Effect of Agitation on Radiation Chemical Reactions Involving Chloral Hydrate Aqueous Solutions

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The location of a radioactive source in the central or inner region of a reactor may be more desirable from the standpoint of the efficiency in use of the source, but it leads to a high nonuniformity in the dose rate distribution. The reaction rates of many radiation chemical reactions are not directly proportional to dose rates and may depend on a power of the dose rate less than 1. For this kind of reaction, it is proved (*1*, *2*) mathematically by the Cauchy-Schwarz inequality that the more uniform distribution of dose rate in time and space gives the higher reaction rate for the same amount of absorbed energy. If there is a sharp nonuniformity of dose rate in a reactor, the overall reaction rate is expected to be increased by agitation when the lifetime of the intermediate is comparable to a time characteristic of the mixing process.

Fredrickson and co-workers (*3*) have discussed the efficiency of the use of radiant energy by culture of algae as functions of mixing, radiation attenuation, and a nonlinear dependence of growing rate. They have shown theoretically the difference of nonmixing and perfect mixing in growth rate and efficiency of light utilization for algal growth chambers. Hill and co-workers (*1*, *4*, *5*) examined theoretically the interaction of mixing, radiation attenuation, and chemical kinetics in a isothermal photoreactor and have discussed time scales of the chemical kinetics and mixing processes by introducing Λ, the ratio of the diffusion mean free path of the radical to the radiation mean free path. They also reported (*6*) experimental results of the effect of mixing in a nonuniformly initiated photopolymerization. The relation between Λ and stirring speed or geometry of the agitated vessel, however, remains to be unfolded.

The purpose of this note is to explore experimentally the effect of agitation on a radiation induced chemical reaction and to suggest a simplified mechanism for the effect.

The radiolysis of chloral hydrate aqueous solution (*7* to *11*) by Cs-137 gamma ray was used as a model reaction.

EXPERIMENTAL

The experimental apparatus is schematically shown in Figure 1*a*. Lead blocks were used to form the high dose rate portion in the reactor by providing a slit width of 5 mm., corresponding to 5.0% of the total cross-sectional area of the reactor. However, it was found experimentally that the collimation was poor and yielded a 10% exposure of the reactor. The Pyrex glass vessel could accommodate four baffles (15 mm. width) and was 125 mm. in diameter. Two sizes of stainless steel agitators were used and are illustrated in Figure 1*b*. Tests were run with the two sizes of agitators, with and without baffles in the reactor vessel. One molar aqueous solution of chloral hydrate was used as the reactant, and the volume was 250 cc. corresponding to 20 mm. in height.

The concentration of hydrochloric acid, which is the main product of the radiolysis, was measured by using a tungsten electrode with a cell constant of 0.27 cm.$^{-1}$. A 900-curie pencil of Cs-137 was used as the gamma ray source. All experiments were carried out in the presence of dissolved oxygen and at 22°C. The agitation speed was varied, yielding 0.5 to 21 sec./rev.

RESULTS AND DISCUSSION

Dosimetry

The average dose rate in the reactor was measured by using an oxygen saturated Fricke solution, with the same amount being used in the reactor as that of the reactant. Irradiations were carried out without agitation for 30 min. An oxygen saturated solution may be used to measure doses up to 5×10^4 rad. Inasmuch as the dose rate of the irradiated portion of the reactor is about 2×10^4 rad./hr., the oxygen break does not occur in any portion of the reactor for the 30-min. irradiation. Thus, the agitation effect on the measurement (*12*) is not significant. The overall dose rate was 30.6 rad./min, and the background dose rate without the slit was 1.0 rad./min.

