Articles

Effects of Noise on a Model of Oscillatory Chemical Reaction

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A simple oscillating reaction model subject to additive Gaussian white noise is investigated as the model is located in the dynamic region of oscillations. The model is composed of three ordinary differential equations representing the time evolutions of X, Y, and Z, respectively. Initially, a uniform random noise is separately added to the three equations to study the effect of noise on the oscillatory cycle of X, Y, and Z. For a given value of noise intensity, the amplitude of oscillation increases monotonically with time. Furthermore, the noise is added to any one of the three equations to study the impact of noise on one species on the bifurcation behavior of the other.

Key Words : Temporal oscillations, Stochastic variable, Noise, Bifurcation, Far from equilibrium and fluctuations

Introduction

The effect of noise on nonlinear systems has attracted considerable attention in recent years. There are many examples showing that noise can have a constructive effect on the formation of order such as noise-induced transitions.[1,2] It is also found that many other interesting phenomena are possible due to the introduction of noise. One can study the effect of noise in two ways. One is by investigating the extent to which a given noise might influence the system. The other is by probing the possible noise-induced phenomena which are of physical interest.[3-5] Noise usually causes destructive effects by weakening the stability of the system[6] and, slowing down the transient processes, and these fluctuations would also cause catastrophe at a higher amplitude. However, it has also been found that some types of noise might either stabilize the system,[6] sustain oscillations,[7] or induce stable steady states.[8-14] In this paper, we study the effect of Gaussian white noise on the oscillatory behavior of a chemical reaction system's simple model by adding a stochastic variable, and then the effect is compared. The paper is organized as follow. In Section II, we present the kinetic model of the chemical reaction, and the differential rate equations; this section also discusses the computation method. In section III, the temporal behavior of the model is discussed, and two bifurcation diagrams are presented. In Section IV, the stochastic formulations of the system are presented. In section V, the stochastic behavior of the system when different conditions are considered is discussed. In section VI, the bifurcation diagrams are constructed by considering the different cases of the stochastic formulations which have been discussed in section V. Finally the conclusion is drawn on the basis of the overall behavior of the system.

Results and Discussions

Kinetic model and the method of calculation. The model that we study here is a slightly modified model of the chaotic chemical reaction scheme which is derived by Hudson *et al.*[15] and which is represented by the following set of reactions R(1)-R(9):

$A + X + Z \rightarrow 2X + Z$	k_1xz	R(1)
$X \rightarrow Y$	k_2x	R(2)
$X \rightarrow P_1$	$k_3xy/(x+K)$	R(3)
$B \rightarrow X$	k_4	R(4)
$Y \rightarrow P_2$	k_5y	R(5)
$C \rightarrow Y$	k_6	R(6)
$D \rightarrow Z$	k_7	R(7)
$Z \rightarrow P_3$	k_8z	R(8)
$X + Z \rightarrow X + P_4$	k_9xz	R(9)

The system is constrained out of equilibrium by keeping the concentrations of species A, B, C, and D constant. Species P_i (i = 1, 2, 3, and 4) are materials produced and x, y, and z denote the concentration of species X, Y and Z, respectively. Where k_i (i = 1, 2, 3, 4, 5, 6, 7, 8, and 9) is the rate constant for each reaction. In here, k_3 is from Michaelis-Menten reaction that catalyzes species X and Y. K is another constant whose value is taken as 0.0001.[15] The system is autonomous in species X, Y and Z. If we assume an ideal

