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Review of the doctoral dissertation

"Photochemistry and spectroscopy of small, cryogenically isolated organopnictogen molecules" by Elavenil Ganesan

The doctoral dissertation of Mr. Elavenil Ganesan (MSc) has a classic layout, typical of PhD theses, where the results of experimental investigations are reported. The dissertation starts with an Introduction (**Chapter 1**) where the basic concepts of matrix-isolation, infrared and UV spectroscopy and photochemistry are briefly introduced. Materials, tools and procedures used in the investigations carried out within this doctoral work are described in **Chapter 2**. The obtained results are presented in the subsequent **Chapters 3, 4, 5** and **6**.

In **Chapter 3** spectroscopic investigations of HCP molecule and of the ·CP radical are described. The main achievements of these studies are: (i) preparation of gaseous sample of HCP (by elimination of HCl molecules from a precursor) in such a way that the obtained product is clean and ready for deposition into a low-temperature matrix; (ii) generation of ·CP radicals by photolysis of matrix-isolated HCP with VUV radiation; (iii) unprecedented observation of quartet – doublet phosphorescence occurring upon UV excitation of matrix-isolated ·CP radicals; (iv) proposition of a plausible mechanism according to which quartet states of ·CP radicals can be populated.

Observations of quartet – doublet phosphorescence are extremely rare. Hence, the case described in Chapter 3 of the dissertation of Mr. Ganesan represents a highly valuable scientific finding. The report on this case has been published in Angewandte Chemie International Edition.

The investigations on HCP and on ·CP radical have been competently conducted.

With respect to the results reported in Chapter 3, I have two questions the Author may wish to answer during the defence of his thesis .

(i) Can the luminescence as well as the luminescence excitation spectra of ·CP radical be presented in a site-selected way? It seems to me, it may be enough to take proper (vertical and horizontal) cuts through the plots presented in Figures 3.5 and 3.8. It looks that an example of a site-selected luminescence excitation spectrum is presented in the upper panel of Figure 3.3. The Author reports annealing of the matrix as a method of dealing with different trapping sites of a matrix; however, the Author does not mention the possibility of taking spectra in a site-selective way.

(ii) It would be nice to record separately the spectra of fast doublet-doublet fluorescence and slow quartet-doublet phosphorescence of ·CP radical. It seems that such measurements should be possible with Setup 2 described in Section 2.4 of the dissertation. Maybe in such a way partial overlap of phosphorescence and fluorescence spectra (shown in Figure 3.6 and Figure 3.7) can be avoided.

Investigations of UV-induced transformations of matrix-isolated methylpnictines (analogues of methylamine CH_3-NH_2, with N-atom substituted by P, As or Sb atoms) are described in **Chapter 4**. Several products of CH_3PH_2 photolysis were identified. Upon exposure of matrix-isolated CH_3PH_2 to UV (λ = 254 nm) radiation, two products CH_4 and HCP were generated. Upon excitation with shorter-wavelength VUV (150 – 190 nm) radiation more photoproducts were created CH_4, HCP, CH_2PH, CP and PH. Analogous photoproducts CH_4, HCAs, CH_2AsH, AsC and AsH were obtained when matrix-isolated CH_3AsH_2 was exposed to UV and VUV radiation. Populations of both analogous products CH_2PH and CH_2AsH, generated upon irradiation with VUV, decrease abruptly upon subsequent excitation with longer-wavelength UV (λ = 254 nm) radiation. The effects of UV irradiation of antimony analogue of methylamine (CH_3-SbH_2) are somewhat different from the effects of UV excitation of CH_3-PH_2 or CH_3-AsH_2. The experiments carried out within the doctoral work of Mr. Elavenil Ganesan demonstrated that alongside the CH_4 and SbH products another species CH_3Sb is also generated. The latter product has no analogues among the species generated from photoexcited CH_3-PH_2 or CH_3-AsH_2. The results of the extensive study on photochemical transformations of CH_3-PH_2, CH_3-AsH_2 and CH_3-SbH_2 are in preparation to publication.

In **Chapter 5** generation of HCCSb molecule by UV-induced dehydrogenation of $HCCSbH_2$ precursor is described. UV absorption and emission spectra of photoproduced HCCSb is reported. Although the spectral identification of this species was not easy, the comparison with the spectrum of analogous HCCAs allowed a tentative, but reasonably plausible, identification of HCCSb. If the identification is correct, that would be the first report on experimental observation of HCCSb molecule. Both HCCAs and HCCSb molecules are triplet in their ground electronic states. Spectral indications of completely dehydrogenated CCAs and CCSb photoproducts were also observed. The obtained results were published in Chemistry – A European Journal.

Products generated by UV (λ = 254 nm) or VUV (150 - 190 nm) photolysis of matrix-isolated $H_2C{=}C{=}C(H)$-PH_2 molecules are presented in **Chapter 6** of the doctoral dissertation. Excitation of $H_2C{=}C{=}C(H)$-PH_2 with UV (λ = 254 nm) radiation led to several transformations of the precursor. One type of observed transformations is photoisomerization (by hydrogen-atom transfer) to HC-$C{\equiv}C$-$C(H_2)$-PH_2. Another photochemical route leads to photodehydrogenation (by loss of 4 hydrogen atoms). The product of this photodehydrogenation is H-C_3-P molecule. Photoinduced cleavage of C-C bonds leads to such products as HCP, HCCP, acetylene and methane. The photochemical transformations of $H_2C{=}C{=}C(H)$-PH_2 excited with UV (λ = 254 nm) radiation were compared with photochemical conversions of H_3C-$C(H_2)$-$C{\equiv}P$ [an isomer of $H_2C{=}C{=}C(H)$-PH_2]. Starting from any of the isomers (both with the formula C_3H_5P), the HC_3P analogue of cyanoacetylene was obtained as a prominent product. Also HCCP and HCP were photogenerated starting from any of the isomeric precursors. Exposure of matrix isolated $H_2C{=}C{=}C(H)$-PH_2 to VUV (150 - 190 nm) radiation led to photogeneration of two main products: HC_3P (which was also generated upon irradiation at 254 nm) and $H_2C{=}C(H)C{\equiv}P$ (which was not generated upon irradiation at 254 nm). Minor products generated upon VUV (150 - 190 nm) irradiation of $H_2C{=}C{=}C(H)$-PH_2 were HCCP and methane.

To sum up, within the doctoral work of Mr. Elavenil Ganesan, the photochemistry of small, cryogenically isolated organopnictogen molecules was extensively and deeply investigated. Several photoproduced chemical species were observed in this work for the first time. The investigations on the infrared and UV-Vis spectra of numerous photogenerated small organopnictogen species provide spectroscopic data which may be of astrochemical relevance.

Conclusion:

I think this is a good thesis, well-written, well-organized, with good results published in journals of high international renown. Therefore, I conclude that the presented dissertation meets all the formal requirements for a PhD thesis and I recommend admission of the Candidate to subsequent stages of the doctoral procedure.

In recognition of the scientific achievements presented in the PhD thesis of Mr. Elavenil Ganesan, I am submitting a motion to award this dissertation with distinction. In my opinion, the results especially eligible for distinction are those concerning spectroscopy (in particular the quartet-doublet phosphorescence) of the ·CP radical. These results were presented in Chapter 3 of the dissertation and published in Angewandte Chemie International Edition (2022) 61, e202210521.

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