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

Murthy S. Gudipati* and Andreas Klein

Institut für Physikalische Chemie, Universität zu Köln,
Luxemburger Strasse 116, D-50939 Köln, Germany

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The first paragraph of the comment by Brauer and Schmidt[1] summarizes our recent publication[2] on the spectroscopy of APO and DMAPO. In the second paragraph these authors gave a nice summary of the historical development that lead to the assignment that in endoperoxides, whether aromatic or aliphatic, the first excited singlet state (S_1) should be of $\sigma^* \leftarrow \pi^*$ character involving the dioxygen bridge of the endoperoxide. Our results were in contradiction with the above assignment. According to our experimental and theoretical results, in APO and DMAPO the first excited singlet state does not have $\sigma^* \leftarrow \pi^*$ character. In our assignment the S_1 state is the S_2 state of the earlier assignment for APO and DMAPO.

Before going further, we would like to touch upon an important aspect of photochemistry. Photochemical reactions from higher excited states, which lead to either different kinetics or different product channels or different electronic states of the products than those reaction products from the first excited state of a given multiplicity, are not unusual but rather common, especially in diatomic and triatomic molecules like O_2, CO_2, O_3, etc. Thus, photochemistry from higher excited states in medium-sized molecules like endoperoxides is not surprising either. However, connecting higher excited state photochemistry to Kasha’s rule[3] is not appropriate and such processes are not exceptions to Kasha’s rule. We have clearly stated to this extent in the introduction of our paper[2] (thanks to one of the referees of our paper to point out this important aspect). Thus, if we gave an impression in the latter part of our paper that higher excited state photochemistry of endoperoxides should not occur, then we want to put our records straight.

Our assignment that the first excited singlet state of APO and DMAPO should be the 1^1B_2 state located at 36360 cm^{-1} in DMAPO is based on the semiempirical predictions that are in excellent agreement with the experimental data. These are as follows: nearly one-to-one correspondence between the predicted and observed energies of the singlet states between 36000 and 62000 cm^{-1} (Figures 2 and 3 in ref 2), excellent agreement between the predicted and experimentally derived oscillator strength of the band at 47000 cm^{-1} due to the 2^1B_2 state of APO (Figure 3 in ref 2), observed and predicted triplet←singlet transition around 21000 cm^{-1}, excellent agreement between the electronic states of APO and its isoelectronic molecule 9,10-dihydro-9,10-ethanoanthracene (EA) (Figure 7 in ref 2), and successful application of exciton-model to interpret the electronic states (singlet and triplet) of APO and EA. If a better and reliable theoretical method can predict the above mentioned spectroscopic features equally well and additionally show that the lowest excited singlet state in APO and DMAPO has $\sigma^* \leftarrow \pi^*$ character involving the dioxygen bridge, then we will be more than glad to withdraw our assignment.

The comparison between nonaromatic endoperoxides like CPO (cyclopentadiene endoperoxide) with aromatic endoperoxides like APO with respect to their spectroscopic behavior is, as we believe, not correct. The main reason is the existence of several occupied MOs of π character from the aromatic units that lie at higher energies than the MO that contains the π^* orbitals of the dioxygen bridge. Similarly, several virtual MOs of the aromatic units lie energetically below the MO that has a significant contribution from the σ^* orbitals of the dioxygen bridge. Thus, only the HOMO-4 has the π^* orbitals of the dioxygen bridge and LUMO+5 has the σ^* orbitals of the dioxygen bridge in APO. On the other hand, in CPO, already the HOMO-1 and LUMO+1 have a significant π^* and σ^* character from the dioxygen bridge, respectively. Thus, it is highly likely that in nonaromatic endoperoxides the $\sigma^* \leftarrow \pi^*$ transitions govern the low-lying excited states. However, in APO and DMAPO this is not the case.

In our laser photolysis experiments of matrix isolated APO and DMAPO at 275 nm, we have not observed any other product than the cycloreversion product, namely, anthracene and DMA, respectively. These results are indeed in contradiction with the results obtained by Brauer and coworkers[4] in the solution environment. This indicates that the environment in which APO/DMAPO exists has also an important role to play. It is possible that after excitation of APO/DMAPO around 275 nm, an intermediate is formed that either leads to photocycloreversion or competes with photocycloreversion. This intermediate may undergo rearrangement in solution. However, due to the matrix cage and due to negligible solute−solvent interactions, in Ar matrices this intermediate may get deactivated back to APO/DMAPO. Thus, in our matrix experiments the photochemical yields of cycloreversion are close to 100%, in consistence with the oscillator strengths derived from the absorption spectra (Figure 3 in ref 2).

