

Salt effect on sensitized photooxidations. A kinetic approach to environmental decomposition of marine contaminants*

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SUMMARY: The salt effect on the kinetics of singlet molecular oxygen [$O_2(^1\Delta_g)$]-mediated photooxidations of sea water contaminants was investigated. Two families of photooxidizable compounds were employed in the study: anthracene derivatives and phenols. The presence of salt (NaCl in H_2O and LiCl in MeCN, in both cases in the range 0-0.45 M) produces changes in the photooxidation rate. For solvent-polarity-dependent reactions, this behavior can be predicted, by knowing the solvent-polarity dependence of the rate constant for chemical reaction of the substrates with $O_2(^1\Delta_g)$ in non-saline solutions (k_r). For the cases of photooxidations possessing solvent-polarity-independent or scantily-dependent k_r values, the photooxidation rates decrease as the salt content in the solution increases, mainly due to a predominance of the physical quenching pathway. In addition, the quantum yield for $O_2(^1\Delta_g)$ generation (Φ_Δ) was determined in a series of saline solutions, in the range of 0-0.45 M in water and MeCN solutions, in the presence of NaCl and LiCl respectively. The Φ_Δ values are independent, within the experimental error on the salt content.

Key words: Anthracene derivatives, phenols, photodecomposition, Salt effect, sensitized photooxidations, singlet molecular oxygen.

INTRODUCTION

The fate of organic contaminants spilt in the marine environment is a topic of great concern, especially from the ecological point of view. The natural degradation of this pollution can arise from several known sources, microbiological and photochemical decontamination routes being the most feasible possibilities (Zafiriou *et al.*, 1984; Ehrhardt

and Petrick, 1985; Payne and Phillips, 1985; Rontani and Giusti, 1987).

Photolytic decomposition of dissolved sea contaminants has been attributed to direct photolysis, radical oxidation and singlet molecular oxygen [$O_2(^1\Delta_g)$]-mediated mechanisms. Nevertheless, the relative importance of the individual pathways remains uncertain (Lichtenthaler *et al.*, 1989).

Specific literature describing the effect of added salts on photooxidative reactions is limited to a few articles (Rubio *et al.*, 1992 a,b; Gutiérrez *et al.*, 1994 and 1995). This effect constitutes an especially interesting point when $O_2(^1\Delta_g)$ -mediated photoreactions

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in the marine environment are considered. The investigations by Rubio *et al.* were made at excessively high salt concentrations to be comparable to those present in the marine environment. They consisted in studies of the salt effect on the $O_2(^1\Delta_g)$ interaction with sodium azide (Rubio *et al.*, 1992b) (through a pure physical quenching process) and with an anthracene derivative (Rubio *et al.*, 1992a) (through a pure reactive quenching). In both cases, at salt concentrations between 1 and 3 M, the rate for the $O_2(^1\Delta_g)$ process was significantly increased as compared with the same process in non saline solutions. The authors explain the observed effect in terms of the stabilization of the charge transfer complex between $O_2(^1\Delta_g)$ and the azide or the anthracene derivative by the added electrolyte.

In 1994 we published some results in this area, which represented the initial step for the present contribution (Gutiérrez *et al.*, 1994). The $O_2(^1\Delta_g)$ -mediated photooxidation of a sulfur-containing amino acid (methionine) and for a polynuclear hydrocarbon (rubrene) were studied as a function of the saline concentration. In a more recent paper (Gutiérrez *et al.*, 1995) we reported preliminary comparative results on the photooxidation rates of ADP and 4M2NP in water and sea water solutions. These results *qualitatively* show that the photooxidation process in sea water is accelerated for the anthracene derivative and inhibited for the phenol.

In this article we present a systematic study on the mechanism of $[O_2(^1\Delta_g)]$ -mediated reactions under different conditions of salinity for two families of known sea-water contaminants: anthracene derivatives and phenols. The strategy of the present work was the estimation of the extent of $O_2(^1\Delta_g)$ -mediated reactions in saline solutions, through a kinetic comparative study with the same reactions in non-saline solutions, a condition in which the mechanistic details are known. In parallel, for the first time according to our knowledge, the quantum yield for $O_2(^1\Delta_g)$ generation (Φ_{Δ}) in saline aqueous and non-aqueous solutions are reported.

