C. E. Herrick, Jr.

Solution of the Partial Differential Equations Describing Photodecomposition in a Light-absorbing Matrix having Light-absorbing Photoproducts

Abstract: A solution has been obtained for the system of partial differential equations describing the photolysis of an arbitrary number of light-sensitive materials contained in a semirigid, nonscattering, actinic light-absorbing matrix. Each photoreactant may produce stable, actinic light-absorbing products. The solutions reduce to known closed form expressions for the simplest cases.

Introduction

In an earlier theoretical study of the sensitometry of positive-working diazotype films we showed that for monochromatic illumination, the shape of the sensitometric curve is fully determined by the initial actinic density of the diazo compound and the initial dye density produced on coupling the diazo to form an azo dye.[1] Without exception, such sensitometric curves possess no linear portion and are unsuitable for many applications.[2] It has recently been shown that the sensitometric curve for diazotype films can be linearized by the use of stratified sensitizing layers if at least one suitably chosen layer contains an inert, actinic light-absorbing substance.[3] As a preliminary step in the development of a sensitometric theory for diazotype composite layers, we have obtained a general solution for the system of partial differential equations applicable to the photolysis of a single such layer. Our results are applicable to systems containing an arbitrary number of light-sensitive materials, each of which may produce actinic light-absorbing photoproducts. The light-sensitive layer, semirigid and nonscattering, is presumed to contain photo-inert, light-absorbing materials as well.

Notation and basic equations

The present treatment is restricted to monochromatic actinic illumination. We shall assume that neither the net quantum efficiency of disappearance, ϕ_i, for each light-sensitive substance nor the chemical nature of the photoproducts arising from each photoreactant changes with exposure. We assume that the final photoproducts, though they may absorb actinic light, are essentially photo-inert. Beer's law is presumed valid for all of the substances throughout the layer. We further assume that any thermal reactions going on proceed instantaneously, yielding final product concentrations linearly related to the nominal primary photoproduct concentrations at all exposures. Actinic light absorption is presumed to remain isotropic throughout the entire exposure.

- *Notation*

$n_i(t)$	*Number of molecules* of the i^{th} photoreactant encountered throughout the film thickness per sq cm, e.g., the total number of molecules of the i^{th} component remaining at time t.
x	*Reduced distance* (l/L) of a particular elementary layer from the film surface receiving the incident actinic light, where l is the actual distance and L is the total thickness.
$C_i(x, t)$	*Concentration*, $\partial n_i(t)/\partial x$, in molecules per sq cm at time t sec and fractional depth x.

$I(x, t)$	*Light intensity* in photons per sq cm per sec at point x and time t.
k_i	*Absorption coefficient* of the i^{th} light-sensitive substance measured in base 10 density units per molecule.
K_i	*Absorption coefficient* of the i^{th} absorbing photoproduct per molecule of i^{th} photoreactant destroyed.
μ	*Product of effective absorption coefficient* of light-stable absorbers by absorber concentration.
α	ratio, base e to base 10 logarithms.

- *Basic equations*

For the system described the rate of change of light intensity with depth is

$$\frac{\partial I(x, t)}{\partial x} = -\alpha\mu I(x, t) - \sum_{i=1}^{m} \alpha k_i C_i(x, t) I(x, t)$$

$$- \sum_{i=1}^{m} \{[C_i(x, 0) - C_i(x, t)]\alpha K_i I(x, t)\}, \qquad (1)$$

where the sequence of terms describes light attenuation due to stable light absorbers, photoreactants, and photoproducts, respectively. The rate of change of concentration of the i^{th} material with time at the point x is

$$\frac{\partial C_i(x, t)}{\partial t} = -\alpha k_i \phi_i C_i(x, t) I(x, t). \qquad (2)$$

For the case of a single light-sensitive substance ($m = 1$), light absorbers absent ($\mu = 0$), and no light absorption by photoproducts ($K_i = 0$), a closed form solution was obtained a number of years ago by W. Wirtinger.[4] More recently Kirkwood[5] obtained a solution for $m = 1$, $K_i = 0$.

Derivation of the general solution

We set

$$\int_0^t I(x, t)\, dt = E(x, t), \qquad (3)$$

with $I(x, t)$ given by

$$I(x, t) = \partial E(x, t)/\partial t. \qquad (4)$$

By using (4), Eq. (2) can be integrated at once to yield

$$C_i(x, t) = C_i(x, 0) e^{-\alpha k_i \phi_i E(x, t)}. \qquad (5)$$

Hereafter, clarity permitting, we will write simply C_i for $C_i(x, t)$, E for $E(x, t)$, and omit summation limits. We will denote $C_i(x, 0)$ by C_i^0.

