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REVIEW ARTICLES

Progress in dynamic study on the triplet excited states and radical ions of DNA and its components*

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Abstract Progress in dynamic study on the triplet excited states and radical ions of DNA and its components is reviewed. It has been found that acetone is the only effective sensitizer for the study of the triplet excited states of DNA components. The transient absorption spectrum of guanyl radical cation resulting from the interaction of triplet acetone and DNA was observed directly, and the original evidence for selective damage of DNA by excited photosensitizer was obtained for the first time, which offered a new pathway for obtaining the main transient species of selective damage of DNA by photonucleases and illustrating initial oxidation mechanism of DNA via electron transfer.

Keywords: DNA, triplet excited state, radical cation, laser flash photolysis.

The triplet excited states of DNA components play a very important role in photophysical and photochemical processes of DNA. Many studies have been focused on the triplet excited states of DNA components for a long time[1—4]. Salet et al.[5, 6] obtained successfully the triplet-triplet (T-T) absorption spectra of triplet excited states of thymine and its nucleoside, nucleotide using laser flash photolysis through direct excitation in 1970s. After that, the study on triplet state behavior of DNA and its components was hampered by the very small yield produced by direct excitation[2, 3]. Utilizing acetone sensitization method, a breakthrough for the detection of T-T absorption spectra and triplet state kinetics of DNA components was made at our laboratory[7—11], and the triplet excited state behavior of DNA components has been studied systematically.

Photoinduced oxidation of DNA by the excited states of photosensitizers has attracted great interest[1, 3, 12]. Radical cations of DNA are the predominant transient species and the direct evidence for electron transfer photooxidation. However, in most studies the formation of radical anions of photosensitizaters has been ascribed as the only initial evidence of photooxidation via electron transfer reaction[13, 14]. Song et al.[15] investigated the dynamics of selective damage of DNA at the guanine moiety by triplet acetone and observed the laser spectrum of guanyl radical cations. Furthermore, the absorption spectra of both radical cations of DNA and its components and the radical anions of quinone photonuclease were obtained simultaneously from selective damage of DNA by photonuclease.

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1 Acetone——an appropriate photosensitizer for study of photoinduced transient species of DNA and its components

1.1 UV photochemistry of acetone

When acetone absorbs far UV light, the transition of $n\rightarrow\pi^*$ should occur ($\lambda_{max} = 266.5$ nm in aqueous solution). The transient species from UV laser photolysis of acetone aqueous solution is triplet acetone ($^3Ac^*$), and derives from intersystem crossing (ISC) of its singlet state.

$$^1Ac^* \xrightarrow{ISC} {}^3Ac^* \quad k_{ISC} = 3.8 \times 10^7\ s^{-1}. \tag{1}$$

$^3Ac^*$ decays via several pathways as follows,

$$^3Ac^* \rightarrow Ac \quad k_0, \tag{2}$$

$$^3Ac^* + Ac \rightarrow 2Ac \quad k_s. \tag{3}$$

T-T excitation transfer occurs in the presence of quencher molecule (M) with lower triplet energy, therefore

$$^3Ac^* + M \rightarrow Ac + {}^3M^* \quad k_T. \tag{4}$$

Triplet acetone decays according to pseudo-first-order kinetics, which is drawn out from eqs. (2), (3) and (4), namely

$$k_{obs} = k_0 + k_s[Ac] + k_T[M]. \tag{5}$$

When energy acceptor is absent and $[Ac] = 0.13\ mol\cdot dm^{-3}$, $k_{obs}(= k_0 + k_s[Ac]) = 3.1 \times 10^5\ s^{-1}$ is determined, thus $\tau_{1/2} = \ln 2/k_{obs} = 2.2\ \mu s$. Related photophysical parameters of $^3Ac^*$ are listed in table 1.

