

The effects of a potassium overlayer on the reaction pathway of CH₂ and C₂H₅ on Rh(111)

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The effect of potassium on the reaction pathways of adsorbed CH₂ and C₂H₅ species on Rh(111) was investigated by means of reflection absorption infrared spectroscopy (RAIRS) and temperature programmed desorption (TDS). Hydrocarbon fragments were produced by thermal and photo-induced dissociation of the corresponding iodo compounds. Potassium adatoms markedly stabilized the adsorbed CH₂ and converted it into C₂H₄, the formation of which was not observed for K-free Rh(111). New routes of the surface reactions of C₂H₅ have been also opened in the presence of potassium, namely its transformation into butane and butene.

KEY WORDS: stability of CH₂ on Rh(111); effects of potassium on the reactions of CH₂; coupling of CH₂ into C₂H₄; stability of C₂H₅ on Rh(111); effects of potassium on the reactions of C₂H₅; formation of butane and butene from C₂H₅

1. Introduction

The study of the effects of alkali promoters on the adsorption and reactions of different compounds on metal single crystal surfaces has been the subject of extensive research in the last two decades [1–3]. This great interest reflects the importance of alkali additives in heterogeneous catalysis, particularly in the catalytic synthesis of hydrocarbons [4,5]. In order to understand the role and the effects of alkali in the latter processes, it appeared important to examine their influence on the chemistry of hydrocarbon intermediates (CH₂, CH₃, C₂H₅, C₃H₇, etc.) transitorily formed in different kinds of hydrocarbon synthesis and reactions. These CH_x fragments, however, exist in a very low concentration on the catalyst surface during the high temperature reaction, which prevented the study of their chemistry earlier. Recently, however, several methods have been described to produce these CH_x species in high surface concentration in pure state which initiated extensive investigations. In the present work we report on the effects of potassium admetal on the stability and reaction pathways of CH₂ and C₂H₅ species on Rh(111) surface, which is the continuation of our recent study performed on the adsorption and reaction of CH₃ on K-dosed Rh(111) [6]. The chemistry of these compounds on clean Rh(111) has been examined before [7–14]. The main features of their reactions will be mentioned in the appropriate parts of the paper.

2. Experimental

The two-level UHV chamber operates at a base pressure of 6×10^{-10} mbar and is pumped by an iongetter

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pump (250 l/s), and an auxiliary turbo pump. The system is equipped with a single pass CMA Auger spectrometer (Physical Electronics) and a quadrupole mass spectrometer (Balzers QMS 200) for thermal desorption spectroscopy (both in the lower chamber). The upper part was equipped with a single beam Fourier transform infrared spectrometer (Mattson Research Series) for reflection absorption infrared spectroscopy (RAIRS). The whole optical path is purged by CO₂- and H₂O-free air generated by a Balston 75–62 FT-IR purge gas generator. All RAIR spectra were averaged over 512 scans using a MCT detector at 2 cm^{-1} resolution. Sample spectra were ratioed against a background taken immediately after the sample by flashing the crystal to 1270 K. The scan was initiated after the crystal temperature had returned to 95 K.

The Rh(111) single crystal was cleaned by cycled heating in oxygen. This was followed by cycles of argon ion bombardment (typically 1–2 kV, 1×10^{-5} mbar argon, 3 μA for 10–30 min) and by annealing at 1270 K. Surface cleanliness was confirmed by AES. The Rh sample was resistively heated, and the temperature was measured with a chromel–alumel thermocouple spot-welded to the edge of the crystal. For low-temperature measurements the sample was cooled via a tantalum braid attached to a liquid nitrogen cooled stainless steel tube. Potassium was deposited on Rh(111) at room temperature by resistively heating a getter wire source (SAES getter) located at 2 cm from the sample. The time required for potassium deposition was 0.5–4 min. The K coverage was calibrated using LEED, AES and TDS yield, and has been described elsewhere [15,16]. A monolayer of potassium on Rh(111) corresponds to a surface density of 5.8×10^{14} atoms/cm² or $\Theta_{\text{K}} = 0.36$ potassium atom per surface rhodium atom.

As a source of CH₂ and C₂H₅ we used the corresponding iodide compounds. As the thermal dissociation of these

compounds at monolayer coverage begins only above 140–180 K, when the reactions of CH₂ and C₂H₅ also set in, these hydrocarbon fragments were also prepared by the photolysis of the adsorbed monolayer at 100 K. The advantage of this procedure is that CH_x species can be produced in relatively high concentration at low temperature where we can exclude the occurrence of their reactions. The photolysis experiments were carried out with 100 W Hg arc lamp.

3. Results and discussion

3.1. Reactions of CH₂

Previous studies showed that CH₂I₂ dissociates on Rh(111) at submonolayer coverage even at 90 K [9,10]. A larger concentration of CH₂ can be obtained, however, only by heating up the molecularly adsorbed CH₂I₂ to higher temperature, when the undissociated CH₂I₂ desorbs from the surface. In figure 1 we show the RAIR spectra of adsorbed CH₂I₂ annealed at different temperatures. Spectral changes occurred at 189 K, when new absorption bands developed at 2937, 2863 and 1103 cm⁻¹. These absorption bands correspond well to the various vibrations of adsorbed CH₂ (see table 1). The stability of CH₂ was followed by measuring the intensity of the two high frequency bands as a function of temperature. As can be seen in figure 2 both bands attenuate at around 180 K, and disappear completely at 300–320 K.

