and cerous ion[14] of 1.07×10^{-8} and 5.0×10^{-10}, second-order rate constants of 1.2×10^4 and 1.7×10^4 l. mole.$^{-1}$ min.$^{-1}$, respectively, are obtained for these ions.

Although these hydroxometallic ions are considerably weaker bases than hydroxyl ion (K_A for hydroxyl ion = 10^{-16}), they are catalytically more active than the latter (for which $k_2 = 2 \times 10^3$).[15] This would tend to lend support to the view that a push-pull mechanism is involved.

Similar effects have also been observed in these laboratories with magnesium, calcium and uranyl ions. As might be expected, both calcium and magnesium, whose hydrated species have very small dissociation constants, showed this behavior only in alkaline media where the large hydrolytic effect of hydroxyl ions prevented quantitative measurement of the part played by the hydroxometallic ions. Uranyl ion, on the other hand, exhibited a marked effect in extremely dilute solution even at low *p*H levels.

Experimental

Reagents.—C.P. grade chemicals were used as purchased, without further purification. Cupric chloride was obtained as the dihydrate, manganous chloride as the tetrahydrate and cerous nitrate as the hexahydrate. GB of high purity was obtained from the Chemical Research Division of the Chemical Warfare Laboratories.

Apparatus.—In early experiments the Beckman model G *p*H meter was used. Later the *p*H was held constant with a Beckman model K automatic titrator set to deliver the smallest possible increments of titrant, and provided with a 5-ml. base-filled microburet graduated to 0.02 ml. Reaction temperature in a jacketed 250-ml. beaker was maintained at 25.0° by a Precision Scientific Co. constant temperature circulating bath. Reaction mixtures were constantly stirred with a 1-inch Teflon-covered magnetic stirring bar. A Klett-Summerson photoelectric colorimeter provided with a No. 42 filter was used in the analysis for GB.

Kinetic Measurements.—Solutions of GB and the metal salt (on the acid side) were mixed in the reaction vessel to give the required concentration of each, and the *p*H was adjusted with base from the microburet. The amount of base, V_1, required to keep the *p*H constant during the course of reaction (hydrolysis liberates one mole each of isopropylmethylphosphonic acid and hydrofluoric acid) was recorded against time. Basic hydrolysis and back titration of an aliquot of the GB stock gave the volume of base (V_∞) required at infinite time. Suitable corrections were applied to the data to account for initial acidity, withdrawal of samples and volume changes, and the corrected values of $(V_\infty - V_1)/V_\infty$, which represents the fraction of GB remaining, were plotted on semi-logarithmic paper. The plots were virtually linear; thus, the reactions exhibited first-order kinetics. In three experiments these results were confirmed by direct analysis for GB by the peroxide-*o*-tolidine method.[16] Most of the experiments were conducted in the *p*H range 5–6.5, in which the spontaneous hydrolysis rate of GB, due to catalysis by water and by hydroxyl and hydronium ions is negligible. From the slopes of the semi-logarithmic plots, the first-order rate constants, *k*, were calculated in the usual manner.[17] These varied with metal ion concentrations and *p*H. In experiments with manganous and cerous ions, nitrogen had to be bubbled through the reaction mixtures to prevent oxidation, which would have changed the concentration of the desired metal ion and caused an anomalous increase in the uptake of base.

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[CONTRIBUTION FROM THE DOW CHEMICAL CO., WESTERN DIVISION]

On the *cis-trans* Equilibria in *o*-Halophenols

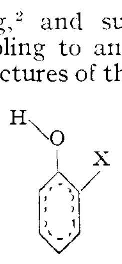
BY ALVIN W. BAKER

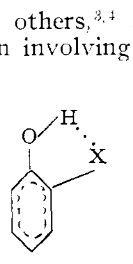
RECEIVED FEBRUARY 24, 1958

The ν_{OH} stretching frequencies of pure *o*-halophenols show a doubled band having a *trans/cis* ratio considerably smaller than previously observed. Both the $\Delta\nu$ shift and the *trans/cis* ratio increase in the order F < Cl < Br < I. An explanation is offered for this effect based on a destabilization of the *trans* configuration compared to that of the *cis*.