EXPERIMENTAL

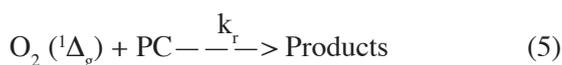
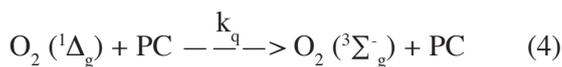
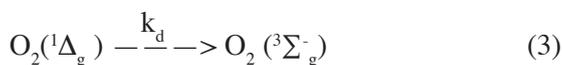
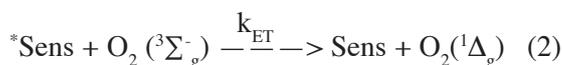
Materials

The chemicals 2-nitrophenol (2NP), 4-methyl-2-nitrophenol (4M2NP), hydroquinone (HQ), 9,10-dimethylanthracene (DMA) and 9,10-anthracene dipropionic acid (ADP), rose bengal

(RB), NaCl and LiCl and KOH were purchased from Aldrich. The solvents MeOH and MeCN were from Sintorgan (Argentine) HPLC grade. Deuterium oxide 99.9% was from Sigma. Water was triply distilled.

Methods

The kinetic scheme accounting for $O_2(^1\Delta_g)$ generation and reaction can be described as follows (Wilkinson and Brummer, 1981):



Sens represent a compound, namely sensitizer (generally a visible-absorbing species), able to absorb radiation in a wavelength range in which the photooxidizable compounds (PC) are transparent. The incident light promotes Sens to electronically excited states (reaction (1)). From these states, an energy transfer reaction to ground state-triplet molecular oxygen [$O_2(^3\Sigma_g^-)$] dissolved in the solution can take place, producing the excited state oxygen species $O_2(^1\Delta_g)$ (reaction (2)). It can decay either by collision with surrounding molecules (the solvent, reaction (3)) or by interaction with PC (4) through pure physical processes. Finally, reaction (5) represents the photooxidation pathway, from which the degradation of PC takes place. The overall rate constant k_t represent the sum of the respective rate constants for the physical and reactive processes ($k_t = k_q + k_r$).

Static photolysis

Samples containing the PC plus RB (the sensitizer) in both saline and non saline solutions were irradiated at wavelengths higher than 400 nm. The irradiation device and procedure was already described (Palumbo *et al.*, 1990a).

For the experiments in a given solvent, the complete set of photooxidation runs for a given PC was made maintaining identical experimental conditions, the saline concentration being the unique difference between the irradiated solutions.

The photooxidation rates were determined by the slopes of the first order plots, as that shown in Fig. 3 (inset) for HQ, where c_0 and c represent either the remaining photooxidizable substrate or the remaining oxygen concentration at times $t = 0$ and $t = t$, respectively, upon sensitized irradiation. Typical initial concentrations for the photooxidizable compounds were in the range of $1-2 \times 10^{-4}$ M. The value for the absorbance of the sensitizer at 560 nm was in all cases *ca.* 0.7. A Hewlett Packard 8452A diode-array spectrophotometer was employed.

The specific oxygen electrode employed in the determination of oxygen concentrations and the irradiation set up has been already described (Palumbo and García, 1990a). The oxygen electrode has a membrane that can be employed only in media containing a high percentage of water (typically more than 95%).

Time resolved photolysis

The kinetic laser spectrophotometer for time-resolved phosphorescence detection (TRPD) of $O_2(^1\Delta_g)$ was previously described (Criado *et al.*, 1995). In the present case RB was employed as a dye sensitizer. Typically, the absorbance of the dye was *ca.* 0.3 at 337 nm. The decay kinetics were first order in all cases. Heavy water instead of normal water was employed as a solvent, in order to enlarge the $O_2(^1\Delta_g)$ lifetime within the detection limits of the spectrophotometer.

The $O_2(^1\Delta_g)$ lifetimes were evaluated in the absence (τ_0) and in the presence (τ) of the quencher and the data was processed according to a simple Stern-Volmer treatment (eq. [1])

$$1/\tau = 1/\tau_0 + k_t [PC] \quad [1]$$

where [PC] represents the molar concentration of the dissolved contaminant.

