# Photochemistry of the Matrix-isolated $\alpha$ , $\beta$ -Unsaturated Aldehydes Acrolein, Methacrolein and Crotonaldehyde at 4.2 K

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The UV photolysis of the  $\alpha$ , $\beta$ -unsaturated aldehydes acrolein, methacrolein and crotonaldehyde in argon matrices at  $\lambda > 300$  nm has shown a major photochemical deactivation pathway to be conformational isomerism to the thermodynamically less stable *s*-*cis* form. This type of isomerization may account for the rapid internal conversion observed in the gas phase. Matrix-isolated crotonaldehyde undergoes further isomerization to ethylketene and *enol*-crotonaldehyde, as observed in the analogous gas-phase photolysis. In addition, another Habstraction product was detected ( $\nu_{OH} = 3674 \text{ cm}^{-1}$ ) which is probably derived from the photolysis of *s*-*cis*crotonaldehyde. At shorter excitation wavelengths ( $\lambda > 230$  nm) acrolein and methacrolein isomerize to methylketene and dimethylketene, respectively.

The photochemistry of simple aldehydes in gas and solution phases is well understood and is usually interpreted in terms of isomerization reactions or decomposition to yield radical fragments.<sup>1,2</sup> The introduction of a conjugating double bond in acrolein (propenal), methacrolein (2-methylpropenal) and crotonaldehyde (3-methylpropenal) shifts the electronic absorption spectra to longer wavelengths from those of the simple aldehydes. It also enhances their 0–0 transitions owing to the molecular planarity of the two lowest singlet states S<sub>0</sub> and S<sub>1</sub>.<sup>1</sup> As a consequence the characteristic nπ\* (S<sub>0</sub>-S<sub>1</sub>) transition is observed in the region 260–380 nm ( $\varepsilon$ , log 1.32) and the second optical transition S<sub>0</sub>-S<sub>2</sub> ( $\pi\pi$ \*) has a maximum at *ca.* 190 nm which is appreciably more intense.<sup>3,4</sup> The measured quantum yields of fluorescence for these aldehydes are less than 10<sup>-6</sup> which indicates rapid internal conversion from the S<sub>1</sub> state.<sup>1</sup>

The effects of irradiation into both these excited singlet states in the gas phase have been well documented for acrolein<sup>5-9</sup> and crotonaldehyde,<sup>10-15</sup> whilst little relating to methacrolein photochemistry or to photolyses in condensed phases has been reported.

Coomber and Pitts<sup>8</sup> observed very little primary photochemical reaction from acrolein at 313 nm ( $S_0 \rightarrow S_1$ ). The reaction products CO,  $C_2H_4$ , CO<sub>2</sub>,  $C_2H_2$  and  $C_4H_6$  were detected in very small quantities with quantum yields ranging from  $5 \times 10^{-3}$  for CO to  $10^{-6}$  for ethyne. A similar photochemical study of crotonaldehyde by the same authors<sup>15</sup> showed CO and propene to be the major products ( $\phi_{CO} =$ 0.3,  $\phi_{propene} = 0.15$ ). The isomers ethylketene (2-ethylethenenone) and *enol*-crotonaldehyde (buta-1,2-dien-1-ol) were also observed and it was suggested the rapid  $S_1$ - $S_0$ internal conversion proceeded *via* isomerization to thermally unstable intermediates (probably ethylketene) in accordance with the ideas expressed by Noyes *et al.*<sup>16</sup>

Direct excitation into the S<sub>2</sub> manifold of acrolein ( $\lambda = 200$  nm) produced vibrationally excited CO. Upon photolysis of methylketene, CO was again observed with a similar non-statistical vibrational energy distribution<sup>9</sup> leading the authors to postulate a role for methylketene in the photolysis of acrolein.

It would seem from the above evidence that the photophysics and photochemistry of the unsaturated aldehydes are linked to the production of unstable photoisomers. The matrix-isolation technique offers an opportunity to characterise spectroscopically such unstable species, which do not exist in the analagous gas-phase experiments. In fact, in the cold, solid environment, isomerization processes are commonly observed upon photolysis of parent compounds because the 'cage effect' often suppresses the identification of radical products. However, only two matrix-isolated *in situ* photolysis experiments (pertaining to acrolein) have been reported<sup>17</sup> in which new post-photolysis IR spectral features were assigned to the production of *s*-*cis*-acrolein, although no detailed spectrum of this isomer was reported in either study. What follows is an investigation of the photolysis mechanism of certain unsaturated aldehydes using FTIR detection of the matrix-isolated products.