Radiolysis of Chloral Hydrate Aqueous Solutions

Although the precise reaction mechanism of the radiolysis is not clear up to the present time, it is reported (*8* to *10*) that this reaction is a chain reaction in the presence of dissolved oxygen, the first and second-order termination reactions for a chain carrier take place, and that the producing rate of hydrochloric acid is proportional to the concentration of the chain carrier. Hence, the reaction mechanism is considered to be similar with the model of chain reaction described below:

Initiation		Reaction rate
$M \rightsquigarrow R\cdot$		GI
Propagation		
$R\cdot + E \xrightarrow{k_1} R\cdot + C$		$k_1 [R\cdot] [E] \equiv K [R\cdot]$
Termination		
$R\cdot + S \xrightarrow{k_2}$	stable by-products	$k_2 [R\cdot] [S] \equiv k [R\cdot]$
$2R\cdot \xrightarrow{l}$		$l [R\cdot]^2$

The concentrations of *M*, *E*, and *S* are assumed to be constant for the low conversion experiments.

The chain radical concentration is given by

$$\frac{dn}{dt} = GI - kn - 2ln^2 \tag{1}$$

The rate of production of the product at steady state is *X* and is expressed by

$$X = Kn = A\left(\sqrt{1 + BI} - 1\right) \tag{2}$$

where

$$A = Kk/4l$$
$$B = 8lG/k^2$$

The values of *A* and *B* are calculated to be 15.2 mole/(liter) (min.) and 5.2×10^{-2} min./rad. from the Lotz and Schmidt data (*9*) which were obtained at 20°C. with 250 kv. X ray, and 13.6 mole/(liter)(min.) and 0.11 min./rad. from the McIntosh, Van Cleave, and Spinks data (*10*) obtained at 25°C. with Co-60 γ ray. The authors also reported (*11*) the values of A, B, and *k* to be 0.45×10^{-5} mho/(cm.) (min.) corresponding to 15.7 mole/(liter) (min.), 0.10 min./rad., and 1.10 sec.$^{-1}$ at 22°C. with Cs-137 γ ray. The experiments were carried out without agitation by using a small reactor (20 mm. ϕ) in which the dose rate was almost uniform.