The vibrational spectra of the *o*-halophenols, first investigated in the near infrared region by Wulf, *et al.*,[1] show a doubling of the hydroxyl stretching frequencies at concentrations low enough to prevent intermolecular association. One of the bands occurs at a nearly normal phenolic position while the other, which is always much more intense, is shifted to lower frequencies by an amount dependent on the halogen. Since comparable effects do not occur in the spectra of phenols *o*-substituted with other types of basic atoms such as oxygen, nitrogen or sulfur, the doubling is somewhat anomalous and a complete explanation has not yet been found.

Pauling,[2] and subsequently others,[3,4] ascribed this doubling to an equilibrium involving *cis* and *trans* structures of the type





According to this hypothesis, the O–H bond is partially constrained to the aromatic plane because of resonance interaction between the aro-

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[1] O. R. Wulf, U. Liddel and S. B. Hendricks, THIS JOURNAL, **58**, 2287 (1936).

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[3] L. R. Zumwalt and R. M. Badger, *ibid.*, **62**, 305 (1940).

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matic π-molecular orbitals and one of the nonbonding electron pairs on the oxygen. The bond type of the oxygen consequently tends toward sp^2 hybridization with two minimum potential energy configurations as shown. In the *cis* position, a hydrogen bond is formed to the halogen thus making the *cis* configuration more stable than the *trans* by 2 to 3 kcal./mole.

Several unpublished criticisms of the above interpretations have led the author, in the course of a more extended investigation of phenols, to reexamine the spectra of the *o*-halophenols for additional data. The critics believed that the higher frequency band in each instance is more likely due to a trace of phenol impurity than to the presence of *trans* isomer, in part because of the difficulty of separating the *o*-halophenols from phenol. This argument is reasonable for *o*-chlorophenol (b.p. 175.6°), but seems much less so for *o*-bromo- and *o*-iodophenol which have boiling points of 194.5° (760 mm.) and 186–187° (160 mm.), respectively, compared to 181.8° (760 mm.) for phenol.

Experimental

Samples of the *o*-halophenols, obtained from Distillation Products and Delta Chemical Co. (*o*-fluorophenol), were exhaustively purified by distillation and then by repeated passes through a chromatographic column or, for *o*-iodophenol, sublimation. Chromatographic rate values[5a,b] of phenol and some chlorophenols on columns of silicic acid are phenol, 0.27; *o*-chlorophenol, 0.64; and *p*-chlorophenol, 0.44. These values indicate that *o*-chlorophenol should be easily separable by chromatography from either phenol or *p*-chlorophenol, the two compounds most likely to be contributing to the "*trans*" O–H band position. No values were listed for either the bromo- or iodophenols, but one would expect that the relative values of the *o* and *p*-isomers would be sufficiently different to allow a clean separation.

A final attempt at the removal of phenol or any phenol unsubstituted in the *o*-position was made by the selective reaction of the hydroxyl groups with hydroxylic reagents such as P_2O_5 and PCl_5. Particularly in the case of PCl_5, rate studies showed that phenols unsubstituted in the *o*-position react faster than the *o*-halophenols. This reaction was run in CCl_4 at concentrations of about 0.07 molar with the purest phenols which could be prepared by the above techniques. The relative intensities of the *cis* and *trans* bands were observed as the reaction proceeded to completion.

The spectra were obtained in the fundamental O–H stretching region at 3600 cm.$^{-1}$ with a Beckman DK-II spectrophotometer. The resolution of the instrument at maximum performance was about 4 cm.$^{-1}$; however, the relative positions of the sharp O–H bands could be measured to about ±1 cm.$^{-1}$ with a day-to-day reproducibility of ±2 cm.$^{-1}$.

