# Kinetics and Mechanism of the Oxidation of Substituted Benzaldehydes by Bis(2,2'-bipyridylyl)copper(II) Permanganate

Kavita Mohnot, Pradeep K. Sharma, and Kalyan K. Banerji\*

Department of Chemistry, J. N. V. University, Jodhpur 342 005, India

Received July 21, 1995<sup>®</sup>

The oxidation of 35 monosubstituted benzaldehydes by bis(2,2'-bipyridylyl)copper(II) permanganate (BBCP) in aqueous acetic acid leads to the formation of the corresponding benzoic acids. The reaction is first order with respect to BBCP. Michaelis–Menten-type kinetics were observed with respect to the aldehyde concentrations. The oxidation of [<sup>2</sup>H]benzaldehyde (PhCDO) indicated the presence of a substantial kinetic isotope effect. The rates of oxidation of meta- and para-substituted benzaldehydes were correlated in terms of Charton's triparametric LDR equation, whereas the oxidation of ortho-substituted benzaldehydes was correlated with the four parametric LDRS equation. The oxidation of para-substituted benzaldehydes is more susceptible to the delocalization effect than is the oxidation of ortho- and meta-substituted compounds which displays a greater dependence on the field effect. The positive value of  $\eta$  suggests the presence of an electron-deficient reaction center in the rate-determining activated complex. The reaction is subjected to steric acceleration when ortho-substituents are present.

Bis(2,2'-bipyridylyl)copper(II) permanganate (BBCP) is a mild and selective oxidant and has been used in the oxidation of a number of organic compounds.<sup>1,2</sup> We have been interested in the mechanistic aspects of oxidation reactions promoted by BBCP. In continuation of our earlier work related to oxidations by BBCP,<sup>3-6</sup> we report here the kinetics of oxidation of 35 monosubstituted benzaldehydes by BBCP in aqueous acetic acid. The oxidation of aldehydes by permanganate has received considerable attention. The oxidation of substituted benzaldehydes by permanganate in alkaline medium exhibited a reaction constant of 1.83.7 In acidic or neutral solutions, however, the effect of structure is small, and formation of a permanganate ester intermediate has been postulated.<sup>7</sup> The oxidation of aliphatic aldehydes by acid permanganate is reported to proceed via the hydrate form of the aldehyde.<sup>8</sup> The major objective of this investigation was to study the structure-reactivity correlation for the substrate undergoing oxidation.

#### Results

Oxidation of the aromatic aldehydes by BBCP results in the formation of the corresponding benzoic acids. Analyses of products and stoichiometric determinations indicate that the overall reaction may be expressed as (1). BBCP is reduced to Mn(IV). To confirm that Mn-

 $3ArCHO + 2Mn(VII) + 3H_2O \rightarrow$ 

$$3\text{ArCOOH} + 2\text{Mn(IV)} + 6\text{H}^+$$
 (1)

(IV) is indeed formed as a result of the oxidation of

| Гable | <b>1.</b> ] | Rate | Const | ants | s for 1 | the  | Oxic | lation | of |
|-------|-------------|------|-------|------|---------|------|------|--------|----|
|       | Ben         | zald | ehyde | by : | BBCI    | P at | 293  | K      |    |

|                                                   | • •                                |                                              |                                                           |
|---------------------------------------------------|------------------------------------|----------------------------------------------|-----------------------------------------------------------|
| 10 <sup>4</sup> [BBCP]<br>(mol dm <sup>-3</sup> ) | [PhCHO]<br>(mol dm <sup>-3</sup> ) | [H <sup>+</sup> ]<br>(mol dm <sup>-3</sup> ) | $\begin{array}{c} 10^4 \ k_{obs} \\ (s^{-1}) \end{array}$ |
| 2.0                                               | 0.1                                | 1.0                                          | 1.33                                                      |
| 2.0                                               | 0.3                                | 1.0                                          | 2.45                                                      |
| 2.0                                               | 0.5                                | 1.0                                          | 2.90                                                      |
| 2.0                                               | 0.8                                | 1.0                                          | 3.21                                                      |
| 2.0                                               | 1.2                                | 1.0                                          | 3.52                                                      |
| 2.0                                               | 1.5                                | 1.0                                          | 3.60                                                      |
| 2.0                                               | 3.0                                | 1.0                                          | 3.85                                                      |
| 2.0                                               | 0.8                                | 1.0                                          | 3.31 <sup>a</sup>                                         |
| 3.0                                               | 0.8                                | 1.0                                          | 3.11                                                      |
| 5.0                                               | 0.8                                | 1.0                                          | 3.27                                                      |
| 8.0                                               | 0.8                                | 1.0                                          | 3.31                                                      |
| 10.0                                              | 0.8                                | 1.0                                          | 3.16                                                      |
|                                                   |                                    |                                              |                                                           |

<sup>a</sup> Contained 0.005 mol dm<sup>-3</sup> of acrylonitrile.

aldehydes by BBCP, rates were determined by monitoring the increase in [Mn(IV)] at 418 nm.<sup>9,10</sup> It could be demonstrated that the rates of decay at 529 nm [Mn-(VII)] and of increase at 418 nm agreed within  $\pm 12\%$ . It was also observed that BBCP has virtually no absorption at 418 nm. This agrees with the observations of earlier workers.<sup>9,10</sup>

The reactions were found to be first order with respect to BBCP. Further, the pseudo-first-order rate constants,  $k_{obs}$ , did not vary with the initial concentration of BBCP. The order with respect to aldehyde is less than 1 (Table 1). A plot of  $1/k_{obs}$  versus 1/[aldehyde] is linear with an intercept at the rate constant ordinate. Thus, Michaelis– Menten-type kinetics are observed with respect to aldehyde concentrations. This leads to the postulation of the following overall mechanism (reactions 2 and 3) and rate law (4).

aldehyde + BBCP 
$$\stackrel{\kappa}{\leftarrow}$$
 [complex] (2)

$$[complex] \xrightarrow{h_2} products \tag{3}$$

rate =  $k_2 K$ [aldehyde][BBCP]/(1 + K[aldehyde]) (4)

The dependence on the concentration of the aldehyde was studied at different temperatures, and the values of

<sup>&</sup>lt;sup>®</sup> Abstract published in *Advance ACS Abstracts*, January 15, 1996. (1) Firouzabadi, H.; Naderi, M.; Sardarian, A.; Vessel, B. *Synth. Commun.* **1983**, *13*, 611.

