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Kinetics of the Formation and Decay of Benzidine Mono Radical Cation in Aqueous Solution

Ponnu Aravindan, Pichai Maruthamuthu,* and Periasamy Dharmalingam

Department of Energy, University of Madras, A.C. College Campus Madras-600025, India

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The oxidation of benzidine by Ce(IV); the oxoanions MnO_4^- and $Cr_2O_7^{2-}$; peroxides, namely potassium peroxomonosulfate ($KHSO_5$), peroxodisulfate ($S_2O_8^{2-}$) and H_2O_2; and halogens viz., Cl_2, Br_2, and I_2, to the benzidine mono radical cation (benzidine$^{\bullet +}$) and further oxidation to the benzidine diradical cation ($^{+\bullet}$benzidine$^{\bullet +}$) by the above-mentioned oxidants, except for Br_2 and I_2, were investigated by a stopped-flow technique. The kinetics of both reactions, the formation and decay of benzidine$^{\bullet +}$, were monitored by following the absorption of the radical cation at $\lambda_{max} = 603$ nm. The reactions were found to follow a total second-order kinetics, first-order each with respect to [benzidine] or [benzidine$^{\bullet +}$] and the [oxidant]. The effects of the pH and temperature on the formation and decay of benzidine$^{\bullet +}$ were also investigated. The kinetic and transition-state parameters were evaluated with a suitable reaction mechanism. The radical cation benzidine$^{\bullet +}$ was converted back to the parent compound, benzidine, by such reducing agents as sulfite (SO_3^{2-}), thiosulfate ($S_2O_3^{2-}$), dithionite ($S_2O_4^{2-}$), and disulfite ($S_2O_5^{2-}$). The rate constants for these reactions were also estimated. The experimentally determined rate constants for the oxidative electron-transfer reactions were correlated theoretically using Marcus theory; the observed and calculated rate constants show good agreement.

Electron-transfer reactions are important in a variety of physical, chemical and biological systems, ranging from semiconductors to cytochromes.[1,2] Studies involving the formation and reactivity of radical cations by thermal[3] and photo-induced[4] reactions have attracted the attention of many researchers because of interesting chemical reactions observed with the radical cations.[5] For example, the synthesis of new compounds, which otherwise may not be possible through the reactions of neutral molecules, and the use of electron sacrificial agents as electron relays in chemical routes to solar-energy conversion[6] and biological-energy conversion[7] processes. There are many organic electron sacrificial agents which form radical cations as transient intermediates by one-electron transfer.[7—10] The oxidation of aromatic amines in solution[11,12] has been investigated by anodic electrochemistry using absorption spectrophotometry and electron-spin resonance to identify the intermediate(s) produced in these redox reactions. The aromatic amines are found to undergo a variety of photophysical and photochemical processes.[13—15] Amino compounds, like *N,N*′-dimethyl-4,4′-bipyridinium^{2+} (MV^{2+}), are used as an electron relay to mediate the reaction in chemical routes to solar-energy conversion.[16] Benzidines and aromatic diamines[9] were found to generate photopotentials in photoelectrochemical cells. Previous studies on the oxidation of benzidine have revealed the formation of a monoradical cation, a diradical cation and an azocompound.[17] In the present investigation, it was found that the oxidation of benzidine by most of the oxidants used was too fast to be monitored by the conventional spectrophotometric method, but slow enough to be investigated by a stopped-flow technique. The successive oxidation of benzidine to the final product, an azo compound, can be given as

$$\text{Benzidine} \rightarrow \text{Benzidine}^{\bullet +} \rightarrow {}^{+\bullet}\text{Benzidine}^{\bullet +} \rightarrow \text{Azo compound.} \quad (1)$$

Hence, the present work aimed at the investigation of the fast kinetics of the formation and decay of the radical cation benzidine$^{\bullet +}$ by one-electron as well as multi-electron oxidizing agents.

Experimental

All of the chemicals used were of analytical grade. Doublly distilled water was always used to prepare the reagent solutions. Benzidine was from Sigma (USA) and potassium peroxomonosulfate,[18] under the trade name 'OXONE', was from DuPont (USA). All of the kinetic measurements were carried out with a stopped-flow spectrophotometer (Model 1705, Applied Photophysics, London). The absorption output was digitized with a Datalab 680 transient recorder equipped with a variable input sensitivity and variable sampling interval, and was monitored by a Trio CS-1562 A oscilloscope; Ca 500—700 data points were collected for each kinetic determination. At least six kinetic measurements were made for each quoted value of k_{obs}. The data were stored and analyzed by a CBM-3032 personal computer. The kinetic plots were plotted on a Hewlett–Packard 7470 graphics plotter. The extent of formation of the radical cation and its decay were monitored at 603 nm, the corresponding absorption maximum of benzidine$^{\bullet +}$. The pH of the reaction medium (pH 3—10) was maintained using a Universal buffer (potassium hydrogen phthalate, potassium dihydrogenphosphate or borax with added acid or base depending upon the pH required).[19]

All of the reactions were performed under pseudo-first-order conditions: [oxidant]>[benzidine] or [benzidine$^{\bullet +}$]; [reductant]>

[benzidine$^{\bullet+}$]. To determine the effect of the temperature on the rates of formation and decay of the radical cation, the experiments were performed in the 15—35 °C temperature range. Duplicate experiments were always carried out, and the rate constants were reproducible within ±10%.

Results and Discussion

a) Formation and Decay of Benzidine$^{\bullet+}$. The kinetics of the oxidation of benzidine by Ce(IV), MnO_4^-, $Cr_2O_7^{2-}$, HSO_5^-, $S_2O_8^{2-}$, H_2O_2, Cl_2, Br_2, and I_2 were carried out under pseudo-first-order conditions with the concentration of the oxidant at least in ten-times excess over that of benzidine, in the 15—35 °C temperature range. ([benzidine] = $1.0—10.0\times10^{-5}$ M (1 M= 1 mol dm^{-3}); [oxidant] = $2.0\times10^{-4}—10.0\times10^{-1}$ M). The changes in the optical density of the radical cation with time were followed at different time scales, depending upon the reactivity of the oxidants. Plots of log (absorbance) against time were found to be linear up to ca. 70% of the reaction with the correlation coefficient ≥0.99. At constant concentrations of the oxidants and with varying concentrations of benzidine, the plots of log $(A_\infty - A_t)$ vs. time were found to be linear. The pseudo-first-order rate constants (k'_f/s^{-1}), evaluated from the slopes of the above plots, were found to be almost constant (within the experimental error), indicating a first-order dependence of the rates on [benzidine]. At a constant concentration of benzidine, but with different concentrations of the oxidants, the evaluated pseudo-first-order rate constants (k'_f/s^{-1}) were found to increase along with an increase in the [oxidant]. The plots of k'_f/s^{-1} vs. [oxidant] were found to be linear, passing through the origin, indicating a first-order dependence of the rates on the [oxidant] (Figs. 1, 2, and 3) and the absence of any reaction un-assisted by the oxidants. From the slopes of the above-mentioned plots, the second-order rate constants (k_{2f}/M^{-1} s^{-1}) for the formation of the radical cation were evaluated (Table 1). From the above results, the following rate law can be proposed for the formation of the benzidine monoradical cation:

