Imidoylketene dimerization and rearrangement†

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FVT of pyrroleidine 10 affords the NH-imidoylketene 11, which is characterized by its matrix isolation IR spectrum (2117 cm$^{-1}$). On warming above 170 K, 11 dimerizes to the oxazinone 13, the X-ray crystal structure of which is reported. Imidoylketene 11 also undergoes a (reversible) 1,3-phenyl shift to afford the detectable α-oxoketenimine 16 (2062 cm$^{-1}$) which at FVT temperatures above 400 °C, isomerizes to 2-cyano-2-phenylacetophenone 18 (optimally at 700 °C). Moreover, imidoylketene 11 can cyclize to azetinone 19, detectable at FVT temperatures up to 570 °C, which undergoes cycloreversion to diphenylacetylene 20 and isocyanic acid (HNCO) 21. Energy profiles calculated at the B3LYP/6-31G** level for the unsubstituted imidoylketene, the diphenylimidoylketene 11 and the N-tert-butylimidoylketene are also reported.

Introduction

Ketenes are highly useful synthetic intermediates. Few ketenes are stable at room temperature, and in the absence of another reaction partner, they will dimerize. The dimers can be useful synthetic intermediates too, sometimes as reservoirs for the ketenes themselves via thermal dedimerization reactions. α-Oxoketenes 1 usually dimerize to form pyrones 2, formally in a [2+4] cycloaddition reaction involving a ketene C=O bond as dienophile. Computational studies by Birney et al. have established the pseudopericyclic nature of related [2+4] cycloaddition reactions of ketenes. A second mode of dimerization of α-oxoketenes involves the ketene C=O bond as dienophile and appears to be favoured under conditions of steric hindrance of the C=O function. Thus, dipivaloylketene 1a dimerizes at room temperature to the 1,3-dioxinone 3a. Depending on reaction conditions, another mode of dimerization of 1a, involving a straightforward addition of one molecule of the oxoketene to a pivaloyl C=O group in the other, is also possible. Both dimers de-dimerize on flash vacuum thermolysis (FVT) and thus can serve as reservoirs for ketene 1. Methoxy carbonyl(pivaloyl)ketene 1b undergoes analogous dimerization across the ketene C=O group to afford 3b (Scheme 1).

Considerably less is known about the chemistry of imidoylketenes, largely because of the occurrence of facile isomerizations. Alkylimidoylketenes 4 carrying an α-hydrogen atom undergo a 1,5-H shift to afford iminoacroleins 5, which may isomerise further. Imidoylketenes may also undergo 1,3-shifts of the α-substituents X to generate α-oxoketenimines, as discussed below (eqn. (1)). Moreover, N-arylimidoylketenes 4 undergo a facile and preparatively useful cyclization to afford quinolones 6, often in high yields.

However, Chuche and coworkers achieved the isolation of the imidoylketene dimer 8a from 7a. This corresponds to the normal behaviour of the ketene C=O bond acting as the dienophile. Very recently, Zhou and Birney have shown that the N-propyl analogue 7b undergoes C=O addition to give 3b in ca. 15% yield, whereas the N-unsubstituted imidoylketene 7e affords the ketene C=O adduct 9 in ca. 7% yield. Smalley and coworkers similarly reported the formation of 3-(2-aminophenyl)benz[d][1,3]oxazin-1-one from the putative imidoylketene by ring opening of benzazetinone. Detailed calculations of the transition structures for the two types of dimerization, involving addition to C=H and C=O bonds, respectively, demonstrated that both followed the minimum energy paths, and both were rationalized as pseudopericyclic reactions with planar transition states.

Here we report the first direct observation of an NH-imidoylketene (11), its dimerization involving the ketene C=O bond as dienophile, its isomerization to the oxoketenimine, 16 and its cyclization to azetinone and cleavage of the latter.

Results and discussion

Observation and dimerization of the imidoylketene

FVT of the pyrrole-2,3-dione 10 at temperatures above 325 °C resulted in the loss of CO (absorbing at 2138 and 2149 cm$^{-1}$) and formation of the imidoylketene 11, characterized by an intense absorption at 2117 cm$^{-1}$ in the IR spectrum of the matrix, 10 K, Fig. 1) or at 2112 cm$^{-1}$ as a neat solid at 77 K. This absorption is...
in good agreement with that computed at the B3LYP/6-31G** level, where the ketene stretch is the only calculated strong band (2119 cm\(^{-1}\), 904 km mol\(^{-1}\)). It is noteworthy that the calculated intensity of the NH band is very small (3330 cm\(^{-1}\), 1 km mol\(^{-1}\)), indeed this band is barely visible in the experimental spectrum. For further details of the calculated spectrum, see the electronic supplementary information.† Doubling of several bands in the experimental IR spectrum is probably due to the presence of more than one conformer of 11 in the matrix (see the calculated energy profile in Fig. 4 below).