## Experimental

A Helipex CS-308 closed-cycle helium refrigeration system (Air Products Inc.) was used to maintain a caesium iodide deposition window at the normal operating temperature of 4.2 K as measured by an Air Products APD-H controller and a helium vapour bulb pressure gauge. IR radiation from an external Perkin-Elmer globar source was passed through the caesium iodide cold window, the outer potassium bromide windows of the vacuum shroud and the emission port of a Digilab FTS-80 Fourier-transform infrared spectrometer fitted with a mercury cadmium telluride detector cooled to liquid-nitrogen temperature. All spectra were taken as single beams at 1 cm<sup>-1</sup> resolution and computed from the coaddition of 1024 interferograms. These were then ratioed against a suitable background to produce the desired absorbance spectrum.

Matrices were deposited on the cold window via the pulsed deposition technique and photolysis light was transmitted through a Spectrosil-B quartz window present in the vacuum shroud. All photolyses were achieved with a high-pressure 1000 W mercury-xenon lamp (Oriel Corp.) fitted with a 10 cm pathlength water filter to eliminate IR radiation. The unfiltered emission from this lamp ranged from  $\lambda > 230$  nm to the near IR and so for photolyses at wavelengths greater than 300 nm a 2 mm thick pyrex filter was inserted in front of the vacuum shroud.

Matrix gas mixtures were prepared on a standard mercuryfree vacuum line fitted with greaseless taps and matrix ratios were calculated from pressure measurements obtained using two MKS baratron units (Models 220B, 222HSA). Argon stated purity 99.999% was purchased from Messer Greisheim (Distillers) and passed though a glass spiral immersed in an appropriate coolant so as to remove residual water vapour

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and carbon dioxide. Acrolein (97% purity), methacrolein (98%) and crotonaldehyde (98%) were purchased from Aldrich Chemicals and were distilled and stored on 4A molecular sieve under vacuum. Each was thoroughly degassed at liquid-nitrogen temperature prior to use.

#### Results

## Photolysis of Acrolein at $\lambda > 300$ nm

When acrolein in argon [matrix ratio (MR), 1:1000] was photolysed exclusively at wavelengths greater than 300 nm for periods of up to 3 h, new bands appeared in the FTIR spectrum which are listed in Table 1. Possible decomposition products such as carbon monoxide (2138 cm<sup>-1</sup>)<sup>18</sup> formyl radicals (1865, 1087 cm<sup>-1</sup>),<sup>19</sup> allyl radicals (1389, 985, 802,  $517 \text{ cm}^{-1})^{20}$  and ethane (1440, 946 cm<sup>-1</sup>)<sup>21</sup> could not be detected. The only other reported UV photolysis study of matrix-isolated acrolein showed conversion of the predominant *s*-trans to the *s*-cis conformer,<sup>17</sup> though few IR bands of the new species were identified. As can be seen from Table 1 there is excellent agreement between the extensive set of IR bands reported here and virtually all those calculated for *s*-cis-acrolein by Bock *et al.*<sup>22</sup>

## Photolysis of Acrolein at $\lambda > 230$ nm

When the unfiltered output from the photolysis lamp was utilized, other products in addition to the *s*-cis conformer were observed. The FTIR spectral region  $2200-2000 \text{ cm}^{-1}$  is shown before and after 4 h of continuous photolysis in Fig. 1 and all new IR bands are listed in Table 2.

