Plasma Dissociation Reaction Kinetics. II. Precursors Related to Methyl Methacrylate: Methyl Crotonate, Methyl Isobutyrate, Ethyl Methacrylate, and Vinyl Acetate

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ABSTRACT: The methodology described in the previous article was utilized to study the plasma chemistry of precursors related to methyl methacrylate (MMA). This article discusses the plasma chemistry of methyl crotonate (MC), methyl isobutyrate (MIB), ethyl methacrylate (EMA), vinyl acetate (VA), isopropanol (IA), and methanol. The monomer structure was found to have strong effects on the dissociation chemistry and product formation. For α,β -unsaturated esters and VA, intramolecular rearrangement (the C—O bond cleavage reaction) and decarboxylations are two efficient dissociation pathways. The intramolecular rearrangement reaction yields a pair of ketene and aldehyde neutrals. Decarboxylations produce CO, CO₂, and a number of radicals that subsequently stabilize to form neutrals. For example, the secondary propyl radicals generated from MMA and EMA decarboxylations form propylene and allene neutrals while the primary propyl radicals generated from MC decarboxylations form propylene and acetylene. The other monomers studied, such as MIB and IA, cannot dissociate via this intramolecular rearrangement mechanism. As a result, they decompose much slower in the plasma. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 17–27, 1999

Key words: plasma chemistry; methyl crotonate; methyl isobutyrate; ethyl methac-rylate; vinyl acetate

INTRODUCTION

Plasmas of organic precursors other than methyl methacrylate (MMA) were studied to further investigate the relationship between monomer

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structure and plasma dissociation chemistry. In particular, two monomers were studied in detail—methyl crotonate (MC, MW = 100) and methyl isobutyrate (MIB, MW = 102). Ethyl methacrylate (EMA), vinyl acetate (VA), isopropanol (IA), and methanol were also investigated.

MC is an α,β -unsaturated ester like MMA, but they have different substituent groups on the C=C double bond. Alkyl ketene ions were found in the electron-impact ionization of a number of α,β -unsaturated esters other than MMA.¹ Thus, the plasma dissociation mechanisms of MMA²⁻⁵ may have applications toward other α,β -unsaturated esters, such as MC and EMA.

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Another precursor closely related to MMA is MIB. Its monomer structure differs from MMA only in the absence of the C=C double bond. Thus, MIB provides a comparative study to investigate the effect of α,β -unsaturation on plasma chemistry. The structures of some of the monomers studied are shown below:



EXPERIMENTAL

The same experimental setup and procedures from the previous article² ("Plasma Dissociation Reaction Kinetics. I. Methyl Methacrylate") were used in this study. In brief, the parallel-plate plasma polymerization reactor is a 13.56-MHz system. An *in situ* FTIR diagnostic tool was utilized to provide information for species identification and gas-phase composition by residual gas analysis.

RESULTS AND DISCUSSION

MC Plasmas

Closed (zero flow rate) MC plasmas were studied in a 2^2 full factorial designed experiment with the same pressure and power settings as those of the closed MMA plasma kinetics study (*pressure* levels: 300 and 500 mT; *power* levels: 75 and 100 W).² In situ FTIR was utilized to provide gasphase information at different plasma reaction times.

An FTIR spectrum of pure MC vapor (500 mT) is shown in Figure 1(a), and the absorption spectrum of the reaction mixture is shown in Figure



Figure 1 In situ FTIR spectra of (a) pure MC vapor at 500 mT, (b) the MC plasma reaction mixture at 100 W after 45 s, and (c) the difference spectrum (see text for species assignment). Resolution is 0.5 cm^{-1} .

1(b) after 45 s of plasma reactions at 100 W of power. A number of MC plasma dissociation products were identified in the plasma difference spectrum [Fig. 1(c)] as denoted by the numbers: 1—acetylene (C_2H_2), 3—propylene (C_3H_6), 4—ethylene (C_2H_4), **5**—methanol (CH_3OH), **6**—methane $(COH_2),$ $(CH_4),$ **7**—formaldehyde **9**—CO, 10-CO₂, and 11-ethyl ketene (EK, CH₃CH₂-CH = C = O, MW = 70. All three categories of dissociation products (intermediate species, small hydrocarbons, and oxygenated species)^{2,3} were observed. Intermediate species of MC plasmas include propylene, methanol, COH₂, and EK. Small hydrocarbons include acetylene, ethylene, and methane. Oxygenated species include CO and CO₂. Two of the MMA intermediate speciesallene and dimethyl ketene (DMK)^{2,3}—were not observed, and a new intermediate species-EKwas observed in MC plasmas instead.

