to decarbonylation of the products arising from 3-methyl-2-butenal hydrogenation rather than reactant 3-methyl-2-butenal itself. Further evidence that citral decomposition may not be responsible for this deactivation behavior via the production of an inhibitor is based on the work of Davis and Barteau, who examined the effect of vinyl substituents on aldehydes and alcohols by studying propanol, allyl alcohol, propionaldehyde, and acrolein (9-11) on Pd surfaces. They suggested that with vinyl substituents adjacent to alcohol and aldehyde functionalities, the principal metal-organic interaction occurs via the oxygen moiety of the organic molecule. Furthermore, they noted that the new reaction pathways opened up by the vinyl substituents accounted for only 20% of the total products. One new pathway opened for allyl alcohol, but not propanol, was C-O bond scission to yield water and propylene, while a new pathway for acrolein, but not propanal, was hydrogenation of acrolein to propanal. In both cases the new reaction channels opened by the vinyl substituents vielded hydrocarbons that desorbed at temperatures below those used in the present study (7). Recently, Carlos de Jesus and Zaera noted that adsorption of crotonaldehyde on Pt(111) yielded significant coordination via the C=C bond via rehybridization; nevertheless, the interaction via the C=O bond was significant (12). In consideration of these results, we suggest that any role in the unusual temperature behavior due to citral decomposition may be best understood by examining the behavior of its more aliphatic counterpart, citronellal. This is consistent with the results at 373 K in the present study which show that hydrogenation of geraniol and that of its more aliphatic counterpart, citronellol, exhibited similar kinetic behavior, i.e., a very high initial activity during the first few minutes of reaction followed by a sharp orders of magnitude drop in the rate. As the following discussion illustrates, it is unlikely that citronellal, and therefore citral, alone can account for the observed activity minimum with temperature.

Hydrogenation of either citronellal or geraniol individually exhibits an activity decrease as the reaction temperature goes from 298 to 373 K, just as observed for citral hydrogenation. The initial TOF for citronellal hydrogenation dropped by only one-half on going from 298 to 373 K whereas the rate of geraniol disappearance at 373 K, after the initial deactivation, was orders of magnitude lower than the initial rate at 298 K. Similar behavior has been observed by Campelo *et al.* during liquid-phase hydrogenation of 2-methyl-2-propen-1-ol over Rh/AlPO4 catalysts at 323 K where a rapid initial hydrogenation rate was observed yielding 22% conversion after which there was negligible activity (13). The behavior observed during geraniol hydrogenation was analogous to that observed during citral hydrogenation at 373 K, i.e., a high initial rate that rapidly decreased to a constant value during the first few minutes of reaction. The high initial activity prior to the constant rate attained during citral hydrogenation at 373 K manifested itself by producing a nonzero intercept (1). Since this deactivation occurs on the time scale of seconds, it is difficult to properly characterize the reaction. The high initial reaction rate during citral hydrogenation is associated primarily with the formation of citronellal along with smaller quantities of geraniol, and we propose that the subsequent decarbonylation of geraniol (or nerol) produces the rapid decrease in activity to a constant value. Further evidence that geraniol and nerol, rather than citronellal, are involved in the deactivation process is provided by the competitive hydrogenation of citronellal and geraniol mixtures. Citronellal hydrogenation alone at 298 K exhibited zero-order kinetics (Fig. 6a), while competitive hydrogenation of citronellal and geraniol at 298 K resulted in a continuous decrease in the activity which eventually led to a nearly complete loss in activity, as seen in Fig. 8. This is further support for the proposal that geraniol and nerol may be responsible for the deactivation via inhibition during citral hydrogenation.

The decomposition pathways for aliphatic alcohols on Pt and Pd surfaces (10, 11, 15–17) and unsaturated alcohols on Pd surfaces (17) have been studied and briefly addressed in the previous paper (1). The decomposition pathway for saturated alcohols occurs via an aldehyde intermediate to yield a surface acyl group, followed by decarbonylation to yield CO and carbonaceous species (10). In that context, it might be argued that decarbonylation of the corresponding unsaturated aldehyde (citral) should also occur. This possibility cannot be discounted, but in view of the previous discussion, geraniol and nerol are considered to be more likely candidates to produce the inhibiting surface species.