$$\text{Rate} = \text{d[Benzidine}^{\bullet+}]/\text{d}t = k'_f[\text{oxidant}] = k_{2f}[\text{benzidine}]\,[\text{oxidant}] \qquad (2)$$

For determining the rate constants for the decay of the radical cation (benzidine$^{\bullet+}$) to the diradical cation of benzidine ($^{+\bullet}$benzidine$^{\bullet+}$), experiments were carried out with the pre-prepared benzidine$^{\bullet+}$. The radical cation benzidine$^{\bullet+}$ was prepared by reacting benzidine and peroxodisulfate ($S_2O_8^{2-}$) in a ratio of 2 : 1, and was kept ready for the reaction. The radical cation was found to be stable for several hours in the absence of any oxidizing or reducing agent and at a low temperature of ca. 4 °C. The kinetics were followed at 603 nm for the variation of [benzidine$^{\bullet+}$] as well as [oxidant] under pseudo-first-order conditions at 15—35 °C. {[benzidine$^{\bullet+}$] = $(1.0—10.0)\times10^{-5}$ M; [oxidant] = $0.5\times10^{-4}—10.0\times10^{-1}$ M}. The variation in the concentrations of the oxidants at a fixed concentration of benzidine$^{\bullet+}$ gave different k'_d values, and plots of k'_d vs. [oxidant] were linear, passing through the origin (Fig. 4)

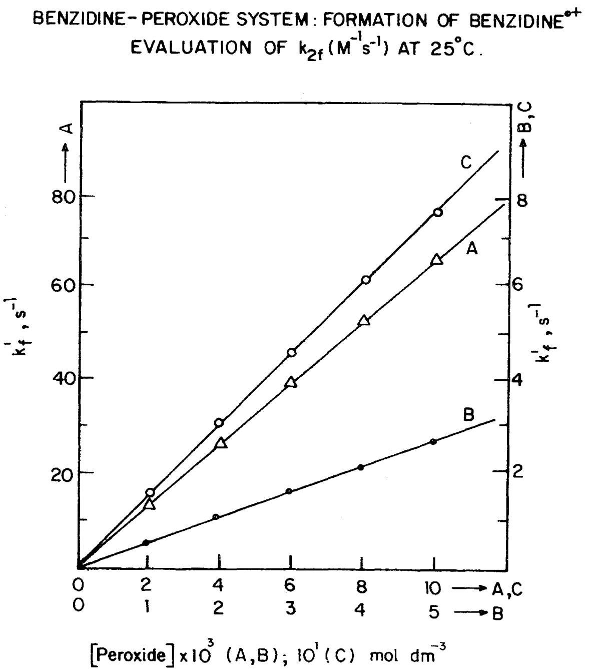


Fig. 1. First-order dependence of the rate on [oxidant] for the formation of benzidine$^{\bullet+}$ at 25 °C. A: HSO_5^-, B: $S_2O_8^{2-}$, C: H_2O_2.

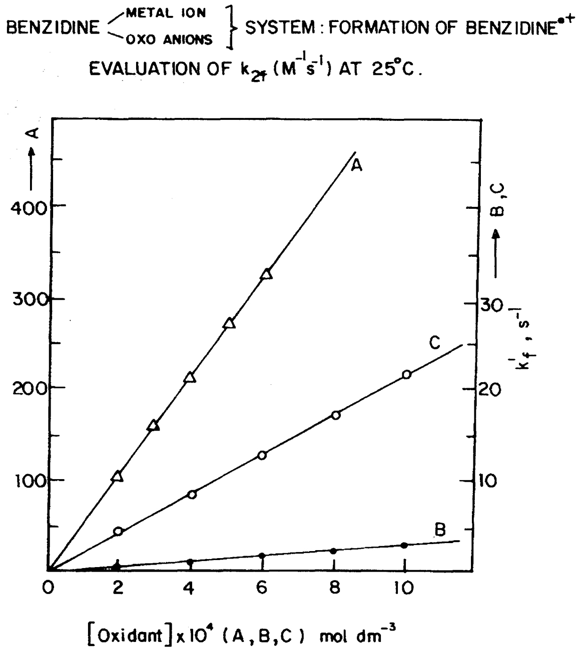


Fig. 2. First-order dependence of the rate on [oxidant] for the formation of benzidine$^{\bullet+}$ at 25 °C. A: MnO_4^-, B: Ce(IV) (0.2 M H_2SO_4), C: $Cr_2O_7^{2-}$ (0.2 M H_2SO_4).

Kinetic analyses similar to those for the formation of the radical cation gave the rate law for the decay process as

$$\text{Rate} = -\text{d[Benzidine}^{\bullet+}]/\text{d}t = k'_d[\text{oxidant}] = k_{2d}[\text{Benzidine}^{\bullet+}]\,[\text{oxidant}]. \qquad (3)$$

The calculated rate constants (k_{2d}/M^{-1}s^{-1}) are given in Table 1.

