Cu(II) Catalyzed Reaction between Phenyl Hydrazine and Toluidine Blue—Dual Role of Acid

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ABSTRACT: The detailed kinetics of Cu(II) catalyzed reduction of toluidine blue (TB^+) by phenyl hydrazine (Pz) in aqueous solution is studied. Toluidine white (TBH) and the diazonium ions are the main products of the reaction. The diazonium ion further decomposes to phenol (PhOH) and nitrogen. At low concentrations of acid, H^+ ion autocatalyzes the uncatalyzed reaction and hampers the Cu(II) catalyzed reaction. At high concentrations, H^+ hinders both the uncatalyzed and Cu(II) catalyzed reactions. Cu(II) catalyzed had stoichiometry similar to the uncatalyzed reaction, $Pz + 2\,TB^+ + H_2O = PhOH + 2\,TBH + 2\,H^+ + N_2$. Cu(II) catalyzed reaction occurs possibly through ternary complex formation between the unprotonated toluidine blue and phenyl hydrazine and catalyst. The rate coefficient for the Cu(II) catalyzed reaction is $2.1 \times 10^4\ M^{-2}\ s^{-1}$. A detailed 13-step mechanistic scheme for the Cu(II) catalyzed reaction is proposed, which is supported by simulations. © 1999 John Wiley & Sons, Inc., Int J Chem Kinet 31: 271–276, 1999

INTRODUCTION

The phenothiazine class dyes have been studied exhaustively because of their useful insecticidal and anthelminite properties [1]. The uncatalyzed and Mo(VI) catalyzed reactions between toluidine blue and Sn(II) in acid were known to exhibit complex kinetics with fractional orders with respect to the reactants [2]. In an earlier communication, we reported the kinetic study of the autocatalyzed reaction between toluidine blue (TB^+) and phenyl hydrazine (Pz) [3]. Based on its selective catalytic efficiency, the suitability of the Cu(II) catalyzed reaction as an indicator reaction for kinetic-catalytic analysis of Cu(II) was explored. Due to the reaction's sensitivity to $[H^+]$, it was found unsuitable for the purpose. The autocatalytic and retarding effects displayed by acid under varied concentration conditions motivated the further studies. Here, we report the kinetics and mechanism of the Cu(II) catalyzed reaction between TB^+ and Pz.

EXPERIMENTAL

Reagents

All the reagents used were of analytical reagent grade, and double distilled water was used in all preparations. A zinc salt of toluidine blue was used in all the studies. A fresh solution of 0.01 M phenyl hydrazine was prepared daily.

Kinetic Measurements

The reagents were kept in a thermostatted water bath at 25°C. The total volume of the reaction mixture was kept at 10 ml. Reagents were mixed in the order to-

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luidine blue, water, and other reagents. The reaction was initiated by the addition of phenyl hydrazine and the homogeneous reaction mixture was then transferred to the cell. Reaction dynamics were monitored at 630 nm using the Cary UV-Visible spectrophotometer thermostatted to (25.0 ± 0.1)°C. For all the kinetic runs, the instrument was set to monitor the reaction 20 s after initiation of the reaction.

Determination of Formation Constants

The alkalimetric titrations were carried out at (25 ± 0.1)°C, using a pH/ISE meter (model EC40, Hach company, USA), with data acquisition facility. Titrations in duplicate were performed for each system in the ranges: Sodium chloride (0.02–0.04 M), phenyl hydrazine (0.01–0.02 M), cupric chloride (0.004 M), and sodium hydroxide (0.2 M). The protonation constants of toluidine blue and phenyl hydrazine and their stability constants with copper were calculated from the alkalimetric data using a nonlinear least-square's program SUPERQUAD [4].

RESULTS AND DISCUSSION

Product Identification and Stoichiometry

Toluidine blue (500 mg in 100 ml water), phenyl hydrazine (5.0 g in 10 ml alcohol), and 0.01 M HCl (10 ml) were mixed and diluted to 200 ml with water. After approximately 24 h, the reaction mixture was extracted in diethyl ether. The ether extract was subsequently dried and the products were analyzed. Thin-layer chromatography and infrared spectroscopy were used to identify the products. A comparison of the infrared spectrum of the product with standard samples showed the presence of phenol (PhOH). A minor product of the reaction was a green solid, thus confirming the presumption of diazonium ion formation and decomposition to phenol in acidic solutions. Toluidine blue was reduced to toluidine white (TBH), a colorless compound [2]. The diazonium ion has been reported as the product of oxidation phenyl hydrazines with lead tetraacetate, chlorine, bromine, and by acidic bromate [5,6]. Based on the stoichiometric ratios and the products identified, the reaction in the presence of the copper ion is the same as the uncatalyzed reaction [3].

