Detection of Gas-Phase Organic Radicals Formed in Gas–Surface Reactions by Photoelectron Spectroscopy: Abstraction of Allylic Hydrogen by Bismuth Oxide

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(Received: May 31, 1983)

Photoelectron spectroscopy has been used to detect gas-phase organic radicals as well as stable products formed in low-pressure gas–surface reactions. The products were sampled directly after exiting the catalyst bed. Allylic hydrogen abstraction by Bi_2O_3 at 760 °C forms gas-phase allyl and 2-methylallyl radicals from propylene and isobutylene, respectively, in the presence of oxygen. CO_2 and H_2O are the other observed products of alkene oxidation over Bi_2O_3. The product distributions and the 2-methylallyl radical yields as a function of oxygen pressure and Bi_2O_3 temperature are discussed.

Introduction

As an extension of our continuing efforts to obtain the photoelectron spectra of organic free radicals,[1-5] we have investigated the possibility of monitoring by photoelectron spectroscopy gas-phase radicals produced by gas–surface reactions. Organic radicals escaping the surface of heated solid catalysts during gas–surface reactions have been detected by matrix isolation ESR spectroscopy,[6,7] mass spectrometry,[8] and matrix isolation IR spectroscopy,[9] but not by photoelectron spectroscopy. Photoelectron spectroscopy has been used to analyze the stable products of heterogeneously catalyzed reactions,[10] and to detect transient species other than organic radicals produced by flowing a gas over a solid reactant. For example, SiF_2 produced by flowing SiF_4 over heated Si has been detected by photoelectron spectroscopy.[11] When photoelectron spectroscopy is used, stable and transient products of a low-pressure gas-surface reaction can be sampled directly after exiting the catalyst bed. Since organic radicals generally have lower ionization potentials than closed-shell organics, photoelectron spectroscopy has a high selectivity for their detection. Furthermore, it has the ability to distinguish between isomers by their ionization potentials and photoelectron band shapes.

In the present study, bismuth oxide catalyst (Bi_2O_3) was chosen as the solid since it has been shown by Lunsford and co-workers using matrix isolation ESR spectroscopy to produce gas-phase allyl radicals upon interaction of propylene with its heated surface.[6,7] Interest in the catalytic properties of bismuth oxide comes primarily from a desire to understand its role as a component of bismuth molybdate catalysts used commercially for heterogeneous oxidation of propylene to acrolein. The results of investigations into the mechanism of selective oxidation of propylene have been reviewed,[12,13] and it is generally accepted that the rate-determining step in this catalytic reaction is the abstraction of an allylic hydrogen in propylene by lattice oxygen. Some experiments have been interpreted to indicate that the lattice oxygens involved in this step are associated with bismuth. Consistent with this, the major stable products of propylene over Bi_2O_3 are the radical coupling product, 1,5-hexadiene, and CO_2.

There are several advantages associated with the selection of allylic radicals for an initial investigation. The first band (adiabatic ionization potential = vertical ionization potential = 8.13 eV) of the allyl radical photoelectron spectrum has sharply resolved vibrational structure[1] and is therefore readily assignable. Several other resonance stabilized organic radicals, which could be produced by abstraction of a hydrogen atom next to a double bond, also have sharply structured first photoelectron bands.[1,5,14] Furthermore, allylic radicals are thermally stable and are not readily pyrolyzed.

Results

The photoelectron spectrometer used in this study is of standard design, modified to study the products of gas-phase pyrolysis.[1] The pyrolyzer consists of a 3-mm i.d. quartz tube, at one end of which a 2.5 cm length is wrapped with a noninductive heater. A thermocouple wedged between the heater and the quartz tube is used to monitor the temperature. Gases flow through the tube, traveling 0.75 cm after leaving the heated region before intersecting the photon beam from the HeI lamp, where they are ionized. The residence time of the gases in the heated region is on the order of 1 ms. For these experiments, the heated section of quartz tube has been filled with Bi_2O_3 chips (~1 mm × 1 mm × 0.5 mm), a small amount of quartz wool at each end being used to keep the chips in place. The Bi_2O_3 chips were made by mixing Bi_2O_3 powder (Alfa Products, 99.8%) with water to form a thick paste, drying this in air up to a temperature of 650 °C, and breaking the material into chips.[6] Before and after each set of experiments, the Bi_2O_3 chips were heated in flowing oxygen for at least 1 h at 500 °C. Spectra were analyzed by comparing them with spectra of reactants and possible products taken from the literature or recorded on our spectrometer using authentic samples.

