COMMENTS

Comment on "New Assignment of the Electronically Excited States of Anthracene-9,10-endoperoxide and Its Derivatives: A Critical Experimental and Theoretical Study"

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Very recently Klein, Kalb, and Gudipati published a paper concerning the assignement of the electronically excited state leading to the cycloreversion of anthracene-9,10-endoperoxide (APO) and of 9,10-dimethylanthracene-9,10-endoperoxide (DMAPO).[1] According to their low temperature Ar-matrix investigation, and in agreement with our previous work,[2] it was found that cyloreversion takes place from the lowest excited $\pi\pi^*$ singlet state. The semiempirical calculations performed indicated that below this state no further excited singlet state should exist. Thus, it was concluded that cycloreversion occurs from the S_1 state.[1] Our previous assignment, whereafter the S_1 state of these endoperoxides corresponds to the $\pi^*\sigma^*$ transition of the peroxide chromophore and S_2 to the lowest excited $\pi\pi^*$ singlet state, which implies that cycloreversion occurs from an upper excited singlet state, was qualified to be wrong. Furthermore, generalizations that the photocycloreversion of other aromatic endoperoxides not containing carbonyl groups proceeds from upper excited singlet states were also said to be wrong.

Already in 1979 Rigaudy et al. reported the dual photochemistry of the endoperoxide of 9,10-diphenylanthracene (DPAPO).[3] Irradiation at $\lambda_{irr} = 254$ nm leads to cycloreversion forming 9,10-diphenylanthracene (DPA) and O_2, whereas irradiation into the weak tail absorption above 350 nm mainly leads to rearrangement following the initial homolytic rupture of the peroxide bridge of DPAPO. Shortly later we quantitatively investigated the photochemistry of DPAPO.[4] We found that the photocycloreversion of DPAPO proceeds adiabatically under formation of singlet oxygen. The quantum yield of cycloreversion of DPAPO is constant $Q_c = 0.28$ for excitation of the $\pi\pi^*$ band and decreases for $\lambda_{irr} > 295$ nm with increasing λ_{irr}. At $\lambda_{irr} = 330$ nm Q_c amounts to only 0.009. Irradiation at $\lambda_{irr} = 330$ nm principally initiates the rearrangement reaction which takes place with the rather large quantum yield $Q_H = 0.08$ determined via the irreversible consumption of DPAPO. At $\lambda_{irr} = 330$ nm the photon energy corresponds to 30300 cm^{-1}, which is by 6000 cm^{-1} smaller than the excitation energy of the first vibrational structure of the $\pi\pi^*$ band of DPAPO.[4] Since irradiation with photons of 30300 cm^{-1} still leads to the consumption of DPAPO, the very broad, structureless, and weak tail absorption must be an integral part of the DPAPO absorption spectrum. The corresponding extinction coefficient ϵ ($M^{-1}cm^{-1}$) increases approximately exponentially with the photon energy and amounts to about 1 at 26000 cm^{-1} and to about 10 at 31000 cm^{-1}.[4] By comparison with the spectra of alkylperoxides and dioxetanes we assigned this weak tail absorption the $\pi^*\sigma^*$ transition of the peroxide chromophore of DPAPO. For example, the absorption spectrum of di-tert-butylperoxide (DTBPO) shows on the low energy side a prominent shoulder with $\epsilon \approx 5$ at about 260 nm. At 310 nm ϵ still amounts to 1. This band is assigned to the $\pi^*\sigma^*$ absorption of the peroxide chromophore.[5] The broadness and the lack of structure indicates the repulsive character of the $\pi^*\sigma^*$ singlet state. Excitation at 254 nm leads to O−O bond homolysis with quantum yield $Q_H = 1.0$.[5] The absorption of the cyclic peroxide tetramethyldioxetane (TMD) is red shifted. Its maximum lies with $\epsilon = 24$ at 280 nm. The absorption even extends into the visible range.[6] At 400 nm ϵ amounts to about 1. The corresponding $\pi^*\sigma^*$ singlet state has again repulsive character. Excitation leads with high quantum yield to bond cleavage and formation of acetone.[6] Because of the similarities of these spectra of typical open-chain and cyclic peroxides with the broad, structureless and weak tail absorption of DPAPO, we conclude that this band of DPAPO is due to the transition to the $S_1(\pi^*\sigma^*)$ state of the peroxide chromophore.[2,4] Due to the broadness and weakness of this band only an estimate of the $S_1(\pi^*\sigma^*)$ excitation energy of about 23000 cm^{-1} could be given.[2] Similar spectral and photochemical results as for DPAPO had been obtained for APO and DMAPO,[2] and for other aromatic endoperoxides without,[7−13] or with ether or carbonyl groups,[14−17] leading us to the conclusion that photocycloreversion of aromatic endoperoxides generally proceeds from upper excited $\pi\pi^*$ singlet states, whereas O−O homolysis with subsequent rearrangement occurs from $S_1(\pi^*\sigma^*)$.

