were prepared by reaction of *tert*-butyllithium with the appropriate ketone; 6–8 were prepared by the one-pot Barbier-type condensation of 1-bromoadamantane with the corresponding ketone by Li metal in ether.[19,20] Products were freed of residual ketone, secondary alcohols, and hydrocarbons by column chromatography on alumina (activity II–III) in ether/petroleum ether mixtures and crystallized from pentane. Yields of new alcohols ranged from 16 (**6**) to 45% (**4**). Alcohol **2** was an oil: IR (CCl_4) 3631 cm^{-1}. Anal. Calcd for $C_{14}H_{30}O$: C, 78.43; H, 14.10. Found: C, 78.20; H, 14.21. Alcohol **4**: mp 42 °C; IR (CCl_4) 3628 cm^{-1}. Anal. Calcd for $C_{17}H_{32}O$: C, 80.95; H, 12.70. Found: C, 81.02; H, 13.01. Alcohol **5** was an oil: IR (CCl_4) 3630 cm^{-1}. Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 81.07; H, 12.55. Alcohol **6**: mp 179.5 °C; IR (CCl_4) 3624 cm^{-1}. Anal. Calcd for $C_{25}H_{40}O$: C, 84.21; H, 11.31. Found: C, 83.99; H, 11.42. Alcohol **7**: mp 157 °C; IR (CCl_4) 3625 cm^{-1}. Anal. Calcd for $C_{23}H_{38}O$: C, 83.57; H, 11.59. Found: C, 83.64; H, 11.51. Alcohol **8**: mp 111 °C; IR (CCl_4) 3627 cm^{-1}. Anal. Calcd for $C_{22}H_{36}O$: C, 83.54; H, 11.39. Found: C, 83.30; H, 11.34.

Thermolysis Kinetics. Samples (25 μL) of a solution of the alcohol (0.1–0.01 M) and a suitable linear saturated hydrocarbon reference (at about half the alcohol concentration) in dodecane were sealed in Pyrex tubes and thermostated in an oil bath at 135–245 °C (45 °C ranges were used for each compound). Samples were withdrawn at convenient times, cooled, and analyzed by GLC on short, lightly loaded SE30 columns. Only compound **6** was too involatile and unstable to be analyzed in this way; its thermolysis could, however, be followed be measuring the IR absorption of the product ketone at 1678 cm^{-1}. For this purpose, rather larger samples (0.5 mL) were required. Measurements on compound **3** by both IR and GLC methods agreed within the experimental error (±3%). The addition of α-methylstyrene in concentrations up to 5 times that of **1** reduced its rate constant by no more than 2%, indicating that induced decomposition does not occur to any appreciable extent.

Product Analyses. One- to two-milligram samples of alcohols were sealed with 25 μL of *n*-dodecane in tubes with a total volume of about 250 μL and were thermostated at temperatures between 150 and 200 °C for times corresponding to 10–15 half-lives. After cooling, the contents were diluted with 0.5 mL of dichloromethane and analyzed by GLC on SE30 columns. Products were identified by comparing their retention times with those of authentic samples and/or by mass spectroscopy. Formation of radicals other than B· was revealed by the presence of anomalous ketones and secondary alcohols or by the appearance of adamantane, in the case of Ad·.

Alcohol **2** gave 69.5, 68.4, 67.5, and 66.7% of products derived from formation of the *tert*-amyl radical at 150, 165, 180 and 200 °C, respectively, while **6** gave 2.6, 3.5, 4.0, and 5.0% Ad· products at the same temperatures. Compounds **3**, **7**, and **8** gave, at 200° C, 1.4, 2.3 (plus 2.5% Oc·), and 2.0% Ad· products, respectively.

Molecular Mechanics Calculations. All calculations were performed on a Digital VAX 780/11 computer through the Iverson–Mislow program[58] BIGSTRN-2 (QCPE 410) and the Allinger-Yuh program[24] MM2 (QCPE 395).

In Allinger's 1971 and Schleyer's force fields the resulting steric energy is converted to ΔH_f (gas) by applying "general group increments", and from this latter quantity the strain energy is obtained by calculating an idealized enthalpy of formation from the "strainless increments".