The procedure for obtaining Φ_Δ values by means of TRPD was as follows: the traces for individual luminescence decay from RB in water (in the absence (o) and in the presence of different NaCl concentrations) and in MeCN (in the absence (o) and in the presence of different LiCl concentrations) were fitted with monoexponential functions to yield

the initial intensity I_0 at time $t=0$. In all cases the linearity between laser pulse energy (typically 1 mJ per pulse) and I_0 was ensured. The respective I_0 values for the saline solutions were plotted against the fraction of absorbed light, yielding linear plots. The slopes of these plots were compared with the slope of the reference sample (RB) without the addition of salt (slope(o)). For RB $\Phi_{\Delta(o)} = 0.7$ in water and $\Phi_{\Delta(o)} = 0.6$ in MeCN (Neckers, 1989). From eq. [2] the respective Φ_Δ values in saline solutions were obtained.

$$\text{slope(o) / slope} = \Phi_{\Delta(o)} / \Phi_\Delta \quad [2]$$

The experimental conditions were: Absorbance RB at 337 nm = 0.4 and air-saturated aqueous and MeCN solutions with and without addition of salt.

RESULTS

Sensitized (static) irradiation of PC saline solutions resulted in both substrate and oxygen consumption. The time evolution of the photooxidative process was monitored by either the decrease in the absorbance of the PC (see Fig. 1 a and b) or by oxygen uptake in aqueous solutions (the latter by means of the described selective electrode for dissolved oxygen on the basis that the only source of oxygen consumption, in the $O_2(^1\Delta_g)$ -mediated photooxidation of anthracenes and phenols, is given by reaction (5) with a 1:1 stoichiometry (Stevens and Pérez, 1974; García 1994).

The two families of PC already described were irradiated in the presence of RB in aqueous and organic media (MeCN) with and without the addition of different amounts of salt (NaCl or LiCl respectively). Two types of kinetic measurements on

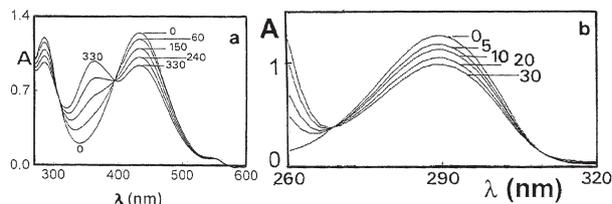


FIG. 1. – Absorption spectra at different irradiation times of PC in the RB-sensitized photooxidation of aerobic saline aqueous solutions. **a:** 4M2NP, 2×10^{-4} M, in the presence of NaCl 0.2 M and NaOH 1×10^{-3} M. **b:** HQ, 1×10^{-4} M, in the presence of NaCl 0.45 M. In both cases: RB $Abs_{330} = 0.7$. Numbers on the spectra represent irradiation time (sec).

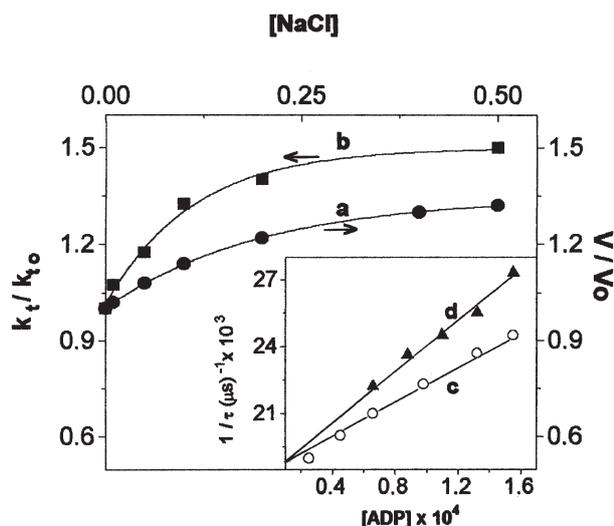


FIG. 2. – a: Dependence of the rates of RB sensitized photooxidation of DMA in MeCN saline solutions, as a function of [LiCl]. V_0 and V represent the photooxidation rates in the absence and in the presence of a given salt concentration respectively. b: Dependence of the overall rate constants (see text) for RB sensitized photooxidation of ADP in saline aqueous solutions, as a function of [NaCl]. The rate constants k_{t_0} and k_t correspond to the absence and to the presence of a given salt concentration, respectively. Inset: Stern-Volmer plots for two runs in determination of k_t for ADP. c: in the absence of salt; d: in the presence of NaCl 0.2 M.