Table 1. Kinetic Data for the Formation and Decay of Benzidine$^{\cdot+}$ (k_2/M^{-1} s^{-1}) at Different Temperatures (15—35 °C)[a)]

Oxidant	15 °C		20 °C		25 °C		35 °C	
	k_{2f}	k_{2d}	k_{2f}	k_{2d}	k_{2f}	k_{2d}	k_{2f}	k_{2d}
Metal ion								
Ce(IV)	1.9×10^3	3.3×10^2	2.9×10^3	5.0×10^2	3.9×10^3	6.6×10^2	7.6×10^3	13.3×10^2
Oxo anions								
MnO_4^-	2.7×10^5	1.1×10^4	4.1×10^5	1.6×10^4	5.5×10^5	2.1×10^4	11.1×10^5	4.2×10^4
$Cr_2O_7^{2-}$	1.1×10^4	2.3×10^3	1.7×10^4	3.4×10^3	2.3×10^4	4.6×10^3	4.5×10^4	9.1×10^3
Peroxides								
HSO_5^-	3.3×10^3	2.2	5.0×10^3	3.4	6.6×10^3	4.5	13.2×10^3	9.0
$S_2O_8^{2-}$	2.8×10^2	1.3	4.1×10^2	2.0	5.5×10^2	2.6	11.1×10^2	5.3
H_2O_2	3.9	0.3	5.8	0.4	7.8	0.6	15.4	1.1
Halogens								
Cl_2	2.5×10^3	2.1×10^2	3.8×10^3	3.2×10^2	5.0×10^3	4.3×10^2	10.0×10^3	8.6×10^2
Br_2	0.6×10^4	—	0.9×10^4	—	1.1×10^4	—	2.2×10^4	—
I_2	1.1×10^5	—	1.7×10^5	—	2.2×10^5	—	4.4×10^5	—

a) The reactions of Ce(IV) and $Cr_2O_7^{2-}$ are in 0.2 M H_2SO_4. All other reactions are carried out at pH 3.0 adjusted with potassium hydrogen phthalate buffer.

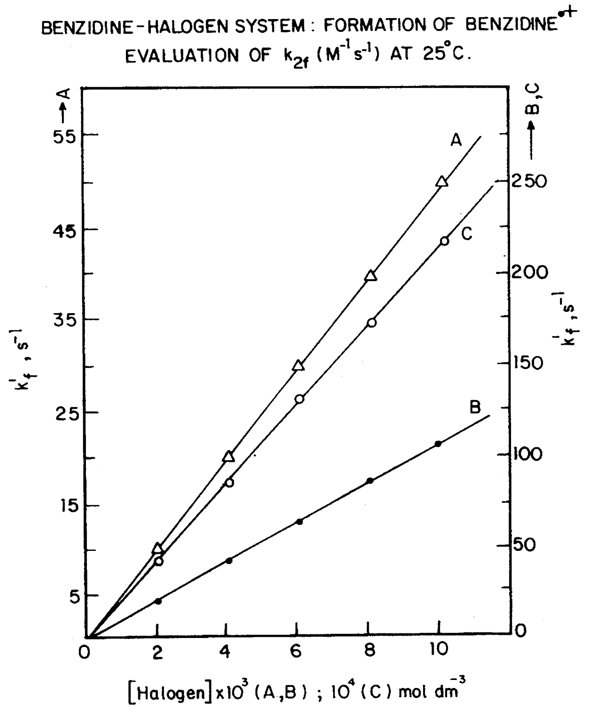


Fig. 3. First-order dependence of the rate on [oxidant] for the formation of benzidine$^{\cdot+}$ at 25 °C. A: Cl_2, B: Br_2, C: I_2.

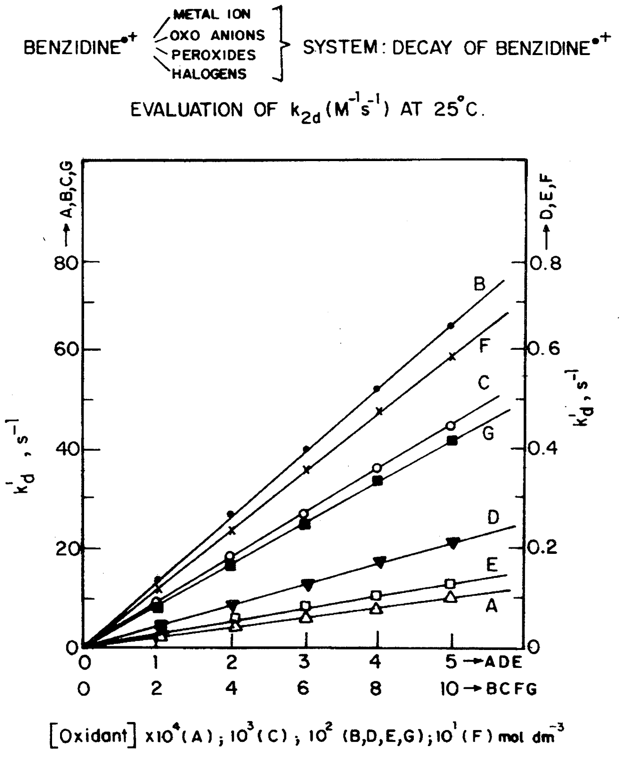
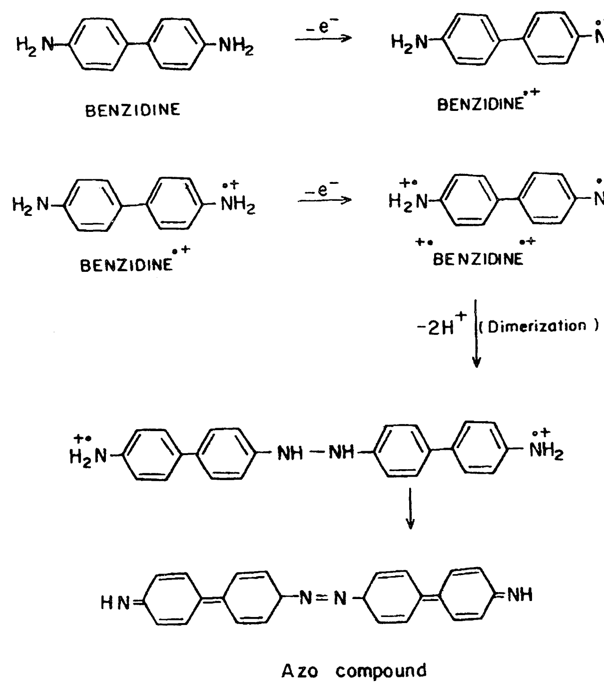


Fig. 4. First-order dependence of the rate on [oxidant] for the decay of benzidine$^{\cdot+}$ at 25 °C. A: MnO_4^-, B: Ce(IV) (0.2 M H_2SO_4), C: $Cr_2O_7^{2-}$ (0.2 M H_2SO_4), D: HSO_5^-, E: $S_2O_8^{2-}$, F: H_2O_2, G: Cl_2.

