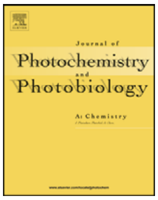
Journal of Photochemistry and Photobiology A: Chemistry 206 (2009) 71–79

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



The photolysis of methyl vinyl ketone at 308 nm

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ARTICLE INFO

Article history:
Received 15 December 2008
Received in revised form 16 April 2009
Accepted 14 May 2009
Available online 29 May 2009

Keywords:
Methyl vinyl ketone
Photochemistry
Quantum yields
Photolysis mechanism

ABSTRACT

The photolysis of methyl vinyl ketone at small conversions has been studied at 308 nm and at temperatures from approximately 300 K to 475 K as a function of the partial pressures of methyl vinyl ketone, argon and oxygen. The main products of photolysis from 300 K to 435 K are propylene and carbon monoxide together with much smaller yields of methane. The absence of measurable yields of ethane, ethylene and 1,3-butadiene indicates that dissociation of methyl vinyl ketone to free radical products is unimportant under these conditions. At 475 K, small yields of ethane, ethylene and 1,3-butadiene were observed suggesting the increased importance of channels producing CH_3 and C_2H_3 radicals which were not observable at the lower temperatures.

The formation of propylene is quenched by methyl vinyl ketone, argon and oxygen. However, the yield of methane is increased by the addition of argon and oxygen but is reduced by increasing the pressure of methyl vinyl ketone. The maximum partial pressures of argon and oxygen used in these experiments were approximately 450 Torr. The maximum pressure of methyl vinyl ketone was limited by its vapour pressure to approximately 45 Torr. The markedly different variation in the yields of propylene and methane with changing pressure and with the addition of argon and oxygen suggests that propylene and methane are formed from different excited states of methyl vinyl ketone. These results are discussed within the context of the energetically accessible states of methyl vinyl ketone.

1. Introduction

The photolysis of methyl vinyl ketone in the $\pi \rightarrow \pi^*$ transition has been thoroughly studied and has been used as a source of vinyl radicals for kinetic experiments [1]. This process at 193 nm proceeds entirely by decomposition to methyl and vinyl radicals and produces comparable yields of ethane, propylene, and 1,3-butadiene as well as smaller amounts of acetylene, ethylene and methane. By contrast, photolysis of methyl vinyl ketone using the $n \rightarrow \pi^*$ transition has received relatively little attention. This transition results in significant absorption of light from about 260 nm to 400 nm [2,3]. The absorption cross-section at 308 nm has been reported [3] to be 5.4×10^{-20} cm^2 and [4] 6.24×10^{-20} cm^2 which is much smaller than that for the $\pi \rightarrow \pi^*$ transition for which the peak absorption cross-section has been reported [1] to be 3.2×10^{-17} cm^2. The electronic absorption in the $n \rightarrow \pi^*$ transition has been reported [3] to have weakly developed vibrational structure which disappears at wavelengths shorter than approximately 310 nm.

Raber and Moortgat [2] studied the photolysis of methyl vinyl ketone as a result of the $n \rightarrow \pi^*$ transition in air under broad-band illumination. Photolysis was initiated with Phillips TL/12 lamps or with Phillips TL/03 lamps having a useful radiation intensity extending from 275 nm to 380 nm and 390 nm to 470 nm respectively. They used long path FTIR spectrometry to detect the photolysis products, of which only formaldehyde, propylene, carbon monoxide and carbon dioxide could be measured accurately. They also reported quantum yields as a function of total pressure for loss of methyl vinyl ketone. It was concluded that the major products, propylene and CO, were largely produced directly from electronically excited methyl vinyl ketone and they proposed an extensive free radical mechanism to account for the other products which were attributed to photo-oxidation. Gierczak et al. [3] also studied the photolysis of methyl vinyl ketone in air. They used lasers to produce well-defined photolysis wavelengths of 308, 337 and 351 nm and used gas chromatography to measure the quantum yield for loss of methyl vinyl ketone as a function of total pressure and laser fluence. They detected acetylene, propylene and methanol as the main reaction products together with smaller amounts of methane, ethane, ethylene, formaldehyde, acetone or propanal, formic acid and acetic acid but did not report the yields of any of these products. More recently, Romero et al. measured the quantum yields at 248, 308 and 320 nm for acyl radical production from a series of ketones [5] and found that, for methyl vinyl ketone, the radical dissociation pathway was a very minor component of the loss of ketone at ambient temperature.

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doi:10.1016/j.jphotochem.2009.05.020

The photolysis of methyl vinyl ketone in the $n \rightarrow \pi^*$ transition is clearly much different from that in the $\pi \rightarrow \pi^*$ transition. However, it is unclear how the observed decomposition at these longer wavelengths is distributed between free radical and molecular reactions and to what extent the presence of oxygen, added to scavenge free radicals, has modified the intrinsic photochemical decomposition. It is evident that the photolysis of methyl vinyl ketone, one of the simplest unsaturated ketones, in the $n \rightarrow \pi^*$ transition is quite different from the analogous photolysis of saturated ketones such as acetone in which photolysis exclusively produces free radicals which then lead to the observed products [6]. If the photolysis of methyl vinyl ketone were to take place via a similar mechanism, one would expect products such as C_2H_6 and 1,3-C_4H_6 which are signatures for CH_3 and C_2H_3 radicals respectively, and a product distribution such as that obtained at 193 nm [1] would be found which is consistent with the known kinetics of recombination and disproportionation of these radicals. We report here experiments to measure the yields of the products of photolysis of methyl vinyl ketone at 308 nm to examine the relative importance of the main channels in the decomposition of methyl vinyl ketone at moderate temperatures on excitation in the $n \rightarrow \pi^*$ transition.

2. Experimental

Photolysis experiments were carried out in a thermostated Pyrex reaction vessel with an optical path length of 20 cm, equipped with quartz windows. Methyl vinyl ketone (Aldrich, 99%) was thoroughly degassed before use and was freshly distilled into the reaction vessel under reduced pressure for each experiment. Gas chromatographic analysis of the methyl vinyl ketone added to the reaction vessel in this way showed only a single peak indicating that this procedure efficiently prevented appreciable amounts of the stabilizer (0.1% hydroquinone, 0.1% acetic acid) and any residual impurities from entering the reaction vessel. Pressures below 10 kPa were measured with a Baratron pressure gauge while larger pressures were measured with a piezoelectric pressure transducer that was calibrated daily. Infrared spectra were measured in a gas cell with a 10 cm path length, using a Nicolet model 330 Avatar FTIR instrument. The detector was DTGS-KBr and Happ-Ganzel apodization was used. The resolution was 1 cm^{-1} and 200 scans were averaged. When FTIR spectra were used for chemical analysis, the absorbance at the relevant wavelength was calibrated against a series of known partial pressures of the analyte. Such plots had slopes with an uncertainty of less than 1% (two standard deviations) and their intercepts were smaller than the standard error of measurement. The gases used in the quenching experiments were argon (Praxair, 99.995%) and oxygen (Praxair, 99.995%) and were used without further purification. Nitrogen dioxide (Matheson, 99.5%), used in the actinometry experiments, was purified by bulb to bulb distillation.