Table 1 Comparison of some triplet state properties* of nucleotide, acetone and benzophenone

Compounds	Φ_{ISC}	$\varepsilon_T/mol^{-1}\cdot dm^3\cdot cm^{-1}(\lambda/nm)$	$\tau_{1/2}/\mu s$	Absorption band/nm	$E_T/kJ\cdot mol^{-1}$
Ac	~0.5[18]	600 ± 100(300)*[19]	2.2	300—380	337[19]
Benzo	—	12 000(550)[17]	65 ± 6[17]	300—700[17]	286[19]
AMP	0.000 4[20]	3 850(470)[21]	9.5	300—700[21]	314[22]
CMP	0.001 5[20]	850(420)[21]	6.2	300—600[21]	321[22]
GMP	0.000 46[20]	13 200(380)[21]	5.6	300—700[21]	317[22]
TMP	0.008 0[20]	2 300(370)[21]	15.4	300—600[21]	310[22]

* Numbers in brackets are monitored wavelengths. a) Intersystem crossing quantum yield (Φ_{ISC}), extinction coefficient (ε_T), life time ($\tau_{1/2}$) and triplet energy (E_T).

1.2 Energy transfer between triplet acetone and DNA components

1.2.1 Excitation energy transfer. Whether or not the excitation energy transfers effectively from $^3Ac^*$ to DNA components only depends on the triplet energy gap, ΔE_T, and the energy transfer rate

constant can be obtained by the Sandros equation[16],

$$k_{ET}(\text{energy transfer}) = \frac{k_{max} e^{-\Delta E_T/RT}}{e^{-\Delta E_T/RT} + 1}, \quad (6)$$

where k_{max} is the maximum rate constant for the system, by which the equilibrium constant for forward energy transfer from $^3Ac^*$ to DNA components and reverse energy transfer from the triplet excited states of DNA components to Ac can be drawn out from eq. (6),

$$\Delta E_T = - RT \ln K. \quad (7)$$

If $\Delta E_T \geqslant 12$ kJ·mol^{-1}, $K \geqslant 127$ (from eq. (7)) and reverse energy transfer is negligible. The data in table 1 show that the triplet energy of acetone is 16 kJ·mol^{-1} and much higher than those of nucleotides. Therefore, the energy of excitation should transfer effectively from triplet acetone to the four nucleotides via T-T energy transfer.

The quantum yield of triplet acetone is 2—3 orders of magnitude higher than those of nucleotides (see table 1). The efficiencies of T-T energy transfer are 0.10—0.23 for thymine and its nucleoside, nucleotide[11], 0.72—0.81 for cytosine and its nucleoside, nucleotide[1]. Hence, the quantum yields of triplet states of DNA components should be enhanced to 1—3 orders of magnitude under acetone sensitization.

Triplet acetone only absorbs the light in the wavelength range 300—380 nm with small molar absorption coefficient and very short life time, thus facilitating the observation on absorption spectra of transient species of DNA components. These distinguished features make acetone-sensitized photolysis experiment and data processing more convenient. But aromatic ketones[17], such as benzophenone (Benzo), are different, namely, they possess low energy of triplet excited state (only can sensitize some bases and nucleosides), long life time and wide absorption band, see table 1.

1.2.2 Free energy change for electron transfer photooxidation. The free energy change (ΔG) for electron transfer between triplet acetone and DNA components can be calculated according to the Rehm-Weller equation:

$$\Delta G = 96.48(E_{ox} - E_{red} - e^2/\varepsilon d) - \Delta E_{0,0}, \quad (8)$$

where the coulombic term $e^2/\varepsilon d$ can be neglected in aqueous solution[23]. The calculated ΔG values are listed in table 2. It shows that an electron cannot transfer from pyrimidines to triplet acetone, but can transfer from purines to triplet acetone efficiently.

Therefore, there are competitive reactions between $^3Ac^*$ and purine components in photolysis of purine components in aqueous solution containing acetone: (i) T-T excitation transfer forming the triplet excited states of all DNA components; (ii) electron transfer producing radical cations of

1) Zuo, Z. H., Study on laser flash photolysis of cytosine, cytidine and dCMP in aqueous solution. MS Thesis: Shanghai Institute of Nuclear Research, Chinese Academy of Sciences, 1992.

