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A Nonlinear Theory for the Brusselator Near the Critical Point Caused by Diffusion

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A nonlinear theory is presented for the fluctuations of intermediates in the Brusselator near the critical point caused by diffusion. The method used is the two time scaling method different from the conventional method in the sense that a slight nonlinear effect is included in the initial time region where the linear approximation is conventionally valid. The result obtained by the nonlinear theory shows that fluctuations close to the critical point approach the value of a stable steady state or deviate infinitely from an unstable steady state, as time goes to infinity, while the linear theory gives approximately time-independent fluctuations. A brief discussion is given for the correlation at a time between fluctuating intermediates when the system approaches a stable steady state.

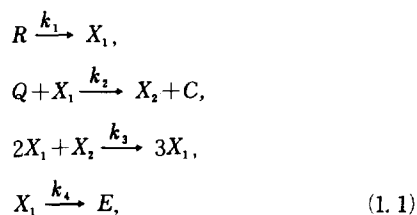
Introduction

Recently, much attention¹⁻⁶ has been given theoretically and experimentally to chemical reactions with instability since Lotka⁷ proposed in 1920 a simple model of autocatalytic chemical reactions which show sustained oscillations in the concentration of the autocatalytic species when open to a flow of matter through the system. Bray⁸ discovered this kind of sustained oscillation in an inorganic redox reaction. In 1952, Turing⁹ showed that stable spatial patterns can be obtained

when chemical reactions are coupled to the process of diffusion. Thus, he laid the foundation for a biochemical theory of morphogenesis. More recently a famous reaction, called the Belousov-Zhabotinsky reaction, which shows temporal oscillations and spatial patterns has been intensively studied by many authors.^{5-6, 10-11}

The model, one of the models with chemical instability, to be considered in this paper is the Brusselator¹, which was invented and carefully studied by Prigogine and his coworkers in the Brussels school. The reaction mechanism for the

Brusselator is given by



where R and Q are reactants maintained at constant concentration, C and E are products, X_1 and X_2 are intermediates, and k_i 's are rate constants.

In this paper we shall discuss the effect of nonlinear terms on fluctuations of intermediates in the Brusselator near the critical point caused by diffusion. With a few exceptions, nonlinear dynamic phenomena can be studied only by approximate methods¹²⁻¹⁷ in various fields such as statistical mechanics, hydrodynamics, chemical reactions, and etc. The approximate method to be used here is the two time scaling method¹²⁻¹⁴ which is one of the most widely used methods. In the two time scaling method the whole range of time is divided into three regions of time. The initial region of time is the range of time where the linear approximation is valid. The second region is the region in which the nonlinear effect becomes important and the system approaches a steady state (or equilibrium state). The final region is the region where the system stays at the steady state (or equilibrium state). The present two time scaling method is different from the conventional method in the sense that a slight nonlinear effect is included in the initial time region where the linear approximation is conventionally valid.

In the present paper, we discuss first the linear case for the Brusselator far from the steady state. Then, the nonlinear case is studied with the aid of the two time scaling method. Finally, the correlation at one time between intermediates is obtained when the system relaxes toward a stable steady state.

Theory

If we consider diffusion effects, the rate equations for the intermediates in the reaction scheme of eq.(1.1) can be written as

$$\begin{aligned} \partial X_1(\vec{r}, t) / \partial t &= D_{11} \nabla^2 X_1(\vec{r}, t) + k_1 R \\ &\quad - (k_2 Q + k_4) X_1(\vec{r}, t) + k_3 X_1(\vec{r}, t)^2 X_2(\vec{r}, t), \\ \partial X_2(\vec{r}, t) / \partial t &= D_{22} \nabla^2 X_2(\vec{r}, t) + k_2 Q X_1(\vec{r}, t) \\ &\quad - k_3 X_1(\vec{r}, t)^2 X_2(\vec{r}, t) \end{aligned} \quad (2.1)$$

where D_{11} and D_{22} are diffusion coefficients for X_1 and X_2 , respectively. In order to simplify the above equations we introduce the following transformations:

$$\begin{aligned} \tau &= k_4 t, \quad a = k_1 R / k_4, \quad b^2 = k_2 Q / k_4, \quad c = k_3 / k_4, \\ \theta^2 &= D_{22} / k_4, \quad d_{11} = D_{11} / k_4. \end{aligned} \quad (2.2)$$