<sup>(2)</sup> Walker, F. A.; Sigel, H.; McCormick, S. Inorg. Chem. 1972, 11, 2756.

<sup>(3)</sup> Kothari, S. Proc. Indian Acad. Sci. (Chem. Sci.) 1991, 103, 747.
(4) Kothari, S.; Sharma, V.; Sharma, P. K.; Banerji, K. K. Proc. Indian Acad. Sci. (Chem. Sci.) 1992, 104, 583.

<sup>(5)</sup> Satsangi, B. K.; Kothari, S.; Banerji, K. K. J. Chem. Res., Synop. 1994, 208; J. Chem. Res., Miniprint 1134.

<sup>(6)</sup> Satsangi, B. K.; Kothari, Ś.; Banerji, K. K. *Transition Met. Chem.* **1995**, *20*, 288.

<sup>(7)</sup> Wiberg, K. B.; Stewart, R. J. Am. Chem. Soc. 1955, 77, 1786.
(8) Jain, A. L.; Banerji, K. K. J. Chem. Res., Synop. 1983, 60; J. Chem. Res., Miniprint 678.

<sup>(9)</sup> Freeman, F.; Kappos, J. C. J. Am. Chem. Soc. **1985**, 107, 6628. (10) Lee, D. G.; Perez-Benito, J. F. J. Org. Chem. **1988**, 53, 5728.

Table 2. Formation Constants and Thermodynamic Parameters for the Substituted Benzaldehyde-BBCP Complexes

|                            |       | $K/dm^3$ | $mol^{-1}$ |       |                                    |                                                   |                                    |
|----------------------------|-------|----------|------------|-------|------------------------------------|---------------------------------------------------|------------------------------------|
| subst                      | 288 K | 298 K    | 308 K      | 318 K | $\Delta H$ (kJ mol <sup>-1</sup> ) | $\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> ) | $\Delta G$ (kJ mol <sup>-1</sup> ) |
| Н                          | 5.66  | 4.82     | 3.97       | 3.13  | $-17.5\pm0.8$                      | $-38\pm3$                                         | $-6.3\pm0.7$                       |
| <i>p</i> -NMe <sub>2</sub> | 5.87  | 5.02     | 4.27       | 3.40  | $-16.2\pm0.8$                      | $-33\pm3$                                         | $-6.5\pm0.6$                       |
| p-CN                       | 5.98  | 5.15     | 4.32       | 3.53  | $-15.8\pm0.6$                      | $-32\pm2$                                         | $-6.5\pm0.5$                       |
| <i>p</i> -NHCOMe           | 5.42  | 4.65     | 3.88       | 3.04  | $-17.0\pm0.9$                      | $-37\pm3$                                         | $-6.2\pm0.7$                       |
| <i>p</i> -OMe              | 5.85  | 5.02     | 4.26       | 3.56  | $-15.1\pm0.4$                      | $-29\pm1$                                         | $-6.5\pm0.3$                       |
| <i>p</i> -SMe              | 6.15  | 5.32     | 4.42       | 3.60  | $-16.0\pm0.7$                      | $-32\pm3$                                         | $-6.8\pm0.5$                       |
| <i>p</i> -Me               | 6.02  | 5.25     | 4.46       | 3.62  | $-15.3\pm0.8$                      | $-30\pm3$                                         | $-6.6\pm0.6$                       |
| <i>p</i> -F                | 5.32  | 4.58     | 3.78       | 3.10  | $-16.3\pm0.6$                      | $-34\pm2$                                         | $-6.2\pm0.5$                       |
| p-Cl                       | 5.45  | 4.62     | 3.85       | 3.08  | $-16.9\pm0.7$                      | $-36\pm2$                                         | $-6.3\pm0.5$                       |
| <i>p</i> -Br               | 5.83  | 5.05     | 4.28       | 3.45  | $-15.7\pm0.8$                      | $-31\pm3$                                         | $-6.5\pm0.6$                       |
| p-CF <sub>3</sub>          | 5.29  | 4.50     | 3.86       | 3.06  | $-16.1\pm0.8$                      | $-34\pm3$                                         | $-6.2\pm0.6$                       |
| <i>p</i> -COOMe            | 6.12  | 5.34     | 4.55       | 3.62  | $-15.5\pm0.9$                      | $-31\pm3$                                         | $-6.6\pm0.7$                       |
| p-NO <sub>2</sub>          | 6.00  | 5.27     | 4.46       | 3.61  | $-15.3\pm0.8$                      | $-30\pm3$                                         | $-6.6\pm0.7$                       |
| <i>m</i> -NHCOMe           | 5.58  | 4.75     | 4.02       | 3.29  | $-15.8\pm0.5$                      | $-32\pm2$                                         | $-6.3\pm0.5$                       |
| <i>m</i> -OMe              | 6.02  | 5.27     | 4.40       | 3.52  | $-16.0\pm0.9$                      | $-32\pm3$                                         | $-6.5\pm0.7$                       |
| <i>m</i> -SMe              | 5.56  | 4.85     | 4.02       | 3.26  | $-16.1\pm0.8$                      | $-33\pm3$                                         | $-6.3\pm0.6$                       |
| <i>m</i> -Me               | 5.96  | 5.12     | 4.32       | 3.48  | $-16.0\pm0.7$                      | $-33\pm2$                                         | $-6.5\pm0.5$                       |
| <i>m</i> -F                | 5.81  | 5.02     | 4.18       | 3.33  | $-16.5\pm0.8$                      | $-34\pm3$                                         | $-6.4\pm0.7$                       |
| <i>m</i> -Cl               | 5.92  | 5.12     | 4.25       | 3.45  | $-16.2\pm0.7$                      | $-33\pm2$                                         | $-6.5\pm0.6$                       |
| <i>m</i> -Br               | 5.86  | 5.02     | 4.20       | 3.38  | $-16.4\pm0.7$                      | $-34\pm2$                                         | $-6.4\pm0.6$                       |
| m-CF <sub>3</sub>          | 5.55  | 4.72     | 3.95       | 3.15  | $-16.7\pm0.7$                      | $-36\pm2$                                         | $-6.3\pm0.6$                       |
| <i>m</i> -CN               | 6.10  | 5.26     | 4.38       | 3.51  | $-16.5\pm0.8$                      | $-34\pm3$                                         | $-6.6\pm0.6$                       |
| m-NO <sub>2</sub>          | 6.28  | 5.46     | 4.58       | 3.67  | $-16.0\pm0.8$                      | $-32\pm3$                                         | $-6.6\pm0.6$                       |
| <i>o</i> -Me               | 5.89  | 5.10     | 4.32       | 3.42  | $-16.1\pm0.9$                      | $-33\pm3$                                         | $-6.5\pm0.7$                       |
| <i>o</i> -F                | 5.68  | 4.86     | 4.05       | 3.20  | $-16.9\pm0.8$                      | $-36\pm3$                                         | $-6.4\pm0.7$                       |
| o-Cl                       | 5.75  | 5.00     | 4.25       | 3.46  | $-15.3\pm0.7$                      | $-30\pm2$                                         | $-6.4\pm0.6$                       |
| <i>o</i> -Br               | 5.82  | 5.05     | 4.23       | 3.40  | $-16.1\pm0.8$                      | $-33\pm3$                                         | $-6.4\pm0.6$                       |
| <i>o</i> -I                | 5.73  | 4.97     | 4.02       | 3.18  | $-17.2\pm0.7$                      | $-37\pm2$                                         | $-6.4\pm0.5$                       |
| o-NO <sub>2</sub>          | 6.05  | 5.24     | 4.42       | 3.52  | $-16.1\pm0.9$                      | $-33\pm3$                                         | $-6.5\pm0.7$                       |
| o-NHCOMe                   | 6.03  | 5.28     | 4.46       | 3.48  | $-16.2\pm1.0$                      | $-33\pm4$                                         | $-6.5\pm0.9$                       |
| o-CF <sub>3</sub>          | 5.76  | 4.82     | 4.05       | 3.26  | $-16.7\pm0.5$                      | $-35\pm2$                                         | $-6.4\pm0.4$                       |
| o-SMe                      | 5.88  | 5.12     | 4.32       | 3.49  | $-15.6\pm0.8$                      | $-31\pm3$                                         | $-6.5\pm0.6$                       |
| o-CN                       | 6.15  | 5.25     | 4.36       | 3.44  | $-17.1\pm0.8$                      | $-36\pm3$                                         | $-6.5\pm0.7$                       |
| o-COOMe                    | 5.93  | 5.16     | 4.38       | 3.47  | $-15.9\pm0.9$                      | $-32\pm3$                                         | $-6.5\pm0.8$                       |
| PhCDO                      | 6.13  | 5.28     | 4.43       | 3.64  | $-15.7\pm0.5$                      | $-31\pm2$                                         | $-6.6\pm0.4$                       |