Figure 2 exhibits the spectral region of ketene carbonyl absorption from MMA and MC plasmas.



Figure 2 FTIR spectra of (a) DMK in MMA plasmas and (b) EK in MC plasmas. Absorption peaks of CO were removed by spectral subtraction.

The spectral interference from CO absorption was removed by spectral subtraction in both cases. There is a clear difference between these two absorption bands shown in Figure 2(a,b). DMK, in Figure 2(a), has been shown to be the species generated in MMA plasmas.^{2–5} The absorption frequency of EK in MC plasmas [Fig. 2(b)] matches the reported frequency of 2132 cm⁻¹ in the literature.⁶

Gas-phase Reaction Kinetics

The plasma chamber pressure was monitored by a Baratron, and the trend is similar to the trend observed in MMA plasmas. For a starting monomer pressure of 300 mT, both MMA² and MC plasmas approached 900 mT of total pressure. Yasuda⁷ used a " γ " factor to describe monomer dissociation in closed systems, where $p_g = \gamma p_0 (p_g$ = plasma pressure and p_0 = initial monomer pressure). When p_0 = 300 mT, γ is 3.0 (at 75 W) and 3.2 (at 100 W) in MC plasmas. The monomer dissociation factor is very similar in MMA plasmas: γ is 3.1 (at 75 W) and 3.3 (at 100 W) at p_0 = 300 mT.

Table IIFactor Effects on the PathwayEfficiencies (x_i) and Volume-AveragedConsumption Rate Coefficients (k_i) in MCPlasmas

	Means	Pressure Effect (%)	Power Effect (%)	Interaction Effect (%)
x _{COH}	0.31	+0	+0	+2
$x_{C_0H_0}$	0.20	+2	+0	+0
$x_{\rm CH,OH}$	0.14	$^{-1}$	+0	$^{-1}$
k	0.015	-30	+12	+1
$k_{\rm COH}$	0.014	-28	+17	-4
$k_{\rm FK}$	0.028	-35	+23	-8
k _{C.H.}	0.007	-35	+15	-5
$k_{\mathrm{CH}_3\mathrm{OH}}^{\mathrm{C}_3\mathrm{H}_6}$	0.005	-35	+23	-5

Effects are shown in percent of the corresponding means.

A number of reaction parameters in the MC plasma gas phase were determined using the kinetic modeling approach as described in the previous article.² They include the volume-averaged consumption rate coefficients (k) of MC, the dissociation reaction pathway efficiencies (x_i) , and the volume-averaged consumption rate coefficients (k_i) of intermediate species—formaldehyde, EK, propylene, and methanol. The kinetic modeling results are summarized in Table I. Overall, the model-to-data fit quality is high.⁸

Effects of Pressure and Power on Reaction Kinetics. Analysis of variance (ANOVA) was used to analyze the effects of pressure and power on the plasma dissociation chemistry of MC. Table II summarizes the factor effects on pathway efficiencies (x_i) and reaction rate coefficients (k_i) .

The factor effects shown in Table II are very similar to those observed in the MMA kinetic study.² First of all, essentially, no pressure and no power effects were observed on the reaction pathway efficiencies. Therefore, the dissociation chem-

Table I Reaction Pathway Efficiencies (x_i) and Volume-Averaged Consumption Rate Coefficients of MC (k) and Intermediate Species (k_i) in Closed MC Plasmas

Pressure (mT)	Power (W)	$x_{\rm COH_2}$	$x_{\mathrm{C_3H_6}}$	$x_{ m CH_3OH}$	k	$k_{ m COH_2}$	$k_{ m EK}$	$k_{ m C_3H_6}$	$k_{ m CH_3OH}$
500	100	0.30	0.20	0.13	0.012	0.014	0.022	0.005	0.004
500	75	0.32	0.20	0.14	0.008	0.008	0.014	0.004	0.003
300	100	0.32	0.20	0.14	0.021	0.020	0.046	0.001	0.009
300	75	0.31	0.19	0.14	0.018	0.015	0.029	0.008	0.006



Figure 3 Two of the electron-impact-induced dissociation pathways in MC plasmas and the corresponding reaction products. *trans*-MC is shown here instead of the *cis* isomer.

istry of MC is unaffected by changes in the reactor power and initial monomer pressure levels. In addition, negative pressure effects (-28% to -35%) and positive power effects (+12% to +23%) were observed on all the rate coefficients. This means that the gas-phase reactions are faster at low initial pressure and high power conditions.