Table 2 The free energy change of electron transfer between DNA components and $^3Ac^*$ [15,24]

DNA components	E_{ox}(SCE)/V	ΔG/kJ·mol^{-1}	DNA components	E_{ox}(SCE)/V	ΔG/kJ·mol^{-1}
Thymine	1.75[25]	54.2	Guanosine	1.05[27]	-13.5
Thymidine	1.63[25]	42.6	dGMP	1.04[28]	-14.3
Cytosine	1.20[26]	0.97	Adenine	1.08[26]	-10.4
Guanine	0.80[26]	-37.4	Adenosine	1.18[27]	-0.96

purine components. Consequently, acetone can be used as the triplet photosensitizer for all DNA components and it interacts selectively with purine components, resulting in the electron transfer oxidation of DNA. Furthermore, because the ΔG values for electron transfer from guanine to triplet acetone are smaller than that of adenine, it is expected that $^3Ac^*$ reacts predominantly with the guanine moiety of DNA.

2 Dynamic study of triplet excited states and radical ions of DNA components

The early studies on photochemistry of DNA components in aqueous solution at room temperature were focused on the separation and identification of photoproducts, while the dynamic study was performed predominately on photoionization using laser flash photolysis, and the observed transient absorption spectra were composed of a strong absorption of hydrated electrons in the visible region with λ_{max} around 700 nm and a weak one of the radical ions in UV band[1, 4].

2.1 Purine components

2.1.1 Guanine components. Kasama et al.[19] investigated the transient absorption spectra from laser photolysis of guanine derivatives using acetone as a photosensitizer, and observed T-T energy transfer from $^3Ac^*$ to 7-methylguanine, but not guanosine (Guo). No electron transfer from guanine derivatives to $^3Ac^*$ was recognized.

Jian et al.[7] studied the laser spectroscopy and kinetics of photochemical reactions of Guo aqueous solution under acetone sensitization. On the basis of detailed kinetic analysis and the estimation of the free energy change of the electron transfer reaction between Guo and triplet acetone, it was suggested, for the first time, that radical cations of Guo and the triplet Guo were produced via electron transfer and T-T excitation transfer respectively.

Song et al.[10] characterized laser-induced transient species of guanine (Gua), Guo and 2′-deoxyguanosine 5′-monophosphoric acid (dGMP) in aqueous solutions with three pH values. The transient species were assigned to the triplet states and the radical cations of Gua, Guo and dGMP (symbolized as G) from acetone sensitization via T-T excitation transfer and electron transfer respectively. In acidic or neutral aqueous solution, the two processes were competitive. The absorption peak of triplet state of G was 360 nm in acidic solution, 370 nm in neutral solution. The kinetic parameters of triplet state of G were determined in acidic and neutral solutions. The radical species in acid, neutral aqueous solutions were identified as radical cations and their deprotonated form[28, 31] respectively, which were characterized by a strong absorption peak at ~310 nm and another weak peak at ~390 nm. In alkaline solution, only electron transfer reaction occurred, and radical anions of G were formed, which was characterized by a strong absorption near 310 nm and another peak at 400 nm for

Gua radical anions, only a peak at 320 nm for Guo or dGMP radical anions. The mechanism of photochemical reaction and the structure of these radicals were elucidated.

2.1.2 Adenine components. Kasama et al.[19] studied the photochemical reactions of triplet acetone with adenine (Ade) or adenosine (Ado) using a KrF laser, and only weak transient absorptions were observed and ascribed to neutral radicals.

Li et al.[9] obtained transient absorption spectra of Ade, Ado and 2′-deoxyadenosine 5′-monophosphate (dAMP) produced upon 248 nm laser flash photolysis by acetone sensitization, and their λ_{max} values were 460 nm, 490 nm, 470 nm respectively. The kinetic parameters are listed in table 3. The deprotonated radical cations of Ade, Ado and dAMP produced by electron transfer oxidation were characterized by an absorption spectrum with λ_{max} at 330 nm. The detail mechanism of photochemical reaction was suggested. Gut et al.[21] determined and verified Li et al.'s results using a 308 nm laser flash photolysis, and suggested a similar mechanism.

