

Kinetic Studies of OH-Radical Initiated Oxidation of Isoprene Using Quadrupole Ion Trap-Time of Flight Mass Spectrometer

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Abstract: The quadrupole ion trap-time of flight mass spectrometer was used to monitor the OH-radical initiated oxidation products of isoprene and formation of its major products, i.e. methyl vinyl ketone (MVK) and methacrolein (MACR) in the smog chamber. Kinetic study of these products was done. Representative ions for isoprene and its products obtained from the dilution experiments were monitored during the isoprene oxidation in the chamber. Reaction profiles were examined and the peak ratios were compared. The values of reaction rate constants were calculated and compared. The K_2/K_1 ratio for MACR was 0.339 ± 0.019 , while this ratio for MVK was 0.172 ± 0.011 which are in agreement with the reported values in literature. The numerical results from the evaluation of the ratio of rate constants illustrate that the instrument is far more capable of analyzing and obtaining quantitative results, even for systems of low concentration.

Key words: Aerosol's • Isoprene • Oxidation products • Time of Flight mass spectrometry

INTRODUCTION

Biogenic volatile organic compounds (VOCs) are emitted in large quantities from vegetation. These compounds emitted globally 1150 TgC/year and dominate anthropogenic sources by five orders of magnitude on a global scale [1]. Due to emission in large quantities and high reactivity, biogenic VOCs have a significant impact on the photochemical processes that lead to the formation of ozone and air quality. Isoprene (2-methyl-1, 3-butadiene) is considered the most abundant biogenic hydrocarbon emitted in to the atmosphere with a global emission rate between 250-500 TgC/yr [2]. In the atmosphere, isoprene is highly reactive with the OH radical. Isoprene and OH radical go through addition reaction and form six peroxy radicals. Four are β -hydroxy peroxy radicals and two are δ -hydroxy peroxy radicals formed as a result of allylic resonance in the initially formed hydroxyl alkyl radicals [3]. Figure 1 shows the structure of the alkoxy radicals formed following reaction of the peroxy radicals with NO. The β -hydroxy peroxy radicals labeled 1 and 2, decompose to give methyl vinyl ketone (MVK) and formaldehyde (HCHO), while those

labeled 3 and 4 decompose to give methacrolein (MACR) and formaldehyde HCHO. The two remaining δ -hydroxy alkoxy radicals undergo isomerization to give δ -hydroxy aldehydes [3].

The main reaction products with the unsaturated δ -hydroxy alkoxy radicals, 5 and 6, are expected to undergo isomerisation to yield the unsaturated δ -hydroxy aldehydes, $\text{HOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ and $\text{HOCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$. The alternative isomerisation of radical 5 by hydrogen atom transfer from the methyl group would lead to the formation of dihydro-aldehyde, $(\text{HOCH}_2)_2\text{C}=\text{CHCHO}$ or hydroxymethacrolin, $\text{CH}_2=\text{C}(\text{CHO})\text{CH}_2\text{OH}$.

The aim of this research was to monitor the OH-initiated oxidation of isoprene and examine the formation of the products, namely methacrolein (MACR) and methyl vinyl ketone (MVK) inside the smog chamber, studying the kinetics of reactions and following the progress throughout the experiment. The Time of Flight Quadrupole Ion Trap Mass Spectrometer was used to monitor the reactants and products. A preliminary experiment known as exponential decay was carried out in order to select representative ions in the chamber using

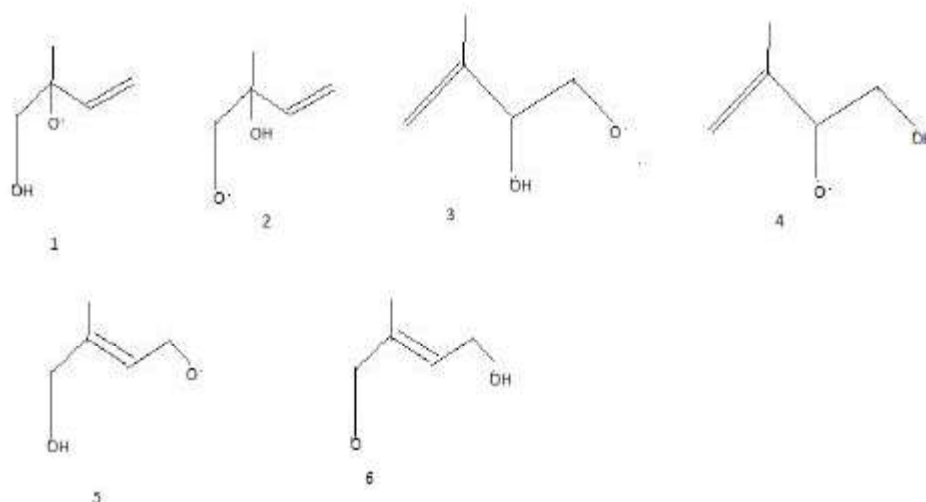


Fig. 1: Six peroxy radicals formed on addition of OH radical with isoprene [3].

