Electronic Supplementary Information

Reactive intermediate detection in real time via paper assisted thermal ionization mass spectrometry

Jiying Pei, Yanbiao Kang,* Guangming Huang*

Department of Chemistry, University of Science and Technology of China, 96 Jinzhai Road, Hefei, Anhui 230026, China

***Corresponding authors:**

Guangming Huang, Ph. D.,
Department of Chemistry
University of Science and Technology of China
96 Jinzhai Road, Hefei, Anhui 230026, P. R. China
Tel.: +86-551-63600706
Fax: +86-551-63600706
E-mail: gmhuang@ustc.edu.cn

Yanbiao Kang, Ph.D.,
Department of Chemistry
University of Science and Technology of China
96 Jinzhai Road, Hefei, Anhui 230026, P. R. China
Tel.: (+) 86 551 63603693
Email: ybkang@ustc.edu.cn

Supplementary Methods

General methods HPLC grade methanol and acetonitrile were purchased from Honeywell Burdick&Jackson Inc. (USA). Formic acid (FA) and acetic acid were obtained from Sigma-Aldrich Chemical Co. Ltd. (USA). Formaldehyde (HCHO), n-dibutylamine (n-DBA) and trifluoromethanesulfonic acid (TfOH) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Beijing, China). PhI(OAc)$_2$, octene and 4-methylstyrene were obtained from J&K Scientific Ltd. (Beijing, China). Styrene was gained from Aladdin Chemistry Co. Ltd. (Shanghai, China). 4-chlorine-substituted styrene was synthesized in the laboratory. All these reagents were used directly without any further purification. Distilled water (18.2 MΩ) was produced by Milli-Q system (Millipore Inc., Bedford, MA, USA).

The probe temperature was controlled by an electric soldering iron (AT936D, Atten Electronic Co. Ltd., Shenzhen, China), and the temperature was measured by a thermocouple (Tenmars Electronics Co. Ltd., Taiwan). Photographs were taken with a Nikon digital camera.

All mass spectrometry measurements were performed using home-made ESI or PATI sources, and a linear ion trap mass spectrometer (LTQ Velos Pro, Thermo Fisher Scientific, San Jose, CA, USA) was used throughout the experiment. The mass spectrometer conditions for PATI were as follows: source voltage, 0 kV; S lens voltage: positive mode, 42%; heated capillary temperature, 275 °C. The maximum ion injection time was set to 100 ms, and the number of microscan was set as one. The mass spectrometer conditions for ESI were the same as those for PATI except that the source voltage, maximum ion injection time and the number of microscan were set as 4.5 kV, 10 ms and 3 respectively.