[†] Contribution No. 6821.

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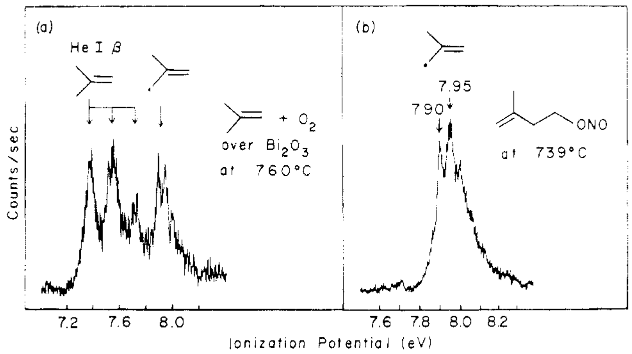

Figure 1. He I photoelectron spectra of 2-methylallyl radical which has been produced by (a) the interaction of isobutylene with Bi_2O_3 at 760 °C in the presence of oxygen and (b) the pyrolysis of 3-methyl-3-buten-1-yl nitrite (adapted from ref 5). In addition to 2-methylallyl radical, the first photoelectron band of isobutylene ionized by the He Iβ line of the He I lamp[17] is observed in (a).

At a temperature of 750 °C and with a ratio of oxygen to propylene of 1:5 (total pressure in the catalyst bed is $\sim 10^{-2}$ torr), ~1% allyl radical, relative to propylene, was observed.[15,16] No significant amount (<5%) of acrolein[17] or 1,5-hexadiene (allyl radical recombination product) and no photoelectron band which could be assigned to the allyl peroxy radical ($C_3H_5O_2\cdot$)[18] were observed. A small amount of CO_2 was observed. A small amount of H_2O, the other product of complete oxidation of hydrocarbons, could also be present but was not detected due to overlapping O_2 and H_2O photoelectron spectra.

To investigate the generality of allylic hydrogen abstraction by Bi_2O_3, we monitored the products of isobutylene interacting with Bi_2O_3. At a temperature of 760 °C and with a ratio of oxygen to isobutylene of 1:5 (total pressure in the catalyst bed is $\sim 10^{-2}$ torr), ~2% 2-methylallyl radical, relative to isobutylene, was observed.[15,16] Our spectral assignment is confirmed by the photoelectron spectra of the 2-methylallyl radical from two different sources shown in Figure 1. For the spectrum shown in Figure 1a, the radical was produced by the interaction of isobutylene with Bi_2O_3 under the experimental conditions described above. Figure 1b presents the spectrum obtained by pyrolysis of an appropriate alkyl nitrite precursor, part of a complete study of C_4H_7 radical photoelectron spectra.[5] No significant amounts (<5%) of methacrolein[19] or 2,4-dimethyl-1,5-hexadiene were observed when isobutylene and oxygen were passed over Bi_2O_3 at 750 °C. No photoelectron band which could be assigned to the 2-methylallyl peroxy radical[18] was observed. Small amounts of CO_2 and H_2O were observed.

The effect of varying the temperature of the catalyst on the production of 2-methylallyl radical was investigated (using a pressure ratio of oxygen to isobutylene of 1:5). The intensity of the 2-methylallyl radical spectrum, compared to the isobutylene He Iβ spectrum, monotonically increased over the temperature range 650–750 °C. Temperatures higher than 750 °C were avoided because the melting point of Bi_2O_3 is 817 °C. Below 650 °C the 2-methylallyl radical band is too weak to quantify. The limited temperature range and low signal levels precluded a more quantitative analysis of the temperature dependence of radical yields. However, our results are consistent with an effective activation energy for radical production in the range of 10–35 kcal/mol.

