

CHEMICAL ACTINOMETRY IN THE UV RANGE BASED ON THE PHOTOHYDROLYSIS OF 3,4-DIMETHOXYNITROBENZENE

Libuše PAVLÍČKOVÁ, Petr KUZMIČ and Milan SOUČEK

*Institute of Organic Chemistry and Biochemistry,
Czechoslovak Academy of Sciences, 166 10 Prague*

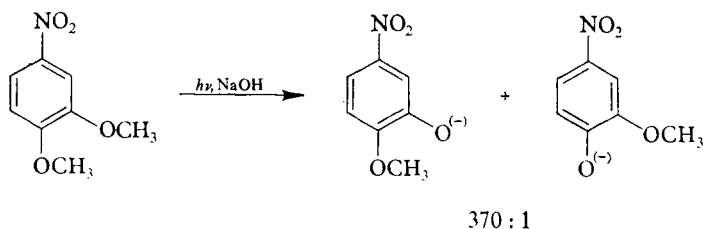
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Photochemical hydrolysis of 3,4-dimethoxynitrobenzene in aqueous potassium hydroxide leading to the formation of 2-methoxy-5-nitrophenolate anion is routinely used for the determination of UV light intensity. The quantum efficiency of the actinometric system is independent on the excitation wavelength (254, 313, 365 nm) and reaches the value of 0.116 ± 0.002 in 0.5 M-KOH. The light intensity determination is based purely on UV/VIS spectral absorption data. A photokinetic model is presented for the reaction which is generally applicable for any photochemical system with the involvement of inner filtration due to products and partial light absorption. The evaluation of primary spectral data is performed by numerical integration of the photokinetic equation.

A chemical actinometer is defined as a system which can be used for the determination of the excitation light intensity on the basis of a light induced chemical process. Among these, one of the classical systems is the ferrioxalate actinometer according to Hatchard and Parker¹ commonly used as an actinometric standard. Unfortunately, this method despite of its universal applicability has some disadvantage in its complexity² and, as for the practical aspects, is rather time consuming in analytical procedures. It is therefore quite frequent that some other chemical actinometers are used³ usually based on the photochemical reactions studied in detail in the particular laboratory. The most important advantage in this approach is that the quantum yield of such an actinometric reaction is similar to those of the reactions under study and the analytical procedures (*e.g.*, chromatography, spectroscopy) are of the same type. In this point our laboratory makes no difference; the system we have chosen as an actinometer belongs to the class of nucleophilic aromatic photo-substitutions which are in the centre of our attention. The reaction of the choice was the photohydrolysis of 3,4-dimethoxynitrobenzene in alkaline media yielding 2-methoxy-5-nitrophenolate as the main product⁴ (Scheme 1).

It is the aim of the present study to illustrate the applicability of the reaction for the actinometry of UV light and to devise its kinetic model. With regard to some basic characteristics of the actinometric system, such a model would be generally applicable to any photochemical system studied under the conditions of a) partial

light transmission and *b*) inner filtration due to photochemical products. As for the total light absorption which is quite often encountered in the literature, it is easy to achieve and removes the necessity of corrections for the transmissivity of the irradiated sample. On the other hand, the high concentrations lead to serious mixing



SCHEME 1

problems and make impossible the direct determination of complete absorption spectra, *i.e.*, the direct spectrophotometric analysis of the reaction mixture. The reverse is true for the photochemistry in weakly absorbing solutions; at low optical densities the errors due to non-ideal mixing are substantially diminished and changes in absorption spectra are detectable in the whole range.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. UV/VIS absorption spectra were recorded on a Cary 219 spectrophotometer (spectral bandwidth 1.5 nm); for the determination of quantum yields the spectral data were collected with the accuracy of ± 0.0002 absorbance units.

3,4-Dimethoxynitrobenzene was prepared according to the described method⁵ and was crystallized twice from water, m.p. 94°C, lit.⁵ m.p. 93–94°C. Traces of oxygen were removed from the argon gas (99.99% purity) using the absorber described by Tenygl⁶ filled with the deoxygenation solution according to Meites⁷. Demineralized water was redistilled from potassium permanganate.

