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Determination of the photolytic decomposition pathways of benzylchlorodiazirine by C_{60} probe technique

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Abstract—By employing C_{60} as a chemical probe, the photolysis of benzylchlorodiazirine has been proposed to form carbene and the rearranged products via the excited state.

Photolysis and thermolysis of diazirines have been widely used to produce carbenes as a photoaffinity labeling reagent in organic chemistry.[1] However, it has also been known that these reactions yield not only carbenes but also diazo compounds as intermolecular rearrangement products.[2] In addition, some diazirines having a C–H bond in the α-position of diazirine carbon may produce olefins by a rearrangement in excited states (RIES).[3] In this context, it is of great importance to understand the various elementary processes in the photochemistry of diazirines.

Photolysis of benzylchlorodiazirine, **1**, produces benzylchlorocarbene (bzcc) which undergoes 1,2-*H* migration to form *E*- and *Z*-β-chlorostyrenes.[4] Upon the addition of a carbene trap such as tetramethylethylene (TME), a cyclopropane adduct is formed. The plots of [addition]/[rearr] versus [TME] are curved. A double inverse plot of [rearr]/[addition] versus 1/[TME] is linear. These results can be understood if a second intermediate contributes to the formation of chlorostyrenes. The additional reactive intermediate was postulated to be a carbene olefin complex, COC.[4] Kinetically, both the RIES and the COC mechanisms account for the nonlinearity of the plots of [addition]/[rearr] versus [TME]. To distinguish between these views, an independent precursor to bzcc is required. With the nonnitrogenous phenanthrene precursor for bzcc, a linear plot of [addition]/[rearr] versus [TME] was obtained.[5] Platz et al. proposed that the second, noncarbene pathway to β-chlorostyrenes in the photolysis of **1** involves a rearrangement in the excited state of diazirine. Thus, the photolysis of diazirine is consistent with the RIES, but not the COC mechanism. However, the extent of the RIES process cannot be quantified up to the present time.

We have recently introduced the C_{60} probe technique, which is a nonspectroscopic method to determine the photolytic decomposition pathways of diazirines.[6] The carbene adds to C_{60} to form a 6,6-closed methanofullerene, whereas the diazo compound reacts with C_{60} to afford a 5,6-open fulleroid. The partitioning of the participation of carbene, diazo, and rearrangement in excited state (RIES) during the reaction is quantitatively and simultaneously achieved. We hereby apply this method to the photolysis of **1** and propose its photolytic decomposition pathways.

We prepared diazirine **1** by the oxidation of the corresponding amidine by NaOCl according to Graham's procedure.[7] A 1,2-dichlorobenzene/C_6D_6 (9/1) solution of diazirine **1** (2.4×10^{-3} M) and C_{60} (2.4×10^{-2} M) was photolyzed with a high-pressure mercury-arc lamp (>300 nm) for 15 h at −30 °C in a sealed Pyrex NMR tube. ^{1}H NMR measurement of the reaction mixture showed a 65% conversion of diazirine (δ 3.04 (s), CH_2) and the formation of *E*- and *Z*-chlorostyrenes (**3-*E***; δ 6.41, 6.62 (d, $J = 13.5$ Hz), **3-*Z***; δ 6.05, 6.39 (d,

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Keywords: C_{60}; Diazirine; Photolytic decomposition; Carbene; RIES process.

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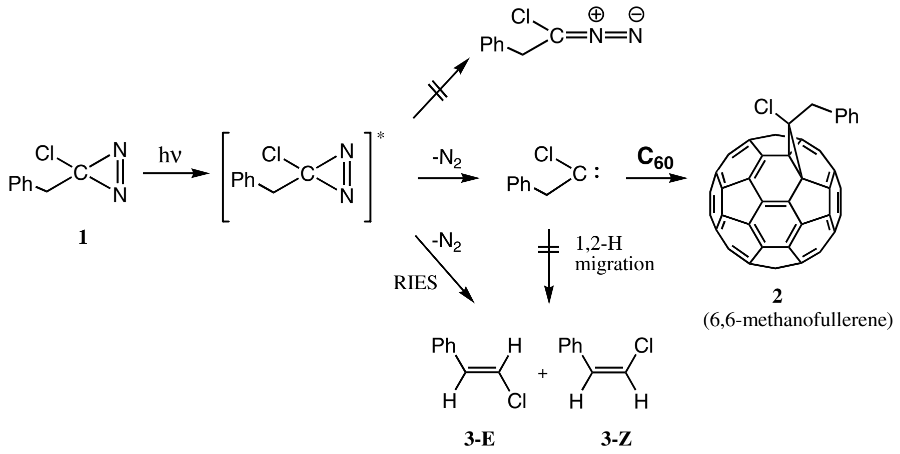

Scheme 1.