$$\mathrm{Pz} + 2\,\mathrm{TB}^+ + \mathrm{H_2O} = \mathrm{PhOH} + 2\,\mathrm{TBH} + 2\,\mathrm{H}^+ + \mathrm{N_2}$$

Reaction Dynamics

In the earlier communication, the first-order dependence of the reaction rate on both TB^+ and Pz, and the autocatalytic role of H^+ ion, was established [3]. In further investigations, it was observed that depending on its relative concentration to Pz, acid acted either as an autocatalyst or an inhibitor for the uncatalyzed reaction. Figure 1 illustrates the dual role played by acid in the uncatalyzed reaction depending on its concentration conditions. Curve **a** shows a typical kinetic curve in absence of added acid, featuring the initial slow reaction, followed by an increasing rate, due to the autocatalytic effect of H^+ ion. Curve **b** shows a swift drop in the $[TB^+]$ confirming the catalyzing effect of H^+ at 0.002 M. Curves **c** and **d** demonstrate the inhibition by acid, at 0.003 and 0.04 M concentrations, respectively.

The effect of variation of [Cu(II)] on the reaction rate was studied, with $[TB^+]$ (5.5×10^{-5} M), excess of Pz (9.0×10^{-3} M), and low concentrations of Cu(II). Figure 2 shows the typical kinetic curves due to variation of the catalyst concentration. The curves **e**, **f**, and **g** show that at low [Cu], the reaction starts slowly and the rate of reaction increases with time. With increased catalyst concentration (curves **h**, **i**, and **j**), the curves change from the autocatalyzed to the exponential decay characteristics. In the preliminary studies, both the initial rates (from the absorbance versus time data) and the rate constants (log absorbance

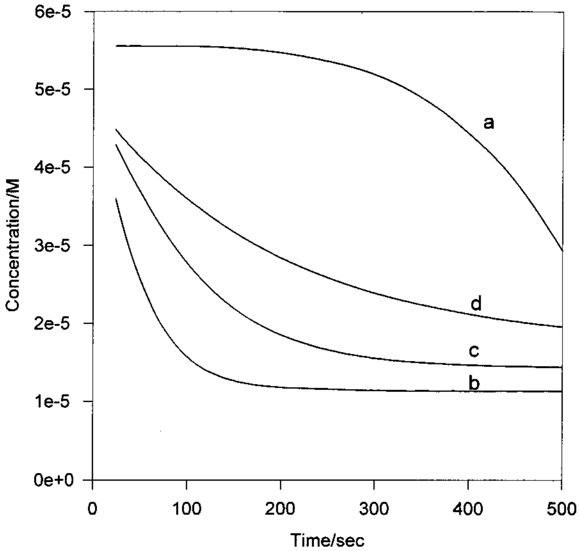

Figure 1 Effect of acid on the uncatalyzed reaction $[TB^+] = 5.5 \times 10^{-5}$ M, $[Pz] = 3.0 \times 10^{-2}$ M. $[H^+]$/M = Curve **a**, Uncatalyzed; **b**, 0.002; **c**, 0.003; and **d**, 0.04.

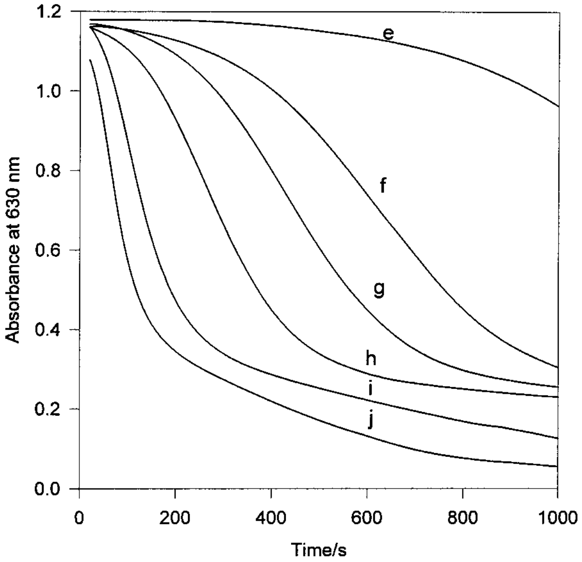

Figure 2 Toluidine blue–phenyl hydrazine reaction—Variation of [Cu(II)]. $[TB^+] = 5.5 \times 10^{-5}$ M and $[Pz] = 9.0 \times 10^{-3}$ M; $Cu(II)/10^{-7}$ M = Curve **e**, 2.0; **f**, 4.0; **g**, 6.0; **h**, 10.0; **i**, 30.0; and **j**, 50.0.

