# Supplemental Material

O. Herbinet, S. Bax, H. Legall, P.A. Glaude, R. Fournet, F. Battin-Leclerc, Z. Zhou, L. Deng, H. Guo, M. Xie, F. Qi, Detailed product analysis during the low-temperature oxidation of *n*-butane, *Phys. Chem. Chem. Phys.*, 2010.

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## I/ Photographies of the reactors used in Hefei and in Nancy

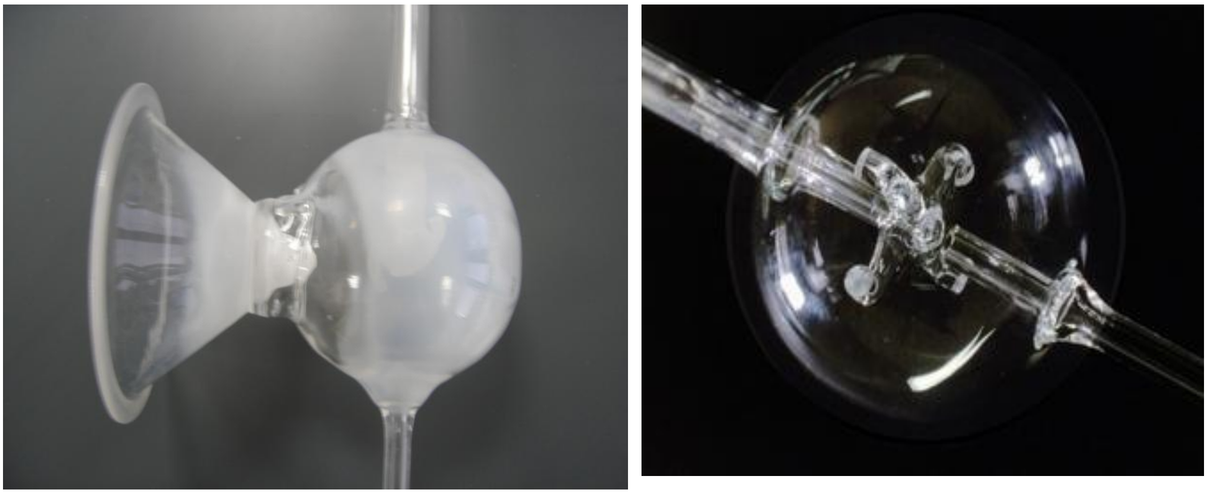

**Figure S1.** Photographies of the reactors used in Hefei and in Nancy (the white color on the reactor used in Hefei has appeared when inserting the cone on the sphere and is due to a lower quality of quartz used to make the cone; it has no incidence on the gas-phase reactions occurring in the vessel).

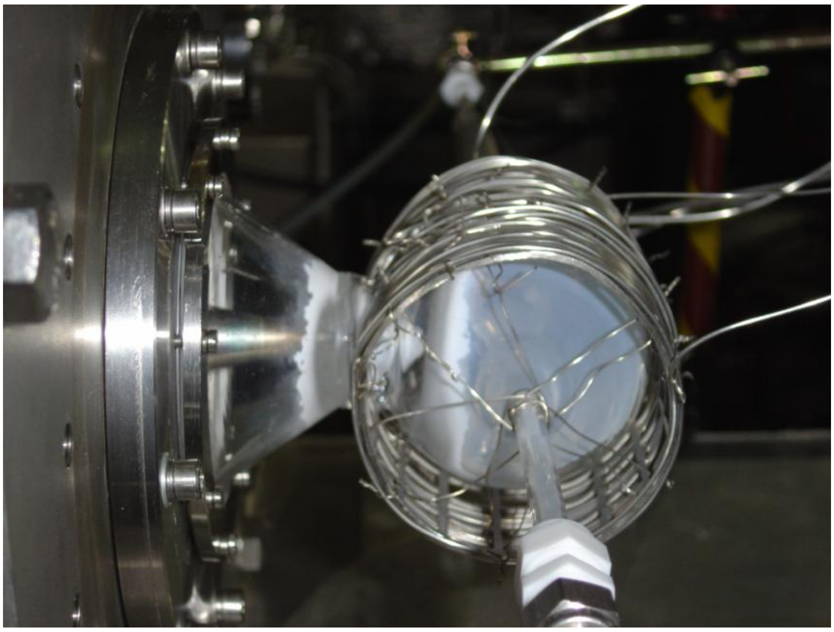

**Figure S2.** Photography of the reactor used in Hefei with a part of the heating resistances and connected to the differential pumped chamber.