The disappearance of the starting material 10 was complete at an FVT temperature of ca. 570 °C. The ketene remained observable in the IR spectrum of the neat solid on warm-up till above 190 K, but its intensity decreased rapidly above 170 K due to dimerization. The dimer was isolated as lemon-yellow rhombohedral crystals in a preparative FVT experiment under the same conditions. The IR spectrum of the matrix-isolated dimer confirmed that this compound was formed on dimerization of the ketene above 170 K. The 13C NMR spectrum of the dimer indicated C1 symmetry. The elemental analysis and strong carbonyl absorption at 1700 cm\(^{-1}\) are consistent with a 1,3-oxazine structure 13 (Scheme 2). Notably, the two NH protons appear at widely different chemical shifts, 5.3 and 10.4 ppm (both broad), which can be ascribed to one of them being engaged in a strong hydrogen bond to the oxazine nitrogen N3 in 13. This structure was confirmed by an X-ray crystal analysis (Fig. 2). The molecular backbone is virtually planar, and the length of the intramolecular hydrogen bond is 1.99 Å. The other hydrogen atom of the amino group is involved in intermolecular H-bonding with the C=O group (O6) in a neighbouring molecule (see the ESI document). The formation of 13 is depicted in Scheme 2 as occurring via a [2+4] cycloaddition of one ketene molecule to the ketene C=O group of another via the transition state 12TS. The calculations by Zhou and Birney demonstrate that this mode of dimerization is favoured in NH-imidoylketenotes due to a stabilization of the transition state by hydrogen bonding.\(^{11}\)

FVT of the dimer 13 at 710 °C generated a small amount of a ketene absorbing at 2117 and 1659 cm\(^{-1}\). This is probably not ketene 11, but a new ketene formed by electrocyclic opening of the oxazine ring in 13. We have investigated similar ring opening reactions of oxazines\(^{12}\) and will publish them in a separate paper.

### Rearrangement

It is known that \(\alpha\)-imidoylketenotes 14 and \(\alpha\)-oxoketenimines 15 can interconvert by a 1,3-shift of the \(\alpha\)-substituent, X (eqn. (1)).\(^{7}\)

\[
R\begin{array}{c}
\text{N} \\
\text{C}=\text{O}
\end{array} \rightleftharpoons R\begin{array}{c}
\text{N} \quad \text{O} \\
\text{C}=\text{N}
\end{array}
\]


This reaction, analogous to the \(\alpha\)-oxoketenamine\(-\alpha\)-oxoketene interconversion,\(^{13}\) is particularly facile when X is an electron donating group which can interact favourably with the low-lying ketene LUMO (NR\(_2\), OR, SR, and halogens).\(^{7,13,14}\) The dimethylamino group has the highest migratory aptitude, and the calculated activation barrier for 14 \(\rightarrow\) 15 (X = NMe\(_2\), R = R\(_1\) = H) is 62 kJ mol\(^{-1}\).\(^{7}\) Thus, this reaction will take place below room temperature.\(^{8}\) However, phenyl groups also undergo the 1,3-shift, typically under FVT conditions at temperatures around 970–1020 K in our apparatus.\(^{14}\) Further computational studies of the activation barriers for 1,3-shifts of a wide range of \(\alpha\)-substituents in \(\alpha\)-oxoketenenes, \(\alpha\)-imidoylketenones and \(\alpha\)-oxoketenimines will be published.\(^{15}\)

Further FVT experiments with matrix isolation, as well as GC-MS of the products, revealed that the intensity of the imidoylketene 11 diminished above 600 °C, although it was still easily detectable at 850 °C. The isomeric nitrile 18 was formed in its place. GC-MS analysis established the optimal temperature for formation of 18 as 700 °C. Compound 18 was also identified by direct comparison of IR and NMR spectra with authentic material.\(^{16}\) A 1,5-hydrogen shift in ketenimine 16 generates hydroxynitrile 17, which is a tautomer of 18. The

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**Fig. 1** FTIR spectrum of imidoylketene 11 (Ar matrix, 10 K). The strongest absorption of 11 is at 2117 cm\(^{-1}\). Weaker bands at 2139 and 2149 cm\(^{-1}\) are due to CO. When 11 is isolated without Ar at 70 K, its main absorption is at 2112 cm\(^{-1}\), and the CO bands are missing. The band at 2340–2345 cm\(^{-1}\) is due to a minor amount of CO\(_2\). Absorbance (A) in arbitrary units.