$J = 8.0$ Hz), olefin protons) and adduct **2** (δ 4.15 (s), CH_2) (Scheme 1). The yields of each product were calculated by the peak areas in ^{1}H NMR of the reaction mixture. To confirm the reproducibility of this reaction, we repeated the experiment four times and averaged the results. Photolysis of diazirine **1** with C_{60} resulted in the formation of 6,6-C_{60} adduct in the yield of 31% (standard deviation (SD) 3.1%) and chlorostyrene in a 57% yield (SD 5.3%, E/Z ratio is 4/1) based on the conversion of **1**. No 5,6-adduct (5,6-open fulleroid) was detected. This is consistent with the very low quantum yield for diazo formation reported by Platz and co-workers.[5]

In order to obtain authentic samples of the $C_{60}CClBz$ adduct, we carried out the experiment using diazirine **1** (85 mg, 2.8×10^{-2} M) and C_{60} (36 mg, 2.8×10^{-3} M) in a preparative scale and isolated the product by HPLC separation with a Buckyprep column (Nacalai Tesque Co). We characterized mono-adduct (**2**) by means of spectroscopic analyses.[8] The UV–vis spectrum of **2** shows an absorption maximum at 431 nm, which is a characteristic feature of a 6,6-adduct of C_{60}.[9] The spectral data of ^{1}H and ^{13}C NMR and 2D NMR (HMQC, HMBC) clearly suggest that **2** has a 6,6-closed methanofullerene structure, which was unambiguously characterized by X-ray crystal analysis (Fig. 1).[10] The redox properties of **2** were also verified by cyclic voltammetry (CV) to be similar to those of the parent C_{60} as shown in Table 1.[11]

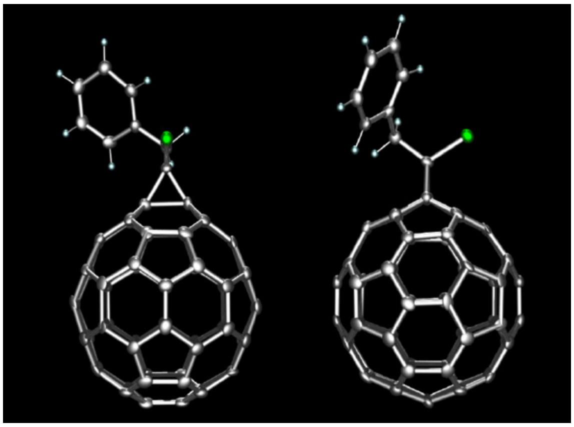

Figure 1. Crystal structure of $C_{60}CClBz$ (**2**). The CS_2 molecules are omitted for clarity.

Table 1. Redox potentials[a] in V of C_{60},[b] **2**, and other adducts

Compound	oxE_1[c]	redE_1	redE_2	redE_3
C_{60}	+1.21	−1.12	−1.50	−1.95
6,6-$C_{60}CClBz$	+1.22	−1.15	−1.54	−2.11
6,6-$C_{60}CClPh$[d]	+1.29	−1.13	−1.54	−2.02
6,6-$C_{60}Ad$[d]	+1.07	−1.21	−1.58	−2.06
5,6-$C_{60}Ad$[d]	+1.10	−1.18	−1.55	−2.02
6,6-$C_{60}CCl(i\text{-}Pr)$[e]	+1.24	−1.14	−1.51	−2.10
5,6-$C_{60}CCl(i\text{-}Pr)$[e]	+1.11	−1.14	−1.51	

[a] Half-cell potentials unless otherwise stated. The values are relative to ferrocene/ferrocenium couple.

[b] Ref. 13.

[c] Irreversible. The value was obtained by differential pulse voltammogram (DPV).

[d] Ref. 6a.

[e] Ref. 6b.