Photolysis was initiated with a Lumonics TE-860-4 excimer laser using the XeCl transition at 308 nm. Laser power was measured with a Scientech pyroelectric power meter. The small variation in power from experiment to experiment was monitored by measuring the scattered laser light at 308 nm in the empty reaction vessel at right angles to the axis of the laser beam before and after each photolysis experiment. The scattered light intensity was verified to vary linearly with laser power. Wire mesh attenuators were used to vary the laser fluence incident on the reactor in experiments where this was required. The extent of conversion of methyl vinyl ketone was kept less than approximately 1% in all the experiments in order to avoid secondary reactions. This small extent of reaction precluded reliable measurement of the quantum yield for loss of methyl vinyl ketone in our experiments. A repetition rate of 4 Hz was used for most of the measurements but experiments in which the product yields were measured over a range of repetition rates indicated that the quantum yield for a given pressure, temperature and sample composition was constant at repetition rates up to at least 20 Hz.

Chemical analysis by gas chromatography used temperature programming and a trap and purge configuration for most of the analyses. A 6′ × 1/8″ SE30 or a 6′ × 1/8″ Carbowax 20M precolumn retained methyl vinyl ketone while passing the reaction products to be measured on to the analytical columns. The analytical columns were a 6′ × 1/8″ Porapak N column followed by a 6′ × 1/8″ Porapak Q column. The flow pattern was switched at a predetermined time so as to vent to the atmosphere compounds such as methyl vinyl ketone with retention times significantly longer than that of 1,3-C_4H_6 before they entered the analytical columns while allowing the analytes with shorter retention times to continue through the analytical columns. This arrangement provided good resolution of CH_4, C_2H_2, C_2H_4, C_2H_6, C_3H_6 and 1,3-C_4H_6 and greatly shortened the analysis time by avoiding the need to wait for complete elution of the large amount of unreacted methyl vinyl ketone. However, compounds with retention times significantly longer than that of 1,3-C_4H_6 were not detected. Initial chromatographic experiments using known hydrocarbon mixtures without the trap and purge arrangement indicated that both the observed hydrocarbon photolysis products and those to be anticipated if free radical reactions were important all eluted before methyl vinyl ketone.

Quantum yields of the photolysis products were measured by comparison of their yields with the extent of photolysis of NO_2 in separate experiments in the same apparatus at the same wavelength. The procedure used has been described in detail by Gierczak et al. [3]. The loss of NO_2 was calculated from the measured absorbance at 450 nm before and after photolysis. The absorbance was measured with a 0.5 m Jarrell-Ash monochrometer equipped with a 1P28 photomultiplier. The spectroscopic source was a tungsten lamp and a shutter was used to isolate the NO_2 sample from this lamp during photolysis by the laser to avoid any extraneous photochemical decomposition. The absorption cross-section of NO_2 at 308 nm was taken from Kirmse et al. [7] and is given by

$$\sigma = 3.765 \times 10^{-23}(\lambda - 240.028)^2 \exp\left\{-\left[\frac{(\lambda - 347.417)}{85.969}\right]^{1.5}\right\} \text{cm}^2$$

Loss of NO_2 at the laser wavelength of 308 nm occurs by the reactions

$$NO_2 + h\nu \rightarrow NO + O$$

$$O + NO_2 \rightarrow NO + O_2$$

The quantum yield for destruction of NO_2 is therefore 2 and this, combined with the measured loss of NO_2 and its known absorption cross-section at 308 nm, allowed calculation of the photon flux into the reactor. The pressures of NO_2 used in the actinometry experiments were sufficiently small that the correction for dimerization of NO_2 was only a few percent at ambient temperature and was negligible at the higher temperatures employed. Laser fluences measured in this way were a few mJ cm^{-2} $pulse^{-1}$ or less. The absorption cross-section of methyl vinyl ketone at 308 nm has been reported [2,3] to be 5.4×10^{-20} cm^2 and [4] 6.24×10^{-20} cm^2. The latter value was recommended in a recent comprehensive evaluation and was used in our calculations. The peak cross-section was reported to vary by less than 2% between 250 K and 298 K [3] and we have assumed that it is approximately constant over the range of temperatures covered in our experiments. This, with the measurements of NO_2 photolysis under the same reaction conditions, allowed calculation of the quantum yields of the products observed in the photolysis of methyl vinyl ketone.

3. Results and discussion

Experiments were conducted at temperatures from approximately 300 K to 475 K. At temperatures of 435 K and below, the only products observed chromatographically were small amounts of CH_4 and much larger amounts of C_3H_6. FTIR spectra of a few of the reaction mixtures after photolysis at ambient temperature indicated the formation of CO, the expected companion product to C_3H_6. The increase in the yield of CO with photolysis time is indicated in Fig. 1. Calibration of the R6 rotational line of the CO spectrum, the most intense peak, against known partial pressures of CO permitted calculation of the partial pressure of CO in each reaction mixture. Even at the longest exposures used in the experiments for Fig. 1, the yield of CO was less than 2% of the initial pressure of methyl vinyl ketone used. The FTIR spectra contained too much overlap of the peaks for methyl vinyl ketone and propylene to permit their use in determining the yields of propylene. However, the partial pressure of CO at exposures typical of our experiments that used chromatographic analysis was comparable to or slightly larger than the partial pressure of C_3H_6 measured under similar conditions of laser power, pressure of methyl vinyl ketone, and length of exposure. Several experiments were made at ambient temperature in which CO was measured by FTIR spectroscopy and the propylene present in the same sample was then measured by gas chromatography. The ratio $[C_3H_6]/[CO]$ found in these experiments was 0.78 ± 0.04 which agrees well with the value 0.7 reported by Raber and Moortgat [2].

The companion product to CH_4 would be either $CH_2{=}C{=}C{=}O$ or $CO + C_2H_2$. We were able to measure small concentrations of C_2H_2 in the photolysis of methyl vinyl ketone at relatively high temperatures and would expect to have observed C_2H_2 in at least some of our higher pressure experiments at lower temperatures if the $CO + C_2H_2$ channel was important. The postulated product CH_2CCO would be formed in a very small yield, equivalent to that of CH_4, and could easily have been missed in the chromatographic analysis either because of peak broadening due to a comparatively long retention time or by loss in the trap and purge arrangement if its retention time was appreciably longer than that of 1,3-C_4H_6. Both potential channels to methane are endothermic and the formation of $CO + C_2H_2$ is expected to be somewhat more endothermic than the formation of $CH_2{=}C{=}C{=}O$ on the basis of average bond energies. On that basis, the latter channel might be considered to be more likely. In the absence of direct information about the companion product to CH_4, it is also arguable that CH_4 might be formed at least in part through a sequence of steps involving reactions such as dimerization rather than in a single elementary reaction.