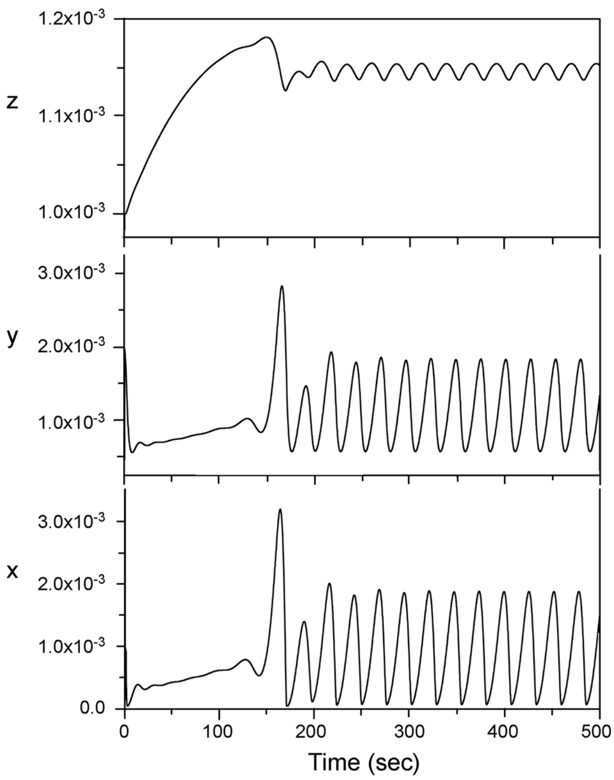

Figure 1. The behavior of time series of x, y, and z at an initial condition of x = 0.0, y = 0.0, and z = 0.0.

mixture and that the reactions take place in a well-stirred reactor, then the governing phenomenological equations of the mass action kinetics read as follows:

$$\frac{dx}{dt} = k_1xz - k_2x - k_3xy/(x+K) + k_4 \quad 2(a)$$

$$\frac{dy}{dt} = k_2x - k_5y + k_6 \quad 2(b)$$

$$\frac{dz}{dt} = k_7 - k_9xz - k_8z \quad 2(c)$$

The coupled systems of Equations (2(a)-2(c)) were solved numerically using the fourth order Runge-Kutta[16] method at the indicated concentrations. Later, the stochastic variables were added to Equations (3(a)-3(c)), we again simulated, and then the behavior was compared.

Oscillatory behavior of species x, y, and z. Figure 1 shows a time series behavior of species x, y, and z at the indicated initial concentrations. We can see that the oscillatory pattern has an initial transient period of about 145 sec, which is similar in x, y and z. It is an induction or a transient period which is required to reach the reactant species to acquire a certain concentration values so that they can give rise to periodic oscillations. Initially also, there is a fall in the concentration in case of x followed by a slow increase, then after a certain time, there is a sudden increase in concentration. Later, it falls rapidly to a lower value of concentration, and then it follows oscillations of rapid increase and decrease in the concentration. The behavior is more or less similar in the case of variable y. However, the behavior in z is somewhat different from x and y. Here, the concentration suddenly increases from a lower value to a higher value, then there is a slow decrease, and finally, oscillations start onwards. These oscillations are sustained and are continued for a longer period of time. These cycles repeat during the course of the reaction without undergoing further changes.

Stochastic formulations. Since the reaction mechanism and the variables x, y, and z are related to external modulations, random elements of various types could affect the dynamic process. Within the framework of white noise formulations, the rate Equations (2(a)-2(c)) turn to be stochastic ones as in Equations (3(a)-3(b)). The fluctuation is included through the term $\xi_{i,t} = \{0,1\}$ such that $< \xi_{i,t}\, \xi_{j,t} > = \delta_{i\,j}\delta(t - t')$ and $\xi_{i,t}$ is Gaussian parameter which is varying with respect to time. The method including these fluctuations is to add a noise term to the above deterministic equations, and the equivalent stochastic differential equations are as follows:

$$\frac{dx}{dt} = k_1xz - k_2x - k_3xy/(x+K) + k_4 + D_1\xi_1g_1(x,y,z) \quad 3(a)$$

$$\frac{dy}{dt} = k_2x - k_5y + k_6 + D_2\xi_{2,t}g_2(x,y,z) \quad 3(b)$$

$$\frac{dz}{dt} = k_7 - k_9xz - k_8z + D_3\xi_{3,t}g_3(x,y,z) \quad 3(c)$$

Equations 3(a)-3(c) represents general form of various types of noise and parameters D_1, D_2 and D_3 (D in general) governs the amplitudes of noisy external force. $g_i(x, y, z)$ is a function represents species x,y and z when affected by noise. Then, various types of noise can be obtained by the general formulation of Equations 3 by forcing a noise to a specific species.

The first type is when the species x is fluctuating or if the rate equation for the x is subjected to an additional random driving as follows:

$g_1(x,y,z) = 1.0$, $D_1 \neq 0$ and $g_2(x,y,z) = 0$, $g_3(x,y,z) = 0$ and $D_2 = D_3 = 0$ (I)

The second is when the species y or its rate is subjected to additional driving as follows:

$g_2(x,y,z) = 1.0$, $D_2 \neq 0$ and $g_1(x,y,z) = 0$, $g_3(x,y,z) = 0$ and $D_1 = D_3 = 0$ (II)

Similarly, in the case when z or its rate is subjected to additional driving, then the following is possible.