Reactions with Peroxomonosulfate (PMS), Peroxodisulfate (PDS), and Hydrogen Peroxide. The oxidation of benzidine with organic peroxides was previously studied both in homogeneous media[20)] and on the surface of montmorillonite clay minerals.[21—25)] In the present investigation, on a shorter time scale (5—20 ms), peroxodisulfate [(1.0—5.0)$\times10^{-3}$ M)] generated only the monoradical cation (benzidine$^{\cdot+}$). However, at longer time scales (20—50 ms) the monoradical cation was found to react further with the oxidant, and decayed to the diradical cation of benzidine. The rate constants determined for the reactions are 5.5×10^2 M^{-1} s^{-1} and 2.6 M^{-1} s^{-1} at 25 °C for the formation of benzidine$^{\cdot+}$ (4) and for the second-stage oxidation (5), respectively.



(4) (5) (6) (7)

All of the peroxides individually reacted with benzidine to generate a monoradical cation, and subsequently oxidised the latter to the diradical cation by a one-electron transfer at each stage. Even though the redox potential for peroxomonosulfate (1.8 V) is less than that of peroxodisulfate (2.0 V) the rate constant for peroxomonosulfate with benzidine is approximately 12-times higher than that of peroxodisulfate. This observation is similar to that encountered in many thermal reaction,[26] wherein the rate constants for the oxidation by peroxomonosulfate were higher than those of peroxodisulfate. Although the reactions of peroxodisulfate are thermodynamically more favorable, the rates of the reactions are, probably, controlled by the kinetic parameters. The reactivity trend observed, $HSO_5^- > S_2O_8^{2-} > H_2O_2$, is not in agreement with the oxidation potentials of the oxidants.

b) Effect of the pH (Peroxomonosulfate). In order to study the effect of the pH on the reaction rates, the oxidant peroxomonosulfate (PMS) was chosen. The kinetics of the oxidation of benzidine by PMS at pHs 3.0, 7.4, and 9.6 were carried out on the time scale of 1—10 ms. The kinetics were followed by monitoring the formation of benzidine$^{\bullet+}$ at various concentrations of the reactants ([benzidine] = 1.0—5.0×10^{-5} M; [PMS] = 1.0—5.0×10^{-3} M). The rate law observed was as that observed with the other oxidants,

$$\text{Rate} = \text{d}[\text{Benzidine}^{\bullet+}]/\text{d}t = k'_\text{f}[\text{PMS}]$$
$$= k_{2\text{f}}[\text{Benzidine}]\,[\text{PMS}]. \quad (8)$$

Irrespective of protonation, the mechanism of the reaction may be given as follows:

$$\text{Benzidine} + \text{HOOSO}_3^- \xrightarrow{\text{Slow}}$$
$$\text{Benzidine}^{\bullet+} + {\cdot}\text{OH} + \text{SO}_4^{2-} \text{ (or) } \text{OH}^- + \text{SO}_4^{\bullet-} \quad (9)$$

$$\text{Benzidine} + {\cdot}\text{OH (or) SO}_4^{\bullet-} \xrightarrow{\text{Fast}} \text{Benzidine}^{\bullet+} + \text{OH}^- \text{ (or) SO}_4^{2-}. \quad (10)$$

The values of the rate constants obtained at different pHs are given below:

pH	$k_{2\text{f}}/\text{M}^{-1}\,\text{s}^{-1}$
3.0	6.3 × 10^3
7.4	10.7 × 10^5
9.6	12.9 × 10^5

The rate constant at pH 7.4 is 170-times higher than that observed at pH 3.0, indicating a higher reactivity of unprotonated benzidine than that of protonated benzidine, due to acid-base equilibrium,[27]

$$\text{BenzidineH}^+ \underset{}{\overset{\text{p}K_\text{a}=4.7}{\rightleftarrows}} \text{Benzidine} + \text{H}^+. \quad (11)$$

Since the pK_a value of PMS is 9.4,[26,28,29] it exists as HOOSO_3^- in the pH range 3.0—7.4, and the rate constant at pH 7.4 is due to the following reaction:

$$\text{Benzidine} + \text{HOOSO}_3^- \longrightarrow \text{Product}. \quad (12)$$

The reaction at pH 9.6 is due to the combination of rate constants for the following reactions:

$$\text{Benzidine} + \text{HOOSO}_3^- \ (40\%) \longrightarrow \text{Product} \quad (13)$$

$$\text{Benzidine} + {}^-\text{OOSO}_3^- \ (60\%) \longrightarrow \text{Product} \quad (14)$$

Since the pK_a of HOOSO_3^- is 9.4, the concentrations of HOOSO_3^- and ${}^-\text{OOSO}_3^-$ at pH 9.6 were calculated to be approximately 40 and 60%, respectively, using the relation

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{salt}]}{[\text{acid}]}. \quad (15)$$

Hence, the rate constant for reaction (14) is 2.2×10^5 M^{-1} s^{-1}, which is approximately 4.9-times slower than that at pH 7.4. This observation is in agreement with the slower reactivity of ${}^-\text{OOSO}_3^-$ than HOOSO_3^- in electron-transfer reactions.[28,30]

In the case of the oxidation of benzidine$^{\bullet+}$ with PMS, the reaction was carried out under pseudo-first-order conditions, [PMS] > [benzidine$^{\bullet+}$], and the kinetics were followed by monitoring the disappearance of benzidine$^{\bullet+}$ on the time scale of 5—50 ms. From the observed kinetic results, the rate law for the disappearance of benzidine$^{\bullet+}$ is as follows:

$$\text{Rate} = -\text{d}[\text{Benzidine}^{\bullet+}]/\text{d}t = k_{2\text{d}}[\text{Benzidine}^{\bullet+}]\,[\text{PMS}] \quad (16)$$

The mechanism of reaction may be given as

$$\text{Benzidine}^{\bullet+} + \text{HOOSO}_3^- \xrightarrow{\text{Slow}}$$
$${}^{+\bullet}\text{Benzidine}^{\bullet+} + {\cdot}\text{OH} + \text{SO}_4^{2-} \text{ (or) } \text{OH}^- + \text{SO}_4^{\bullet-} \quad (17)$$

$$\text{Benzidine}^{\bullet+} + {\cdot}\text{OH (or) SO}_4^{\bullet-} \xrightarrow{\text{Fast}}$$
$${}^{+\bullet}\text{Benzidine}^{\bullet+} + \text{OH}^- \text{ (or) SO}_4^{2-}. \quad (18)$$