It was previously assumed that each of the hydrogenation steps in Fig. 1 was described by assuming quasi-equilibrium for adsorption of the reactants, competitive adsorption between hydrogen and organic, and addition of a second H atom as the rate-determining step. The general form of the rate expression developed previously for each of the steps was (1)

$$r = \frac{kK_{\mathrm{H}_2}K_{\mathrm{Org}}K_{\mathrm{Org}} + C_{\mathrm{Org}}P_{\mathrm{H}_2}}{(1 + K_{\mathrm{Org}}C_{\mathrm{Org}})^2},$$
 [2]

where k is the rate constant,  $K_{\text{Org}}$  are the adsorption equilibrium constants for the organic reactants, and  $K_{\text{Org-H}}$ is the equilibrium constant for formation of the halfhydrogenated surface species. BOC estimates of the enthalpy of reaction associated with addition of the first H atom to either a C=C or a C=O bond yield a similar value of  $1 \pm 2$  kcal/mol (18–20). Therefore,  $K_{\text{Org-H}}$  does not vary much and the major differences in the rates among the different compounds are expected to arise from the rate constant *k* and the adsorption equilibrium constants  $K_{\text{Org.}}$ . The adsorption equilibrium constants for the reactants and intermediates of citral hydrogenation at 298 K can be ordered as

> $K_{\text{citral}} > K_{\text{citronellal}} > K_{\text{geraniol}},$  $K_{\text{nerol}} > K_{\text{citronellol}} > K_{3.7\text{-dimethyloctanol}}$

based on the hydrogenation rates of the intermediates alone along with competitive hydrogenation of a mixture of the intermediates. The argument for this ordering is as follows. Hydrogenation of 1 M geraniol in hexane at 298 K yielded primarily citronellol until the geraniol was depleted, at which point citronellol was further hydrogenated to 3,7dimethyloctanol. Such behavior suggests that at 298 K,  $K_{\text{geraniol}} > K_{\text{citronellol}} > K_{3,7-\text{dimethyloctanol}}$ . This is in accord with what one would predict a priori. Since 3,7-dimethyloctanol has no unsaturated bonds, its adsorption equilibrium constant should be significantly lower than those of compounds that contain unsaturated C=C bonds such as citral, citronellal, and geraniol. Geraniol or nerol would be expected to have greater absorption bond strength compared with citronellol due to the presence of the vinyl substituent next to the alcohol functionality, which provides additional coordination sites with the surface in addition to the alcohol funcitonality (9). The initial rates during competitive hydrogenation of geraniol and citronellal at 298 K further indicate that citronellal is more strongly bound than geraniol. Competitive hydrogenation of 0.5 M geraniol and 0.4 M citronellal yielded an initial TOF for geraniol disappearance of 0.18 s<sup>-1</sup>, in contrast to a value of 1.2 s<sup>-1</sup> during hydrogenation of 0.5 M geraniol alone, thus representing a sixfold decrease in the rate during competitive hydrogenation as opposed to hydrogenation of the alcohol alone. The initial rate of disappearance of citronellal, on the other hand, was  $0.08 \text{ s}^{-1}$  during competitive hydrogenation with geraniol compared with  $0.11 \text{ s}^{-1}$  during hydrogenation of 0.5 M citronellal alone, which represents a decrease of only 30% in the rate. The large decrease in the rate of geraniol disappearance during competitive hydrogenation and the small reduction in the rate of citronellal hydrogenation are strong evidence that the latter compound displaces geraniol from the catalyst surface. The higher rate for geraniol compared with citronellal during competitive hydrogenation is due to a higher rate constant for the alcohol. This is in agreement with results in the literature that indicate that the rate of hydrogenation of a C = C bond is more than an order of magnitude greater than that for hydrogenation of a C=O bond (21). In fact, it is because activation of a C=C bond is easier than that of a C=O bond that selective hydrogenation

of the carbonyl functionality in  $\alpha$ , $\beta$ -unsaturated aldehydes is difficult. Consequently, one can further conclude that at 298 K,  $K_{\text{citronellal}} > K_{\text{geraniol}}$ . In addition, from Fig. 10b, it can be concluded that  $K_{citral} > K_{citronellal}$  because addition of citronellal during citral hydrogenation at 298 K resulted in no change in reaction kinetics. However, the addition of geraniol to a reaction mixture of citral at 298 K resulted in a twofold increase in the rate of H<sub>2</sub> uptake (Fig. 9a). The increase in TOF for H<sub>2</sub> uptake, as mentioned earlier, is attributed to the larger rate constant for of hydrogenation of geraniol to citronellol. Therefore, even though the surface may be primarily covered by citral, the rate of H<sub>2</sub> uptake goes up due to the more rapid hydrogenation of the small amount of geraniol that does adsorb. Over time the rate of H<sub>2</sub> uptake decreases to that which would have been obtained had no geraniol been introduced. This behavior is not completely understood but it may be due to a surface equilibration involving adsorption and decomposition of geraniol being established on the time scale of the overall reaction.