Taking that d_{11} is unity, the rate equations become

$$\begin{aligned} \partial X_1(\vec{r}, \tau) / \partial \tau &= \nabla^2 X_1(\vec{r}, \tau) + a - (1 + b^2) X_1(\vec{r}, \tau) \\ &\quad + c X_1(\vec{r}, \tau)^2 X_2(\vec{r}, \tau), \\ \partial X_2(\vec{r}, \tau) / \partial \tau &= \theta^2 \nabla^2 X_2(\vec{r}, \tau) + b^2 X_1(\vec{r}, \tau) \\ &\quad - c X_1(\vec{r}, \tau)^2 X_2(\vec{r}, \tau) \end{aligned} \quad (2.3)$$

with the homogeneous steady state value

$$X_1^0 = a, \quad X_2^0 = b^2 / ac. \quad (2.4)$$

Expansion in terms of $y_i = X_i - X_i^0$ leads to

$$\partial \mathbf{y}(\vec{r}, \tau) / \partial \tau = M_{\theta, \vec{r}} \mathbf{y} + (2ac y_2 + b^2 y_1 / a + c y_1 y_2) \mathbf{y}_1 (1, -1)^T \quad (2.5)$$

where

$$\mathbf{y} = (y_1, y_2)^T, \quad M_{\theta, \vec{r}} = \begin{pmatrix} \nabla^2 + b^2 - 1, & a^2 c \\ -b^2, & \theta^2 \nabla^2 - a^2 c \end{pmatrix}$$

Linear Case. Neglecting the nonlinear terms in eq.(2.5) and considering one dimensional diffusion for simplicity, we take the solution of the form $y(\vec{r}, \tau) = y(\tau) \cos kx$. Then eq.(2.5) becomes

$$d\mathbf{y}/d\tau = M_{\theta, k} \mathbf{y}; \quad M_{\theta, k} = \begin{pmatrix} -k^2 + b^2 - 1, & a^2 c \\ -b^2, & -\theta^2 k^2 - a^2 c \end{pmatrix} \quad (2.6)$$

Since the concentrations of reactants are kept constant, the controllable variables are θ and k . Thus, the system can be stable or unstable, depending on the values of these variables.

If we carry out usual linear stability analysis²³, the stability criteria can be obtained as follows:

$$\begin{aligned} (k^2 + 1 - b^2) (\theta^2 k^2 + a^2 c) + a^2 b^2 c &> 0 \\ a^2 c &> (b - 1)^2 \end{aligned} \quad (2.7)$$

The first criterion which corresponds to the positiveness of the determinant of $M_{\theta, k}$ together with the second criterion ensures the real negative normal mode frequencies leading to the linear stability. As shown in Figure 1, the minimum point of the boundary between the stable and unstable regions is the critical point of the system. At the critical point the variables k and θ have the critical values of

$$k_c^2 = b - 1, \quad \theta_c = a\sqrt{c} / (b - 1). \quad (2.8)$$

As k_c^2 and θ_c are positive, the following conditions should be satisfied.

$$b > 1. \quad (2.9)$$

In order to analyze the asymptotic behavior of the solution of eq.(2.6) as $\tau \rightarrow \infty$ it is sufficient to find the eigenvalues and eigenvectors of $M_{\theta, k}$.²³ The eigenvalues of the matrix near the critical point are

$$\begin{aligned} \lambda_1 &= \eta (\theta - \theta_c) + O(\theta - \theta_c)^2 \\ \lambda_2 &= -b[a^2 c - (b - 1)^2] / (b - 1) + O(\theta - \theta_c) \\ \eta &= 2a\sqrt{c} (b - 1)^2 / [a^2 c - (b - 1)^2]. \end{aligned} \quad (2.10)$$

