

Mechanistical Aspects of Thermal Plates

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Abstract

Two fundamental pathways can be distinguished acting in light sensitive formulations containing IR dyes: (1) transformation of the incident IR energy into heat followed by several thermal processes; (2) interaction between excited states of the IR dye and the ground state of another compound leading to reactive intermediates, which then react with other components to final products. Based on general accepted theories of excited state chemistry, estimations and conclusions for both pathways will be made for systems containing IR dyes. As follows, electron transfer reactions can be compete successfully with the fast physical deactivation processes of excited dye molecules. Some results for such reactions will be presented.

Introduction

In the last few years, there has been keen interest in computer-to-plate (CtP) systems, where a document or graphic stored in a computer is written directly to a printing plate. Among all types of CtP offset printing plates, the IR sensitive ones ("thermal plates") play an important role. A lot of information about design and formulation ingredients of these plates have been published, mainly in patents.¹ Contrary, only few data are available about the mechanisms taking place in these formulations

In this paper we discuss fundamental mechanisms possible in such formulations from a very photochemical point of view. The basis of this discussion is the so-called Jablonski diagram of excited states, which is widely accepted in the scientific literature² for describing of processes of excited states; see Fig. 1. In the following we transfer this scheme to excited IR dye molecules.

Within the framework of this model, only these molecular orbitals (MO's) between which a light-induced electron transition takes place are involved in the formal energy terms. In the electronic ground state the MO's are occupied by electrons in pairs, this state has the multiplicity of 1 and the total spin moment $S=0$. Therefore, it is designated as the singlet ground state S_0 . The absorption of an IR photon (process $h\nu$) generates dye molecules in both electronically and vibrationally excited state, with a very short life-time. Since the total spin moment is conserved, an excited singlet state S_1 (or S_n) is formed. The deactivation of this excited state occurs via release of heat (internal conversion; ic- and d-processes), light emission (fluorescence, f-process), or photochemical conversion to a product either in presence or absence of reaction partner B in its ground state.

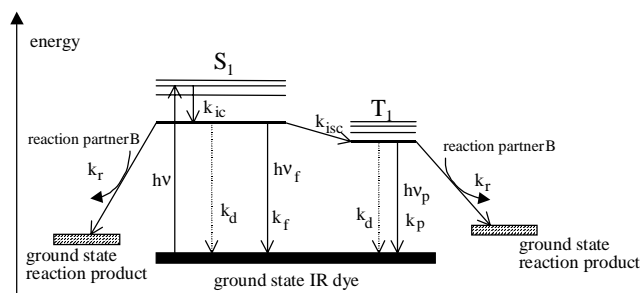


Figure 1. Jablonski diagram of an IR dye molecule

Moreover, it is possible by spin conversion (intersystem crossing; isc-process) to occupy an energetically lower lying triplet state T_1 in which both electrons have a parallel spin. The deactivation $T_1 \rightarrow S_0$ (d-process) is spin-forbidden, and therefore proceeds relatively slowly with release of heat, emission of light (phosphorescence; p-process), or photochemical conversion to a product.

As follows from this diagram, in principle two processes can be used for thermal plate formulations: heat generation and generation of reactive intermediates formed by chemical deactivation of excited IR dye molecules.

Heat Generation Mode

As known, the energy (E) pumped into a CtP formulation by exposure depends on the wavelength (λ) of incident IR light. By means of the Einstein Eq. 1, the energy of important wavelengths 830 nm (used in Creo/Heidelberg IR exposure devices) can be calculated to be $E = 33.5$ kcal/mol, and that of 1060 nm (used in Barco IR exposure devices) to be $E = 26.3$ kcal/mol. Assuming that all other pathways outlined in Fig. 1 are not active, than this energy represents this heat energy (Q) generated by deactivation of 1 mol of excited dye, which corresponds the deactivation of 6.022×10^{23} excited dye molecules. Refer to 1 molecule, the energies are 5.54×10^{-20} cal/molecule (830 nm) and 4.37×10^{-20} cal/molecule (1060 nm), which is this heat released into the immediate environment of a single dye molecule. However, an efficient interaction of IR photons with the ground state of this dye molecule is a fundamental prerequisite to reach this heat energy increase. By variation of IR dye concentration of a given formulation, the optimal ratio between laser irradiance and dye concentration can be found.^{3,4}

$$E = h \nu = h c / \lambda \quad (1)$$

For an estimation, which temperature increase is connected with the heat release, we assume following model formulation: 14.2 mass % IR dye (molecular weight 450 g/mol), 76.2 % cresol novolak (2400) and 9.6 % thermally decomposable compound (300). Such formulation represents a typical example described in several patents. In this formulation 1 dye molecule is surrounded by 20 phenolic units and by 1 molecule thermally decomposable compound. This triple formed a kind of reaction cell. Each phenolic unit of this cell occupies on average a volume of 200 \AA^3 ,⁵ and a 20-fold cell will than occupy a volume of about 4000 \AA^3 , corresponding to a mass of $4000 \times 10^{-24} \text{ g}$. The specific heat of this cell is approximately $0.25 \text{ cal/}^\circ\text{C}$, which leads to a heat capacity for the cell of $c = 4000 \times 10^{-24} \times 0.25 = 1 \times 10^{-21} \text{ cal/}^\circ\text{C}$.

