

Supporting information for

Alkyl groups as synthetic vehicles in gold-mediated oxidative-coupling reactions

Bingjun Xu¹, Robert J. Madix², Cynthia M. Friend^{1,2,}*

¹Department of Chemistry and Chemical Biology, Harvard University, Cambridge, MA 02138

(USA)

²School of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138 (USA)

E-mail: cfriend@seas.harvard.edu

Table S1 Relative ion yields for the product of the reaction of methoxycarbonyl with methyl, ethyl and phenyl iodides on O/Au(111)

<i>Molecule</i>	Mass	<i>Mass fragments measured: relative intensity</i>	<i>Mass fragments reference: relative intensity</i>
CH ₃ CH ₃	30 (parent)	0.95	0.79 ^a
	27	1	1 ^a
	26	0.68	0.70 ^a
CH ₃ CH ₂ CH ₂ CH ₃	58 (parent)	0.11	0.12 ^a
	43	1	1 ^a
	41	0.30	0.28 ^a
C ₆ H ₅ C ₆ H ₅	154 (parent)	1	1 ^a
	76	0.22	0.2 ^a
CH ₃ OCH ₃	46	0.51	0.61 ^a
	45	1	1 ^a
	29	0.41	0.39 ^a
CH ₃ CH ₂ OCH ₂ CH ₃	74 (parent)	0.41	0.35 ^b
	59	0.67	0.76 ^b
	45	1	1 ^b
CH ₃ C(=O)H	44 (parent)	1	1 ^b
	43	0.66	0.63 ^b
	42	0.18	0.19 ^b
CH ₃ C(=O)OCH ₂ CH ₃	88 (parent)	0.83	0.84 ^b
	73	1	1 ^b

^a Data adopted from NIST (Stein, S. E.; Linstrom, P. J., (Ed.); Mallard, W. G., (Ed.); Institute of Standards and Technology, Gaithersburg MD, 20899).

^b Measured from the molecular desorption of the authentic sample from Au(111).

Procedure for selectivity calculations

Selectivity towards different products is calculated on a molar basis, according to the following formulae:

$$S_{diethylether} = \frac{n_{diethylether}}{n_{diethylether} + n_{ethylacetate} + n_{butane} + n_{acetaldehyde} + n_{CO_2}}$$

$$S_{ethylacetate} = \frac{n_{ethylacetate}}{n_{diethylether} + n_{ethylacetate} + n_{butane} + n_{acetaldehyde} + n_{CO_2}}$$

$$S_{butane} = \frac{n_{butane}}{n_{diethylether} + n_{ethylacetate} + n_{butane} + n_{acetaldehyde} + n_{CO_2}}$$

$$S_{acetaldehyde} = \frac{n_{acetaldehyde}}{n_{diethylether} + n_{ethylacetate} + n_{butane} + n_{acetaldehyde} + n_{CO_2}}$$

$$S_{CO_2} = \frac{n_{CO_2}}{n_{diethylether} + n_{ethylacetate} + n_{butane} + n_{acetaldehyde} + n_{CO_2}}$$

where S and n stand for the selectivity and the number density of molecules in the ionizer of the mass spectrometer, respectively. n for various species were calculated according to the following formula (The derivation is described in the supporting information of *J. Am. Chem. Soc.* **2010**, 132, 16571.):

$$n_i \approx I_i \approx \sum_j I_{ij} = \sigma_i^{-1} \cdot \sum_j \frac{s_{ij}}{T_{ij} \cdot \delta_{ij}} = \frac{\sigma_i^{-1} \cdot s_{ik}}{T_{ik} \cdot \delta_{ik}} \cdot \left(1 + \sum_{j, j \neq k} \frac{s_{ij} \cdot T_{ik} \cdot \delta_{ik}}{s_{ik} \cdot T_{ij} \cdot \delta_{ij}} \right)$$

where

s_{ij} is the measured mass spectrometer signal of the j th mass fragment of molecule i ,

s_{ij}/s_{ik} is the ratio of signals of the j th and k th fragments of molecule i determined separate calibrations of the neat parent molecule i ,

T_{ik} is the transmission coefficient of the k th fragment of molecule i ,

δ_{ik} is the detection coefficient of the k th fragment of molecule i .

Parent masses are used as signature masses for all species in the quantification (Table S1). The constants used in the quantification are summarized in Table S2.