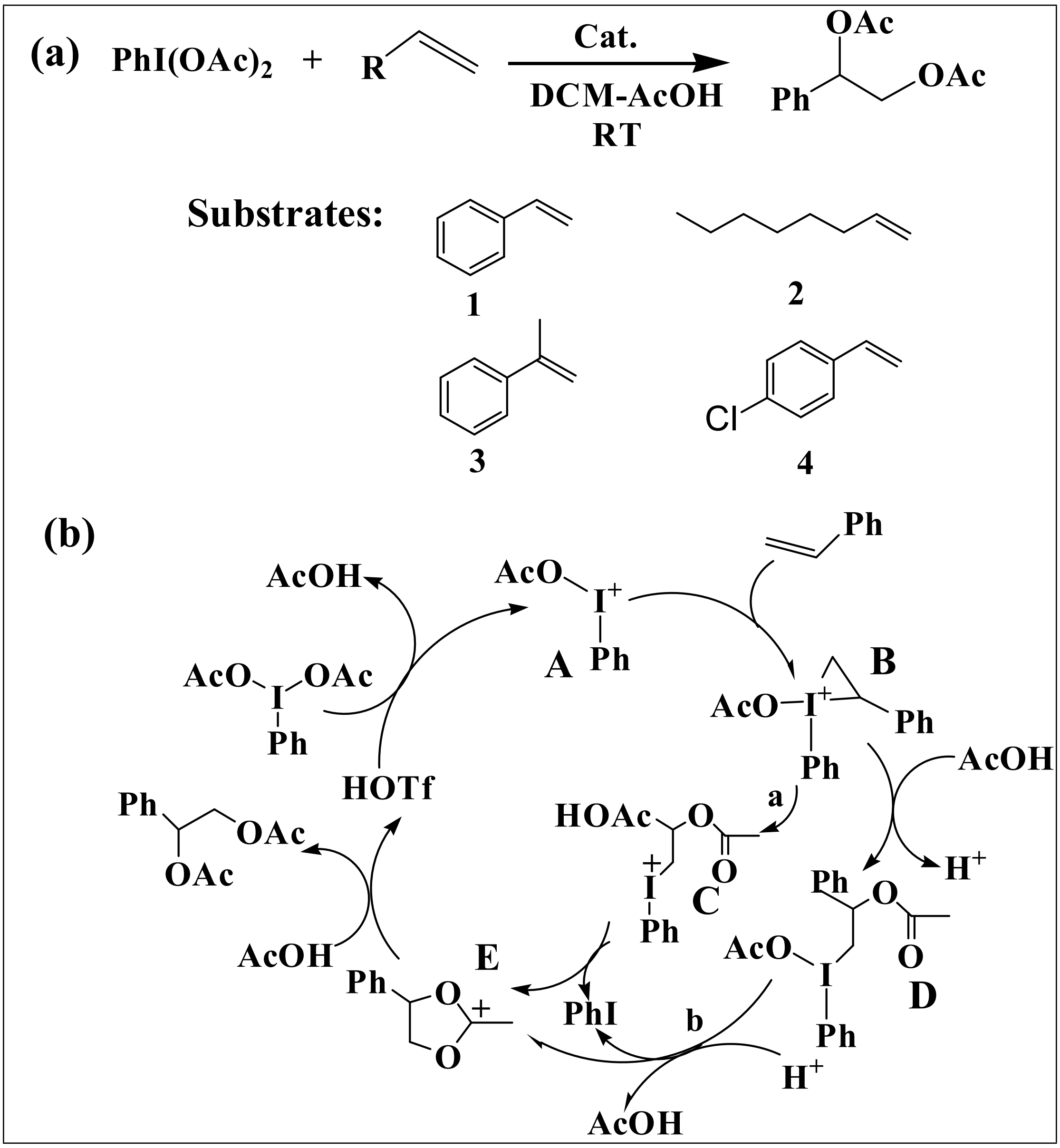
PATI Setup PATI is made up of a heated metal probe which is positioned horizontally 0.5-1 cm away from the MS inlet. The probe temperature was controlled by a regulated heater and measured by a thermocouple. For sample analysis, the probe temperature was maintained at 90 °C and 125 °C for solvent dichloromethane (CH_2Cl_2, DCM) and CH_3OH/H_2O (v/v, 1:1) respectively first. Then, a small volume of sample solution (2-5 μL) was loaded onto the heated filter paper with a home-made silica capillary-pipette tip. The home-made silica capillary-pipette tip is composed of a 10 μL pipette tip and a 2 cm long fused silica capillary. One end of the capillary is inserted into the conventional 10 μL pipette tip while the other end is used for sample loading. Polyimide coating of the top 5 mm of the capillary is burned to avoid possible interference.

Conventional ESI MS for E-C reaction. A heating reflux unit was put up to initiate the reaction of E-C methylation. The solvent used was CH_3OH/H_2O (v/v, 1:1) and the refluxing temperature was set as 76 ^{o}C. After 60 mins' reaction, the round-bottom flask was lifted up for naturally cooling. Then 10 μL of the bulk solution was taken out to be diluted with CH_3OH/H_2O (v/v, 1:1) for MS analysis. Two groups of E-C reactions with different reactant concentrations were conducted independently. Reactant concentrations 1 corresponded to $C_{n\text{-}DBA} = 0.6$ mM, $C_{HCHO} = 36$ mM and $C_{FA} = 54$ mM, while concentrations 2 were 10 times improvement of all the reactants. Before MS analysis, the bulk solutions with low and high reactant concentrations are diluted 100 and 1000 times respectively.

