Supporting Information: Vibrational Excitation of Both Products of the Reaction of CN Radicals with Acetone in Solution

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I. TIME RESOLVED ELECTRONIC ABSORPTION SPECTROSCOPY OF ICN / CDCl$_3$ AND ACETONE / CDCl$_3$ SOLUTIONS

This section shows and explains the time resolved electronic absorption spectra (TEAS) of two binary mixtures, whose analysis helps to explain the spectra of the ternary mixtures reported in the main document. The TEAS of a 0.36 M ICN solution in CDCl$_3$ generated the spectra shown in panel (a) of **Figure S1**. Previous analysis,[1-2] and recent work by our group provide a satisfactory interpretation of these TEAS spectra. The transient features are a result of the CN B$^2\Sigma^+\leftarrow$X$^2\Sigma^+$ absorption and an I*(^{2}P$_{1/2}$)-CDCl$_3$ charge transfer band. The corresponding I(^{2}P$_{3/2}$)-CDCl$_3$ charge transfer band will underlie the strong features on the short wavelength side of the spectra. The CN absorption band has contributions from radicals in two distinct environments. Uncomplexed ("free") CN produces a sharp absorption band centred at 389 nm that is similar to the gas-phase spectrum. A broad feature at wavelengths < 550 nm is assigned to CDCl$_3$-CN complexes

("solvated CN"), which have a stabilisation energy estimated to be ~1800 cm^{-1}.[3] The decomposition of one of the TEAS spectra into these features is shown in panel (b) of **Figure S1**.
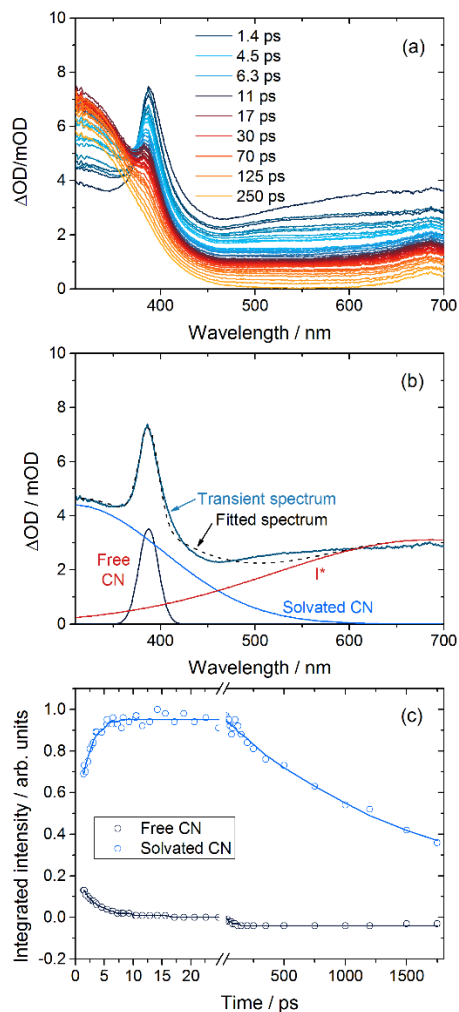

Figure S1: Transient electronic absorption spectroscopy of ICN dissolved in CHCl$_3$. (a) Time resolved electronic absorption spectra following 267 nm photolysis of the ICN; representative time delays are identified in the inset key. (b) Decomposition of one transient absorption spectrum (at a time delay of 1.5 ps) into electronic absorption bands of free and solvated CN, with a longer-wavelength contribution attributed to I*(^{2}P$_{1/2}$) atoms. (c) Time dependence of the band intensities for the free and solvated CN, and fits to double exponential functions.

The photolysis of ICN produces CN radicals in both the complexed and uncomplexed states. In CDCl$_3$ solutions containing ICN, the decay of uncomplexed, possibly rotationally hot[2, 4] CN has a time constant of 2.7 ± 0.8 ps (2 SD uncertainties) which, within the experimental uncertainty, matches the 3.1 ± 1.0 ps initial rise in the complexed CN band. The results from Moskun and Bradforth,[2] which had a higher time resolution than the current work, displayed rapid in-cage recombination to ICN/INC in the first 500 fs. The solvated CN band decays with a time constant of 1200 ± 400 ps, which has previously been attributed to reaction with CDCl$_3$.[5]

TEAS spectra were also obtained for 1 M acetone solutions in CDCl$_3$ to observe time dependent absorptions following the 266 nm photoexcitation of acetone. Example spectra are presented in **Figure S2**. An ultraviolet band was observed with a lifetime greater than the timescale of the experiment (2 ns). The feature was attributed to acetone absorption from the T$_1$ or S$_1$ states, which both have nanosecond lifetimes.[6] Calculations for acetone (T$_1$) in CHCl$_3$ (using a polarizable continuum solvent model as explained in the main document) predicted an absorption feature at 295 nm which corresponds to the T$_2$←T$_1$ transition, a reasonable assignment for the feature we see whose maximum is outside our probing window.