As shown in the above results, λ_1 is positive or negative, depending on the value of θ , while λ_2 is always negative. Let the set of the right and left eigenvectors of the matrix belonging to the eigenvalue λ_o be ψ^o and $\bar{\psi}^o$, respectively. Then we have¹⁸

$$\begin{aligned} \psi^1 &= (a^2 c / [b(1 - b)], 1)^T, \quad \psi^2 = ((1 - b) / b, 1)^T \\ \bar{\psi}^1 &= (b - 1)^2 [(b - 1)^2 - a^2 c]^{-1} (b / (b - 1), 1) \\ \bar{\psi}^2 &= [a^2 c - (b - 1)^2]^{-1} (b(b - 1), a^2 c). \end{aligned} \quad (2.11)$$

It can be easily checked that the eigenvectors satisfy the following orthonormalization conditions

$$\sum_i \bar{\psi}_i^o \psi_i^o = \delta_{oo}, \quad \sum_a \bar{\psi}_i^a \psi_j^a = \delta_{ij}, \quad (2.12)$$

where $\delta_{\alpha\beta}$ is the Kronecker delta. Later we shall use the above conditions with respect not only to eigenvectors but also to position. Thus, the complete orthonormalization condition to be used is

$$\int_0^{n\pi/k_c} dx (\bar{\psi}^\alpha, \psi^\beta) \cos lk_c x \cos mk_c x = \delta_{\alpha\beta} \delta_{lm} n\pi/k_c, \quad (n, l, m=1, 2, 3, \dots) \quad (2.13)$$

The solution in the linear case near the critical point is

$$\mathbf{y}(x, \tau) = [A\psi^1 \exp(\lambda_1 \tau) + B\psi^2 \exp(\lambda_2 \tau)] \cos k_c x. \quad (2.14)$$

The fluctuations are stable when θ is smaller than the critical value θ_c according to eq.(2.10). Thus, the fluctuations not only remain finite but also, in fact, approach zero as $\tau \rightarrow \infty$. When $\theta > \theta_c$, the system is unstable and the first mode in eq.(2.14) becomes infinite as time goes to infinity. The region to be considered in this paper is near the critical point. In the region very close to the critical point where $\theta \cong \theta_c$, eq.(2.14) becomes

$$\mathbf{y}(x, \tau) \cong A\psi^1 \cos k_c x. \quad (2.15)$$

The above result shows that fluctuations are time-independent near the critical point, which does not describe the actual phenomena properly. Thus, to discuss the actual phenomena the nonlinear terms should be included.

Nonlinear Case. In order to study nonlinear stability for the Brusselator we shall apply two time scaling method. The whole range of time is divided into three regions. The initial region of time denoted by τ_0 is the range of time where the linear approximation is conventionally valid. In the present paper, however, we shall define the initial region as the region where not only the linear approximation is valid but also a slight nonlinear effect is included to obtain more accurate nonlinear effect. The second region of time, τ_1 , is the region in which the nonlinear effect becomes important and the system approaches a stable steady state. The final region is the region where the system stays at the stable steady state. Let us scale the time and eigenvectors as

$$\tau_m = \epsilon^{2m} \tau, \quad m=0, 1$$

$$\mathbf{y}_j = \sum_i \epsilon^i \mathbf{y}_{ij}, \quad i, j=1, 2 \quad (2.16)$$

where ϵ is a parameter to be defined later. We assume that fluctuations depend on τ_0 and τ_1 through the amplitude of fluctuations, A . That is,

$$\mathbf{y}(x, \tau_0, \tau_1) \cong A(\tau_0, \tau_1) \psi^1 \cos k_c x. \quad (2.17)$$