Table I Pseudo First-Order Rate Coefficients (k') for Cu(II) Catalyzed Reaction between Toluidine Blue and Phenyl Hydrazine
$[TB^+] = 5.5 \times 10^{-5}$ M and $[Pz] = 9.0 \times 10^{-3}$ M

$[Cu]/10^{-6}$ M	$k'/10^{-3}$ s^{-1}*
0.5	0.23
0.6	0.25
0.7	0.27
1.0	0.35
2.0	0.53
3.0	0.76
5.0	1.14
7.0	1.57
10.0	2.19

* Mean of duplicate experiments with less than 5% deviation.

versus time data) were investigated. Table I summarizes the pseudo first-order rate coefficients, k' for different [Cu(II)]. A plot of k' versus [Cu(II)] gave a linear curve with gradient 206 ± 2 (Corr. Coeff. 0.988) and an intercept of $(1.29 \pm 0.15) \times 10^{-4}$ s^{-1}. The ratio of the intercept to [Pz] was in agreement with the experimentally determined second-order rate constant for the uncatalyzed reaction [3]. Further, the mean value of the gradient to the [Pz] gave the rate coefficient for the Cu(II) catalyzed reaction as $(2.1 \pm 0.1) \times 10^4$ M^{-2} s^{-1}. Considering that acid exhibits both autocatalytic and inhibiting effects on the uncatalyzed reaction, the influence of H^+ on the copper catalyzed reaction was investigated.

In Figure 3, curves **k**, **l**, **m**, and **n** illustrate the hampering effect of added acid. With a raise in $[H^+]$ to 4.0×10^{-3} M (curve **j**) the reaction slowed down significantly. To further establish the role of acid, the dynamics of Cu(II) catalyzed reactions were studied with TB^+ (5.5 × 10−5 M) and higher Pz (3.0×10^{-2} M). Figure 4 compares the uncatalyzed (curve **a**) and Cu catalyzed (curve **o**) kinetic runs. Curves **p** and **q** demonstrate the effect of added acid on the Cu catalyzed reaction. This confirms that H^+ ions at all concentrations interfere and hinder the copper catalyzed pathway. Although added acid hampers the Cu catalyzed reaction, at high [Pz] it is interesting to note that the reaction rate is still faster than that for the uncatalyzed reaction. For typical mixtures, initial pH values for uncatalyzed and Cu catalyzed reactions were 7.527 and 7.561, respectively. By the completion of the reaction, the values decreased to 7.379 and 7.433, respectively. The marginal change in the pH of the reactions points towards the formation H^+ ions and swift protonation of organic moieties in the system.

To explain the dual role of acid in the reaction, the equilibrium chemistry of toluidine blue and phenyl hydrazine was further investigated. The protonation constants of Pz and TB^+, their stability constants with Cu(II), and stability of ternary complex of TB^+,

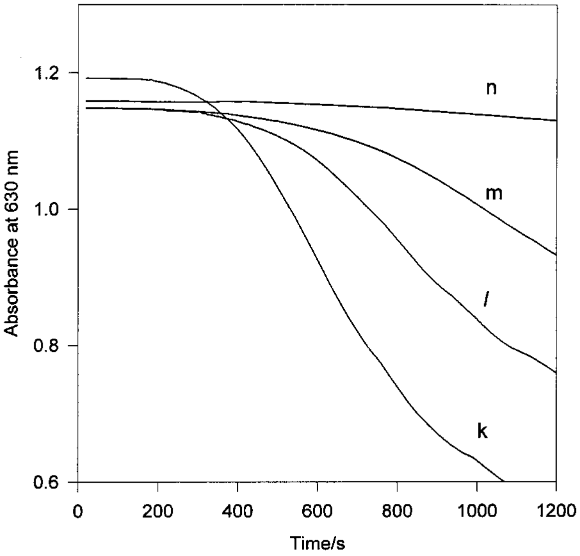

Figure 3 Effect of acid on the Cu(II) catalyzed reaction. $[TB^+] = 5.5 \times 10^{-5}$ M, $[Pz] = 9.0 \times 10^{-3}$ M, and $Cu(II) = 5.0 \times 10^{-7}$ M. $[H^+]$/M = Curve **k**, 0.001; ***l***, 0.002; **m**, 0.003; and **n**, 0.004.