PC photooxidation were performed: the determination of the rate constant k_t for ADP and HQ and the determination of photooxidation rates for DMA, HQ, 4M2NP and 2NP. The values for the rate constants k_t (normally evaluated through comparative methods) could not be determined due to the absence of an adequate reference compound of known k_t at different saline concentrations.

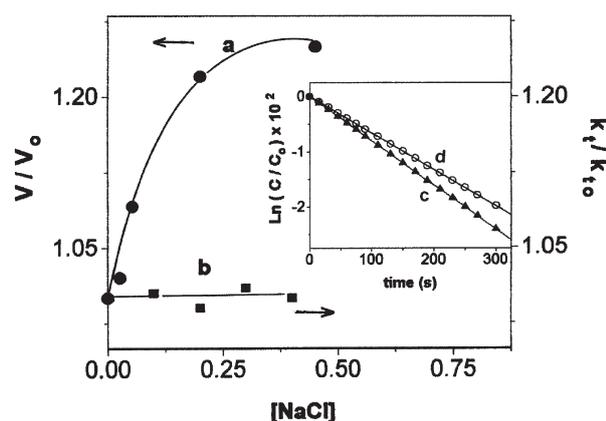


FIG. 3. – Salt effect on the sensitized photooxidation of HQ in aqueous solutions. a: Change of the photooxidation rate (V) as a function of the saline concentration (left ordinate axis). V_0 represents the photooxidation rate in the absence of salt. b: Behavior of the overall rate constant (k_t) as a function of the salt concentration (right ordinate axis). k_{t_0} represent the rate constant in the absence of salt. Inset: first order plots for oxygen uptake of aqueous saline (NaCl 0.2 M (c)) and non saline (d) solutions.

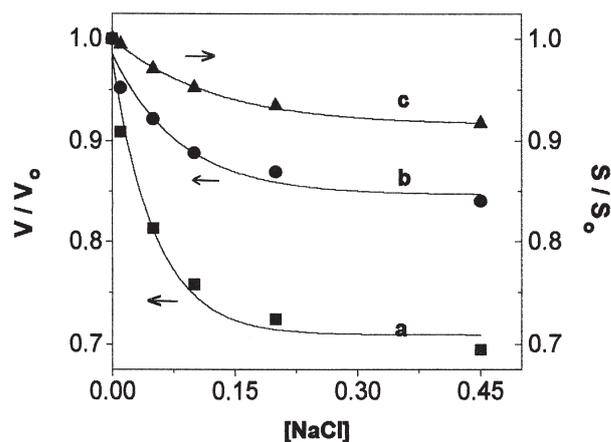


FIG. 4. – Inhibition of the oxidation rate of phenols in water containing NaOH 1×10^{-3} M, in the absence (V_0) and in the presence (V) of salt, as a function of the saline concentration [NaCl] in solution. a: 4M2NP. b: 2NP. The profile c represents the dissolved oxygen concentration, in water, as a function of [NaCl] in the presence of NaOH 1×10^{-3} M. S_0 and S are the measured oxygen solubilities for [NaCl] = 0 and for a given [NaCl] respectively. Sensitizer RB $Abs_{530} = 0.7$.

In order to make the presentation of the data easy, the photooxidation rates and the rate constants in the presence of salt (V and k_t respectively) were referred to the values in the absence of salt (V_0 and k_{t_0} respectively). Experimental results are shown in Figs. 2-4. From the observation of Fig. 2 (inset) arises that τ_0 values are the same in the absence and in the presence of the salt.

As can be seen, for some compounds a smooth increase in the k_t values (ADP in Fig. 2) and in the photooxidation rates (DMA in Fig. 2, and HQ in Fig. 3) is observed as the saline concentration increases. To the contrary, for the hydroxy-derivatives (4M2NP and 2NP, Fig. 4) the photooxidation rates decrease with the saline content.

