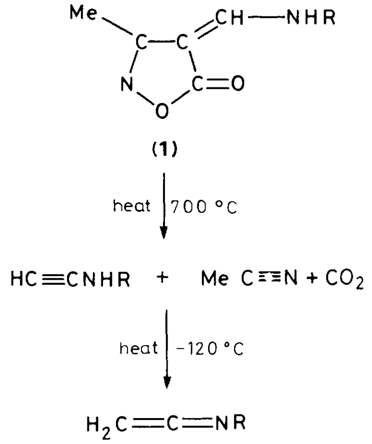
F.T.I.R. Study of Ynamines and Ketenimines Produced by Thermolysis of Substituted Isoxazolones

Julie August, Klaus Klemm,† Harold W. Kroto,* and David R. M. Walton
School of Chemistry and Molecular Sciences, University of Sussex, Falmer, Brighton BN1 9QJ

Gas phase flow thermolysis of 3-methyl-4-(methylaminomethylidene)isoxazol-5(4*H*)-one yielded *N*-methylethynamine, $HC\equiv CNHMe$, and *N*-methylketenimine, $H_2C{=}C{=}NMe$, which were observed by f.t.i.r. spectroscopy. Attempts to detect the simplest ynamine, $HC\equiv CNH_2$, and ketenimine, $H_2C{=}C{=}NH$, by an analogous route using the appropriately substituted isoxazolone were unsuccessful.

Winter and Wentrup[1,2] and Briehl[3] generated various ynamines, $HC\equiv CNHR$ and ketenimines, $CH_2{=}C{=}NR$, by thermolysis of various substituted isoxazolones (**1**) (Scheme). The products were trapped at low temperature and identified by their characteristic i.r. frequencies at *ca.* 2 120 cm^{-1} ($HC\equiv CNHR$) and *ca.* 2 040 cm^{-1} ($CH_2{=}C{=}NR$). This is the first reported observation of a secondary aminoalkyne (ynamine). The results are consistent with the proposed reaction Scheme.

The aim of this work was to detect ynamines and ketenimines in the gas phase by f.t.i.r. spectroscopy using the method of Winter, Wentrup, and Briehl.[1–3] In particular we had hoped to detect ethynamine, $HC\equiv CNH_2$, and ketenimine, $CH_2{=}C{=}NH$, using precursor (**1**; R = H). Matrix-trapped $CH_2{=}C{=}NH$ has been detected by Jacox in an i.r. study of the reaction of $HC\equiv CH$ with the NH radical.[4] Our study has confirmed that the Scheme operates efficiently in the gas phase with (**1**; R = Me). Bands analogous to those detected in the matrix studies[1,3] have been observed and assigned, however, when R = H the parent ynamine, $HC\equiv CNH_2$, and ketenimine $H_2C{=}C{=}NH$ were not observed. During the course of our work Amatatsu, Hamada, and Tsuboi[5] obtained *N*-methyketenimine by the thermolysis of *N*-chloropropyleneimine. Our assignment is, with one or two refinements, broadly consistent with theirs. Rodler *et al.*[6] have detected ketenimine in the gas phase by microwave spectroscopy in the thermolysis products of 3-hydroxypropionitrile, $HOCH_2CH_2CN$ and we have used this approach to measure the f.t.i.r. spectrum.[7] Recently Wentrup and co-workers have succeeded in detecting the elusive ethynamines $HC\equiv CNH_2$ and $PhC\equiv CNH_2$.[8]



Scheme.

Experimental

The precursors were prepared from 3-methylisoxazolone by a method analogous to the general procedure described by Wentrup and co-workers.[1–3] 3-Methyl-4-(methylaminomethylidene)isoxazol-5(4*H*)-one was prepared by the addition of $HC(OEt)_3$ (30 cm^3) to 3-methylisoxazolone (3.27 g) in a three-necked flask fitted with a reflux condenser and stirrer. Methylamine was added using a gas inlet tube and the reaction mixture was boiled under reflux for 30 min. The product (m.p. 218 °C) was recrystallized from EtOH. 3-Methyl-4-(aminomethylidene) isoxazol-5(4*H*)-one was prepared in the same way using NH_3 instead of $MeNH_2$.