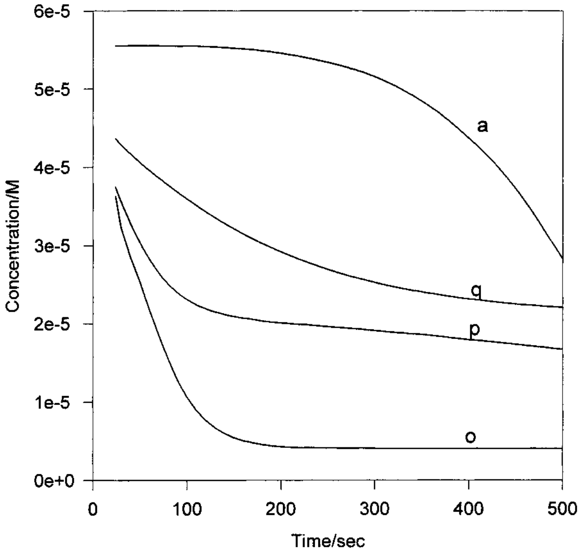

Figure 4 Effect of acid on the Cu(II) catalyzed reaction at high [Pz]. $[TB^+] = 5.5 \times 10^{-5}$ M, $[Pz] = 3.0 \times 10^{-2}$ M, Cu(II) $= 5.0 \times 10^{-6}$ M. Curve **a**, Uncatalyzed; **o**, Cu only and no acid; **p**, Cu plus $[H^+]$ 0.002 M; **q**, Cu plus $[H^+]$ 0.04 M.

Table II Protonation and Stability Constants of Toluidine Blue, Phenyl Hydrazine, and Their Complexes with Copper
T = 25°C; Computer program = SUPERQUAD

System	log K	Number of points
TB^{+}*	7.20 ± 0.01	89
Pz	5.18 ± 0.03	75
TB^{+}—Cu(II)*	7.17 ± 0.01	94
Pz—Cu(II)	4.85 ± 0.07	90
TB^{+}—Cu(II)—Pz	13.02 ± 0.03	104

* (Ref. 7)

Cu(II), and Pz [4,7] were calculated from the alkalimetric titration data (Table II). Based on the magnitudes of protonation and stability constants, dual behavior exhibited by acid can be explained. In absence of the catalyst, the observed autocatalytic effect of H^+ implies that protonated toluidine blue (TBH^{2+}) reacts faster than TB^+ with Pz [2,3]. Autocatalytic effect of acid at low concentrations is explainable in terms of favored protonation of TB^+ over Pz. Protonated toluidine blue (TBH^{2+}) undergoes reduction faster, while the protonated phenyl hydrazine (PzH^+) is oxidized slowly. With excess [Pz] as in the present case and at low $[H^+]$, the TBH^{2+} to Pz reaction will dominate over the slower TBH^{2+} to PzH^+ reaction, hence the autocatalytic effect of H^+ is observed. At high $[H^+]$, due to the increased $[PzH^+]$, the slow reaction becomes increasingly significant and the overall reaction is hampered. In the Cu(II) catalyzed reaction, at very low $[H^+]$, the $\{TB^+$—Cu(II)$\}$ complex accelerates the oxidation of Pz, by the formation of the ternary complex, $\{TB^+$—Cu(II)—Pz$\}$. At higher $[H^+]$, considering the higher protonation constants of TB^+ Pz relative to their stability constants with Cu(II), TB^+ and Pz get readily protonated. These phenomena interfere in the formation of ternary complex between TB^+, Cu(II), and Pz, resulting in lower catalytic efficiency by Cu(II).

The reduction of toluidine blue to leuco-toluidine blue (toluidine white, TBH) is a reversible reaction involving the gain of two electrons [8]. The present experimental results suggest that in the rate limiting step, toluidine blue is also involved in a two-electron reduction step, as one-electron step for toluidine blue would have resulted in fractional order [4,9–11]. Consistent with the reaction orders and products, the following mechanistic steps may be proposed for the reaction sequence in presence of copper cations. The proposed mechanism involves the oxidation of phenyl hydrazine to its corresponding imide and to diazonium ion as the reaction intermediate species and the formation of toluidine white (TBH) and phenol as the major products.