## II/ Method used for calculating mole fraction from mass spectrometer ion signal

As described by Cool et al.[15], the ion signal (integrated ion count $S_i(T)$) for a species of mass i may be written as:

$$S_i(T) = CX_i(T)\sigma_i(E)D_i\Phi_p(E)F(T) \qquad (1)$$

With: C: Constant of proportionality,

$X_i(T)$: Mole fraction of the species at the temperature T,

$\sigma_i(E)$: Photoionization cross-section at the photon energy E,

$D_i$: Mass discrimination factor,

$\Phi_p(E)$: Photon flux,

F(T): Empirical instrumental sampling function, which relates the molecular beam molar density in the ionization region to the temperature and pressure inside the reactor.

Since F(T) is the same for all component species, we have for a given species, at a given ionization energy:

$$X_i(T) = X_i(560K) \times \left[\frac{S_i(T)}{S_i(560K)} \cdot \frac{F(T)}{F(560K)}\right] \qquad (2)$$

The values F(560K)/F(T) can be deduced from the ion signal obtained at a photon energy of 16.20 eV for argon (mass = 40 g/mol) which acted as an internal standard.

$$\frac{F(T)}{F(560K)} = \frac{S_{40}(T)}{S_{40}(560K)} = FKT \qquad (3)$$

In our experiments, the values of this parameter vary from 1 at 560 K to 0.747 at 780 K.

For knowing the complete evolution with temperature of the experimental mole fraction of a species, it is then only necessary to have a calibration at one given temperature. The mole fractions of oxygen and *n*-butane were then directly derived from the ion signals normalized by FTK at mass 32 and 58, respectively, considering that no reaction occurred below 590 K.

It can be deduced from equation (1), that the mole fraction of a species of mass i can be obtained from that of a reference species, of mass ref, at a given temperature and energy:

$$\frac{S_i(T)}{S_{ref}(T)} = \frac{X_i(T)}{X_{ref}(T)} \cdot \frac{\sigma_i(T)}{\sigma_{ref}(T)} \cdot \frac{D_i(T)}{D_{ref}(T)} \qquad (4)$$

# III/ Evolution with temperature of concentration of the $C_1$-$C_3$ organic compounds

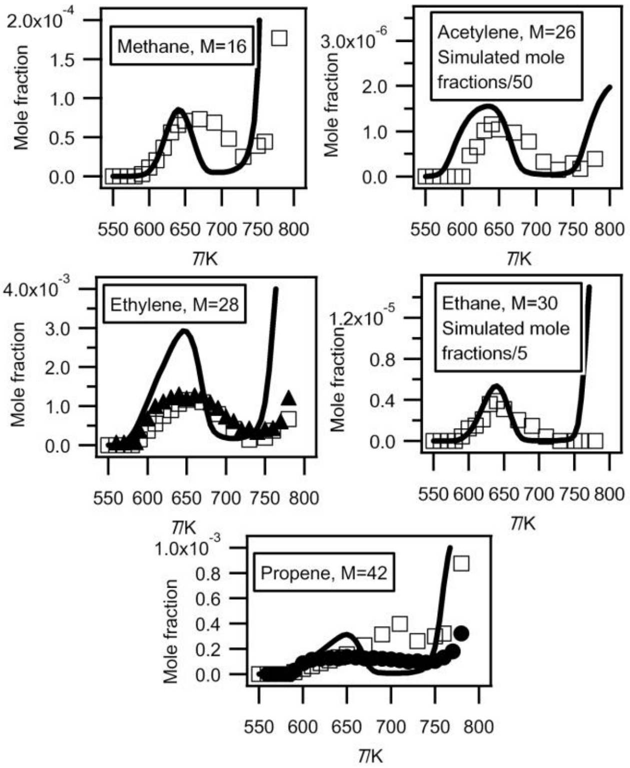

**Figure S2:** Evolution with temperature of the experimental (black circles for the data obtained by RTOF-MS (black triangles for ethylene, the mole fraction of which has been normalized by its maximum mole fractions obtained by GC), white squares for those obtained by GC) and simulated (full line) mole fractions of $C_1$-$C_3$ hydrocarbons (M in g/mol).