The spectra were observed using a Bomem DA3.002 f.t.i.r. spectrometer at 1.0 cm^{-1} resolution. Up to 100 interferograms were co-added and InSb and MCT detectors, cooled to liquid nitrogen temperatures, were used between 1 800–3 700 and 800–3 700 cm^{-1}, respectively. The thermolysis apparatus consisted of a 5 mm i.d. quartz tube of length 30 cm, closed at one end and located directly in the side (15 cm from one end) of a 50 cm multiple traversal cell, which was set for a 20 m path length. The exit was 15 cm from the other end on the opposite side, so the gas flow followed a chicane path. A 12 cm furnace, surrounding the quartz tube and heating it to *ca.* 700 °C, was placed as close as possible to the cell, *ca.* 3 cm from the joint. The distance from the end of the pyrolysis zone to the cell cavity was *ca.* 10 cm. The powdered sample was placed in the closed end of the quartz tube, roughly half-filling the last 10 cm, and the sample was sublimed as carefully as possible (using heating tape of *ca.* 150 °C) into the hot zone. The system was pumped, using a standard liquid nitrogen trap, by an Edwards EDM18 rotary pump.

Results

The i.r. spectra recorded in the 1 800–2 500 cm^{-1} region are shown in Figure 1. The result obtained on thermolysis of (**1**; R = Me), using the fastest flow-rate obtainable with the apparatus described in the previous section and heating the precursor to maintain a pressure of *ca.* 1 Torr, is shown in Figure 1(*a*). A flow rate restricted by closing a 10 mm tap between the trap and the rotary pump by a factor of *ca.* 0.75 generated the spectrum in Figure 1(*b*). If the thermolysis products are condensed at −196 °C, and the contents of the

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† Abteilung für Chemie, Ruhr-Universität Bochum, Bochum, West Germany.