The effect of potassium on the infrared spectrum and on the stability of adsorbed CH₂ species was examined in the following way. Adsorbed CH₂I₂ was annealed at 190 K and then potassium was deposited on this surface at 100 K. As shown in figure 1(B), potassium influenced only slightly the positions of CH₂ bands. It exerted, however, a significant stabilization on adsorbed CH₂ species. Its vibration bands were eliminated only at 390–405 K, without any sign of the formation of new absorption features.

Following the desorbing products from a clean Rh(111) we detected CH₄ ($T_p = 230$ K), and H₂ ($T_p = 330$ K). In the presence of potassium, the peak temperature of CH₄ desorption remained the same, but its amount decreased significantly with the increase of potassium coverage (figure 3). As

Table 1
Vibrational characteristics (in cm⁻¹) for CH₂I₂ and CH₂ species.

Assignment	CH ₂ I ₂ (g) [17]	CH ₂ I ₂ /Rh(111) present work	CH ₂ /Rh(111) present work	CH ₂ /Rh(111) HREELS [10]
$\nu_{as}(\text{CH}_2)$	3047	3044	2937	2940
$\nu_s(\text{CH}_2)$	2968	2968	2863	
$\delta(\text{CH}_2)$	1353			
$\gamma(\text{CH}_2)$	1106	1111		
$\omega(\text{CH}_2)$			1103	1190
$\rho(\text{CH}_2)$	717			780
$\nu_{as}(\text{C-I}_2)$	571			
$\nu_s(\text{C-I}_2)$	486			
$\nu_{as}(\text{M-C})$				650
$\nu_s(\text{M-C})$				

was expected, the desorption of H₂ shifted to higher temperature in the presence of potassium. A new desorption product is ethylene which is released in two peaks with $T_p = 250$ and 380 K. Its amount clearly increased with the rise of the potassium coverage. This suggests that the potassium adlayer promotes the coupling of CH₂ species into C₂H₄. The fact that we could not detect adsorbed ethylene by means of infrared spectroscopy implies that ethylene desorbed at once after its formation. This is consistent with the observation that potassium induces the desorption of ethylene at low temperature from Pt(111) surface: at monolayer K coverage, most of the ethylene desorbed with a peak temperature of 150 K, and only a very little fraction remained on the surface to decompose at around 500 K [18–20].

In the next experiments CH₂ was produced at 100 K by the photolysis of an adsorbed CH₂I₂ layer on Rh(111). In this way we could avoid any thermal reaction occurring during the heating up of the adsorbed layer to 190 K, and at the same time, we could increase the surface concentration of adsorbed CH₂ at 100–110 K. As a result of photolysis, a larger amount of ethylene was produced than in the dark experiments: the enhancement was 30% at $\Theta_K = 0.24$ and 60% at $\Theta_K = 0.36$. In this case more ethylene desorbed in the low temperature peak, $T_p = 200$ K. A slight formation of ethylene, with $T_p = 190$ K, was also observed for the clean surface. Post-irradiation TPD spectra for ethylene are presented in figure 3(C).

In the explanation of the stabilizing effect of potassium we assume the formation of a surface complex between adsorbed CH₂ molecules and K adatoms. Such compound exists between CH₃ and K, which exhibits a relatively high thermal stability [21]. We are inclined to think that the simple site blocking and electronic effects play a less important role. It is very likely that the coupling of CH₂ species to ethylene proceeds in this surface complex.

3.2. Reactions of C₂H₅

The infrared spectrum of adsorbed C₂H₅I at 100 K is shown in figure 4(A). The observed vibrational feature corresponds to that measured for gas-phase and adsorbed C₂H₅I on Pt(111) [22–24]. The assignments of the absorption bands are given in table 2. Annealing the adsorbed layer caused a spectral change at 180–200 K, where the weakly adsorbed C₂H₅I already desorbed. The remaining absorption bands at 2908, 1420 and 1190 cm⁻¹ belong to the vibrations of adsorbed C₂H₅ (table 2), which suggests that most of the strongly bound C₂H₅I molecules underwent dissociation. Heating the adsorbed layer further to 240 K, the features of C₂H₅ disappeared, and new bands developed at 2975, 2879, 1380, 1125 and 940 cm⁻¹. These peaks are characteristic of ethylidyne [25–27]. However, in the case of Pt(111) the calculation revealed that the asymmetric stretch of CCH₃ is a dipole inactive in IR [28]. If this is valid for Rh(111), then we may assume that the band at 2975 cm⁻¹ is due to the symmetric stretch of di- σ -bonded ethylene. All these bands disappeared at 320 K, and only a very weak sig-