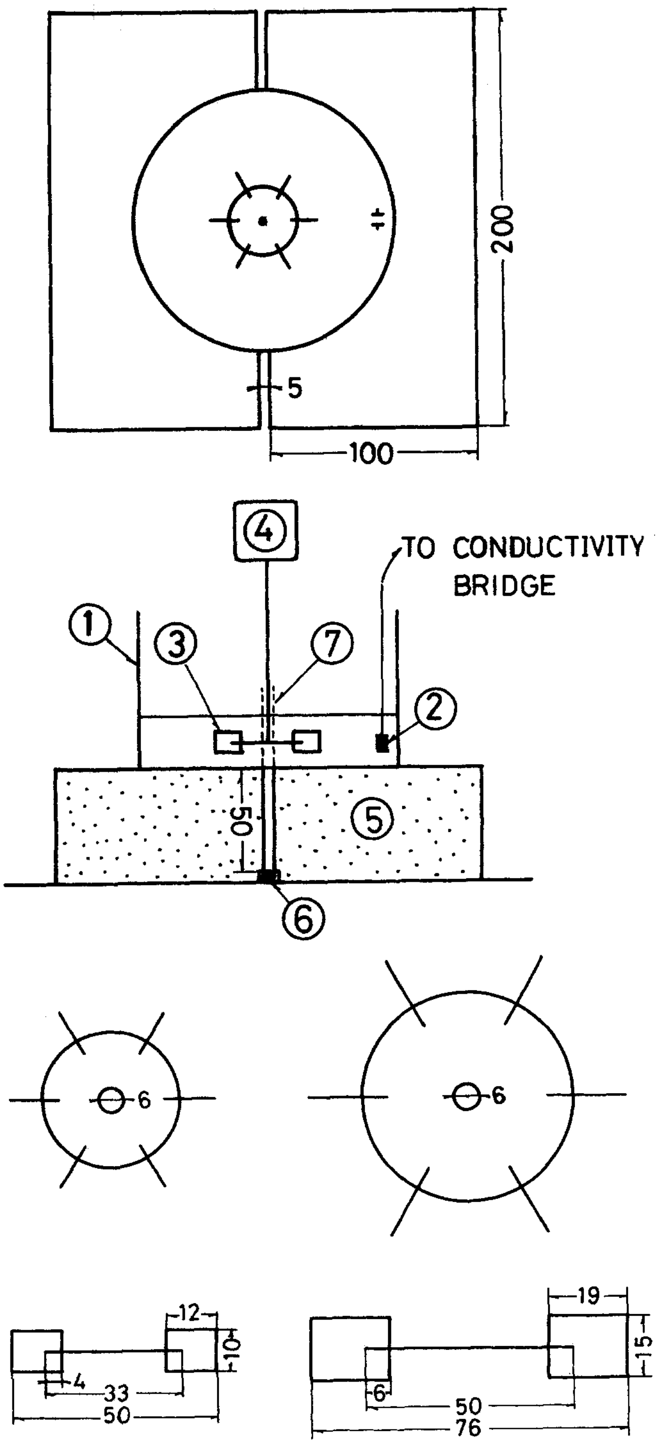

Fig. 1. Experimental apparatus. (a) Reactor system: (1) reactor, (2) tungsten electrode, (3) agitator, (4) motor for agitation, (5) shielding leads, (6) Cs-137 source pencil, (7) separator plates; (b) agitators (dimensions are in millimeters).

The reaction rates of this radiolysis Y $(=X/A)$ are shown as a function of dose rate in Figure 2. The reaction rate is not directly proportional to the dose rate but is related by Equation (2) which is presented as the solid curve.

Effect of Agitation on the Reaction

The reaction rates for the perfect mixing (Y_p) and nonmixing (Y_n) cases are evaluated as follow:

$$Y_p = Y(\bar{I}) = 1.04$$

$$\bar{I} = \kappa I_1 + (1-\kappa) I_2 = 30.6$$

$$Y_n = \kappa Y(I_1) + (1-\kappa) Y(I_2) = 0.51$$

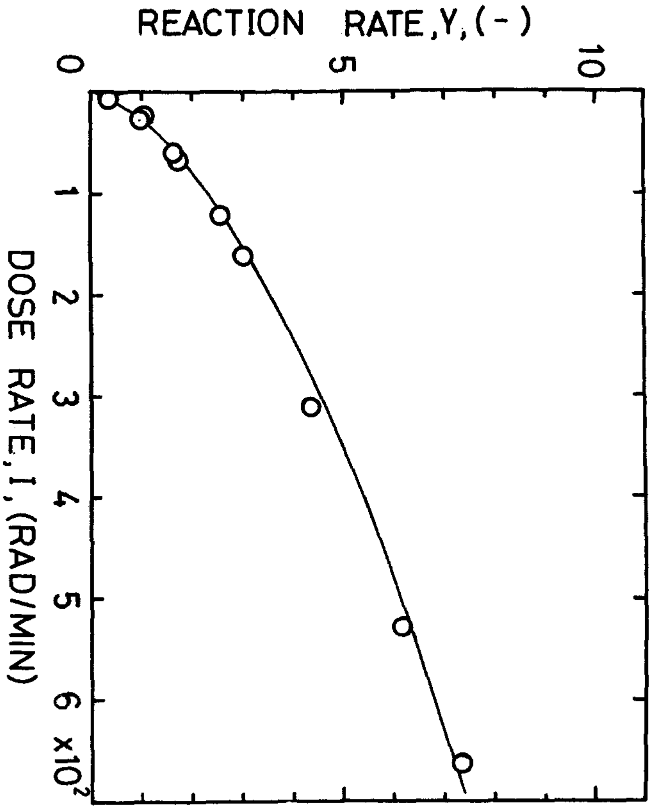

Fig. 2. Rate of formation of hydrochloric acid vs. dose rate. The solid line is based on Equation (2); (○) are measured values.

by using κ, the volume fraction of reactor in the high dose rate, to be 0.1 to match the experimental values of $Y_n = 0.54$.

The experimental results of the effects of agitation on the reaction rate are shown in Figure 3. This graph indicates that the reaction rate depends on the agitation speed, the size of agitator, and the presence of baffles.