Again no trace of HCO could be detected, in contrast to the gas-phase molecular beam photolysis conducted by Shin-

**Table 1** New bands in the FTIR spectrum of acrolein after photolysis at  $\lambda > 300$  nm

band <sup>a</sup> /cm <sup>-1</sup>	relative intensity (%)	Bock et al. <sup>b</sup>	Krantz et al. <sup>c</sup>	assignment
		162		
		282		
546.3	10	545	547	V17
672.4		672		v <sub>12</sub>
914.8	52	928	918	V <sub>10</sub>
916.6				10
970.0	25	972	970	v <sub>16</sub>
985.4	11	989	995	V <sub>14</sub>
992.0	18			14
1005.9	10	1017		V15
1052.4	3	1068		v <sub>11</sub>
1092.0	2			
1286.7	4	1293		vo
1397.7	10	1393		V
1405.3	90	1420	1402	v7
1616.9	60	1616	1616	Vo
1714.3	100	1711		V .
1715.7				•
1830.6	4			
1935.7	27			
1938.9				
2747.7	25			
2750.3				
		2801		v <sub>4</sub>
2840.3	26			
2834.5				
		3041		v <sub>3</sub>
		3065		$v_2$
		3131		$v_1^-$

<sup>a</sup> This work. <sup>b</sup> Spectrum predicted by Bock *et al.*<sup>22</sup> <sup>c</sup> Matrix photolysis of acrolein by Krantz *et al.*<sup>25</sup>

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Fig. 1 Spectral region 2000–2200 cm<sup>-1</sup> of the post-photolysis FTIR spectrum (b) of acrolein ( $\lambda > 230$  nm), (a) before photolysis

ohara and Nishi.<sup>23</sup> It is clear from the post-photolysis spectrum that both ethane and CO are reaction products. Furthermore, very strong bands at 2125.9 and 2129.2 cm<sup>-1</sup> are produced, the identities of which are now discussed.

The IR spectrum of matrix-isolated ketene<sup>24</sup> contains an intense feature at 2142 cm<sup>-1</sup> due to the asymmetric CCO stretch which completely dominates the remaining spectrum. Upon partial or full deuteration this band shifts to 2132 or 2113 cm<sup>-1</sup>, respectively. This intense band is characteristic of all ketene-type molecules and its absolute spectral position depends upon the attached substituents. For example, ethoxyketene exhibits its strongest feature at 2120 cm<sup>-1,25</sup> Thus it is concluded that the bands present in this region in the post-photolysis spectrum of acrolein, namely, those at 2125.9 and 2129.3 cm<sup>-1</sup>, represent the formation of a ketene, probably methylketene, via a 1,3-hydrogen migration. Unfortunately, the detailed IR spectrum of methylketene is difficult to obtain owing to a rapid thermal polymerization even at low partial pressures.<sup>26</sup> However, reference to the spectra of ketene and gaseous dimethylketene<sup>26</sup> (DMK) allows some qualitative assignments to be made. The spectrum of DMK shows a strong band at 1389  $cm^{-1}$  due to the symmetric

**Table 2** New bands in the FTIR spectrum of acrolein after photolysis at  $\lambda > 230$  nm

band <sup>a</sup> /cm <sup>-1</sup>	relative intensity (%)	assignment
521.4	5	methylketene
532.9	6	methylketene
730.6	1	•
736.7	1	
948.9	10	ethene
1363.4	0.1	
1385.4	0.1	methylketene
1440.0	7	ethene
2025.9	0.1	
2077.0	0.1	
2125.9	50	methylketene
2129.3	100	methylketene
2138.0	87	CO
2146.2	10	CO (complex)
2269.8	0.1	

" Bands for s-cis-acrolein are not listed.

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methyl deformation. It is well known<sup>27</sup> that such vibrations appear with strikingly similar frequencies in different molecules and so the moderately intense band at 1385 cm<sup>-1</sup> in the post-photolysis spectrum of acrolein is assigned to a similar vibration in methylketene. In the spectrum of the parent ketene molecule the strongest bands below 2000 cm<sup>-1</sup> are those associated with out-of-plane hydrogenic deformation at 588 and 528 cm<sup>-1</sup>. Such modes must also be present in the spectrum of methylketene, possibly those observed at 521 and 532 cm<sup>-1</sup>. There still exist, however, several unassigned bands, notably at 730.6, 736.7, 1363.4, 2025.9, 2077.0 and 2269.8 cm<sup>-1</sup>; their origin will be discussed below.

