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M. Churio, K. Angermund, S. Braslavsky. Molecular volume changes in cyanines. A laser-induced optoacoustic study. Journal de Physique IV Proceedings, 1994, 04 (C7), pp.C7-323-C7-325. 10.1051/jp4:1994777 . jpa-00253306

HAL Id: jpa-00253306

<https://hal.science/jpa-00253306>

Submitted on 1 Jan 1994

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Molecular volume changes in cyanines. A laser-induced optoacoustic study

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Abstract: The molecular movements taking place during the *E-Z* photoisomerization of the carbocyanines 3,3'-diethyloxadicarbocyanine iodide (DODCI) and 3,3'-diethyloxacarbocyanine iodide (DOCI) were studied in ethanol-water mixtures using solvent- and temperature-dependent laser-induced optoacoustic spectroscopy (LIOAS) with nanosecond excitation and 1- μ s heat integration time. The contraction measured for the DODCI photoisomerization is attributed to solvent rearrangement around the DODCI isomers with different dipole moments, as evaluated using force field calculations. No volume change was observed for the DOCI photoisomerization⁽¹⁾.

1. INTRODUCTION

Photothermal techniques, in particular laser-induced optoacoustic spectroscopy (LIOAS) have been used for the determination of molecular movements concomitant with photoinduced reactions [1-4]. The proper selection of the heat integration time permits to assign the movement to a particular molecular step. The time can be selected from several picoseconds [5] to micro or milliseconds [1-4] depending on the particular technique used. With LIOAS, time windows from several ns to μ s can be studied.

Callis *et al.* [1] pointed out that there are two possible contributions to the volume change in a photoinduced reaction in solution: a) the difference in volume between products and reactants, and b) the expansion or contraction of the medium upon release of heat. Only the second part depends on the thermoelastic parameters of the solution (c_p , the heat capacity at constant pressure, β , the volume expansion coefficient, and ρ , the solution density). LIOAS measurements as a function of these parameters can separate both terms, thus allowing the calculation of molecular volume changes.

In order to test the potential and limitations of this type of measurements, we studied by LIOAS the photoisomerization of two symmetric carbocyanines in solution: 3,3'-diethyloxadicarbocyanine iodide (DODCI) and 3,3'-diethyloxacarbocyanine iodide (DOCI).

⁽¹⁾ The results presented in this contribution are part of the paper by the same authors in *J.Phys. Chem.* **98** (1994) 1776-1782.

DODCI

DOCI

2. RESULTS AND DISCUSSION

Upon irradiation, cyanines undergo a reversible *E-Z* isomerization in their polymethynic chain. While the deactivation of the first excited state takes only a few ns, the photoisomer *P* is considered the final state in our measurements since the heat integration time in LIOAS (determined by the transit time of the acoustic wave through the laser beam diameter), was shorter than the lifetime of *P* in all cases and under all conditions studied (lifetimes in the range of ms). The absorption characteristics of *P* and *N*, the normal state, are such that permit preferential excitation of *N* when using wavelengths in the blue flank of the absorption spectrum of *N*. The absorption spectrum of *P* for DODCI was determined accurately by LIOAS [6]. The absorption spectrum of *P* for DOCI was determined in this work by flash photolysis with optical detection.

The solutions of DODCI and DOCI were excited with 8ns dye laser pulses and the acoustic signal was measured with a piezoelectric ceramic. The amplitude of the signal was measured and the data evaluated as described in [7]. The amplitude of the optoacoustic signal depended in every case linearly on the laser energy. CoCl₂, bromocresol green, and evans blue were used as calorimetric references [8].