*K* and  $k_2$  were calculated from the double reciprocal plots. The thermodynamic parameters for the complex formation and the activation parameters for the decomposition of the complexes were calculated from the values of *K* and  $k_2$ , respectively, at different temperatures (Tables 2 and 3). The oxidation of benzaldehyde, in an atmosphere of nitrogen, failed to induce polymerization of acrylonitrile. Further, the addition of acrylonitrile had no effect on the reaction rate (Table 1).

**Kinetic Isotope Effect.** To ascertain the importance of the cleavage of the aldehydic C–H bond in the ratedetermining step, the oxidation of [<sup>2</sup>H]benzaldehyde (PhCDO) was studied. It was observed that the value of the formation constant for the complex, *K*, is slightly but consistently higher in the oxidation of PhCDO than that of PhCHO. We do not have an explanation for this observation at the present time. The rates of decomposition of the complex,  $k_2$ , however, exhibited a substantial kinetic isotope effect ( $k_{\rm H}/k_{\rm D} = 4.35$  at 298 K).

**Effect of 2,2'-Bipyridine Concentration.** The rates of oxidation were not affected by the addition of 2,2'-bipyridine (Table 4).

**Effect of Acidity.** The reaction rate increases with an increase in the concentration of hydrogen ions (Table 5). A plot of rate versus  $[H^+]$  is concave to the rate axis and makes an intercept on the rate axis. The dependence of the reaction rate on the concentration of benzaldehyde was studied at  $[H^+] = 0.02$ , 0.45, and 1.5 mol dm<sup>-3</sup>. It was observed that the formation constant, *K*, does not vary appreciably with the hydrogen ion concentration, while the rate constant for the decomposition of the complex,  $k_2$ , is affected by the changes in the hydrogen ion concentration.

**Effect of Solvent Composition.** The rate of oxidation was determined in solvents containing different amounts of acetic acid and water. It was observed that the rate increased with an increase in the amount of acetic acid in the solvent.

To ascertain whether the change in the solvent composition is affecting the formation constant for the complex and/or the rate of its decomposition, the dependence of the reaction rate on the concentration of benzaldehyde was studied in solvents of different compositions. The results recorded in Table 6 show that the rate constant of the decomposition of the complex increases with an increase in the amount of acetic acid in the solvent. The formation constant, *K*, remains practically constant.

### Discussion

Not much is known about the structure of BBCP. In particular, the nature of the bonding of the permanganate anions with the [bpy<sub>2</sub>Cu(II)] cation is not certain. However, in the corresponding halide complexes, it has been shown that one halide ion is joined to the central atom by a covalent bond and another by an electrovalent bond.<sup>11</sup> On the basis of that analogy, BBCP may also be represented as [bpy<sub>2</sub>Cu(MnO<sub>4</sub>)]MnO<sub>4</sub>, although we do not have any direct evidence to support our contention that permanganate acts as a ligand to copper(II).

