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Direct Observation of Acyl Azide Excited States and Their Decay Processes by Ultrafast Time Resolved Infrared Spectroscopy

Jacek Kubicki,[†] Yunlong Zhang,[‡] Jin Wang,[‡] Hoi Ling Luk,[‡] Huo-Lei Peng,[‡] Shubham Vyas,[‡] and Matthew S. Platz*,[‡]

Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland, and Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio, 43210

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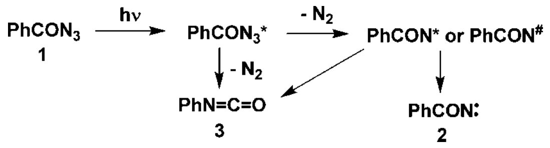
The thermochemistry and photochemistry of acyl azides have fascinated chemists for decades.[1,2] The light induced fragmentation of benzoyl azide **1** produces carbonyl nitrene **2** and isocyanate **3** (Scheme 1). Chemical analysis of the products of photolysis of **1** and other acyl azides[3,4] demonstrates that the isocyanate products arise either from electronically excited states of the acyl azides or via electronically or vibrationally excited carbonyl nitrenes[5] (including dynamical effects) rather than from the relaxed ground states of carbonyl nitrenes.[6]

Scheme 1. Photochemical Reactions of Benzoyl Azide



The photochemical Curtius Rearrangement is analogous to the Wolf Rearrangement, a reaction which was recently studied by femtosecond time-resolved infrared (fs TRIR) spectroscopy. Those experiments confirmed the long suspected ultrafast formation of a ketene from a diazo excited state[7] and have motivated the present study. We examined the photochemistry of benzoyl azide (PhCON$_3$), 2-naphthoyl azide (2-NpCON$_3$), and pivaloyl azide (*t*-BuCON$_3$) in chloroform solution at ambient temperature by fs TRIR spectroscopy. Typical TRIR data obtained following 270 nm excitation of 2-NpCON$_3$ and PhCON$_3$ are shown in Figure 1 and in Figure S1. Three broad positive bands are observed within the 300 fs excitation. Two of these bands narrow and shift to the blue over 100 ps, then stabilize at 2265 and 1760 cm^{-1} (for PhCON$_3$) or at 1740 cm^{-1} (for 2-NpCON$_3$), and do not decay over 3 ns (Figure S2). The 2265 cm^{-1} band does grow in intensity after the laser pulse. The blue shift and band narrowing of the positive bands are characteristic of vibrational cooling (VC) of intermediates born with excess vibrational energy.[14] The 2265 and 1740 cm^{-1} (1760 cm^{-1}) bands can be readily assigned to the appropriate isocyanates and ground-state singlet aroyl nitrenes, respectively, on the basis of prior ns TRIR and UV−vis spectroscopy, matrix spectroscopy, chemical analysis studies, and quantum chemical calculations[8−13] and, in the case of the isocyanates, steady state IR absorption spectra (Figure S3). Calculations predict that **2** has a structure intermediate between the nitrene and oxazirine.[10] Benzoyl nitrene is not stable in solution, but its lifetime in dichloromethane, cyclohexane, and deuterated acetonitrile is on the order of microseconds[8] which is consistent with the absence of nitrene signal decay in chloroform over 3 ns.

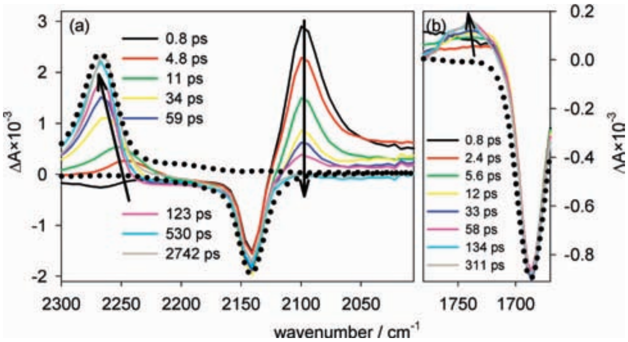


Figure 1. Transient IR spectra produced upon photolysis of 2-NpCON$_3$ (λ_{ex} = 270 nm) in chloroform. The spectra of isocyanate (2265 cm^{-1}) and the N$_3$ stretch of the excited azide (2100 cm^{-1}) and the carbonyl stretch of the nitrene (1740 cm^{-1}) are given at selected time delays. The normalized steady state IR absorption spectra of 2-NpCON$_3$ and 2-NpNCO are shown as dotted lines.

