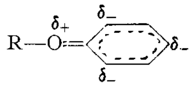
> Cl > Br > I. Therefore, this should be the series for an *increasing* hydroxyl interaction with the ring since such effects are partially mutually exclusive. As a consequence, resonance interaction probably constrains the O–H bond direction to the aromatic plane to the least extent in *o*-fluorophenol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

[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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[1] J. H. Kastle and A. S. Lovenhart, THIS JOURNAL, **21**, 262 (1899); H. Wieland and A. Wingler, *Ann.*, **431**, 301 (1923).

[2] K. Wirtz and K. F. Bonhoeffer, *Z. physik. Chem.*, **B32**, 108 (1936); J. B. Jaillet and C. Quellet, *Can. J. Chem.*, **29**, 1046 (1951); *C. A.*, **47**, 5230a (1953); E. Abel, *Z. physik. Chem.* (*Neue Folge*), **7**, 101 (1956).

[3] J. Hollnta and A. Mutschin, *ibid.*, **150**, 381 (1930).

[4] C. E. H. Bawn and A. G. White, *J. Chem. Soc.*, 343 (1951); G. Hargreaves and L. H. Sutcliffe, *Trans. Faraday Soc.*, **51**, 786 (1955).

[5] G. Hargreaves and L. H. Sutcliffe, *ibid.*, **51**, 1105 (1955).

[6] F. H. Pollard and R. M. H. Wyatt, *ibid.*, **45**, 760 (1949); F. H. Pollard and P. Woodward, *ibid.*, **45**, 767 (1949).

[7] E. C. A. Horner and D. W. G. Style, *ibid.*, **50**, 1197 (1954); E. C. A. Horner, D. W. G. Style and D. Summars, *ibid.*, **50**, 1201 (1954); J. C. Ghosh and S. K. Nandy, *J. Indian Chem. Soc.*, **6**, 975 (1929).

[8] R. J. Williams and M. A. Woods, THIS JOURNAL, **59**, 1408 (1937).

[9] J. H. Payne and G. F. Lemon, *ibid.*, **63**, 226 (1941); L. Reiner, *Z. anorg. allgem. Chem.*, **141**, 363 (1925).

[10] N. N. Melnikov and M. S. Rokitskaya, *J. Gen. Chem., U.S.S.R.*, **7**, 2738 (1937); see G. R. Waitkins and C. W. Clark, *Chem. Revs.*, **36**, 250 (1945).

[11] F. C. Tompkins, *Trans. Faraday Soc.*, **39**, 280 (1943); K. B. Wiberg and R. Stewart, THIS JOURNAL, **77**, 1786 (1955).

[12] A. Y. Drummond and W. A. Waters, *J. Chem. Soc.*, 435 (1953).

[13] C. A. McDowell and J. H. Thomas, *Trans. Faraday Soc.*, **46**, 1030 (1950); A. E. Pedler and F. H. Pollard, *ibid.*, **53**, 44 (1957).

[14] C. E. H. Bawn and J. B. Williamson, *ibid.*, **47**, 721 (1951); **47**, 735 (1951); J. B. Farmer and C. A. McDowell, *ibid.*, **48**, 624 (1952).

[15] E. Lucchi, *Boll. sci. facolta chim. ind. Bologna*, **II**, 208 (1940); **II**, 333 (1940); **2**, 165 (1941); *Gazz. chim. ital.*, **71**, 729, 752 (1941).

[16] V. Antony and A. C. Chatterji, unpublished work.

Since A.R. formaldehyde is not suitable for kinetic work as it contains about 10% methyl alcohol which was found to be reactive toward chromic acid, stock solutions were prepared freshly for each experiment by decomposing paraformaldehyde (Merck) with barium peroxide (Merck) and collecting the gas in ice-cold conductivity water. Concentrations were then estimated by iodine titration.[17]

Perchloric acid (Thomas Tyrer & Co.) solutions were prepared in conductivity water and standardized against carbon dioxide-free sodium hydroxide. All other chemicals were either B.D.H. or Merck (C.P.) and were further purified, if necessary.

(2) **Kinetic Study.**—The thermostat was controlled within 0.05°. The progress of the reaction was followed by pipetting out 25-cc. aliquot portions of the reaction mixture at regular intervals into ice-cold water containing potassium iodide and then adding 5 cc. of about 9% A.R. hydrochloric acid and titrating the liberated iodine against standard thiosulfate.

(3) **Identification and Estimation of Product of the Reaction.**—Formic acid was the main product of oxidation as detected by the chromotropic acid reaction. In an experiment the chromic acid was taken in excess (10 cc. of 1.00 *N* chromic acid, 5 cc. of 0.7346 *N* formaldehyde, 20 cc. of 1.359 *N* perchloric acid and 15 cc. of water) and after completion of the reaction (2 days) the reaction mixture was distilled and the fraction between 99–102° was collected. This solution was first tested for formaldehyde, if any, by the chromotropic acid reaction, which was negative. A portion of the solution was then reduced with magnesium and hydrochloric acid and again tested for formaldehyde, which confirmed the formation of formic acid.[18] Formic acid was then estimated by conductometric titration of mixed acids containing liberated formic acid and the unused portion of the perchloric acid.[19]

Ten cc. of 1.00 *N* chromic acid, 20 cc. of 0.58 *N* perchloric acid and 40 cc. of 0.6779 *N* formaldehyde were taken in a 100-cc. volumetric flask and the mixture was made up to the final volume. The solution was then allowed to stand for about 4 days at room temperature and then 10 cc. of the solution was titrated with standard carbon dioxide-free sodium hydroxide solution conductometrically. The yield of formic acid has been found to be 92.3%. It may be concluded that complete oxidation to formic acid occurs.

