ON THE USE OF 9,10-DIMETHYLANTHRACENE AS CHEMICAL RATE CONSTANT ACTINOMETER IN SINGLET MOLECULAR OXYGEN REACTIONS

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SUMMARY

Time resolved near IR luminescence detection of singlet oxygen, $O_2(^1\Delta_g)$, and steady-state photolysis experiments were performed to study in detail limitations and approaches involved when 9,10-dimethylanthracene (DMA) is used as actinometer to measure the chemical rate constants, k_r, for the reaction between excited oxygen and a given substrate. Our results show that in solvents in which singlet oxygen lifetime is long, the actinometer opens an additional pathway to the singlet oxygen disappearance at a rate of similar magnitude to the decay rate constant of $O_2(^1\Delta_g)$, k_Δ. This reactive pathway decreases singlet oxygen concentration. In this case erroneous values of the chemical reaction constant, k_r^M, for the reaction between singlet oxygen and a given substrate M will be obtained. Additionally, we have found that not in all the solvents, can the total rate constant, k_T^{DMA}, for the reaction between singlet oxygen and 9,10-dimethylanthracene obtained from time resolved experiments be taken as the "reactive" rate constant, k_r^{DMA}, when DMA is employed as an actinometer. The chemical reaction constant, k_r^M, for the reaction between singlet oxygen and a given substrate M obtained in these conditions will be smaller than the true values. Then, to employ DMA as actinometer, k_T^{DMA} and k_r^{DMA} must be previously evaluated. If k_T^{DMA} and k_r^{DMA} values are very close, nearly ideal conditions to employ DMA as actinometer are fulfilled. Moreover, if k_T^{DMA} and k_r^{DMA} differ in a greater extent, further corrections must be applied to improve k_r^M values.

KEYWORDS: 9,10-Dimethylanhracene, Singlet Oxygen, Actinometry, Photo-oxidations, Chemical Rate Constant.

RESUMEN

Se utilizaron experimentos de fotólisis en condiciones estacionarias y detección resuelta en el tiempo de la luminiscencia IR del oxígeno molecular singulete, $O_2(^1\Delta_g)$, para estudiar en detalle las limitaciones y aproximaciones involucradas en el uso del 9,10-dimetilantraceno, DMA, como actinómetro para medir constantes de reacción química entre el oxígeno excitado y un determinado sustrato. Nuestros resultados muestran que en aquellos solventes en los que el tiempo de vida del oxígeno molecular singulete es largo, la presencia del actinómetro abre un camino adicional para la desaparición del $O_2(^1\Delta_g)$, cuya velocidad es de similar magnitud a la constante de velocidad de decaimiento, k_Δ, del oxígeno singulete en el mismo solvente. Esta vía reactiva disminuye la concentración estacionaria del $O_2(^1\Delta_g)$. En estos casos, se obtendrán valores erróneos de la constante de reacción química, k_r^M, para reacciones entre el oxígeno excitado y un sustrato dado M. Además, se encontró que en no todos los solventes es posible considerar la constante de velocidad total, k_T^{DMA}, para la reacción entre 9,10-dimetilantraceno y oxígeno singulete, obtenida de experimentos resueltos en el tiempo, como la constante de velocidad "reactiva" cuando el DMA se emplea como actinómetro. Las constantes de reacción química, k_r^M,

obtenidas en estas condiciones, para la reacción entre oxígeno molecular singulete y el sustrato M, tendrán valores menores que los verdaderos. Luego, para emplear DMA como actinómetro, se deben evaluar previamente k_T^{DMA} y k_r^{DMA}. Si los valores obtenidos son muy similares, se dan condiciones muy cercanas a la situación ideal para utilizar este actinómetro. Por el contrario, si los valores de k_T^{DMA} y k_r^{DMA} son sustancialmente diferentes, se deben aplicar las correcciones apropiadas para obtener valores de k_r^M más exactos.