The regularities in the chemical kinetics of MC plasmas were checked using the time-scale transformation technique based on monomer decomposition half-lives $(t_{1/2})$.² The kinetics of the monomer and dissociation products were found to be invariant of the process condition using $t_{1/2}$ as the time unit.⁸

Dissociation Mechanisms in MC Plasmas

The plasma dissociation mechanisms of MC are similar to those of MMA because of the α,β -un-saturation. However, different reaction products are produced as a result of the different substituent groups on the C=C double bond. Figure 3 illustrates the electron-impact-induced dissociation pathways and reaction products in MC plasmas, and they are discussed below:

The C—O Bond Cleavage Reaction EK and formaldehyde are products of the same C—O bond cleavage dissociation reaction that yields DMK and formaldehyde in MMA plasmas. However, the EK/COH₂ production efficiency (average = 0.31) is smaller than the DMK/COH₂ production efficiency (average = 0.48) in MMA plasmas² as shown in Figure 4.

The less efficient production of EK/COH_2 is related to the monomer structure of MC. As illus-

trated in Figure 3, the formation of the five-member ring is not hindered by the methyl group in the *trans* isomer of MC. However, there may be some hindrance effects for the *cis* isomer. Since MMA does not have structural isomers, the DMK/ COH_2 pathway in MMA plasmas is more efficient than is the EK/COH₂ pathway in MC plasmas.

Besides a lower EK/COH_2 production efficiency, Figure 4 also shows a higher production efficiency for C_3H_6 (propylene) and methanol in MC plasmas, an indication of a higher decarboxylation efficiency as a result of the lower C—O bond cleavage efficiency.

Decarboxylations. Decarboxylations of MC produce propyl, methoxy, and methyl radicals and CO and CO_2 as shown in Figure 3. The different substituent groups on the C=C double bond also have effects on the formation of neutral decarboxylation products. Contrary to the secondary propyl radicals (CH2=C•-CH3) formed in MMA plasmas, primary propyl radicals (*CH=CH- CH_3) are produced in MC plasmas. The different propyl radicals stabilize to different neutrals: Secondary propyl radicals can produce neutral propylene ($CH_2 = C - CH_3$) and allene ($CH_2 = C = CH_2$) molecules. Primary propyl radicals produce neutral propylene as well. However, instead of producing allene, primary propyl radicals fragment to acetylene molecules (CH=CH) and [•]CH₃ radicals. This also explains in part why 60% more acetylene is observed in MC plasmas compared to MMA plasmas. Thus, propylene is associated with both primary and secondary propyl radicals, and allene is associated only with secondary propyl radicals.



Figure 4 Dissociation pathway efficiencies (x_i) in MMA and MC plasma systems.



Figure 5 Difference spectrum of an MIB plasma reaction mixture at 100 W after 45 s (see text for species assignment). Resolution is 0.5 cm^{-1} .

MIB Plasmas

Closed MIB plasmas were studied in the same fashion as were closed MMA and closed MC plasmas. The plasma dissociation products are identified in the difference spectrum of an MIB plasma reaction mixture after 45 s at 100 W of power (Fig. 5). Small hydrocarbons (1, 4, 6), oxygenated species (9, 10), and intermediate species (3, 7, 8, 12) were observed: **1**—*acetylene*, **2**—*allene*, **3**—*propylene*, **4**—*ethylene*, **5**—*methanol*, **6**—*methane*, **7**—*formaldehyde*, **8**—*DMK*, **9**—CO, **10**—CO₂, and **12**—*ketene* (H₂C==C=O, MW = 42). Allene (#2) was not observed in MIB plasmas, and a new species, ketene (#12), was.