Table S2 Constants used in the quantitative mass spectrometry analysis

<i>Mass/amu</i>	<i>T^a</i>	<i>δ^b</i>	<i>Molecule</i>	<i>σ</i>
0-20	1	1.5	Ethane	4.85 ^c
21-30	1	1	Ethene ^g	-
31-40	1	0.9	Butane	9.34 ^c
41-50	1	0.8	Acetaldehyde	6.7 ^d
51-60	1	0.7	Diethyl ether	14.2 ^d
61-70	1	0.65	Ethyl acetate	13.02 ^e
71-80	0.9	0.6	CO ₂	3.5 ^f
81-90	0.8	0.55		

^a Adapted from manual of the Pfeiffer 6.3 mm triple-filtered analyzer.

^b Adapted from manual of the UTI 100C mass spectrometer.

^c Adapted from *Chem. Phys.* **280**, 309-329 (2002).

^d *International Journal of Mass Spectrometry* **273**, 53-57 (2008).

^e Calculated according to equation 3 of *Int. J. Mass spectrom.* 248 (2006) 42-46.

^f Adapted from *J. Phys. B: At. Mol. Opt. Phys.* 37 (2004) 445-455.

^g calculated based on the 1:1 molar ratio of ethane and ethene.

Table S3 X-ray photoelectron peak assignments

<i>Surface intermediate</i>	<i>I (3d_{5/2})</i>	<i>Surface intermediate</i>	<i>O (1s)</i>
	<i>Binding energy (eV)*</i>		<i>Binding energy (eV)*</i>
I_(a)	619.0	O_(a)	529.5
CH₃I_(a)	620.5	C₂H₅OH_(a)	532.4
C₂H₅I_(a)	620.5	C₂H₅O_(a)	531.5
C₆H₅I_(a)	620.5		

*Binding energies refer to the letters in bold.

Table S4 I (3d_{5/2}) peak areas in the X-ray photoelectron spectra

I (3d_{5/2})	Temperature (K)	Peak area (a. u.)	
		Alkyl iodide 620.5 eV	I_(a) 619.0 eV
CH₃I on Au(111) (Figure 2)	150	7788	228
	200	1516	1377
	300	1026	1605
C₂H₅I on Au(111) (Figure 3a)	150	4691	2139
	200	1573	2445
	300	251	2033
C₆H₅I on Au(111) (Figure 3b)	150	7013	0
	200	3705	554
	300	996	759
C₂H₅I on O/Au(111) (θ₀ = 0.1 ML) (Figure 5b)	150	3239	2327
	200	2195	2776
	300	259	2447

Table S5 O (1s) peak areas in X-ray photoelectron spectra

O (1s) (Figure 5a)	Peak area (a. u.)		
	O_(a) 529.5 eV	Ethoxy 531.5 eV	Ethanol 532.4 eV
Bottom	270	-	-
Middle	61	218	-
Top	110	325	24

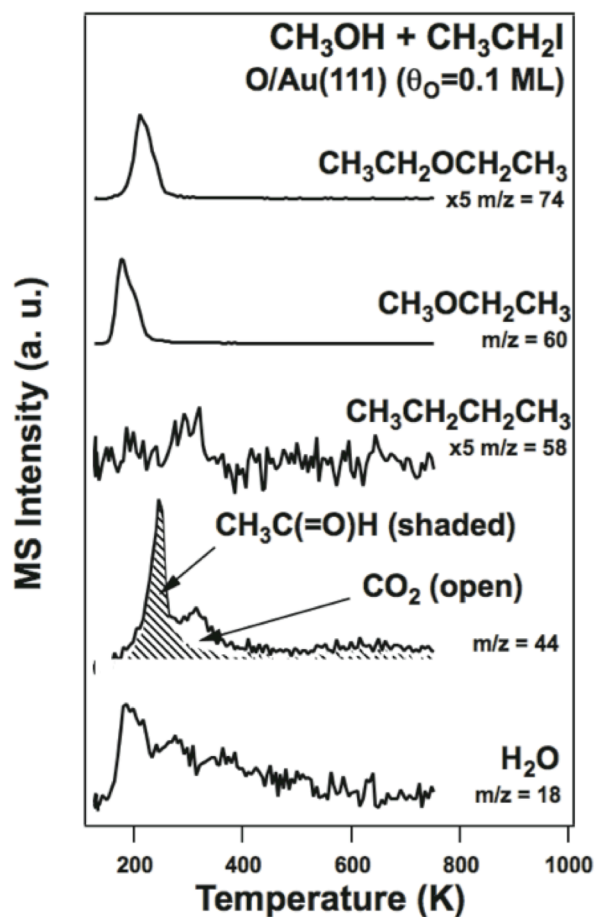


Fig. S1. Coupling of ethyl iodide with methanol on O/Au(111) ($\theta_0 = 0.1$ ML) forming diethyl ether. 6 L of CH₃OH and CH₃CH₂I were sequentially introduced at 150 K to O/Au(111) ($\theta_0 = 0.1$ ML). The heating rate is 5 K/s. Surface oxygen was prepared by ozone exposure at 200 K.