The absorption band observed for the 1 M acetone solution has an intensity approximately 20 % that of the solvated CN feature evident in **Figure S1 (a)**, and the two bands significantly overlap. An attempt to decompose the TEAS spectra of solutions containing ICN, acetone and CDCl$_3$ with separate functions describing the acetone and CN bands was unsuccessful because of the similarity of spectral features. The chlorinated solvents are known to undergo two-photon induced photochemistry at 267 nm,[7] but the time resolved signals obtained from CDCl$_3$ were at least a factor of 20 smaller than the features observed from the photolysis of ICN and acetone.
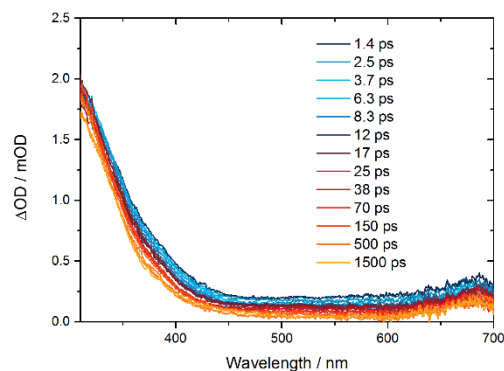
Figure S2: Time dependent electronic absorption spectra obtained following 267 nm excitation of a 1.0 M solution of acetone in CHCl₃. The inset key identifies spectra obtained at selected time delays.

Figure S3 shows TEAS data for a solution of ICN in acetone. The band centered near 400 nm resembles that seen at long times in spectra obtained with both ICN and acetone in CDCl₃ (**Figure 2** of the main text), and tentatively assigned to CN-acetone complexes.
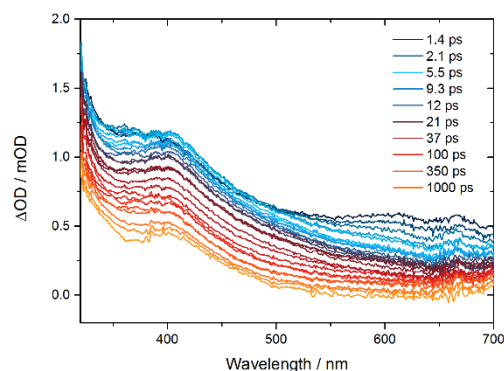

Figure S3: Time-resolved electronic absorption spectra obtained following 267-nm excitation of a solution of ICN in acetone. The inset key identifies time delays associated with selected spectra.

The band centered near 400 nm has a rise time constant of 0.5 ps and decays with biexponenital time constants of 36 and 1400 ps. The fast rise may be a consequence of overlap of free CN and

CN-acetone complex bands. The slow decay is consistent with observation of this band at long times in experiments performed on ICN and acetone in chloroform solution.

II. TIME RESOLVED VIBRATIONAL SPECTRA OF ICN AND ACETONE SOLUTIONS IN CDCl$_3$

TVAS measurements of solutions of ICN and acetone in CDCl$_3$ following 267-nm excitation were made in both the C=N and C=O stretching regions. The assignments of bands in the latter region are discussed in the main text. The C=N stretching region is congested, with several neighbouring and overlapping bands. **Figure S4** illustrates the decomposition of the features in this spectral region into bands assigned to ICN, INC, HCN and CN-radical complexes.
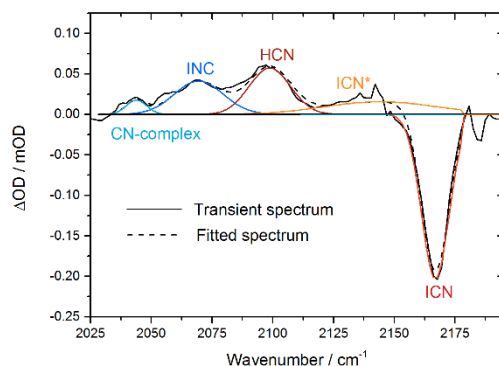

Figure S4: Decompostion of a single TVAS spectrum following 267-nm excitation of a solution of ICN and 0.5 M acetone in CDCl$_3$. The spectral features are modelled using 5 Gaussian functions, with the assignments indicated in the figure.

III. ELECTRONIC STRUCTURE CALCULATIONS OF REACTION ENERGIES

Reaction exothermicities were calculated by optimization of reactants and products in the Gaussian 09 program,[8] and the results are listed in **Table S1**. The CBS-QB3 method, which was explicitly designed for efficient computation of accurate molecular energies,[9-10] is deemed to give reliable results for gas-phase molecules. Previous calculations of exothermicities of other hydrogen abstraction reactions by CN gave values around -100 kJmol^{-1}; the greater energy release for the acetone reaction is likely to be a consequence of the resonance stabilization of $CH_3C(O)CH_2$.

Table S1: Computed Enthalpy Changes at 0 K for the CN + $CH_3C(O)CH_3 \rightarrow$ HCN + $CH_3C(O)CH_2$ Reaction.[a]

Computational Method	$\Delta_r H_{0K}$ / kJ mol^{-1}
B3LYP 6-31G	-142.3
B3LYP 6-31++G(*d,p*)	-140.4
B3LYP 6-31++G(*d,p*) with solvent	-153.5 [b]
M06-2X/aug-cc-pVDZ	-134.3
MPW1K/6-31G(d,p)	-121.8
MPW1K/aug-cc-pVDZ	-95.0
BB1K/6-31+G(*d,p*)	-115.4
CBS-QB3	-125.0
CBS-QB3 with solvent	-134.7 [b]

[a] Values are reported for calculations at a range of theoretical levels. [b] A chloroform solvent was incorporated in the B3LYP 6-31++G(*d,p*) and CBS-QB3 calculations as explained in the text.

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