The rate constants estimated at three different pHs are:

pH	k_{2d}/M^{-1} s^{-1}
3.0	4.7
7.4	6.2×10^3
9.6	5.2×10^4

From the magnitudes of the rate constants for the decay of the radical cation, the rate constant at pH 7.4 is ca. 1300-times higher than that at pH3.0. This indicates that the radical cation at pH 3.0 is protonated, and that the protonated radical cation is more difficult to oxidize than the unprotonated one. Hence, the actual reaction at pH 3.0 would be

$$\text{BenzidineH}^{2+\bullet} + \text{HOOSO}_3{}^- \rightarrow {}^{+\bullet}\text{Benzidine}^{\bullet+} + \cdot\text{OH} + \text{HSO}_4{}^- \text{ (or) } \text{H}_2\text{O} + \text{SO}_4{}^{\bullet-}. \tag{19}$$

The rate constant at pH 9.6 is ca. one order of magnitude higher than that at pH 7.4, indicating a higher reactivity of $^-\text{OOSO}_3{}^-$ (60%) with benzidine$^{\bullet+}$ at pH 9.6. From the rate constants at pH 7.4 and 9.6, the rate constant for the reaction

$$\text{Benzidine}^{\bullet+} + {}^-\text{OOSO}_3{}^- \rightarrow \text{Product} \tag{20}$$

was calculated to be 4.6×10^4 M^{-1} s^{-1}.

Reactions of Ce(IV), $\mathbf{MnO_4{}^-}$ and $\mathbf{Cr_2O_7{}^{2-}}$. The fast kinetics of the reaction of benzidine ([Benzidine]=1.0—10.0×10^{-5} M; [oxidant]=2.0—10.0×10^{-4} M) with $\text{MnO}_4{}^-$, $\text{Cr}_2\text{O}_7{}^{2-}$ and Ce(IV) (0.2 M H_2SO_4) to generate the benzidine mono radical cation and further oxidation at a longer time scale, or with a higher concentrations of the oxidants at a shorter time scale, were studied by following the absorption and decay of the radical cation. The rate constants are given in Table 1. Upon comparing the second-order rate constants, the reactivity of the above-mentioned oxidants with benzidine and benzidine$^{\bullet+}$ was found to be in the order $\text{MnO}_4{}^- > \text{Cr}_2\text{O}_7{}^{2-} >$ Ce(IV). The rate constants are in line with the oxidation potentials[31] of the oxidants, $\text{MnO}_4{}^-$ (1.7 V) and $\text{Cr}_2\text{O}_7{}^{2-}$ (1.4 V, 0.2 M H_2SO_4). In the case of Ce(IV) (1.4V, 0.2 M H_2SO_4), it was found to be less reactive than $\text{Cr}_2\text{O}_7{}^{2-}$, probably due to the complexing[32] ability of Ce(IV) with groups containing electron donors.

Reactions of Halogens. There was a very fast rise in the signal at 603 nm, even at the lowest concentration of I_2 (2.0×10^{-4} M), and no decay of the transient was seen, even at the highest concentration of I_2 (2.0×10^{-2} M). The observed transient may be a charge-transfer complex between benzidine and I_2, and not the product of a complete electron-transfer reaction. Iodine is well known to form such a charge-transfer complex,[33,34] and the calculated rate constants for such a process in the present investigation was found to be 2.2×10^5 M^{-1} s^{-1} at 25 °C. Molecular Br_2 in water (or) aqueous Br_2/KBr oxidized benzidine to benzidine$^{\bullet+}$ on a 2.0 ms time scale; also, the rate constant for the reaction

$$\text{Benzidine} + \text{Br}_2 \rightarrow \text{Benzidine}^{\bullet+} + \text{Br}_2^{\bullet-} \tag{21}$$

is 1.1×10^4 M^{-1} s^{-1} at 25 °C. No attempt was made to investigate the fate of $\text{Br}_2{}^{\bullet-}$, since it has been postulated to decay by a bimolecular reaction at a diffusion controlled rate,[35]

$$2\text{Br}_2{}^{\bullet-} \rightarrow \text{Br}^- + \text{Br}_3^-. \tag{22}$$

There was no observed reaction of Br_2 with benzidine$^{\bullet+}$. In the case of chlorine, the rate constants of the first-stage oxidation (4) is 5.0×10^3 M^{-1} s^{-1} at 25 °C, and the kinetics of the decay of the radical cation was also found to be total second-order, first-order each with respect to [benzidine$^{\bullet+}$] and [Cl_2]. The rate constant is 4.3×10^2 M^{-1} s^{-1} at 25 °C. In the case of the oxidation of benzidine$^{\bullet+}$→$^{+\bullet}$benzidine$^{\bullet+}$, judging from the magnitude of the oxidation potential of Cl_2 (1.4 V) and the magnitude of the rate constant for the reaction, benzidine$^{\bullet+}$+Cl_2→$^{+\bullet}$benzidine$^{\bullet+}$, it is not surprising that Br_2 (oxidation potential 1.1 V) hardly reacts with benzidine$^{\bullet+}$.

c) Reduction of Benzidine$^{\bullet+}$ by Various Reducing Agents. The radical cation benzidine$^{\bullet+}$ was converted back to the parent compound, benzidine, by reducing agents, (sulfite ($\text{SO}_3{}^{2-}$), thiosulfate ($\text{S}_2\text{O}_3{}^{2-}$), dithionite ($\text{S}_2\text{O}_4{}^{2-}$) and disulfite ($\text{S}_2\text{O}_5{}^{2-}$)), suggesting many room-temperature oxidations by benzidine$^{\bullet+}$,

$$\text{Benzidine}^{\bullet+} \xrightarrow{+e^-} \text{Benzidine}. \tag{23}$$

Since the benzidine$^{\bullet+}$ could be prepared in a stable form, its individual reactions with various reducing agents (mentioned above) could be carried out. The kinetics of these reduction reactions were carried out under pseudo-first-order conditions, [reducing agent] > [benzidine$^{\bullet+}$], by following the disappearance of the radical cation (benzidine$^{\bullet+}$) at 25 °C. ([benzidine$^{\bullet+}$]=(1.0—10.0)×10^{-5} M; [reducing agents]=2.0×10^{-4}—2.0×10^{-1} M). The reactions of all the sulfur compounds were conducted at pH 6.0.