Applying the scaling relation to eq.(2.5) and matching terms

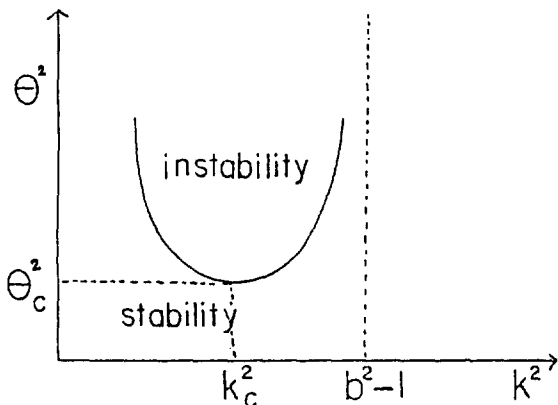


Figure 1. Stability diagram.

in orders of ϵ and ϵ^2 , respectively, we obtain the following equations in the initial time region:

$$d(\mathbf{y}_{11}, \mathbf{y}_{12})^T / d\tau_0 = M_{\theta_c, k_c}(\mathbf{y}_{11}, \mathbf{y}_{12})^T, \quad (2.18a)$$

$$d(\mathbf{y}_{21}, \mathbf{y}_{22})^T / d\tau_0 = M_{\theta_c, k_c}(\mathbf{y}_{21}, \mathbf{y}_{22})^T + (2ac\mathbf{y}_{12} + b^2\mathbf{y}_{11}/a)\mathbf{y}_{11}(1, -1)^T. \quad (2.18b)$$

Eq.(2.18a) is just the linear equation already discussed. From eqs.(2.17) and (2.18a) we can see that A is approximately independent of τ_0 in the critical region. That is, $A(\tau_0, \tau_1) \cong A(\tau_1)$. Substituting eq.(2.17) into eq.(2.18b), we have the particular solution for $(\mathbf{y}_{21}, \mathbf{y}_{22})^T$ as (Appendix)

$$(\mathbf{y}_{21}, \mathbf{y}_{22})^T = A(\tau_1)^2 \mathbf{g} [M_{\theta_c}^{-1} + M_{\theta_c, k_c}^{-1} \times \cos 2k_c x] (1, -1)^T, \quad (2.19)$$

where M^{-1} is the inverse matrix of M and \mathbf{g} is given by

$$\mathbf{g} = -\frac{1}{2} [2ac\phi_2^1 + (b^2/a)\phi_1^1] \phi_1^1. \quad (2.20)$$

The complete solution in the initial region of time near the critical point is

$$\mathbf{y}(x, \tau_1) = \epsilon A(\tau_1) \psi^1 \cos k_c x + \epsilon^2 A(\tau_1)^2 \mathbf{g} \times (\phi^1 + \phi^2 \cos 2k_c x), \quad (2.21)$$

with

$$\phi^1 = (a^2c)^{-1} (0, 1)^T, \quad \phi^2 = (9a^2c)^{-1} (4a^2c/(1-b), 4b-3)^T. \quad (2.22)$$

The solution is more accurate than the linear case in the sense that a slight nonlinear effect is included.

Now, let us define the parameter ϵ as

$$\epsilon^2 = |\theta - \theta_c|. \quad (2.23)$$

From the above definition λ_1 is given as

$$\lambda_1 = \eta \epsilon^2, \quad \text{sign } \eta = \text{sign}(\theta - \theta_c). \quad (2.24)$$

Substituting eq.(2.21) into eq.(2.5) and matching terms of the third order in ϵ , we have

$$[dA(\tau_1)/d\tau_1] \psi^1 \cos k_c x = \eta \psi^1 A(\tau_1) \cos k_c x + A(\tau_1)^3 \{ [gac(\phi_2^1 \phi_2^1 + \phi_1^1 \phi_2^2 + 2\phi_1^1 \phi_2^1)] + (b^2g/a)\phi_1^1 \phi_1^2 + (3c/4)\phi_1^2 \phi_2^1 \} \cos k_c x + [gac(\phi_1^1 \phi_2^1 + \phi_1^1 \phi_2^2) + (b^2g/a)\phi_1^1 \phi_1^2 + (c/4)\phi_1^2 \phi_2^1] \cos 3k_c x (1, -1)^T. \quad (2.25)$$