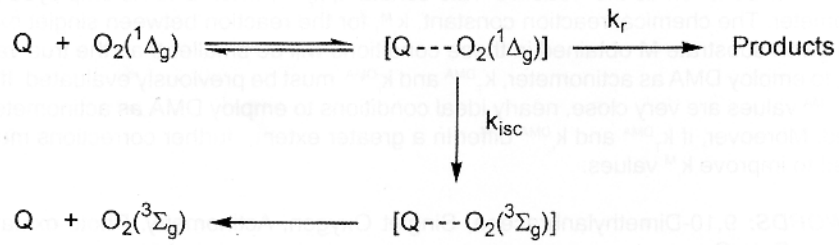
PALABRAS CLAVES: 9,10-Dimetilantraceno, Oxígeno Singulete, Actinometría, Fotooxidaciones, Constantes de Velocidad de Reacción Química.

INTRODUCTION

Reactions of singlet oxygen, $O_2(^1\Delta_g)$, with organic and/or biological substrates have been a subject of major research effort over the last three decades, mainly due to the role that these reactions play in biological systems.[1-6] Quenching processes may be physical or chemical in nature and in living systems they would be related to biological protection or biological damage, respectively. Singlet molecular oxygen reactions are generally non-diffusion-controlled processes, and the extent of the reaction in homogeneous solution depends on the $O_2(^1\Delta_g)$ steady-state concentration and on the bimolecular rate constant. In a complex biological system, the $O_2(^1\Delta_g)$ steady-state concentration near the reactive substrate and the bimolecular rate constant expressed in terms of local concentrations must be considered. The mechanistic aspects of such reactions have been thoroughly reviewed. It is accepted that reactions of $O_2(^1\Delta_g)$ in general occur according to the mechanism summarized in Scheme 1.[7,8]

Scheme 1 shows that both processes, physical quenching and chemical reaction proceed via the intermediacy of an exciplex formed rapidly and reversibly.

Scheme 1



In the pre-equilibrium limit, the experimental total rate constant for the quenching process ($k_T^{exp} = k_P + k_Q$, where k_P and k_Q accounts for the chemical reaction and the physical quenching, respectively) is currently obtained in most solvents, with the aid of infrared luminescence detection systems, by observing the effect of the quencher on the lifetime of the singlet oxygen in time resolved experiments.[9,10]

However, measurements of rate constants for chemical reaction inevitably involve steady-state photolysis conditions.[9,10] To obtain the chemical rate constant from these experiments, it is necessary to use a reference compound that reacts with singlet oxygen at a previously determined rate. The use of an actinometer allows to take into account singlet oxygen stationary concentration, which depends on the sensitizer employed and its concentration, on light intensity and on the system geometry. An ideal actinometer must meet several requirements to obtain reliable values of k_r: i) the absorption spectra of actinometer and sensitizer must not overlap; ii) basal and excited state interactions between actinometer and substrate must not occur; iii) the reaction between the actinometer and $O_2(^1\Delta_g)$ must be only chemical in nature and physical quenching must be negligible (the reaction products must be non-reactive in the reaction conditions, i.e. back reaction does not occur and the products does not react with the actinometer

and/or singlet oxygen); and iv) the presence of the actinometer must not modify the singlet oxygen steady-state concentration. A large number of compounds have been employed as actinometer to evaluate chemical reaction rates in processes involving singlet molecular oxygen.[9,10] Nevertheless, in many experiments actinometer requirements are not completely fulfilled. In general, only the two first points are considered, but not the last ones.

In this study we discuss in detail limitations and approaches involved when 9,10-dimethylanthracene (DMA) is used as actinometer to evaluate $O_2(^1\Delta_g)$ steady-state concentration in experiments leading to measure k_r for the reaction between excited oxygen and a given substrate. Our results can be applied to other molecules employed as reference compounds in this type of reactions performed under similar experimental conditions.

EXPERIMENTAL

The compounds 9,10-dimethylanthracene (DMA), 1,3-diphenylisobenzofurane (DPBF) and 5,10,15,20-tetraphenyl-21H,23H-porphine (TPP) (*Aldrich Chemical Co.*) were used without further purification. All the solvents used (*Merck*) were of spectroscopic or HPLC quality.

UV - VIS absorption spectra and steady state kinetic experiments were performed in a *Unicam UV - 4* spectrophotometer interfaced with a *DTK* personal computer. The cell holder was maintained at 22 ±0.5 °C by circulating water from a Haake thermoregulated bath.