The rates of the disappearance of benzidine$^{\bullet+}$ in the presence of the reducing agents individually investigated were found to obey overall second-order kinetics, but first-order each on [benzidine$^{\bullet+}$] and [reducing agent]. The linearity of the plots of $\log A_t$ vs. time and the absence of any appreciable change in the pseudo-first-order decay rate constant, (k'_r/s^{-1}) for various initial concentrations of benzidine$^{\bullet+}$ confirm the first-order dependence of the rate on [benzidine$^{\bullet+}$]. The k'_r(s^{-1}) values were found to increase along with increasing concentrations of the reducing agents (Fig. 5); also, the plots of k'_r(s^{-1}) versus [reductant] are linear, passing through the origin, thus indicating the first-order dependence of the rate on the [reducing agent]. The overall second-order rate constants ($k_{2\text{r}}$/M^{-1} s^{-1}), evaluated from the slopes of the above-mentioned plots are given in Table 2. The general rate law for reducing the radical cation may be given as

$$\begin{aligned}\text{Rate} &= -\text{d}[\text{Benzidine}^{\bullet+}]/\text{d}t = k'_\text{r}[\text{reducing agent}] \\ &= k_{2\text{r}}[\text{Benzidine}^{\bullet+}]\,[\text{reducing agent}].\end{aligned} \tag{24}$$

With the exception of $\text{HSO}_3{}^-$, the reducing sulfur compounds and benzidine$^{\bullet+}$ exist as such without protonation at pH 6.0. The pK_a value for $\text{HSO}_3{}^-$ is 7.2,[36] and, hence, at pH 6.0 the sulfite ions exist as a mixture of $\text{HSO}_3{}^-$ (approximately 94%) and $\text{SO}_3{}^{2-}$ (6%). Thus, the measured rate constants may be a combination of those due to

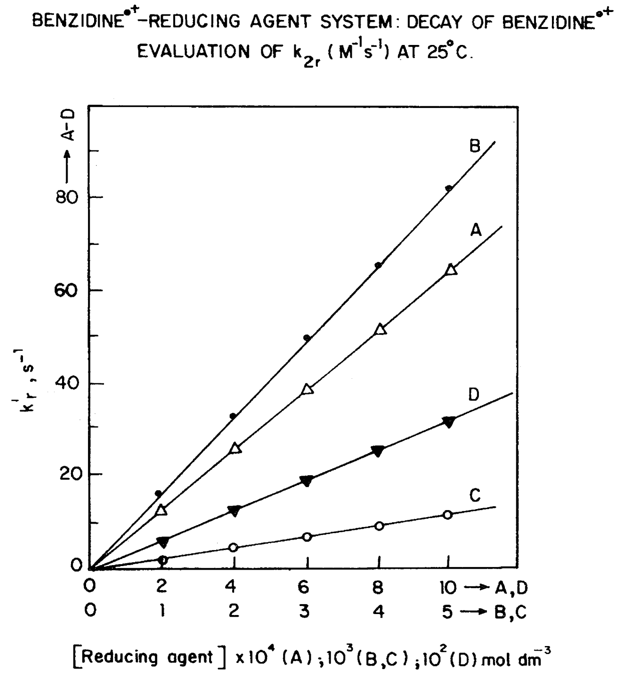


Fig. 5. First-order dependence of the rate on [Reducing agent] for the reduction of benzidine$^{\bullet +}$ to benzidine at 25 °C. A: $S_2O_3{}^{2-}$, B: $S_2O_5{}^{2-}$, C: $HSO_3{}^{-}$, D: $S_2O_4{}^{2-}$.

Table 2. Kinetic Data for the Reduction of Benzidine$^{\bullet +}$ at 25 °C (pH=6.0)

Reductant	k_{2r}/M^{-1} s^{-1}
$S_2O_3{}^{2-}$	6.5×10^4
$S_2O_5{}^{2-}$	1.7×10^4
$HSO_3{}^{-}$	2.5×10^3
$S_2O_4{}^{2-}$	3.2×10^2

the reactions, benzidine$^{\bullet +}$+$SO_3{}^{2-}$ and benzidine$^{\bullet +}$+$HSO_3{}^{-}$. However, separate experiments carried out at pH 4.5 (100% $HSO_3{}^{-}$) exhibited almost the same rate constant as that observed at pH 6.0, thus proving the reaction to be

$$\text{Benzidine}^{\bullet +} + HSO_3{}^{-} \longrightarrow \text{Benzidine} + SO_3{}^{\bullet -} + H^{+}. \qquad (25)$$

In all of the reactions, the radical cation benzidine$^{\bullet +}$ was found to be reduced to the parent compound, benzidine. The following mechanisms are proposed for the electron-transfer reactions of benzidine$^{\bullet +}$ with the reducing agents:

$$\text{Benzidine}^{\bullet +} + HSO_3{}^{-} \longrightarrow \text{Benzidine} + H^{+} + SO_3{}^{\bullet -}, \qquad (26a)$$

$$2SO_3{}^{\bullet -} \longrightarrow S_2O_6{}^{2-}, \qquad (26b)$$

$$\text{Benzidine}^{\bullet +} + S_2O_n{}^{2-} \longrightarrow \text{Benzidine} + S_2O_n{}^{\bullet -}, \qquad (27a)$$

$$2S_2O_n{}^{\bullet -} \longrightarrow S_4O_6{}^{2-} + (n-3)O_2, \qquad (27b)$$

where $n = 3$, 4, and 5.

In all of the above reactions, the radical anions, formed from the reducing agents, are proposed to undergo self-termination. Though these radical anions could behave as oxidizing agents,[37] there is no equilibrium reaction (as indicated below) observed under the present experimental condition ([reductant]≫[benzidine$^{\bullet +}$]):

$$\text{Benzidine}^{\bullet +} + R^{2-} \rightleftharpoons \text{Benzidine} + R^{\bullet -}$$

(where R^{2-} represents a reducing agent). (28)

Such an equilibrium formation between $SO_3{}^{\bullet -}$ and chloropromazine was observed in a pulse radiolytic reaction investigated by Huie and Neta.[38] However, no equilibrium was observed between $SO_3{}^{\bullet -}$ and benzidine$^{\bullet +}$ in the present investigation.