If the molecular heats after deactivation of excited dye molecule, $q = 5.54 \times 10^{-20} \text{ cal}$ and $4.37 \times 10^{-20} \text{ cal}$, respectively, are released into the cell instantaneously, and if heat losses into the surroundings can be neglected, the temperature of this cell will increase by $\Delta T = q/c = (5.54 \times 10^{-20})/(1 \times 10^{-21}) = 55.4 \text{ }^\circ\text{C}$ (in case of 830 nm exposure), and $\Delta T = (4.37 \times 10^{-20})/(1 \times 10^{-21}) = 43.7 \text{ }^\circ\text{C}$ (in case of 1060 nm exposure). Based on calculations with analogous UV sensitive systems (5), it can be expected that the quantity of the heat flow into neighborhood cells lies in the range of 0.01 % of the heat energy generated by a single IR dye molecule.

The estimated heat energies and, as a result, temperature increases of a reaction cell are, at a glance, unexpected low. Taking into account that dissociation energies for bond breaking are between $7.2 \times 10^{-20} \text{ cal/molecule}$ (for O-O bond cleavage of peroxides) and $14.6 \times 10^{-20} \text{ cal/molecule}$ (for C-C bond cleavage of alkanes), then thermal decompositions of compounds with the above estimated heat energies are questionable. However, in practice such reactions are well established; see ablative thermal plates with their total thermal decomposition of compounds.⁽¹⁾ Therefore, we have to assume a multiple excitation/ deactivation cycle of the IR dye molecule within the reaction cell during the dwell time of the laser spot to overcome this obvious discrepancy.

To repeat such cycles, the IR dye molecule must have two fundamental properties: 1st - the life-time of its excited state must be much shorter as the laser dwell time, and 2nd - the dye must be stable against IR light exposure.

Because almost no experimental data about life-times of excited IR dyes are published, we estimated the life time of S^1 state (τ^1) for IR dye A and IR dye B (see Fig. 2) by means of Strickler-Berg Eq. 2. (2). The wave number ν and extinction coefficient ϵ_{max} can be taken from the NIR spectra. The parameters for both dyes, which are of practical importance for plates sensitive at 830 nm (dye A) and at 1060 nm, respectively, (dye B), are summarized in Table 1.

$$\tau^1 = 3.5 \times 10^8 / \nu^2 \times \epsilon_{\text{max}} \times \delta\nu_{1/2} \quad (2)$$

Both dyes have short lived S^1 states in the ns-region. Therefore, during usual employed laser dwell times between 10^{-6} and 10^{-7} sec multiple deactivation (d-process in Fig. 1)

and re-excitation steps are possible. By this way, high enough heat energy can be generated in a reaction cell, required for thermal decompositions. As a result of such processes either ablation occurs or intermediates are formed, which then function as catalyst for thermo-induced crosslinking reactions (pre-heat type of thermal plates). (1)

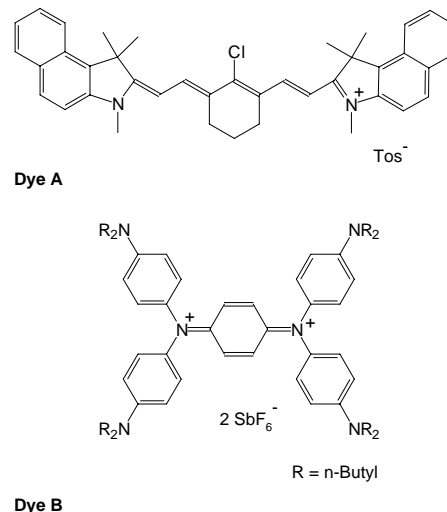


Figure 2. Structures of IR dyes A and B

Table 1. Parameters for estimation of life-times of S^1 states based on Eq. 2 of IR dye A and B.