The chemical reaction rate constant for the reaction between DMA and singlet oxygen was determined by irradiation of solutions of appropriate concentration in a 1 cm spectrophotometer cuvette fit in a cell holder equipped with a filter support that allows irradiation with light of a selected wavelength by using a *Shott* cut-off filter. The cell holder was thermostated by circulating water at 22 ± 0.5 °C. TPP was employed as a sensitizer. Illumination was performed with a visible, 200 W, Par lamp. The distance between the light source and the cell was set for each experiment so that the initial substrate concentration would diminish about 50% in 15 min. In these experiments DMA consumption was evaluated by observing the decrease in the absorbance of DMA. 1,3-Diphenylisobenzofurane was employed to evaluate the steady-state concentration of O_2 ($^1\Delta_g$). 1,3-Diphenylisobenzofuran solutions daily prepared in a dark room and an appropriate cut-off filter were used in these experiments. Autooxidation of this compound, measured using UV-VIS spectrophotometry, was lower than 1% under our experimental conditions.

Time resolved phosphorescence measurements were carried out in 1 cm-path fluorescence cuvettes. TPP excitation was by absorption of the 500-ps light pulse of a *PTI model PL-202* dye laser (419 nm, ca. 200 μJ per pulse). A *PTI model PL-2300* nitrogen laser was employed to pump the dye laser. A liquid nitrogen-cooled *North Coast model EO-817P* germanium photodiode detector equipped with a built-in preamplifier was used to detect infrared radiation emitted from the cuvette. The detector was coupled to the cuvette in right-angle geometry. The only elements between the cuvette face and the diode cover plate were an interference filter (1270 nm, *Spectrogon US, Inc.*) and a cut-off filter (995 nm, *Andover Corp.*). The output of the preamplifier was fed into the MΩ input of a *Hewlett Packard model 54540 A* digitizing oscilloscope. Computerized experiment control, data acquisition and analysis were performed by means of a LabView based software developed in our laboratory.

RESULTS AND DISCUSSION

The most widely employed actinometer, which can be considered as the "universal" actinometer to monitor $O_2(^1\Delta_g)$ generation in experiments performed under continuous illumination, is 1,3-diphenylisobenzofuran.[11-19] Due to DPBF is highly reactive and completely traps photogenerated singlet oxygen, it does not accomplish requirement iv). Otherwise, depending on the media and reaction conditions, other types of compounds such as furane derivatives,[20-28] olefins,[29-36] compounds of biological interest (e.g. bacteriochlorophyll,[37] carotene,[33] bilirubin,[38] cholesterol,[39] histidine,[40-43] methionine,[44-47]) and aromatic policyclic hydrocarbons,[29, 48,49] are used as actinometers. In the last group of compounds, the most currently employed are anthracene derivatives, mainly 9,10-dimethylanthracene.[29, 41, 44-46, 48, 50-54]

To obtain chemical rate constants, k_r, for reactions between singlet oxygen and a given substrate, M, under steady-state conditions, substrate consumption is monitored using a reliable analytical procedure, frequently UV-VIS spectrophotometry, GLC or HPLC. Normally, experimental set-up is established so that data will fit a pseudo-first-order kinetics, with an experimental rate constant that includes $O_2(^1\Delta_g)$ stationary concentration. As mentioned previously, in order to determine absolute values of k_r, from the experimental measured values, a reference compound must be used. It must be a very effective actinometer that traps all the generated singlet oxygen or an actinometer whose chemical rate constant with $O_2(^1\Delta_g)$ is previously known.

In these conditions (Type I processes excluded), and in the presence of a substrate M, the photosensitized production of singlet oxygen and its different pathways of decay can be represented by the equations included in Scheme 2:

Scheme 2

Photoexcitation of sensitizer	$\text{Sens} \xrightarrow{I_a} \text{Sens}^*$	(1)
Quenching by oxygen	$\text{Sens}^* + {}^3O_2 \xrightarrow{k_{S\Delta}} {}^1O_2 + \text{Sens}$	(2)
Chemical reaction	$^1O_2 + M \xrightarrow{k_r^M} \text{Products}$	(3)
Physical quenching	$^1O_2 + M \xrightarrow{k_q^M} M + {}^3O_2$	(4)
$^1O_2$ decay pathways	$^1O_2 \xrightarrow{k_\Delta} {}^3O_2$	(5)

From Scheme 2, $O_2(^1\Delta_g)$ steady-state concentration is given by eq. (6):

$$\left[{}^1O_2\right] = \frac{v_f}{k_\Delta + \left(k^M{}_r + k^M{}_q\right)[M]} \tag{6}$$

where v_f is the production rate of singlet oxygen.

