

# The Curtius Rearrangement of Acyl Azides Revisited – Formation of Cyanate (R–O–CN)

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The Curtius rearrangement is a synthesis of isocyanates (R–N=C=O) by thermal or photochemical rearrangement of acyl azides and/or acylnitrenes. The photochemical rearrangement of benzoyl azide is now shown for the first time to pro-

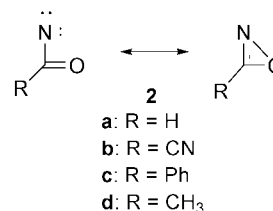
duce a small amount of phenyl cyanate (Ph–O–CN) together with phenyl isocyanate. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

## Introduction

The Curtius rearrangement<sup>[1]</sup> of acyl azides R–CO–N<sub>3</sub> (**1**) to isocyanates R–N=C=O (**3**) can take place either thermally or photochemically.<sup>[2]</sup> There is general consensus that the thermal Curtius rearrangement is a concerted reaction of the azides, not involving acylnitrenes (**2**). It is usually believed that the photochemical rearrangement can take two distinct paths: (i) Concerted Curtius rearrangement to isocyanate, and (ii) nitrene formation, which may or may not lead to isocyanate.<sup>[2]</sup> Experiments<sup>[3]</sup> and calculations indicate that acylnitrenes have singlet ground states. Calculations on the lowest singlet states of formylnitrene (**2a**),<sup>[3,4]</sup> cyanocarbonylnitrene NC–CO–N (**2b**),<sup>[5]</sup> benzoylnitrene (**2c**),<sup>[6]</sup> 2-naphthoylnitrene<sup>[6]</sup> and acetylnitrene<sup>[7]</sup> (**2d**) have revealed structures that are intermediate between nitrenes and oxazirenes with very long N–O bonds of the order of 1.73–1.82 Å at G2(MP2,SVP), BLYP/6-31G\* and CCSD(T)/cc-pVTZ levels of theory.

Moreover, the calculated NCO angle is nearly 90°. The stabilization of the singlet state of the nitrene can be ascribed to the N–O bonding interaction.<sup>[4–7]</sup> Thus, the singlet acylnitrenes may be regarded as resonance hybrids of nitrene and oxazirene structures (Scheme 1). Recent work by Pritchina et al. revealed that Ar matrix photolysis of benzoyl azide PhCON<sub>3</sub> leads to phenyl isocyanate PhNCO by two paths: (i) Concerted, and (ii) via benzoylnitrene Ph–CO–N, which was observed by IR spectroscopy.<sup>[8]</sup>

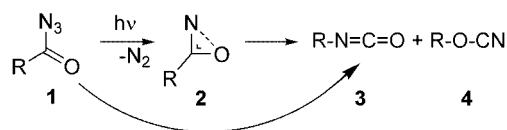
We have a long-standing interest in alkyl and aryl cyanates,<sup>[9]</sup> and we wondered why apparently nobody had ever considered the formation of cyanates in the Curtius rearrangement. Therefore, we have reexamined the photochemical Curtius rearrangement of benzoyl azide (**1c**).



Scheme 1.

## Results and Discussion

Photolysis of benzoyl azide isolated in Ar matrix at 12 K at 308 nm afforded the IR spectrum shown in Figure 1 (full IR spectra are shown in the Supporting Information; for details see also the footnote on the first page of this article). It is readily seen that small amounts of phenyl cyanate (**4c**) are formed together with the main product, phenyl isocyanate, PhNCO (**3c**). Phenyl cyanate (**4c**) is identified by its prominent C–O–C stretch at 1193 cm<sup>−1</sup>; all the other bands of PhOCN were also identified.



In contrast, flash vacuum thermolysis (FVT) of the azide afforded only the isocyanate PhNCO (**3c**) (FVT is not necessary in order to produce the isocyanate; this takes place already on mild heating of the azide). In order to examine the photochemical rearrangement of benzoylnitrene (**2c**) itself, the matrix-isolated azide was irradiated at 254 nm until all the azide had been consumed (5–20 min depending on the concentration and amount of azide). This affords a mixture of benzoylnitrene (**2c**),<sup>[8]</sup> phenyl isocyanate (**3c**) and phenyl cyanate (**4c**). Further photolysis of this mixture at 308 nm for 5 min caused transformation of the benzoylni-