The processes of protonation of $Ac^{\cdot -}$ (pKa − 2) and deprotonation of $Pur^{\cdot +}$ (pKa 3.9 for Guo, < 1 for Ade) should proceed very fast, thus the dissociation of geminate ions ($Ac^{\cdot -}$-$Pur^{\cdot +}$, vide infra) can occur simultaneously and be facilitated. We suggested the electron transfer processes between $^3Ac^*$ and purine components as follows[7, 9, 10, 15]:

$$^3Ac^* + Pur \rightarrow {}^3[Ac - Pur]^* \rightarrow [Ac^{\cdot -} - Pur^{\cdot +}] \rightarrow Ac(+H)^{\cdot} + Pur(-H)^{\cdot}$$

2.2 Pyrimidine components

2.2.1 Thymine components. The quantum yields of triplet excited states of thymine components (T) are the highest in DNA components, and their T-T absorption spectra can be observed by direct laser excitation. Therefore, the studies about triplet states of thymine components were mostly reported in DNA components.

Salet et al.[5] obtained the k_0, k_s values of triplet thymine (Thy) in acetonitrile by direct laser excitation, and afterwards the corresponding values of thymidine (Thd) in aqueous solution, thymidine 5′-monophosphate (TMP) in ethanol were also obtained[6]. These kinetic parameters were obtained from different solvents, thus could not be compared. No headway in the study had been made up to the beginning of 1990s[3].

Song et al.[11] obtained the transient absorption spectra and the kinetic parameters of the triplet states of thymine and its nucleoside, nucleotide from acetone sensitization in aqueous solution. The scheme of the formation and the decay can be displayed by eqs. (1)—(3), (9)—(11),

$$^3Ac^* + T \rightarrow Ac + {}^3T^* \quad k_T, \tag{9}$$

$$^3T^* \rightarrow T \quad k_0, \tag{10}$$

$$^3T^* + T \rightarrow 2T, T_2 \quad k_s, \tag{11}$$

where k_T is the rate constants of T-T energy transfer from $^3Ac^*$ to Thy, Thd and TMP, respectively,

and is obtained from eq. (5) since energy transfer is the only pathway for the interaction between $^3Ac^*$ and pyrimidine components. Furthermore, T-T energy transfer efficiency $\rho_T\left(=\frac{k_T[T]}{k_{obs}}\right)$ from $^3Ac^*$ to thymine components has been obtained. Meanwhile, the k_0, k_s values have been obtained by direct laser excitation. The rate constants from direct excitation are in reasonable agreement with those from acetone sensitization. Moreover, the advantages of acetone sensitization were clarified by the characteristics of triplet acetone and enhanced yields of triplet thymine components.

2.2.2 Cytosine components. Due to their low intersystem crossing quantum yields, short lifetimes and small molar absorption coefficients at room temperature, the information on the excited states of cytosine components is relatively rare. The transient absorption spectra of their triplet states had not been reported until Zuo et al.'s work[8].

Table 3 Kinetic parameters of triplet excited states of DNA components[a)]

DNA components	pH	$k_0\times10^{-5}/s^{-1}$	$k_s\times10^{-8}/dm^3\cdot mol^{-1}\cdot s^{-1}$	$k_q\times10^{-8}/dm^3\cdot mol^{-1}\cdot s^{-1}$ Mn^{2+}	Reference
Gua	1.0	1.4	3.9	1.8	[10]
Guo	1.0	1.2	1.5	1.4	[10]
	7.0	1.3	1.7	1.5	[10]
dGMP	1.0	1.0	1.2	2.3	[10]
	7.0	1.1	1.3	2.5	[10]
GMP	7	-	0.62	-	[21]
Ade	7.0	1.1	6.9	4.2	[9]
Ado	7.0	0.79	8.3	3.5	[9]
dAMP	7.0	0.37	3.6	6.0	[9]
AMP	7	-	3.3	-	[21]
Cyt	7.0	0.55	4.2	0.8	[8]
Cyd	7.0	0.76	2.4	2.5	[8]
dCMP	7.0	0.94	1.8	1.7	[8]
CMP	7	-	4.1	-	[21]
					[5][b)]
Thy	CH_3CN	1.0	6	-	[11]
	7.0	0.31	12	-	[6][b)]
					[11]
Thd	7	0.40	1	-	[11]
	7.0	0.50	2.8	-	[6][b)]
					[21]
TMP	7.0	0.42	0.30	-	
	C_2H_5OH	0.40	2.0	-	
	7	-	0.27	-	

a) Obtained from acetone sensitization by laser photolysis unless indicated else; b) obtained from direct photolysis.