Considering that $O_2(^1\Delta_g)$ stationary concentration corresponds to the ratio of the excited oxygen production rate to the summatory on the rate of all the processes that consume it, the substrate consumption rate takes up the form:

$$-\frac{\partial[M]}{\partial t} = \frac{v_f}{k_\Delta + (k^M{}_r + k^M{}_q)[M]} k^M{}_r[M] \tag{7}$$

A first point not always considered, is that a first-order raction take place only at low substrate concentration or when the data are extrapolated to zero substrate concentration. In this limit, the condition $k_\Delta >> (k_r^M + k_q^M)$ [M] is accomplished, and the reduction of steady-state singlet oxygen concentration by substrate quenching is negligible. Under this approach the expression for substrate consumption takes up the form:

$$-\frac{\partial[M]}{\partial t} = v_f \frac{k^M_r}{k_\Delta}[M] = k^M_{exp}[M] \qquad (8)$$

Eq. (8) shows that to evaluate the chemical rate constant for the reaction between M and $O_2(^1\Delta_g)$, it is necessary to know the singlet oxygen steady-state concentration or the singlet oxygen production rate, which depend on experimental conditions (e.g. solvent, sensitizer, radiation source, system geometry). These parameters, singlet oxygen steady-state concentration or their production rate must be obtained employing an actinometer, A.

Depending on actinometer reactivity towards $O_2(^1\Delta_g)$, there are two different possible limiting behaviors:

When A is a highly reactive molecule, in which the chemical reaction with singlet oxygen predominates far above the physical quenching, it will trap the entire singlet oxygen produced and k_r^A [A] >> k_Δ. If this condition is fulfilled, the actinometer consumption rate is equal to the singlet oxygen production:

$$-\frac{\partial[A]}{\partial t} = v_f \qquad (10)$$

This behavior has been described for DPBF[20-25] and α-terpinene.[35,36] When these compounds are employed as actinometers to determine the chemical rate constant for the reaction between M and $O_2(^1\Delta_g)$, only the pseudo-order zero rate of the actinometer disappearance can be measured.

In the situation in which A is a less reactive actinometer, the most important singlet oxygen consumption path corresponds to solvent quenching. In this condition, $(k_r^A + k_q^A)[A] >> k_\Delta$, then actinometer disappearance rate takes up the form:

$$-\frac{\partial[A]}{\partial t} = v_f \frac{k^A_r}{k_\Delta}[A] = k^A_{exp}[A] \qquad (11)$$

From eqns. (8) and (11) it is found that:

$$\frac{k^M_{exp}}{k^A_{exp}} = \frac{k^M_r}{k^A_r} \qquad (12)$$

Eq. (12) shows that in order to determine k_r^M it is necessary to know the chemical rate constant for the reaction between the actinometer and $O_2(^1\Delta_g)$, which is the situation when 9,10-dimethylanthracene is employed.

To obtain a precise idea of the limitations associated to the use of DMA as an actinometer, first we verify if the steady-state singlet oxygen concentration is the same in the reaction with DMA as that with M. DMA presence could affect considerably the $O_2(^1\Delta_g)$ steady-state concentration. To analyze this point we