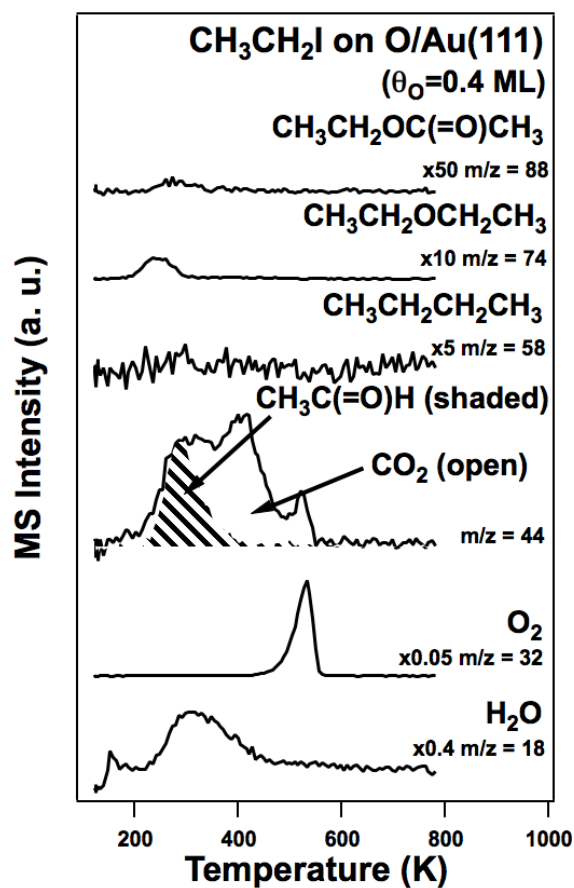
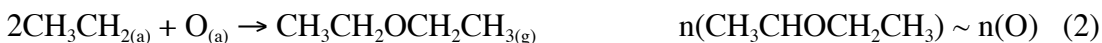
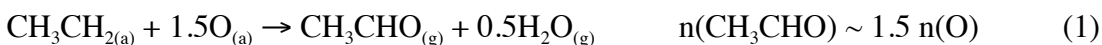


Fig. S2. Oxidation of ethyl iodide on O/Au(111) ($\theta_0 = 0.4$ ML). 6 L of CH₃CH₂I were introduced at 150 K to O/Au(111) ($\theta_0 = 0.4$ ML). The heating rate is 5 K/s. Surface oxygen was prepared by ozone exposure at 200 K.

Mass balance calculations for the oxidation of ethyl iodide on O/Au(111) ($\theta_{\text{O}} = 0.1$ ML)

The total amount of oxygen in the system is 0.1 ML adsorbed prior to the introduction of ethyl iodide at 150 K, calibrated by both temperature programmed desorption and XPS measurements.

The oxygenates formed in the oxidation of ethyl iodide on O/Au(111) ($\theta_{\text{O}} = 0.1$ ML), *i.e.* acetaldehyde and diethyl ether, have the following stoichiometric relationship with atomic oxygen:



Combining (1) and (2), together with the fact that total amount of atomic available is 0.1 ML, we get:

$$1.5n(\text{CH}_3\text{CHO}) + n(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3) = 0.1 \text{ ML} \quad (3)$$

From the product distribution in Figure 6, the selectivities for CH_3CHO , $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ are 57%, 20% and 23%, respectively. Therefore, the amounts of CH_3CHO , $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ can be inferred:

$$n(\text{CH}_3\text{CHO}) = 0.054 \text{ ML}$$

$$n(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3) = 0.019 \text{ ML}$$

$$n(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3) = 0.022 \text{ ML}$$

The total amount of ethyl distributed in the products is:

$$n(\text{CH}_3\text{CH}_2) = n(\text{CH}_3\text{CHO}) + 2 n(\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3) + 2n(\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3) = 0.136 \text{ ML}$$

The total amount of decomposed ethyl iodide on O/Au(111) ($\theta_{\text{O}} = 0.1$ ML) during reaction is estimated to be 0.11 ML, based on the maximum amount of $\text{I}_{(a)}$ measured by XPS (Table S4).

The error of the mass balance for the oxidation of ethyl iodide on O/Au(111) ($\theta_o = 0.1$ ML) can be estimated as:

$$error\% = \frac{n(CH_3CH_2) - n(I)}{0.5n(CH_3CH_2) + 0.5n(I)} \times 100\% = 20\%$$