A plot of log  $k_2$  at 288 K is linearly related to log  $k_2$  at 318 K (r = 0.9989, slope = 0.880  $\pm$  0.007). The value of

<sup>(11)</sup> Baclay, G. A.; Hoskins, B. F.; Kennard, C. H. L. J. Chem. Soc. 1963, 5691.

| Table 3. | Rate Constants for the Decomposition of the Benzaldehyde-BBCP Complexes and the Corresponding |
|----------|-----------------------------------------------------------------------------------------------|
|          | Activation Parameters                                                                         |

|                            |       | $10^4 k_2 (\mathrm{dm}^3)$ | <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> ) |       |                                               |                                                              |                                               |
|----------------------------|-------|----------------------------|--------------------------------------------------|-------|-----------------------------------------------|--------------------------------------------------------------|-----------------------------------------------|
| subst                      | 288 K | 298 K                      | 308 K                                            | 318 K | $\Delta H^{\ddagger}$ (kJ mol <sup>-1</sup> ) | $\Delta S^{\ddagger}$ (J mol <sup>-1</sup> K <sup>-1</sup> ) | $\Delta G^{\ddagger}$ (kJ mol <sup>-1</sup> ) |
| Н                          | 1.63  | 4.10                       | 10.3                                             | 25.2  | $66.9\pm0.7$                                  | $-87\pm2$                                                    | $92.3\pm0.6$                                  |
| <i>p</i> -Me               | 2.95  | 7.31                       | 18.2                                             | 43.1  | $65.6\pm0.6$                                  | $-85\pm2$                                                    | $90.8\pm0.5$                                  |
| p-OM <sup>e</sup>          | 5.10  | 12.9                       | 31.3                                             | 71.0  | $64.8 \pm 0.2$                                | $-83\pm1$                                                    | $89.5\pm0.1$                                  |
| <i>p</i> -NHCOMe           | 2.75  | 6.75                       | 17.0                                             | 40.0  | $65.6\pm0.7$                                  | $-86\pm2$                                                    | $91.0\pm0.6$                                  |
| p-CN                       | 0.15  | 0.46                       | 1.26                                             | 3.50  | $77.1\pm0.5$                                  | $-70\pm2$                                                    | $97.8\pm0.4$                                  |
| <i>p</i> -SMe              | 3.10  | 3.50                       | 19.2                                             | 45.0  | $65.7\pm0.9$                                  | $-84\pm3$                                                    | $90.7\pm0.7$                                  |
| <i>p</i> -Br               | 1.00  | 2.54                       | 6.66                                             | 16.5  | $68.8 \pm 0.8$                                | $-83\pm3$                                                    | $93.4\pm0.7$                                  |
| <i>p</i> -F                | 1.60  | 3.92                       | 10.5                                             | 25.2  | $67.9 \pm 1.0$                                | $-82\pm4$                                                    | $92.3\pm0.9$                                  |
| p-Cl                       | 1.02  | 2.67                       | 6.73                                             | 16.3  | $67.8\pm0.4$                                  | $-86\pm1$                                                    | $93.4\pm0.3$                                  |
| p-CF <sub>3</sub>          | 0.25  | 0.78                       | 2.10                                             | 5.15  | $74.2\pm0.9$                                  | $-76\pm3$                                                    | $96.5\pm0.7$                                  |
| <i>p</i> -COOMe            | 0.38  | 0.94                       | 2.40                                             | 6.37  | $68.9 \pm 1.5$                                | $-91\pm5$                                                    | $95.8 \pm 1.0$                                |
| p-NO <sub>2</sub>          | 0.12  | 0.27                       | 0.85                                             | 2.21  | $72.6\pm3.0$                                  | $-88\pm9$                                                    | $98.7\pm2.0$                                  |
| <i>p</i> -NMe <sub>2</sub> | 15.0  | 36.4                       | 86.4                                             | 188   | $61.8\pm0.7$                                  | $-85\pm1$                                                    | $86.1 \pm 6.0$                                |
| <i>m</i> -SMe              | 1.48  | 3.80                       | 9.25                                             | 21.8  | $65.9\pm0.5$                                  | $-90\pm2$                                                    | $92.5\pm0.4$                                  |
| <i>m</i> -NHCOMe           | 1.5   | 3.66                       | 8.84                                             | 21.6  | $65.2 \pm 1.0$                                | $-92\pm4$                                                    | $92.6\pm0.9$                                  |
| <i>m</i> -OMe              | 2.15  | 5.38                       | 12.5                                             | 30.2  | $64.2\pm0.7$                                  | $-93\pm2$                                                    | $91.6\pm0.6$                                  |
| <i>m</i> -Me               | 2.42  | 6.10                       | 15.0                                             | 35.3  | $65.5\pm0.4$                                  | $-87\pm1$                                                    | $91.3\pm0.3$                                  |
| <i>m</i> -F                | 0.72  | 1.75                       | 4.52                                             | 10.7  | $66.2\pm0.8$                                  | $-95\pm2$                                                    | $94.3\pm0.6$                                  |
| <i>m</i> -Br               | 0.50  | 1.40                       | 3.44                                             | 9.02  | $70.4 \pm 0.8$                                | $-83\pm3$                                                    | $95.0\pm0.6$                                  |
| <i>m</i> -Cl               | 0.55  | 1.45                       | 3.82                                             | 9.50  | $69.6\pm0.3$                                  | $-85\pm1$                                                    | $94.8\pm0.3$                                  |
| m-CF <sub>3</sub>          | 0.26  | 0.71                       | 1.86                                             | 4.98  | $71.8\pm0.9$                                  | $-90\pm2$                                                    | $96.6\pm0.7$                                  |
| <i>m</i> -CN               | 0.14  | 0.40                       | 1.12                                             | 3.00  | $75.1\pm0.4$                                  | $-77 \pm 1$                                                  | $98.0\pm0.3$                                  |
| $m-NO_2$                   | 0.09  | 0.23                       | 0.72                                             | 1.88  | $75.8\pm2.0$                                  | $-79\pm8$                                                    | $99.3\pm2.0$                                  |
| <i>o</i> -Me               | 9.71  | 21.9                       | 51.9                                             | 116   | $60.6\pm0.9$                                  | $-93\pm3$                                                    | $88.1\pm0.7$                                  |
| <i>o</i> -F                | 1.92  | 4.52                       | 11.8                                             | 28.5  | $66.3 \pm 1.0$                                | $-86\pm4$                                                    | $91.9 \pm 1.0$                                |
| o-Cl                       | 2.72  | 6.35                       | 16.7                                             | 38.2  | $65.1 \pm 1.0$                                | $-88\pm4$                                                    | $91.1\pm0.9$                                  |
| <i>o</i> -Br               | 3.45  | 8.06                       | 19.9                                             | 44.8  | $62.9\pm0.8$                                  | $-93\pm3$                                                    | $90.6\pm0.7$                                  |
| <i>o</i> -I                | 5.01  | 11.6                       | 28.3                                             | 63.6  | $62.3\pm0.8$                                  | $-92\pm3$                                                    | $89.7\pm0.7$                                  |
| o-NO <sub>2</sub>          | 0.21  | 0.53                       | 1.51                                             | 4.28  | $74.2\pm2.0$                                  | $-78\pm7$                                                    | $97.2\pm2.0$                                  |
| o-NHCOMe                   | 0.8   | 25.1                       | 58.7                                             | 128   | $60.4\pm0.5$                                  | $-92\pm2$                                                    | $87.8 \pm 0.4$                                |
| o-CF <sub>3</sub>          | 2.22  | 5.65                       | 13.4                                             | 31.2  | $64.4\pm0.3$                                  | $-92\pm1$                                                    | $91.5\pm0.2$                                  |
| o-SMe                      | 9.91  | 22.7                       | 53.9                                             | 120   | $60.9\pm0.7$                                  | $-91\pm2$                                                    | $88.0\pm0.6$                                  |
| <i>o</i> -OMe              | 7.83  | 18.2                       | 44.9                                             | 100   | $62.5\pm0.8$                                  | $-88\pm3$                                                    | $88.5\pm0.7$                                  |
| o-COOMe                    | 1.05  | 2.76                       | 7.01                                             | 16.9  | $68.0\pm0.3$                                  | $-85\pm1$                                                    | $93.3\pm0.3$                                  |
| o-CN                       | 0.39  | 1.01                       | 2.58                                             | 6.38  | $68.4\pm0.6$                                  | $-92\pm2$                                                    | $95.8\pm0.5$                                  |
| PhCDO                      | 0.38  | 0.94                       | 2.35                                             | 5.80  | $66.7\pm0.9$                                  | $-99\pm3$                                                    | $95.9\pm0.7$                                  |
| $k_{\rm H}/k_{\rm D}$      | 4.29  | 4.36                       | 4.38                                             | 4.34  |                                               |                                                              |                                               |

