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A CALCULATION ON THE EFFECT OF
NONHOMOGENEITY ON THE DETERMINATION
OF THE RATE CONSTANT OF A BIMOLECULAR,
SECOND-ORDER REACTION

by

Myran C. Sauer, Jr.

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May 1967

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ABSTRACT

In pulse-radiolysis experiments, where a beam of electrons is absorbed by a sample, thereby producing chemical transients, the concentration of the transients is often not uniform, due to attenuation and scattering of the electron beam as it passes through the sample. This report presents a calculation showing that, for a chemical transient that disappears by a bimolecular, second-order reaction, wide variation in initial concentration throughout the reaction cell has a negligible effect on the slope of a plot of the reciprocal of concentration vs time, which is contrary to intuition.

DISCUSSION

Although the calculations to be shown are generally applicable, the calculation has been made specifically to analyze the situation in which a cylindrical cell,¹ 13 cm long and about $2\frac{1}{2}$ cm in diameter, is irradiated with a 12 to 15-MeV electron beam, which enters the cell from one end. If the cell is filled with argon at 900 psi, the energy deposited per unit volume in the gas drops by a factor of about 3.5, going from the front to the back of the cell, due mainly to scattering of the electron beam. Hence, the distribution of transient species is quite nonuniform. Calculations have been made for two assumed situations: (A) where the energy deposited decreases linearly along the cell length, and (B) where the decrease is exponential. The average concentration of transient is determined by the absorption of a beam of light passing lengthwise through the cell.¹

A. Linear Decrease in Energy Deposition

The initial concentration of transient through the cell is defined by the following equation:

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¹M. C. Sauer, Jr. and L. M. Dorfman, J. Am. Chem. Soc. 87, 3801 (1965).

$$C_{0,x} = C_0^0 \left[1 - \left(\frac{1-r}{x_f} \right) x \right], \quad (1)$$

where

$C_{0,x}$ = initial concentration of transient at position x in cell,

C_0^0 = initial concentration of transient at front end of cell
(where the electron beam enters),

x = distance along cell, measured from front end = zero,

x_f = length of cell,

and

r = ratio of the initial concentration of transient at front end
to that at back end of cell.

If the transient would disappear by a bimolecular, second-order process in the absence of effects due to nonuniformity of concentration, then at any position x in the cell (neglecting diffusion),

$$\frac{1}{C_{t,x}} = \frac{1}{C_{0,x}} + at, \quad (2)$$

where $C_{t,x}$ is the concentration at time t and position x , a is the rate constant, and t is the time, measured relative to zero time being the end of the electron pulse.

Equations 1 and 2 can be combined and rearranged to yield

$$C_{t,x} = \frac{C_0^0 \left[1 - \left(\frac{1-r}{x_f} \right) x \right]}{1 + C_0^0 \left[1 - \left(\frac{1-r}{x_f} \right) x \right] at}. \quad (3)$$

The average concentration as a function of time is given by

$$C_{avg} = \frac{\int_{x=0}^{x=x_f} C_{t,x} dx}{x_f}. \quad (4)$$

Integration of Eq. 4 yields

$$C_{avg} = \frac{C_0^0}{T} \left[1 + \frac{1}{T(1-r)} \log_e \left(\frac{1+rT}{1+T} \right) \right], \quad (5)$$

where $T = C_0^0 at$.

Using Eq. 5, we can examine the behavior of the average concentration (which is equivalent to what we observe experimentally) as a function of time. Table I gives C_0^0/C_{avg} for various values of T , as well as the slopes of C_0^0/C_{avg} between successive points, for several values of r , including the case of uniform concentration, $r = 1.0$.

TABLE I. Linear Decrease in Energy Deposition

T	r = 0		r = 0.1		r = 0.2		r = 0.5		r = 1.0	
	$C_0^0/C_{avg}^{(b)}$	Slope	C_0^0/C_{avg}	Slope	C_0^0/C_{avg}	Slope	C_0^0/C_{avg}	Slope	C_0^0/C_{avg}	Slope
0(a)	2.00		1.817		1.667		1.333		1.00	
		1.24		1.16		1.09		1.03		1.00
1	3.24		2.98		2.76		2.36		2.00	
		1.14		1.06		1.03		1.00		1.00
5	7.78		7.22		6.89		6.37		6.00	
		1.08		1.02		1.01		1.00		1.00
10	13.17		12.32		11.95		11.38		11.0	
		1.02		1.005		1.00		1.00		1.00
50	54.1		52.5		52.0		51.4		51.0	
		1.01		1.00		1.00		1.00		1.00
100	104.8		102.4		102.0		101.4		101.0	

(a) The value of C_0^0/C_{avg} for $T = 0$ can be shown to be given by $2/(1+r)$.

(b) The values of C_0^0/C_{avg} reflect the value of C_{avg} , since C_0^0 is a constant.

In many experimental situations, the decay of C_{avg} cannot be followed over more than three half-lives. Therefore, the values of C_0^0/C_{avg} for $T = 0$ through 10 are the most significant. In this range of T , C_{avg} decreases by a factor of $1/6.58$ for $r = 0$, and $1/11$ for $r = 1.0$. The value of the slope for $r = 1.0$ is, of course, 1.00; the deviation from this value for other values of r indicates the error in the determination of the rate constant, a , resulting from the nonhomogeneous concentration. The important fact is that if $r \geq 0.2$, and the experimental results are analyzed over two or three half-lives, an error in the value of a of no more than 5% will result. Even for smaller values of r , the error will not be more than about 10%, under the same conditions of analysis.

B. Exponential Decrease in Energy Deposition

Using the same symbolism as before, we obtain

$$C_{0,x} = C_0^0 e^{-bx}, \quad (6)$$

where b is given by

$$e^{-bx_f} = r. \quad (7)$$

These equations take the place of Eq. 1, and the same process of determining C_{avg} is followed. In this case, the result of the integration is

$$C_{avg} = \frac{C_0^0}{T} \left\{ 1 - \frac{1}{\log_e r} \left[\log_e \left(\frac{T+1}{T+1/r} \right) \right] \right\} \quad (8)$$

In this case also, the value of the slope, determined over the first three half-lives, is within about 5% of the correct value (1.00), as can be seen from the results in Table II for $r = 0.2$.

TABLE II. Exponential Decrease in Energy Deposition for $r = 0.2$

T	C_0^0/C_{avg}	Slope
0(a)	2.02	
		1.13
1	3.15	
		1.04
5	7.32	
		1.01
10	12.38	
		1.00
50	52.4	
		1.00
100	102.5	

(a) The values of C_0^0/C_{avg} for $T = 0$ can be shown to be given by $(1-r)/\log_e(1/r)$.

The effect of diffusion on the initial distribution of transient has not been considered. However, this would cause the distribution to become more uniform throughout the cell, and would therefore lead to a nearer approximation of the slope to the actual rate constant.