In his later force field (QCPE 395), Allinger calculates ΔH_f slightly differently, allowing for translation/rotation and torsional contributions explicitly, while two quantities, "inherent strain" and "strain energy", are defined. Rüchardt uses another quantity, the "strain enthalpy", H_{sp}, defined as the difference between the calculated enthalpy of formation and the specific reference value, ΔH_f^N, calculated from group increments.[16] Normally this would be simply 2.4 kcal·mol^{-1} greater than Allinger's strain energy, but Rüchardt uses strainless increments taken from an earlier source,[59] although the currently proposed general increments, translation/rotation term, and torsional contributions are used to calculate ΔH_f. In order to maintain consistency between alkane and alcohol data, we have used Allinger's 1980 values throughout.

Acknowledgment. We are indebted to A. Adenier for invaluable technical assistance, to B. Galland and Drs. P. K. Luong and T. Couesnon for help in modifying and running the molecular mechanics programs, and to Professor Ch. Rüchardt and Dr. H.-D. Beckhaus for fruitful discussions and correspondance.

Registry No. 1, 41902-42-5; 2, 82902-97-4; 3, 66951-98-2; 4, 82902-98-5; 5, 82902-99-6; 6, 80514-85-8; 7, 82903-00-2; 8, 82903-01-3.

Supplementary Material Available: Tables IV to VII containing calculated steric energies, heats of formation, and strain energies of alkanes, carbocations and alcohols (4 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of Oxidation of Aromatic Aldehydes by Acid Bromate

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The kinetics of oxidation of benzaldehyde by potassium bromate in an acetic acid medium have been studied. The reaction is first order with respect to oxidant concentration whereas the order with respect to substrate is less than one. Hydrogen ion accelerates the rate of reaction. A mechanism involving the formation of an unstable bromate ester which decomposes to the reaction products has been suggested. The activation parameters associated with the rate-determining step and the thermodynamic values associated with the equilibrium stage have been computed. The effects of various functional groups on the ring at the ortho, meta, and para positions of benzaldehyde have also been examined.

It is well-known that potassium bromate is a strong oxidizing agent, having an oxidation potential of 1.44 V in an acidic medium.[1] This readily available reagent offers trouble-free workup of the reaction product compared to the other oxidizing agents.[2] The bromate ion oxidation of metal ions has been studied with different inorganic reductants. The reaction exhibits a remarkable variety of

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mechanistic behavior.[3-11] Surprisingly, the application of potassium bromate for oxidizing organic compounds is rather scanty.

The bromate oxidations of some alcohols and α-hydroxy acids were investigated in acid media.[12] Although some aromatic as well as aliphatic aldehydes have been oxidized in boiling acetic acid with this reagent,[13] the mechanism of oxidation of aromatic aldehyde by this oxidant is yet to be established. Hence it was of interest to study the mechanism of oxidation of aromatic aldehydes by this oxidant in acetic acid medium.

Experimental Section

Reagents. All the organic compounds were of AR grade and were further purified by either recrystallization or redistillation just before use. Acetic acid was heated under reflux for 6 h with excess of potassium dichromate and distilled just before use. Potassium bromate was of BDH grade. All solutions of benzaldehyde and substituted benzaldehydes were prepared in acetic acid.

Rate Measurements. The reaction was followed by withdrawing aliquots of the reaction mixture at known intervals of time and quenching the reaction by adding it to excess of potassium iodide solution. During the oxidation, interference by the liberated bromine was prevented by adding a calculated quantity of mercuric acetate[14] whereby the bromide ion formed from potassium bromate was removed as complex. The concentration of mercuric acetate was adjusted to 2.0×10^{-2} M in each run. It has been shown earlier that mercuric acetate is inert toward oxidation of benzaldehyde to benzoic acid.[2] The liberated iodine was estimated by titrating it against standard thiosulfate solution and using starch solution as an indicator. The pseudo-first-order rate constants (k_{obsd}) were calculated from the slopes of log[bromate] vs. time plots. The duplicate experiments were always reproducible to ±5%.