Kinetic parameters for the reaction of bzcc with TME have been investigated by Liu and Bonneau, $E_a = -4.7$ kcal/mol and $\log A = 5.3$, hence k (−30 °C) = $3 \times 10^9\ M^{-1}\ s^{-1}$.[12] To establish the rate constant for the reaction of C_{60} with bzcc, we carried out the photolysis of **1** at −30 °C in the presence of an equal amount of C_{60} and TME (**1**: 4.2×10^{-3} M; C_{60} and TME: 2.1×10^{-2} M). The product ratio of two adducts, **2** and TME–CBzCl, was calculated by the peak areas in the ^{1}H NMR of the reaction mixture. The results suggest that C_{60} traps the bzcc 4.1 times (SD 0.6 times) faster than TME does and that the rate constant for bzcc addition to C_{60} is on the order of $10^{10}\ M^{-1}\ s^{-1}$. In this respect, the C_{60} trapping (2.1×10^{-2} M) is more efficient than the 1,2-*H* migration of bzcc [k (−30 °C) = $10^7\ s^{-1}$][4c] and thus the chlorostyrenes must come only from the RIES process. Our present data suggest that the amount of adduct **2** reveals the generation of bzcc and that the amount of chlorostyrenes indicates the extent of the RIES mechanism in the photolysis of **1** (Scheme 1). The formation ratio of carbene/RIES in this reaction was estimated to be 35/65. We believe that this Letter presents the first set of unambiguous and quantitative results in the assignment of decomposition pathways in the photolysis of benzylchlorodiazirine.

In conclusion, we are convinced that the C_{60} probe technique is a valuable tool for the detection of carbene, diazo, and excited chemistry in the photolysis of diazirines especially the decomposition pathways, which are so varied from one diazirine to the next.

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Supplementary data

HPLC profiles, ^{1}H NMR, ^{13}C NMR, HMQC, HMBC, mass, and UV–vis spectral data, X-ray crystallographic data, and CV and DPV spectra for $C_{60}CClBz$ adduct. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.11.145.

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8. MALDI-TOF mass (Matrix: 1,1,4,4-tetraphenyl-1,3-butadiene, negative mode): m/z 858, UV–vis (toluene) λ 431 nm (ε1900), ^{1}H NMR (500 MHz, $CS_2/CDCl_3$ (4/1)) δ 4.26 (s, 2H), 7.34 (t, $J = 7.4$ Hz, 1H), 7.41 (t, $J = 7.4$ Hz, 2H), 7.64 (d, $J = 7.4$ Hz, 2H), ^{13}C NMR (125 MHz, $CS_2/CDCl_3$ (4/1)) δ 39.15 (t, 1C), 57.42 (s, 1C), 78.86 (s, 2C), 127.48 (d, 1C), 128.62 (d, 2C), 129.96 (d, 2C), 135.44 (s, 1C), 137.22 (s, 2C), 138.85 (s, 2C), 140.76 (s, 2C), 141.04 (s, 2C), 141.62 (s, 2C), 141.90 (s, 2C), 141.96 (s, 2C), 142.10 (s, 2C), 142.66 (s, 1C), 142.75 (s, 1C), 142.80 (s, 2C), 142.84 (s, 2C × 2), 143.08 (s, 2C), 143.39 (s, 2C), 143.48 (s, 2C), 144.20 (s, 2C), 144.27 (s, 1C), 144.31 (s, 2C), 144.32 (s, 2C), 144.38 (s, 2C, 1C), 144.60 (s, 2C), 144.75 (s, 2C × 2), 144.87 (s, 2C), 144.94 (s, 2C), 144.98 (s, 2C × 2), 145.53 (s, 2C), 145.83 (s, 2C).
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10. Crystallographic data for **2**: $C_{137}H_{14}Cl_2S_2$, $FW = 1794.50$, black crystals, $0.25 \times 0.10 \times 0.10$ mm^3, monoclinic, $P21/m$ (no. 11), $a = 16.1072(19)$, $b = 10.1377(13)$, $c = 21.406(3)$ Å, $\beta = 96.259(5)°$, $V = 3474.6(8)$ Å^3, $Z = 2$, $D_c = 1.715$ g cm^{-3}, $T = 110$ K, 32,293 reflections that were collected, 8380 were unique ($R_{int} = 0.113$) and 4380 refractions ($I > 2.0\sigma(I)$), $R_1 = 0.099$, $wR_2 = 0.261$, GOF = 1.063, 1231 refined parameters, 1560 restraints. The maximum and minimum residual electron density is equal to 0.83 and -0.55 e Å^{-3}, respectively. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 622039. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].
11. Measuring conditions; solvent: 1,2-dichlorobenzene; supporting electrolyte: 0.1 M $TBAPF_6$; scan rate: 50 mV/s; working electrode: Pt disc; counter electrode: Pt wire; reference electrode: SCE.
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