Isopropyl nitrite (IPN), Isoprene and its products during the oxidation. Chemical ionization of these organic compounds was achieved by using O_2^+ . O_2^+ reacts with many molecules through charge transfer and hydride ion transfer processes [4].

Experimental: The set of experiments were conducted which comprises of,

- Exponential dilution of isoprene, acetone, methacrolein (MACR), methyl vinyl ketone (MVK) by using a 3litre flask.
- Investigating the oxidation of isoprene and its products inside the smog chamber.
- Examining the Isopropyl Nitrite (IPN) photolysis inside the smog chamber.

All experiments were done by using the Quadrupole Ion Trap-Time of Flight Mass Spectrometer assembled by R.M.Jordan Co. (Grass valley, CA, USA). The ion source chamber pressure was maintained between $9.8-10.2 \times 10^{-5}$ Torr by using Turbo 550 pump. The sample was ionized by using a 70 eV electron beam (E-gun model C-950, using a C-1251 power supply by R.M.Jordan). For experiments, emission of 600 μA was used.

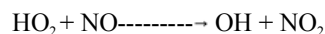
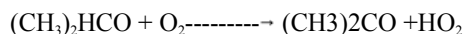
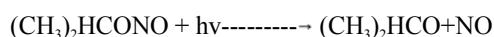
Dilution Experiments Setup: Dilution experiments for isoprene and its major oxidation products, methacrolein (MACR) and methyl vinyl ketone (MVK) were conducted separately in 3L flask. Decay experiment for acetone was also performed as it is a major product of the Isopropyl Nitrite (IPN) photolysis that occurs inside the smog chamber and was expected to have a significant amount.

The purpose of these experiments was to select representative ions for each of the target organic compounds, create a reference spectrum for each and determine the ratios/abundance of these fragment ions. Hypothetically the signal response of a representative ion had a linear relationship with that of the ion with the strongest signal for that particular organic compound. It will also be investigated whether or not the ratios of these representative ions would be comparable to that of the ions in the isoprene oxidation in the smog chamber experiments. This was a way of accounting for the peaks that would have significant presence in the chamber. It is important to note that these preliminary experiments were not conducted in to the smog chamber.

Dilution Experiments Procedure: 1 μL of the sample was injected through syringe into a continuous supply of air (dry, clean and particle free) stream inside a 3L flask. Flow rates of AADCO purified air for isoprene was 1000 cc/min, while for MACR and MVK it was 500cc/min. Only very small flow was drawn into the TOF. A flow meter was used to control the flow of the sample gas into the leak valve located at the back of the source chamber. After five minutes the valve was switched to the dilution mode. In dilution mode 5000 cc/min of pure air passes through the 3L flask to dilute the sample. The variation of each ion during the reaction with O_2^+ ions was noted and ions showing high response and significant change were selected as representative ions for isoprene, MACR, MVK and acetone.

In order to collect the reference spectrum of IPN, a chamber experiment was carried out with only IPN as the analyte so as to account for all the species generated and consumed throughout the experiment. For the chamber experiment 400 ppb of IPN was injected into the chamber through a septum. Period of about 45 minutes was allowed for IPN to be mixed in the chamber, after which UV lights were turned on to initiate the reaction.

Oxidation of Isoprene and IPN Photolysis in the Smog Chamber: The OH radical initiated oxidation of isoprene and formation of its oxidation products, MACR and MVK in the smog chamber was monitored. The chamber is cylindrical in shape, Teflon coated aluminum endplates and transparent Teflon walls. It is about 8m³ in volume. OH radicals were produced by the photolysis of IPN with UV radiation by the following reaction.



Twelve UV lamps were attached inside the chamber. Prior to the injection of isoprene into the chamber, the mass spectrometer was allowed to warm up for 30 minutes, while taking blank readings. The valve was switched toward sampling through chamber. 21.5 µL Isoprene was injected into a septum located at the back of the chamber followed by IPN (21.5 µL). A flow meter was used to control the flow of NO into the chamber. After one hour and ten minutes of mixing the reactants, the UV lights were turned on to initiate the production of OH radical. The reaction was allowed to proceed for three hours, with one full scan mass spectrum in every minute. After three hours, the UV lamps were turned off and the experiment was allowed to run for another an hour a separate experiment was conducted in the chamber to study the IPN photolysis only. This was done to examine the possibility that IPN has some of the same fragments as acetone.