Results

After the above purification procedures, the spectra of all of the *o*-halophenols except *o*-fluorophenol still showed the hydroxyl doublet. The *trans/cis* ratios did not decrease during the chemical reaction technique although this ratio could be improved on samples known to be impure. However, the *trans/cis* ratios were very much smaller than those previously reported, thus indicating that impurities were indeed present in the earlier samples. The doublet could not be detected for *o*-fluorophenol, but this may have been due to the fact that the *trans* band is very weak in *o*-fluorophenol and occurs on the high-frequency side of the main band with a very small wave number separation. The relevant data are given in Table I.

TABLE I

O–H FREQUENCIES OF *o*-HALOPHENOLS

Phenol	ν_{OH}, cm.$^{-1}$ *Trans*	*Cis*	*Trans/cis* ratio Present	Previous	$\Delta\nu$ (*trans* − *cis*)
o-Fluoro-		3584			<20
o-Chloro-	3600	3542	1/56	1/11	58
o-Bromo-	3598	3524	1/38		74
o-Iodo-	3593	3500	1/13.5		93

Two factors argue in favor of the high purity of these samples; these are (1) complete reaction of the O–H group or additional passes through the chromatographic column did not reduce the *trans/cis* ratios, and (2) the frequencies of the *trans* bands are detectably different from those of the suspected impurities. This is particularly evident for *o*-iodophenol which has a *trans* band at 3593 cm.$^{-1}$ whereas the hydroxyl frequencies in phenol and *p*-iodophenol are at 3604 and 3599 cm.$^{-1}$, respectively. The values of ν_{O-H} for the *p*-halophenols are listed in Table II for comparison.

TABLE II

O–H FREQUENCIES FOR PHENOL AND *p*-HALOPHENOLS

Phenol	ν, cm.$^{-1}$	Phenol	ν, cm.$^{-1}$
p-Fluoro-	3607	*p*-Bromo-	3600
Phenol	3604	*p*-Iodo-	3599
p-Chloro-	3602	*m*-Bromo-	3597

The data of Table I show that both the *trans/cis* ratio and the $\Delta\nu$ shift increase in the order F < Cl < Br < I. This is also the order which is shown for the size of the atomic diameters of the halogens.[6] Since the strength of the hydrogen bond increases as the amount of the donor electron overlap and the acidity of the O–H group increase, one would expect the $\Delta\nu$ shift to increase according to this series despite a decreasing electronegativity of the halogen. The fact that both the *trans/cis* ratio and the $\Delta\nu$ shift increase in the same order appears to argue against the applicability of Badger's rule[7] which states that the progressive shift to lower frequencies is an indication of increasing strength of the hydrogen bond. If the rule is valid here, one would expect the *trans/cis* ratios to decrease from chloro to iodo, whereas the reverse is true.

A logical explanation of this anomaly is that the $\Delta\nu$ shifts are valid measures of the strength of the hydrogen bonds but that the *trans* isomers are destabilized with respect to the *cis* isomers according to the sequence F > Cl > Br > I. Two possible mechanisms which might be contributing to this destabilization are as follows: When the oxygen bonds rehybridize because of conjugation with the ring, the sp^2 type orbital of one of the non-bonding pairs of electrons probably overlaps a similar rehybridized orbital on the halogen leading to a repulsive interaction. Secondly, and possibly more important, ability of the halogens to participate in such an effect decreases markedly in the series F

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(5) (a) A. L. LeRosen, J. K. Carlton and P. B. Moseley, *Anal. Chem.*, **25** 666 (1953). (b) Rate values as used here are defined as the ratio of the rate of movement of the adsorptive in the column to the rate of movement of the developing solvent.