## Methacrolein Photolysis at $\lambda > 300$ nm

Methacrolein (MR, 1:1000) photolysed for periods of up to 4 h produced new bands in the FTIR spectrum of which none could be associated with the dissociation products HCO, CO or propene.<sup>21</sup> The post-photolysis IR bands are listed in Table 3, from which it can be seen that several of the new peaks lie very close to those of methacrolein before photolysis. For example, the bands at 1712.1, 1715.7 and 2739.5 cm<sup>-1</sup> are typical of aldehydic C=O and C-H stretches and it is reasonable to assume that in the absence of any dissociation products the photolysis at wavelengths longer than 300 nm results in the *s*-trans  $\rightarrow$  s-cis isomerization as is observed with acrolein.

## Methacrolein Photolysis at $\lambda > 230$ nm

When matrix-isolated methacrolein (MR, 1:1000) is subjected to photolysis at shorter wavelengths more complicated photochemistry is observed. For instance, the post-photolysis FTIR spectrum shows several strong bands in the spectral region  $2060-2160 \text{ cm}^{-1}$  (Fig. 2) which can be assigned to DMK<sup>26</sup> and CO: Table 3 lists all new IR bands. As an aid to identifying the different products, a serial photolysis experiment was undertaken in which the peak height intensity of each product IR band (where the signal-to-noise ratio allowed reproducible measurements) was monitored as a function of photolysis time. Several such plots are displayed in Fig. 3. The temporal profiles fall into four distinct categories labelled A, B, C and D each of which represents the

DMK 0.09 0.08 0.07 units) 0.06 absorbance (abs. 0.05 0.04 0.03 0.02 (a) 0.01 0.00 (b) 2160 2140 2120 2100 2080 2060 wavenumber/cm<sup>-1</sup>

Fig. 2 Spectral region 2060–2160 cm<sup>-1</sup> of the post-photolysis FTIR spectrum (b) of methacrolein ( $\lambda > 230$  nm), (a) before photolysis

 
 Table 3
 New bands in the post-photolysis FTIR spectrum of methacrolein

methacrolein	methacrolein		
alter $1 > 200 \text{ nm}^{4}$	alter $1 > 230 \text{ nm}^{a}$	assignment <sup>b</sup>	
λ > 500 mm	λ > 250 mm		
	579.7 (0.7)	propene	(A)
594.1	594.1 (0.6)	s-cis	<b>(B)</b>
	630.9 (sh)		
	732.8 (0.7)	DMK	(C)
	740.5 (0.3)	DMK?	
865.8 (6.5)	865.8 (6.0)	s-cis–DMM	
	911.3 (7.5)	propene	
	927.0 (2.7)	DMM	(D)
945.0 (4.2)	945.0 (4.0)	s-cis	<b>(B</b> )
952.3 (3.6)	952.3 (3.0)	s-cis	<b>(B)</b>
	954.3 (1.9)	DMM	(D)
	985.4 (2.0)	DMM	(D)
	990.8 (2.5)	DMM	(D)
	1032.6 (4.7)	DMM	(D)
	1100.5 (0.5)		
	1110.6 (0.4)		
	1141.2 (0.6)		(C)
	1151.7 (2.9)		(C)
	1215.5 (0.4)	DMM	(D)
1257.4 (1.7)	1257.4 (1.5)	s-cis	(B)
	1274.8 (1.0)	DMM	(D)
	1296.1 (0.3)		
1374.7	1374.7	s-cis	
	1389.0 (w)		
1441.3	1440.2		
	1453.9		
1627.1 (1.6)	1627.1 (1.7)	s-cis	
1639.5 (0.7)	1639.5 (0.8)	s-cis	
1712.1 (10.1)	1712.1 (10.0)	s-cis	
1715.7 (sh)	1/15./ (sh)	s-cis	
1737.2 (4.7)	1737.2 (4.0)	S-C1S	
	2104.4 (1.7)		(C)
	2113.5 (2.1)		(C)
	2124.3 (6.3)	DMK	(C)
	2127.1 (9.5)	DMK	(C)
	2130.2 (6.3)	DMK	(C)
	2135.8 (6.7)	CO	(A)
	2136.8 (7.4)	CO	( <b>A</b> )
	2138.4 (4.4) 2615.4	CO	(A)
2730 5	2740.9	s-cis	
5.5	2747 9 (m)	s-cis	
	2764.2		
	2921 7	DMK	
	2922.6	DMK	
2950.5	2949.8 2985.0	s-cis propene	