Substitution of (4) in (1) gives

$$\frac{\partial\left(\frac{\partial E}{\partial t}\right)}{\partial x} = -\alpha\mu \frac{\partial E}{\partial t} - \sum \alpha k_i C_i \frac{\partial E}{\partial t}$$

$$- \sum \left\{[C_i^0 - C_i]\alpha K_i \frac{\partial E}{\partial t}\right\}. \qquad (6)$$

The replacement of C_i in (6) with the exponential expression of (5) yields

$$\frac{\partial\left(\frac{\partial E}{\partial t}\right)}{\partial x} = -\alpha\mu \frac{\partial E}{\partial t} - \sum \alpha k_i C_i^0 e^{-\alpha k_i \phi_i E} \frac{\partial E}{\partial t}$$

$$- \sum \left\{C_i^0[1 - e^{-\alpha k_i \phi_i E}]\alpha K_i \frac{\partial E}{\partial t}\right\}. \qquad (7)$$

We now note that

$$\frac{\partial\left(\frac{\partial E}{\partial t}\right)}{\partial x} = \frac{\partial^2 E}{\partial t\, \partial x} = \frac{\partial\left(\frac{\partial E}{\partial x}\right)}{\partial t}, \qquad (8)$$

$$-\sum \alpha k_i C_i^0 e^{-\alpha k_i \phi_i E} \frac{\partial E}{\partial t} = \sum \frac{\partial}{\partial t} \left\{\frac{C_i^0}{\phi_i} e^{-\alpha k_i \phi_i E}\right\} \qquad (9)$$

and

$$-\sum \alpha K_i C_i^0 [1 - e^{-\alpha k_i \phi_i E}] \frac{\partial E}{\partial t}$$

$$= -\sum \frac{\partial}{\partial t} \left\{\frac{K_i C_i^0}{k_i \phi_i} (\alpha k_i \phi_i E + e^{-\alpha k_i \phi_i E})\right\}. \qquad (10)$$

Using (8), (9) and (10) we may now write (7) as

$$\frac{\partial}{\partial t} \left\{\frac{\partial E}{\partial x} + \alpha\mu E - \sum \frac{C_i^0}{\phi_i} e^{-\alpha k_i \phi_i E}\right.$$

$$\left. + \sum \frac{K_i C_i^0}{k_i \phi_i} (\alpha k_i \phi_i E + e^{-\alpha k_i \phi_i E})\right\} = 0. \qquad (11)$$

Integration of (11) yields on the right-hand side a function of x alone which we take as $K(x)$. By differentiation of (5) with respect to x we may readily establish that at $t = 0$,

$$\frac{\partial E(x, 0)}{\partial x} = 0 \qquad (12)$$

whence

$$K(x) = \sum \frac{C_i^0}{\phi_i} \left(\frac{K_i}{k_i} - 1\right). \qquad (13)$$

The differential equation resulting from the time integration of (11) can be written as

$$dx = \frac{dE}{K(x) + \sum \frac{C_i^0}{\phi_i} \left(1 - \frac{K_i}{k_i}\right) e^{-\alpha k_i \phi_i E} - (\alpha\mu + \sum \alpha K_i C_i^0) E}. \qquad (14)$$

If we now take the various components to have been uniformly distributed throughout the layer at zero exposure, (14) is immediately (numerically) integrable. Thus,

$$x = \int_{E(0,t)}^{E(x,t)} \frac{dE}{\sum \left\{ \frac{C_i^0}{\phi_i} \left(\frac{K_i}{k_i} - 1 \right) (1 - e^{-\alpha k_i \phi_i E}) \right\} - E(\alpha\mu + \sum \alpha K_i C_i^0)} . \tag{15}$$

In practical computation, we choose an arbitrary value of the exposure at the incident light side, that is, a value of the lower limit $E(0, t)$, and we integrate to that particular upper limit that produces a value of unity for the definite integral. Each $E(0, t)$ is associated with a particular upper limit $E(1, t)$ in this way. By (15), $E(1, t)$ is the exposure which the extreme back side of the layer has received, e.g., the exposure at $x = 1$. In many cases we may take $E(0, t) = I_0 t$ although the equations are not limited to a uniform incident intensity. The value of the definite integral produced by an arbitrary value of the upper limit ($\int_{E(0,t)}^{E(x,t)} \leq 1$) gives the exposure received by the layer at the fractional depth x. Such values of $E(x, t)$ may be substituted in (5) and a concentration profile constructed for the layer as a function of the incident exposure parameter $E(0, t)$. For sensitometric purposes, however, such concentration profiles are of no great interest. We need instead, the total number of molecules of the i^{th} species present in the layer as a function of $E(0, t)$, e.g., we wish to evaluate

$$\int_0^1 C_i(x, t)\, dx = n_i(E(0, t)). \tag{16}$$

We may do this for every species by combining (14) and (5) to produce

$$n_i(E(0, t)) = \int_{E(0,t)}^{E(1,t)} \frac{C_i^0 e^{-\alpha k_i \phi_i E}\, dE}{\sum \left\{ \frac{C_i^0}{\phi_i} \left(\frac{K_i}{k_i} - 1 \right) (1 - e^{-\alpha k_i \phi_i E}) \right\} - E\left(\alpha\mu + \sum \alpha K_i C_i^0\right)} . \tag{17}$$

where the limits are to be determined, as outlined above, with the aid of (15).