Table 4.Effect of 2,2'-Bipyridine on the Oxidation of<br/>Benzaldehyde by BBCP<sup>a</sup>

| [bpy] (mol dm <sup>-3</sup> )                     | 0.00 | 0.01 | 0.02 | 0.03 | 0.05 | 0.10 |  |
|---------------------------------------------------|------|------|------|------|------|------|--|
| $k_{\rm obs}$ (10 <sup>-4</sup> s <sup>-1</sup> ) | 2.90 | 3.02 | 2.97 | 2.81 | 3.15 | 2.88 |  |
|                                                   |      |      |      |      |      |      |  |

 $^a\,[{\rm BBCP}]=0.0002\ {\rm mol}\ {\rm dm}^{-3},\ [{\rm PhCHO}]=0.50\ {\rm mol}\ {\rm dm}^{-3},\ [{\rm H}^+]=1.0\ {\rm mol}\ {\rm dm}^{-3},\ T=298\ {\rm K}.$ 

Table 5. Dependence of the Rate of Oxidation of<br/>Benzaldehyde by BBCP on the Hydrogen Ion<br/>Concentration<sup>a</sup>

| $[{ m H^+}] \ ({ m mol} \ { m dm^{-3}}) \ 10^4 k_{ m obs} \ ({ m s^{-1}})$ | 0.10 | 0.20 | 0.30 | 0.50 | 0.75 | 1.00 |
|----------------------------------------------------------------------------|------|------|------|------|------|------|
|                                                                            | 0.54 | 0.86 | 1.10 | 1.60 | 2.21 | 2.90 |
| [H <sup>+</sup> ] (mol dm <sup>-3</sup> )                                  | 1.50 | 1.80 | 2.50 | 3.75 | 5.00 |      |
| $10^4 k_{\rm obs} \ ({\rm s}^{-1})$                                        | 5.37 | 7.80 | 14.8 | 34.5 | 60.0 |      |

 $^a$  [BBCP] = 0.0002 mol dm^-3, [aldehyde] = 0.50 mol dm^-3,  $T\!=\!298$  K.

the isokinetic temperature is 1410  $\pm$  32 K. A linear isokinetic relationship is a necessary condition for the validity of linear free energy relationships.^{12} It also implies that all the aldehydes for which the rates of oxidation are so correlated are oxidized by the same mechanism.^{12}

An analysis of the hydrogen ion dependence of the reaction rate showed that at  $[H^+] \leq 1.0 \text{ mol } \text{dm}^{-3}$  the dependence has the form  $k_{\text{obs}} = a + b[\text{H}^+]$  ( $a = (3.14 \pm 0.22) \times 10^{-4} \text{ s}^{-1}$ ,  $b = (2.57 \pm 0.04) \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , r = 0.9996). At  $[\text{H}^+] > 1.0 \text{ mol } \text{dm}^{-3}$ , the dependence has the form  $k_{\text{obs}} = c[\text{H}^+]^2$  ( $c = (2.41 \pm 0.02) \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ , r = 0.9998). This is reminiscent of the effect

| Table 6.  | Dependence of <i>k</i> <sub>obs</sub> for Benzalde | hyde    |
|-----------|----------------------------------------------------|---------|
| Oxidation | by BBCP on Substrate Concentra                     | tion in |
| Sol       | vents of Different Compositions <sup>a</sup>       |         |

| 10 <sup>2</sup> [PhCHO]        | $10^4 k_{obs} (s^{-1})$ [at % AcOH (v/v)] |      |      |      |      |      |  |  |
|--------------------------------|-------------------------------------------|------|------|------|------|------|--|--|
| (mol dm <sup>-3</sup> )        | 20                                        | 40   | 50   | 60   | 70   | 80   |  |  |
| 0.1                            | 0.46                                      | 0.82 | 1.33 | 2.29 | 8.9  | 35.0 |  |  |
| 0.3                            | 0.92                                      | 1.51 | 2.45 | 4.21 | 16.1 | 63   |  |  |
| 0.5                            | 1.00                                      | 1.72 | 2.90 | 5.12 | 19.2 | 76   |  |  |
| 0.8                            | 1.14                                      | 1.99 | 3.21 | 5.68 | 21.3 | 85   |  |  |
| 1.2                            | 1.22                                      | 2.16 | 3.52 | 6.04 | 22.9 | 91   |  |  |
| 1.5                            | 1.26                                      | 2.24 | 3.60 | 6.21 | 23.4 | 93   |  |  |
| 3.0                            | 1.35                                      | 2.36 | 3.85 | 6.61 | 25.5 | 101  |  |  |
| $K (\mathrm{dm^3 \ mol^{-1}})$ | 5.07                                      | 4.78 | 4.82 | 4.93 | 5.00 | 4.69 |  |  |
| $k_2 (10^{-4} \text{ s}^{-1})$ | 1.42                                      | 2.51 | 4.10 | 7.03 | 26.7 | 107  |  |  |