The rate of citral disappearance at 373 K was not affected by addition of either citronellal or geraniol. This is consistent with the kinetics observed during hydrogenation of citral alone at 373 K, which exhibited a zero-order dependence on citral concentration. Addition of citronellal also did not affect the rate of disappearance of citral but a significant enhancement in the rate of citronellal hydrogenation to citronellol and isomerization to isopulegol did occur (Table 2). Furthermore, the rate of disappearance of citronellal, after its addition to a citral hydrogenation reaction mixture, was almost 20-fold lower as compared with hydrogenation of citronellal alone at 373 K. This is strongly indicative of our earlier assertion that  $K_{citral} > K_{citronellal}$ .

The results described in Table 2 also suggest that the rate of hydrogenation of geraniol to citronellol under citral hydrogenation conditions is negligible. Addition of geraniol to 1 M citral at 373 K did not affect the rate of formation/ disappearance of geraniol or citronellol. However, addition of citronellal to an identical reaction mixture significantly enhanced the rate of citronellal disappearance and rates of isopulegol and citronellol formation. Therefore, hydrogenation of the unsaturated alcohol (geraniol + nerol) to citronellol is kinetically insignificant during citral hydrogenation at 373 K, and the primary route for citronellol formation is via citronellal hydrogenation.

The reaction temperature has a pronounced effect on product distribution during hydrogenation of citronellal alone. It was previously shown that the selectivity to geraniol during citral hydrogenation was greater at 373 K than at 298 K (1). Similarly, the results in the present study indicate that activation of the C=O bond can be accomplished much more selectively at higher reaction temperatures, such as 373 K, than at 298 K where substantial activation of C=C bonds also occurs. This is clearly demonstrated

by the different product distributions for citronellal hydrogenation at 298 and 373 K (Figs. 7a, 7b). At 298 K and a citronellal conversion of 20%, selectivities of 60% for hydrogenation of the C=C bond, 20% for hydrogenation of both C=O and C=C bonds, and only 20% for hydrogenation of the C=O bond were obtained. At 373 K the only products detected were those involving selective hydrogenation of the C=O bond to give citronellol and isomerization of citronellal to the cyclic isopulegol. No hydrogenation of the C=C bond was detected. The more selective activation of C=O bonds compared with C=C bonds at higher reaction temperatures can be rationalized in terms of bond dissociation energies as well as heats of adsorption for coordination via each of the moieties. The gas-phase bond dissociation energy of the C=C bond is approximately 141 kcal/mol compared with 174 kcal/mol for the C=O bond; thus, higher reaction temperatures should enhance activation of the C=O bond to a greater extent (22). Furthermore, a calculated value of 14 kcal/mol from BOC theory for the heat of adsorption of formaldehyde (20) is in close agreement with 17 kcal/mol reported experimentally (23), as compared with 9 kcal/mol reported for ethylene (24). Therefore, reaction at higher temperatures will favor hydrogenation of the C=O bond since a greater fraction of the adsorbed unsaturated aldehydes should be coordinated via the C=O bond.

Hydrogenation of 0.5 M geraniol at 298 K yielded an initial TOF of 1.2 s<sup>-1</sup>. Simultaneous hydrogenation of 0.5 M geraniol and 0.5 M nerol yielded a TOF of 0.5 s<sup>-1</sup> for each of the intermediates, representing a twofold drop as compared with hydrogenation of the intermediate alone at an identical concentration of 0.5 M (Table 1). Such a decrease in rate during competitive hydrogenation is expected due to competitive adsorption between geraniol and nerol. However, it is worthwhile to note that the total hydrogenation rate of geraniol + nerol during the competitive hydrogenation reaction is also half of that observed during hydrogenation of 1 M geraniol during which a TOF of  $1.9 \text{ s}^{-1}$  was observed. This reduced activity during the competitive hydrogenation reaction is not well understood, but it may be related to the inhibition involving the decarbonylation reaction. Isomerization of geraniol and nerol to citronellal was negligible under the conditions of the present study, in contrast to vapor-phase studies of crotonaldehyde in which significant isomerization to butyraldehyde has been observed (25, 26).

Based on the initial hydrogenation rate, the reactivity of the compounds investigated in the present study can be ordered as follows: geraniol > nerol > citronellol > *E*citral ~ citronellal > *Z*-citral. As expected from literature, the reactivity of the C=C bond toward hydrogenation is greater than that of the C=O bond (21). Furthermore, it is apparent that the *trans* isomer exhibits a slightly higher hydrogenation rate as compared with the *cis* isomer, presumably due to steric constraints present for the *cis* isomer but not for the *trans* isomer. The rate of hydrogenation of the *trans* isomer of the unsaturated alcohol (geraniol) is  $1.9 \text{ s}^{-1}$  compared with  $1.5 \text{ s}^{-1}$  for the *cis* isomer (nerol). Furthermore, the initial TOF for disappearance of *E*-citral (*trans* isomer) is double that of *Z*-citral (*cis* isomer).