Zuo et al.[8] carried out laser photolysis of cytosine (Cyt), cytidine (Cyd) and 2'-deoxycytidine 5'-monophosphate (dCMP) under acetone sensitization in aqueous solution, and the absorption spectra ($\lambda_{max}\leqslant320$ nm) of triplet Cyt, Cyd and dCMP were recorded. The molar absorption coefficients of triplet cytosine components were estimated as 200 $mol^{-1}\cdot dm^3\cdot cm^{-1}$ (340 nm) for Cyt, 200 $mol^{-1}\cdot dm^3\cdot cm^{-1}$ (350 nm) for Cyd and 400 $mol^{-1}\cdot dm^3\cdot cm^{-1}$ (450 nm) for dCMP, and the corresponding value of dCMP is very close to that of Gut et al.[21] Görner cited these results in his invited review[4].

3 Dynamic study of the mechanism of photooxidation of DNA via electron transfer

The radical cations of DNA bases are predominant transient species resulting from primary oxidizing damage of DNA by ionizing radiation, monophotonic or multiphotonic ionization, one-electron oxidizing agents and excited state of photosensitizer. However, only a few studies have reported the time-resolved spectroscopic evidence of electron transfer from nucleobases of DNA to excited states of photosensitizers[13, 14, 29].

Jovanovic and Simic[28] studied the DNA-guanyl radical cation from one-electron oxidation of single-stranded DNA by pulse radiolytically produced thallic ions (Tl^{2+}), which was found to oxidize ssDNA producing DNA-guanyl radical cation exclusively. In order to mimic the direct effect of ionizing radiation, Steenken et al.[31] obtained transient absorption spectrum of the radical cations of dinucleotide phosphate of G and A from monophotonic ionization by 193 nm light, which was very similar to that of guanyl radical cations[30]. The transient absorption spectra from photoionization of G-containing oligonucleotides by 193 nm light were similar to that of guanyl radical cations[32]. However, the transient absorption spectra from photoionization of DNA by 193 nm light were only somewhat similar to that from guanyl radical cations[33].

The laser flash photolysis study of transient intermediates was reported in the photocleavage of oligodeoxynucleotides by a photosensitizer, lysine derivative possessing a naphthalimide chromophore. The synchronization of growth of radical anions of lysine derivative with its triplet decay offered a time-resolved spectroscopic evidence for the electron transfer from a guanine base in duplex oligonucleotide to a triplet photosensitizer for the first time[13]. Breslin and Schuster's[13] investigation of photooxidation of DNA by excited states of anthraquinone derivatives obtained similar results. However, the elucidation of the electron transfer mechanism for interaction of excited photosensitizer and DNA is still restricted to the formation of radical anions of photosensitizer due to the failure of direct observation of radical cations of DNA.

For the first time, Song et al.[15] reported a time-resolved spectroscopic and kinetic evidence for the photosensitized selective modification of DNA at guanine moiety by triplet acetone.

In the laser photolysis of DNA components under acetone sensitization, triplet acetone only interacts with purine components, and generates purinyl radical cations. Moreover, on the basis of a remarkable similarity of the transient absorption spectra of the radical species produced from the interaction of triplet acetone with ssDNA to those of dGMP, Poly[G] and Poly[A,G], and the rate constant of interaction of triplet acetone with polyG is one-order of magnitude higher than that with Poly[A]. It is concluded that the predominant species produced in Poly[A, G], and ssDNA are guanyl radical cations, Poly[A, G]-$G^{\cdot+}$, and ssDNA-$G^{\cdot+}$.

Our results of acetone sensitization of polynucleotide are in agreement with the sensitizer-nucleotide work by Gut et al.[21] In their laser flash photolysis studies, the efficient chemical quenching of triplet sensitizer by nucleotides was obtained even when energy transfer was not observed. The rate constants of sensitizer-nucleotide reaction for the systems in which no energy transfer occurs are much higher for GMP, which are comparable with our efficient chemical quenching of triplet acetone by

polynucleotide, i.e. the highest reactivity is obtained from Poly[G] in particular.