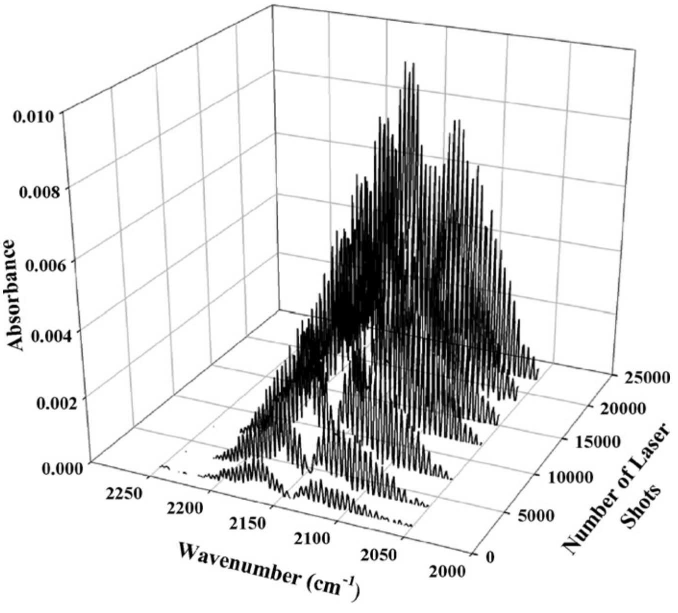

Fig. 1. Evolution of CO yield with increased extent of photolysis of methyl vinyl ketone at ambient temperature. Initial pressure of methyl vinyl ketone = 56.7 Torr, laser repetition rate = 4 Hz, laser power = 0.04 W.

The absence of detectable yields of C_2H_6 and 1,3-C_4H_6, products that would be expected as a result of recombination of CH_3 and C_2H_3 radicals respectively via reactions (1) and (2) below, indicates

$$2C_2H_3 \rightarrow 1,3\text{-}C_4H_6 \tag{1}$$

$$2CH_3 \rightarrow C_2H_6 \tag{2}$$

that the photochemical decomposition of methyl vinyl ketone under our conditions is primarily a molecular process rather than a free radical one. The observation of small yields of C_2H_2, C_2H_4, C_2H_6 and 1,3-C_4H_6 at high temperatures, products that are consistent with a free radical channel under those conditions, suggests that a free radical channel might also operate to a very minor extent at lower temperatures although it was not observable at the very small conversions of methyl vinyl ketone in our experiments. This is consistent with recent measurements of the extent of free radical channels in the photolysis of methyl vinyl ketone [5] in which production of free radicals was shown to result from dissociation of methyl vinyl ketone into C_2H_3 and CH_3CO. At our photolysis wavelength of 308 nm, which is slightly below the threshold of 295.3 nm for this dissociation process, they measured a radical yield of only 2% in the zero pressure limit. The absence of a radical channel to CH_4 is also supported by the observation that the yield of C_3H_6 was typically roughly 100 times the yield of CH_4 which is far greater than would be consistent with the disproportionation and cross combination processes represented by reactions (3) and (4). In this respect, it differs markedly from the photolysis of methyl vinyl ketone

$$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4 \tag{3}$$

$$C_2H_3 + CH_3 \rightarrow C_3H_6 \tag{4}$$

using the shorter wavelength $\pi \rightarrow \pi^*$ transition. Photolysis at these shorter wavelengths has been demonstrated to take place entirely by decomposition to CH_3 and C_2H_3 radicals [1] and produces a ratio of yields of C_3H_6 and CH_4 which is very different from that found under our conditions.

The quantum yields of C_3H_6 scaled linearly with laser power over a factor of 16 in power. We conclude from this that the production of C_3H_6 is not due to multiphoton processes. The yields of CH_4 in experiments with pure methyl vinyl ketone were approximately 1% of the yields of propylene. Consequently, the CH_4 yields could only be measured accurately at the higher laser powers precluding a similar analysis of the variation of CH_4 yield with laser fluence. The quantum yields of both CH_4 and C_3H_6 at a given pressure, temperature and laser power were independent of the repetition rate of the laser from 4 Hz to 20 Hz and of the number of laser pulses over a factor of more than five. The yields of both methane and propylene, normalized to a constant incident power, scaled linearly with the number of laser pulses with an intercept very close to zero and much smaller than the standard error of fit. This suggests that secondary photochemical processes were not significant under our conditions.

These observations are generally consistent with earlier work. Raber and Moortgat [2] reported minor products such as formaldehyde and methanol which they attributed to photo-oxidation as a result of their use of air as a bath gas. The yields they observed were a few percent or less of the yields of the major products, CO and C_3H_6. This is below our detection limits at the small extents of consumption of methyl vinyl ketone, less than 1%, in our experiments. Formaldehyde and methanol would presumably have been absent in our experiments in argon and pure methyl vinyl ketone if they were a result of photo-oxidation in air. The variation with pressure of the quantum yield for loss of methyl vinyl ketone which both they and Gierczak et al. [3] observed is also consistent with the pressure dependence of the quantum yields of C_3H_6 and CH_4 which we observed. While the consumption of methyl vinyl ketone in our experiments was too small to permit direct measurement of the quantum yields for loss of methyl vinyl ketone, those reported for ambient temperature by Raber and Moortgat [2] at up to 20% consumption of methyl vinyl ketone and by Gierczak et al. [3] are comparable to the quantum yields of the major product, C_3H_6, in our experiments made with pure methyl vinyl ketone at ambient temperature. Gierczak et al. also reported C_2H_2 and CH_3OH in addition to C_3H_6 as major products of the photolysis of methyl vinyl ketone in air although they do not give numerical values of the yields of these products. We did not observe either C_2H_2 or CH_3OH in our experiments. The retention time of CH_3OH was measured under our chromatographic conditions and was so long that it would have been purged to the atmosphere together with the residual methyl vinyl ketone. It is also probable that the CH_3OH was formed in their experiments in air as a result of photo-oxidation. Analysis of samples containing known quantities of C_2H_2 indicated that the chromatograph was equally sensitive to C_2H_2 and CH_4 so we should have been able to measure C_2H_2 if it had been formed in yields comparable to those of CH_4. In fact, small yields of C_2H_2 were observed in our experiments at 475 K but not at the lower temperatures. In this respect, our results are more consistent with those of Raber and Moortgat who found only small amounts of methanol and did not report C_2H_2 as a product. The origin of this difference in behaviour is not clear. Gierczak et al. report small yields of CH_4 which we also observe. It is likely that small yields of CH_4 would have been difficult to detect in the experiments of Raber and Moortgat. It may also be relevant that our extent of conversion of methyl vinyl ketone was significantly less than that of the experiments in references [2,3] and that most of our experiments were made with pure methyl vinyl ketone or in a bath of argon.