Although MIB can form a five-member ring, the lack of a double bond has strongly diminished the dissociation rate of MIB and the formation rate of DMK. Figure 6 shows the absorption spectrum of ketene in MIB plasmas. Also shown in the figure is a spectrum of DMK in MMA plasmas. Spectral interference from CO absorption was removed by spectral subtraction. The ketene absorption is at a higher wavenumber than is DMK, and it matches the reported ketene absorption frequency (2151 cm⁻¹) in the literature.⁹

However, the asymmetric shape of the ketene absorption band in Figure 6 suggests that there is another absorption peak around 2130 cm⁻¹. As will be shown later (Fig. 11), the absorption band of ketene consists of three branches (P, Q, R), and the P-branch at a lower wavenumber actually has a smaller peak height than has the R-branch at a higher wavenumber. Thus, the lower wavenumber peak around 2130 cm⁻¹ is probably associated with DMK and/or methyl ketene (CH₃CH=C=O). It is difficult to determine which alkyl ketene is

present due to the severe spectral overlap of the two ketenes. The Q-branch of the DMK absorption band was observed at 2134.4 cm⁻¹, ² and the gas-phase absorption peak of methyl ketene was observed at 2132 cm⁻¹ in the literature.¹⁰

The observation of ketene and substituted ketenes suggests a mechanism involving elimination processes as shown below. A similar molecule, methyl 3-hydroxylbutyrate, was proposed to undergo a similar methyl group elimination upon electron-impact ionization.¹¹ A ketene-ion complex then was formed by intramolecular rearrangement to yield a ketene ion¹¹:



MIB plasma chamber pressure exhibits a higher total chamber pressure than that of MMA and MC plasmas. The monomer dissociation factor (γ) is 3.5 (at 75 W) and >3.6 (at 100 W) for MIB plasmas at $p_0 = 300$ mT. The most likely cause for the higher MIB plasma pressure is the higher dehydrogenation and increased H₂ concentration associated with a saturated species over the unsaturated counterpart.¹² As a result, the γ factor in MIB plasmas is considerably higher.

The gas-phase reaction parameters $(k_i \text{ and } x_i)$ of MIB plasmas were determined based on kinetic



Figure 6 Absorption spectra of (a) DMK in MMA plasmas and (b) ketene and DMK in MIB plasmas. Spectral subtraction was performed to remove the CO interference. Resolution is 0.5 cm^{-1} .

Pressure (mT)	Power (W)	$x_{ m COH_2}$	$x_{\mathrm{C_3H_6}}$	$x_{ m CH_3OH}$	k	$k_{ m COH_2}$	$k_{ m K}$	$k_{ m C_3H_6}$	$k_{ m CH_3OH}$
500	100	0.32	0.16	0.92	0.006	0.014	0.028	0.005	0.004
500	75	0.32	0.10	0.22	0.000	0.014	0.020	0.005	0.004
300	100	0.28	0.10	0.16	0.010	0.022	0.039	0.004	0.005
300	75	0.28	0.11	0.16	0.008	0.016	0.032	0.004	0.003

Table III Reaction Pathway Efficiencies (x_i) and Volume-Averaged Consumption Rate Coefficients of MIB (k) and Intermediate Species (k_i) in Closed MIB Plasmas

modeling. Table III summarizes x_i and k_i for the monomer and plasma species including COH₂, ketenes, propylene, and methanol.⁸ A number of observations besides the γ factor indicate that MIB plasma chemistry is significantly different from that of the α , β -unsaturated esters:

- Slower MIB plasma decomposition rates,
- Ethylene as an intermediate species in MIB plasmas, and
- Different factor effects on the decomposition kinetics.

Monomer Decomposition Rates

Figure 7 shows the averaged rate coefficients of monomer and other plasma species in MMA,² MC, and MIB plasmas. The MMA decomposition rate is slightly higher than that of MC, but the MMA and MC decomposition rates are significantly higher than that of MIB. The other plasma species, such as COH_2 , ketenes, propylene, and



Figure 7 Averaged decomposition rate coefficients of monomer, formaldehyde, ketenes, propylene, methanol, and ethylene in MMA, MC, and MIB plasmas. Ketenes are the most reactive neutrals.

methanol, have roughly the same decomposition rates in all three systems.

Ethylene: An Intermediate Species in MIB Plasmas

Besides the intermediate species discussed above, ethylene appears to be an important intermediate species in MIB plasmas. Figure 8 shows the quality of fit between the ethylene data and the kinetic model for intermediate species.