In order to check the effect, if any, of the saline concentration on the quantum yield for $O_2(^1\Delta_g)$ generation, the Φ_Δ values in saline aqueous (NaCl) and MeCN (LiCl) solutions were determined employing RB as a dye sensitizer. As shown in Fig. 5 A and B, the Φ_Δ values obtained were practically the same in the range 0-0.45 M. In other words: all Φ_Δ values lie within the experimental error, estimated in $\pm 10\%$. In addition, the expected effect of slight decrease in Φ_Δ as the salt content increases (due to the reduction in oxygen solubility) was also included within the experimental error.

It is known that the concentration of dissolved oxygen in a given solution is dependent on the dis-

solved electrolytes. These concentrations, for a series of solvents and solvent mixtures, were reported by Battino *et al.*, 1983. Nevertheless, in order to evaluate the concentration of triplet oxygen dissolved under our precise experimental conditions, we made the following determinations: by means of the specific oxygen electrode we determined the change of these concentrations in the saline range 0-0.45 M. For comparative purposes, the oxygen concentration profile is plotted as the quotient of the concentration in the presence and in the absence of the salt (S and S_0 respectively), as a function of the salt content (see Fig. 4). As can be seen, the change in molecular oxygen dissolved only reaches the minimum value $S/S_0 = 0.92$ at salt concentration 0.45 M.

DISCUSSION

In order to properly discuss the salt effect in our present results, two aspects should be pointed out: a) the general factors that could influence the determination of $O_2(^1\Delta_g)$ -mediated photooxidation rates (V) and b) the particular or specific kinetic effects on the photooxidation of each PC studied. It should be emphasized that k_t values are determined in an absolute fashion and hence are not influenced by the general factors (a). As already mentioned, the specific effects (b) are known for all the PC studied in non-saline media, under a variety of experimental conditions.

Under constant irradiation dose and dissolved ground state oxygen concentration, the rate of photooxidation (V) is proportional (a) to the following factors, as indicated in eq. [3].

$$V \propto I_a \Phi_{\Delta} \tau_o k_r \quad [3]$$

where I_a is the light intensity absorbed by the sensitizer (constant for all the runs), Φ_{Δ} is the quantum yield for $O_2(^1\Delta_g)$ generation by the irradiated sensitizer and τ_o is the $O_2(^1\Delta_g)$ lifetime (the reciprocal of k_d , reaction. (3)).

According to our results τ_o and Φ_{Δ} are not affected by the addition of salt, within the experimental error (see Figs. 2, inset and 5).

Thus, the only factor that apparently could affect the behavior of the photooxidation rate, as the salt content varies, is given by the photooxidation rate constant k_r .

The mechanism and kinetics for the photooxidation of the families of compounds here studied have

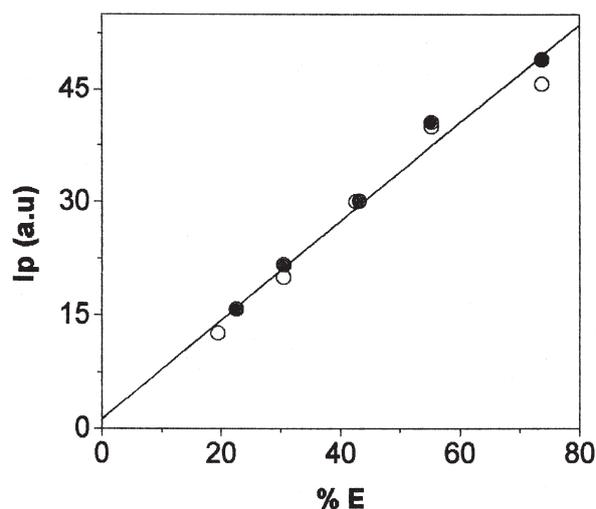


FIG. 5. – Plot of initial intensity of the $O_2(^1\Delta_g)$ phosphorescence signal (I_p) as a function of the absorbed laser energy (%E) for different LiCl concentrations. (○): in the absence of salt; (●) in the presence of LiCl 0.1 M. Sensitizer RB, $Abs_{337} = 0.2$. Solvent MeCN.

been previously reported, in non saline solutions, by other researchers (Carlsson *et al.*, 1974; Stevens *et al.*, 1974) and by ourselves (Palumbo *et al.*, 1990 a; Mártire *et al.*, 1991; Luiz *et al.*, 1993; Bocco *et al.*, 1994; García, 1994).