At the highest temperature, 474 K, small yields of C_2H_2, C_2H_4, C_2H_6 and 1,3-C_4H_6 were observed in addition to somewhat increased yields of CH_4 and C_3H_6. These new products are consistent with the emergence of a decomposition channel producing C_2H_3 and CH_3 radicals which then lead to the observed new products via the recombination, disproportionation and hydrogen abstraction reactions

$$2C_2H_3 \rightarrow 1,3\text{-}C_4H_6 \tag{1}$$

$$2CH_3 \rightarrow C_2H_6 \tag{2}$$

$$C_2H_3 + CH_3 \rightarrow C_2H_2 + CH_4 \tag{3}$$

$$C_2H_3 + CH_3COC_2H_3 \rightarrow C_2H_4 + C_3H_5CO \tag{5}$$

In addition to contributing an additional channel for production of CH_4 via reaction (3) above, the production of CH_3 and C_2H_3 would be expected to result in additional channels for CH_4 and C_3H_6 via the reactions

$$CH_3 + CH_3COC_2H_3 \rightarrow CH_4 + C_3H_5CO \tag{6}$$

$$C_2H_3 + CH_3 \rightarrow C_3H_6 \tag{4}$$

For this reason, most of our measurements were restricted to temperatures below 475 K to isolate the molecular decomposition channel from the free radical one and the complications resulting from its consequent additional chemical reactions. The small decrease in the Stern–Volmer slopes at 474 K seen later in Table 1 for the quantum yields in pure methyl vinyl ketone may be attributable to the onset of these additional sources of CH_4 and C_3H_6.

Table 1

Slopes and intercepts of the Stern–Volmer plots for quenching C_3H_6 and CH_4 and the initial linear portions of plots of CH_4 quantum yield against partial pressure of added Ar and O_2. Uncertainties are calculated at the 95% confidence level.

Absolute temperature	Slope ($L\,mol^{-1}$)	Intercept
Quenching of C_3H_6 by methyl vinyl ketone		
300	$(1.04 \pm 0.06) \times 10^4$	3.6 ± 0.7
355	$(2.7 \pm 0.3) \times 10^4$	4 ± 4
474	$(1.9 \pm 0.2) \times 10^4$	1.3 ± 0.9
Quenching of CH_4 by methyl vinyl ketone		
300	$(1.7 \pm 0.1) \times 10^6$	-30 ± 140
355	$(3.5 \pm 0.2) \times 10^6$	200 ± 200
474	$(5 \pm 1) \times 10^5$	25 ± 50
Quenching of C_3H_6 by Ar		
298	$(1.3 \pm 0.2) \times 10^4$	35 ± 12
299	$(2.0 \pm 0.2) \times 10^4$	9 ± 12
300	$(2.8 \pm 0.5) \times 10^4$	6 ± 7
350	$(1.2 \pm 0.2) \times 10^4$	17 ± 7
355	$(2.0 \pm 0.6) \times 10^4$	37 ± 26
405	$(8.5 \pm 1.8) \times 10^3$	-33 ± 21
Quenching of C_3H_6 by O_2		
300	$(2.1 \pm 0.1) \times 10^4$	21 ± 6
355	$(4.0 \pm 0.2) \times 10^4$	8 ± 9
Generation of CH_4 by Ar		
300	0.37 ± 0.06	$1.2 \times 10^{-3} \pm 2 \times 10^{-4}$
355	0.07 ± 0.02	$4.4 \times 10^{-4} \pm 0.8 \times 10^{-4}$
Generation of CH_4 by O_2		
300	0.84 ± 0.07	$5.7 \times 10^{-4} \pm 1.2 \times 10^{-4}$
355	0.55 ± 0.02	$6.1 \times 10^{-4} \pm 0.8 \times 10^{-4}$

The quantum yields of propylene and methane in experiments with pure methyl vinyl ketone at a pressure of 10 Torr and a temperature of 300 K were respectively 0.08 ± 0.02 and $9 \times 10^{-4} \pm 1 \times 10^{-4}$. This is somewhat smaller than the quantum yield of 0.17 calculated for loss of methyl vinyl ketone at 10 Torr using the relation reported by Gierczak et al. [3] or approximately 0.1 reported by Raber and Moortgat [2]. The results of Raber and Moortgat indicate that $[C_3H_6]/\Delta[MVK]$ is approximately 0.3 at a pressure of 500 Torr in the limit of very small photolysis times. They also provide data at other pressures from which one can calculate this ratio to be approximately 0.4 at 54 Torr and 0.2 at 760 Torr, suggesting that some pressure dependent reaction may be preferentially depleting the precursor to C_3H_6. They attribute this difference between the loss of methyl vinyl ketone and the yield of C_3H_6 to loss of a significant proportion of excited methyl vinyl ketone to form adducts rather than leading to C_3H_6. Combining the lower pressure factor of 0.4 with our quantum yields of propylene indicates a quantum yield of 0.2 for loss of methyl vinyl ketone based on the measured quantum yield of propylene in our lower pressure experiments. On the assumption that this factor would continue to increase with decreasing pressure, it seems reasonable to conclude that our quantum yields for propylene at a pressure of 10 Torr are consistent with the previous work, particularly since their measurements were made at larger extents of reaction and higher pressures than ours and there is evidence of photo-oxidation in their experiments as a result of using air as the bath gas. The quantum yields measured in our experiments in 10 Torr of pure methyl vinyl ketone decreased with increasing temperature so that above approximately 400 K the quantum yield of methane could not be measured reliably. Evidently some temperature dependent process competes with the photochemical decomposition of methyl vinyl ketone to methane and propylene. Our experiments do not provide direct identification of this temperature-dependent process. However, this would be consistent with the indication above, based on the work of others, that some unidentified chemical reaction leads to loss of methyl vinyl ketone that is significantly larger than that implied by the yields of propylene, carbon monoxide and methane.

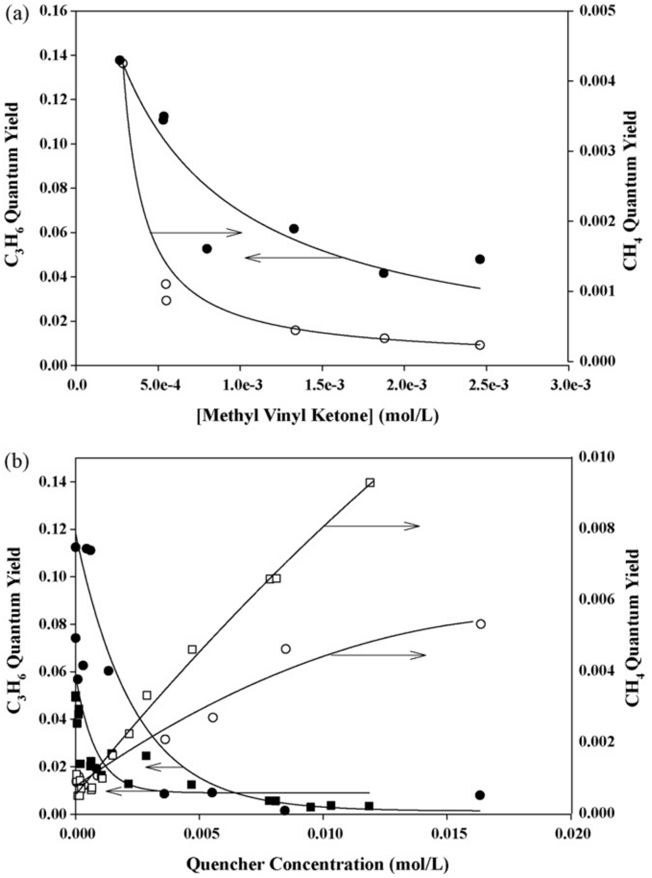

Fig. 2. (a) Variation of quantum yields with concentration of methyl vinyl ketone at 300 K. The lines represent a smoothed fit to the data and are intended only to guide the reader's eye. ○ CH_4; ● C_3H_6. (b) Effects of argon and oxygen on quantum yields of methane and propylene at 300 K with a fixed partial pressure of 10 Torr of methyl vinyl ketone. The lines represent a smoothed fit to the data and are intended only to guide the reader's eye. C_3H_6: ● quenching by Ar, ■ quenching by O_2. CH_4: ○ quenching by Ar, □ quenching by O_2.