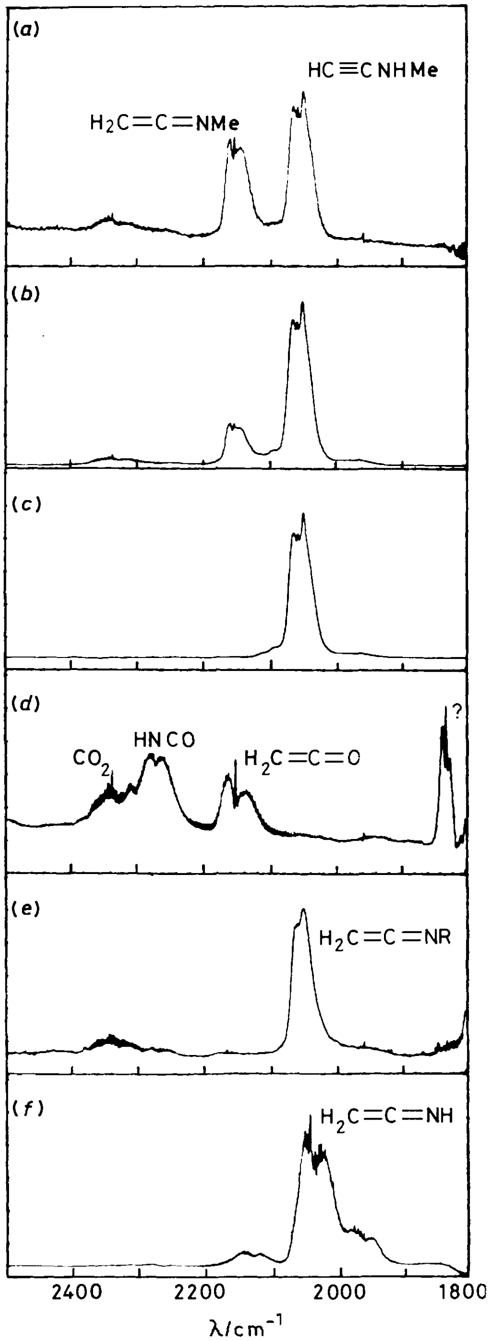

Figure 1. (*a*) The i.r. spectrum products of pyrolysis of the parent isoxazolone (**1**; R = Me) using a very fast flow rate. (*b*) The i.r. spectrum under more moderate flow rates than in (*a*). (*c*) The i.r. spectrum of the species revaporized at −95 °C from the trapped (−196 °C) products of the pyrolysis of (**1**) under conditions similar to those used in (*a*). (*d*) The i.r. spectrum of the products of pyrolysis of the isoxazolone (**1**; R = H). CO_2, HNCO and H_2CCO were all conclusively identified by a very high resolution study. The peak at 1 830 cm^{-1} has not been identified. (*e*) The spectrum of the species revaporized at −95 °C from the trapped (at −196 °C) products of pyrolysis of (**1**; R = H). The peak is very similar to the ketenimine stretch vibration shown in (*a*)–(*c*) but appears to be slightly narrower. (*f*) The i.r. spectrum of CH_2=C=NH produced by pyrolysis of 3-hydroxypropionitrile.[6]

trap pumped for a few minutes at −126 °C and revaporized at −95 °C, the spectrum shown in Figure 1(*c*) is obtained. Only under the fastest flow conditions is the 2 152 cm^{-1} band assigned to HC≡CNHMe detected strongly, and this peak together with that at 2 060 cm^{-1} assigned to CH_2=C=NMe are then roughly of equivalent intensity [Figure 1(*a*)]. The gas-phase spectra are entirely consistent with (and confirm) the matrix measurements.[1–3]

When the precursor (**1**; R = H) is used, the thermolysis route (Scheme) does not appear to be followed to any significant extent under our conditions. The spectra of the products are shown in Figure 1(*d*) where the PQR contour band centred at 2 152 cm^{-1} belongs to ketene and the PR contour band centred at 2 267 cm^{-1} belongs to HNCO. These assignments have been unequivocally confirmed by an accurate comparison of the rotationally resolved spectra taken at 0.008 cm^{-1} resolution with published high resolution measurements for ketene[9] and HNCO.[10] The other, weaker features belong to CO and CO_2. The PQR contour band at 1 830 cm^{-1} has not been identified but its narrow width indicates a significantly smaller *B* value than the methyl-substituted ynamine or eneimine would have. When these products were trapped at −196 °C, pumped at −126 °C and then revaporized at −95 °C the product yielded a spectrum with a very strong band at the frequency characteristic for an enimine [Figure 1(*e*)]. This band appears to be similar, though not identical to the analogous CH_2=C=NMe band and, in particular, it is slightly narrower, suggesting that a CH_2=C=NX species has been produced with an X group somewhat heavier than Me. Further work is necessary to elucidate the complicated chemistry involved in this particular experiment. The spectrum of ketenimine obtained by thermolysis of 3-hydroxypropionitrile[7] is presented for comparison in Figure 1(*f*).

Assignment of Spectra.—The i.r. spectrum in the range 3 500–800 cm^{-1}, corresponding to Figure 1(*b*), is shown in Figure 2(*a*), whilst that in Figure 2(*b*) corresponds to Figure 1(*c*) (*i.e.* the species revaporized). Almost all the features in Figure 2(*b*) belong to *N*-methylketenimine. The spectrum in Figure 2(*c*) is obtained by scaled subtraction of the spectrum in Figure 2(*b*) from that in Figure 2(*a*). Some of the weaker features have been assigned to MeCN and CO_2 but all the main features belong to *N*-methylethynamine. The distinct PQR feature at 3 345 cm^{-1}, which is readily assigned to the ≡C–H stretch mode, parallels the intensity variation behaviour of the C≡C stretch mode at 2 152 cm^{-1}, adding conclusive support for the proposed identification. The other C–H stretch modes lie in a broad more-or-less featureless contour centred at *ca.* 2 930 cm^{-1}, Figure 2(*c*) which has some very weak sharp lines of MeCN superimposed. Two further features in Figure 2(*c*) are reliably assigned to HC≡CNHMe. These are the NH stretch band at 3 442 cm^{-1} and a band at 1 136 cm^{-1} which most likely belongs to the CNH bending vibration. The latter is expected to lie at a frequency close to the analogous vibrations in keteneimine[7] and hydrogen azide[11] which lie at 1 004 cm^{-1} and 1 150 cm^{-1}, respectively. (Note that the latter appears to be mixed with the N–N stretch at 1 274 cm^{-1}.)