$g_3(x,y,z) = 1.0$, $D_3 \neq 0$ and $g_3(x,y,z) = 0$, $g_1(x,y,z) = 0$ and $D_1 = D_3 = 0$ (III)

In addition, there can also be another ways to study the effect of noise by taking any combinations above. In our study, the effect of noise altogether is considered in such a way that $g_1(x,y, z) = g_2(x,y,z) = g_3(x,y,z) = 1$ and $D_1 = D_2 = D_3 = D$. And then, type I, II and III were considered separately in order to study the effect of noise on selective

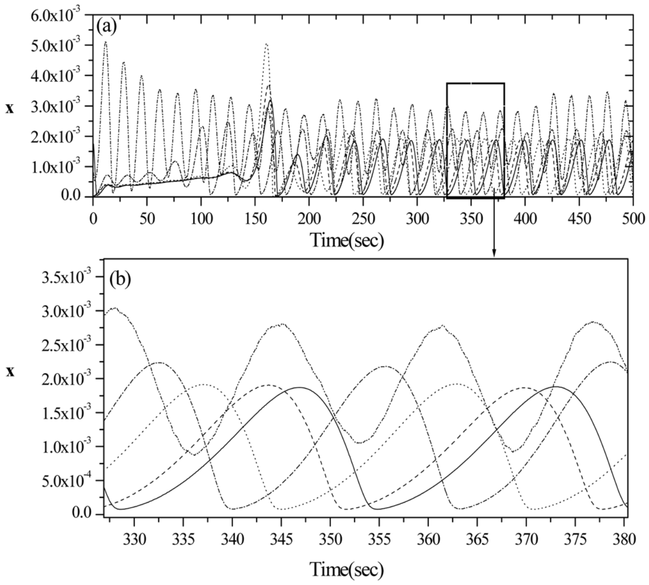

Figure 2. The behavior of time series of x at D = 0.0 (———), $D = 10^{-6}$ (- - - -), $D = 10^{-5}$ (...........), $D = 10^{-4}$ (...........) at an initial condition of x = 0.0, y = 0.0, and z = 0.0. (a) is the original behavior, and (b) is enlarged.

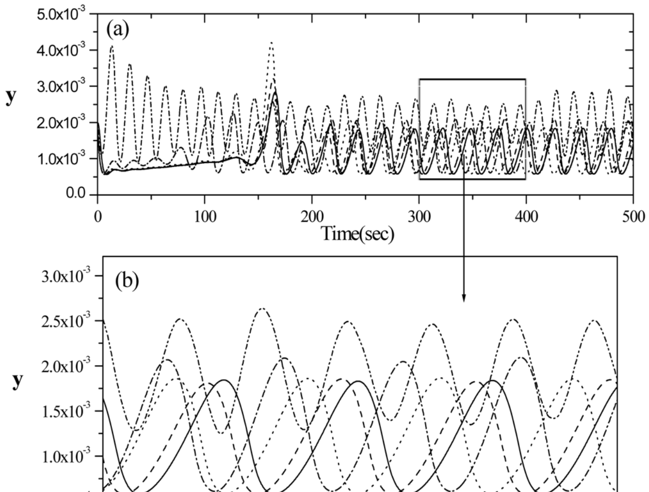

Figure 3. The behavior of time series of y at D = 0.0 (———), $D = 10^{-6}$ (- - - -), $D = 10^{-5}$ (...........), $D = 10^{-4}$ (...........) at an initial condition of x = 0.0, y = 0.0, and z = 0.0. (a) is the original behavior, and (b) is enlarged.