Closed form comparisons

We may check (15) against a closed form result if we place $\mu = 0$, $K_i = 0$, and $m = 1$. For this case, (15) reduces to

$$x = \int_{I_0 t}^{E_x} \frac{dE}{\frac{-C_0}{\phi} (1 - e^{-\alpha k \phi E})} \tag{18}$$

We set

$$-\alpha k C_0 x = \ln T_0, \tag{19}$$

where T_0 is the initial actinic transmission of the layer. Integration and the insertion of limits gives

$$E_x = \frac{1}{\phi k} \ln \left[1 + T_0(e^{\alpha k \phi I_0 t} - 1)\right] \tag{20}$$

for the total exposure emerging from the back side of the layer.

In our earlier work[1] we showed that the transmission of a layer containing a single photobleaching material was given by

$$T = \frac{1}{\left(\frac{1}{T_0} - 1 \right) e^{-\alpha k \phi I_0 t} + 1} . \tag{21}$$

The exposure transmitted by such a film is evidently

$$E_x = \int_0^t I_0 T\, dt = \int_0^t \frac{I_0\, dt}{\left(\frac{1}{T_0} - 1 \right) e^{-\alpha k \phi I_0 t} + 1} . \tag{22}$$

Integration and insertion of limits gives

$$E_x = \frac{1}{\phi k} \ln \left[1 + T_0(e^{\alpha k \phi I_0 t} - 1)\right] \tag{23}$$

in agreement with the result, (20), obtained from (15).

With the now-verified result for E_x we may check (17) via a closed form expression. We have

$$n(E_x) = \int_{I_0 t}^{E_x} \frac{-\phi e^{-\alpha k \phi E}\, dE}{1 - e^{-\alpha k \phi E}} . \tag{24}$$

Integration, insertion of limits and simplification yields

$$e^{-\alpha k n} = \frac{1}{\left(\frac{1}{T_0} - 1 \right) e^{-\alpha k \phi I_0 t} + 1} = T, \tag{25}$$

in agreement with (21).

We may show that Eq. (15) reduces to Kirkwood's integral by setting $K_i = 0$, $m = 1$, and taking $kC_0 = \beta$ to obtain

$$\beta X = \int_{E(0,t)}^{E(x,t)} \frac{dE}{\frac{-1}{\phi k}(1 - e^{-\alpha k \phi E}) - (\alpha\mu/\beta)E}. \qquad (26)$$

Equation (5) gives $E = -(1/\alpha k\phi)y$, which on substitution in (26) yields

$$\beta X = \frac{1}{\alpha}\int_{y_0}^{y} \frac{dy}{1 - e^y - (\mu/\beta)y}.$$

Results

Extension of Eqs. (1) and (2) to the case of polychromatic illumination is straightforward although the resulting system of equations must be solved numerically.[6] Using a program devised by L. A. Skinner, polychromatic illumination sensitometric curves for a variety of complex diazo film systems have been calculated on the IBM 7094, and these checked against the corresponding experimental systems with excellent agreement in all cases.[7] The assumptions as to the constancy of quantum efficiency with exposure and the applicability of Beer's law are evidently correct for the materials studied.

Appendix

We transcribe here Professor Kirkwood's solution:

$$\frac{\partial I}{\partial x} = -\mu I - kCI$$

$$\frac{\partial C}{\partial t} = -\phi kCI$$

$$\begin{cases} I = I_0 \exp\left\{-\mu x - k\int_0^x C(X', t)\, dx'\right\} \\ \dfrac{\partial I}{\partial x} + \mu I = -kCI = \dfrac{1}{\phi}\dfrac{\partial C}{\partial t} = -\dfrac{1}{\phi k}\dfrac{\partial \ln C}{\partial t} \end{cases}$$

$$\frac{\partial}{\partial t}\left\{\ln C + k\int_0^x e^{\mu(x'-x)} C(x', t)\, dx'\right\} = -\phi k I_0 e^{-\mu x}$$

$$\ln\frac{C}{C_0} + k\int_0^x e^{\mu(x'-x)}[C(x', t) - C(x', 0)]\, dx'$$

$$= -\phi k I_0 e^{-\mu x t}$$

$$y = \ln C/C_0 \qquad \beta = kC_0$$

$$\frac{\partial y}{\partial x} + \mu y + \beta(e^y - 1) = 0$$

$$y_0 = -\phi k I_0 t \quad \text{at} \quad x = 0$$

$$\int_{y_0}^{y} \frac{dy}{1 - e^y - (\mu/\beta)y} = +\beta x.$$

References

1. C. E. Herrick, Jr., *J. Opt. Soc. Am.* **42**, 904–910 (1952).
2. R. Alfaya, *Photographic Science and Engineering* **6**, 258–264 (1962).
3. C. E. Herrick, Jr., U. S. Patent 3,069,268.
4. R. Wegscheider, *Z. Physik, Chem.* **103**, 273 (1923).
5. J. G. Kirkwood, private communication, 1947. (Professor Kirkwood's notes are reproduced in an appendix.)
6. Due to L. A. Skinner.
7. E. M. Evleth, et al., *1965 Symposium on Photography in Information Storage and Retrieval*, Washington, D.C., Oct. 22, 1965.

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