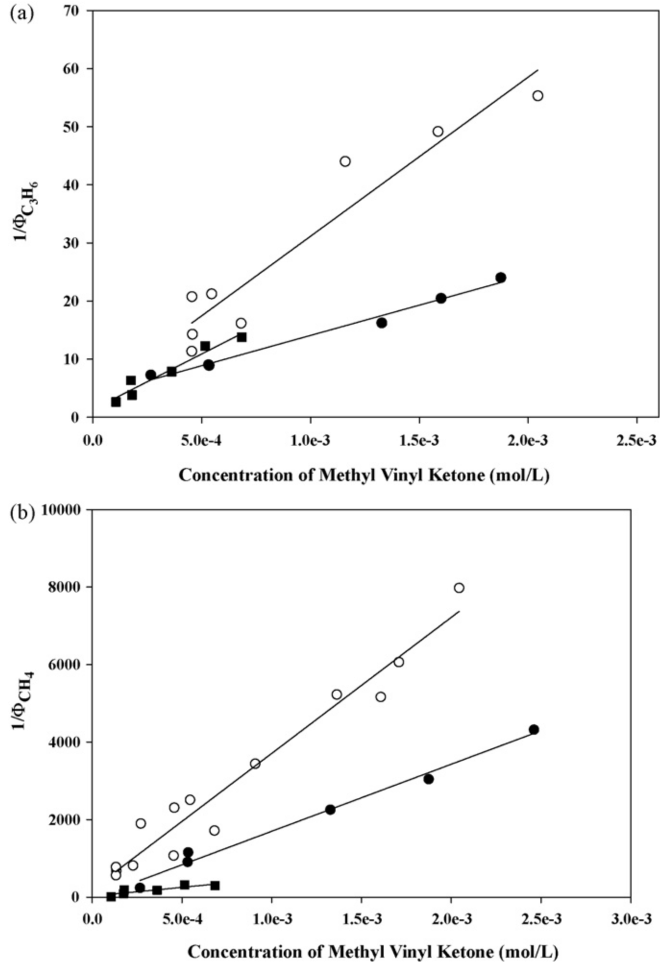

Fig. 3. (a) Quenching of C_3H_6 by methyl vinyl ketone. ● 300 K, ○ 355 K, ■ 474 K. (b) Quenching of CH_4 by methyl vinyl ketone. ● 300 K, ○ 355 K, ■ 474 K.

The quantum yields of both CH_4 and C_3H_6 decreased with increasing concentration of methyl vinyl ketone at a fixed temperature in the absence of added gases. Representative results for a temperature of 300 K are shown in Fig. 2(a). As indicated earlier, the precision of the quantum yields is approximately ±0.02 (about 20%) for the larger propylene quantum yields and the precision decreases somewhat as the quantum yields decrease. While the quality of the data is less than might be desired, it is typical of the precision of the quantum yields reported by others for loss of methyl vinyl ketone [2,3] and may be due in part to the small magnitude of the quantum yields and to the small extent of reaction in our experiments. The quantum yields for methane have similar precision even though they are much smaller than the quantum yields of propylene. Methane is quenched by methyl vinyl ketone more efficiently than propylene, and this behaviour continues at the other temperatures examined.

The effect of added argon or added oxygen on the quantum yields of methane, relative to propylene, obtained using a fixed partial pressure of methyl vinyl ketone is quite different from that produced by varying the pressure of pure methyl vinyl ketone. Representative data are presented for a temperature of 300 K in Fig. 2(b) and Table 1. The effects of varying the pressure of Ar, O_2 and methyl vinyl ketone on the quantum yield of C_3H_6 are comparable at this temperature, consistent with its formation from a singlet state rather than a triplet. While Ar, O_2 and methyl vinyl ketone all quench C_3H_6, in contrast the quantum yield of CH_4 increases with increasing pressure of Ar and O_2. This suggests that propylene and methane are produced from different species with Ar and O_2 removing the precursor to C_3H_6 and generating the precursor to CH_4. As with the quenching by methyl vinyl ketone, the qualitative behaviour of the quantum yields of CH_4 and C_3H_6 on addition of Ar and O_2 is the same at all the temperatures examined.

The quenching can be represented in linear form by Stern–Volmer plots, as indicated in Figs. 3(a), (b) and 4. The data points in these plots are quite scattered but several distinct trends are none the less apparent. The growth of CH_4 with increasing pressure is approximately linear except at the higher pressures of Ar or O_2 where curvature becomes evident as indicated in Fig. 2(b). The slopes and intercepts of the Stern-Volmer plots and of the linear portion of the plots of quantum yield of CH_4 against pressure of added Ar or O_2 are presented in Table 1. The slopes in Table 1 for the experiments in pure methyl vinyl ketone increase with temperature from 300 K to 355 K for both CH_4 and C_3H_6 but then decrease at the highest temperature, 474 K. As suggested earlier, this decrease at the highest temperature might be attributable to the onset of new reaction channels producing new products, ethane and butadiene, that are signatures of methyl and vinyl radicals. These channels, which need not be photochemical, provide additional routes to both methane and propylene, leading to measured quantum yields that are larger than would otherwise be the case. The increase in the slope from 300 K to 355 K suggests that at least some of the quenching of the precursors to CH_4 and C_3H_6 might be due to a chemical reaction with methyl vinyl ketone rather than to energy transfer.

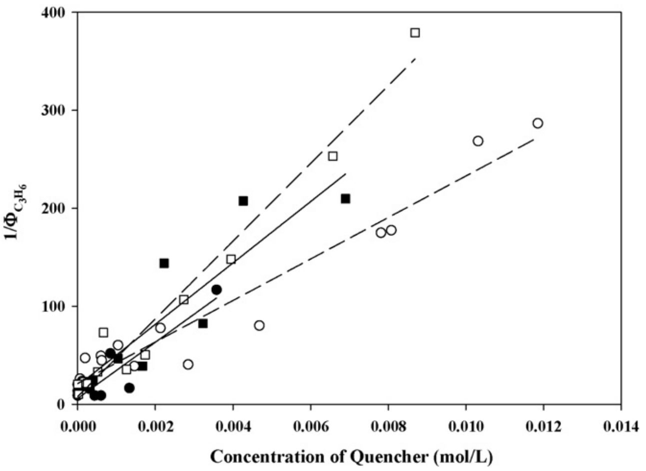

Fig. 4. Quenching of C_3H_6 by Ar and O_2. ●, Ar, 300 K; ○, O_2, 300 K; ■, Ar, 355 K; □, O_2, 355 K.

