# Similarity of photodissociation waves and experimental determination of the primary period of the photochemical process

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A method for the experimental determination of the duration of the primary process of photolysis and of the start of secondary chemical reactions, based on the similarity properties of photodissociation waves, is described. First experimental results are presented.

It is customary to subdivide the photolysis process into the primary act of photodissociation and subsequent secondary chemical reactions[1]. Depending on the type of the secondary chemical processes, photodissociation waves can be of three types:

1) Free photodissociation waves, i.e., the concentration profile of the photoactive substance is not perturbed by the products of the secondary chemical processes[2].

2) Accelerated photodissociation waves, i.e., the secondary chemical processes lead to additional decomposition of the photoactive process and thereby accelerate the propagation of photodissociation waves[3].

3) Slowed photodissociation waves, i.e., the secondary processes lead to the regeneration of the initial photoactive substance which, at a sufficiently high rate of the recombination reactions, may slow down or stop completely the propagation of photodissociation waves.

The use of the photodissociation process for creating an inversion[4] or for the initiation of secondary reactions leading to an inversion[5] demands a detailed study of the whole photochemical process, since the secondary chemical reactions may exert either a favorable or unfavorable effect on the generated energy yield.

In view of the usual complexity of the mechanism of the secondary reactions and of the essential nonlinearity of the equations of the chemical kinetics it is reasonable to examine, as a starting approximation, the development and the propagation of photodissociation waves of all three types under the assumption that the secondary products and processes have no effect on the structure of the photodissociation waves. This assumption which, generally speaking, is clearly inaccurate for accelerated and slowed photodissociation waves, may be a reasonably good approximation during the first stage of photolysis, i.e., the primary period, when the accumulation of secondary products is still insufficient to have any observable effect on the structure and the propagation of photodissociation waves. Thus, any given photodissociation wave is free during the primary period, and an analysis of the photolysis process during this stage can be made on the basis of an independent study of free photodissociation waves and of their accompanying local chemical reactions.

There arises the question of determining the time interval during which a given photodissociation wave can be regarded as free. It is clear that the method used for determining the duration of the primary period must meet the requirement that all the experimental conditions be close to the conditions under which this information may be used. The reason for this requirement is that most processes accompanying the photolysis are essentially not in equilibrium. Therefore, for example, study of the recombination of a photoactive substance, carried out under high-dilution and quasi-equilibrium conditions and under weak steady-state irradiation, yields very little information suitable for use under strongly nonequilibrium conditions, with intensive pulsed photolysis at high concentrations of the substance.

As a method meeting these requirements, it is here proposed to use the experimental verification of the similarity of free photodissociation waves, i.e., of a property established by the present authors[6] from an analysis of the system of equations for a physical model of these objects, under definite initial and boundary conditions.

Similarity properties exist for a broad class of system geometries, and can be established in two manners: either by an analysis of the dimensionalities of the physical quantities that determine the course of the process, or by a study of the analytically-obtainable solutions of the initial equations, which can be obtained analytically. Both methods have been used, and have led to identical results.

As an illustration of the basic idea, let us consider the case of a plane free photodissociation wave, which admits of a quadrature solution of a system of nonlinear partial integro-differential equations. The form of the photolysis wave in the working substance N(x, t), with a radiation flux density P(x, t, $\nu$, $\theta$), is determined by the system of equations

$$\partial P/\partial x = -P\sigma N,$$

$$\partial N/\partial t = -2\pi c N \int_0^{\pi/2} d\theta \sin\theta \int_0^{\infty} d\nu\sigma(\nu) P(x, t, \nu, \theta)$$

with the initial and boundary conditions

$$N(x, 0) = N_0, \quad P(x_0, t, \nu, \theta) = P_0(\nu, \theta).$$

where x and t are reckoned from the position of the source and the instant when it is turned on; $\nu$ and $\theta$ are parameters that determine the frequency and angular distribution of the source; $\sigma(\nu)$ is the absorption cross section and depends on the frequency; c is the speed of light.

By introducing a new independent variable of the optical thickness type

$$\tau = \int_0^x N(x', t)\, dx'$$

the system that is nonlinear with respect to N reduces to the linear equation

$$\frac{\partial N(\tau,t)}{\partial t}-\Phi(\tau)\frac{\partial N(\tau,t)}{\partial\tau}=-N(\tau,t)F(\tau),$$

where

$$\Phi(\tau)=-2\pi c\int_0^\infty\int_0^{\pi/2}\sin\theta\cos\theta[1-\exp(-\sigma(\nu)\tau/\cos\theta)]P_0(\nu,\theta)\,d\nu\,d\theta,$$

$$F(\tau)=-2\pi c\int_0^{\pi/2}\sin\theta\,d\theta\int_0^\infty\sigma(\nu)P_0(\nu,\theta)\exp[-\sigma(\nu)\tau/\cos\theta]\,d\nu.$$

If we wish to return to the variables x and t, we must solve the equation

$$\partial\tau/\partial t=-\Phi(\tau)$$

with the initial condition $\tau_0 = N_0x$. It is evident from this that $\tau(x, t)$ is a universal function of the combination $\tau_0 = N_0x$. From the nonlinearity of the equation for $N(\tau, t)$ it follows that the normalized profile of the photolysis wave $N/N_0 = \psi(\tau, t)$ also depends in a universal manner on the combination $\tau_0 = N_0x$. Thus, if the photolysis wave is independent of the subsequent reactions, all plane photolysis waves, when plotted in the coordinates $N/N_0$ and $N_0x$, coincide at all instants of time (see Fig. 1). This similarity makes it possible to set up experiments to verify the model of a free photodissociation wave by comparing standard reference radiation fluxes that have passed originally through identical optical densities $\tau_0 = N_0'x' = N_0''x''$ of physically different systems $N_0' \neq N_0''$, $x' \neq x''$.