Expressing the nonlinear parts in terms of the linear combination of ψ^1 and ψ^2 and using the orthonormalization condition given in eq.(2.13), the following equation is obtained:

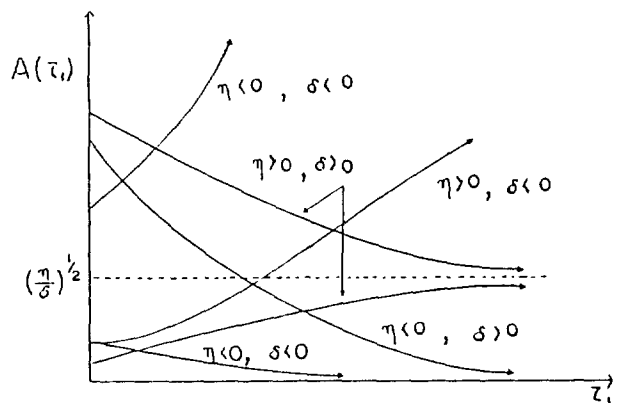


Figure 2. The dependence of $A(\tau_1)$ on time τ_1 .

$$dA(\tau_1)/d\tau_1 = \eta A(\tau_1) - \delta A(\tau_1)^2, \quad (2.26)$$

where

$$\delta = (\phi_1^2 + \phi_2^2) \{g[ac(\phi_1^2\phi_2^2 + \phi_1^1\phi_2^2 + 2\phi_1^1\phi_2^1) + b^2\phi_1^1\phi_2^1/a] + 3c\phi_1^2\phi_2^2/4\} / (\phi_1^2\phi_2^2 - \phi_1^1\phi_2^1). \quad (2.27)$$

Rewriting δ in terms of constants given in eq.(2.2), we obtain

$$\delta = (a^4c^3/36b^2) [2(2-b)(4b^2+7b-15) + 27(b-1)^2(b-1)^{-3}[a^2c - (b-1)^2]^{-1}. \quad (2.28)$$

The coefficients, η and δ , can be positive or negative. If η and δ are positive, $\pm(\eta/\delta)^{1/2}$ correspond to stable steady states and $A=0$ is an unstable steady state. The amplitude of fluctuations approaches the stable steady states as τ_1 goes to infinity. In the case that η and δ are negative, $A=0$ is a stable steady state and $\pm(\eta/\delta)^{1/2}$ are unstable steady states. When the initial state is between $(\eta/\delta)^{1/2}$ and $-(\eta/\delta)^{1/2}$, the amplitude becomes zero as $\tau_1 \rightarrow \infty$. Otherwise, A becomes divergent. When $\eta > 0$ and $\delta < 0$, there is only one steady state which is unstable. Thus, the amplitude deviates infinitely from the unstable steady state. If $\eta < 0$ and $\delta > 0$, the system has a stable steady state corresponding to $A=0$ and approaches the stable steady state as time goes to infinity. The dependence of amplitude of fluctuations on time is shown in Figure 2.

Correlation Between Fluctuating Intermediates. Let us consider the correlation between fluctuating intermediates in the second region of time when the system relaxes toward a stable steady state. When no stable steady state is obtained, higher order terms become important. Such cases will not be considered in the present paper. The correlation at one time between y_i and y_j is

$$\langle y_i(\tau_1)y_j(\tau_1) \rangle = \langle A(\tau_1)^2 \rangle \phi_i^1\phi_j^1 \cos^2 k_c x. \quad (2.29)$$