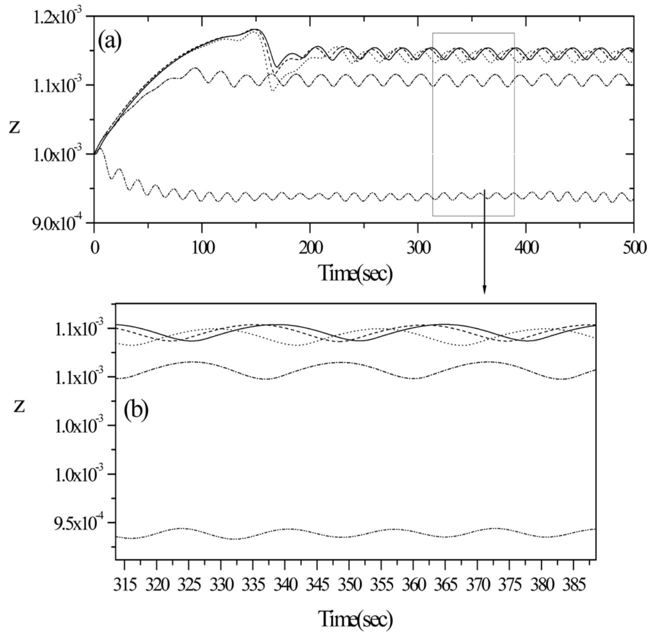

Figure 4. The behavior of time series of y at D = 0.0 (———), $D = 10^{-6}$ (- - - -), $D = 10^{-5}$ (...........), $D = 10^{-4}$ (...........) at an initial condition of x = 0.0, y = 0.0, and z = 0.0. (a) is the original behavior, and (b) is enlarged.

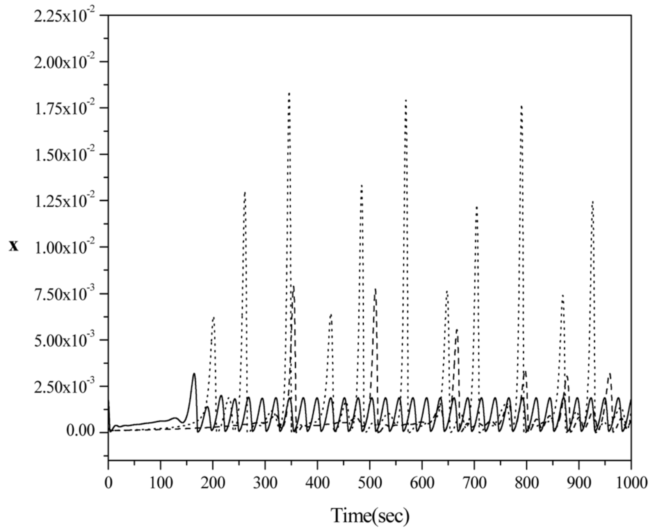

Figure 5. Noise induced transition of a limit cycle of x, at $D_1 = D_2 = D_3 = 0$, (———), $D_2 = 2.5 \times 10^{-5}$, $D_1 = D_3 = 0$ (- - - -) and $D_3 = 4.0 \times 10^{-6}$, $D_1 = D_2 = 0$ (...........) at an initial condition of x = 0.0, y = 0.0, and z = 0.0.

species i.e. the impact of noise on the other species when one of them is affected. The range of noise intensity studied here is $D = 10^{-6}$ to 10^{-1}.

The stochastic behavior obtained by the stochastic formulations. Adding the stochastic variable into each equation in order to study the effect of noise performed numerical simulations. Initially, we have considered the effect of noise by controlling the value of amplitudes of noise on each term of coupled Equations (3(a)-3(c)) and the oscillatory behavior of species x, y, and z were observed. These results are indicated in Figures 2, 3 and 4 which show the effect of noise on x, y, and z, respectively. Here, Figure 2(a), 3(a), and 4(a) show the effect of noise of different amplitude on the limit cycle behavior, and Figure 2(b), 3(b), and 4(b) are extended portion showing the effect more clearly. It has been found that the oscillatory region gets shifted to the neighboring deterministic values due to the presence of noise in case of the species x and y, while the case is reversed in z. For small and moderate noise amplitude, transient processes and asymptotic properties of the