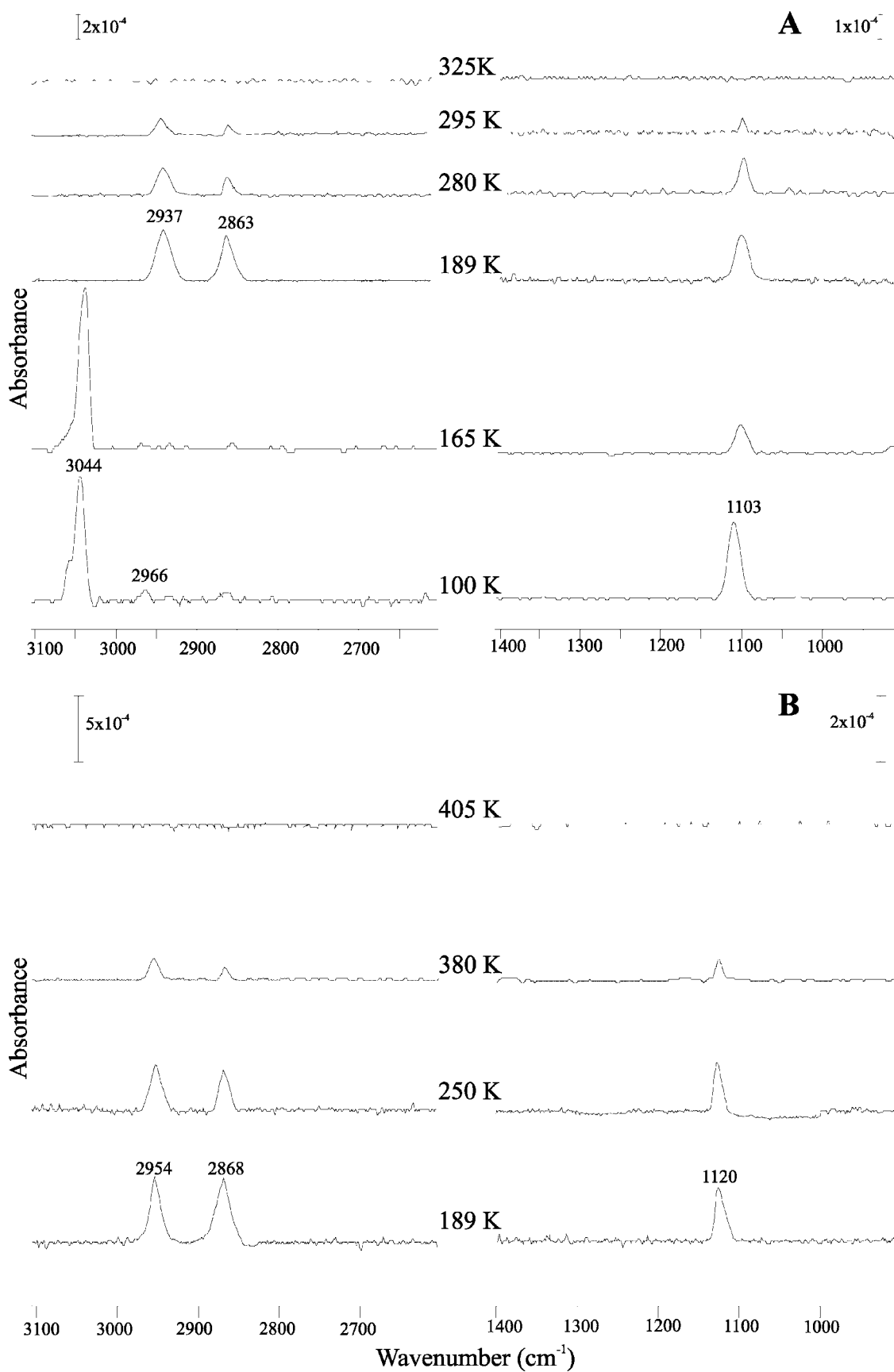


Figure 1. Effects of temperature on the RAIIR spectra of adsorbed CH_2I_2 on Rh(111). (A) Clean Rh(111); (B) K-dosed Rh(111), $\Theta_{\text{K}} = 0.36$. In the latter case, potassium was deposited on the adsorbed CH_2I_2 heated to 189 K.