Parameter	IR dye A	IR dye B
$\nu \times 10^8 (\text{cm}^{-1})$	1.4	0.9
$\epsilon_{\text{max}} \times 10^4 (\text{l/mol} \times \text{cm})$	24	7.3
$\Delta\nu_{1/2} \times 10^4 (\text{cm}^{-1})$	1	1.4
$\tau^1 \times 10^9 (\text{sec})$	1	40

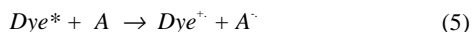
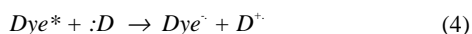
Chemical Deactivation Mode

In principle, the excited state of an IR dye molecule can be also deactivated by a chemical reaction; see Fig. 1. However, this decay pathway must compete with the physical deactivation (d-process). Only when the condition of the kinetic Eq. 3 is obeyed, then such process can participate to a remarkable extent at the overall deactivation of S^1 (or T^1) states.

$$k_r \times [B] \geq k_d \quad (3)$$

The value of k_d needed for an estimation of Eq. 3 corresponds to $k_d = 1/\tau^1$.² Using the data of Tab. 1 the following quantities can be calculated: for dye A - $k_d = 1 \times 10^9 \text{ s}^{-1}$, for dye B - $k_d = 2.5 \times 10^7 \text{ s}^{-1}$. In solid formulation of printing plates, die concentration of reaction partner B could be $[B] \approx 1 \times 10^{-1} \text{ mol/l}$. As a consequence of Eq. 3, then the value of k_r must be between 10^7 and $10^9 \text{ mol/l} \times \text{s}$. There are only very few bimolecular reactions having such high reaction constants. One of these reactions are single electron transfer reactions (SET), well known for many excited state molecules.⁶

In SET, an electron migrates between an excited and ground-state species; in the case discussed in this paper, between excited state on an IR dye (D^*) and the reaction partner B. As with other dyes,⁷ two fundamental possibilities exist: reduction of IR dye by electron donors (D) (Eq. 4), and oxidation of IR dye by electron acceptors (A) (Eq. 5).



In Eq. 4, the dye molecule acts as electron acceptor, in opposition to Eq. 5, where the IR dye functions as electron donor. As a consequence, the reaction partner B must be either the donor (Eq. 4) or the acceptor (Eq. 5).

From an energetic point of view, the free reaction enthalpy ΔG_{et} of these electron transfer processes can be estimated with the use of the Rehm-Weller equation⁸:

$$\Delta G_{et} = IP - EA - E_{0,0} - E_{coul} \quad (6)$$

where IP denotes the ionization potential (or oxidation potential) of the donor, EA denotes the electron affinity (or reduction potential) of the acceptor, $E_{0,0}$ denotes the excitation energy of the dye, and E_{coul} denotes the term for the electrostatic interaction (which usually can be neglected).

If a reaction is to proceed effectively, ΔG_{et} must be negative. The limiting value of ΔG_{et} for which an electron transfer is still possible is 0.2 eV.

Important for the topic discussed in this paper, the formed reactive intermediates of both pathways or their fragmentation products are able to react with other ingredients of plate formulations. At the end of all these processes, chemical changes take place suited to differentiate between exposed and unexposed areas of a CtP plate.

Table 2. Free reaction enthalpies ΔG_{et} (calculated with Eq. 6) and changes in normalized optical density $\Delta O.D._n$ at absorption maximum of IR dye A derivative by exposure with a x 0.36 W laser power ($\lambda = 810$ nm; [dye] = 0.05 mol/l; [onium salt] = 0.017 mol/l).

Onium Salt	ΔG_{et} (in eV)	$\Delta O.D._n$
4-Chlorobenzenediazonium tetrafluoroborate	- 0.6	0.37
Diphenyliodonium chloride	- 0.3	0.28
Triphenylsulfonium chloride	+ 0.2	0.09
N-Benzylisoquinolinium hexafluorophosphate		0.10
Triphenylpyrylium perchlorate		0.12

The oxydation of a derivative of IR dye A (see Fig. 2) by several onium salts was employed as a model to study whether reactions based on Eq. 5 can occur upon IR irradiation. The results of calculations for these processes based on Eq. 6 are summarized in Tab. 2. The $E_{0,0}$ -value was evaluate from the longwavelength absorption maximum by

means of Eq. 1. The oxydation and reduction potentials of the reaction partners was taken from the literature. As show the ΔG_{et} values, such processes are thermodynamically allowed with diazonium and iodonium salts, contrary to the situation with sulfonium salts.

For experimental verification of these calculations, both IR dye and onium salt were dissolved together with a model methacrylics in a solvent mixture. This solution was coated at a polyester substrate. After drying, a small piece of this IR sensitive formulation was mounted on a rotating drum, and imaged with a 810 nm laser diode to obtain exposed areas. The emitted power of the laser diode varies with electrical current given to this diode. Thus, a variation of laser power is easily achievable. Due to constant drum rotation speeds used in all experiments, the IR light energy varies in same ratio as the electrical current is changed.