The spectrum of CH_2=C=NMe observed by Amatatsu, Hamada, and Tsuboi[5] was assigned on the basis of *ab initio* calculations and our assignment is consistent with theirs as far as the strongest features are concerned. There are, however, alternative assignments for some weaker features on the basis of comparisons with related molecules, in particular thioketene.[12]

The very strong C=C=N stretching mode of CH_2=C=NMe dominates the spectrum in Figure 2(*b*). The lower frequency C=C=N stretch mode has been assigned to the 1 234 cm^{-1} band. In CH_2=C=NH a value of 1 127 cm^{-1} is observed for this vibration.[7] The C–H stretching frequencies are bunched together in a complicated group between 3 046–2 881 cm^{-1}. Three bands with PR contours lie at 1 468, 1 409, and 1 366

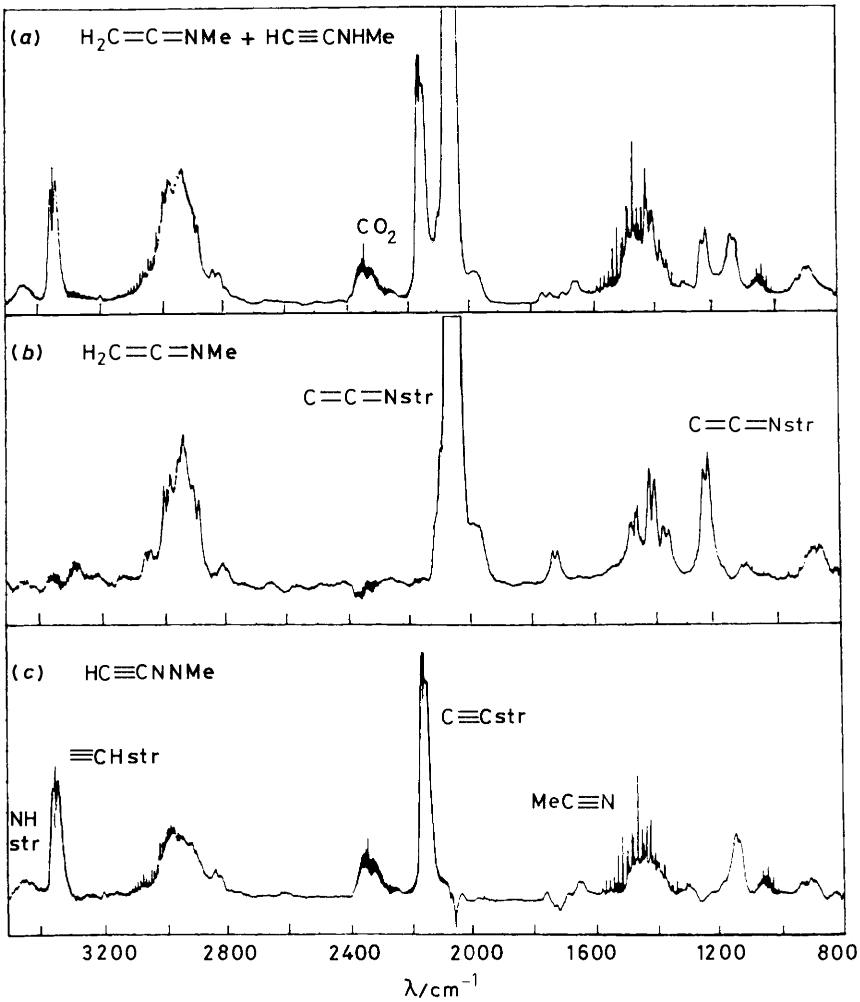

Figure 2. (*a*) The i.r. spectrum in the range 800–3 500 cm^{-1} for the products of pyrolysis of the isoxazolone (**1**; Re = Me) under moderately fast flow conditions [as in Figure 1(*b*)]. (*b*) The i.r. spectrum of $CH_2=C=NMe$ revaporized at −95 °C from the trapped products of Figure 2(*a*) at −196 °C. (*c*) The difference spectrum obtained by scaled subtraction of 2(*b*) from 2(*a*). The main features belong to HC≡CNMe. Minor contaminants are MeCN and CO_2.