The effect of varying the oxygen to isobutylene pressure ratios on the production of 2-methylallyl radicals at 750 °C was also investigated. The amount of 2-methylallyl radicals produced was constant for oxygen to isobutylene ratios between 1:4 and 1:8. Only with very low oxygen pressures (ratios less than ~1:100) was a marked decrease in production of 2-methylallyl radicals observed. With no oxygen flowing, radical production was still observed.

No 2-methylallyl radicals were observed at 750 °C when the catalyst and quartz wool were absent. To demonstrate that the Bi_2O_3 chips and quartz wool plugs do not simply increase the residence time of isobutylene in the heated region, thus allowing pyrolysis or gas-phase oxidation of isobutylene, the Bi_2O_3 chips were replaced with similarly sized quartz chips and the amount and configuration of the quartz wool were reproduced. No 2-methylallyl radicals were observed at 750 °C with this experimental arrangement.

Discussion

Using photoelectron spectroscopy, we have been able to detect gas-phase organic radicals formed in gas–surface reactions. Allyl and 2-methylallyl radicals were formed by allylic hydrogen abstraction by Bi_2O_3 from propylene and isobutylene, respectively, in the presence of oxygen. CO_2 and H_2O are the other observed products of alkene oxidation over Bi_2O_3. In experiments where only stable products could be detected, 1,5-hexadiene and CO_2 were the major products of propylene oxidation over Bi_2O_3.[12,13] Martir and Lunsford concluded by comparison of allyl radical and 1,5-hexadiene concentrations over Bi_2O_3 that gas-phase radical recombination reactions served as a major pathway for the formation of 1,5-hexadiene.[6] With direct sampling of a low-pressure reaction region and a somewhat lower sensitivity for the detection of dienes than allylic radicals, it is not unexpected that we observed no diene production in our experiments.

The production of 2-methylallyl radical from isobutylene and oxygen flowing over Bi_2O_3 increases with the catalyst temperature, indicating its formation is an activated process. Lunsford and co-workers reported apparent activation energies of 14[6] and 16.1 ± 1.6[7] kcal/mol for the formation of allyl radical from propylene over Bi_2O_3. An activation energy of 22 kcal/mol has been reported for the reaction of propylene in the presence of oxygen to form 1,5-hexadiene over Bi_2O_3[20] and values of 27.5[21] and 29.0[20] kcal/mol have been reported for the reaction of propylene with Bi_2O_3 in the absence of oxygen. Although a precise

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(15) Relative concentrations of allylic radical and alkene were estimated by comparing the intensity of their He Iα first photoelectron bands (counts/s at their maxima). This was accomplished by directly comparing the He Iα first photoelectron band of the radical and the He Iβ first photoelectron band of the alkene. The relative intensity (3:100) of the He Iβ to the He Iα band is then taken into account. Since absolute cross sections are not known, this method was chosen for its convenience and should yield a value within a factor of five of the actual relative concentration.

(16) The major line of the He I lamp, He Iα, is at 21.22 eV and an impurity line, He Iβ, is at 23.09 eV with a relative intensity to He Iα of 3:100. Electrons ionized by the He Iα line have 1.87 eV higher kinetic energy than those ionized by He Iα and therefore appear in the He I spectrum at lower ionization potential by 1.87 eV from the major He Iα bands.

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activation energy could not be extracted from our results for isobutylene over Bi_2O_3, the observed change in the intensity of the radical spectrum with temperature is consistent with an effective activation energy for the formation of 2-methylallyl radical in the range of 10–35 kcal/mol. Thus, our results for the temperature dependence of the allylic hydrogen abstraction by Bi_2O_3 from isobutylene are consistent with activation energies determined for the reaction of propylene over Bi_2O_3. This is not unexpected since the allylic C–H bond energies in propylene and isobutylene differ by only 1.6 kcal/mol.[22]

The yield of 2-methylallyl radical decreases if the pressure of oxygen flowing with the isobutylene over the Bi_2O_3 is decreased to a very low level, although radicals are still observed with no oxygen flowing. Martir and Lunsford also observed a decrease in the yield of allyl radical production from propylene over Bi_2O_3 at very low levels of oxygen.[6] These results are consistent with Bi_2O_3 being an oxidant, in the absence of gas-phase oxygen, for the dehydrodimerization of propylene to form 1,5-hexadiene.[21] When gas-phase oxygen is present, it can replenish the lattice oxygens, regenerating the active site for hydrogen abstraction. Thus, over the timescale of our experiments (1–2 h), if the oxygen pressure is too low, the activity of the Bi_2O_3 decreases.