Mechanistic Scheme

1. $TB^+ + Pz \rightarrow TBH_2^+ + I_1$
2. $TB^+ + H^+ \rightleftharpoons TBH^{+2}$
3. $Pz + H^+ \rightleftharpoons PzH^+$
4. $TBH + H^+ \rightleftharpoons TBH_2^+$
5. $TBH^{+2} + Pz \rightarrow TBH + I_1 + 2\,H^+$
6. $PzH^+ + TBH^{+2} \rightleftharpoons TBH_2^+ + I_1 + 2\,H^+$
7. $TBH^{+2} + I_1 \rightleftharpoons TBH_2^+ + I_2^+$
8. $TB^+ + Cu(II) \rightleftharpoons [TB^+ - Cu(II)]$
9. $[TB^+—Cu(II)] + Pz \rightleftharpoons [TB^+—Cu(II)—Pz]$
10. $[TB^+—Cu(II)—Pz] \rightarrow TBH_2^+ + I_1 + Cu(II)$
11. $[TB^+—Cu(II)] + PzH^+ \rightleftharpoons [TB^+—Cu(II)—PzH^+]$
12. $[TB^+—Cu(II)—PzH^+] \rightarrow TBH_2^+ + I_1 + H^+ + Cu(II)$
13. $TBH^{2+} + Cu(II) \rightleftharpoons [TBH^{2+}—Cu(II)]$
14. $[TBH^{2+}—Cu(II)] + Pz \rightleftharpoons [TBH^{2+}—Cu(II)—Pz]$
15. $[TBH^{2+}—Cu(II)—Pz] \rightarrow TBH_2^+ + I_1 + H^+ + Cu(II)$
16. $[TBH^{2+}—Cu(II)] + PzH^+ \rightleftharpoons [TBH^{2+}—Cu(II)—PzH^+]$

17. $[\mathrm{TBH^{2+}—Cu(II)—PzH^{+}}] \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1} + 2\,\mathrm{H^{+}} + \mathrm{Cu(II)}$
18. $\mathrm{Pz} + \mathrm{Cu(II)} \rightleftharpoons [\mathrm{Pz—Cu(II)}]$
19. $[\mathrm{Pz—Cu(II)}] + \mathrm{TB^{+}} \rightleftharpoons [\mathrm{TB^{+}—Cu(II)—Pz}]$
20. $\mathrm{TB^{+}} + \mathrm{I_1} \rightarrow \mathrm{TBH} + \mathrm{I_2^{+}}$
21. $\mathrm{PzH^{+}} + \mathrm{TB^{+}} \rightleftharpoons \mathrm{TBH_2^{+}} + \mathrm{I_1} + \mathrm{H^{+}}$
22. $\mathrm{I_1} + \mathrm{H^{+}} \rightleftharpoons \mathrm{I_1H^{+}}$
23. $\mathrm{I_2^{+}} + \mathrm{Pz} \rightarrow \mathrm{Azo} + \mathrm{H^{+}}$
24. $\mathrm{I_2^{+}} + \mathrm{H_2O} \rightarrow \mathrm{PhOH} + \mathrm{N_2} + \mathrm{H^{+}}$

$\mathrm{I_1}$ = imide, $\mathrm{I_2^{+}}$ = diazonium ion, and Azo = azo compound.

RATE LAW

$$-d[\mathrm{TB}]/dt = \text{Uncatalyzed reaction rate} + \text{Acid catalyzed rate} + \text{Cu(II) catalyzed rate}$$

$$-d[\mathrm{TB}]/dt = k_1[\mathrm{TB^{+}}][\mathrm{Pz}] + k_5[\mathrm{TB^{+}}][\mathrm{H^{+}}][\mathrm{Pz}] + k_{10}[\mathrm{TB^{+}}][\mathrm{Pz}][\mathrm{Cu^{2+}}]$$

$$-d[\mathrm{TB}]/dt = \{k_1[\mathrm{Pz}] + k_{10}[\mathrm{Pz}][\mathrm{Cu^{2+}}] + k_5[\mathrm{H^{+}}][\mathrm{Pz}]\}[\mathrm{TB^{+}}]$$

where k_1, k_5, and k_{10}, are respectively the rate coefficients for the uncatalyzed, $\mathrm{H^{+}}$ catalyzed, and Cu(II) catalyzed reactions. Under excess [Pz] conditions, reaction initially exhibits pseudo first-order behavior with respect to toluidine blue.