The third positive band (2100 cm^{-1}) was not previously observed by ns TRIR spectroscopy. This band is formed within the 300 fs excitation pulse, and for PhCON$_3$ its decay can be fit to a biexponential function ($\tau_1 = 1.6 \pm 0.4$ ps, $\tau_2 = 15 \pm 4$ ps). The carrier of this transient absorption is assigned to the N$_3$ stretch of the first singlet excited azide S$_1$, as it is located close to the N$_3$ stretch of the ground state of benzoyl azide and its lifetime of several picoseconds is too long to be consistent with its assignment to an upper excited-state S$_n$. The lifetime is too short to be associated with the triplet state of 2-NpCON$_3$ which is known to be much longer.[9] We have not detected the transient IR spectrum of the triplet state of 2-NpCON$_3$ either because of overlapping absorption with the ground state (DFT calculations (Table S1) predict only a 14 cm^{-1} difference) or low signal intensity.

The fast decay lifetime of the S$_1$ state can be attributed to a mixture of IVR and VC[15,16] and Curtius Rearrangement of hot S$_1$, and the longer decay lifetime is associated with the decay of the thermally relaxed S$_1$ state of benzoyl azide. The 2100 cm^{-1} band is not assigned to the hot electronic ground state of the azide, as the relaxed S$_1$ band does not undergo a characteristic blue shift and narrowing as it decays and the ground-state vibration does not recover as this band decays.

The integrated intensities of the growth of the phenyl isocyanate band and the decay of the N$_3$ stretch of the excited state of benzoyl azide are shown in Figure S4. As the positive band at 2100 cm^{-1} decays, the isocyanate band at 2265 cm^{-1} becomes more intense. A global fit of the data demonstrates that both changes can be simultaneously described by a two-exponential function (Table S2). The fast decay component is assigned again to the hot S$_1$ state, and the slower component, to the relaxed S$_1$ state of the acyl azide.

[†] Adam Mickiewicz University.
[‡] The Ohio State University.

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About twice as much phenyl isocyanate is formed in the fast process relative to the slower process.

Analogous experiments were performed with 2-NpCON$_3$, and similar results were obtained. The integrated intensity of the 2100 cm^{-1} band decays biexponentially (6.8 ± 1.3 and 120 ± 30 ps, Figure 2, Table S3).

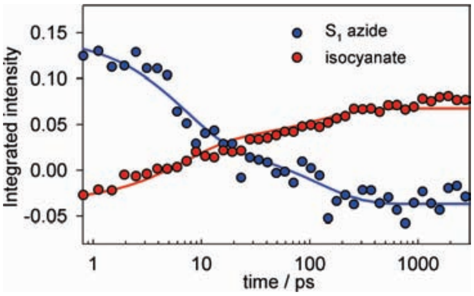


Figure 2. Integrated intensities of isocyanate (red) and excited azide (blue) bands for 2-NpCON$_3$ in chloroform.

Our work is consistent with the finding of Autrey and Schuster[9] that the lifetime of the S$_1$ state of 2-naphthoyl azide, as determined by fluorescence spectroscopy, is less than 2 ns at ambient temperature. The lifetime of S$_1$ is 13 ns at 77 K. These observations reveal that there is a finite barrier to decomposition of the S$_1$ state.