The semiempirical calculations of Klein, Kalb and Gudipati gave no indication of a low lying $\pi^*\sigma^*$ singlet state. However, they resulted in low energy triplet states around 21000 cm^{-1} (INDO/S) or 27000 cm^{-1} (CNDO/S). Actually, a heavy-atom-enhanced absorption band with a maximum value of $\epsilon \approx 3$ at 21000 cm^{-1} was found with DMAPO in C_2H_5I. It was therefore proposed by these authors that the homolytic O−O bond cleavage of these endoperoxides should occur in the triplet manifold, whereas cycloreversion should occur from the $S_1(\pi\pi^*)$ state.[1]

This interpretation is in severe conflict with the finding that rearrangement also takes place, if the $\pi\pi^*$ states of APO, DMAPO, or of other endoperoxides are excited.[2,7,8,10,18] For example, irradiation at 270 nm into the $\pi\pi^*$ band leads to rearrangement with quantum yield 0.75 for APO and 0.22 for DMAPO, whereas cycloreversion takes place with quantum yield 0.22 for APO and 0.35 for DMAPO.[2] It has been shown that photocyloreversion of endoperoxides occurs as a two step reaction,[19−21] whereby the best measurements indicate that the rupture of the first C-O bond occurs in less than 350 fs.[21] If cycloreversion would take place from $S_1(\pi\pi^*)$ and rearrangement from the triplet manifold, intersystem crossing would have to occur in much less than 1 ps to be consistent with these results. Such fast intersystem crossing is unknown for light-atom compounds. Efficient competition of rearrangement and cycloreversion upon excitation of a $\pi\pi^*$ singlet state is only possible, if the deactivation to the state of lower energy, from which rearrangement occurs, is very fast, i.e., spin allowed. Therefore, the lowest $\pi\pi^*$ singlet state must be the S_2 state.

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Thus, our conclusion that cycloreversion of these endoperoxides occurs from an upper excited singlet state is not disproved by the work of Klein, Kalb and Gudipati, but correct. The above discussed spectral and photochemical similarities of the peroxide chromophores of DTBPO and TMD with APO, DMAPO and DPAPO strongly indicate that the lowest excited singlet state, from which homolytic cleavage of the O−O bond and subsequent rearrangement occurs, has $\pi^*\sigma^*$ character.

The result that the semiempirical calculations of Klein, Kalb, and Gudipati gave no indication of a low lying $\pi^*\sigma^*$ singlet state is actually astonishing considering the existence of the weak tail absorption bands of APO, DMAPO, and DPAPO. Further support of our spectral data has been given by the group of Rigaudy, which recorded in the 300 to 400 nm range a very similar absorption spectrum of APO like the one published in ref 2.[22] We are somewhat surprised why Klein, Kalb, and Gudipati neither performed calculations on peroxides such as DTBPO or TMD, to test their semiempirical methods with respect to the excited states of peroxide chromophores, nor investigated experimentally the weak tail absorption bands of APO, DMAPO, or DPAPO. It is true that these bands can easily be disturbed and overlapped by the strong absorption bands of the parent aromatic hydrocarbons being present as contaminations. However, the preparation procedures of highly purified endoperoxides have been published.[2,4] The residual contamination of DPAPO by DPA can, for example, be as low as 3ppm.[4]

In our further extended investigations of this dual and state selective photochemistry we found that for the endoperoxides of several other aromatic hydrocarbons not containing carbonyl groups, e.g., of 1,4,9,10-tetraphenylanthracene,[8] of tetracene, 9,10-diphenyltetracene and rubrene,[9] of tetrabenzopentacene,[10] of mesodiphenylhelianthrene,[11] of 1,4-dimethyl-1,9-diphenylanthracene,[12] and of 1,2,3,4-teramethylanthracene and 1,2,3,4-teramethyl-9,10-diphenylanthracene,[13] the quantum yield of cycloreversion significantly depends on λ_{irr} in the wavelenth range of $\pi\pi^*$ singlet states. These results demonstrate that cycloreversion originates for these endoperoxides not only from the lowest excited $\pi\pi^*$ singlet state but even from higher excited $\pi\pi^*$ singlet states. Thus, our finding that the photocycloreversion of other aromatic endoperoxides not containing carbonyl groups proceeds from upper excited singlet states is correct, in contrast to the assertions of Klein, Kalb, and Gudipati. Only for reasons of completeness it should be mentioned that cycloreversion of enoperoxides also occurs upper excited $\pi\pi^*$ triplet states, as was first shown by Stevens and Glauser.[23−25]

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References and Notes

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