The rate of chemical quenching might be expected to increase with increasing temperature if the reaction responsible for the quenching has an appreciable activation energy. It is also worth noting that the Stern–Volmer coefficients for CH_4 are roughly two orders of magnitude larger than those for C_3H_6. This supports the conclusion that C_3H_6 and CH_4 are produced from different precursors.

The data for quenching of C_3H_6 by argon do not show a systematic temperature dependence within the scatter of the results suggesting that in this case quenching is due entirely to energy transfer. The results obtained on adding O_2 again indicate an increase in quenching with increasing temperature which could also be due to chemical reaction of O_2 with a precursor to C_3H_6. This would be consistent with the evidence for production of photooxidation products in the results reported for photolysis of methyl vinyl ketone in air [2,3]. It is worth noting that a small yield of free radicals has been found [5] on irradiation of methyl vinyl ketone at 308 nm, due to its dissociation to C_2H_3 and CH_3CO. The CH_3CO radical is known to react rapidly with O_2 forming a peroxy radical that quickly produces OH radicals. The rapid reaction of OH with methyl vinyl ketone might well complicate the interpretation of the results obtained in O_2. The increase in the quantum yield of CH_4 with increasing partial pressures of argon and of oxygen presumably represents a balance between processes that quench a precursor and those that form it. The observed decrease in efficiency of generation of CH_4 with increasing temperature would be consistent with the suggestion above that the quenching process might be due at least in part to a chemical reaction having a significant activation energy. This would cause the relative contribution of quenching to increase with increasing temperature, decreasing the yield of CH_4.

Although the data of Table 1 suggest that the effect of O_2 is somewhat greater for methane than that of Ar, this may be a reflection of the experimental difficulty in measuring the very small quantum yields of methane. The Stern–Volmer coefficients in Table 1 are based on plots of $1/\Phi$ against concentration of quencher rather than the more customary plots of Φ_0/Φ for which an intercept of unity would be expected. Consequently, for the addition of varying partial pressures of Ar or O_2 to a fixed partial pressure of methyl vinyl ketone, the intercept is the reciprocal of the quantum yield for experiments with this fixed concentration of pure methyl vinyl ketone. For the experiments with pure methyl vinyl ketone, the intercept can only be predicted with reference to a reaction mechanism. As a result, little mechanistic information can be obtained from the intercepts in Table 1, many of which have standard deviations that are at least ±100%. However in spite of the degree of scatter evident in the plots of Fig. 4, it is clear from the slopes in Table 1 that the efficiency of quenching of propylene is comparable for methyl vinyl ketone, argon and oxygen while methyl vinyl ketone quenches methane approximately two orders of magnitude more efficiently than it quenches propylene.

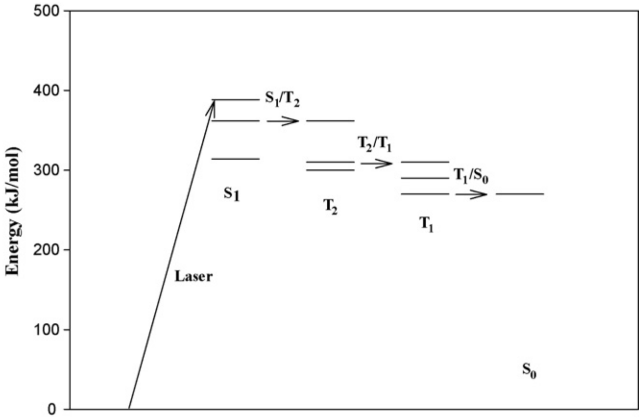

Fig. 5. Schematic representation of the singlet and triplet states of methyl vinyl ketone accessible to our laser radiation and the conical intersections between them.

The laser wavelength of 308 nm excites the $n \rightarrow \pi^*$ transition of methyl vinyl ketone with sufficient excess energy to populate vibrational levels approximately 75 kJ mol^{-1} above the minimum of the first excited singlet but well below the minimum of the second excited singlet. The subsequent decomposition of methyl vinyl ketone and the products formed in this process must therefore emanate from the first excited singlet (S_1) and precursor species that are formed from it. The accessible states of methyl vinyl ketone other than S_1 that might be considered are the triplet and the vibrationally excited ground state singlet. The photochemistry of ketones is influenced by intersystem crossings and the role of conical intersections between states has been reviewed [8]. The dynamics of excited states of α,β-enones has received a significant amount of recent attention [9–12]. While much of that work has focused on acrolein, a significant effort has also been extended to other small molecules including methyl vinyl ketone [10–12].

The states that are accessible from the first excited singlet of methyl vinyl ketone, S_1, are two triplets, T_1 and T_2, and the ground state singlet, S_0. Intersystem crossing between these states is facilitated by a set of conical intersections [10,12]. The relative energies of these states and of the conical intersections between them are indicated schematically in Fig. 5. The S_1/S_0 conical intersection lies 49 kJ mol^{-1} above the minimum of the S_1 state [12], approximately 26 kJ mol^{-1} lower than the highest vibrational levels accessible with our 308 nm laser radiation. By analogy with acrolein [9,10], the S_1/T_2 conical intersection in methyl vinyl ketone is expected to lie significantly below the S_1/S_0 intersection and close to the S_1 minimum. Other conical intersections are anticipated at somewhat lower energies culminating in an intersection with S_0. Two non-radiative channels therefore exist. Relaxation via the S_1/S_0 conical intersection has been reported [12] to have a relaxation time of 1040 fs and is accessed by S_1 species with significant vibrational excitation. The second channel results from crossing to the triplet through a S_1/T_2 conical intersection with an estimated [11] relaxation time of about 2 ps. Evidence for this channel comes from the observation [5] of a small yield of free radicals which presumably requires formation of triplet methyl vinyl ketone and from observation of transient triplet absorption [13] from which a triplet relaxation time of 8 ns has been reported. Further relaxation to S_0 from the triplet can then occur, facilitated by conical intersections [10]. This second non-radiative channel is the only one accessible to vibrational levels of S_1 below the S_1/S_0 intersection. Passage through the T_2/S_0 intersection with has been proposed [10] to be the rate limiting step for relaxation of the triplet to S_0 in acrolein and a similar situation might be anticipated in methyl vinyl ketone. The triplet lifetime of methyl vinyl ketone has been reported [13] to be 8 ns based on measurements in cyclohexane, suggesting that this is a much less efficient relaxation mechanism than the higher energy channel through the S_1/S_0 intersection. Both channels are expected to efficiently populate high vibrational levels of S_0 methyl vinyl ketone. It has been suggested [12] that the dominant relaxation process for S_1 is via the S_1/S_0 conical intersection and is so efficient that fluorescence from S_1 cannot compete. Relaxation via the triplet channel would be expected to be far less effective than that via the S_1/S_0 intersection. In spite of this, transient absorption has been observed in several α,β-enones including methyl vinyl ketone [13] verifying that an appreciable fraction of S_1 species is able to bypass the S_1/S_0 conical intersection. Some of the features of the conical intersections in methyl vinyl ketone and several other simple α,β-enones that can result in avoidance of the S_1/S_0 conical intersection have been discussed elsewhere relative to their measured relaxation times [12].