measure the consumption rate of anthracene as a function of its initial concentration, using TPP and acetonitrile as the sensitizer and the solvent, respectively. It should be taken in consideration that in acetonitrile $k_\Delta \approx (k_r^{DMA} + k_q^{DMA})$ [DMA]. Then DMA would reduce the $O_2(^1\Delta_g)$ steady-state concentration. Furthermore, a decrease in $O_2(^1\Delta_g)$ steady-state concentration due to the quenching of TPP by DMA can be disregarded because the intensity at zero time, of the time resolved IR luminescence of $O_2(^1\Delta_g)$, is not modified by increasing DMA concentration. Similar experiments were done to determine the dependence of the consumption rate of 2,5-diphenylisobenzofuran, DPBF, as a function of its initial concentration. In these experiments DPBF concentrations that fit pseudo order zero kinetics were employed. Figure 1 shows the results obtained, expressed as the ratio between the experimental zero order rate constant obtained at a given actinometer concentration and the value extrapolated at zero actinometer concentration. As is observed, the zero order experimental rate constant for the DPBF consumption is independent, within experimental error, of the initial concentration of the actinometer, in agreement with eq. (10). Furthermore, the first-order experimental rate constant for the DMA consumption diminishes noticeably with the increase on DMA concentration. This result implies that in acetonitrile, greater DMA concentrations decrease the $O_2(^1\Delta_g)$ steady-state concentration. From eq. (6) it is clear that the decrease in $O_2(^1\Delta_g)$ steady-state concentration occurs because the condition $k_\Delta >> (k_r^{DMA} + k_q^{DMA})$ [DMA] is not accomplished due to the relatively large singlet oxygen lifetime, $\tau^{^1O_2}$, in this solvent.

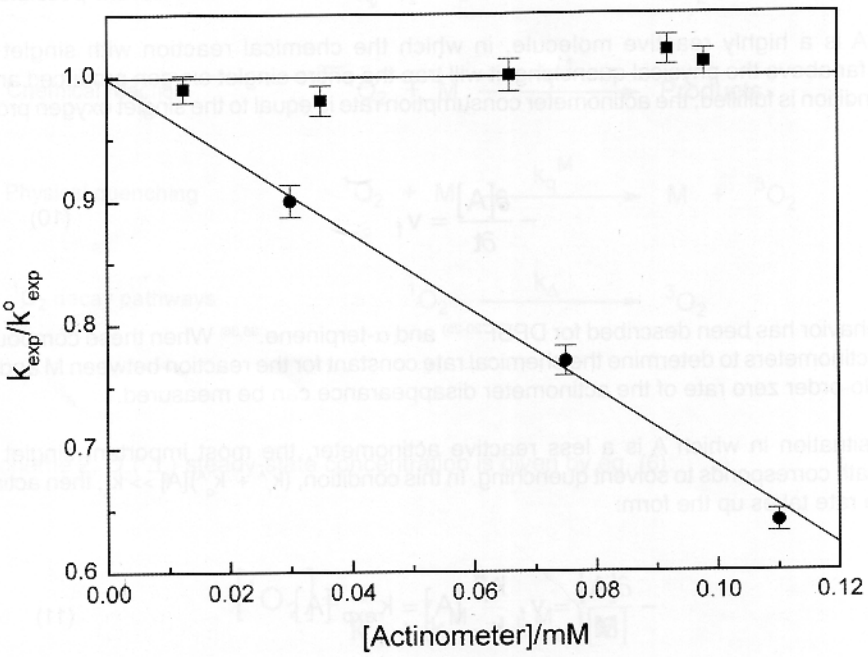


Fig.1. Dependence of the experimental rate constant for DMA (•) and DPBF ( ) consumption on actinometer concentration. Values are expressed relative to the experimental rate constant extrapolated to zero actinometer concentration.Solvent: acetonitrile. Sensitizer: TPP.

In Table I we include DMA kinetic parameters and $\tau^{^1O_2}$ in four different solvents. Singlet oxygen lifetime values correspond to the mean value obtained in our laboratory in a large number of experiments employing several sensitizers and pulse sources. Values of $k_T^{DMA} = (k_r^{DMA} + k_q^{DMA})$, were determined by measuring the decrease of the time resolved IR luminescence of $O_2(^1\Delta_g)$ with DMA addition. We also included the product k_T^{DMA} [DMA] and the ratio k_T^{DMA} [DMA]/k_Δ, taking a DMA concentration equal to 8×10^{-5} M, which corresponds to an absorbance of approximately 0.7, typically employed in actinometry experiments.

Table I. Kinetic parameters of 9,10-dimethylanthracene in several solvents at 22 °C.