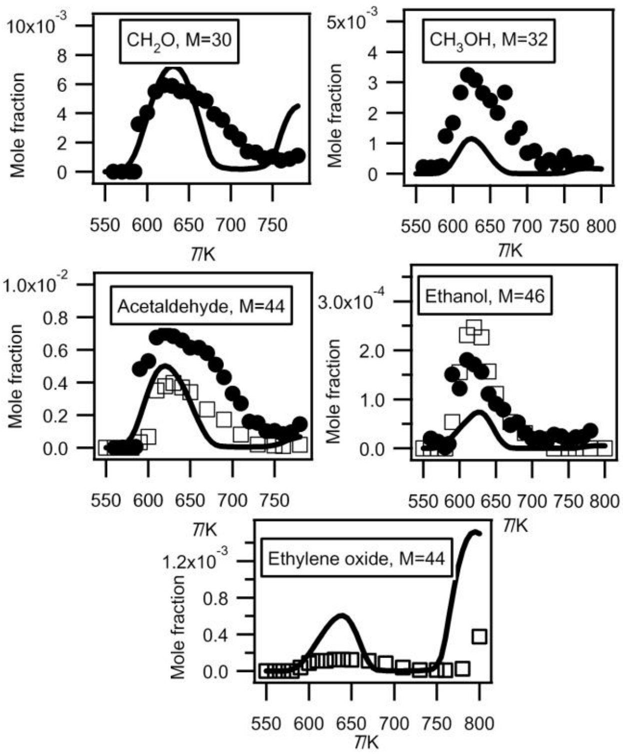

**Figure S4:** Evolution with temperature of the experimental (black circles for the data obtained by RTOF-MS, white squares for those obtained by GC) and simulated (full line) mole fractions of ethylene oxide and $C_1$-$C_2$ aldehydes and alcohols (M in g/mol).

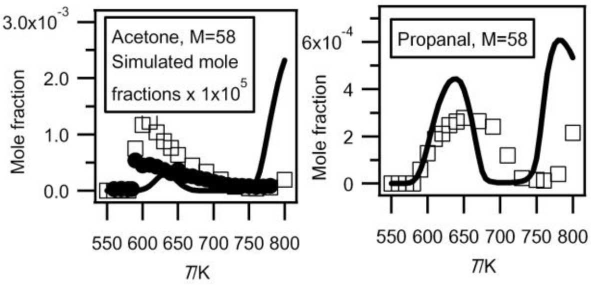

**Figure S5:** Evolution with temperature of the experimental (black circles for the data obtained by RTOF-MS, white squares for those obtained by GC) and simulated (full line) mole fractions of $C_3$ saturated carbonyl compounds (M in g/mol).

# IV/ Contribution of ketene to mass 42

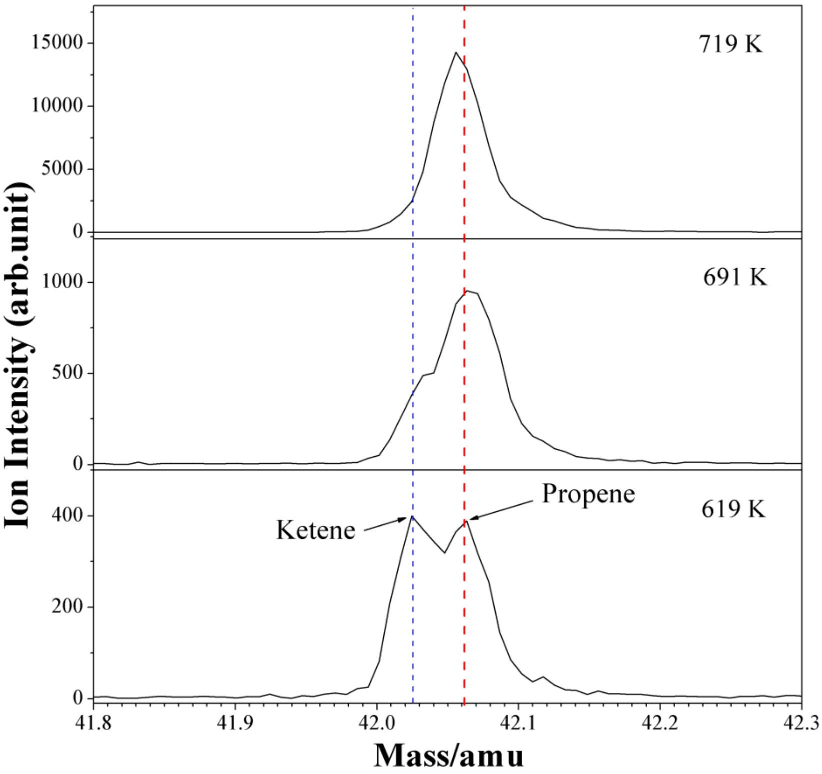

**Figure S6:** Contribution of ketene to mass 42 for temperatures between 619 and 719 K.