In some static experiments, two stainless steel plates were placed in the reactor along the direction of the beam formed by the slit to prevent diffusion of the radical from the high dose rate portions of the reactor. No essential difference was observed in the experiments with and without separator plates, thus indicating that mixing by diffusion is slow compared with reaction rate.

Model Proposed

The mixing process in agitated vessels is considered to be composed of two stages: a macroscale mixing or eddy diffusion process developed by circulation of the fluid in the vessel and a microscale mixing produced by molecular diffusion. In a first step, the degree of segregation may be considered to be kept nearly constant, whereas the scale of segregation is reduced. After that, mixing by molecular diffusion proceeds, reducing the degree of segregation to finally a molecularly uniform concentration. Except for viscous fluids, mixing times by a macroscale process are longer than those by a microscale process (*13* to *15*).

The mixing characteristics are used to formulate a period T for fluid elements to be in the high and low dose rates. In addition, interaction of the fluid elements are introduced through an empirical mass transfer coefficient U. These effects are combined with the treatment for the periodical irradiation exposure to formulate an overall rate equation.

The concentrations of the radical in a fluid element at steady state $(i >> 1)$ are given by

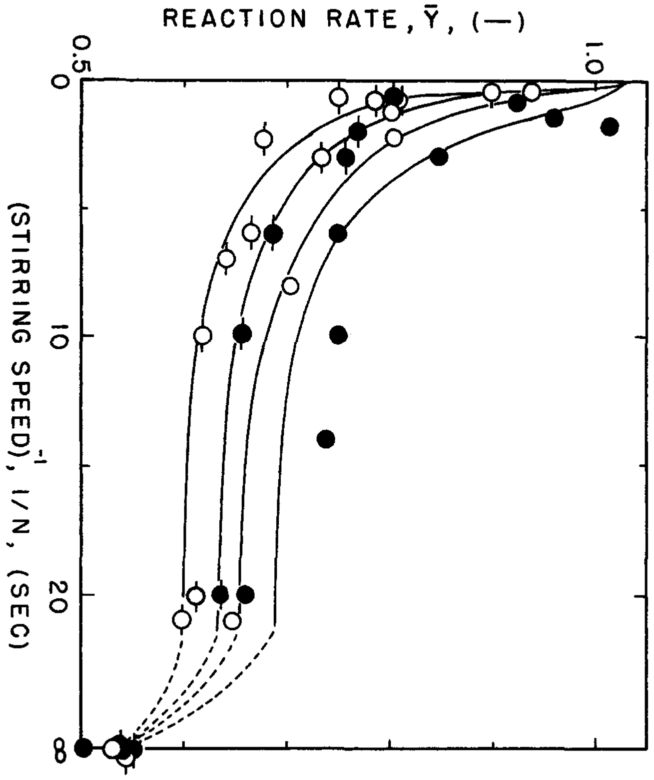

Fig. 3. Rate of formation of hydrochloric acid under agitation vs. reciprocal of stirring speed. (—○—) agitator diameter 50 mm. unbaffled, (○) agitator diameter 76 mm. unbaffled, (—●—) agitator diameter 50 mm. baffled, (●) agitator diameter 76 mm. baffled.

$iT \leqq t < iT + \kappa T$ (high dose rate portion)

$$dn/dt = GI_1 - kn - 2ln^2 + U(\bar{n} - n) \qquad (4)$$

and

$iT + \kappa T \leqq t < (i+1)\,T$ (low dose rate portion)

$$dn/dt = GI_2 - kn - 2ln^2 + U(\bar{n} - n) \qquad (5)$$

where

$$\bar{n} = \frac{1}{T}\int_{iT}^{(i+1)T} n\,dt \qquad (6)$$

The last term provides for the rate of mass transfer based on interactions between fluid elements. Each fluid element is assumed to have interaction with all other fluid elements in the vessel. The age of these fluid elements can be considered to distributed uniformly between iT and $(i + 1)\ T$. The mean concentration for these fluid elements, therefore, is given by $\bar{n}$.