SIMULATIONS

Computer simulations using the proposed mechanistic scheme were carried out. The semi-implicate Runge-Kutta method in PASCAL language (TURBO PASCAL 7.0 version) devised by Kaps and Rentrop, which solves autonomous ordinary differential equation systems, was implemented [12]. Based on the responses using the 24-step mechanism and after assessing the significance of each step, the 24-step scheme with 40 parameters was simplified and reduced to a 13-step scheme with 18 parameters. Basic features of the reaction mechanism were maintained. The two sets of two steps involving the formation of ternary complex and their decompositions were reduced to two single steps. All reactions involving the reaction of toluidine blue copper complexes with protonated Pz ($\mathrm{PzH^{+}}$) were excluded. The two steps involving diazonium ion giving final products were combined to one. Table III summarizes the simplified reaction scheme and the rate parameters used for the simulations.

For the three kinetically controlled steps, uncatalyzed (k_1), $\mathrm{H^{+}}$ ion catalyzed (k_5) [3], and Cu(II) catalyzed (k_{10}) reactions, the experimental rate constants were used. For the equations 2, 3, and 9, experimentally determined protonation and stability constants were used as the ratios for the forward to reverse rate constants (Table II). For these reactions, the ratios were kept identical to their protonation or stability constants, and the magnitudes of rate coefficients were then estimated. Simulations were very sensitive to the values of the experimentally determined parameters, k_1, k_5, and k_{10}. The values of k_7 and k_8 were kept larger than k_5 and k_{10}. Other rate constants and other estimated coefficients were adjusted until the theoretical curves matched with the experimental curves. With a fixed set of experimental and estimated rate coefficients, simulations were repeated for varied concentrations Cu(II) of reactants. Each simulated curve represents toluidine blue as the sum of $[\mathrm{TB^{+}}]$ and $[\mathrm{TBH_2^{+}}]$, as protonated toluidine blue has no phase shift. Figure 5 shows the simulated curves (**e′**, **h′**, and **i′**) for the variation of Cu(II) superimposed on the cor-

Table III Simulations: Rate Equations and Rate Coefficients

1. $\mathrm{TB^{+}} + \mathrm{Pz} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1}$	$k_1 = 1.4e-2$;
2. $\mathrm{TB^{+}} + \mathrm{H^{+}} \rightleftharpoons \mathrm{TBH^{+2}}$;	$k_2 = 9.6$; $k_{-2} = 6e-7$
3. $\mathrm{Pz} + \mathrm{H^{+}} \rightleftharpoons \mathrm{PzH^{+}}$;	$k_3 = 4.8e1$; $k_{-3} = 4e-4$;
4. $\mathrm{TBH} + \mathrm{H^{+}} \rightleftharpoons \mathrm{TBH_2^{+}}$;	$k_4 = 1.5e-3$; $k_{-4} = 1e-8$;
5. $\mathrm{TBH^{+2}} + \mathrm{Pz} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1} + \mathrm{H^{+}}$;	$k_5 = 2e2$;
6. $\mathrm{TBH^{+2}} + \mathrm{PzH^{+}} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1} + 2\,\mathrm{H^{+}}$;	$k_6 = 1e-2$;
7. $\mathrm{TBH^{+2}} + \mathrm{I_1} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_2^{+}}$;	$k_7 = 2e4$;
8. $\mathrm{I_2^{+}} \rightarrow \mathrm{Products} + \mathrm{H^{+}}$;	$k_8 = 1e5$;
9. $\mathrm{TB^{+}} + \mathrm{Cu(II)} \rightleftharpoons [\mathrm{TB^{+}—Cu(II)}]$;	$k_9 = 1.3e4$; $k_{-9} = 1e-3$;
10. $[\mathrm{TB^{+}—Cu(II)}] + \mathrm{Pz} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1} + \mathrm{Cu(II)}$;	$k_{10} = 2.1e4$;
11. $\mathrm{TBH^{2+}} + \mathrm{Cu(II)} \rightleftharpoons [\mathrm{TBH^{2+}—Cu(II)}]$;	$k_{11} = 2.1e—1$; $k_{11} = 1e1$;
12. $[\mathrm{TBH^{2+}—Cu(II)}] + \mathrm{Pz} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1} + \mathrm{Cu(II)} + \mathrm{H^{+}}$;	$k_{12} = 20$;
13. $[\mathrm{TBH^{2+}—Cu(II)}] + \mathrm{PzH^{+}} \rightarrow \mathrm{TBH_2^{+}} + \mathrm{I_1} + \mathrm{Cu(II)} + 2\,\mathrm{H^{+}}$;	$k_{13} = 1e-1$;