The changes in optical density (O.D.) of such area at the longwavelength absorption maximum using an aryl diazonium salt as electron acceptor are shown in Fig. 3. As follows, the exposure of the formulation with different laser energies decreases the O.D. of the IR dye. Contrary, the O.D values remain almost constant after exposure with a x 0.36 W (highest laser power of Fig. 3) in absence of any electron acceptor in the formulation (for this case $\Delta O.D. = 0.03$). Because the optical density is direct proportional to the dye concentration (see Lambert-Beer law), changes in O.D. indicate changed concentrations of the dye. Therefore, the data of Fig. 3 support the assumption of a SET process between ground-state diazonium ion and excited IR dye followed by dye molecule decomposition.

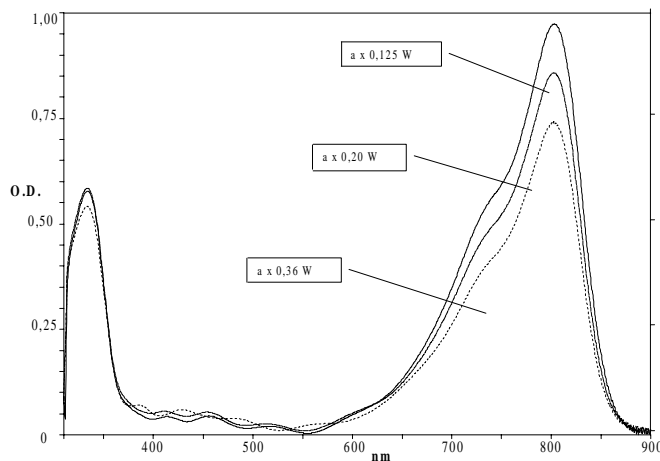


Figure 3. Changes in optical density (O.D.) of dye A derivative in dependence of laser power in presence of 4-chlorobenzene-diazonium tetrafluoroborate (experimental conditions see caption of Tab. 2)

The $\Delta O.D.$ value with other electron acceptors of the onium salt type are summarized in Tab. 2. There is a clear correlation with the estimated free reaction enthalpy. The lower the reduction potential of the electron acceptor the lower the extent of dye bleaching, as predicted by Eq. 6. These results also indicate the SET character of the process leading to bleaching of the IR dye.

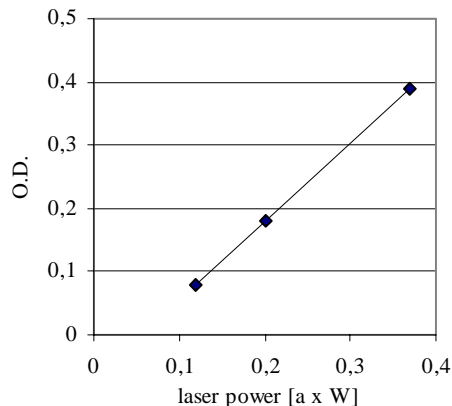


Figure 4. Relation between optical density changes of dye A derivative in dependence of laser power (4-chloro-benzene-diazonium tetrafluoroborate as electron acceptor; other experimental conditions see caption of Tab. 2)

Based on the kinetics of SET processes, the extent of dye bleaching should linearly depend on the laser power. A correlation between Δ O.D. and laser power is given in Fig. 4. Similar linear relationships have been found also with other IR dye/onium salt combinations.

As expected, the Δ O.D. value depends also on the concentration of electron acceptor, as verified with the diazonium salt and IR dye A derivative. Due to the bimolecular character of SET's, at higher concentrations the Δ O.D. approaches a limiting value.

Conclusion

Two fundamental pathways acting in formulations of thermal plates, containing IR dyes, were discussed with regard of their theoretical prerequisites: heat generation mode and chemical deactivation mode. Calculations from

the energetic point of view predict that a multiple excitation of a given IR dye molecule is required to approach an energy level needed either for ablation or other decomposition processes. Electron transfer processes also can be participate at the decay of excited states of the IR dye. It seems that the portion of both modes depends primarily on the redox properties of the reaction partners.

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Biography

Hans-Joachim Timpe received his B.S. degree in Chemistry from the Technical University at Dresden (Germany) in 1963 and a Ph.D. in Organic Chemistry from Technical University Leuna-Merseburg (Germany) in 1966. Since 1967 he has worked in this University, since 1980 he headed a chair of photochemistry. His work was primarily focused on photoinitiator systems and photo-induced polymerisations. The results of this research were published in 5 books, more than 250 reviews and papers, and in 53 patents. In 1991 he joined the Kodak Polychrome Graphics company and works since that time on formulations for offset printing plates.