The correlation depends on time through $\langle A^2 \rangle$. To discuss $\langle A^2 \rangle$ let us consider that A is a stochastic rather than deterministic variable. Then, the following Fokker-Planck equation is satisfied²¹

$$\partial P(A, \tau_1)/\partial \tau_1 = -\partial[(\eta A - \delta A^2)P(A, \tau_1)]/\partial A + D\partial^2 P(A, \tau_1)/\partial A^2 \quad (2.30)$$

where D is the diffusion coefficient with respect to A . From the Fokker-Planck equation $\langle A^2 \rangle$ satisfies

$$d\langle A^2 \rangle/d\tau_1 = 2[\eta \langle A^2 \rangle - \delta \langle A^4 \rangle + D]. \quad (2.31)$$

If $\eta < 0$, the linear approximation can be used since $\langle A^4 \rangle$ decays much more rapidly than $\langle A^2 \rangle$. Thus, $\langle A^2 \rangle$ becomes

$$\langle A^2 \rangle_{\tau_1} \cong \langle A^2 \rangle_0 \exp(-2\eta' \tau_1) + D[1 - \exp(-2\eta' \tau_1)]/\eta' \quad (2.32)$$

where $\eta' = -\eta > 0$. In the case of $\eta > 0$ and $\delta > 0$, the linear approximation breaks down for $\exp(2\eta\tau_1) \geq 1$ since $\langle A^4 \rangle$ is proportional to $\exp(4\eta\tau_1)$. Therefore, we have to sum up all the most dominant terms up to infinite order for $\exp(2\eta\tau_1) \sim 1$ to obtain $\langle A^2 \rangle$. Shimizu¹⁹ used a system-size expansion method to sum up all the most dominant terms up to infinite order. The more efficient method is, however, to obtain the probability distribution. Some authors^{14,20-22} have obtained the probability distribution satisfying eq.(2.30) and discussed very interesting dynamic phenomena for the laser model, the time-dependent Ginzburg-Landau model, and the Schlögl models. Referring the detailed discussion to the previous papers^{14,20-22}, the probability distribution in the second region of time is given by

$$P(A, \tau_1; A_0) = G'(A) [2\pi\sigma(\tau_1)]^{-1/2} \times \exp\{-[G(A) - A_0 \exp(\eta\tau_1)]^2/2\sigma(\tau_1)\}, \quad (2.33)$$

where A_0 is the initial value of A , the prime in G denotes the differentiation with respect to A , and G and σ are given by

$$G(A) = A(1 - \delta A^2/\eta)^{-1/2}, \\ A = A_0 \exp(\eta\tau_1) [1 + (\delta/\eta)A_0^2 \exp(2\eta\tau_1)]^{-1/2}, \\ \sigma(\tau_1) = (D/\eta) \exp(2\eta\tau_1). \quad (2.34)$$

In eq.(2.34) the initial value of σ has been neglected. It should be mentioned that the probability distribution given in eq.(2.33) holds only in the case that A is between the two stable steady states. In this case, we may start from $A_0=0$ since there is no difference in physical meaning. Thus, $\langle A^2 \rangle_{\tau_1}$ is

$$\langle A^2 \rangle_{\tau_1} = \int_0^{\sqrt{\eta/\delta}} dA A^2 P(A, \tau_1) / \int_0^{\sqrt{\eta/\delta}} dA P(A, \tau_1) \\ = \eta [1 - \sqrt{\pi} x \exp(x^2) \operatorname{erfc}(x)]/\delta. \quad (2.35)$$

where

$$x = [2\delta\sigma(\tau_1)/\eta]^{-1/2} \quad (2.36)$$

and $\operatorname{erfc}(x)$ is the complementary error function. For very long time, $\langle A^2 \rangle_{\tau_1}$ becomes

$$\langle A^2 \rangle_{\tau_1} \cong \eta/\delta \quad (2.37)$$

which is the same result obtained from the steady state solution of the deterministic equation [eq.(2.26)].