Although there are strong factor (pressure and power) effects, one-third to one-half of MIB monomers yield ethylene as a plasma decomposition intermediate according to the model. In comparison, the model does not identify ethylene as an intermediate species in MMA² and MC plasmas. Hence, ethylene only becomes a significant decomposition intermediate in the absence of mono-



Figure 8 Goodness of fit between the kinetic model and ethylene in MIB plasmas. The kinetics parameters (x: production efficiency, k: decomposition rate coefficient in s^{-1}) of ethylene are listed for the four process conditions.

	Means	Pressure Effect (%)	Power Effect (%)	Interaction (%)
x _{COH}	0.30	+6	+2	+1
$x_{C_0H_0}$	0.13	+20	-2	+2
$x_{C_{0}H_{1}}$	0.41	+21	-1	$^{-1}$
$x_{\rm CH_{2}OH}$	0.19	+15	-1	$^{-1}$
k	0.0067	-31	+17	-2
$k_{\rm COH_0}$	0.0155	-23	+15	-5
k _{K/DMK}	0.0328	-9	+4	-7
$k_{\rm CoHe}$	0.0044	+7	-4	+4
$k_{\rm CoH}$	0.0048	+1	+1	-6
$k_{\rm CH_3OH}^{O_2 II_4}$	0.0039	-3	-20	-5

Table IV Factor Effects on the Pathway Efficiencies (x_i) and Reaction Rate Coefficients (k_i) in MIB Plasmas

Effects are shown in percent of the corresponding means.

mer dissociation via intramolecular rearrangement.

Effects of Pressure and Power on Reaction Kinetics

ANOVA was used to examine the reactor parameter effects on x_i and k_i . Table IV summarizes the factor effects which are quite different from the α,β -unsaturated esters (MMA² and MC). Power exhibits no significant effect on x_i , but pressure exhibits a +20% effect on propylene and ethylene production efficiencies and a +15% effect on methanol production efficiencies. This suggests that the dissociation chemistry of the saturated ester, MIB, is less predictable than that of the unsaturated ester, MMA, when the initial monomer pressure is changed.

More pronounced differences between MIB and MMA plasmas are observed in the rate coefficient analysis. Pressure effects on the *k*'s range widely from -31% for the monomer to +7% for propylene, and power effects also range widely from +17% for MIB to -20% for CH₃OH. In comparison, analyses on the plasmas of the unsaturated esters revealed only negative pressure effects and positive power effects on all the *k*'s. This is shown in Figure 9, which displays the factor effects on the decomposition rate coefficients of the monomers and intermediates of MMA,² MC, and MIB plasmas. Once again, this indicates a much less predictable dissociation chemistry of the saturated MIB in the plasma.

The regularities in the chemical kinetics of MIB plasmas were checked using the time-scale

transformation technique based on monomer decomposition half-lives $(t_{1/2})$.² Although it has been shown to reduce the effects of reactor condition on the kinetics of monomer and dissociation products in MMA and MC plasmas, this technique failed to do so for MIB plasmas.⁸

Other Organic Plasmas

Four additional monomers other than MMA, MC and MIB were studied. Dissociation products identified in different organic plasmas, including MMA,^{2,3} MC, MIB, EMA, VA, IA, methanol, tetramethyl-1,3-cyclobutandione (TMCB),¹³ and formaldehyde,¹³ are summarized in Table V. They include **1**—*acetylene* (C₂H₂), **2**—*allene* (C₃H₄), **3**—*propylene* (C₃H₆), **4**—*ethylene* (C₂H₄), **5**—*methanol* (CH₃OH), **6**—*methane* (CH₄), **7**—*formaldehyde* (COH₂), **8**—*dimethyl ketene* [DMK, (CH₃)₂C=C=O], **9**—CO, **10**—CO₂, **11**—



Figure 9 Factor (pressure and power) effects on the consumption rate coefficients of different species in MMA, MC, and MIB plasmas. The factor effects are similar for α,β -unsaturated monomers, MMA and MC. However, they are significantly different for MIB plasmas.