Determination of quantum yields. The isolation of monochromatic light from the spectrum of a high pressure mercury lamp (HBO-200) was achieved using an Applied Photophysics M-300 high intensity monochromator (dispersion 0.25 mm/nm). Its intensity was determined by ferrioxalate actinometry² under the conditions identical with the subsequent photolyses of 3,4-dimethoxynitrobenzene (temperature $25 \pm 1^\circ\text{C}$, irradiated volume 3.00 ml, fixed optical arrangement). Solutions of 3,4-dimethoxynitrobenzene ($1.36 \cdot 10^{-4} \text{ mol l}^{-1}$) in aqueous potassium hydroxide of given concentration were irradiated in a magnetically stirred quartz cuvette. Before and after the completion of each run the absorbance at the excitation wavelength was determined and the reaction course was followed by monitoring the absorbance at 450 nm at regular time intervals (15.0 s, total irradiation time 60.0–90.0 s). The absorbance data were plotted against the irradiation time to check the linearity of the dependence and were evaluated by the numerical procedure described below.

RESULTS AND DISCUSSION

The photolysis of 3,4-dimethoxynitrobenzene in aqueous potassium hydroxide is accompanied by spectral changes shown in Fig. 1. It is apparent that the position of the isosbestic point at 384 nm is retained up to the total conversion of the starting compound. It means that during the whole irradiation period the reaction follows a well-defined course corresponding to the formation of either a single photoproduct or a product mixture with constant distribution. Van Riel and coworkers⁴ have in fact found that a small amount (0.3%) of 2-methoxy-4-nitrophenolate anion is formed beside the isomeric main product (99.7%, Scheme 1). From the kinetic point of view we can nevertheless consider the photohydrolysis of 3,4-dimethoxynitrobenzene as a simple reaction of the type $S \rightarrow P$, where the starting compound S is irreversibly transformed into the only photoproduct P , its absorption spectrum being identical with that of the reaction mixture at infinite irradiation time. The most important spectral characteristics of S and P lies in molar absorption coefficients at certain selected wavelengths, *i.e.*, at the excitation wavelength and an arbitrarily chosen analytical one. Thus, the molar absorption coefficients of S at 254, 313, 365 and 450 nm are 315, 593, 568 and $3 \text{ m}^2 \text{ mol}^{-1}$, while 1047, 452, 280 and $304 \text{ m}^2 \text{ mol}^{-1}$ could be ascribed to P at the same wavelengths.

The quantum yield Φ of the reaction $S \rightarrow P$ is defined by equations (1)–(4),

$$\Phi = n_r / I_{\text{abs}} , \quad (1)$$

$$I_{\text{abs}} = \int_{t_0}^{t_r} I_a \, dt , \quad (2)$$

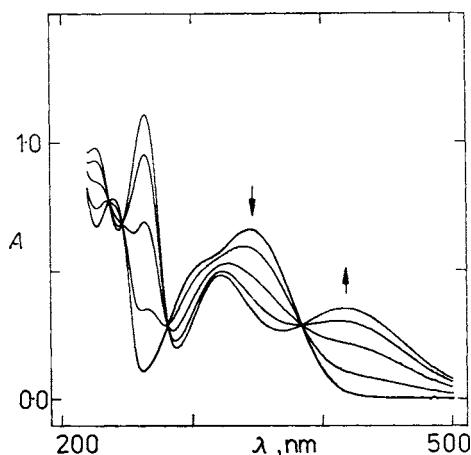


FIG. 1
Spectral changes during the irradiation of an air saturated solution of 3,4-dimethoxynitrobenzene in 0.5 M-KOH with monochromatic light ($365 \pm 10 \text{ nm}$). Spectra were recorded at 0, 1, 3, 6 and 20 min

$$I_a = I_0(1 - 10^{-A}) c_S \epsilon_S / (c_S \epsilon_S + c_P \epsilon_P), \quad (3)$$

