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**G. W. Cushing, J. K. Navin, S. B. Donald, L. Valadez, V. Johánek, and I. Harrison\*:** C−H Bond Activation of Light Alkanes on Pt(111): Dissociative Sticking Coefficients, Evans−Polanyi Relation, and Gas−Surface Energy Transfer

Page 17222. It has come to our attention that the alkane dissociative sticking coefficients measured with effusive molecular beams in our original report[1] should be systematically lower (e.g., by a factor of 2.45 for methane). After cutting open the effusive molecular beam nozzle used in the original report's experiments, it was found that the actual thickness of the nozzle orifice wall was 0.060 in. rather than the design specification of 0.010 in. The nozzle orifice diameter was 0.0197 in. (0.5 mm). A thicker orifice wall serves to sharpen the angular distribution of an effusive beam. Consequently, more flux was hitting the surface along the beam axis in our experiments than we had previously calculated according to Pauly's effusive beam model[2] under the assumption of an orifice wall thickness of 0.010 in. The result is that the originally reported dissociative sticking coefficients along the direction of the surface normal, $S_n(T_g, T_s)$, should be systematically lower. Updated figures for the paper are provided as Supporting Information. The corrected $S_n(T_g, T_s)$ for methane and ethane are in good accord with those previously measured.[3,4] The methane $S_n(T_g, T_s)$ are ~6 times smaller than expectations (see Supporting Information, Figure 2) based on a PC-MURT model[3] of dissociative sticking that replicates supersonic molecular beam dissociative sticking coefficients[5] very well. The conclusions of the original paper are unchanged as is the Evans−Polanyi plot relating the activation energy for quasi-thermal dissociative sticking to the alkane desorption energy. Nevertheless, it is important to provide accurate values for the effusive beam dissociative sticking coefficients. The asymmetry in the rotational populations prepared in supersonic and effusive molecular beams is believed to provide theoretical opportunities to better understand the role of rotational energy in dissociative sticking by comparing dissociative sticking coefficients derived from studies using these two different kinds of molecular beam.

**TABLE 1: MURT Dissociative Sticking, Energy Transfer, and Desorption Parameters for Alkanes on Pt(111)**

| | MURT | | | | Desorption | |
|---|---|---|---|---|---|---|
| | $E_0$ (kJ/mol) | $s$ | $\nu_D$ (cm$^{-1}$) | $\alpha$ (cm$^{-1}$) | $E_D$ (kJ/mol)[7] | $\tau_D(E^* = E_0)$ (ps) |
| methane | 48.2 | 4 | 315 | 50 | 15.7 | 0.078 |
| ethane | 34.4 | 4 | 145 | 700 | 32.9 | 1.56 |
| propane | 21.2 | 4 | 70 | 1400 | 41.4 | 59.1 |

**TABLE 2: Arrhenius Fit Parameters to Experimental $S_n(T)$ and Theoretical ME-MURT $S(T)$ for Alkanes on Pt(111)**

| | $S_n(T) = S_0 \exp(-E_a/RT)$ | | | $S(T) = S_0 \exp(-E_a/RT)$ | | |
|---|---|---|---|---|---|---|
| | $S_0$ | $E_a$ (kJ/mol) | $S_n(700\ K)$ | $S_0$ | $E_a$ (kJ/mol) | $S(700\ K)$ |
| methane | 1.65 | 58.0 | $7.74 \times 10^{-5}$ | 0.33 | 52.5 | $4.00 \times 10^{-5}$ |
| ethane | 0.53 | 42.5 | $3.60 \times 10^{-4}$ | 0.32 | 41.8 | $2.48 \times 10^{-4}$ |
| propane | 0.82 | 33.6 | $2.58 \times 10^{-3}$ | 0.42 | 30.2 | $2.43 \times 10^{-3}$ |

Revised Tables 1 and 2 above summarize an analysis of the corrected $S_n(T_g, T_s)$ values. One theoretical improvement was incorporated into the model of the physisorbed complexes that is used in calculation of the desorption lifetimes at the reaction threshold energy, $\tau_D(E^* = E_0)$, in Table 1 and also in ME-MURT calculations. In the past, we have assumed the physisorbed complexes have frequencies for the three frustrated rotations and frustrated translation along the surface normal that are degenerate and the same as in the transition state for chemisorption where that degenerate frequency is $\nu_D$, a fitting parameter. The improvement used here is to more directly obtain these frequencies for the physisorbed complexes from experiments. The vibrational frequency along the direction of the surface normal for physisorbed $n$-alkanes on Pt(111) has been determined by inelastic He beam scattering[6] to be $\nu_n = 68.6$ cm$^{-1}$. The remaining three low frequency vibrations corresponding to frustrated rotations were fixed by setting all three frequencies as equal to one another and adjusted to recover the appropriate pre-exponential factor for the desorption rate constant measured in alkane thermal programmed desorption experiments.[7] This change in physisorbed complex modeling had no impact on the PC-MURT calculations that require no knowledge of the physisorbed complex properties, and the change had a modest impact on the ME-MURT calculations (cf., original and revised Table 1). However, the calculated desorption lifetimes for physisorbed complexes at the apparent threshold energy for dissociative chemisorption, $E_0$, are consistently shorter in the revised Table 1 where they were calculated according to

$$\tau_D(E^* = E_0) = \frac{\rho(E_0)}{W_D^{\ddagger}(E_0)}$$

where $\rho(E^*)$ is the physisorbed complex density of states; $W_D^{\ddagger}(E^*)$ is the sum of states for the desorption transition state; and the $E^*$ energy scale has its zero when the alkanes are in the gas phase far from the surface.

**Supporting Information Available:** Revised Figures 2−6 for the original paper are available here. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**

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