We begin development of a mechanism to account for our observations and those in the literature by consideration of the main photolysis product, propylene. The minimum set of reactions requiring consideration is

$$S_0 + h\nu \rightarrow S_1 \tag{7}$$

$$S_1 \rightarrow S_0^{\dagger} \tag{8}$$

$$S_1 \rightarrow C_3H_6 + CO \tag{9}$$

$$S_0^{\dagger} \rightarrow C_3H_6 + CO \tag{10}$$

$$S_0^{\dagger} + M \rightarrow S_0 + M \tag{11}$$

Reaction (8) represents relaxation of the excited singlet to the region of the S_1/S_0 conical intersection and its immediate passage through the intersection forming the vibrationally hot ground state singlet. Given the very short lifetime measured [12] for S_1, collisional relaxation should be too slow to be significant on this time scale and reaction (8) is represented as first order internal relaxation. Reactions (9) and (10) represent two channels by which C_3H_6 could be formed, consistent with the indication from the quenching experiments that C_3H_6 is formed from singlet states. Steady-state analysis of this system gives the following expression for the quantum yield of propylene.

$$\Phi_{C_3H_6} = \frac{k_9}{k_8 + k_9} + \frac{k_{10}k_8}{(k_{10} + k_{11}[M])(k_8 + k_9)}$$

If collisional relaxation was important, reaction (8) would have two channels and the expression for the quantum yield of propylene would be modified by replacing k_8 with $k_{8a} + k_{8b}[M]$. If reaction (9) was the dominant source of C_3H_6, Stern–Volmer quenching would require both channels for reaction (8) and the first term above would dominate. In that case, plots such as those in Fig. 4 would have a slope of k_{8b}/k_9 and an intercept of $(k_{8a}/k_9 + 1)$. Unless decomposition of S_1 to propylene is rapid relative to internal relaxation, these intercepts would be much larger than the values reported in Table 1. Such rapid decomposition to propylene would be inconsistent with the very small quantum yields measured and we conclude that reaction (10) is more likely to be the dominant source of propylene. In that case, the second term above should dominate and k_9 should be much smaller than k_8 giving a Stern–Volmer slope of k_{11}/k_{10} and an intercept of unity. This would be more consistent with the parameters recorded in Table 1.

Analysis of the production of methane is much more difficult, partly because its quantum yield is so much smaller than that of propylene. The substantial difference in pressure dependence of its quantum yields compared to the behaviour of propylene indicates that methane is produced from a different precursor than propylene and is not dependent on the same electronic state of methyl vinyl ketone. In the absence of Ar or O_2, normal Stern–Volmer behaviour is observed for CH_4 but the Stern–Volmer coefficient is roughly two orders of magnitude larger than that for quenching of the C_3H_6 quantum yield by methyl vinyl ketone. This makes it unlikely that either S_1 or $S_0^{\dagger}$ can be responsible for production of CH_4. Two triplet states, $T_2(\pi,\pi^*)$ and $T_1(n,\pi^*)$, are located at energies close to the S_1 minimum. A S_1/T_2 conical intersection exists near the S_1 minimum with an estimated [11] lifetime for crossing from S_1 to T_2 of about 2 ps. Indirect evidence for production of triplet methyl vinyl ketone has also been found [5] through the formation of small yields of free radicals on excitation of S_1 at 308 nm. Although the radical yields were small, they suggest sufficient intersystem crossing to account for the very small quantum yields of methane we observe although it is not expected to be produced from a free radical precursor. Given the short lifetime of S_1 as a result of relaxation through the S_1/S_0 conical intersection, it is likely that production of triplet methyl vinyl ketone would be very limited with correspondingly small yields of species produced from a triplet. The existence of an efficient S_1/T_2 conical intersection suggests that intersystem crossing should be described by the first order process

$$S_1 \rightarrow T \tag{12}$$

in which we have made no effort to distinguish between the accessible triplet states. The normal relaxation processes and the formation of CH_4 would then be accommodated in pure methyl vinyl ketone by the following sequence of steps. The extensive occurrence of conical intersections postulated for other enones suggests that relaxation of the triplet could be both collisional (reaction (13)) and internal (reaction (14)). Reaction (15) is not intended to be an elementary step. Indeed, it is likely to be a more complex process than indicated. Unfortunately, our results do not provide sufficient information to deduce the detailed nature of reaction (15). Steady-state analysis of the reaction sequence (12) through (15), on the assumption that it does not appreciably perturb the mechanism for production of C_3H_6, leads to the following expression for production of CH_4 in pure methyl vinyl ketone.

$$T + S_0 \rightarrow \text{products} \tag{13}$$

$$T \rightarrow S_0 \tag{14}$$

$$T \rightarrow CH_4 + \text{other products} \tag{15}$$

$$\Phi_{CH_4} = \frac{k_{12}k_{15}}{k_8(k_{13}[S_0] + k_{14} + k_{15})}$$

While this results in Stern-Volmer quenching, the uncertainty regarding the nature of reaction (15) prevents further analysis of the Stern–Volmer coefficients.

The results obtained by adding Ar or O_2 to a fixed concentration of methyl vinyl ketone were entirely unexpected and their interpretation is more difficult. Addition of Ar would be expected to quench the triplet, reducing the quantum yield of methane. However, adding Ar increased the methane quantum yield, suggesting that it generates a precursor to CH_4. Addition of O_2 would be expected to quench the triplet more readily than Ar but instead it increased the methane quantum yield to much the same extent as Ar. This is inconsistent with reaction (15) as a simple process and suggests that an immediate precursor to methane is produced in a pressure dependent channel. In addition, it appears that quenching of the triplet by methyl vinyl ketone is particularly efficient so that comparatively large concentrations of either Ar or O_2 are required before quenching is able to compete with the generation step, producing a decrease in the effectiveness of the generation process. An important distinction between methyl vinyl ketone and Ar is that while methyl vinyl ketone can remove a methane precursor either by chemical reaction or by collisional energy transfer, Ar can only participate in collisional energy transfer. Since methane is produced both in the presence and absence of Ar or O_2, two channels for methane production are required, one of which could be facilitated by energy transfer.