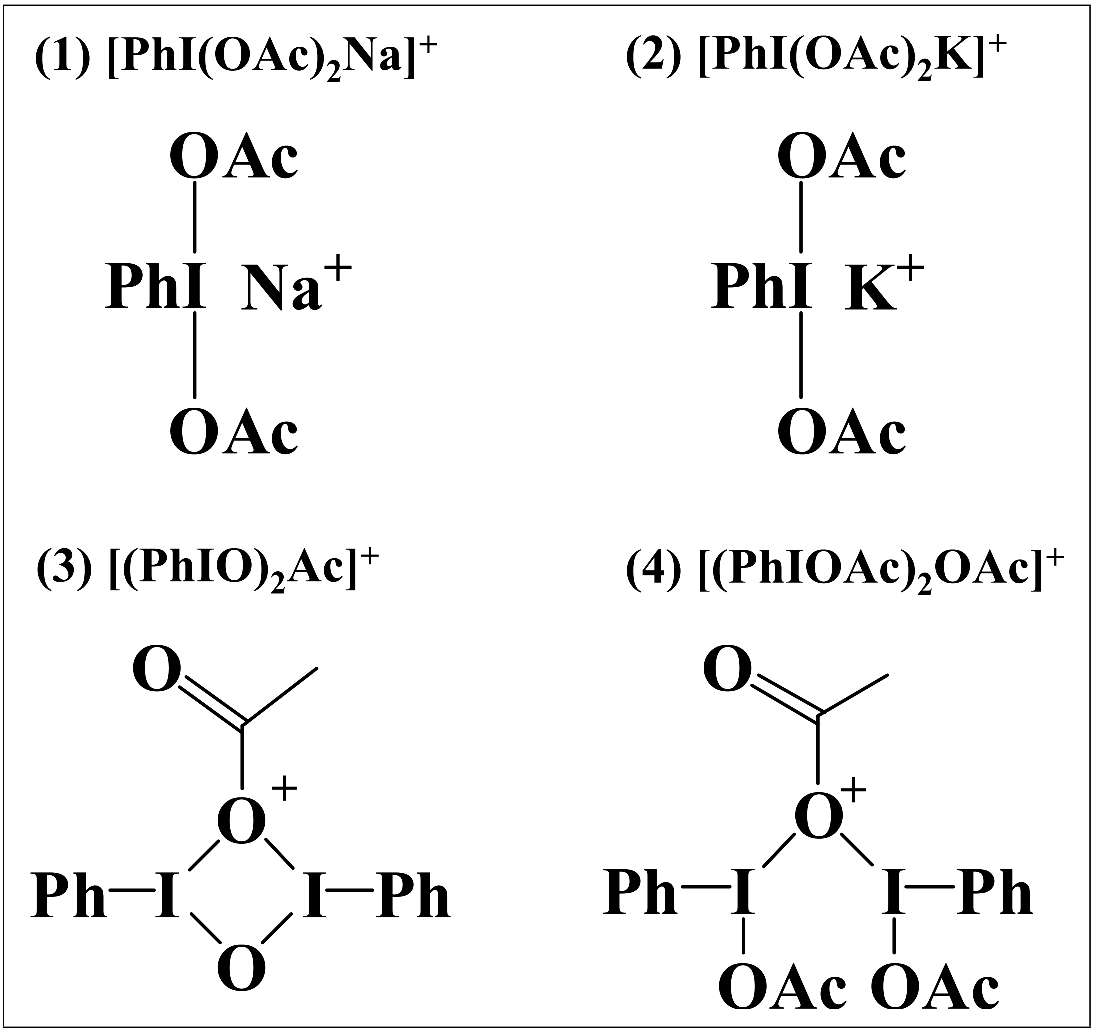
PATI MS for E-C reaction. Before analysis, the probe temperature was regulated to maintain at 125 °C first, then 5 μL of the bulk reaction solution was loaded onto the heated filter paper with a home-made silica capillary-pipette tip. When solution contacts the heated filter paper, the solvent evaporates, accompanying with the transfer of reagents, products and intermediates from liquid phase to gas phase for MS analysis.

Conventional ESI MS for alkenes dioxygenation. $PhI(OAc)_2$, HOAc, TfOH and one of the substrates (styrene, octene, 4-methylstyrene and 4-chlorostyrene) were dissolved by CH_2Cl_2 with the final concentrations of 0.19 M, 0.13 M, 10% (m/m) and 5 mM respectively. After 30 mins' reaction, 5 μL of the bulk solution was taken out to be diluted 10000 times with CH_3CN/H_2O (v/v, 1:1) for MS analysis.

PATI MS for alkenes dioxygenation. Before analysis, the probe temperature was regulated to maintain at 90 °C first. Then, two reaction solutions held in two separate pipette tips were added to the filter paper heated simultaneously. One solution was the mixture of $PhI(OAc)_2$ (0.38 M), substrate (0.25 M) and 20% of HOAc (v/v) in CH_2Cl_2, while the other one was 10 mM TfOH as catalyst in CH_2Cl_2. When the two solutions contacted on the heated filter paper, the reaction was initiated and the intermediate ions were detected upon solvent evaporatation.



Scheme S1. Proposed mechanism for the TfOH-catalyzed intermolecular diacetoxylation of styrene. Reprinted with permission from Kang (2011). Copyright 2011, American Chemical Society



(1) $[PhI(OAc)_2Na]^+$

(2) $[PhI(OAc)_2K]^+$

(3) $[(PhIO)_2Ac]^+$

(4) $[(PhIOAc)_2OAc]^+$

Scheme S2. Structures of monomer and dimer cations of $PhI(OAc)_2$ reagent in alkenes dioxygenation reaction ($[PhI(OAc)_2 + Na]^+$, $[PhI(OAc)_2 + K]^+$, $[(PhIO)_2Ac]^+$ and $[(PhIOAc)_2OAc]^+$).