Solvent	$\tau^{1}O_2$ /μs	$k_T^{DMA}/10^7$ $M^{-1}s^{-1}$	$k_\Delta/10^4$ s^{-1}	$k_T^{DMA}[DMA]/10^4$ s^{-1}	$k_T^{DMA}[DMA]/k_\Delta$
Acetonitrile	82 ± 4	8.8 ± 0.4	1.22 ± 0.06	0.71	0.58
Benzene	31 ± 2	2.1 ± 0.08	3.23 ± 0.22	0.17	0.05
Chloroform	198 ± 9	9.3 ± 0.5	0.51 ± 0.02	0.74	1.45
Methanol	10 ± 0.6	6.8 ± 0.3	10 ± 0.6	0.54	0.05

From the data in Table I it is possible to establish that in solvents in which singlet oxygen lifetime is short and the k_T^{DMA} value is moderate, there are no difficulties to employ DMA as actinometer and that the $O_2(^1\Delta_g)$ steady-state concentration remains constant, independently of the actinometer. However, in solvents such as chloroform or acetonitrile, where $\tau^{1}O_2$ is large, the actinometer opens an additional pathway to singlet oxygen disappearance with a pseudo first-order rate constant of similar magnitude to k_Δ and the singlet oxygen concentration decreases. In this case erroneous values of the chemical reaction constant, k_r^M, will be obtained for the reaction between singlet oxygen and a given substrate M. Two approaches could be employed to improve k_r^M values determined by using DMA as actinometer. The first one, involves diminish the DMA concentration and measure its consumption employing fluorescence methods. DMA concentration would be reduced in a factor 10^2 - 10^3 and the condition $k_\Delta >> (k_r^{DMA} + k_q^{DMA})$ [DMA] can be accomplished. The second approach requires measure k_r^{DMA} and k_T^{DMA} in separate experiments. The correct kr^M value will be obtained multiplying the value calculated in the usual manner (with k_r^{DMA} previously measured) by the factor $(1 + (k_T^{DMA}/k_\Delta)[DMA])$, where [DMA] is the DMA concentration employed to perform the actinometry. It is obvious from this approach, that determining k_{exp}^M as a function of the k_{exp}^{DMA} actinometer concentration, the correct k_r^M value will be obtained extrapolating to zero actinometer concentration if k_r^{DMA} was previously measured.

A second point to consider is related to the requirement: the reaction between the actinometer and $O_2(^1\Delta_g)$ must be only chemical in nature and physical quenching must be negligible, which 9,10-dimethylanthracene does not always accomplish. In order to know the fraction of the DMA-singlet oxygen encounters that yield products, we compare k_T^{DMA}, obtained from time resolved experiments, with k_r^{DMA}, determined by observing the anthracene derivative consumption using UV-VIS spectrophotometry and extrapolating to zero concentration of DMA. In the last experiments DPBF was used as actinometer. Table II summarizes these results.

Table II. Total rate, k_T^{DMA}, and chemical rate constants, k_r^{DMA}, for the reaction between $O_2(^1\Delta_g)$ and DMA at 22 °C.

Solvent	$k_T^{DMA}/10^7$ M^{-1} s^{-1}	$k_r^{DMA}/10^7$ M^{-1} s^{-1}	k_T^{DMA}/k_r^{DMA}
Methanol	6.8 ± 0.3	6.3 ± 0.4	1.07
Acetonitrile	8.8 ± 0.4	5.3 ± 0.3	1.66

Data in Table II shows that with acetonitrile as solvent, the chemical reaction rate constant is approximately 40% smaller than the total quenching constant whereas with methanol the difference is negligible. These results imply that it is not possible to use DMA in solvents whose behavior is similar to the one observed in acetonitrile. In these systems the consumption rate of the anthracene derivative will not reflect singlet oxygen quenching by the actinometer. Then, the chemical reaction constant, k_r^M, for the reaction between singlet oxygen and a given substrate M obtained in these conditions will be smaller than the true values. To correct it, is necessary to determine k_r^{DMA} quantifying DMA consumption by means UV-VIS, fluorescence or chromatographic methods.

Summing up, when DMA or compounds of similar behavior are employed as actinometers, precaution must taken to quantify the errors associated to the experimental method and to include the appropriate correction factors.

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