From the calculated second-order rate constants, the following reactivity trend of the reducing agents with benzidine$^{\bullet +}$ may be given as

$$S_2O_3{}^{2-} > S_2O_5{}^{2-} > SO_3{}^{2-} > S_2O_4{}^{2-}. \qquad (29)$$

Although benzidine$^{\bullet +}$ behaves as a mild oxidizing agent, the present investigation demonstrates that this radical cation undergoes fast electron-transfer reactions with the above-mentioned reducing agents, proving the reversibility of the reaction to form the parent compound, benzidine,

$$\text{Benzidine}^{\bullet +} + \text{reducing agent} \longrightarrow \text{Benzidine} + \text{product}. \qquad (30)$$

d) Effect of Temperature (Correlation of Rate and Activation Parameters). The reaction temperature was varied over the range 15—35 °C for both the formation and decay of the radical cation benzidine$^{\bullet +}$ with all of the oxidants. The values of the pre-exponential factor (A) and the transition state parameters ($\Delta H^{\#}$, $\Delta S^{\#}$, and $\Delta G^{\#}$) were calculated, and are presented in Table 3. All of the rate constants are collectively presented in Table 1. From the Tables, it can be seen that the observed second-order rate constants (k_{2f} and k_{2d} (M^{-1} s^{-1})) for both the formation and decay of benzidine$^{\bullet +}$ exhibit the reactivity trend $MnO_4{}^{-} > Cr_2O_7{}^{2-} >$ Ce(IV); peroxomonosulfate > peroxodisulfate > H_2O_2 and $I_2 > Br_2 > Cl_2$. This observation is in accordance with the $\Delta G^{\#}$ values. However, the energy of activation (E_a) for both the formation and decay of the radical cation are almost the same. For each oxidant, the rate constants for the formation of a radical cation are higher than that for the decay, which is usually expected. The high positive $\Delta S^{\#}$ values favor the reactions of $MnO_4{}^{-}$ and I_2 to proceed at a faster rates in the formation of the radical cation. The high negative values of $\Delta S^{\#}$ for the reactions of peroxides may indicate the more polar nature of the activated complex than the reactants. In another words, the reactions of the peroxides involve a high charge development and severe steric requirements in the formation of an activated complex.

Comparison of the Experimental Rate Constants for the Oxidation of Benzidine with Those of a Theoretical Calculation Using the Marcus Theory. The observed rate constants for the electron-transfer reactions in the present investigation were correlated theoretically using the Marcus theory.[39] In many calculations, it has been assumed that λ_i, the inner-sphere reorganization energy, can be neglected when compared with λ_o;[40] also, it has been substantiated[41] that in almost all cases the values of λ_i, are less than 5 % of

Table 3. Calculated Kinetic and Transition State Parameters for the Formation and Decay of Benzidine$^{\bullet+}$ [a)]

Oxidants	$A/\mathrm{M^{-1}\,s^{-1}}$		$E_a/\mathrm{kJ\,mol^{-1}}$		$\Delta H^{\neq}/\mathrm{kJ\,mol^{-1}}$		$\Delta S^{\neq}/\mathrm{J\,K^{-1}\,mol^{-1}}$		At 298 K $\Delta G^{\neq}/\mathrm{kJ\,mol^{-1}}$	
	k_{2f}	k_{2d}	k_{2f}	k_{2d}	k_{2f}	k_{2d}	k_{2f}	k_{2d}	k_{2f}	k_{2d}
Metal ion										
Ce(IV)	1.5×10^{12}	3.2×10^{11}	49.1	49.6	46.6	47.7	−19.9	−32.7	52.6	57.5
Oxo anions										
MnO_4^-	3.0×10^{14}	9.8×10^{12}	49.9	49.5	47.5	47.1	24.3	−4.3	40.2	48.3
$Cr_2O_7^{2-}$	1.0×10^{13}	2.2×10^{12}	49.5	49.5	47.0	47.1	−3.9	−16.9	48.2	52.1
Peroxides										
HSO_5^-	3.0×10^{12}	2.2×10^{9}	49.4	49.6	47.0	47.2	−14.2	−74.1	51.2	69.3
$S_2O_8^{2-}$	2.7×10^{11}	1.4×10^{9}	49.6	49.8	47.3	47.4	−33.8	−78.0	57.4	70.6
H_2O_2	3.2×10^{9}	4.2×10^{8}	49.1	50.7	46.7	48.3	−71.2	−88.0	67.9	74.5
Halogens										
Cl_2	2.2×10^{12}	2.2×10^{11}	49.4	49.7	47.0	47.3	−16.6	−35.9	51.9	57.9
Br_2	3.2×10^{12}	—	48.3	—	45.9	—	−13.5	—	49.9	—
I_2	7.8×10^{13}	—	48.8	—	46.3	—	12.9	—	42.5	—

a) The reactions of Ce(IV) and $Cr_2O_7^{2-}$ are in 0.2 M H_2SO_4. All other reactions are carried out at pH 3.0 adjusted with potassium hydrogen phthalate buffer.

λ_o. The classical theory of Marcus[42,43)] requires an estimate of the solvent reorganization energy (λ), which is considered to be equal to λ_o, (assuming λ_i is very small when compared to λ_o) the outer sphere solvent reorganization energy from the expression

$$\lambda_o = \frac{e^2}{4\pi\varepsilon_o}\left(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{r_{12}}\right)\left(\frac{1}{D_o}-\frac{1}{D_s}\right), \tag{31}$$

where 'e' represents the electronic charge, ε_o, the permittivity of free space, D_o the optical relative permittivity (equal to the square of the refractive index), and D_s the static relative permittivity of the solvent (78.4 for water); r_1 and r_2 are the radii of the two colliding molecules, and $r_{12}=r_1+r_2$.

Since the Marcus theory assumes that both molecules are spherical, an approximate estimation of the radii was obtained from the software PC Model.[44)]

From the λ values (Table 4) the activation energy was calculated using the equation

$$\Delta G^{\#} = \frac{(\lambda+\Delta G^{\circ})^2}{4\lambda}. \tag{32}$$

The values of ΔG° were calculated using the reported potentials ($\Delta G^{\circ} = -\mathrm{n}FE^{\circ}$). Using $\Delta G^{\#}$ obtained from Eq. 32, the theoretical rate constants were estimated using the relation

$$k_{\mathrm{cal}} = Z\exp(-\Delta G^{\#}/k_{\mathrm{B}}T). \tag{33}$$

Here, Z is the collision number (10^{11})[42,43,45)] and k_{B} is the Boltzmann constant.