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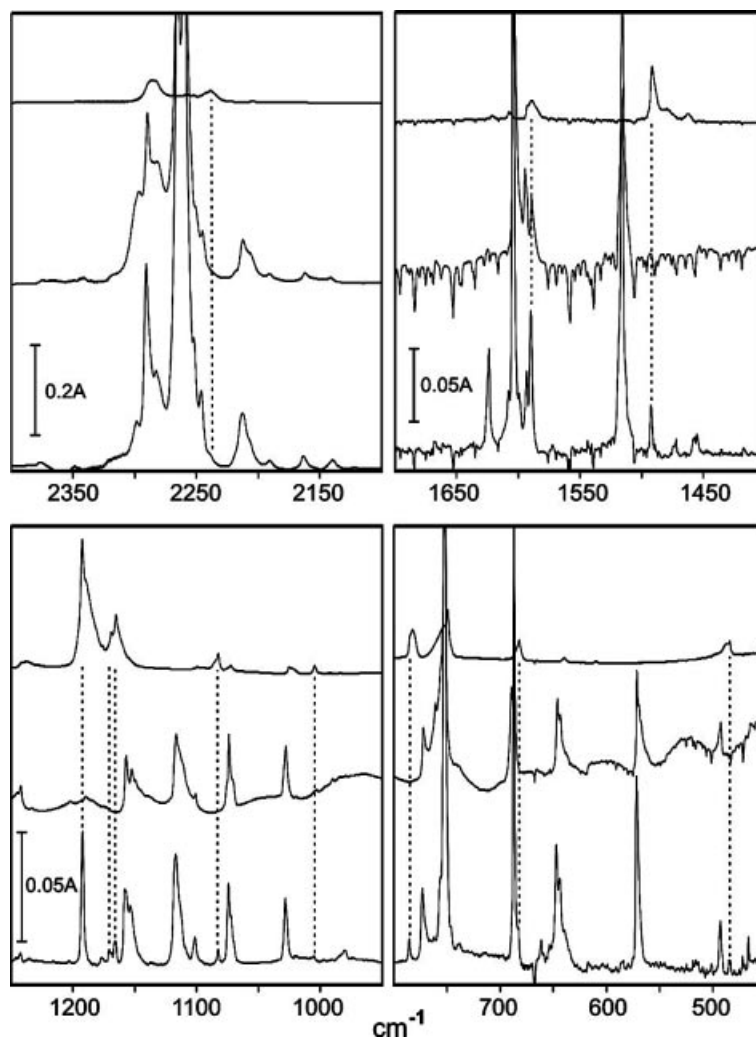


Figure 1. Ar matrix spectra at 12 K. Top: authentic sample of phenyl cyanate PhOCN; middle: phenyl isocyanate PhNCO from FVT of PhCON<sub>3</sub> at 450 °C; bottom: photolysis of PhCON<sub>3</sub> at 254 nm (15 min) and at 308 nm (5 min).

trene to products, producing a spectrum similar to Figure 1, whereby the amount of isocyanate had increased strongly, and the amount of cyanate had increased slightly. Thus, the nitrene **2c** undergoes photo-rearrangement to isocyanate and cyanate; most likely these two products are also formed in a direct photo-reaction of the azide.

In a control experiment phenyl isocyanate (**3c**) was irradiated in an Ar matrix at 254 nm for 90 min, followed by 308 nm for 15 min. No isomerization to phenyl cyanate (**4c**) was observed at either wavelength. In order to prove beyond doubt that phenyl cyanate (**3c**) is really formed, the product of the photolysis was rinsed from the cryostat with dichloromethane after warming to room temperature, and the resulting solution was examined by GC-MS. Direct comparison with authentic samples of phenyl cyanate and phenyl isocyanate proved the formation of the cyanate and isocyanate in relative yields of 1:85 (uncorrected relative peak areas). This experiment was repeated several times with the same results. The mass spectra of phenyl cyanate and phenyl isocyanate are very characteristic and easily distinguished.<sup>[10]</sup> For example, PhNCO gives a strong peak due

to PhN<sup>+</sup> at *m/z* 91, whereas for PhOCN the strongest peak is due to Ph<sup>+</sup> at *m/z* 77. The spectra are shown in the supporting information.

It is interesting to note that a peak is also present at 1193 cm<sup>-1</sup> in the matrix IR spectrum of Pritchina, Bally, et al.<sup>[3]</sup> This was ascribed to an artefact due to the spectral subtraction but is undoubtedly due to phenyl cyanate (**4c**), formed by photolysis of the nitrene/oxazirene **2c**.