(6) The acidity of the *p*-halophenols increases in the same order. Since the *ortho* inductive effects are as large or larger than the *para*, the increasing acidity will aid formation of the hydrogen bond; A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

(7) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937)

> Cl > Br > I. Therefore, this should be the series for an *increasing* hydroxyl interaction with the ring since such effects are partially mutually exclusive. As a consequence, resonance interaction probably constrains the O–H bond direction to the aromatic plane to the least extent in *o*-fluorophenol and to the greatest extent in *o*-iodophenol.[8]

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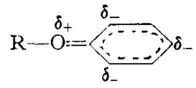
(8) For phenols having an *o*-alkoxy group, a single O-H band is observed which has a $\Delta\nu$ shift of about 55 cm.$^{-1}$ from the phenol position. This is compatible with the above explanation because the alkoxy interaction of the type



is even greater than the comparable interaction shown by the fluoro group. This again would decrease the stability of the *trans* O-H position. On the other hand, this type of resonance interaction is less important for sulfur than for oxygen because of the greater difficulty in forming πp bonds, but again the O-H band is single. This is probably due to the much greater strength of the O–H. . .S hydrogen bond as evidenced by a $\Delta\nu$ shift of about 150 cm.$^{-1}$; A. W. Baker, *J. Phys. Chem.*, **62**, 744 (1958).

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[Contribution from the Chemistry Department, Lucknow University]

Mechanism of Chromic Acid Oxidations. Part IV. Oxidation of Formaldehyde by Chromic Acid

By A. C. Chatterji and Samir Kumar Mukherjee

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A kinetic study of the oxidation of formaldehyde with chromic acid has been made. The order of the reaction with respect to chromic acid, formaldehyde and H$^+$ ion has been found to be first, first and second at all hydrogen ion concentrations. The temperature coefficients for the temperature range between 25 and 55° at various concentrations have been determined. The product of the reaction, formic acid, was detected by the chromotropic acid reaction and then estimated by conductometric titration. The effects of light is negligible. The effects of some salts on the oxidation rates have been studied. The induction factor for the induced oxidation of manganous sulfate to manganese dioxide has been found to be 0.5. From a knowledge of the above results a possible mechanism for the oxidation of formaldehyde by chromic acid has been proposed.

Introduction

A survey of the literature reveals that although a large number of oxidizing agents have been used to oxidize aliphatic as well as aromatic aldehydes only a few workers have studied the oxidation of these in sufficient detail to interpret their results in terms of a detailed mechanism of the reactions.

Kinetic studies on the oxidation of formaldehyde by hydrogen peroxide,[1] hydrogen peroxide in alkaline solution,[2] potassium permanganate,[3] cobaltic ions,[4] ceric ions,[5] nitrogen dioxide,[6] and photochemical oxidations[7] have been made in some detail. Williams and Woods[8] found that aromatic and aliphatic aldehydes are oxidized by iodic acid. Studies on the oxidations of other aldehydes by hydrogen peroxide,[9] selenium dioxide,[10] potassium permanganate in neutral, acidic and alkaline medium,[11] manganic pyrophosphate,[12] nitrogen dioxide[13] and by molecular oxygen[14] also have been made. In spite of these investigations, the detailed nature of the rate-determining step still remains obscure.

Lucchi[15] studied in some detail the oxidation of substituted aromatic aldehydes by chromic acid in acetic acid–sulfuric acid solutions. From his data it is impossible to determine which ion of chromium is the active oxidizing agent. Oxidation of acetaldehyde, *n*-butyraldehyde and isobutyraldehyde by chromic acid also has been studied in detail.[16]

In the present paper the oxidation of formaldehyde has been studied with chromic acid at constant ionic strength of 0.4 in the hope of throwing light on the detailed mechanism of the oxidation of aldehydes by chromic acid. Further we have attempted to find out whether there is any similarity in the mechanisms of oxidation of alcohols and aldehydes by chromic acid.

Experimental

(1) **Chemicals.**—Merck (C.P.) chromium trioxide was recrystallized from conductivity water, and stock solutions were prepared in conductivity water. The chromic acid content was determined iodometrically.

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