Our results of acetone modification of ssDNA at guanine moiety are also in good agreement with alkaline-labile lesions of DNA fragment at guanine site, when DNA was irradiated with 313 nm light in the presence of acetone[34]. The alkaline-labile product may represent the additional product produced from the substitution of the hydrogen atoms on guanine moiety by ketyl radical. Additionally, the guanine photoproducts of this type have been implicated as premutagenic DNA lesions.

A study by Epe et al.[35] showed that the photochemical modification of DNA by acetone resulted in the formation of substitution products including 8-hydroxyguanine. The latter may be a final product from electron transfer oxidation of guanine moiety by triplet acetone.

Wood and Redmond's studies on the fate of the triplet state of bases in DNA have indicated that the triplet-mediated electron transfer from purine to pyrimidine is the predominant route for enhanced purine radical formation[22]. The most efficient interbase electron transfer from guanine to cytosine results in the enhancement of guanine radical formation[36]. Thus, the interbase electron transfer route may be an additional pathway for acetone sensitization of DNA at guanine moiety.

In short, our work dealt with transient spectroscopy and kinetics of DNA polynucleotides under acetone sensitization has demonstrated that the predominant species from chemical quenching of triplet acetone by DNA and Poly[A,G] are guanyl radical cations. These novel findings have offered spectroscopic and kinetic evidences for photochemical selective modification of DNA and Poly[A,G] at the guanine moiety for the first time[15]. The investigations on selective photocleavage of DNA by quinone photonuclease[37], anthroquinone-2-sulfonate and 2-methyl-1,4-naphthaquinone have acquired, for the first time, the transient spectra and kinetic parameters of initial radical ion pairs from electron transfer oxidation of four kinds of DNA components. Additionally, the rate constants and free energy changes of the electron transfer reaction display that the highest reactivity is obtained from guanine components. Furthermore, the transient spectra and kinetic parameters of radical cations of DNA and radical anions of quinone photonuclease have also been obtained[1)]. Thus, the initial process of long range migration and localization of excited holes on guanine sequence has been illustrated.

4 Concluding remark

The time resolved study of interaction of laser induced triplet acetone with DNA components has made two original contributions to the bioorganic photochemistry. First, the acetone sensitized excitation of DNA components offered a complete set of transient absorption spectra and kinetic parameters of DNA bases, nucleosides and nucleotides, which have been confirmed by Gut and Redmond[21] of Wellman Laboratories of Photomedicine. Thus, the systematic study of laser spectroscopy and kinetics of triplet DNA components has been fully achieved. Secondly, the reaction mechanism for electron transfer oxidation of purine components by triplet acetone and the produced radical cations have also been identified. Furthermore, the spectroscopic and kinetic evidences for electron transfer oxidation of

1) Lin Nianyun, Progress in laser photolysis study of radical cation of DNA, Report on China Congress of Photophysics of High Intensity Light in 1998, Wushi, Jiangsu, November 2—4, 1998.

DNA at guanine moiety have also been obtained. In short, our studies regarding acetone sensitization of DNA components offered a good example for studying competitive triplet energy transfer and electron transfer reactions in the field of bioorganic photochemistry, and have further confirmed and developed the basic principle of "three transfer mechanisms of radioprotection and radiosensitization"[38].

The intensive studies of photocleavage of DNA by photonuclease have demonstrated that the electron transfer oxidation depends on base sequence. An insight into the photosensitized damage at base sequence level should assist in the illustration of detailed mechanism of selective photocleavage. Artificial photonuclease[29, 39—42] can be used for blocking of oncogene expression via electron transfer oxidation of DNA at its homopurine sequence, which reveals the bright prospects for application to biology and medicine, such as for therapeutic application to genetic disorder.

Molecular orbital calculations[41] have predicted that the ionization potential of stacked homoguanine decreases with increasing number of stacked base sequence ($-G_n-$), which has been identified as the specific localization site of photoexited holes from long range electron transfer oxidation of DNA[39]. The time-resolved studies on photocleavage of DNA by triplet acetone and triplet quinone photonuclease have attained novel achievement of direct observation of primary radical ion pairs from photooxidation of DNA, which opens a new pathway to fully elucidate the electron transfer oxidation mechanism.

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