Theoretical calculations were carried out in an effort to determine the differences in activation barriers for cyanate and isocyanate formation. Previous efforts to describe the HCNO energy surface<sup>[4,11]</sup> demonstrate that this is not a trivial task. Fueno et al.<sup>[4a]</sup> reported a very small barrier for the isomerization of **2a** to HNCO (**TS1a**) and a 16.5 kcal/mol higher transition state for the isomerization of singlet oxazirene (**2a**) (<sup>1</sup>A') to HOCN (**TS2a**) using CASSCF(6,10) and MRD-CI/6-31G(d,p) calculations. HOCN was found to be 21 kcal/mol less stable than HNCO at this computational level.

Morokuma et al.<sup>[4b]</sup> failed to locate **TS1a** on the singlet surface at the B3LYP/6-311G(d,p) level, but they located

**TS2a** lying only 0.7 kcal/mol above the oxazirene structure **2a**. Note however that the structure of their **TS2a** corresponds very closely to our **TS3a** ( $\text{HOCN} \rightarrow \text{HNCO}$ ), which lies 5.5 kcal/mol higher than **2a** at the B3LYP/6-31G(d,p) level.

HOCN was found to be 28.7 kcal/mol less stable than HNCO at the B3LYP/6-311G(d,p) level. The triplet nitrene **2a** ( $^3\text{A}''$ ) did rearrange to HNCO and HOCN.

Shapley and Backskay<sup>[4c]</sup> located **TS1a** ( $^1\text{A}'$  oxazirene  $\rightarrow$  HNCO) lying 30 kcal/mol above oxazirene (**2a**) when using the G2 computational method, but a direct path from **2a** to HOCN (**TS2a**) was not reported. HOCN was 25.4 kcal/mol less stable than HNCO, and the direct isomerization HNCO  $\rightarrow$  HOCN had a barrier (**TS3a**) of 88 kcal/mol (HOCN  $\rightarrow$  HNCO has a barrier of 62.6 kcal/mol).

We found **TS1a** (oxazirene  $\rightarrow$  HNCO, 15.8 kcal/mol) by using B3LYP/6-31G(d) for the parent compound **2a**, but **TS2a** (oxazirene  $\rightarrow$  HOCN) was not located on the singlet surface. At the HF/6-31G(d,p) level, **TS1a** and **TS2a** were located. At the CASSCF(8,8) level, **TS1a** was securely located with both Gaussian03 and Molpro; it is about 20 kcal/mol above **2a**. When using CASSCF(12,12) this energy difference increases to 25.5 kcal/mol, which is in better agreement with the literature.<sup>[4c]</sup> As for **TS2a**, it appeared to be ca. 6 kcal/mol above **TS1a**, but it is most likely that all structures obtained for **TS2a** at CASSCF levels are artifacts, since in neither case could they be verified by IRC calculations.

Similar calculations were carried out for the phenyl derivatives **2c**, **3c** and **4c** and the corresponding transition states **TS1c**, **TS2c** and **TS3c**. At the B3LYP/6-31G(d) level we found **TS1c** (phenyloxazirene  $\rightarrow$  PhNCO, 14.7 kcal/mol), and **TS2c** (phenyloxazirene  $\rightarrow$  PhOCN, 19.3 kcal/mol). At the HF/6-31G(d,p) level, **TS2c** was at 20.5 kcal/mol, but all efforts to locate **TS1c** failed at this level. At the CASSCF(8,8) level, **TS2c** was 17.6 kcal/mol above **TS1c**. Thus, in spite of some quantitative differences and failure to locate some transition states at all attempted levels of theory, all the computations agree that the barrier for cyanate formation is significantly higher than the one for isocyanate formation. This explains the absence of cyanate formation in the thermal Curtius rearrangement. It should be pointed out that all the calculations pertain to the ground state energy surface, whereas the photochemical rearrangements are likely to take place on excited state surfaces.

**TS3c**, the transition state for isocyanate-cyanate rearrangement, was computed to lie close to **TS2c** in energy, at 20.1 kcal/mol above the oxazirene structure **2c** (94 kcal/mol above the isocyanate PhNCO) at the B3LYP/6-31G(d) level. The cyanate was 31 kcal/mol less stable than the isocyanate at this level. Experimentally, it is known that alkyl cyanates rearrange thermally to alkyl isocyanates, but aryl cyanates do not rearrange to aryl isocyanates.<sup>[9]</sup>

During a search for a concerted pathway from the azide to the cyanate, **1**  $\rightarrow$  **4**, we found instead a carbene intermediate,  $\text{RO}-\text{C}-\text{N}_3$ , formed from the azide  $\text{HCON}_3$  (**1a**) with a barrier of 81.4 kcal/mol, and from the azide  $\text{PhCON}_3$  (**1c**) with a barrier of 95.9 kcal/mol. These carbenes decompose

to cyanate HOCN and  $\text{PhOCN} + \text{N}_2$  with barriers of less than 1 kcal/mol. We do not believe these carbene intermediates are realistic; concerted rearrangement on the excited state energy surfaces of the azides is more likely.