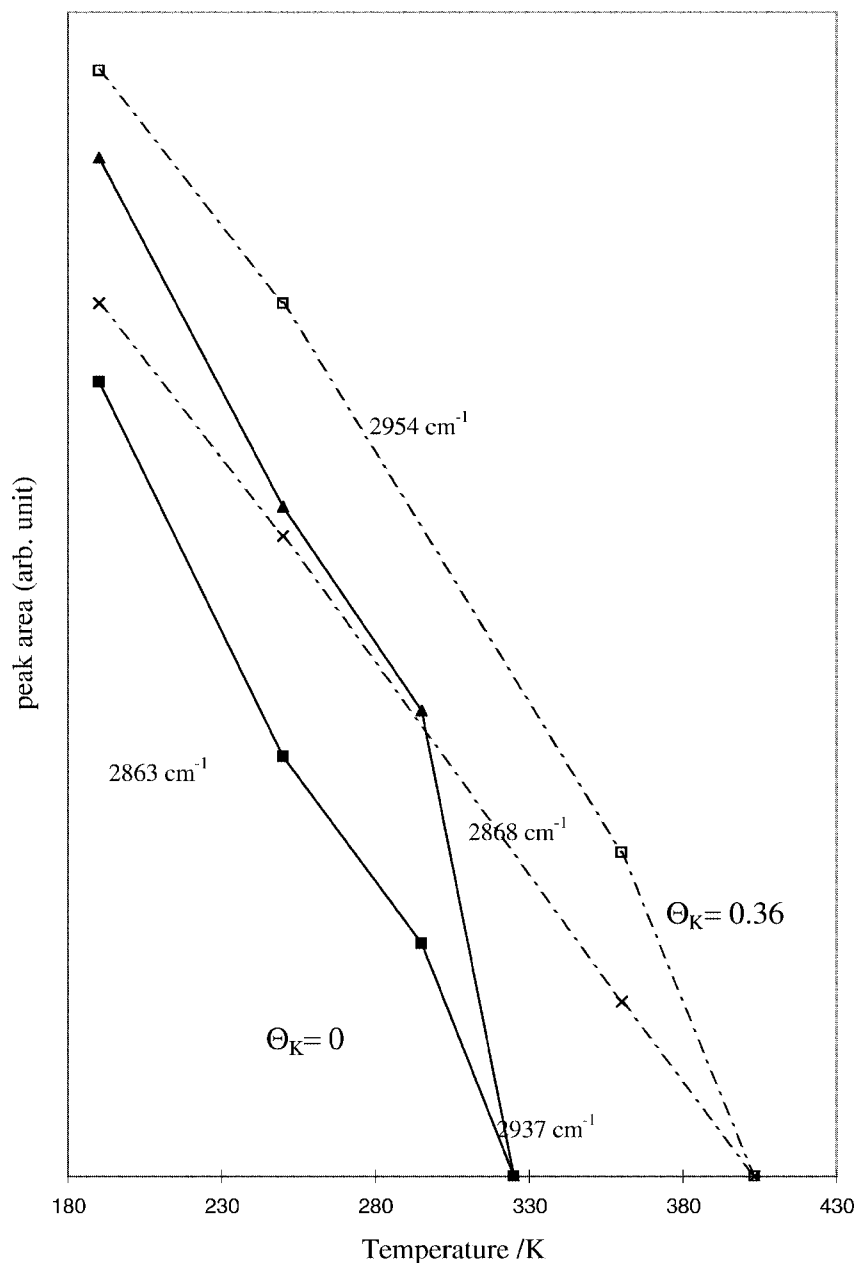


Figure 2. Effects of temperature on the absorbances of CH_2 bands on clean and K-dosed Rh(111) surfaces.

nal was detected at 3030 cm^{-1} very likely due to the stable CCH species.

Evaporation of potassium on the C_2H_5 -containing Rh(111) caused no spectral change, and it exerted no influence on the stability of C_2H_5 species. At 190 K, a new band appeared at 2947 (and 1117 cm^{-1}) (figure 4(B)), which was also observed on potassium-promoted Pt(111) surface after adsorption of C_2H_4 [19]. This feature was attributed to the formation of ethylidene (CHCH_3) [19]. All these bands disappeared at 247 K, and there were no signs of the bands of ethylidyne or other hydrocarbon fragments observed for the clean surface.

Following the reactions of adsorbed C_2H_5 on clean Rh(111) by TPD we detected no methane in the desorbing gases. The main routes of reactions of C_2H_5 were the de-

hydrogenation and hydrogenation of C_2H_5 resulting in the formation of C_2H_4 ($T_p = 180\text{ K}$) and C_2H_6 ($T_p = 170\text{ K}$). In addition, the formation of H_2 (between 350 and 500 K) was also observed as a result of the complete decomposition of ethylidyne to carbon and hydrogen. This feature is consistent with that observed in our previous study [14]. TPD spectra are presented in figure 5(A).

Potassium adatoms markedly influenced the reaction pathways of C_2H_5 : the formation of ethane and ethylene radically decreased. A completely new feature is the desorption of butane ($T_p = 135, 190$ and 220 K (shoulder)) and butene ($T_p = 180\text{--}220\text{ K}$). The amount of both compounds grew with the increase of potassium coverage up to $\Theta_K = 0.24$, when ethane and ethylene were not detectable among the desorption products (figure 5). Accordingly, new routes of the