<sup>*a*</sup> [BBCP] = 0.0002 mol dm<sup>-3</sup>, [H<sup>+</sup>] = 1.0 mol dm<sup>-3</sup>, T = 298 K.

observed in the oxidation of aliphatic alcohols and methionine.<sup>5,6</sup> Therefore, it can be suggested that the oxidation of benzaldehyde by BBCP follows an acidindependent path and two acid-dependent paths involving singly protonated and doubly protonated forms of reactant as reactive species at moderate and higher concentrations of hydrogen ion, respectively.

The Hammett acidity function,  $H_0$ , for low concentrations of perchloric acid in a series of acetic acid–water mixtures has been determined.<sup>13</sup> The acidity increases as the water concentration decreases. Since the reaction under investigation is an acid-catalyzed one, an increase in the proportion of acetic acid in the solvent results in an increase in the rate of oxidation.

 Table 7. Temperature Dependence for the Reaction Constants for the Oxidation of Substituted Benzaldehydes by

 BBCP

| <i>T</i> (K)     | L                 | D              | R              | S             | η    | $R^2$  | sd   |      | $P_{\mathrm{D}}$ | Ps   |
|------------------|-------------------|----------------|----------------|---------------|------|--------|------|------|------------------|------|
| Para-Substituted |                   |                |                |               |      |        |      |      |                  |      |
| 288              | $-1.40\pm0.05$    | $-1.61\pm0.04$ | $-0.67\pm0.16$ |               | 0.42 | 0.9975 | 0.04 | 0.04 | 53.5             |      |
| 298              | $-1.39\pm0.02$    | $-1.57\pm0.01$ | $-0.57\pm0.05$ |               | 0.36 | 0.9997 | 0.01 | 0.01 | 53.1             |      |
| 308              | $-1.30\pm0.05$    | $-1.52\pm0.04$ | $-0.59\pm0.16$ |               | 0.39 | 0.9998 | 0.01 | 0.01 | 53.9             |      |
| 318              | $-1.25\pm0.01$    | $-1.45\pm0.01$ | $-0.55\pm0.03$ |               | 0.38 | 0.9998 | 0.01 | 0.01 | 53.7             |      |
| Meta-Substituted |                   |                |                |               |      |        |      |      |                  |      |
| 288              | $-1.64\pm0.03$    | $-1.09\pm0.03$ | $-0.32\pm0.13$ |               | 0.29 | 0.9988 | 0.02 | 0.03 | 40.7             |      |
| 298              | $-1.60\pm0.01$    | $-1.05\pm0.01$ | $-0.31\pm0.06$ |               | 0.30 | 0.9998 | 0.01 | 0.01 | 39.6             |      |
| 308              | $-1.51\pm0.02$    | $-0.96\pm0.02$ | $-0.32\pm0.10$ |               | 0.31 | 0.9992 | 0.02 | 0.02 | 38.9             |      |
| 318              | $-1.46\pm0.02$    | $-0.91\pm0.01$ | $-0.28\pm0.01$ |               | 0.31 | 0.9998 | 0.01 | 0.01 | 37.6             |      |
|                  | Ortho-Substituted |                |                |               |      |        |      |      |                  |      |
| 288              | $-1.57\pm0.02$    | $-1.38\pm0.01$ | $-0.48\pm0.08$ | $1.04\pm0.01$ | 0.35 | 0.9997 | 0.01 | 0.02 | 35.3             | 26.1 |
| 298              | $-1.55\pm0.01$    | $-1.31\pm0.01$ | $-0.48\pm0.04$ | $1.02\pm0.01$ | 0.37 | 0.9999 | 0.01 | 0.01 | 35.7             | 26.3 |
| 308              | $-1.46\pm0.01$    | $-1.28\pm0.01$ | $-0.47\pm0.06$ | $0.95\pm0.01$ | 0.37 | 0.9998 | 0.01 | 0.01 | 34.7             | 25.7 |
| 318              | $-1.38\pm0.03$    | $-1.22\pm0.02$ | $-0.53\pm0.13$ | $0.88\pm0.02$ | 0.43 | 0.9989 | 0.02 | 0.01 | 33.8             | 25.3 |

**Correlation Analysis of Reactivity.** A perusal of the data recorded in Tables 2 and 3 reveals that the formation constants, *K*, for the ArCHO–BBCP complexes are not very sensitive to the nature of the substituent in the aldehyde substrate. This may be because of the fact that the formation constant, K, is a composite value of two preequilibria (the first two steps of Scheme 1 and 2) and that the electronic requirements of the two steps are opposite and almost equal. The rate constant for decomposition of the complex,  $k_2$ , however, showed considerable variation as a function of substituent in the substrate. Similar observations have been previously recorded in the oxidation of benzyl alcohols<sup>14</sup> and mandelic acids<sup>15</sup> by ceric ammonium nitrate and of aliphatic primary alcohols by BBCP,5 pyridinium fluorochromate,16 and pyridinium hydrobromide perbromide.<sup>17</sup>

Since the discovery of significant effects of substituents on reactivity, many workers have attempted correlations with the Hammett equation<sup>18</sup> or with dual substituentparameter equations.<sup>19,20</sup> In the 1980's, Charton<sup>21</sup> introduced a triparametric LDR equation for the quantitative description of structural effects on chemical reactivities. This triparametric equation results from the fact that substituent types differ in their mode of electron delocalization. This difference is reflected in a different sensitivity to the electronic demand for the phenomenon being studied. It has the advantage of not requiring a choice of parameters, as the same three substituent constants are reported to cover the entire range of electrical effects of substituents. We have, therefore, begun a study of structural effects on reactivity by means of the LDR equation. In this work, we have applied the LDR equation (eq 5) to the rate constants,  $k_2$ . Here,  $\sigma_1$ 