<sup>a</sup> Relative intensity (%) given in parentheses. <sup>b</sup> Temporal profile.

formation of a different product or pair of products. The three bands at 2138.4, 2136.8 and 2135.8  $\text{cm}^{-1}$  all share a common profile (type A) which is linear initially but then has an increasing gradient after 2-3 h of photolysis. The bands are readily identified with carbon monoxide in three slightly different matrix sites. Furthermore, the bands at 579.7 and 911.3 cm<sup>-1</sup> exhibit the same type A profile and, after reference to spectra reported by Barnes et al.,<sup>21</sup> are assigned to the strong bands of propene. Those bands that are present in both the photolyses at  $\lambda > 300$  nm and  $\lambda > 230$  nm are assigned to the formation of s-cis-methacrolein. All of these bands display a temporal profile which reaches a maximum very early and then decays monotonically (type B), indicating the presence of removal processes, e.g. secondary photolysis. A further set of bands displays two linear regions where the gradient decreases after ca. 2-3 h photolysis and these bands



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Fig. 3 Peak height intensity of new product FTIR bands plotted as a function of photolysis time for methacrolein ( $\lambda > 230$  nm). A, (a) 857, (b) 1033, (c) 927, 991, (d) 954, (e) 985, 1251, 1275; B, (a) 2127, (b) 2130, (c) 2124; C, 945, 952; D, (a) 2137, (b) 2138 cm<sup>-1</sup>

are associated with DMK formation (type C). The fourth and final set consists of bands which reach a maximum intensity after ca. 3 h photolysis but then gradually decay upon further irradiation (type D). Such profiles are indicative of a molecule which undergoes competing formation and destruction processes. The identity of the type D bands is also more difficult to establish as they correspond to no obvious dissociation product or valence isomer of methacrolein such as dimethyloxirene.<sup>28</sup>

#### Crotonaldehyde Photolysis at $\lambda > 300$ nm

The post-photolysis FTIR spectrum of matrix-isolated crotonaldehyde (MR 1:1000) displays several interesting new features, all of which are listed in Table 4. The spectral regions 1600–1800, 2100–2200 and 3600-3700 cm<sup>-1</sup> are illustrated in Fig. 4.

The bands at 3623.1 and 3674.2  $\text{cm}^{-1}$  are both indicative of OH stretches and represent the formation of two different



Fig. 4 Spectral regions of the post-photolysis FTIR spectrum (b) of crotonaldehyde ( $\lambda > 300$  nm), (a) before photolysis

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Table 4 New bands in the post-photolysis FTIR spectrum of crotonaldehyde

protonaldehyde after $\lambda > 300 \text{ nm}$	assignment
610.6 (0.2%)	s-cis
613.2 (2.8%)	5 015
668.2 (2.8%)	
679.8 (0.8)	s-cis
683 5 (0.8)	s-cis
688 9 (2 2)	alcohol <sup>a</sup>
693.1 (1.8)	alcohol <sup>a</sup>
718.3 (2.0)	s-cis
721.1 (2.1)	s-cis
729.8 (4.7)	s-cis
731.0 (4.8)	s-cis
732.7 (7.2)	s-cis
786.1 (2.9)	s-cis
792.8 (1.5)	s-cis
882.8 (3.0)	s-cis
894.3 (9.5)	alcohol <sup>a</sup>
908.3 (1.2)	$C_2H_4$ /alcohol
911.9 (1.1)	$C_2H_4$ /alcohol
919.8 (0.5)	
1029.1 (12.3)	alcohol <sup>a</sup>
1118.0 (0.4)	
1217.8 (6.5)	alcohol <sup>a</sup>
1233.7 (2.1)	s-cis
1239.9 (0.9)	s-cis
1244.2 (1.0)	s-cis
1253.0 (6.7)	alcohol <sup>a</sup>
1256.7 (5.3)	alcohol"
1291.2 (2.6)	s-cis
1354.0 (0.6)	
1365.1 (1.0)	
1634.1 (7.6)	s-cis
1636.4 (9.1)	s-cis
1638.1 (15.2)	s-cis
1696.1 (33.5)	s-cis
2124.0 (0.3)	ethylketene
2139.2 (0.9)	CO
2742.8 (1.7)	s-cis
2755.7 (2.3)	s-cis
3623.1 (3.4)	enol
3674.2 (4.4)	cyclopropenol