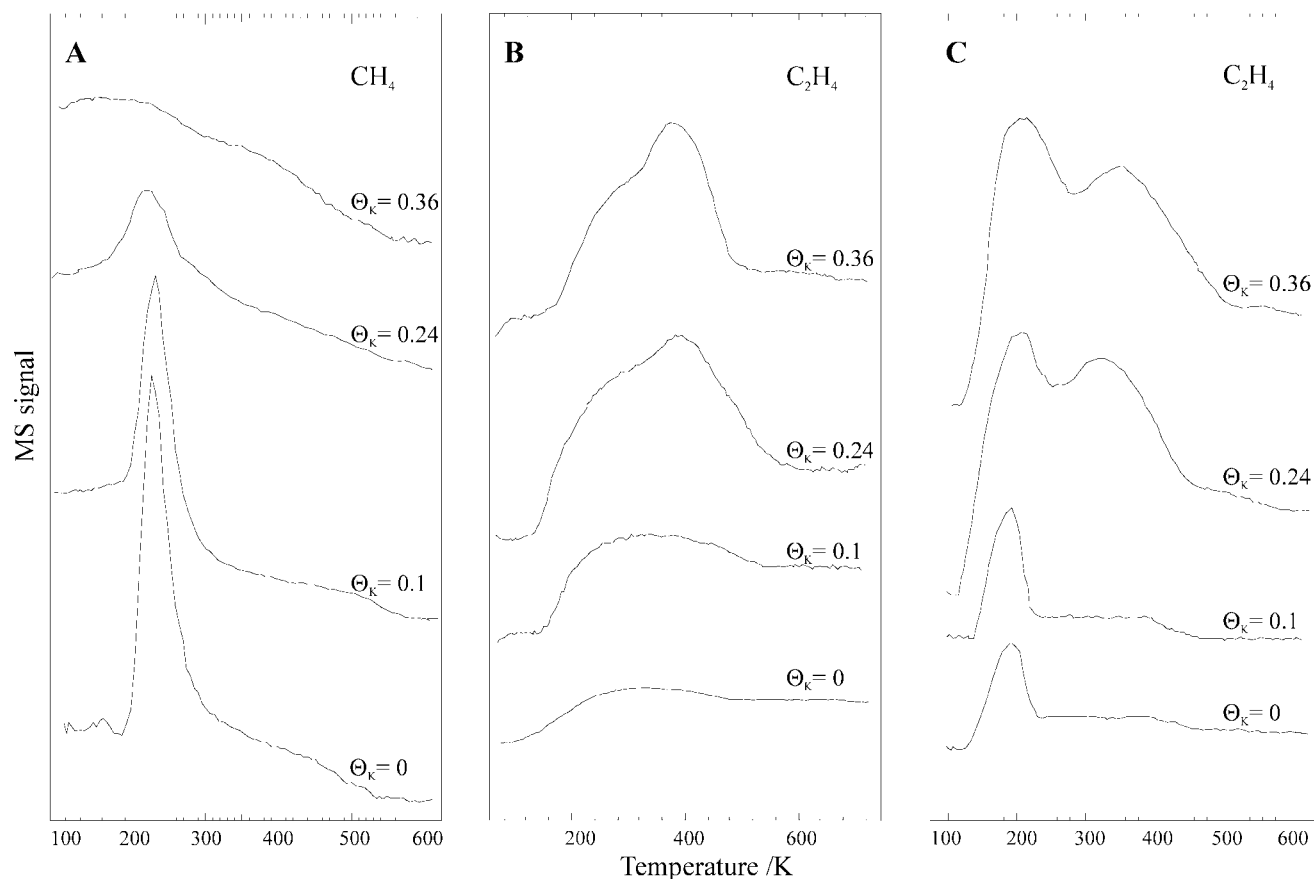


Figure 3. TPD spectra following the reactions of CH₂ on clean and K-dosed Rh(111). (A,B) CH₂ was produced by the thermal dissociation of adsorbed CH₂I₂; (C) CH₂ was produced by the photolysis of adsorbed CH₂I₂.

Table 2
Vibrational characteristics (in cm⁻¹) of C₂H₅I and C₂H₅ species.

Assignment	C ₂ H ₅ I/Pt(111) RAIRS [24]	C ₂ H ₅ I/Rh(111) present work	C ₂ H ₅ /Rh(111) present work	C ₂ H ₅ /Rh(111) HREELS [14]
$\nu_{\text{as}}(\text{CH}_3)$	2969	2969		
$\nu_{\text{s}}(\text{CH}_3)$	2914	2913	2908	2910
$2\delta_{\text{a}}(\text{CH}_3)$	2864	2853		
$\delta_{\text{a}}(\text{CH}_3)$	1454	1455	1420	1420
$\delta(\text{CH}_2)$	1438	1438		
$\delta_{\text{s}}(\text{CH}_2)$	1377	1376		
$\nu(\text{CC}) + \delta(\text{CCI})$	1212			
$\omega(\text{CH}_2)$	1203	1205	1190	1150
$\nu(\text{CC})$	952	951	940	940

reaction of C₂H₅ have been opened in the presence of potassium. Considering the sensitivity of mass spectrometer to these compounds the ratio of butane/butene was calculated to be 13 ± 3.0 .