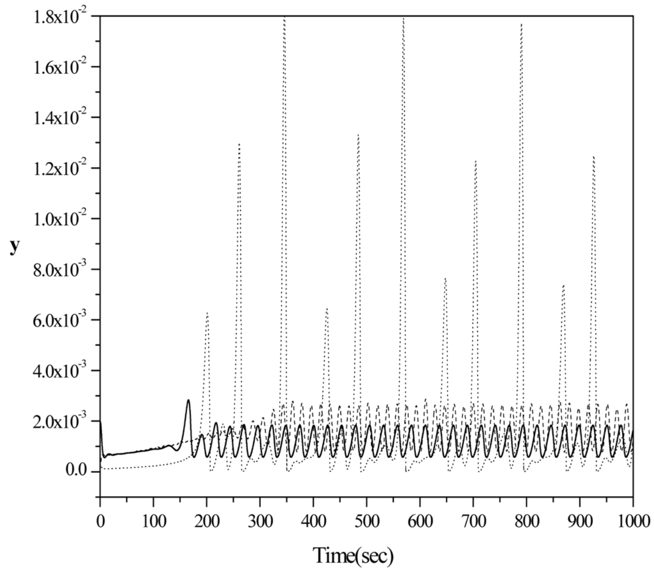

Figure 6. Noise induced transition of a limit cycle of y, at $D_1 = D_2 = D_3 = 0$ (——), $D_1 = 6.0 \times 10^{-4}$, $D_2 = D_3 = 0$ (- - - -) and $D_3 = 4.0 \times 10^{-6}$, $D_1 = D_2 = 0$ (............) at an initial condition of x = 0.0, y = 0.0, and z = 0.0.

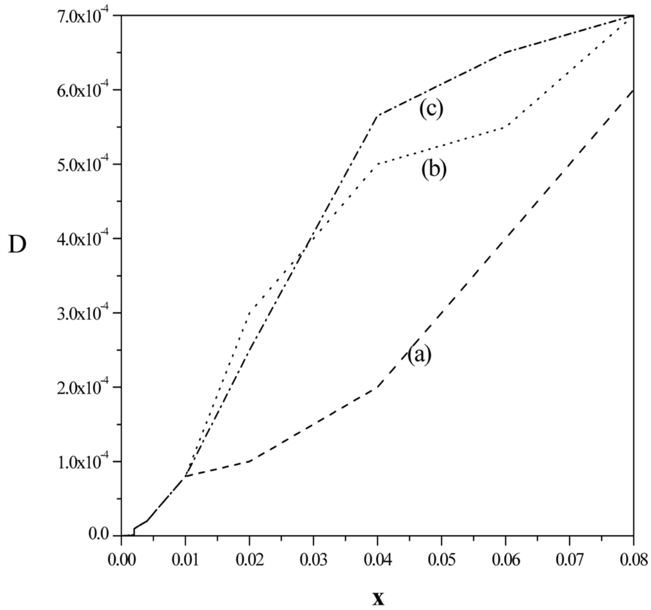

Figure 8. Phase boundaries of fixed point and limit cycle attractors for x at an initial condition of x = 0.0, y = 0.0, and z = 0.0, (a) $D_1 \neq 0$, $D_2 = D_3 = 0$, (b) $D_2 \neq 0$, $D_1 = D_3 = 0$, (c) $D_3 \neq 0$, $D_1 = D_2 = 0$.

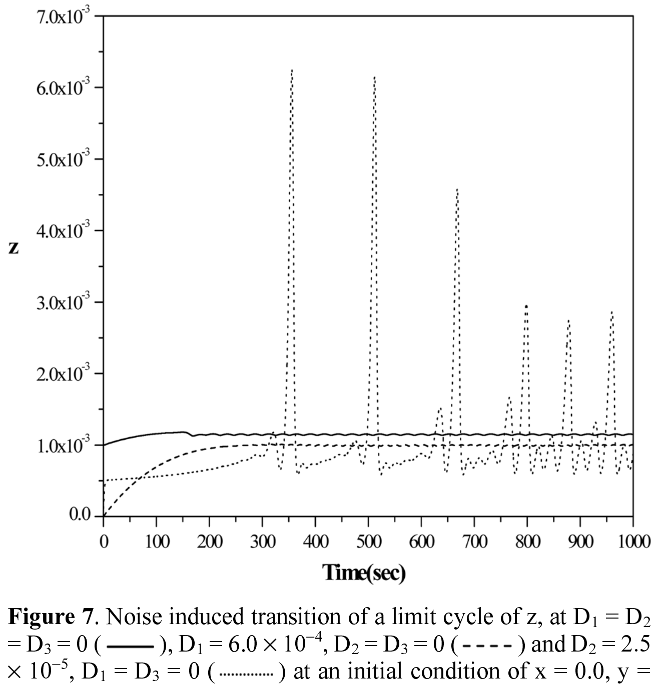

Figure 7. Noise induced transition of a limit cycle of z, at $D_1 = D_2 = D_3 = 0$ (——), $D_1 = 6.0 \times 10^{-4}$, $D_2 = D_3 = 0$ (- - - -) and $D_2 = 2.5 \times 10^{-5}$, $D_1 = D_3 = 0$ (............) at an initial condition of x = 0.0, y = 0.0, and z = 0.0.