" Exact identity discussed in text.

alcohols by hydrogen abstraction reactions. Only a single band at 3630 cm<sup>-1</sup> was observed in the gas-phase photolysis of crotonaldehyde.<sup>15</sup> Carbon monoxide (2138 cm<sup>-1</sup>) and ethylketene (2124.0 cm<sup>-1</sup>) are also formed but in much smaller quantities. In fact, the most intense feature in the spectra of ketene-type molecules is the asymmetric stretch at ca. 2130 cm<sup>-1</sup> and since the observed band of ethylketene is only 0.003 absorbance units it is unlikely that any further features due to this molecule are present in the post-photolysis spectrum. Also, since the amount of CO observed is small (0.018 absorbance units) then little  $C_3H_6$  is expected to be identified. From Fig. 4 a new carbonyl absorption is observed at 1711.3  $cm^{-1}$  as well as features at 2742.8 and 2755.7  $cm^{-1}$ , all indicative of aldehyde formation. To confirm this assignment a serial photolysis was again conducted up to a total photolysis time of 2.5 h (Fig. 5). In an entirely analogous fashion to that observed for methacrolein there exists a set of bands which reach a maximum very early and then decrease monotonically. This group includes the bands cited at 1711.3, 2742.8 and 2755.7  $cm^{-1}$  and indicates s-cis aldehyde formation. From Fig. 5 it is apparent that there exists a set of bands which increase linearly with time and which cannot be assigned to known dissociation products such as HCO and

Fig. 5 Peak height intensity of new product FTIR bands plotted as a function of photolysis time for crotonaldehyde ( $\lambda > 300$  nm). A, (a) 733, (b) 730, 731, (c) 883, (d) 1291; B, (a) 1029, (b) 894, (c) 1218, (d)  $1257 \text{ cm}^{-1}$ 

t/min

propene. Although temporal profiles for the alcohol bands at 3623.1 and 3674.2 cm<sup>-1</sup> could not be plotted accurately (owing to spectral noise in this region) the growth of these bands was definitely observed with time and hence they are probably to be included with those definitely identified as possessing linear profiles. The alcohol with  $v_{OH} = 3623.1$  $cm^{-1}$  is almost certainly *enol*-crotonaldehyde. This feature is directly comparable to a band observed in the gas-phase photolysis of crotonaldehyde at 3630 cm<sup>-1</sup>, but is slightly shifted by the argon matrix.

## Discussion

## Acrolein and Methacrolein

20 40 60 80

0

All three  $\alpha,\beta$ -unsaturated aldehydes can exist in two distinct conformational forms, the s-trans and the s-cis. At ambient temperatures the equilibrium favours the s-trans and this form predominates at room temperature (>98%).<sup>29-31</sup>

s-cis-Acrolein is definitely a product of the photolysis at  $\lambda > 300$  nm of acrolein as evidenced by the characteristic aldehydic bands at 1714.3, 1715.7, 2747.7 and 2750.3 cm<sup>-1</sup> and by the excellent agreement of the observed bands with

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those predicted for s-cis-acrolein by Bock et al.<sup>22</sup> From the post-photolysis spectra and in the absence of any identifiable dissociation products, the matrix photochemistry of meth-acrolein at  $\lambda > 300$  nm can be proposed to bring about the same steady-state s-trans  $\rightarrow$  s-cis interconversion as is observed for acrolein. In the gas phase it is probable that once the less stable s-cis conformer is formed a reversion takes place, so bringing about a process of rapid internal conversion (as evidenced by the low measured quantum yields of fluorescence for these molecules).