The instant of time at which the transmitted fluxes start to differ (in intensity or in spectral composition) determines the duration of the primary period, i.e., the limits of applicability of the model of a free photodissociation wave that are essential in practice, and offers the possibility of evaluating the characteristic rates of the secondary chemical reactions, in particular, of rapid reactions with radicals and excited molecules. A schematic diagram of the scheme of apparatus[7] for this differential spectrokinetic analysis is given in Fig. 2.

The main difference between this unit and the well known Norrish, Porter, and Thrush apparatus[8] for pulsed kinetic spectroscopy consists in the presence of several channels, along which at least two cells of different sizes, containing a photoactive substance are probed simultaneously; the filling of the cells is such that the original optical densities are equal. The cells are arranged in a geometrically similar fashion with respect to the source of photolysis light. The structural variants of this arrangement can vary considerably.

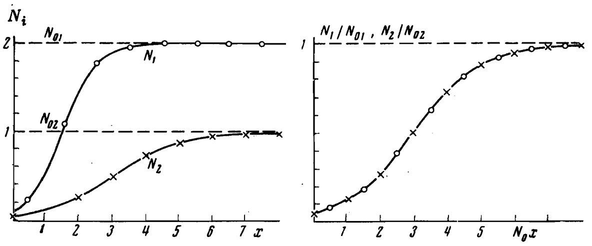

FIG. 1. Curves for the treatment of a photoactive substances as a function of the distance x (left-hand figure) and of the optical density $N_0x$ (right-hand figure), in arbitrary units.

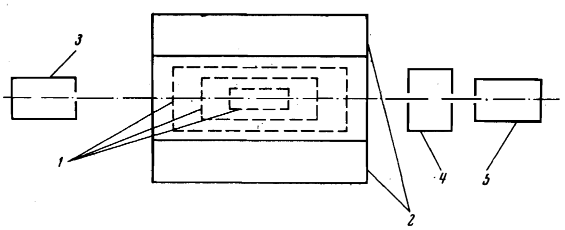

FIG. 2. Apparatus for pulsed photolysis: 1) arrangement of reaction cell in different experiments; 2) pulsed photolysis light source; 3) spectroscopic pulsed light source; 4) monochromator; 5) radiation detector (spectrograph).

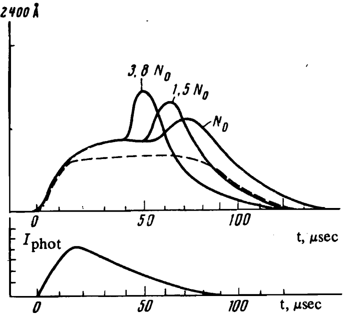

FIG. 3. Results of analysis of oscillograms.

Figure 3 gives data from the analysis of oscillograms of the time variation of the intensity of a probing light source with a wave length of 2400 Å, passing through initially equal optical thicknesses of three sample cells containing $CF_3I$ gas. Quartz cells of similar form, with diameters of 5, 13, and 19 mm, were used in the experiments. The length of the largest cell was 80 cm. The pressure of the gas in the cell was, respectively, 26, 10, and 6.8 Torr. The lower part of Fig. 3 shows the photolysis radiation source, pulse waveform, while the upper part shows plots of the intensity of a probing signal with λ = 2400 Å for the above three experiments. The dashed line illustrates the form of the signal of an EV-45 light source, recorded using a photomultiplier in the absence of photodissociation. The source of the photolysis radiation was a coaxial flash lamp fed from a 75 μF capacitor bank, with an initial voltage of 15 kV. In this series of experiments, tests were carried out in accordance with a sequential scheme, which demanded special monitoring of the reproducibility of the pulses of the probing and photolysis light sources. If a simultaneous multichannel testing scheme is used, the necessity for this type of monitoring is obviated, and the form of the pulses may be arbitrary.

The fact that three curves have identical initial sections points to the existance of free photodissociation wave conditions at the given initial densities and the given intensity of the photolysis light. The curves begin to differ after the 45-th microsecond of the process; it appears first of all for the cell in which the original pressure was maximal. In the cells with a lower pressure, the duration of the primary period is naturally longer, since the secondary processes (pyrolysis in this case) take place in them at a lower rate. The dependence of the duration of the primary period on the concentration and the intensity of the photolysis light, provides a new type of information on the rates and the mechanisms of the secondary reactions.

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135