Introducing a dimensionless reaction rate $Y(= Kn/A)$ $iT \leqq t < iT + \kappa T$, we get

$$dY/dt = k(a - Y)(b + Y)/2 \qquad (7)$$

$iT + \kappa T \leqq t < (i + 1)T$

$$dY/dt = k(c - Y)(d + Y)/2 \qquad (8)$$

where

$$a = [\sqrt{1 + p^2\,(BI_1 + 2U\bar{Y}/p)} - 1]/p$$

$$b = a + 2/p$$

$$c = [\sqrt{1 + p^2\,(BI_2 + 2U\bar{Y}/p)} - 1]/p$$

$$d = c + 2/p$$

$$p = k/(k + U)$$

$$\bar{Y} = \frac{1}{T}\int_{iT}^{(i+1)T} Y\,dt \qquad (9)$$

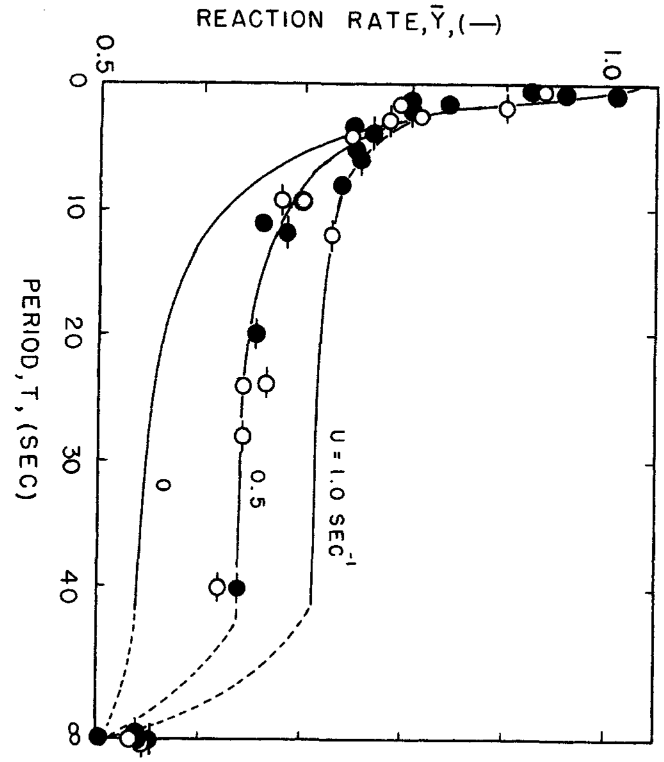

Fig. 4. Reaction rate under agitation vs. period. Notes are same as Figure 3. The solid lines are based on Equation (10).

$\bar{Y}$ represents the average reaction rate in one period producing hydrochloric acid in the fluid element and corresponds to the overall reaction rate in the stirred vessel. $\bar{Y}$ is given by Equation (10):

$$\bar{Y} = \frac{2}{kT}\,ln\left(\frac{r+b}{s+b}\,\frac{s+d}{r+d}\right) + \kappa a + (1 - \kappa)c \qquad (10)$$

r and s are solution of the following equations:

$$\left(\frac{b+s}{a-s}\,\frac{a-r}{b+r}\right) = \exp\,[\kappa kT(a + b)/2] \qquad (11)$$

$$\left(\frac{r+d}{r-c}\,\frac{s-c}{s+d}\right) = \exp\,[(1 - \kappa)kT(c + d)/2] \qquad (12)$$