**Fig. 2** ORTEP drawing of the crystal structure of 13.
existence of a solvent dependent mixture of two Z/E isomers of enol 17 (17a and 17b) and ketone 18 has been reported, and our own NMR measurements support a ratio of 80 : 8 : 12 of the two isomers of enol 17 and ketone 18 (DMSO-d<sub>6</sub> solution).

The ketenimine 16 was itself observable as a weak peak at 2062 cm<sup>-1</sup> in the matrix IR spectra at very mild FVT temperatures, 350–500 °C; the imidoylketene peak at 2117 cm<sup>-1</sup> always remained the strongest peak. The reason for this is easily understood: although more ketenimine 16 should be formed in equilibrium with ketene 11 at higher temperatures, 16 is removed by isomerization to the nitrile 18. N-Unsubstituted ketenimines always tautomerize very easily to nitriles under FVT conditions, probably due to wall-catalyzed reactions. An analogous reaction is known: generation of the ketenimine 7a above 700 °C results in elimination of isobutene and rearrangement to the corresponding ketenimine, which isomerizes to the tautomeric mixture of 3-oxopropionitrile and 3-hydroxyacrylonitrile.

Furthermore, a second isomerization pathway with a lower activation energy also removes imidoylketene 11 and therefore also hinders any build-up of ketenimine 16: the cyclization of 11 to azetinone 19. The latter compound is observable by means of a weak peak at 1814 cm<sup>-1</sup> in the matrix IR spectra only at the mildest FVT temperatures, 325–400 °C. The weakness of this peak can be ascribed to a fragmentation to diphenylacetylene 20 and HNCO 21 (Scheme 3 and Fig. 4). Diphenylacetylene 20 was identified by GC-MS comparison with authentic material, its yield increasing with the temperature, and HNCO was identified by its characteristic matrix IR spectrum (2259 cm<sup>-1</sup>). The rearrangement and fragmentation modes leading to 18 and 20 became major reactions above 700 °C. In addition, benzonitrile was always formed as a by-product in the high temperature range. The mechanism of formation of benzonitrile is not known.

We have calculated the energy profiles for the relevant rearrangements of the unsubstituted imidoylketene 11a (Fig. 3), the diphenylimidoylketene 11 (Fig. 4), and the N-tert-butylphenylmethylimidoylketene 11b (Fig. 5) at the B3LYP/6-31G** level of theory. The energies of some of the species and transition states (TS2) were also computed at the 6-311+G(3df,2p)//B3LYP/6-31G* level. Transition states were verified by intrinsic reaction coordinate calculations and imaginary vibrational frequencies (listed in the electronic supplementary information).† Part of the energy profile of the unsubstituted compounds, including ketene 11a, ketenimine 16a and azetinone 19a has been calculated previously at the MP4(SDQ)/6-31G**//MP2/6-31G** level. Our results (Fig. 3) are in good accord. The N-tert-butyl derivative in Fig. 5 is a model for the corresponding N-adamantyl-phenylmethyl derivative, which has been the subject of a previous investigation, where the thermal conversion of the N-adamantylimidoylketene to the N-adamantyloxoketenimine, the cyclization of N-adamantylimidoylketene to the N-adamantylazetinone (observed at 1814 and 1819 cm<sup>-1</sup> in the Ar matrix IR spectrum), and the fragmentation of the latter to 1-phenyl-1-propyne and adamantyl isocyanate on FVT above 450 °C were observed. The energy profiles in Figs. 4 and 5 reveal that the activation barrier for the 1,3-phenyl shift interconverting imidoylketenes and oxoketenimines, ca. 150 kJ mol<sup>−1</sup>, is well within the expectations for FVT reactions. The calculated 1,3-shift barrier for a phenyl group in the otherwise unsubstituted imidoylketene is 186 kJ mol<sup>−1</sup>. Thus, the two phenyl groups in 11 have a significant stabilizing effect on TS2 (Fig. 4). We have found that electron donating substituents (D) in the migrating phenyl group, and electron-withdrawing ones (W) in the other can lower this 1,3-phenyl migration barrier (TS2) in α-oxoketenones (Z = O).