$$A = (c_S \epsilon_S + c_P \epsilon_P) d, \quad (4)$$

where n_r (mol) is the amount of S converted at the final irradiation time t_r (s), I_{abs} (mol quanta) is the integrated light intensity absorbed at t_r by the starting compound, I_a (mol quanta s^{-1}) is the corresponding actual light intensity, I_0 (mol quanta s^{-1}) is the intensity of the incident monochromatic light approaching the front wall of the reaction cuvette, A is the absorbance of the irradiated sample at the excitation wavelength, ϵ_S , ϵ_P , c_S , c_P are the respective molar absorption coefficients and concentrations and d is the optical path length. For the determination of the quantum yield Φ it is necessary to determine the incident light intensity I_0 and to evaluate the integral on the right side of the equation (5),

$$I_{\text{abs}} = I_0 \int_{t_0}^{t_r} (1 - 10^{-A}) \frac{1 - x}{1 - x(1 - \epsilon_P/\epsilon_S)} dt, \quad (5)$$

where x is the actual conversion degree defined as $x(t) = (c_S(0) - c_S(t))/c_S(0)$. This integral, further denoted as the correction factor F (Eq. (6)), can be numerically evaluated provided the functions $x(t)$ and $A(t)$ are analytically expressed. It is of great advantage if the final conversion, x_r , is kept relatively low, not to exceed the range where $x(t)$ is roughly linearly dependent on time. The absorbance experimentally determined at the analytical wavelength (450 nm) is plotted against the irradiation time in Fig. 2. It can be concluded from the data shown in Fig. 2 that the linear approximation of $x(t)$ is valid at least up to the conversion degree of 0.25. Of course, at this time the inner filtration is far from being negligible (see the values of absorption coefficients mentioned above) but in our approach it causes no difficulty because the inner filtration effect is quantitatively evaluated and thus eliminated.

It is especially convenient to use for the evaluation of the integrated intensity a programmable calculator or an on-line microcomputer/spectrophotometer system. In this laboratory we use a programmable calculator which first performs the linear regression analysis of the absorbance data to find the analytical expression of the functions $A(t)$, $x(t)$ and then makes the numerical integration according to equations (6) and (7),

$$F = \Delta t \left(\frac{1}{2} f_1 + \frac{1}{2} f_n + \sum_{i=2}^{n-1} f_i \right), \quad (6)$$

$$f_i = (1 - 10^{-(k_1 + k_2 i \Delta t)}) \frac{1 - k_3 i \Delta t}{1 - k_3 i \Delta t (1 - \epsilon_P/\epsilon_S)}, \quad (7)$$

where the coefficients k_1 , k_2 , and k_3 characterize the empirically found linear functions $A(t) = k_1 + k_2t$, $x(t) = k_3t$ and Δt is the integration step defined as t_r/n . In the preliminary experiments using ferrioxalate actinometry we have determined the quantum yield for the photolysis of 3,4-dimethoxynitrobenzene in air saturated solutions of 0.5 M-KOH. At all of the excitation wavelengths 254 ± 10 , 313 ± 10 , and 365 ± 10 nm we found the identical value of $\Phi = 0.116 \pm 0.002$. This value we currently use for the determination of the incident light intensity according to the equation (8),

$$I_0 = \frac{x_r c_0 V}{0.116 F}, \quad (8)$$

where c_0 is the initial concentration of 3,4-dimethoxynitrobenzene (both x_r and c_0 are calculated from the spectral data), V is the volume of the irradiated sample and F is the correction factor defined by Eq. (6).