The flow rate discharged from an agitator in stirred vessels may be expressed in the following form (*16* to *19*):

$$Q = fND^3 \qquad (13)$$

Rushton and co-workers (*16, 17*) reported values of f to be 0.47 for a turbine with four blades, 0.5 for three blades [6 in. turbine (baffled)], and 0.59 for four blades [6 in. turbine baffled)]. Marr and Johnson (*20*) reported f to be 0.61 for a propeller, using tracer circulation measurements. Nagata and co-workers (*18, 19*) reported the coefficient ranging from 0.17 to 2.9, depending upon the geometrical condition of the agitator and the vessel, and also reported the effect of baffles on the coefficient. Fluid elements circulate in the reactor with a mean circulation time given by

$$\theta = V/Q \qquad (14)$$

With the geometry used, the period representing the interval for the motion of the fluid elements in the vessel is taken as $\theta/2$. It is recognized that there is a distribution of circulation time for the motion of fluid in the agitated vessel, and the ratio of staying time in the two limits of dose rate is not necessary κ: $1 - \kappa$. However, a first approximation, V/Q, and κ: $1 - \kappa$ are used as their mean values.

The mass transfer between fluid elements is considered to be caused mainly by coalescence and dispersion, and thus the overall mass transfer coefficient may be dependent on frequency of coalescence and dispersion, contact time, and contact area of fluid elements. Although U might be expected to vary with agitation speed, we assumed U to be a constant. The values of $\bar{Y}$ were computed for parametric values of U, with $k = 1.10$, $B = 0.10$, $\kappa = 0.10$, $I_1 = 297$, and $I_2 = 1.0$. In Figure 4, the calculated values of $\bar{Y}$ are plotted vs. the period T together with the experimental results by using $f = 0.5$ for baffled and 0.25 for unbaffled vessels. A comprehensive geometrical model has not been made. For periods greater than 10 sec., the calculated reaction rates are relatively insensitive to period but are dependent upon the mass transfer rate. At small periods, the reaction rates is insensitive to the mass transfer rates.

The analytical and experimental methods for the chloral hydrate system indicate sufficient concurrence to merit reporting the simple approaches used for the model.

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NOTATION

A = defined by Equation (3), mole/(liter (min.) or mho./(cm.) (min.)
a = defined by Equation (9)
B = defined by Equation (3), min./rad.
b, c = defined by Equation (9)
C = product
D = diameter of agitator, cm.
d = defined by Equation (9)
E = reactant
f = coefficient of impeller discharge.
G = G value of initiation reaction, mole/rad.
I = dose rate, rad./min.
I_1, I_2 = dose rate of high and low dose rate portion, rad./min.
$\bar{I}$ = average dose rate in the reactor, rad./min.
i = number of cycle times per fluid element in the reactor
K = apparent rate constant of the propagation reaction, sec.$^{-1}$
k = apparent rate constant of the termination reaction, sec.$^{-1}$
k_1, k_2 = propagation and termination rate constant, liter/(mole) (sec.)
l = termination rate constant, liter/(mole) (sec.)
M = reactant
N = agitation speed, rev./sec.
n = concentration of chain carrier, mole/liter; $[R\cdot]$ = concentration of $R\cdot$ designated by n
$\bar{n}$ = defined by Equation (6), mole/liter
p = defined by Equation (9)
Q = discharge rate of agitator, cc./sec.
$R\cdot$ = chain carrier radical
r, s = solutions of Equations (11) and (12)
S = scavenger
T = period of motion of fluid element in the reactor, sec.
t = time, sec.
U = overall mass transfer coefficient based on interaction between fluid elements, sec.$^{-1}$
V = reactant volume, cc.
X = rate of production of the product, mole/(liter) (min.) or mho./(cm.) (min.)
Y = X/A, dimensionless reaction rate
$\bar{Y}$ = defined by Equation (9).

Greek Letters

κ = fraction of high dose rate portion in the reactor
θ = mean circulation time of fluid in the reactor, sec.

Subscripts

n = nonmixing
p = perfect mixing

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Drag Reduction Correlations

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We would like to point out a more general drag reduction correlation to which the one presented by Astarita, Greco, and Nicodemo (*1*) is very similar. The older correlation, which was proposed and tested for many polymers and solvents by Rodriguez, Zakin, and Patterson (*2*, *3*) was of the form f/f_{pv} vs. $U\tau_1/D^{0.2}$, where τ_1 is the