

Review

Photochemistry of azide-moiety containing inorganic compounds

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Accepted 9 March 2006

Available online 16 March 2006

Contents

1. Introduction	2325
2. Photophysical processes involving azide anions and azido complexes	2326
2.1. Photophysical processes of free azide anion	2326
2.2. Photophysical processes involving excited azido complexes	2326
3. Photochemical processes of inorganic azides and azido complexes	2326
3.1. Free and protonated azide anion, and azide salts	2326
3.2. Photochemical reactions of azido complexes	2327
3.2.1. Nitrene intermediate formation	2328
3.2.2. Nitrido complexes formation	2329
3.2.3. Azidyl radical formation	2330
3.2.4. Non-redox photoeliminations, photosubstitutions and photoisomerizations	2331
3.2.5. Photochemical processes not involving azido ligand	2332
3.2.6. Photoreactions of organic azido ligands	2332
4. Conclusion	2333
Acknowledgements	2333
References	2333

Abstract

Results obtained to date document that inorganic compounds containing azide-moiety undergo several kinds of photochemical processes, the most extensively studied being (i) singlet or triplet six-electron nitrene ($-N$) intermediate formation at a dinitrogen molecule elimination from the azido ligand preserving the central atom oxidation state; (ii) transformation of azido ($-N_3$) to nitrido ($\equiv N$) complexes associated with a two-electron oxidation of the central atom; (iii) oxidation of azido anionic ligand (N_3^-) to its radical (N_3^\bullet) accompanied by a one-electron reduction of the central atom; (iv) non-redox photoejection of azido ligands from the coordination sphere or its substitution, usually for a solvent molecule; (v) photoisomerization reaction; (vi) reaction of other than azido ligand in the primary coordination sphere; (vii) reactions of azido group being peripheral part of organic ligands. Moreover, azido complexes are involved in pure photophysical deactivation processes without any chemical change. This contribution is aimed at reviewing all of the mentioned deactivations.

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Keywords: Photochemistry; Azide complexes; Redox processes; Azidyl radical; Nitrene formation; Nitrido ligand

1. Introduction

Systems of free azides or azido-moiety containing compounds may, in principle, be grouped into four classes:

1. organic azido compounds (e.g. azidobenzene $C_6H_5N_3$);

2. inorganic compounds containing free (e.g. ionic salts such as NaN_3) and protonated (HN_3) azide anions;
3. coordination compounds with azido ligand(s) covalently bonded to the central atom (e.g. $[Co(NH_3)_5(N_3)]^{2+}$);
4. coordination compounds containing organic azido ligand(s) (e.g. azidoferrocene $[Fe(C_5H_5)(C_5H_4N_3)]$).

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Members of each of the mentioned groups have been subjected to photochemical investigation and a wide variety of

photochemical processes has been unveiled. The photochemical behaviour of organic azides (class 1) lies usually outside the interest of the chemist engaged in inorganic or coordination chemistry. However, the knowledge obtained through investigation of organic azides may be very inspiring and helpful in the interpretation of behaviour of inorganic azido complexes and salts. This opinion can be exemplified by a transfer of information on nitrene intermediates – which is very deeply elaborated in the photochemistry of organic azides – to the realm of photochemistry of azido complexes. In spite of its stimulating impact to inorganic photochemistry, the area of photochemical behaviour of organic azides remains beyond the scope of this contribution and will not be covered in this paper. The reader may find necessary information elsewhere (see e.g. [1–4]).

Up to now, the photochemistry of inorganic azides or azido complexes has been focused mainly on unveiling the mechanisms of photophysical and photochemical deactivation processes, frequently stimulated by a vision of practical applications of the acquired knowledge. In this contribution this aspect is reviewed with a stress put on the photochemistry of iron(III) compounds.

Most of the fundamental results obtained before 1990 are described in comprehensive monographs [5,6] and reviews [7,8]. This contribution treats in particular, subsequent information, however, some older principal papers are also mentioned. Individual photophysical processes and photochemical reactions are tentatively classified based on the primary deactivation processes and/or their products.