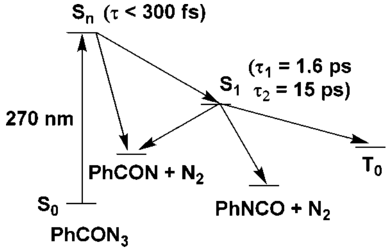
The transient IR spectra obtained upon 270 nm photolysis of *t*-BuCON$_3$ in chloroform are shown in Figure S5. The same pattern of results noted previously with PhCON$_3$ and 2-NpCON$_3$ was observed with the alkyl acyl azide; the prompt formation of isocyanate (2260 cm^{-1}) and nitrene (1750 cm^{-1}) and the ultrafast formation and subsequent decay of the excited singlet state of acyl azide (2100 cm^{-1}) S$_1$ were monitored. The positive bands behave similarly to those observed for PhCON$_3$ and 2-NpCON$_3$ although the fast lifetime of the S$_1$ state is particularly short ($\tau_1 = 0.6 \pm 0.2$ ps, $\tau_2 = 23 \pm 5$ ps, Table S4). As with PhCON$_3$ and 2-NpCON$_3$, the decay of the excited azide band (2100 cm^{-1}) is correlated with the growth of the isocyanate band (Figure S6).

The intensities of the benzoyl, 2-naphthoyl, and pivaloyl nitrene IR bands are very weak (the signal-to-noise ratio is ~3:1). The IR bands are also relatively broad; thus the integration of the nitrene bands is very uncertain. It is clear, however, that the acyl nitrenes are present immediately after the 270 nm, 300 fs laser pulse (Figure S7). We do not observe a slower formation of acylnitrene corresponding to the decay of the IR active S$_1$ states detected as the integrated nitrene signal intensity is constant or, in the case of pivavoylnitrene, actually undergoes decay. We deduce that 270 nm excitation of the acyl azides must initially populate a highly excited singlet state S$_n$ which decays within 300 fs to form both carbonylnitrene and the IR active S$_1$ state. Chemical analysis studies of Autrey and Schuster[9] demonstrate that S$_1$ of 2-NpCON$_3$ decomposes to form nitrene, a result we have confirmed with 355 nm laser photolysis of this azide. Thus, our inability to detect the growth of the acylnitrene signal following 270 nm excitation must be due to the low yield of S$_1$ with this wavelength and the resultant low signal intensity of nitrene growth derived from S$_1$.

Two negative bands are observed at 1692 and 2140 cm^{-1} (Figures 1, S1, and S5) due to depletion of the PhCON$_3$, 2-NpCON$_3$, and *t*-BuCON$_3$ ground states. The 1692 cm^{-1} band is due to depletion of the C=O stretch, and the 2140 cm^{-1} band is related to the depletion of the N$_3$ stretch of the acyl azides. The amplitudes of the negative bands do not change over 3 ns (Figure S8). This demonstrates that the ground states of PhCON$_3$, 2-NpCON$_3$, and *t*-BuCON$_3$ are not replenished within 3 ns of initial light induced depletion. Our results indicate that the quantum yield of disappearance of these three acyl azides is large with 270 nm light.[17] Autrey and Schuster[9] report a quantum yield of 0.5 with broadband 350 nm light, and we have found a value of 0.68−0.94 with monochromatic 355 nm light.

In conclusion, ultrafast IR spectroscopy is a valuable tool for studying the photochemistry of acyl azides. Upon 270 nm excitation, upper excited states of PhCON$_3$, 2-NpCON$_3$, and *t*-BuCON$_3$ are produced. These states decay by two processes: relaxation to S$_1$ and nitrene formation, within 300 fs. The S$_1$ states of 2-naphthyl carbonyl azide, benzoyl azide, and pivaloyl azide are IR active, and their decay correlates with the formation of isocyanate. This is the first direct detection of an acyl azide singlet excited state by time-resolved vibrational spectroscopy and the first direct demonstration that the S$_1$ states of these azides undergo Curtius Rearrangement to form isocyanates. The concentration of isocyanate rises biexponentially as it is formed from both hot S$_1$ (or S$_n$) (major) and the relaxed S$_1$ state (minor) of excited azide. The S$_1$ states also decay by the formation of triplet azide and carbonylnitrene (Scheme 2).[9]

Scheme 2. New Insights into the Photochemistry of Benzoyl Azide



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Supporting Information Available: FTIR spectra, transient spectra, kinetic traces (Figures S1−S8), and Tables S1−S4. This material is available free of charge via Internet at http://pubs.acs.org.

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(17) Recovery of ground state absorption by intersystem crossing of triplet 2-NpCON$_3$ is longer than 3 ns and would not be detected in these experiments.

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