Using simple energy balance considerations, the following expression is obtained which relates the ratio of the LIOAS energy-normalized signals (H_n) for sample (s) and calorimetric reference (ref) with other parameters of the reaction:

$$\frac{H_n^s}{H_n^{ref}} + \Phi_f \frac{E_f}{E_\lambda} + \Phi_{NP} \frac{\Delta E_{NP}}{E_\lambda} = 1 + \frac{\Phi_{NP} \Delta V_{NP}}{E_\lambda} \left(\frac{c_p \rho}{\beta} \right)$$

Φ_f and E_f are the fluorescence quantum yield and emission maximum, respectively, Φ_{NP} and ΔE_{NP} are the isomerization quantum yield and the energy content of *P*, and ΔV_{NP} is the molar volume change occurring during the isomerization. E_λ is the molar energy of the laser pulse.

Since β in water or dilute aqueous solutions strongly depends on the temperature between 4°C and room temperature, and also appreciably increases on going from water to organic solvents, temperature- and solvent-dependent LIOAS experiments afford ΔV_{NP} from the slope of the plot using the eq. above.

The fluorescence quantum yield was measured as a function of the temperature and solvent composition. The term accounting for the energy stored by the isomer (third term of the left hand side of the previous eq.) was calculated using the data determined in a previous work [6]. In any case this term accounted for less than 5% of the energy absorbed. The left hand side of the previous equation was plotted vs $(c_p \rho / \beta)$. The variation of β was achieved either by changing the temperature between 5-30°C in a 30% ethanol/water solution, or by changing the ethanol/water ratio at 25°C.

The value of $(c_p, \rho/\beta)$ for each solution and temperature was determined by using a calorimetric reference and measuring the compressibility factor, ρv_a^2 , in each case.

For DODCI, the slope of the temperature-dependent plot afforded a value of $\Delta V_{NP} = -29 \pm 12$ ml/mol corresponding to a volume contraction of $48 \text{ \AA}^3/\text{molecule}$. Semiempiric calculations of the properties of the various possible configurational isomers of the dicarbocyanine revealed that the largest difference between them lies in their dipole moment. Thus, the molecular movement was attributed to solvent rearrangement around the isomers with different dipole moments. The configuration of **P** was assigned by comparison of the data obtained with the calculated energy content and dipole moment of the various possible configuration isomers. The linear regression for the solvent-dependent plot for DODCI was not good, indicating a change in solvation energy with different solvent composition.

For DOCI, a value $\Phi_{NP}\Delta V_{NP} = 0$ was derived from the plots, both at variable temperature and at variable solvent composition. This could be the result of a too low value of the quantum yield (a value of $\Phi_{NP} = 0.012 \pm 0.007$ was determined using the comparative method in flash photolysis [9]) or a truly zero volume change. Assuming the latter, a provisional assignment of the photoisomer structure was made.

Acknowledgements: We are indebted to Professor Kurt Schaffner for his constant support of this work.

References

- [1] Callis, J. B., Parson, W. W., and Gouterman, M., *Biochim. Biophys. Acta* **267** (1972) 348-362.
- [2] Hung, R. R. and Grabowski, J. J., *J. Am. Chem. Soc.* **114** (1992) 351-352.
- [3] Herman, M. S. and Goodman, J. L., *J. Am. Chem. Soc.* **111** (1989) 1849-1854.
- [4] Peters, K. S. and Snyder, G. J., *Science* **241** (1988) 1053-1057.
- [5] Morais, J., Ma, J., and Zimmt, M.B., *J. Phys. Chem.* **95** (1991) 3885-3888.
- [6] Bilmes, G.M., Tocho, J.O., and Braslavsky, S.E., *J. Phys. Chem.* **92** (1988) 5958-5962.
- [7] Braslavsky, S.E. and Heihoff, K. (CRC-Handbook of Organic Photochemistry), Scaiano, J.C., ed., CRC Press, Boca Raton, Florida, 1989) Vol. 1, chapter 14.
- [8] Braslavsky, S.E. and Heibel, G.E., *Chem. Rev.* **92** (1992) 1381-1410.
- [9] Bensasson, R.V., Goldschmidt, C.R., Land, E.J., and Truscott, T.G., *Photochem. Photobiol.* **28** (1978) 277-281.