	$MMA^{2,3}$	MC	MIB	EMA	VA	IA	MeOH	$TMCB^{13}$	$\mathrm{COH_2}^{13}$
1—C _a H _a	./	./	./	./	./	./	./	./	
$2 - C_3 H_4$	ý	v	v	v V	v	v	v	ý	
$3-C_3H_6$	ý	\checkmark	\checkmark	ý		\checkmark		·	
$4-C_2H_4$, ,	, ,	, ,	\checkmark	\checkmark		\checkmark	
5—MeOH	\checkmark	\checkmark	\checkmark				_		
$6-CH_4$	\checkmark								
$7-COH_2$	\checkmark	\checkmark	\checkmark						
8—DMK	\checkmark		?	\checkmark				\checkmark	
9—СО	\checkmark								
$10-CO_2$	\checkmark								
11—EK		\checkmark							
12—Ketene			\checkmark		\checkmark	\checkmark			
$13 - C_2 H_4 O$				\checkmark	\checkmark				
$14 - H_2O$						\checkmark	\checkmark		
Methyl ketene			?						

Table V Summary of Plasma Dissociation Products of Various Precursors Identified by In Situ FTIR

ethyl ketene (EK, CH_3CH_2 —CH=C=O), **12** ketene (CH_2 =C=O), **13**—acetaldehyde (CH_3 — CHO), and **14**—water. This section discusses the findings on EMA, VA, IA, and methanol plasmas.

EMA Plasmas

EMA is an α,β -unsaturated ester; thus, the dissociation mechanisms in EMA plasmas should be similar to those in MMA and MC plasmas. Figure 10 illustrates the electron-impact-induced dissociation chemistry and reaction products in EMA plasmas. The C—O bond cleavage reaction and decarboxylations are the two predominant dissociation pathways. DMK and acetaldehyde are produced from the C—O bond cleavage reaction. Propylene, allene, CO, CO₂, and ethanol are produced from decarboxylations. All the intermediate species illustrated in Figure 10 were identified except ethanol, probably due to the increased difficulty to identify the wider absorption peaks of ethanol. In addition, small hydrocarbons (acetylene, ethylene, and methane) and oxygenated species (CO and CO_2) were observed by FTIR as well.

VA Plasmas

Plasmas of VA (MW = 86) were studied to examine these issues related to ketene formation: (1) effects of isolated unsaturation, that is, the C=C double bond and the C=O carbonyl bond are separated by at least one single bond, and (2) effects of the five-member ring configuration.

FTIR measurement revealed the presence of small hydrocarbons (acetylene, ethylene, and



Figure 10 Dissociation reaction pathways in EMA plasmas and the reaction products.

methane), oxygenated species (CO and CO_2), and intermediate species (ketene and acetaldehyde) in VA plasmas. Allene and propylene, two common three-carbon species, were not detected due to the lack of three-carbon linkages (—C—C— C—) in the monomer structure.

Based on the observation of ketene and acetaldehyde as the only intermediate species, the following decomposition pathway is proposed for VA plasmas:



Therefore, plasma dissociation via the intramolecular rearrangement mechanism and ketene formation is an important process for unsaturated oxygen-containing hydrocarbons besides α,β -unsaturated esters (MMA, MC, and EMA). This mechanism might be an important dissociation reaction in a number of unsaturated oxygen-containing hydrocarbons other than those investigated so far.

IA and Methanol Plasmas

IA (CH₃CH₂CH₂—OH, MW = 60) plasmas were investigated to examine the possibility of ketene formation in the absence of carbonyl functional groups in the monomer. Small hydrocarbons (acetylene, ethylene, and methane), oxygenated species (CO and CO₂), intermediate species (propylene and ketene), and water were observed in the plasma. Species such as allene, methanol, formaldehyde, acetaldehyde, DMK, and EK were not observed.

Because IA has four carbon and oxygen atoms, it cannot arrange itself into a five-member ring configuration. The production of ketene in IA plasmas, then, occurs via other mechanisms. For example, the following pathway yields ketene through a radical intermediate:

$$\begin{array}{c} \overset{H}{\overset{H}} \overset{H}} \overset{H}{\overset{H}} \overset{H}} \overset{H}{\overset{H}} \overset{H}{\overset{H}} \overset{$$

Methanol (CH₃OH, MW = 32), on the other hand, cannot generate such a radical intermediate in the plasma. As a result, ketene was not detected in methanol plasmas. The only decomposition products of a methanol plasma are small hydrocarbons (acetylene, ethylene, and methane),



Figure 11 Spectrally subtracted spectra of (a) ketene (MIB, IA, and VA plasmas), (b) DMK (MMA and EMA plasmas), and EK (MC plasmas) obtained under the same process conditions.

oxygenated species (CO and CO_2), and water. Ketenes, aldehydes (such as COH_2), and alcohols were not observed in methanol plasmas. Thus, the formation of ketenes, aldehydes, and alcohols can only be accomplished by monomer dissociation and not by recombination in an experimental condition similar to ours.