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + h \tag{5}$$

is a localized (field and/or inductive) effect parameter,  $\sigma_d$  is the intrinsic delocalized (resonance) electrical effect parameter when active site electronic demand is minimal, and  $\sigma_e$  represents the sensitivity of the substituent to changes in electronic demand by the active site. The latter two substituent parameters are related by eq 6.

$$\sigma_{\rm D} = \eta \sigma_{\rm e} + \sigma_{\rm d} \tag{6}$$

where  $\eta$  represents the electronic demand of the reaction site which is given by  $\eta = R/D$  and  $\sigma_D$  represents the delocalized electrical parameter of the diparametric LD equation. For ortho-substituted compounds, it is necessary to account for the possibility of steric effects, and Charton, therefore, modified the LDR equation to generate the LDRS equation (7)<sup>21</sup>

$$\log k_2 = L\sigma_1 + D\sigma_d + R\sigma_e + SV + h \tag{7}$$

where V is the well known Charton's steric parameter based on van der Waals radii.<sup>22</sup>

The rates of oxidation of ortho-, meta-, and parasubstituted benzaldehydes show excellent correlations with structure via the LDR/LDRS equations (Table 7). All three series of substituted benzaldehydes meet the requirement of a minimum number of substituents for analysis by LDR and LDRS equations.<sup>21</sup> We have used the standard deviation (sd), the coefficient of multiple determination ( $R^2$ ), and Exner's<sup>23</sup> parameter,  $\psi$ , as measures of goodness of fit.

The comparison of the L and D values for the substituted benzaldehydes showed that the oxidation of parasubstituted benzaldehydes is more susceptible to the delocalization effect than to the localized effect. However, the oxidation of ortho- and meta-substituted compounds exhibited a greater dependence on the field effect. In all cases, the magnitude of the reaction constants decreases with an increase in the temperature, pointing to a decrease in selectivity with an increase in temperature.

All three regression coefficients, *L*, *D*, and *R*, are negative, indicating an electron-deficient carbon center in the activated complex for the rate-determining step. The positive value of  $\eta$  adds a negative increment to  $\sigma_d$  (eq 6), reflecting the electron-donating power of the substituent and its capacity to stablize a cationic species. The positive value of *S* indicates that the reaction is subject to steric acceleration by an ortho-substituent.

To test the significance of localized, delocalized, and steric effects in the ortho-substituted benzaldehydes,

- (14) Young, Y. B.; Trahanovsky, W. S. J. Am. Chem. Soc. 1969, 91, 5060.
  - (15) Banerji, K. K. J. Indian Chem. Soc. 1975, 52, 573.
  - (16) Banerji, K. K. J. Chem. Soc., Perkin Trans. 2 1988, 1547.
     (17) Mathur, D.; Sharma, P. K.; Banerji, K. K. J. Chem. Soc., Perkin
- *Trans. 2* **1993**, 205.
- (18) Johnson, C. D. *The Hammett Equation*; Cambridge University Press: Cambridge 1973; p 78.
- (19) Dayal, S. K.; Ehrenson, S.; Taft, R. W. J. Am. Chem. Soc. 1974, 94, 9113.

(20) Swain, C. G.; Unger, S. H.; Rosenquest, N. R.; Swain, M. S. J. Am. Chem. Soc. **1983**, *105*, 492.

(21) Charton, M.; Charton, B. Bull. Soc. Chim. Fr. 1988, 199 and references cited therein.

(22) Charton, M. J. Org. Chem. 1975, 40, 407.

(23) Exner, O. Collect. Czech. Chem. Commun. 1966, 31, 3222.

multiple linear regression analyses were carried out with L, D, and R, D, R, and S, and L, R, and S. The absence of significant correlations (eqs 8–10) showed that all four substituent constants are significant.

$$\log k_2 = (-1.21 \pm 0.32)\sigma_1 - (1.28 \pm 0.25)\sigma_d - (2.22 \pm 1.46)\sigma_e - 2.31$$
(8)

$$R^2 = 0.8336$$
, sd = 0.22,  $n = 12$ ,  $\psi = 0.34$ 

log  $k_2 = (-1.34 \pm 0.36)\sigma_d - (0.97 \pm 2.21)\sigma_e +$ (0.65 ± 0.40)v - 3.03 (9)

$$R^2 = 0.6676$$
, sd = 0.31,  $n = 12$ ,  $\psi = 0.49$ 

$$\log k_2 = (-1.57 \pm 0.52)\sigma_1 - (0.11 \pm 2.49)\sigma_e + (0.98 \pm 0.47)v - 2.37 (10)$$

$$R^2 = 0.5763$$
, sd = 0.35,  $n = 12$ ,  $\psi = 0.57$ 

Similarly, in the cases of the oxidation of para- and meta-substituted benzaldehydes, multiple regression analyses indicated that both localization and delocalization effects are significant. There is no significant colinearity between the various substituent constants for the three series.

The percent contribution<sup>22</sup> of the delocalized effect,  $P_D$  is given by the following equation (11).

$$P_{\rm d} = \frac{100D}{(L+D)}$$
(11)

Similarly, the percent contribution of the steric parameter<sup>22</sup> to the total effect of the substituent,  $P_{\rm S}$ , was determined by using eq 12.

$$P_{\rm S} = \frac{100S}{(L+D+S)}$$
(12)

The values of  $P_D$  and  $P_S$  are also recorded in Table 7. The value of  $P_D$  for the oxidation of para-substituted benzaldehydes is *ca.* 53%, whereas the corresponding values for the meta- and ortho-sobstituted aldehydes are *ca.* 39 and 34%, respectively. This shows that the balance of localization and delocalization effects is different for differently substituted benzaldehydes. The less pronounced resonance effect from the ortho-position than from the para-position may be due to the twisting away of the aldehydic group from the plane of the benzene ring. The magnitude of the  $P_S$  value shows that the steric effect is significant in this reaction.

#### Mechanism

The cleavage of the aldehydic C-H bond in the ratedetermining step is confirmed by the presence of a substantial kinetic isotope effect. The negative values of the localization and delocalization electrical effects, i.e., of *L*, *D*, and *R*, points to an electron-deficient reaction center in the rate-determining activated complex. Further, it is confirmed by the positive value of  $\eta$  which indicates that the substituent is better able to stabilize a cationic or electron-deficient reactive site. Therefore, a hydride ion transfer in the rate-determining step is suggested.