Stoichiometry and Product Analysis. The stoichiometry and products of oxidation were determined as follows.[2] The mixtures of benzaldehyde (60 mM, in each case), acetic acid (10 mL), and varying amounts of potassium bromate (2.1, 4.2, 8, 12, and 16.2 mM) were heated under reflux for 10 min in each experiment. The reaction mixture was poured onto water and extracted with chloroform (3 × 50 mL). The organic layer was washed successively with water, sodium bicarbonate solution, and water and dried over anhydrous sodium sulfate. On removal of the solvent, the unreacted benzaldehyde was obtained (50, 42, 31, 19, and 7.5 mM, respectively) which was characterized through a 2,4-dinitrophenylhydrazone derivative. The aforementioned sodium bicarbonate extract was cooled in ice and acidified with dilute sulfuric acid (using congo red as an indicator), and the precipitated benzoic acid was extracted with pure ether (3 × 30 mL). The ethereal solution was washed with a little water and dried over sodium sulfate. On removal of the solvent, benzoic acid was obtained as colorless flakes (6.1, 12.3, 23, 34, and 45 mM, respectively) with a melting point of 121 °C which remained undepressed on admixture with an authentic sample of benzoic acid. It had been shown that 1 molar equiv of potassium bromate oxidized approximately 3 molar equiv of benzaldehyde under the experimental conditions, taking into consideration the potassium bromide formed in the reaction and its subsequent consumption of bromate.

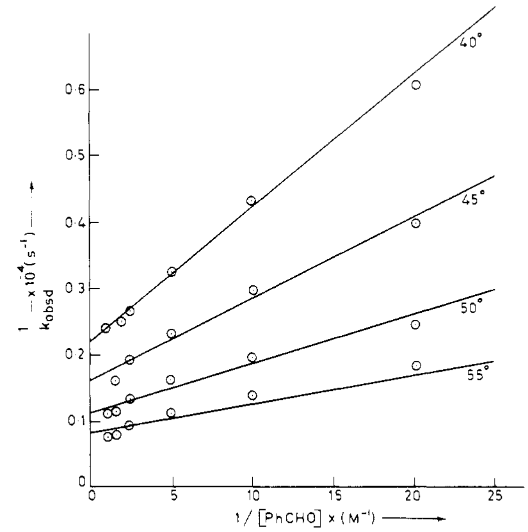

Figure 1. Variation of pseudo-first-order rate constant with substrate concentrations. Plots of $1/k_{obsd}$ against 1/[PhCHO] at different temperatures. $[BrO_3^-] = 1 \times 10^{-2}$ M and [AcOH] = 70% (v/v).

Table I. Effect of Acetic Acid on the Reaction Rate[a]

% [AcOH] (v/v)	50	60	70	80	90
$10^5 k_{obsd}$, s^{-1}	3.83	10.5	23.0	56.0	92.2

[a] $[PhCHO] = 7 \times 10^{-1}$ M; $[BrO_3^-] = 1 \times 10^{-2}$ M; temperature = 50 °C.

Thus, various substituted benzaldehydes had been oxidized, and the derived acids have melting points generally within 2 °C of the reported values and were confirmed through mixture melting point determination with authentic samples, neutralization equivalent determination, and IR spectra. The results further indicated that benzaldehyde and substituted benzaldehydes are not brominated in the acetic acid medium under these experimental conditions.

Results

Effect of Reactant Concentrations. The oxidation of benzaldehyde by acid bromate has been studied at various initial concentrations (5×10^{-3}–25×10^{-3} M) of oxidant, keeping the benzaldehyde concentration, acetic acid concentration, and temperature constant (at 7×10^{-1} M, 90% (v/v), and 50 °C, respectively). The observed pseudo-first-order rate constant is found to be $(2.73 \pm 0.13) \times 10^{-4}$ s^{-1}. Thus, the pseudo-first-order rate constant is independent of the initial concentration of oxidant. This indicates that the reaction is first order with respect to bromate concentration. The effect of changing substrate concentration has also been studied at a constant oxidant concentration and constant acidity at four different temperatures. An increase of the benzaldehyde concentration enhances the rate of oxidation. The plot of $1/k_{obsd}$ against 1/[PhCHO] at each temperature gives a straight line making an intercept on the y axis (Figure 1). This indicates that the reaction is initiated by the formation of an intermediate compound. The equilibrium constant (K) associated with the substrate–oxidant equilibrium and the disproportionation constant (k) associated with the slow step have been evaluated at different temperatures as has been mentioned earlier.[15a]

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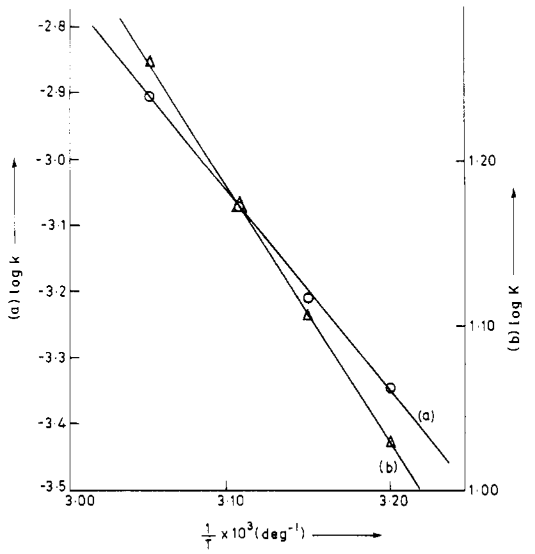

Figure 2. Variation of disproportionation and equilibrium constants with temperature. Plots of (a) log k against $1/T$ and (b) log K against $1/T$.