In order to know more about the formation mechanism of two compounds, we determined their main desorption characteristics following their adsorption on K-dosed Rh(111) at 100 K. The peak temperatures were in both cases 140 K, which were independent of the coverage. This low temperature peak suggests that the evolution of both compounds is a reaction limited process. The rather broad desorption peak for butane in figure 5(B) implies two ways of bu-

tane formation. One is the coupling of C₂H₅. The other one is the hydrogenation of butene. Control experiments showed that a small fraction of butene is hydrogenated around 180–200 K under the present experimental conditions.

RAIR spectra of annealed adsorbed layer were consistent with these features. Whereas the reaction of C₂H₅ on a clean Rh(111) produced the characteristic peaks for ethylidyne – possibly through the formation of di- σ -bonded ethylene and then vinylic species [29,30], in the presence of potassium we could not detect any vibrations attributable to these adsorbates.

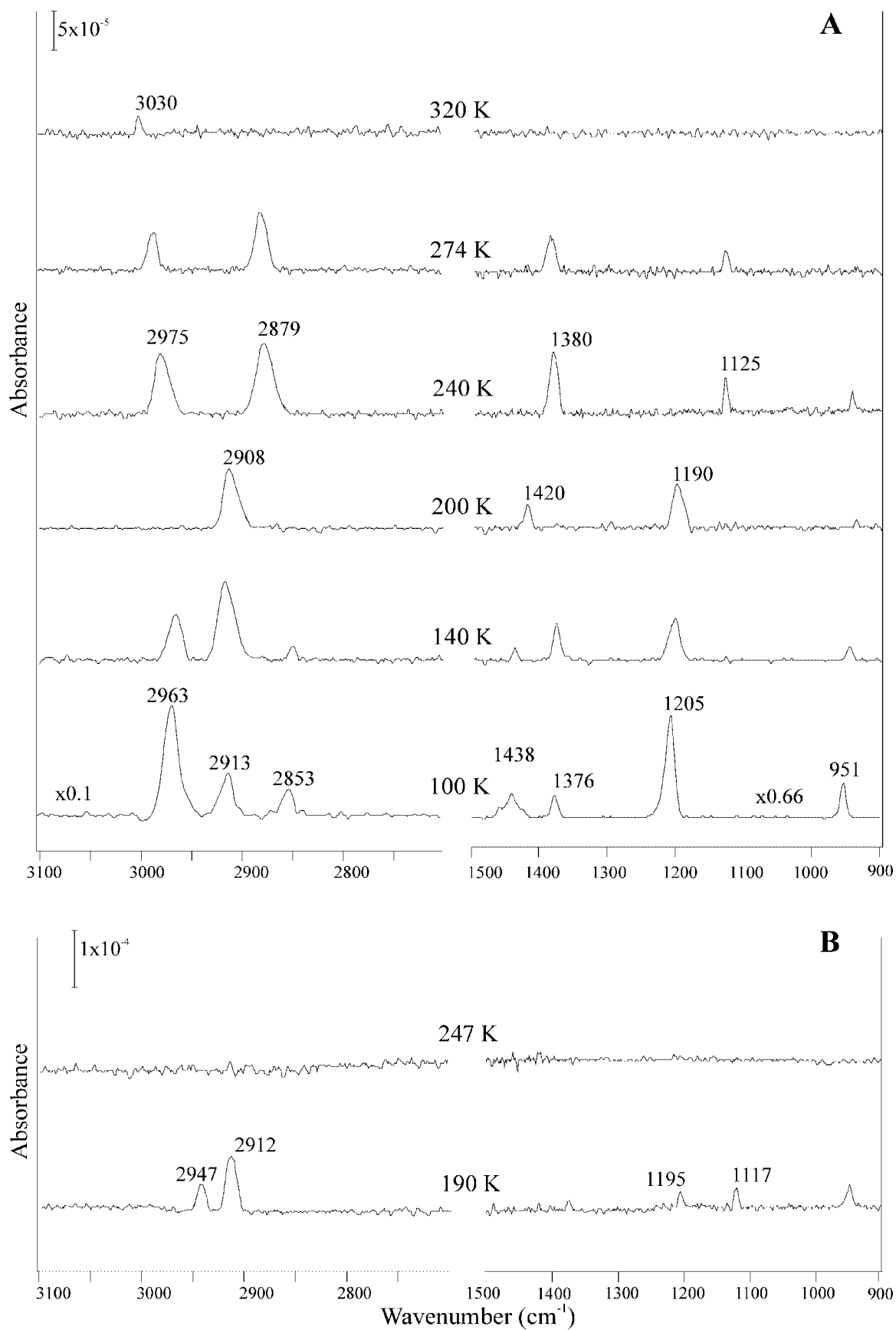


Figure 4. Effects of temperature on the RAI spectra of adsorbed $\text{C}_2\text{H}_5\text{I}$ on Rh(111). (A) Clean Rh(111); (B) K-dosed Rh(111), $\Theta_{\text{K}} = 0.36$. In the latter case, potassium was deposited on the adsorbed $\text{C}_2\text{H}_5\text{I}$ heated to 190 K.