The small magnitude of  $\eta$ , which represents the electronic demand at the reaction center, indicates a less

acid-independent path:

$$\begin{array}{c} \text{ArCHOMnO}_{3} + \text{H}^{+} \underbrace{\text{fast}}_{O^{-}} & \text{ArCHOMnO}_{3} \\ I \\ O^{-} & + \text{H}^{+} \underbrace{\overset{\text{fast}}{\longrightarrow}}_{OH} & \text{ArCHOMnO}_{3} \\ OH \\ \text{Ar} - \underbrace{\overset{\text{OH}}{C} - \bigcirc & \text{MnO}_{2} & \underbrace{\text{slow}}_{Mn(V)} & \text{HMnO}_{3} + \text{ArCOOH} \\ I \\ H \\ O \\ & \text{Mn(V)} & \underbrace{\text{fast}}_{2Mn(IV)} + \text{Mn(VII)} \end{array}$$

## Scheme 2

acid-dependent path:

$$[bpy_2Cu(MnO_4)]MnO_4 + ArCHO \longrightarrow [bpy_2Cu(MnO_4)]^+ + ArCHOMnO_3$$

$$\begin{array}{c} O^{-} \\ ArCHOMnO_{3} \\ I \\ O^{-} \\ + H^{+} \underbrace{fast}_{OH} \\ ArCH(OH)OMnO_{3} + H^{+} \underbrace{fast}_{OH} \\ ArCH(OH)OMnO_{2}OH]^{+} \\ ArCH(OH)OMnO_{2}OH]^{+} + H^{+} \underbrace{}_{OH} [ArCH(OH)OMnO(OH)_{2}]^{2+} \\ [ArCH(OH)OMnO_{2}OH]^{+} \\ ArCOOH + [MnO(OH)_{2}]^{2+} \\ Mn(V) \\ [ArCH(OH)OMnO(OH)_{2}]^{2+} \\ Mn(V) \\ ArCOOH + [MnO(OH)_{3}]^{2+} \\ Mn(V) \\ 3Mn(V) \\ \underbrace{fast}_{SMn(V)} \\ ArcooH + [MnV] \\ Mn(V) \\ Mn$$

pronounced charge separation in the activated complex and suggests a mechanism involving a hydride ion transfer via a permanganate ester. The mechanisms depicted in Schemes 1 and 2 are consistant with all the available data. The aldehyde first suffers a nucleophilic attack by BBCP to yield an anion which is rapidly protonated to form a permanganate ester. The ester then decomposes in the rate-determining step to yield the ultimate products. The rate-determining decomposition of an ester intermediate is supported by the steric acceleration due to the presence of an ortho-substituent in the substrate. As the tetrahedral carbon atom in the ester changes to a trigonal carbon atom in the activated complex, there is an increase in steric relief with increasing crowding at the reaction center. The formation of an electron-deficient reaction center in the activated complex indicates that the cleavage of the C-H bond is ahead of the formation of the C=O bond.

## **Experimental Section**

**Materials.** The preparation and purification of the aldehydes has been reported earlier.<sup>24</sup> BBCP was prepared and purified by a reported method.<sup>1</sup> [<sup>2</sup>H]Benzaldehyde (PhCDO) was also prepared by a reported method.<sup>25</sup> Acetic acid was refluxed with chromic oxide and acetic anhydride for 3 h and fractionated.

**Product Analysis.** The product analysis was carried out under kinetic conditions. In a typical experiment, freshly distilled benzaldehyde (5.25 g, 0.05 mol) and BBCP (6.15 g, 0.01 mol) were made up to 100 mL in 1:1 (v/v) acetic acid– water in the presence of 0.1 mol dm<sup>-3</sup> of perchloric acid. The reaction mixture was allowed to stand for *ca.* 6 h to ensure completion of the reaction. It was rendered alkaline with NaOH and filtered and the filtrate evaporated to dryness

<sup>(24)</sup> Banerji, K. K. J. Org. Chem. 1988, 53, 2154.

<sup>(25)</sup> Wiberg, K. B. J. Am. Chem. Soc. 1954, 76, 5371.

under reduced pressure. The residue was dissolved in a minimum quantity of dilute HCl and cooled in crushed ice to yield the crude acid (2.0 g), which was recrystallized from hot water to produce pure benzoic acid (1.74 g, 95%, mp 121 °C). Iodometric determinations of the oxidation state of manganese, in a spent reaction mixture, indicated it to be 4.03  $\pm$  0.15.

**Stoichiometry.** To determine the stoichiometry, BBCP (3.07 g, 0.005 mol) and benzaldehyde (0.11 g, 0.001 mol) were made up to 100 mL in 1:1 (v/v) acetic acid–water in the presence of 0.1 mol dm<sup>-3</sup> of perchloric acid. The reaction was allowed to stand for *ca.* 10 h to ensure the completion of the reaction. The residual BBCP was determined spectrophotometrically at 529 nm. Several determinations with differently substituted benzaldehydes showed that 2 mol of BBCP is consumed for every 3 mol of the aldehyde oxidized.

**Kinetic Measurements.** The reactions were carried out under pseudo-first-order conditions by maintaining a large excess of the aldehyde ( $\times 15$  or more) over BBCP. The solvent was a 1:1 (v/v) acetic acid–water mixture (pH = 2.04), unless

otherwise mentioned. The reactions were carried out at a constant temperature ( $\pm 0.1$  K) and followed up to 80% reaction by monitoring the decrease in absorption due to [BBCP] at 529 nm. The pseudo-first-order rate constants,  $k_{obs}$ , were computed from the linear (r > 990) least-squares plots of log-[BBCP] versus time. Duplicate kinetic runs showed that the rate constants were reproducible within  $\pm 4\%$ . The average errors in the values of K and  $k_2$  are  $\pm 5\%$  and  $\pm 4\%$ , respectively. Preliminary experiments showed that the oxidation is not sensitive to ionic strength: therefore, no attempt was made to keep it constant. All kinetic measurements, except those to study acid catalysis, were performed in the absence of any added mineral acid.

**Acknowledgment.** Thanks are due to the Council of Scientific and Industrial Research (India) for financial support.

JO9513424