Effect of Changing Hydrogen Ion Concentration. In order to find out the effect of hydrogen ion concentration on the rate of the reaction, it has been studied at a constant acetic acid concentration of 80% (v/v) while the acidity is changed by the addition of perchloric acid. When the perchloric acid concentration was changed from 1.0×10^{-3} to 1.0×10^{-2} M, the rate was found to increase by 60%. The reaction could not be studied at high perchloric acid concentrations because it might complicate the reaction by inducing bromination of benzaldehyde as experienced in sulfuric acid medium.[2]

Effect of Changing Acetic Acid Concentration. The kinetics of the reaction have been studied by changing the composition of acetic acid in the reaction mixture, while keeping the oxidant and substrate concentrations unchanged. It has been found that the reaction is slow at lower compositions (<40%) of acetic acid. However, the reaction takes place smoothly at much higher acetic acid concentrations (Table I), and the pseudo-first-order rate constant changes from 3.83×10^{-5} to 9.22×10^{-4} s^{-1} for a change of acetic acid concentration from 50% to 90%. The increase in rate in acetic acid is high enough to indicate that the dielectric constant[15b] of the medium may play an important role. However, for a reaction between ions of similar charge, the rate decreases with the decrease in dielectric constant of the medium. On the other hand, the rate increases with the decrease in dielectric constant when a reaction takes place between ions of opposite charges.[15c] The results presented in Table I suggest that the reaction may take place between ions of opposite charge.

Effect of Temperature. The influence of temperature on k and K has been studied at 40, 45, 50, and 55 °C. The values of k are found to be (4.55, 6.25, 8.95, and 12.50) $\times 10^{-4}$ s^{-1}, respectively, whereas K values are 10.7, 12.8, 15.1, and 18.2 at the respective temperatures. A least-squares fit of the plot of log k against $1/T$ (Figure 2) has been used to evaluate the energy of activation (E_a) which is 57.8 kJ mol^{-1}. The entropy and free energy of activation have been calculated as usual[15a] and are found to be −133.2 J K^{-1} mol^{-1} and 97.8 kJ mol^{-1}, respectively. The enthalpy, entropy, and free energy changes associated with the equilibrium stage have been computed to be 29.9 kJ mol^{-1}, 115.1 J K^{-1} mol^{-1}, and 7.03 kJ mol^{-1}, respectively.

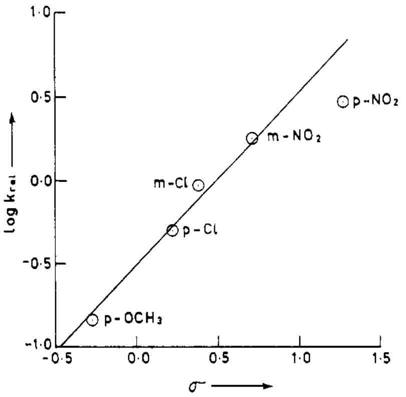

Figure 3. Effect of substituents upon the pseudo-first-order rate constants. The plots of the logarithm of the relative rates against the Hammett σ values.

Effect of Substituents. The rates of oxidation of ortho-, meta-, and para-substituted benzaldehydes were examined in aqueous acetic acid of concentration 70% (v/v). The experiments were carried at a [PhCHO], [BrO_3^-], and temperature of 5.0×10^{-1} M, 1.0×10^{-1} M, and 50 °C, respectively. The observed pseuso-first-order rate constants (s^{-1} $\times 10^5$) for the oxidations of benzaldehyde and *p*-methoxy-, *o*-chloro-, *m*-chloro-, *p*-chloro-, *o*-nitro-, *m*-nitro-, and *p*-nitrobenzaldehydes are 23.3, 3.33, 15.7, 21.8, 11.5, 31.4, 42.2, and 69.0, respectively. The results, therefore, indicate that the rate of oxidation decreases with the presence of electron-donating groups and increases with electron-withdrawing groups on the aromatic ring. A plot of the logarithm of the relative rates against the Hammett σ values is shown in Figure 3. The slope (ρ) of the plot is 1.05 which is nearer that ($\rho = 1.02$) reported by Wiberg and Mill in connection with the chromic acid oxidation of aromatic aldehydes.[17a]