Ketene production through the radical intermediate mechanism is, however, less effective than is the intramolecular rearrangement mechanism. Figure 11 shows the spectra of different ketenes generated by the various monomers under the same process condition (500 mT of starting monomer pressure, 100 W of power, and zero flow rate). Spectral subtraction was performed to remove the CO spectral interference in all cases.

The spectral intensities of ketenes in IA and MIB plasmas were about five times smaller than those in MMA, EMA, MC, and VA plasmas. Although the absorption coefficients of the ketenes are slightly different (the dipole moment of ketene is 1.43, and it is 1.87 for DMK in benzene),¹⁴ it is an indication of less effective ketene formation via radical intermediates in IA and MIB plasmas.

Summary and Additional Observations

Based on the FTIR measurements, a few other observations on the plasma product formation are presented below:

1. Water is present only in plasmas of IA and methanol, but not in ester plasmas. Possible sources of water include recombination reactions between ${}^{\bullet}OH$ and H^{\bullet} radicals and direct elimination of a water molecule from the alcohol.

- 2. Neither propylene or allene is observed in plasmas of monomers without three-carbon linkages, such as VA and methanol. Therefore, the three-carbon species are produced directly from the monomer dissociation and not from the recombination of C_xH_y species. In addition, allene is observed so far only when the monomer has a structure that can give rise to unsaturated secondary propyl radicals—monomers like MMA and EMA.
- 3. The two-carbon species, like ethylene and acetylene, are observed in all the organic plasmas investigated so far regardless of the monomer structure. Particularly, the formation chemistry of ethylene may differ significantly from one plasma to another. For example, ethylene is produced directly from the monomer in MIB plasma. However, since methanol has only one carbon, the two-carbon species (ethylene and acetylene) in methanol plasmas must have also been formed by recombination reactions of CH_x species.
- 4. The oxygenated species (CO and CO_2) are produced in all the plasmas. They can be produced from the dissociation of the monomer and intermediate species. In addition, they are also the stable final products.

Therefore, CO, CO₂, acetylene, ethylene, and methane can be expected in the plasmas of all the oxygen-containing hydrocarbons. However, the production chemistry of other plasma species like ketenes, alcohols, and aldehydes—are controlled by the monomer structure in the experimental regime similar to those used in the study. Identification of these intermediate species can provide significant insights to the plasma dissociation reaction mechanism of the monomer.

CONCLUSIONS

The monomers used in this study fall into two groups: The first group includes the unsaturated species of MMA, MC, EMA, and VA. These monomers exhibit two decomposition pathways: intramolecular rearrangement (C—O bond cleavage reaction) and decarboxylations.

Due to the different substituent groups, the C-O bond cleavage reaction yields different products in different plasmas: neutral DMK and COH_2 in MMA plasmas, EK and COH_2 in MC plasmas, and DMK and acetaldehyde in EMA plasmas. The second reaction, decarboxylations, produces propyl radicals which then stabilize into propylene or allene (if it is a secondary radical as in MMA and EMA plasmas) or acetylene (if it is a primary radical as in MC plasmas). The methoxy radicals produced in MMA and MC plasmas form methanol, and the ethoxy radicals in EMA plasmas probably form ethanol. Although VA has a slightly different structure from the α , β -unsaturated esters, it has very similar plasma dissociation mechanisms that also involve the formation of ketene and aldehyde species via intramolecular rearrangement.

The second category of monomers includes saturated monomers, such as IA and MIB. These monomers are not able to undergo the intramolecular rearrangement dissociation. MIB does not have the C=C double bond to facilitate the formation of ketene and aldehyde although it can form a five-member ring configuration. For these monomers, a radical intermediate mechanism becomes the dominant dissociation pathway. Radicals containing at least one oxygen and two carbon atoms can stabilize to ketene species. But the radical mechanism is much less efficient in ketene production than is the intramolecular rearrangement mechanism. The kinetic modeling used in this work reveals a much more complex and less predictable dependence of the MIB plasma dissociation chemistry on the process parameters than its α,β -unsaturated counterpart, MMA.

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