In conclusion, phenyl cyanate (**4c**) is formed in small amount along with the main product, phenyl isocyanate (**3c**) on photolysis of benzoyl azide (**1c**). Both cyanate and isocyanate are formed on photolysis of the (singlet) nitrene/oxazirine **2c** at 308 nm. Both cyanate and isocyanate are also formed on photolysis of the azide **1c** at 254 nm; this may be a direct reaction of an excited state of the azide, or it may be a rapid reaction via the nitrene. The thermal Curtius rearrangement produces only the isocyanate **3c**. Further experimental and theoretical work on the Curtius rearrangement is envisaged, e. g. an examination of substituent effects on the barrier heights for cyanate and isocyanate formation. No direct evidence for the formation of nitrile oxides, RCNO, in the Curtius rearrangement has been found so far, although such a rearrangement cannot be excluded.<sup>[12]</sup>

## Experimental Section

Benzoyl azide was prepared following the procedure of Barrett and Porter,<sup>[13]</sup> and phenyl cyanate by the procedure of Murray and Zweifel.<sup>[14]</sup>

**Matrix Isolation Procedure:** A gaseous mixture of argon and benzoyl azide (ratio  $\approx$  1000:1) is deposited slowly onto a CsBr window at 20 K. The matrix is irradiated with a 254-nm low-pressure mercury lamp (75 W; Graentzel, Karlsruhe, Germany) for 5 to 20 min (depending on the amount of azide), which leads to the complete decomposition of the azide and the formation of phenyl isocyanate, phenyl cyanate and singlet benzoylnitrene. Prolonged photolysis for 2–5 min with 308 nm excimer lamp (50 mW/cm<sup>2</sup>; Ushio, Singapore) results in larger amounts of phenyl isocyanate, while the amount of phenyl cyanate increases slightly. Relevant IR spectra are shown in the supporting information. GC/MS analysis: For GC/MS analysis of the products of the matrix photolysis, the cold window and the inner surfaces of the cryostat cold head are rinsed with dichloromethane after warming to room temperature and examined on a 30 m capillary column DB-5ms, diameter 0.32 mm, stationary phase thickness 0.25  $\mu\text{m}$ ; helium flow rate 1.3 mL/min; temperature program: 50 °C for 3 min, then 15 °C/min till 260 °C, and maintain this temperature for 8 min; injector: 200 °C; detector: 250 °C. GC retention times and mass spectra:

Authentic samples: Phenyl cyanate:  $R_t$  = 7.28 min, MS [ $m/z$  (rel. int. %)]: 120 (4), 119 (49), 92 (2), 91 (17), 78 (7), 77 (100), 75 (3), 74 (4), 65 (6), 64 (5), 63 (4), 51 (27), 50 (12). Phenyl isocyanate:  $R_t$  = 6.18 min, MS [ $m/z$  (rel. int. %)]: 120 (9), 119 (100), 92 (4), 91 (43), 77 (1), 74 (3), 65 (6), 64 (28), 63 (12), 62 (4), 61 (2), 60(4), 52(3), 51 (6), 50 (6).

Samples collected after matrix isolation: Phenyl cyanate:  $R_t$  = 7.28 min, MS [ $m/z$  (rel. int. %)]: 120 (9), 119 (56), 91 (14), 78 (13), 77 (100), 65 (11), 63 (8), 57 (47), 51 (53), 50 (24). Phenyl isocyanate:  $R_t$  = 6.18 min, MS [ $m/z$  (rel. int. %)]: 120 (8), 119 (100), 92 (4), 91 (50), 90 (3), 77 (2), 74 (3), 65 (7), 64 (34), 63 (13), 62 (4), 59 (5), 51 (7), 50 (6). Integration of GC peak areas: First run (rel. integrated area): PhOCN 0.48, PhNCO 41.19, ratio 1:85. Second run: PhOCN 0.20, PhNCO 17.13, ratio 1:86. Third run: PhOCN 0.25, PhNCO 21.00, ratio 1:84.

**Supporting Information** (see footnote on the first page of this article): Contains IR spectra of matrix photolysates of benzoyl azide and of authentic PhOCN and PhNCO, GC-mass spectra of PhOCN and PhNCO isolated from the matrix photolysates as well as the mass spectra of authentic PhOCN and PhNCO, and tables of calculated energies and Cartesian coordinates of ground state and transition structures.

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