#### SUMMARY

The unusual activity minimum that occurs for citral hydrogenation as the temperature is increased from 298 to 373 K is duplicated during hydrogenation of citronellal, geraniol, and citronellol. Decomposition of geraniol and nerol to form adsorbed CO on Pt as an inhibitor is proposed to be responsible for the activity minimum observed during citral hydrogenation. Relative rates during hydrogenation of the pure reaction intermediates as well as competitive hydrogenation at 298 K allows the following ordering of the adsorption equilibrium constants:  $K_{\text{citral}} >$  $K_{\text{citronellal}} > K_{\text{geraniol}} > K_{\text{citronellol}} > K_{3,7-\text{dimethyloctanol}}$ . The relative rates of hydrogenation of the compounds investigated in the present study indicate that the hydrogenation rate of the C=C bond in this family of compounds is greater than that of the C=O bond, as evidenced by the ordering of the hydrogenation activity: geraniol > nerol > citronellol > *E*-citral > citronellal > *Z*-citral. Furthermore, the product distributions obtained during hydrogenation of citronellal indicate that higher reaction temperatures favor activation of the C=O bond relative to the C=C bond.

#### ACKNOWLEDGMENT

This study was supported by the DOE, Division of Basic Energy Sciences, under Grant DE-FE02-84ER13276.

#### REFERENCES

- 1. Singh, U. K., and Vannice, M. A., J. Catal. 190 (2000).
- 2. Gallezot, P., and Richard, D., *Catal. Rev. Sci. Eng.* **40**, 81 (1998).
- 3. Singh, U. K., Ph.D. thesis, Pennsylvania State University, in progress.
- Weast, R. C., "Handbook of Chemistry and Physics," 59th ed. CRC Press, Boca Raton, FL, 1979.
- Fogler, H. S., "Elements of Chemical Reaction Engineering," 2nd ed., p. 62. Prentice–Hall, Englewood Cliffs, NJ, 1992.
- 6. Kulson, P., and Cerveny, L., Appl. Catal A 128, 13 (1995).
- Mercadante, L., Neri, G., Milone, A., Donato, A., and Galvagno, S., J. Mol. Catal. 105, 93 (1996).
- Waghray, A., and Blackmond, D. G., J. Phys. Chem. 97, 6002 (1993).
- 9. Davis, J. L., and Barteau, M., J. Mol. Catal. 77, 109 (1992).
- 10. Davis, J. L., and Barteau, M., Surf. Sci. 235, 235 (1990).
- 11. Davis, J. L., and Barteau, M., Surf. Sci. 187, 387 (1987).
- 12. Carlos de Jesus, J., and Zaera, F., Surf. Sci., in press.
- Campelo, J. M., Garcia, A., Luna, D., and Marinas, J. M., *J. Catal.* 113, 172 (1988).
- 14. Shekhar, R., and Barteau, M., Catal. Lett. 31, 221 (1995).

- 15. Rendulic, K. D., and Sexton, B. A., J. Catal. 78, 126 (1982).
- Sexton, B. A., Rendulic, K. D., and Hughes, A. E., Surf. Sci. 121, 181 (1982).
- 17. Shekhar, R., and Barteau, M., Surf. Sci. 319, 298 (1994).
- Dumesic, J. A., Rudd, D. F., Aparicio, L. M., Rekoske, J. E., and Trevino, A. A., "The Microkinetics of Heterogeneous Catalysis," p. 129. Am. Chem. Soc., Washington, DC, 1993.
- 19. Sen, B., and Vannice, M. A., J. Catal. 78, 126 (1982).
- 20. Shustorovich, E., Adv. Catal. 37, 101 (1990).

- Beccat, P., Bertolini, J. C., Gauthier, Y., Massardier, J., and Ruiz, P., J. Catal. 126, 451 (1990).
- Patil, A., Banares, M. A., Lei, X., Fehlner, T. P., and Wolf, E. E., J. Catal. 159, 458 (1996).
- 23. Abbas, N. M., and Madix, R. J., Appl. Surf. Sci. 7, 241 (1981).
- Godbey, D., Zaera, F., Yeates, R., and Somorjai, G. A., Surf. Sci. 167, 150 (1986).
- 25. Sen, B., and Vannice, M. A., J. Catal. 115, 65 (1989).
- 26. Dandekar, A. B., and Vannice, M. A., J. Catal. 183, 344 (1999).