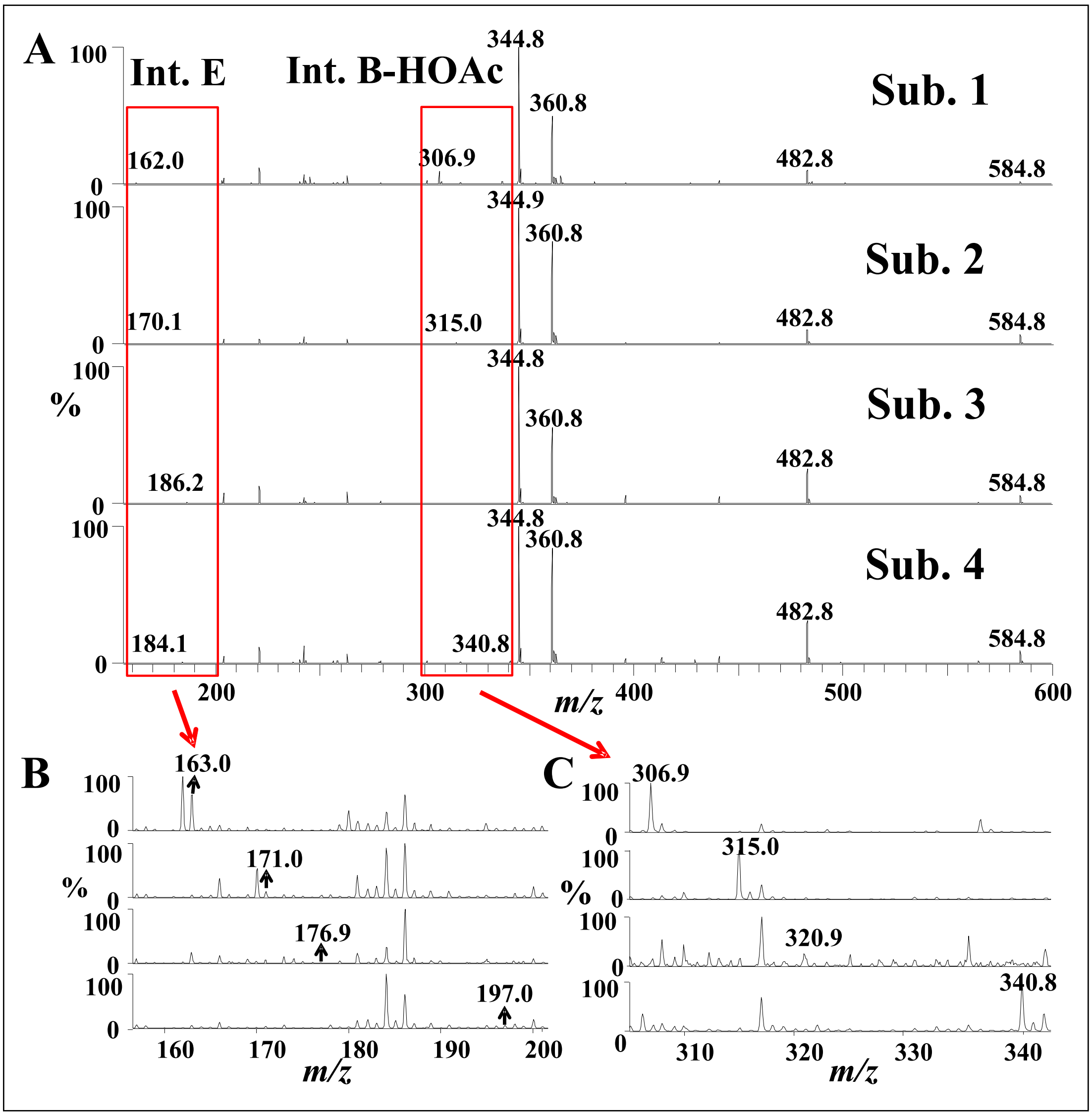


Figure S1. (A) Mass spectra of alkenes dioxygenation reaction with different substrates monitored by ESI MS. Substrates 1-4 corresponded to styrene, octene, 4-methylstyrene and 4-chlorostyrene respectively. Reaction conditions: C($PhI(OAc)_2$) = 0.19 M, C(substrate) = 0.13 M, C(HAc) = 10% (m/m), C(TfOH) = 5 mM in CH_2Cl_2. The solution was diluted 10000 times with CH_3CN/H_2O (v/v, 1:1) before ESI MS analysis. (B, C) Amplification of the spectra corresponding to the mass ranges of intermediates E and B-HOAc.

Figure S2. Adsorption behavior of filter paper to the extra reagents of alkenes dioxygenation reaction.