2. Photophysical processes involving azide anions and azido complexes

Photophysical processes form an integral part of all deactivation processes of excited molecules. As typical examples, vibrational and rotational relaxation accompanying almost all chemical deactivations may be introduced. In this section, only systems with exclusively photophysical deactivation (i.e. without observable chemical change) are briefly mentioned. Of the known photophysical deactivations, mainly physical deactivation yielding the ground state reactants, intersystem crossing (*isc*) and energy transfer (*ent*) processes are typical of the systems containing free azide anions or excited azido complexes.

2.1. Photophysical processes of free azide anion

Free anion N_3^- behaves in its ground state as an efficient quencher of singlet dioxygen molecules $^1\text{O}_2$ in water, organic solvents and mixed aqueous–organic media. The rate constants of the quenching k_q ranging from $2.24 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (ethanol– D_2O mixture) up to $2.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (acetonitrile– D_2O mixture) were determined for several solvents and their mixtures [9,10]. Such constants are routinely used as standards to calculate k_q values for the $^1\text{O}_2$ quenching by various substrates. The measured values showed that the quenching rate constants in most mixtures cannot be reliably predicted using simple additivity rules estimating from the

k_q values obtained for pure solvents. The activation energy for the $^1\text{O}_2$ quenching by azide in D_2O is 11.3 kJ mol^{-1} [9]. With respect to the quenching mechanism, it is generally believed that the interaction proceeds through a partial charge transfer intermediate followed by its dissociation to ground state reactants without any chemical change [11]:

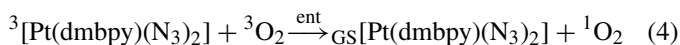
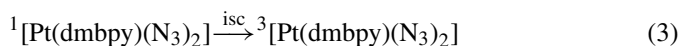
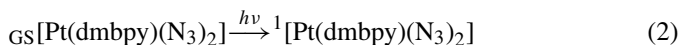


In practical application only the anionic form N_3^- is able to effectively quench the $^1\text{O}_2$, HN_3 is almost inactive in this process.

2.2. Photophysical processes involving excited azido complexes

In connection with the photochemistry of the environment, photodynamic therapy and other attractive fields of human medicine, energy transfer processes generating $^1\text{O}_2$ or other active oxygen species have been extensively investigated. Simultaneously, azido complexes have been involved in research of industrial importance, mainly on the photooxidation of organic compounds by $^1\text{O}_2$ catalyzed by inorganic complexes.

Anbalagan [12] presents the results of the generation of the $^1\text{O}_2$ by energy transfer processes involving platinum(II) or palladium(II) complexes in their MLCT excited states. Among several other compounds, two azido complexes, $[\text{Pt}(\text{dmbpy})(\text{N}_3)_2]$ and $[\text{Pd}(\text{dmbpy})(\text{N}_3)_2]$ ($\text{dmbpy} = 4,4'$ -dimethyl-2,2'-bipyridine) dissolved in DMF were subjected to the study. Of all the complexes investigated, the excited $[\text{Pt}(\text{dmbpy})(\text{N}_3)_2]$ was most effective in $^1\text{O}_2$ production. The suggested mechanism of formation of $^1\text{O}_2$ consists of three steps (GS = the singlet ground state of the complex, left superscripts denote the multiplicity of molecules):



The generated $^1\text{O}_2$ subsequently acts as an oxidizing agent towards industrial organic substances. The author did not mention any photochemical changes in platinum or palladium complexes within the study. From the formal point of view, the generation of $^1\text{O}_2$ can be taken as the opposite process to its quenching, which is a typical property of free azide anion [9,10].

3. Photochemical processes of inorganic azides and azido complexes

3.1. Free and protonated azide anion, and azide salts

Free anion N_3^- or hydroazoic acid HN_3 are involved predominantly in two kinds of photochemical and/or photophysical processes: the previously mentioned quenching of $^1\text{O}_2$, and the generation of the nitrene anion N^- .

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