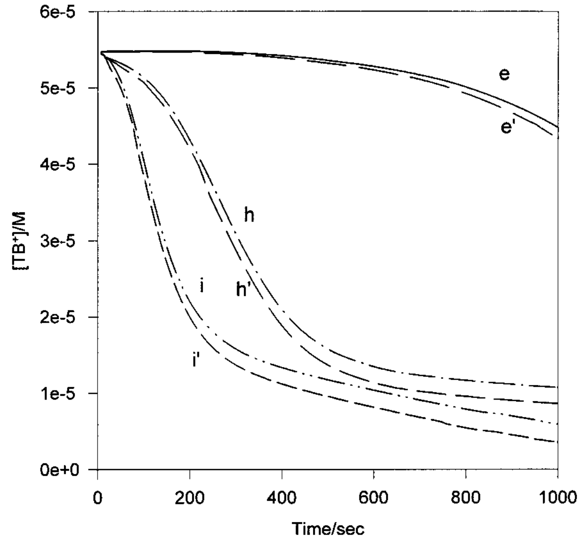

Figure 5 Simulated curves. For curves **e**, **h**, and **i**—Conditions are same as in Figure 2. Curves **e′**, **h′**, and **i′** are the respective simulated curves by varying [Cu(II)].

responding experimental curves (**e**, **h**, and **i**). A perusal of the curves show that the computed curves are in good agreement with the experimental runs. Further, the effect of acid on the simulations in the presence and absence of the copper ion was investigated under different reactant conditions. Figure 6 illustrates the results with $[TB^+] = 5.5 \times 10^{-5}$ M and $[Pz] = 3.0 \times 10^{-2}$ M. Curves **d′**, **o′**, and **q′** were produced under identical concentration conditions to the respective experimental curves, **d**, **o**, and **q** in Figures 1 and 4. Curve **d′** illustrates the effect of the addition of H^+ (0.04 M). Curve **o′** shows the effect of the addition of Cu(II) (5×10^{-6} M). Curve **q′** indicates the effect of the addition of both Cu(II) and acid. The computations are based on the fact that the proposed mechanism could generate the catalytic effect of Cu(II), the autocatalytic effect of H^+ at low concentrations on the uncatalyzed reaction, and the retarding effect of acid on the Cu catalyzed reaction. These simulations also demonstrate the retarding effect of acid on the uncatalyzed reaction at high $[H^+] = 0.10$ M (curve **r′**). Consistency in the characteristics of the experimental and simulated curves for varied concentrations of the reactants, catalyst and acid, support the proposed mechanism as a plausible scheme for the reaction between toluidine blue and phenyl hydrazine.

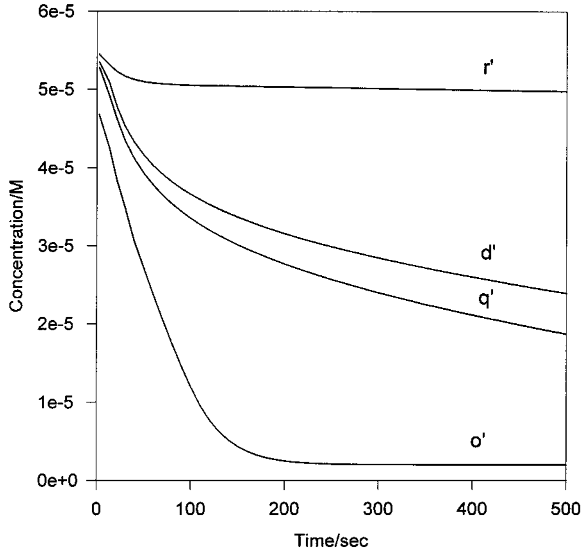

Figure 6 Simulated curves. Curves **d′**, **o′**, and **q′** and are simulated curves under identical conditions as experimental curves **d**, **o**, and **q** in Figure 4. Curve **r′**: Simulated curve under excess acid (0.01 M) with no Cu(II).

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