cm^{-1} and all appear to be associated with $CH_2=C=NMe$. The pattern bears a remarkably similarity to the same region in $CH_2=C=S$[12] (which has two PR contour bands at 1 421 and 1 331 cm^{-1}) with the addition of an extra middle band, which almost certainly belongs to a CH_3 deformation. This similarity has led us to suggest an alternative assignment to that of Amatatsu *et al.*,[5] namely that the 1 366 cm^{-1} band belongs to the CH_2 deformation which in $CH_2=C=NH$ lies at 1 355 cm^{-1} and in $CH_2=C=S$ at 1 331 cm^{-1}. The 'extra' middle band (not observed in the thioketene spectrum) lies at 1 409 cm^{-1} and is assigned to a CH_3 deformation. The third band at 1 421 cm^{-1} is assigned to two quanta of the CH_2 wagging vibration on the basis of the near identical pattern and frequency (1 421 cm^{-1}) of that observed in thioketene $CH_2=C=S$.[12] In thioketene the observation of the second harmonic appears to be due to Fermi resonance. The weak band at 1 113 cm^{-1} in Figure 2(*b*) has not been assigned. It appears very weakly in the spectrum of Amatasu *et al.*[5] who also observe a very broad feature at *ca.* 950 cm^{-1} which is not evident in our sample and thus must be an impurity. The last distinct feature is weak and broad and centred at *ca.* 876 cm^{-1}. It may have an A/B hybrid-type contour and is likely to belong to the C–N stretching mode, though CH_2 rocking is also possible. In CH_2CS and CH_2CO the rocking frequencies are 922 and 977 cm^{-1} respectively.[12,9] Amatatsu *et al.*[5] have assigned this frequency to the C–N stretch.

Discussion

Using fast-flow thermolysis techniques together with f.t.i.r. detection it has proved possible to study the production of unstable *N*-substituted ketenimines and ynamines in the gas phase from appropriately substituted isoxazolones. Unfortunately, attempts to observe $HC≡CNH_2$ and $CH_2=C=NH$ by this route were unsuccessful. Only under the fastest flow rates can the ynamine HC≡CNHMe be detected, indicating significant instability. Methyl substitution stabilizes the ketenimines and in fact $CH_2=C=NMe$ was successfully revaporized from a trap. The experiments show that substituted ynamines and ketenimines are quite efficiently produced by this method, and this could be a useful synthetic route. The study has also enabled reliable vibrational assignments to be made. Further i.r. and photoelectron work on these systems is in progress; in particular the spectra (including high resolution i.r.) of the simplest ketenimine, $CH_2=C=NH$,[7,13] are the subject of further study.

Table. I.r. frequencies (cm^{-1}) and assignments.

HC≡CNHMe	CH_2=C=NMe	Other	Intensity	Contour	Assignment
3 442			w	br	NH str
3 345			s	PQR	H–C≡ str
		3 310	vw		HCN
	3 046		vw	PQR	CH str
	2 995		m	sharp	CH str
	2 974		m	sharp	CH str
	2 931		m	sharp	CH str
	2 898		m	sharp	CH str
	2 881		m	sharp	CH str
		2 822	w	PR	—
	2 797		w	PR	—
		2 336	w	PR	CO_2
		2 266	vw	PQR	$CH_3C≡N$
2 152			s	PQR	C≡C str
	2 094		w		sh
	2 060		vvs	PQR	C=C=N str
	1 978		w	br	sh
1 755			w		—
		1 730	w		—
	(1 724)		w	PR	(–)
		1 690	w		—
1 647			w	PR	—
		1 580–1 330	m	Q	$CH_3C≡N$
	1 468		w	PR	2 × CH_2 wag
	1 409		m	PR	CH_3 def
	1 366		w	PR	CH_2 def
	1 234		m	PR	C=C=N str
1 136			w	PR	CNH bend
		1 040	w	Q	$CH_3C≡N$
		920	w		$CH_3C≡N$
	896		w		—
	876		w		CN str?

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