The observed rate constants for the formation of radical cations from benzidine with nine different oxidants were correlated theoretically (Table 4) using the above-derived expressions of the Marcus theory. The thus-calculated values theoretically coincides well with the experimentally observed rate constants for all of the oxidants, except for I_2. In the case of I_2, the observed high rate constants may be due to the formation of a charge-transfer complex between benzidine and I_2, and not due to a complete electron-transfer reaction.[33,34)]

Table 4. The Observed and Calculated Rate Constants for Electron Transfer Reactions between Benzidine and Oxidants for the Formation of Benzidine$^{\bullet+}$ at 25 °C[a)]

Oxidant	k_{2f} / $\mathrm{M^{-1}\,s^{-1}}$	$k_{2f(cal)}$ / $\mathrm{M^{-1}\,s^{-1}}$	λ / $\mathrm{kJ\,mol^{-1}}$
Metal ion			
Ce(IV)	3.9×10^{3}	1.4×10^{3}	247.3
Oxo anions			
MnO_4^-	5.5×10^{5}	4.5×10^{5}	228.3
$Cr_2O_7^{2-}$	2.3×10^{4}	1.5×10^{4}	223.2
Peroxides			
HSO_5^-	6.7×10^{3}	4.4×10^{3}	299.5
$S_2O_8^{2-}$	5.5×10^{2}	1.7×10^{2}	360.3
H_2O_2	7.8	1.9	369.0
Halogens			
Cl_2	5.0×10^{3}	4.7×10^{3}	219.8
Br_2	1.1×10^{4}	1.1×10^{4}	159.2
I_2	2.2×10^{5}	2.1×10^{1}	93.9

a) The reactions of Ce(IV) and $Cr_2O_7^{2-}$ are in 0.2 M H_2SO_4. All other reactions are carried out at pH 3.0 adjusted with potassium hydrogen phthalate buffer.

Further, to test the present experimental results with a Marcus plot, the following equation was used:

$$k_{(\mathrm{obs})} \text{ or } k_{(\mathrm{cal})} = \frac{k_{\mathrm{d}}}{1+A\exp(\{W+\Delta G^{\#}(0)\,[1+\Delta G^{\circ}/4\Delta G^{\#}(0)]^2\}/RT)}, \tag{34}$$

where the values of A and W (work function) are assumed to be 1 and 0, respectively, and k_{d}, the diffusion-controlled limit[46)] for water (1.1×10^{10}). $\Delta G^{\#}(0)$ was calculated to be

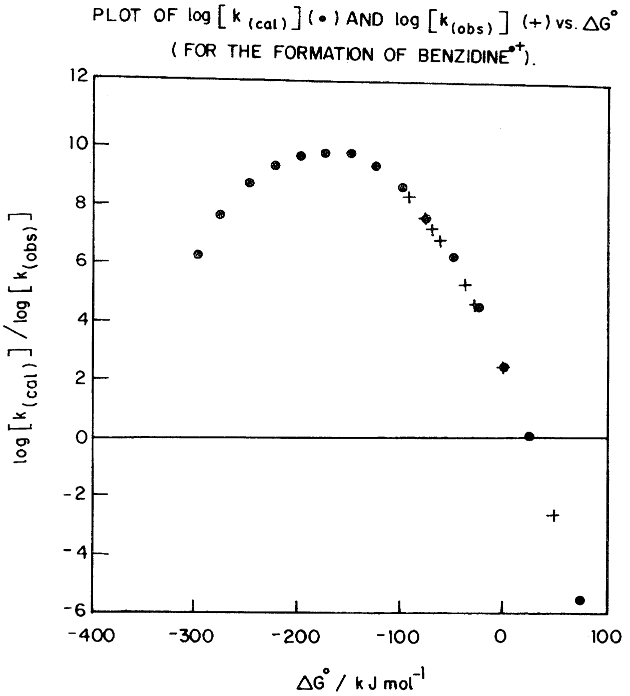


Fig. 6. Plot of log $k_{(\mathrm{cal})}$ (•) and log $k_{(\mathrm{obs})}$ (+) vs. $\Delta G°$.

44 kJ mol^{-1} for benzidine. The values of $k_{(\mathrm{obs})}$ vs. $\Delta G°$ and $k_{(\mathrm{cal})}$ vs. $\Delta G°$ are plotted in Fig. 6; $k_{(\mathrm{obs})}$ is the rate constants obtained from experiments concerning the reaction of benzidine with the oxidants, and $\Delta G°$ is the standard Gibbs-energy change for the respective redox pair; $k_{(\mathrm{cal})}$ is the value calculated for $\Delta G°$, ranging from -300 to $+75$ kJ mol^{-1}. An inflexion is seen for $k_{(\mathrm{cal})}$ at a more negative $\Delta G°$ for all of the plots. As far as the trend is concerned, from the plot, the experimentally obtained rate constants are in excellent agreement with the calculated values.

Conclusions

1) The following trends were observed concerning the reactivity of the oxidants:

a) In the formation of benzidine$^{\bullet+}$,

$MnO_4^- > I_2 > Cr_2O_7^{2-} > Br_2 > PMS > Cl_2 > Ce(IV) > PDS > H_2O_2$.

b) In the decay of benzidine$^{\bullet+}$,

$MnO_4^- > Cr_2O_7^{2-} > Ce(IV) > Cl_2 > PMS > PDS > H_2O_2$.

2) The effect of the pH on the reaction of benzidine and potassium peroxomonosulfate reveals that benzidineH$^+$ and benzidineH$^{2+\bullet}$ are more difficult to oxidize than the corresponding deprotonated species.

3) The reduction of benzidine$^{\bullet+}$ by the reducing agents used generated back the parent compound, benzidine, thus proving the reversibility of the reaction.

$$\text{benzidine}^{\bullet+} \xrightarrow{+e^-} \text{benzidine},$$

as long as benzidine$^{\bullet+}$ is not oxidised further (similar to MV$^{\bullet+}$). This supports the fact that benzidine may be used as a potential electron sacrificial agent.

4) The experimentally determined second-order rate constants for the formation of a radical cation were found to be in good agreement with those calculated on the basis of the Marcus theory.

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