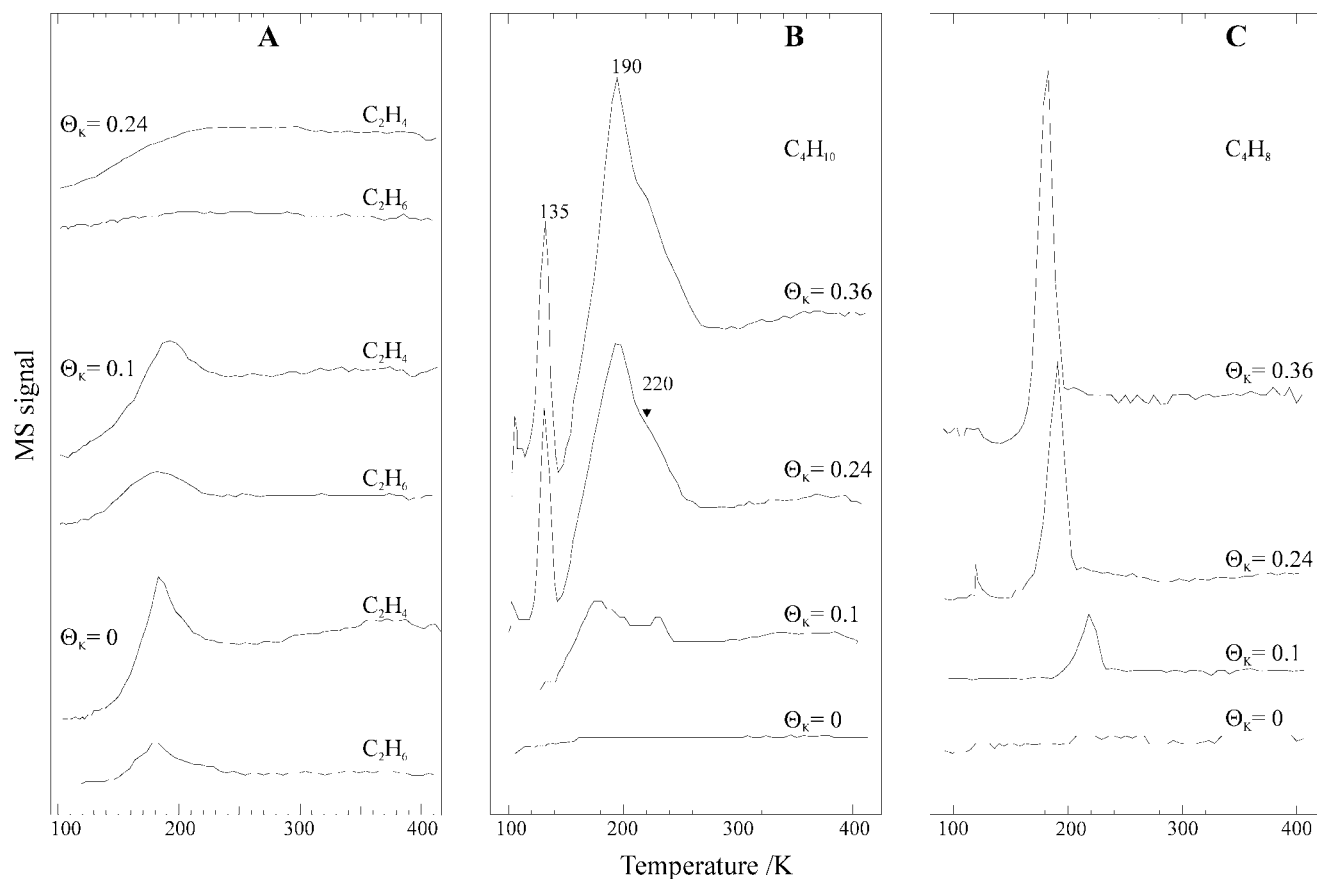


Figure 5. TPD spectra following the reactions of C_2H_5 on clean and K-dosed Rh(111).

In this case we also attempted to produce C_2H_5 at 100 K by the photolysis of the adsorbed $\text{C}_2\text{H}_5\text{I}$ on Rh(111) to avoid thermal reaction occurring during annealing of the adsorbed layer. As regards the effect of potassium, we observed the same features as above. As a result of the larger surface concentration of C_2H_5 produced by photolysis, the coupling of C_2H_5 to C_4H_{10} proceeded to a small extent even on the clean surface. However, potassium adatoms enhanced the production of both butane and butene in this case, too. Compared to the dark experiments, the amount of butane increased by a factor of 1.5 at monolayer K coverage. This factor was 3.7 in the case of the formation of butene.