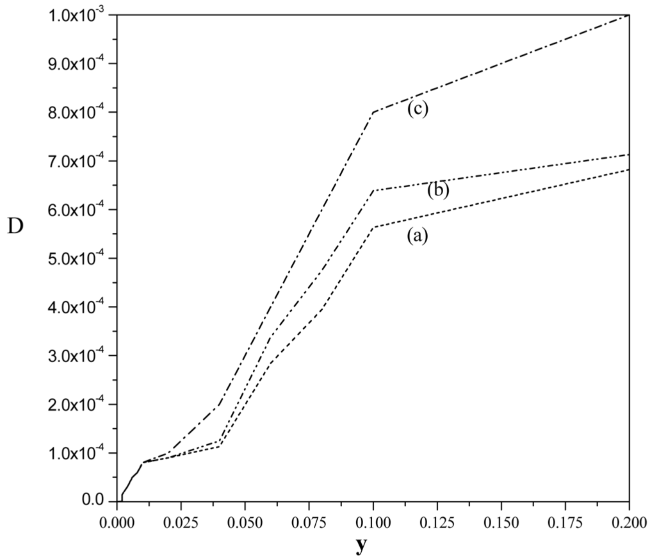

Figure 9. Phase boundaries of fixed point and limit cycle attractors for y at an initial condition of x = 0.0, y = 0.0, and z = 0.0 with (a) $D_2 \neq 0$, $D_1 = D_3 = 0$, (b) $D_1 \neq 0$, $D_2 = D_3 = 0$, (c) $D_3 \neq 0$, $D_1 = D_2 = 0$.

system are more or less deterministic, deviation from deterministic behaviors occurs at higher amplitude. As it is evident that spiraling amplitudes are compressed and the relaxation time is reduced.[13] Due to the effect of noise that plays a dissipative role to suppress the intrinsic mechanism of self-sustaining oscillation.[14]

Figures 5, 6, and 7 show the impact of the oscillatory behavior for a specific species when one of them is affected by noise. Figure 5 indicates the oscillatory behavior of x when the other two, namely, y and z are affected by noise. It has been found that the effect of noise on the species; say y and z, causing an enhancement of oscillatory period in x. Further the effect of noise on z enhances the period of oscillation in x further when compared to the effect of noise on y. Figures 6 shows the behavioral changes in the y when x and z are affected by noise when noise was considered on each species, separately. Here the effect of noise on z enhancing the period of oscillation in y is higher than the effect on x. Similarly Figure 7 shows the impact on the oscillatory behavior of z when x and y are affected noise when the noise parameter is considered on each species separately. Here the effect of noise on y enhances the period

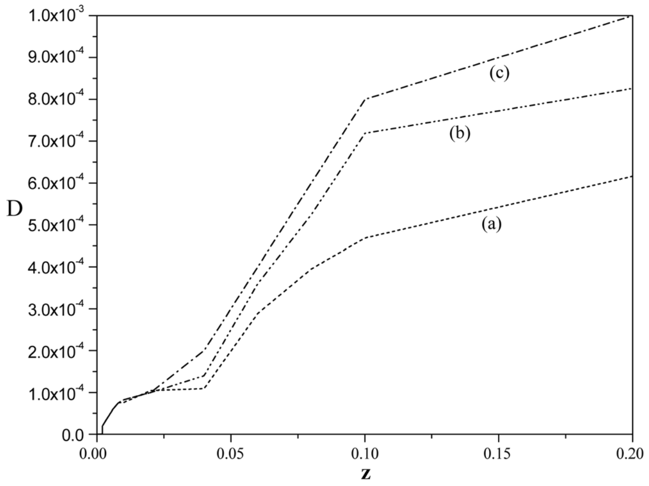

Figure 10. Phase boundaries of fixed point and limit cycle attractors for z at an initial condition of x = 0.0, y = 0.0, and z = 0.0 with (a) $D_3 \neq 0$, $D_1 = D_2 = 0$, (b) $D_2 \neq 0$, $D_1 = D_3 = 0$, (c) $D_1 \neq 0$, $D_2 = D_3 = 0$.

of oscillations in z highly compared to the noise on x, and it almost has little effect on z.