From the point of view of practical use it is important to know the dependence of Φ on different experimental conditions as for example the concentration of reactants, wavelength of the exciting radiation, presence of oxygen or the reaction temperature. In fact we have found that deoxygenation of the reaction mixture by extensive bubbling with high purity argon gas has no effect on the quantum yield, despite of the fact that the reaction mechanism involves most probably the triplet excited state⁴. In our case, however, the effect of oxygen as a triplet quencher could not be observed due to very high (limiting) concentration of the nucleophilic anion. As for the effect of temperature we have determined that going from 25°C to 35°C

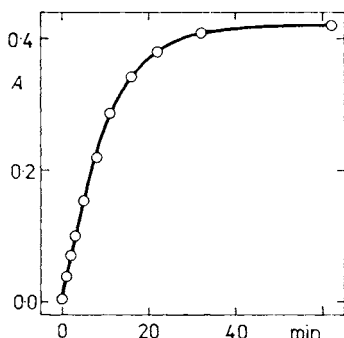


FIG. 2

Absorbance at 450 nm vs irradiation time during the photolysis (365 ± 10 nm) of an air saturated solution of 3,4-dimethoxynitrobenzene in 0.5 M-KOH

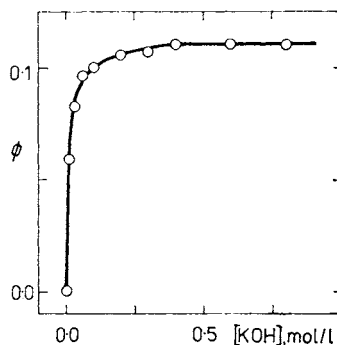


FIG. 3

Quantum yield of photohydrolysis (365 ± 10 nm) of 3,4-dimethoxynitrobenzene vs potassium hydroxide concentration

the quantum yield raises from 0.116 to 0.125; it means that to assure sufficient reproducibility it is needed only to keep temperature within the limits of $\pm 2^\circ\text{C}$ which is easily achievable. The dependence of the quantum yield on the concentration of potassium hydroxide is shown in Fig. 3. In the concentration range 0.4 to 0.6 mol \cdot l^{-1} the quantum yield has virtually constant value, *i.e.*, is independent on the exact concentration of hydroxide. This is quite an advantage for the reproducibility of preparation of the actinometric solution. Another substantial advantage is the independence of Φ on the exciting wavelength mentioned above which is to be expected in case a reaction runs from a single lowest excited state (singlet or triplet). In our case it makes the actinometer universal throughout the whole UV range while the diffuse daylight is completely ineffective.

Reproducibility is one of the most important features of any chemical actinometer; it is determined not only by experimental errors in ordinary sense but also by some inherent instability, say due to chain reactions (quantum yield higher than 1.00) in the ferrioxalate actinometry. The raw absorbance data obtained in two subsequent determinations of light intensity (365 ± 10 nm), before and after a series of photokinetic experiments, are collected in Table I. It follows from the data shown in Table I that the dependence of absorbance at 450 nm on the irradiation time is strictly linear, despite of the fact that the final conversion degree was 0.17. Linear regression analysis gave almost identical results for the two runs and the intensity calculated by the method described above was $9.55 \cdot 10^{-9}$ and $9.61 \cdot 10^{-9}$ mol quanta \cdot s^{-1} , respectively.

We can conclude that the photochemical hydrolysis of 3,4-dimethoxynitrobenzene in 0.5 M-KOH proves to be a well defined chemical actinometer for UV light intensity

TABLE I

Absorbance data for the determination of light intensity (365 ± 10 nm) obtained during the photolysis of an air saturated solution of 3,4-dimethoxynitrobenzene ($1.36 \cdot 10^{-4}$ mol l^{-1}) in 0.5 M-KOH

Time, s	Exp. 1		Exp. 2	
	A_{365}	A_{450}	A_{365}	A_{450}
0	0.7710	0.0063	0.7705	0.0075
15	—	0.0196	—	0.0189
30	—	0.0310	—	0.0310
45	—	0.0429	—	0.0416
60	—	0.0536	—	0.0533
75	—	0.0652	—	0.0646
90	0.7095	0.0760	0.7098	0.0763

determinations, the results being obtained in a fairly quick and reproducible way. We recommend this method for use in any photochemical laboratory equipped with a high quality spectrophotometer with digital output for the collection of experimental data and a programable calculator or an on-line computer for their numerical evaluation.

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