The mechanism of $O_2(^1\Delta_g)$ photooxidation for phenols and anthracene derivatives have been postulated to occur through an intermediate excited complex [$PC-O_2(^1\Delta_g)$], possessing a variable degree of charge transfer character. (Bocco *et al.*, 1994; Gutiérrez *et al.*, 1994; Luiz *et al.*, 1993; Mártire *et al.*, 1991; Palumbo *et al.*, 1990 a; Cazin *et al.*, 1986). This component is dominant in the case of some phenols (for a review see García, 1994), where the solvent polarity greatly contribute to the stabilization of the mentioned charge transfer-like excited complex. The k_r value for HQ dramatically increases in changing the solvent from MeCN to water (Mártire *et al.*, 1991) whereas the k_r value for 4M2NP remains unchanged going from a benzene-methanol mixture to water as solvents (Luiz *et al.*, 1993).

On the other hand, the reactivity of pure hydrocarbons such as DMA towards $O_2(^1\Delta_g)$ (the reaction is a [4+2] cycloaddition) is sensitive, in kinetic terms, to the solvent polarity. The reported k_r values for DMA in benzene and methanol are $2.1 \times 10^7 M^{-1} s^{-1}$ and $1.2 \times 10^7 M^{-1} s^{-1}$ respectively (Stevens *et al.*, 1974; Wilkinson and Brummer, 1981).

The kinetic profiles in Figs. 2-4 can be interpreted on the basis of stabilization-destabilization of the

intermediate charge-transfer complex, due to the presence of charged species in solution.

The case of the anthracene derivatives (Fig. 2) clearly obey this pattern: the reactivity towards $O_2(^1\Delta_g)$ increases with the addition of salt.

For HQ the photooxidation rate increases as the salt content increases, whereas k_t remains practically unchanged (Fig. 3). This is in agreement with our previous results on solvent effect in the kinetics of HQ photooxidation (Mártire *et al.*, 1991). In that paper we show that the k_q/k_r ratios are much lower in water than in MeCN, indicating that the reactive dissociation of the encounter complex is related to the solvent polarity. In MeCN k_q/k_r ratio is 60 whereas in water the ratio only reaches the value of 11. Besides, in the less polar solvent MeCN, the relatively high k_q/k_r ratio and the extremely low value of k_r consistently render the chemical reaction with $O_2(^1\Delta_g)$ negligible. In these cases the formation of the intermediate complex [PC- $O_2(^1\Delta_g)$] should be favored by the presence of charged species in the solution.

The kinetic behavior of the nitrophenols (4M2NP and 2NP) shows a common characteristic: the photooxidation rate is decreased by the presence of increasing amounts of salt (Fig. 4). A quite plausible explanation for our results arises from the already postulated mechanism of inhibition of photolytic reactions by the addition of a salt (Loupy *et al.*, 1992). The authors describe the effect as a dislocation of the reaction partners within the reaction encounter complex by the added salt. The result can be visualized as the removal of the reactive pairs from each other, as a measure of the replacement of the solvent molecules by the ions of the salt in the complex. As can be seen in Fig. 4, even when the decrease in the concentration of dissolved oxygen in solution, as the salt content increases, would play an inhibitory role in the kinetic profile (see S/S_0 axis), such an effect is significantly lower than the inhibition of the respective oxidation rates (see V/V_0 axis). The result for both nitrophenols can be also discussed in terms of the k_t/k_r values as the solvent polarity changes: for 2NP this quotient is 1 in alkaline MeOH/Bz (2:3, v/v) and 94 in water, pH 11 (Bocco *et al.*, 1994), whereas for 4M2NP these values are 1.6 and 86 respectively. This indicates that the non reactive dissociation route for the encounter complex ($O_2(^1\Delta_g)$) is dramatically favored by the increase in solvent polarity, or, as in our case by the presence of charged particles in solution.

CONCLUSIONS

We show that the behavior of the photooxidation rates as a function of the salt concentration in solution (in a $O_2(^1\Delta_g)$ -mediated mechanism), can be predicted, by knowing the solvent-polarity effect on k_r in non-saline solutions. For photooxidative reactions exhibiting solvent-polarity-independent or scantily-dependent k_r values, the photooxidation rates decrease as the salt content in the solution increases. In this case the relative weights for reactive and physical quenching of $O_2(^1\Delta_g)$ play a decisive role.

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