Methylketene has been identified as an intermediate involved in acrolein photolyses after excitation into the S<sub>2</sub> manifold in accordance with the suggestion of Umstead et al.<sup>9</sup> CO and ethane were also identified as photolysis products. Unfortunately, the gas-phase IR spectrum of methylketene is difficult to record and it is not possible, therefore, to assign all the bands of methylketene observed in the postphotolysis spectrum of acrolein. The doublet of bands at 2125.9 and 2129.3 cm<sup>-1</sup>, assigned to methylketene, indicates that this molecule is formed in at least two distinct crystalline sites, perhaps originating from the two different conformers of methacrolein. CO is also formed in two sites as evidenced by the bands at 2138.0 and 2146.2 cm<sup>-1</sup>. The former absorption is well characterised and is due to 'unperturbed' CO, whereas the latter band is due to a complex as previously observed (e.g. CO-H<sub>2</sub>O at 2148 cm<sup>-1 18</sup>). The two features can arise in the present experiments for a variety of reasons. For example, only one of the methylketene sites may promote complexation with the partner CO. Alternatively, secondary photolysis may occur to leave CO in two forms in certain sites: ketenes are known to dissociate at the wavelengths employed here to yield methylene-type products.<sup>32</sup> The expected products from methylketene would be CO and ethylidene (H<sub>3</sub>CCH), which can isomerize to ethene. (In the gas phase, the activation barrier to this rearrangement is only 21 kJ mol<sup>-1 33</sup>.) Thus in a matrix, a fraction of the ethylidene might be stabilized and the remainder isomerizes to give the observed ethene. Hence two types of cage partner give rise to the observed CO frequencies: the 'unperturbed' CO-ethene pair and the complexed CO-ethylidene pair. The unassigned bands in this work at 730.6, 736.7, 1363.4, 2025.9, 2077.0 and 2269.8  $\text{cm}^{-1}$  may thus be due to ethylidyne. A combination of both effects is probably operative in the present experiments.

A similar photolysis experiment with methacrolein results in valence isomerization to DMK as well as the formation of the products CO, propene and s-cis-methacrolein. The serial photolysis of matrix-isolated methacrolein also revealed a product with IR bands displaying a different temporal profile (type D) to those of the products already mentioned. The IR bands cannot be associated with any obvious valence isomer of methacrolein such as dimethyloxirene and so they can be assumed to belong to a dissociation product. It is known that ketene-type molecules dissociate photolytically and thermally to give methylenes and carbon monoxide. Furthermore, methylenes can rearrange easily by means of 1,2-hydrogen migrations to yield alkenes.<sup>33</sup> Since the matrix photolysis of methacrolein produces propene, CO and DMK, it is possible that dimethylmethylene (DMM) is also formed and has been trapped in the inert matrix environment. The type D IR bands reach a maximum intensity and then decay, indicating the existence of a loss mechanism, probably a secondary photolysis. Methylenes are known to possess two low-lying states, one a triplet and one a singlet. The parent methylene (CH<sub>2</sub>) has a triplet ground state and the first allowed electronic transition is well into the vacuum UV (ca. 140 nm); the first singlet-singlet transition lies in the visible region of the electromagnetic spectrum.<sup>32</sup> However, upon substitution, the

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energy difference between the singlet and triplet states decreases and it is possible that the relative ordering changes,<sup>33</sup> so that DMM may in fact possess a singlet ground state and thus be able to absorb the light emitted from the photolysis lamp employed in the present study. However, the evolution of CO and propene (type A) increases after ca. 3 h photolysis, and the rate of DMK production, although smaller, remains linear with time (type C). Hence it is unlikely that DMK undergoes a secondary photolysis to form the observed CO and propene, as a temporal profile tending to an asymptote would be expected. Therefore the 'extra' CO cannot be a result of the photolysis of DMK. The formation of CO and propene could be explained if the type D bands did, in fact, belong to a valence isomer of methacrolein which underwent a secondary photolysis to yield propene and CO. As has already been stressed, the behaviour of the type D IR bands is consistent with this suggestion, as they possess the appropriate temporal profile. In summary, it is clear that the D-bands cannot be assigned definitely to a particular species, although it seems more likely that they belong to an isomer of methacrolein rather than to dimethylmethylene. The suggested photolysis scheme for methacrolein is shown in Fig. 6 where \* represents an electronically or vibrationally excited molecule.

The temporal profile of DMK formation exhibits a decrease in its linear growth as indicated by a change in slope. However, the experiments reported here contain an added complication in that photochemistry may occur from two different conformations.