![Scheme 3](image-url)

**Fig. 3** Calculated energy profile for the rearrangements of the unsubstituted imidoylketene 11a at the B3LYP/6-31G** level of theory, corrected for zero-point vibrational energies (ZPVE).
and imidoylketenes \((Z = NR)\) further still.

![Diagram](image)

Comparison of the three energy profiles also reveals that an \(N\text{-}tert\)-butyl group significantly destabilizes the ketene 11, probably due to steric strain, and conversely stabilizes the ketenimine isomer 16a, in agreement with the observation that the analogous \(N\text{-}adamantyl\) imidoylketene underwent isomerization to the isolable \(N\text{-}adamantyloxoketenimine\) on FVT above 600 °C.\(^{14}\)

The phenyl substitution lowers the energy of the azetinone 19 (Fig. 4) very significantly, compared with the unsubstituted case (Fig. 3), and the \(N\text{-}tert\)-butyl group lowers this energy even further (Fig. 5) relative to the ketene 11. This is in accord with the finding that the \(N\text{-}adamantyl\) case was the only one where significant amounts of the azetinone could be matrix isolated.\(^{14}\)

In the case of the diphenyl derivative, Fig. 4, 19, 11 and 16 all have very similar calculated energies, and only a trace of the azetinone 19 is observable under FVT conditions. As mentioned above, this can be ascribed to the cleavage to diphenylacetylene 20 and HNCO 21 as well as the isomerization of the easily formed ketenimine 16 to nitrile 18.

### Conclusion

The \(NH\)-imidoylketene 11 is stable in the gas phase under conditions of FVT at moderate temperatures. It is also stable...
in the solid phase till ca. −100 °C, when it dimerizes to the 1,3-oxazinone 13. At FVT temperatures above 700 °C, 11 undergoes a 1,3-phenyl shift to afford the NH-ketenimine 16, which tautomerizes to nitrile 18. Imidoylketene 11 also cyclizes to azetinone 19, which fragments to diphenylacetylene and HNCO. All the processes are summarized in Scheme 4.

**Experimental**

The apparatus for FVT and matrix isolation was as previously reported. For GC-MS conditions see ref. 20. The pyroreldione 10 was prepared according to the literature, mp 189–191 °C; IR (KBr) 3270 m, 1735 vs, 1700 vs, 1615 m cm⁻¹; ¹³C NMR (DMSO-d₆) δ 159.9 (C2), 183.3 (C3), 110.4 (C4), 163.6 (C5), 127.1, 128.3, 128.5, 128.6, 128.7, 129.1, 130.0, 132.3. 2-Cyano-2-phenylacetophenone 18 was prepared according to the literature. ¹H NMR (DMSO-d₆) the spectrum scanned till 15 ppm showed peaks at δ 12.0 (OH), 11.6 (OH) and 6.6 (CH) in the integrated ratio 80 : 8 : 12 corresponding to enol 17a : enol 17b : ketone 18, together with phenyl signals at δ 8.0 to 7.0; ¹³C NMR (DMSO-d₆) δ 167.9 (CO of main enol 17), 120.0 (CN of main enol 17a), 88.0 (CH of main enol 17a), 87.8 (CH of isomeric enol 17b), 45.9 (CH of ketone 18). The eight phenyl group signals of the major tautomer 17a are at 135.9, 132.9, 130.4, 128.4, 128.3 (two signals), 127.3, and 126.7 (cf. ref. 16c). The assignment of the ¹³C NMR data was supported by a DEPT spectrum.

**Crystallography**

Cell constants were determined by least-squares fits to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo Kα radiation (0.71073 Å) and operating in the o-2θ scan mode. Data reduction was performed with the WinGX package. The structure of compound 13 was solved by direct methods with SHELXS and refined by full-matrix least-squares analysis with SHELXL-97. All non-H atoms were refined with anisotropic thermal parameters. H-atoms attached to carbon were included in estimated positions using a riding model whereas those attached to nitrogen were located from difference maps in the first instance then restrained also using a riding model. The drawing of the molecule (Fig. 2) was produced with ORTEP.