Discussion

The oxidation of benzaldehyde to benzoic acid by potassium permanganate and chromic acid has been studied.[17a] The reaction of the former reagent has been established to be acid-catalyzed and is accelerated slightly by the presence of electron-donating groups. It is believed to proceed through the formation and subsequent decomposition of permanganate ester. Under basic conditions, however, the reaction is accelerated by electron-withdrawing groups and is supposed to be a free-radical chain process[16a] or to involve a hydride transfer.[16b] Likewise, the chromic acid oxidation of benzaldehyde has been shown to proceed through the formation of chromate ester.[17] The results plotted in Figure 1 indicate that the oxidation of aldehyde by potassium bromate seems to occur through the formation of an intermediate compound followed by its decomposition to give products of reaction. The rate expression at constant acidity is

$$-\frac{\mathrm{d[oxidant]}}{\mathrm{d}t} = \frac{kK\mathrm{[oxidant][aldehyde]}}{1 + K\mathrm{[aldehyde]}} \qquad (1)$$

where k is the disproportionation constant of the intermediate compound and K is the equilibrium constant of the complex formed between the substrate and the reactive species of the oxidant. The hydrates of aliphatic aldehydes are well-known,[18] and the oxidations of some aliphatic

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(16) (a) K. B. Wiberg and R. Stewart, *J. Am. Chem. Soc.*, **77**, 1786 (1955); (b) F. Freeman, J. B. Brant, N. B. Hester, A. A. Kamego, M. L. Kasner, T. G. McLaughlin, and E. W. Paull, *J. Org. Chem.*, **35**, 982 (1970).

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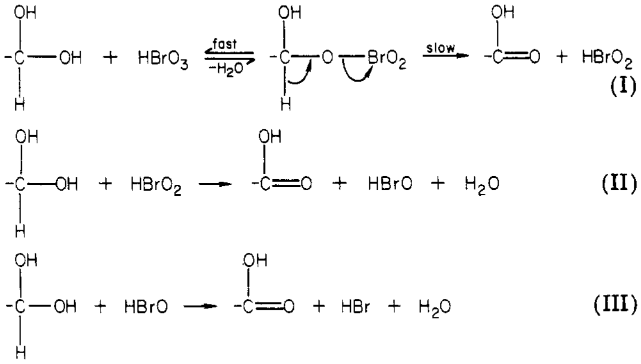
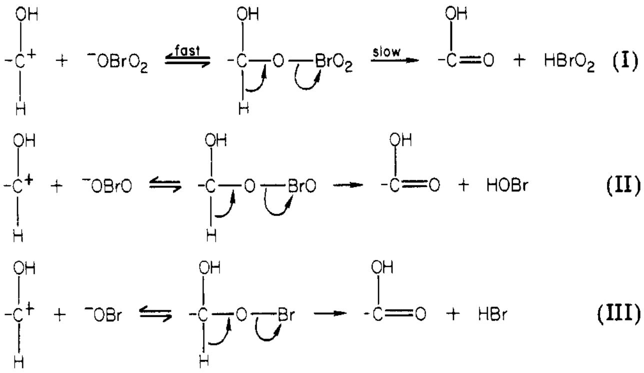
Scheme I