The dramatic effect of potassium on the reaction of C_2H_5 can be attributed to the electron donation from potassium to the antibonding orbital of Rh–C bond. This may occur through the Rh metal, or at high potassium coverage directly from the potassium. As was demonstrated before in the case of adsorbed ethylene on Pt(111), this charge transfer leads to the stabilization of C–H bond, and to the destabilization of carbon–metal σ bonds [19]. In addition, we assume that potassium layer initiates the formation of a surface compound between adsorbed C_2H_5 molecules, which decomposes to gaseous butane. This process is illustrated in a scheme shown in figure 6. This idea is supported by the fact that the extent of the promoter effect, e.g., the change in the reaction pathway is markedly enhanced with the in-

crease of the surface concentration of potassium adatoms (figure 5). A rough calculation showed that the maximum surface concentration of C_2H_2 is $4\text{--}5 \times 10^{14}$ molecules/cm². Taking into account the number of K atoms near saturation we propose that one potassium is combined with one C_2H_5 species. Note that the largest work function decrease of Rh(111) (3.5 eV) was measured at lower potassium coverage, $\Theta_{\text{K}} = 0.15$ [16], which exerted only a moderate promoter influence on the chemistry of adsorbed C_2H_5 .

A further question is the formation of butene. A possible reaction is the coupling of ethylene into butene. As we found no report on the production of butene from ethylene on a clean and K-dosed metal surfaces, some control measurements were performed under the present reaction conditions. We found no signs of butene desorption following ethylene adsorption on Rh(111) containing different amounts of potassium. This suggests that potassium may also induce a compound formation between CHCH_3 , occurring in the partially dehydrogenated C_2H_5 species, the decomposition of which produces butene. This is also shown in figure 6.

4. Conclusions

- (i) Potassium adatoms stabilized the CH_2 adsorbed on Rh(111) surface and induced its coupling into C_2H_4 .

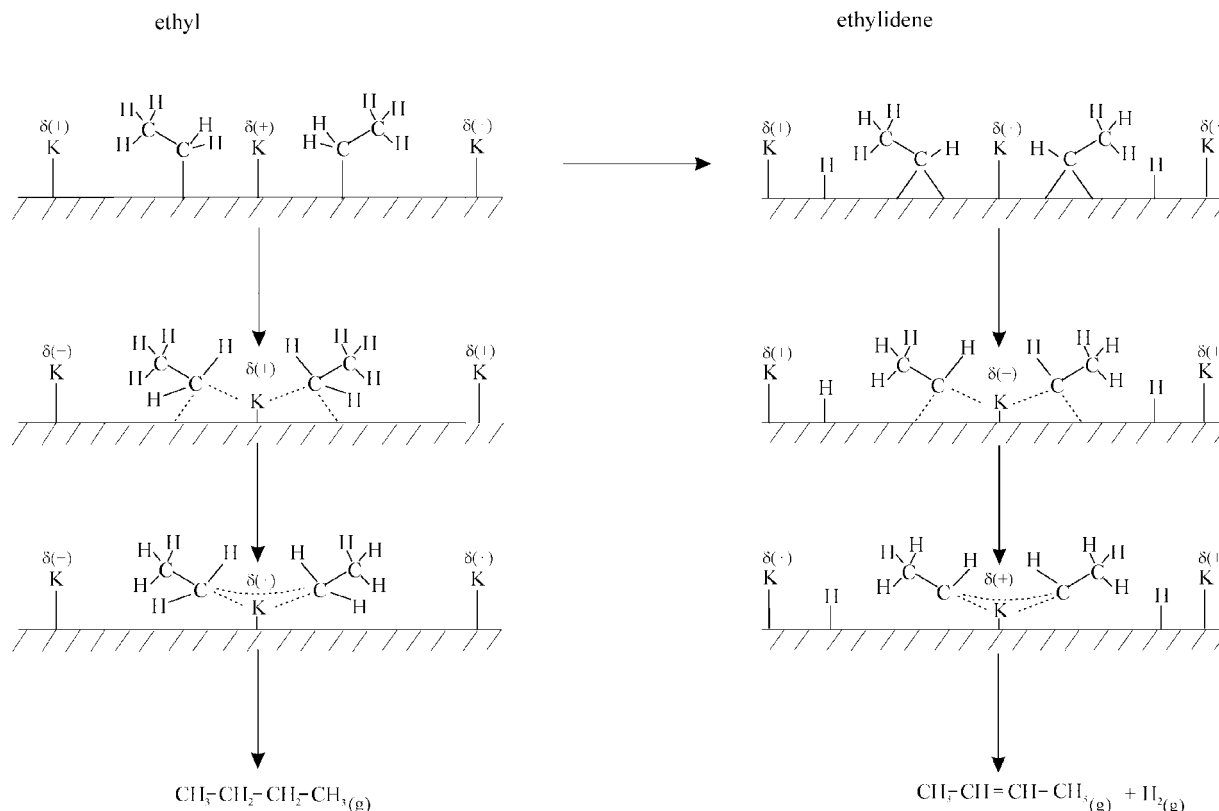


Figure 6. Effects of potassium on the reactions of adsorbed C₂H₅ on Rh(111).

- (ii) The reaction pathways of C₂H₅ were also influenced by potassium, the formation of butane and butene was observed which did not occur on the clean surface.
- (iii) The new routes of the reactions of both CH₂ and C₂H₅ are attributed to the formation of surface compounds between C_xH_y and K adatoms and to the operation of an electronic factor.

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