**FVT and matrix isolation**

Pyroreldione 10 was sublimed into the FVT tube in a stream of Ar at 100 °C and thermolysed at temperatures ranging from 300–800 °C. No reaction took place at 250 °C. The products were isolated in an Ar matrix at 20 K, and FTIR spectra were recorded at ca. 10 K. A typical IR spectrum is shown in Fig. 2. Bands due to imidoylketene 11 are at 3456 wv, 3071 wv, 2117 vs, 1595 m, 1575 m, 1498 m, 1361 m, 1351 m, 1180 w, 1046 84 w, 862 w, 775 w, 756 m, 699 m, 655 w cm⁻¹. Bands at 2138 and 2149 cm⁻¹ are due to CO. The band at 2340–2345 cm⁻¹ is due to a minor amount of CO₂. Similar FVT of 10 using Ar as a carrier gas but with isolation at 70 K (i.e. without Ar and CO condensing), afforded 11 with its main absorption at 2112 cm⁻¹, and the CO bands were missing under these conditions.

FVT temperatures above 700 °C caused formation of nitrile 18 in amounts increasing with the temperature and identified by GC-MS, IR and NMR comparison of the isolated product with the spectra of authentic material. Benzonitrile (identified by GC-MS and IR comparison with authentic material), diphenylacetylene (identified by GC-MS comparison with authentic material), and isocyanic acid HNCO (identified by its Ar matrix IR absorption at 2259 cm⁻¹) were formed at the same time. GC retention times in min (relative peak abundance in %) for the products formed at 700 °C; benzonitrile 2.95 (100), diphenylacetylene 9.4 (60), 2-cyano-2-phenylacetophenone 18 11.6 (75).

**4,5-Diphenyl-2-(1,2-diphenyl-2-aminoethyl)-1,3-oxazinone-6-one 13**

Pyroreldione 10 (300 mg; 1.20 mmol) was sublimed into the FVT apparatus at 110 °C and thermolysed at 570 °C in the course of 2.5 h. The product was collected in a liquid nitrogen-cooled U-tube and after the end of the experiment dissolved in acetonitrile-methanol. Preparative thin layer chromatography on SiO₂, eluting with methylene chloride, afforded a yellow solid (80 mg; 30%), which crystallized as lemon-yellow rhombohedra of C₃₀H₂₂N₂O₂, m/z 442.1688. Bands due to imidoylketene 11 are at 3456 vw, 3071 vw, 2117 vs, 1595 m, 1575 m, 1498 m, 1361 m, 1351 m, 1180 w, 1046 84 w, 862 w, 775 w, 756 m, 699 m, 655 w cm⁻¹. At FVT temperatures above 700 °C, nitrile 18 was sublimed into the FVT tube in a stream of Ar at 100 °C and thermolysed at temperatures ranging from 300–800 °C. No reaction took place at 250 °C. The products were isolated in an Ar matrix at 20 K, and FTIR spectra were recorded at ca. 10 K. A typical IR spectrum is shown in Fig. 2. Bands due to imidoylketene 11 are at 3456 wv, 3071 wv, 2117 vs, 1595 m, 1575 m, 1498 m, 1361 m, 1351 m, 1180 w, 1046 84 w, 862 w, 775 w, 756 m, 699 m, 655 w cm⁻¹. Bands at 2138 and 2149 cm⁻¹ are due to CO. The band at 2340–2345 cm⁻¹ is due to a minor amount of CO₂. Similar FVT of 10 using Ar as a carrier gas but with isolation at 70 K (i.e. without Ar and CO condensing), afforded 11 with its main absorption at 2112 cm⁻¹, and the CO bands were missing under these conditions.

**Crystal data**

C₃₀H₂₂N₂O₂, M = 442.50, monoclinic, space group P2ₐ, a = 11.209(3), b = 6.6731(8), c = 16.500(4) Å, α = 90°, β = 108.47(2)°, V = 1170.64(4) Å³, Z = 2, D = 1.255 g cm⁻³, μ = 0.79 cm⁻¹. 2165 unique reflections (R₁ = 0.000), R₁ = 0.0409 (for 927 observed data, I > 2σ(I)), wR₂ = 0.1210 (all data).

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**References**


‡ CCDC reference number 233531. See http://www.rsc.org/suppdata/ob/bt/b4i2530d/ for crystallographic data in .cif format.