If one considers the geometry of the *s*-trans and *c*-cis conformers, then it is apparent for the formation of DMK that H(1) must migrate to carbon C(1). The distances travelled by H(1) are different for the two conformers. Indeed, the distance is considerably shorter for *s*-trans-methacrolein and, according to the 'principle of least nuclear motion',<sup>34</sup> the favoured elementary reactions are those which involve the least change in atomic positions and electronic configuration. Thus, the isomerization to DMK from the *s*-trans conformer should proceed more easily than that from the *s*-cis conformer. During the photolysis of matrix-isolated methacrolein appreciable quantities of the *s*-cis conformer are produced (as evidenced by the FTIR spectrum) and it is therefore not surprising that the reduced concentration of *s*-trans decreases the rate of DMK formation.

The post-photolysis spectrum of methacrolein still contains several unassigned bands. For example, the bands at 1141.2, 1151.5, 2104.4 and 2113.5 cm<sup>-1</sup> all share the same temporal evolution as that associated with DMK, but do not match the gas-phase IR spectrum of this molecule particularly well. It is not possible to guarantee 100% isolation of each methacrolein molecule in the initially deposited matrix and thus



Fig. 6 Schematic representation of methacrolein photolysis



Fig. 7 Schematic representation of crotonaldehyde photolysis

the quoted bands may result from bimolecular interactions of reaction products with themselves or with unreacted methacrolein within the matrix cage.

### Crotonaldehyde

The photolysis of crotonaldehyde at  $\lambda > 300$  nm produces small amounts of carbon monoxide, ethylketene (2121.0 cm<sup>-1</sup>) and possibly propene (911.0 cm<sup>-1</sup>), although not in sufficient quantities to enable identification of more than one band for the latter two compounds. In the gas phase it has been noted<sup>15</sup> that a vibrationally excited  $S_1$  state is responsible for ethylketene production. In the matrix it is expected that vibrational relaxation to the zeroth level will be rapid and this may explain why only small quantities of ethylketene are observed.

Again, the most readily formed photolysis product is the s-cis conformer of crotonaldehyde, identified by the characteristic group frequencies (1771.3, 2742.8, 2755.7 cm<sup>-1</sup>) and the temporal profile which reaches its maximum very early in the photolysis and then decays monotonically as is observed for methacrolein.

The most interesting feature of the post-photolysis IR spectrum is the emergence of bands at 3632.1 and 3674.2 cm<sup>-</sup> both of which are indicative of alcohol formation. These bands increase in intensity with time and are associated with the bands possessing linear temporal profiles and are thus distinct from those features of s-cis crotonaldehyde. The gasphase photolysis of crotonaldehyde gives rise to a product absorption at 3630 cm<sup>-1</sup> which was assigned to enolcrotonaldehyde. However, in the gas phase there exists only the s-trans conformer, whereas in the matrix a sizeable concentration of the s-cis conformer co-exists after short photolysis times. Therefore, if this conformer also undergoes the geometrically most favourable hydrogen abstraction reaction then a different alcohol, possibly methylcyclopropenol, will be formed, as is illustrated in Fig. 7.

#### Conclusion

The photolysis of acrolein, methacrolein and crotonaldehyde at wavelengths greater than 300 nm in inert matrices has been shown to yield the s-cis conformer in large quantities. This isomerization may offer a pathway for enhanced internal conversion in the gas phase and explains the observed low quantum yields of fluorescence for these molecules. This is the first occasion that the IR spectra of s-cismethacrolein and s-cis-crotonaldehyde have been reported. In addition, crotonaldehyde isomerizes to give enolcrotonaldehyde and ethylketene, as is observed in the analogous gas-phase photolysis. A second H-abstraction reaction is also observed, which is thought to derive from the photolysis of s-cis-crotonaldehyde. This alcohol is tentatively assigned as methylcyclopropenol.

Excitation at shorter wavelengths ( $\lambda > 230$  nm) causes acrolein and methacrolein to isomerize to methylketene and dimethylketene, respectively. Evidence has also been presented to support the existence of a further valence isomer of methacrolein upon photolysis at these wavelengths.

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