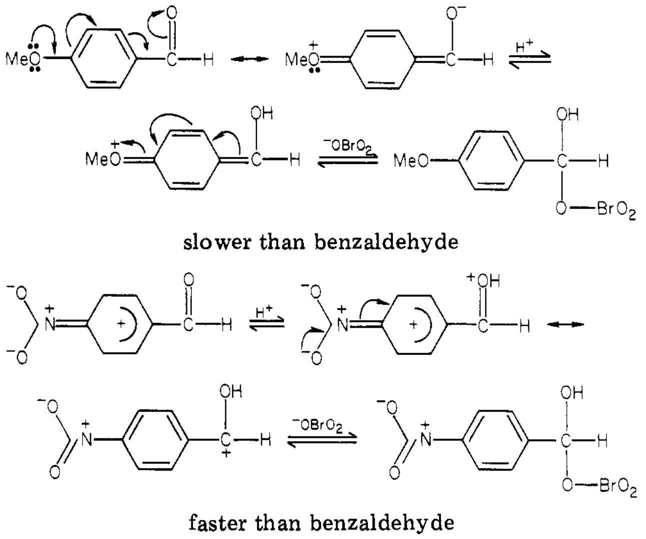
Scheme II



aldehydes have been shown to occur through intermediate hydrates. Though the hydrate of benzaldehyde has escaped detection in earlier studies,[19] later reports indicate that the oxidation of benzaldehyde by some other oxidants also takes place through partially hydrated benzaldehyde.[20] Thus, protonation of the bromate ion to give bromic acid followed by its reaction with the hydrated form of benzaldehyde may take place. It is also possible that the aldehyde molecule remains in the protonated form which may react with nucleophilic bromate ion to give products. The intermediate ester formation with aromatic aldehydes has been reported in the oxidations by transition metal ions,[16,17] but there is no supporting evidence, kinetic or otherwise. Regardless of which scheme is correct, one piece of information is obtained with certainty: the oxidation of benzaldehyde by bromate ion occurs through intermediate bromate ester. Two alternative mechanistic paths (Schemes I and II) are shown, and the last two steps in each scheme are fast.

If the foregoing mechanism (Scheme II) is correct, the attack of the bromate anion on the carbonyl carbon is very crucial, and it will be favored by the generation of a carbonium ion on that carbon. Any structural feature tending to diminish the accumulation of positive charge on this carbon should retard the rate of oxidation. Thus, an electron-releasing group (e.g., a methoxyl group, particularly at ortho and para positions) attached to benzaldehyde should make the rate of oxidation slower (Scheme III) while an electron-attracting group (e.g., a nitro group) should exhibit the opposite effect, and chlorine will retard the rate slightly when compared to that of unsubstituted benzaldehyde. This is found to be true experimentally.

Scheme III



The protonation of carbonyl oxygen preceds the attack of the bromate anion, and it is very likely that a step following the protonation may be rate determining.

Thus it becomes evident that the rate of oxidation of substituted benzaldehyde is highly influenced by the nature of the subsituents. In connection with the oxidations of inorganic compounds by bromate ion, it has been shown[7,8,10] that the oxidations also take place with $H_2BrO_3^+$. However, participation of $H_2BrO_3^+$ seems unlikely in the present study since the reactions have been carried out in acetic acid medium, unlike those done by previous workers with a high concentration of perchloric acid. On the other hand, the species $H_2BrO_3^+$ is so reactive with respect to reduction that its reactions are essentially diffusion-controlled[10] outer-sphere processes. In connection with the oxidation of benzaldehyde by chromic acid, Wiberg and Mill[17a] have shown that the oxidation takes place between H_2CrO_4 and the hydrated form of benzaldehyde. On the other hand, in the permanganate oxidation of some aromatic aldehydes[16a] in neutral and fairly acidic solutions it has been shown that MnO_4^- reacts with protonated aldehyde to give permanganate ester prior to electron transfer. The observed decrease in the pseudo-first-order rate constant with an increasing dielectric constant of the medium further indicates that the reaction may take place between two oppositely charged species, and hence the alternative mechanism (Scheme II) which has been suggested cannot be totally ruled out.

The rate of the chromic acid oxidation of benzaldehyde increases with the first power of the concentration of acid chromate ion as well as of benzaldehyde. The permanganate oxidation of benzaldehyde also proceeds at a rate which is proportional to the concentrations of the aldehyde and permanganate ion. The bromate oxidation of aromatic aldehydes which has been studied in acetic acid medium is kinetically dissimilar, and hence the present rate constant values cannot be compared with those obtained earlier with chromic acid or permanganate. However, from the results it appears that even in acetic acid medium bromate oxidations of the aldehydes proceed at appreciable rates, and hence bromate ion is in no way inferior to other oxidizing agents.

Registry No. PhCHO, 100-52-7; p-$CH_3OC_6H_4CHO$, 123-11-5; o-ClC_6H_4CHO, 89-98-5; m-ClC_6H_4CHO, 587-04-2; p-ClC_6H_4CHO, 104-88-1; o-$NO_2C_6H_4CHO$, 552-89-6; m-$NO_2C_6H_4CHO$, 99-61-6; p-$NO_2C_6H_4CHO$, 555-16-8; potassium bromate, 7758-01-2.

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