Phase diagram of stochastic bifurcation. Bifurcation between the fixed point and limit cycle attractors is a result of the competition between the intrinsic mechanism of dissipation and self-sustaining oscillation. When the random noise is under consideration, both the competing mechanism and the asymptotic attractors are perturbed. Limit cycle is more vulnerable to noise effects than the fixed point. Figures 8, 9, and 10 present the bifurcation diagram showing the transition in the phase boundaries of the fixed point and the limit cycle attractors of x, y, and z, respectively. Figure 8(a) shows the behavior of bifurcation for x when $D_1 \neq 0$, $D_2 = D_3 = 0$ *i.e.*, where there is no noise in the term containing y and z at the Equations 3(a)-3(c) of the system. Figure 8(b) shows the behavior of bifurcation for x when $D_2 \neq 0$, $D_1 = D_3 = 0$, *i.e.*, where there is no noise in the term containing x and z at the Equations 3(a)-3(c) of the system. Figure 8(c) shows the behavior of bifurcation for x when $D_3 \neq 0$, $D_1 = D_2 = 0$, *i.e.*, where there is no noise in the term containing x and y at the Equations 3(a)-3(c) of the system. Figure 9(a) shows the behavior of bifurcation for y when $D_2 \neq 0$, $D_1 = D_3 = 0$, *i.e.*, where there is no noise in the term containing x and z at the Equations 3(a)-3(c) of the system. Figure 9(b) shows the behavior of bifurcation for y when $D_1 \neq 0$, $D_2 = D_3 = 0$, *i.e.*, where there is no noise in the term containing y and z at the Equations 3(a)-3(c) of the system. Figure 9(c) shows the behavior of bifurcation for y when $D_3 \neq 0$, $D_1 = D_2 = 0$, *i.e.*, where there is no noise in the term containing x and y at the Equations 3(a)-3(c) of the system. Figure 10(a) shows the behavior of bifurcation for z when $D_3 \neq 0$, $D_1 = D_2 = 0$ *i.e.*, where there is no noise in the term containing x and y at the Equations 3(a)-3(c) of the system. Figure 10(b) shows the behavior of bifurcation for z when $D_2 \neq 0$, $D_1 = D_3 = 0$ i.e. where there is no noise in the term containing x and z at the Equations 3(a)-3(c) of the system. Figure 10(c) shows the behavior of bifurcation for z when $D_1 \neq 0$, $D_2 = D_3 = 0$, *i.e.*, where there is no noise in the term containing y and z at the Equations 3(a)-3(c) of the system. All the three types of additive noise discussed above do not qualitatively have the same effects on the transition, since the effect of noise on one parameter also affects the behavior of others as can be observed from Figures 8, 9, and 10. The minimum noise amplitude required to do so is found to be nearly $D_1^{min} = D_2^{min} = D_3^{min} = 8 \times 10^{-5}$ as in the case of x and y (shown in Figures 8 and 9), but is slightly different in the case of z (Figure 10) as $D_1^{min} = 8.5 \times 10^{-5}$, $D_2^{min} = 7.5 \times 10^{-5}$, and $D_3^{min} = 8.75 \times 10^{-5}$. However, the transition points of x, y, and z are all similar as 0.01, 0.012, and 0.021, respectively.

Conclusion

Extensive studies show that the transition from a limit cycle to a fixed point occurs only for specific types of noise with considerably large noise amplitudes. Noise effect is an interesting topic since noise plays constructive as well as destructive roles. The nonlinearity of the systems, which provides a rich scenario in deterministic dynamics, causes interesting response to noisy perturbations. In this paper, we have studied oscillatory behavior and the bifurcation of a simple oscillating chemical reaction system when noise is added to each of the three ordinary differential equations. It is interesting to observe the occurrence of stochastic resonance-like behavior at lower values of amplitude, which, however, causes destructive effects at much higher values of noise amplitude. Effect of selective noise on z has an increasing effect on x and y. In contrary y enhances the oscillatory period on z than x. This is an evident for the effect of noise on the intrinsic behavior of the mechanism, which is also evident from the bifurcation diagrams. There are some reports where the presence of noise was responsible for the generation of temporal oscillations, and the appearance of spatial patterns does not arise in the deterministic model.[17-22] However, we have reported here that the system retains its characteristic time scale and does not require any external drive. Environmental noise does not always play a destructive role of wiping out the coherent behavior in such systems. There are several biological and chemical systems, specifically those which can be modeled by the above systems and by stochastic resonance without external periodic drive, which may have interesting applications there. Everything depends upon the system that we have chosen to study. Noise has its own role to play either in a constructive or destructive way, but one needs of course a careful analysis of the behavior for a better understanding of it.

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