We proposed an alternative way of interpreting the dual-photochemistry of DPAPO reported by Rigaudy et al.[5], who observed photocycloreversion as the major channel when irradiated at shorter wavelengths than 280 nm and O−O bond cleavage when irradiated at longer wavelengths than 280 nm. We stated that the photocycloreversion should occur from the S_1 state and O−O bond cleavage from the triplet manifold (according to our assignment). Our statement is aimed at explaining the major channels of photochemistry in DPAPO rather than to imply that only one channel of photoreaction is active for below 280 nm and only one channel for above 280 nm irradiation. Thus, our statement is not in contradiction with the observations of Brauer and co-workers[4] as well as the femtosecond reaction dynamics mentioned by Brauer and Schmidt in their comment.[1]

We need to shift thinking from a static picture that we use to deal with vertical electronic transitions (within Born-Oppenheimer approximation) to evolution of the electronic states with time, the dynamical aspects, when trying to understand and explain photochemistry. After initial electronic excitation, the electronic states evolve with time through changes in nuclear coordinates. Along this evolution, the electronic states and their energies need not follow their original order at the time of vertical excitation. Energetically higher states may become low-lying states and vice versa. On the multidimensional potential

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* Corresponding author. E-mail: murthy.gudipati@uni-koeln.de.

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hypersurface of these electronic states of endoperoxides (we limit our proposal only to APO and DMAPO), the first C-O bond breakage (that may occur within 350 fs[6]) may happen at a region where higher singlet state(s) already have crossed the first excited singlet state. Unfortunately, there is too little theoretical information at hand to speak of these reaction dynamics. Hence we prefer not to speculate further. Thorough theoretical treatment of this problem is necessary.

Finally, the broad absorption tail of endoperoxides at longer wavelengths than the first and rather sharp absorption band around 280 nm needs to be commented. Our experiments under matrix-isolated conditions were carried out at high dilutions. In fact, subliming APO and DMAPO to get enough substance into the Ar matrix without thermal decomposition was a significant achievement. Due to high dilutions and small amount of the substance, our absorption spectra are not accurate enough to see this long wavelength absorption tail. According to Brauer and Schmidt,[1,4] the extinction coefficient (ϵ) of the absorption tail ranges between 1 and 15 for APO, DMAPO and DPAPO. Such a weak absorption need not necessarily originate from a singlet excited state of the isolated molecule. We speculate over a few possibilities. Coupling of the triplet states with strongly allowed singlet states and thus gaining more one-photon allowed character. Due to rather high dipolemoment of these molecules (for example, according to ab initio calculations dipolemoment of APO in the ground state is 4.48 D) formation of complexes with the solvent, when the solvent has halogen or oxygen atoms or when the solvent is polar is highly probable; in nonpolar solvents a part of these molecules may aggregate and form dimers. In all these cases one can expect a weak longer wavelength absorption tail.

We conclude our reply as follows. According to the theoretical interpretation of our spectroscopic data under matrix-isolated conditions at 22 K, the lowest excited singlet state of APO and DMAPO is located at around 36000 cm^{-1}. Its symmetry is $^1B_2$ and the transition into this state has $\pi^* \leftarrow \pi$ character involving the aromatic units. Reliable potential energy surfaces of the excited states (both singlet and triplet) at ab initio level are necessary to understand how these states evolve to the states of the product(s). We believe that the generalization of the spectroscopic/photochemical properties of nonaromatic and aromatic endoperoxides may not be appropriate.

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References and Notes

(1) Brauer, H.-D.; Schmidt, R. *J. Phys. Chem. A.* **1999**, *103*, 164 and references therein.

(2) Klein, A.; Kalb, M.; Gudipati, M. S. *J. Phys. Chem. A* **1999**, *103*, 3843.

(3) Kasha, M. *Discuss. Faraday Soc.* **1950**, *9*, 14.

(4) Schmidt, R.; Schaffner, K.; Trost, W.; Brauer, H.-D. *J. Phys. Chem.* **1984**, *88*, 956.

(5) Rigaudy, J.; Breliere, C.; Scribe, P. *Tetrahedron Lett.* **1978**, (7), 687.

(6) Ernsting, N. P.; Schmidt, R.; Brauer, H.-D. *J. Phys. Chem.* **1990**, *94*, 5252.