The importance of surface-initiated gas-phase reactions, in which gas-phase oxygen may participate, has been demonstrated under certain conditions for the oxidation of propylene over bismuth molybdate catalysts.[12] In the experiments of Martir and Lunsford,[6] allyl radical production over Bi_2O_3 reached a maximum with a ratio of ~1:50 for oxygen to propylene. They explained the decrease at higher oxygen pressures as due to increased peroxy radical production via the association reaction of gas-phase allyl radical and oxygen in the cooler post-catalytic volume. Our experimental arrangement allows us to sample the gases immediately after they leave the catalyst, and thus we observe no decreased radical production at higher oxygen pressures.

To further test the generality and selectivity of heated Bi_2O_3 to abstract allylic or other labile hydrogens and to form gas-phase radicals to be detected by photoelectron spectroscopy, we have examined briefly the reactions of other organic molecules over Bi_2O_3 in the presence of oxygen. Although the energetics of forming benzyl radicals, which have an adiabatic and vertical ionization potential of 7.20 eV,[1] are favorable, none were detected (<1%) when toluene was passed over Bi_2O_3 at 760 °C. Cycloheptatriene produced at 760 °C ~2% tropyl radicals, which have an adiabatic ionization potential of 6.28 eV.[14] The major reaction observed, however, was the isomerization of approximately half the cycloheptatriene to toluene. CO_2 and H_2O were also produced. A significant fraction of trimethylsilane was oxidized to H_2O and CO_2 at 625 °C. No trimethylsilyl radicals, for which an estimated ionization potential is 6.30 eV,[23] were observed. Trimethylamine produced no (<1%) dimethylaminomethyl radicals ($(CH_3)_2NCH_2$) at 760 °C. An estimated ionization potential for this radical is 5.7 eV.[24] In an effort to obtain the photoelectron spectrum of cyclopentadienyl radical, cyclopentadiene and oxygen were passed over heated Bi_2O_3. At 550 °C large amounts of CO_2 and H_2O were formed in addition to a product whose first photoelectron band has an adiabatic and vertical ionization potential coinciding at 8.16 ± 0.03 eV. Two other bands in the photoelectron spectrum of the products of cyclopentadiene over Bi_2O_3, with vertical ionization potentials of 9.0 and 11.2 eV, have intensities that remain proportional to the band at 8.16 eV as the catalyst temperature is varied and therefore may arise from the same reaction product. We have not been able to assign this spectrum. The ionization potential is lower than 8.41 eV, the value determined for cyclopentadienyl radical by Lossing and Traeger using an electron monochromator–mass spectrometer combination.[25] Although dimerization products were not observed in the reactions of alkenes, this possibility must be considered in view of the fact that Bi_2O_3 is more reactive toward cyclopentadiene. In this system the production of a large amount of cyclopentadienyl radicals may occur and result in the formation of dimerization products. However, the unidentified band cannot be due to the radical recombination product since it has an ionization potential of 7.75 eV.[26] Perhaps dimerization and then dehydrogenation could occur to form fulvalene. No experimental value for the ionization potential of this transient species is available. Naphthalene, the stable isomer of fulvalene, is ruled out by a comparison of the photoelectron spectrum of this species to that observed in the present work. The spectrum cannot be assigned to cyclopentadienone, a possible oxidation product of cyclopentadiene, which has a first vertical ionization potential of 9.41 eV.[27] We are continuing our efforts to obtain the photoelectron spectrum of cyclopentadienyl radical using other radical sources.

Other catalysts can also be tested for their ability to produce gas-phase organic and inorganic radicals.[28] These studies may provide information about the gas–surface reactions as well as lead to a means of producing radicals not yet observed by photoelectron spectroscopy and thus allow their spectrum to be obtained. Photoelectron spectroscopy has been used extensively to optimize desired stable products of gas-phase reactions with heterogeneous catalysts.[10] As shown in this work, photoelectron spectroscopy may be used to sample directly both the transient and stable products of gas–surface processes.

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