Discussion

In this work we have investigated the fluctuations of intermediates in the Brusselator in the presence of diffusion. The linear case shows that the fluctuations are time-independent near the critical point. Analysis of the nonlinear case has been carried out by the two time scaling method and the result in eq.(2.21) shows that the solution contains a higher order correction in the initial region of time near the critical point. It is interesting to notice that the amplitude of fluctuations which contains the time-dependence depends on τ_1 rather than τ_0 due to eq.(2.18a). This fact stems from the inclusion of the nonlinear term in eq.(2.5).

Another interesting point is that eq.(2.26) governing the time-dependence of the amplitude of fluctuations is of the same form as the Schlögl model investigated earlier by Lee, et al.²¹ The correlation between fluctuating intermediates can be obtained from eq.(2.29) and results in eqs.(2.32) and (2.35) clearly show that the dominating contribution comes from the nonlinear term in eq.(2.26) in the nonlinear analysis.

In the forthcoming paper we shall discuss how the Brusselator behaves near the critical point when an external disturbance is added.

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Appendix Since $A(\tau_0, \tau_1) \cong A(\tau_1)$ and the time-dependence of $(y_{21}, y_{22})^T$ is contained only in $A(\tau_1)$, the LHS of eq.(2.18b) vanishes. Then, substitution of eq.(2.17) into the nonlinear terms in eq.(2.18b) gives

$$M_{\theta_c, x_c}(y_{21}, y_{22})^T = -A(\tau_1)^2 (2ac\phi_1^1\phi_2^2 + b\phi_1^2/a) \\ \times \cos^2 k_c x (1, -1)^T \\ = -A(\tau_1)^2 g(1 + \cos 2k_c x) (1, -1)^T \quad (A1)$$

At the critical point the inverse matrix M_{θ, k_c}^{-1} becomes singular. But the above equation can be solved by recognizing that $1 = \cos 0x$ and when inverse matrix is applied to the RHS, the subscript k_c should be replaced by 0 for the first term and by $2k_c$ for the second term as in eq.(2.19).

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The Photoaddition Reaction of 1,4-Diphenyl-1,3-butadiyne with 5-Fluorouracil

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Diacetylene compound, 1,4-diphenyl-1,3-butadiyne, was photolyzed with 5-fluorouracil as a model reaction of the phototoxic conjugated poly-yne with DNA or RNA and obtained a [2+2] photocycloadduct. The structure of the photoadduct was determined by spectral methods and compared with the [2+2] photoadducts of 1,4-diphenyl-1,3-butadiyne with tetramethylethylene and dimethyl fumarate.

Introduction

Certain naturally occurring conjugated poly-yne (polyacetylenes) have been reported to be phototoxic to a variety of microorganisms, human skin fibroblasts, Syrian hamster cells, mosquito larvae and Paramecium.¹⁻⁶ For example, 1-phenylhepta-1,3,5-triyne (PHT) which is a conjugated poly-yne occurring in high concentration in the leaves of the tropical weed *Bidens pilosa* L. is phototoxic toward various organisms containing membranes, including eukaryotic cells, fungi, bacteria, and viruses in the presence of long wave UV.⁷ PHT, unlike the naturally occurring photoactive psoralens, does not form interstrand cross-links with calf thymus DNA^{8,9} while furanocoumarins inactivate viruses by cross-linking the DNA.⁹ Instead, PHT exerts its phototoxic action via the

viral membrane damage which inactivates DNA or RNA to replicate.⁸ However, nothing is known about the photochemistry of poly-yne even though it is essential to understand the molecular mechanism of phototoxicity of the compounds. This membrane damage may involve the modification of cellular DNA or RNA.

The conjugated di-yne are reported to be less toxic than the conjugated tri-yne¹ but the cross-addition products were isolated and characterized in the photochemical reaction of diacetylene compound 1,4-diphenyl-1,3-butadiyne (DPB) and some olefins.¹⁰

We now report for the first time the photocycloaddition of DPB with 5-fluorouracil (5-FU) as a model photoreaction of conjugated poly-yne with DNA or RNA possibly in the membranes of various organisms.