These considerations lead to the following expansion of reaction (15) and division of reaction (13) into two channels, allowing methyl vinyl ketone to have significantly different quenching efficiency than either Ar or O_2. Reaction (13a) is intended to represent a chemical reaction such as the well-known

$$\mathrm{T} + \mathrm{S_0} \rightarrow \text{products} \tag{13a}$$

$$\mathrm{T} + \mathrm{M} \rightarrow \text{products} \tag{13b}$$

$$\mathrm{T} \rightarrow \mathrm{CH_4} + \text{products} \tag{15}$$

$$\mathrm{T} + \mathrm{M} \rightarrow \mathrm{X} + \mathrm{M} \tag{16}$$

$$\mathrm{X} \rightarrow \mathrm{CH_4} + \text{products} \tag{17}$$

propensity for triplet enones to form adducts [14] while reaction (13b) is intended to represent collisional energy transfer by either methyl vinyl ketone or some additive such as Ar or O_2. Reactions (15) and (17) might still represent complex processes although formation of $CH_4 + CH_2CCO$ would be possible if the carbene product was formed as a triplet. Formation of $C_2H_2 + CO$ would be less likely since it would not conserve spin. This would account for our failure to detect acetylene among the reaction products. The species “X” might be an isomeric structure which more readily decomposes to methane. For example, two conformers of methyl vinyl ketone, the *syn*-periplaner and *anti*-periplaner forms, are well known [15,16]. These have comparable stability in the ground state and are separated in the ground state by a small potential barrier. Their structures suggest that there might be a significant difference in their ability to undergo the intramolecular hydrogen transfer that would be required for production of methane. Other isomeric possibilities for “X” are also possible. Steady-state analysis of the system consisting of reactions (12) through (17) leads to the following expression for production of methane in the presence of Ar or O_2.

$$\Phi_{\mathrm{CH_4}} = \frac{k_{12}(k_{15} + k_{16}[\mathrm{M}])/k_8}{(k_{13\mathrm{a}}[\mathrm{S_0}] + k_{13b}[\mathrm{M}] + k_{14} + k_{15} + k_{16}[\mathrm{M}])}$$

In the absence of the additive, M, this reduces to the previous equation for the quantum yield of methane in pure methyl vinyl ketone.

The full equation for the quantum yield of methane can be made to fit the experimental data for the experiments in argon and in oxygen with a range of values of the rate constants. The degree of fit is illustrated in Fig. 6. The lifetime [12] of S_1 was used to provide a value of k_8, the estimated time [11] for the $S_1 \rightarrow T$ intersystem crossing (2 ps) was used to estimate k_{12}, and the reported [13] lifetime for the triplet (8 ns) was used to estimate an upper limit for k_{14}. Values of k_{15}/k_8 were selected to provide consistency with the measured values of the Stern–Volmer coefficients in pure methyl vinyl ketone using a representative value of 10^6. The steady-state analysis predicts that the Stern–Volmer coefficients are given by $K_{SV} = k_{13a}k_8/k_{12}k_{15}$. These conditions reduced the number of freely adjustable parameters significantly although these constraints remain somewhat flexible given the experimental uncertainties in the present work and the nature of the approximations required in some of the reported estimates of lifetimes. Representative values used for the freely adjustable parameters are $k_{15}/k_8 = 2 \times 10^{-8}$, $k_{16}/k_8 = 10^{-4}$, $k_{13a}/k_{12} = 0.02$, and $k_{13b}/k_{12} = 0.02$. These parameters have a range of degrees of sensitivity in determining the methane quantum yields and, given the degree of uncertainty in their estimates and in the experimental data, they should be regarded only as representing the order of magnitude of the values required to qualitatively represent our observations.

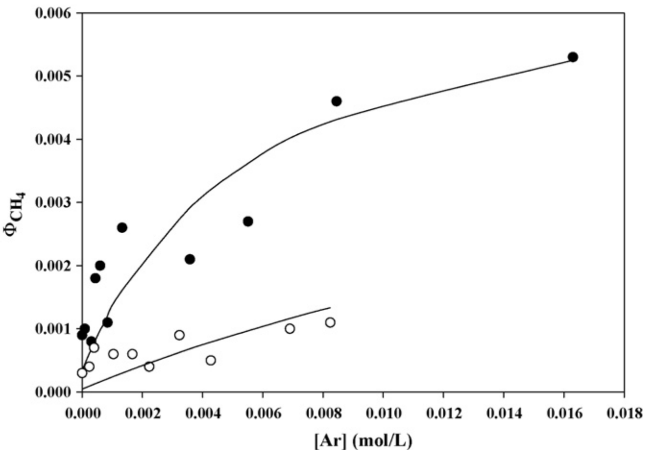

Fig. 6. Model fits to the experimental data for methane quantum yields as a function of argon concentration at a fixed concentration of methyl vinyl ketone. ● 300 K, 10 Torr methyl vinyl ketone; ○ 355 K, 10 Torr methyl vinyl ketone.

4. Conclusions

The photolysis of methyl vinyl ketone below 475 K is dominated by molecular processes giving rise primarily to propylene and carbon monoxide with much smaller yields of methane. No evidence was found for free radical reactions under our conditions. However, the very small extent of free radical production reported by others [5] would have been extremely difficult to detect at our very small conversions using the analytical techniques at our disposal. The quantum yields measured in argon and in oxygen are very similar. Steady-state analysis of a mechanism for production of propylene suggests that the variation of the quantum yields of propylene with pressure of methyl vinyl ketone, argon and oxygen is best described if propylene is produced from high vibrational levels of the ground state singlet of methyl vinyl ketone. The very different behaviour of methane, particularly when Ar or O_2 is added, suggests that it is produced from a different state which we postulate is a triplet. Steady-state analysis of a minimal mechanism for production of methane is consistent with this postulate. Our results are consistent with the following mechanism which also accommodates the observations of others [2,3]. In particular, it

$$\mathrm{S_0} + h\nu \rightarrow \mathrm{S_1} \tag{7}$$

$$\mathrm{S_1} \rightarrow \mathrm{S_0}^{\dagger} \tag{8}$$

$$\mathrm{S_0}^{\dagger} \rightarrow \mathrm{C_3H_6} + \mathrm{CO} \tag{10}$$

$$\mathrm{S_0}^{\dagger} + \mathrm{M} \rightarrow \mathrm{S_0} + \mathrm{M} \tag{11}$$

$$\mathrm{S_1} \rightarrow \mathrm{T} \tag{12}$$

$$\mathrm{T} + \mathrm{S_0} \rightarrow \text{products} \tag{13a}$$

$$\mathrm{T} + \mathrm{M} \rightarrow \text{products} \tag{13b}$$

$$\mathrm{T} \rightarrow \mathrm{CH_4} + \text{products} \tag{15}$$

$$\mathrm{T} + \mathrm{M} \rightarrow \mathrm{X} + \mathrm{M} \tag{16}$$

$$\mathrm{X} \rightarrow \mathrm{CH_4} + \text{products} \tag{17}$$

makes allowance for consumption of significantly more methyl vinyl ketone than would be implied by the yields of C_3H_6 and CH_4. It also provides the possibility for production of CO among the other unspecified “products” which would be consistent with the observation in our experiments as well as those of others [2] that the quantum yield of CO is somewhat larger than the quantum yield of C_3H_6.

Acknowledgements

The authors are indebted to the Natural Sciences and Engineering Research Council Canada for financial support of this work. The assistance of Nancy Djogbenou, Bradley Hayley and Sherri MacLeod in some of the experiments is gratefully acknowledged.

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