The DAQ program produces a mass spectrum of the data collected, as signal / count versus time of flight (ns). The data was translated into mass to charge ratio (m/z) units using a fitting routine in Igor pro 6 software.

RESULTS AND DISCUSSION

Exponential dilution experiments were performed for organic compounds that were suspected to be present in

Table 1: Relative Abundance of the Representative Ions of Isoprene, MACR, MVK and Acetone

Ions m/z	Isoprene	MACR	MVK	Acetone
39	11.3	-	-	-
40	-	7.6	-	-
41	4.5	69.3		
42		26		58
43			20	100
44				28
51	5			
53	28			
55			100	
56			3	
58				13.3
59				58
65	4			
67	100			
68	26			
69		67.6		
70		100	6	
85		43.6		

the OH radical initiated oxidation of isoprene inside the smog chamber. The intensity of the signals obtained for any m/z ion represents the concentration of the ion. The variation of each ion during the decay of a particular compound was examined. The ion showing the highest response was selected and it was determined whether or not a linear relationship exists between the strongest ion and the rest of the ions showing high response and significant change. Ions that have a strongest linear relationship with the strongest ion for the four organic compounds are summarized in Table 1.

O₂⁺ reacts with isoprene to form three major fragments at m/z=53, 67 and 68 with the strongest signal at m/z=67. The decay rate followed a double exponential decay. The exponential dilution experiment was carried out at a very high isoprene mixing ratio (11ppm), the C₇H₁₀ species was considered as an impurity (21.4% of the total signal), the peak appears only when isoprene concentration was high, as the concentration of isoprene decreased to 1ppm that particular peak was also disappeared.

IPN alone was injected in the smog chamber to obtain reference spectrum. We observed two groups of fragments of IPN. The first was fragments of IPN itself which was consumed during photolysis and the second group of fragments was of acetone that was the main product of the reaction.

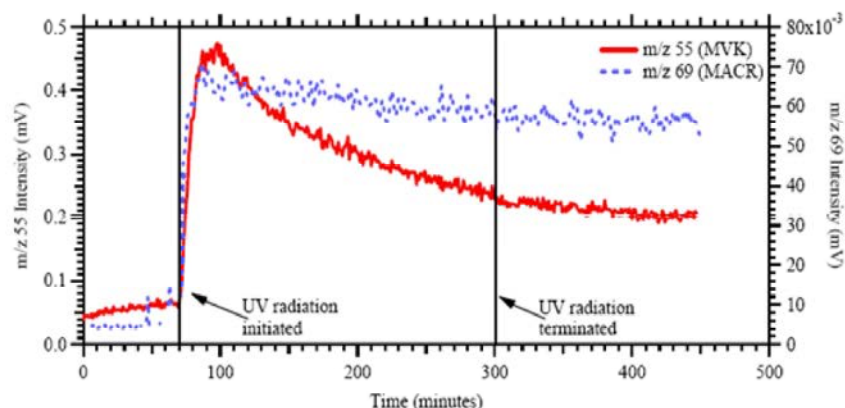


Fig. 2: Time Profile of Production and consumption of MVK and MACR

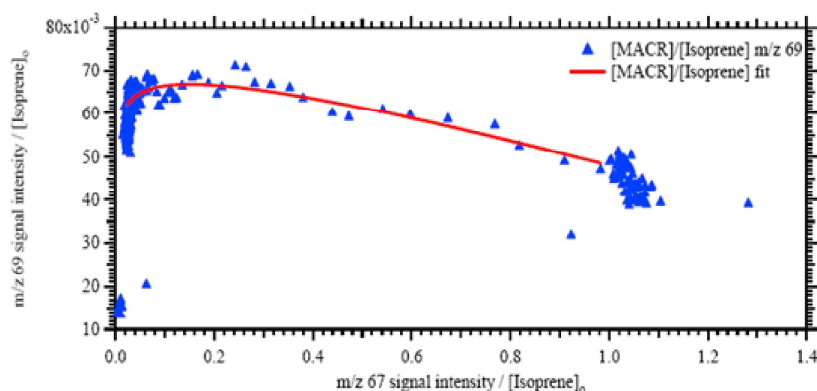


Fig. 3: Intensity fit of [MACR] as a function of [Isoprene]

Oxidation of Isoprene and IPN Photolysis in the Smog Chamber:

Oxidation of isoprene by OH radicals is a process that has been extensively studied. During this reaction, OH radical can attack the isoprene by addition at any of the carbons in the conjugated system; the following reactions show only one of the pathways leading to generation of the major products of isoprene oxidation: methyl vinyl ketone (MVK) and Methacrolein (MACR) [5]. Tuazon *et al.* [1990] reported [6] MVK and MACR as major products of isoprene oxidation with OH. The reported molar yields for these molecules are respectively 0.32 and 0.23. Even though there are many other products such as methyl-furan, organic nitrates and esters which are formed throughout this reaction our goal here remained limited to the identification of the 2 named products, studying their kinetics of reaction and following their progress throughout the experiment. For this purpose exponential dilution tests were carried out on MVK and MACR and reference spectra were extracted. Both MACR and MVK spectra clearly show their parent peaks at m/z 70 as well as a prominent peak at m/z 55,

which corresponds to loss of a single methyl group from the parent. As can be seen from figures 2 and 3 that the two products share most of the same fragments; this makes identification of MVK and MACR more challenging; in order to differentiate the two compounds from each other the unique mass at 69 from the MACR spectrum was used. Hence in the following diagram, masses 69 and 55 were chosen respectively to represent the two products.

The behavior of the two carbonyl products seen in the above diagram can be explained by the following equations. Reactions 1-6 show that isoprene decays as a result of reacting by OH. The limiting rate constant for the consumption of isoprene and route to production of MVK and MACR is the first step [5] [2004], i.e. oxidation by OH (Reaction 1), from this reaction we have:

$$d[\text{Isoprene}]/dt = -k_1[\text{OH}][\text{Isoprene}] \quad (1)$$

$$d[\text{MACR}]/dt = \beta k_1[\text{OH}][\text{Isoprene}] - k_2[\text{OH}][\text{MACR}] \quad (2)$$

Dividing Equation 2 by Equation 1 we have

$$d[MACR] / d[Isoprene] = [k_2 / k_1] [MACR] / [Isoprene] - \beta \quad (3)$$

Equation 3 can be written for y: =

$$[MACR] / [Isoprene]_o, x: = [Isoprene] / [Isoprene]_o \text{ and}$$

m: = k_2 / k_1 as follows:

$$dy/dx = m y/x - \beta \quad (3)$$

Multiplying both sides by dx, dividing both sides by x^m and rearranging gives:

$$dy/x^m + (\beta/x^{m+1} - m y/x^{m+1}) dx = 0 \quad (4)$$

Equation 4 is an exactly differential equation for $y_o = 0$ and $x_o = 1$ (i.e. no products present at the beginning of the reaction) it can be integrated to give:

$$1/x^m (y + \beta x/1-m) = \beta/1-m \quad (5)$$

Rearranging equation 5 to solve for y gives:

$$y = (\beta/1-m)(x^m - x) \quad (6)$$

or

$$\frac{[MVK]}{[Isoprene]} = \left(\frac{\beta}{1 - \frac{k_2}{k_1}} \right) \left[\frac{[Isoprene]^{k_1}}{[Isoprene]_o} - \frac{[Isoprene]}{[Isoprene]_o} \right]$$

Equation 6 can then be used to determine the ratio of rate constants k_2/k_1

The value of k_2/k_1 can be easily determined by fitting the MACR signal against that of isoprene. Figure 2 shows this obtained fit, which results in evaluation of the desired ratio: 0.339 ± 0.019 . This is in complete agreement with the literature values [7] for the decay rates of Isoprene ($k_1 = 9.26 \times 10^{-11} \text{S}^{-1}$) and MACR ($k_2 = 3.14 \times 10^{-11} \text{S}^{-1}$) in oxidation by OH radicals. The K_2/K_1 ratio from the literature is therefore 0.334. Similarly for MVK, as shown in figure 3, [MVK] can be fitted as a function of [Isoprene]. The resulting K_2/K_1 ratio is 0.172 ± 0.011 ; while, the value listed in the literature is 0.193.

This value is obtained from the decay rate constant listed for oxidation of MVK by OH radicals ($k_2 = 1.79 \times 10^{-11} \text{S}^{-1}$) [7]. The reason for this deviation (0.021) is still not known. The numerical result from the evaluation of the ratio of rate constants illustrate that the instrument is far more capable of analyzing and obtaining quantitative results, even from systems of low concentration.

ACKNOWLEDGEMENT

We are thankful to Higher Education Commission (HEC), Government of Pakistan for providing Post Doctoral Fellowship to complete the work reported in this paper.

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