Order of the Reaction and Temperature Coefficient.—The order with respect to chromic acid, formaldehyde and H^+ ions has been determined by the same method as applied in the case of alcohols.[20] The order with respect to chromic acid, formaldehyde and H^+ ions has been found to be first, first and second at all hydrogen ion concentrations (0.02–0.5 *M*). The velocity constants of the reaction with respect to chromic acid have been calculated using natural logarithms at various concentrations and temperatures. From these values the order, temperature coefficient and energy of activation were calculated. The values of rate constants, as shown in the tables, represent the mean values. The summarized results are given in the Tables I and II.

Effect of Light.—While studying the reaction in the dark, the bottle in which the reaction was carried out was covered with several layers of black glazed paper. For studying the reaction in the light the bottle was exposed to light from a 500 watt tungsten filament lamp placed 20 to 30 cm. away. No evidence was found for any appreciable photochemical reaction in this oxidation process in presence of perchloric acid.

Effect of Metallic Salts on the Oxidation Rate.—The reaction was studied in the presence of small quantities of metallic salts. The difference in the velocity constants with respect to chromic acid of the reaction in the presence of the salt from that in the absence of the salt shows the effect of the salt used. The results are given in Table III. The quantity of salt used in each case was approximately 0.1 g. The result shows that the retarding action of $MnSO_4$, $MnCl_2$, $Ce(NO_3)_3$, $(NH_4)_2MoO_4$ and $BeSO_4$ are very pronounced; $AlCl_3$, $CdCl_2$ and $Mg_3(PO_4)_2$ also retard the reaction; $Zr(SO_4)_2$ accelerates the reaction slightly; manganous and cerous salts retard the reaction considerably.

TABLE I

OXIDATION OF FORMALDEHYDE BY CHROMIC ACID AT 35°: ORDER OF REACTION

Order determining reactant	Concn., *M*	Concn. of other reactants, *M*	Mean value of *k*, sec.$^{-1}$	Order	Total order
Chromic acid	0.0005	Formaldehyde,	9.13×10^{-4}	1	
	.001	0.0583	9.05×10^{-4}	1	
	.002	Perchloric	8.51×10^{-4}	1	
	.005	acid, 0.2175	7.58×10^{-4}	1	
	.01		6.51×10^{-4}	1	
Formaldehyde	0.0104	Chromic acid,	1.29×10^{-4}	1.01	
	.0208	0.002	2.60×10^{-4}		
	.0278	Perchloric	3.46×10^{-4}	0.99	
	.0417	acid, 0.2175	5.33×10^{-4}	1.06	
	.0568		8.13×10^{-4}	1.36	
	.0757		1.10×10^{-3}	1.07	
Perchloric acid	0.0217	Formaldehyde,	1.45×10^{-5}	1.93	Four at all hydrogen ion concn.
	.0544	0.0686	8.52×10^{-5}		
	.1087	Chromic acid,	2.87×10^{-4}	1.75	
	.2175	0.002	1.12×10^{-3}	1.97	
	.3263		2.28×10^{-4}	1.89	
	.4350		3.76×10^{-3}	1.71	

TABLE II

OXIDATION OF FORMALDEHYDE BY CHROMIC ACID: TEMPERATURE COEFFICIENT AND ENERGY OF ACTIVATION

Concn. of the reactants[a]	Temp. range, °C.	Mean values of $k \times 10^3$, sec.$^{-1}$	Temperature coefficient	Energy of activation, kcal.
a	25–35	1.00 1.65	1.65	9.1
a	35--45	1.65 2.71	1.64	9.6
a	45–55	2.71 4.06	1.50	8.4
b	25–35	0.519 0.862	1.66	9.3
b	35–45	0.862 1.39	1.61	9.3
b	45–55	1.39 2.28	1.64	10.3
c	25–35	1.16 1.83	1.58	8.3
c	35–45	1.83 3.19	1.74	10.8

[a] a, 0.1099 *M* formaldehyde, 0.002 *M* chromic acid, 0.2175 *M* perchloric acid; b, 0.0584 *M* formaldehyde, 0.002 *M* chromic acid, 0.2175 *M* perchloric acid; c, 0.0393 *M* formaldehyde, 0.002 *M* chromic acid, 0.4350 *M* perchloric acid.

TABLE III

EFFECT OF METALLIC SALTS ON THE OXIDATION OF FORMALDEHYDE BY CHROMIC ACID AT 35°

Formaldehyde, 0.0899 *M*; chromic acid, 0.002 *M*; perchloric acid, 0.2175 *M*

Metallic salt	$k \times 10^3$, sec.$^{-1}$	Metallic salt	$k \times 10^3$, sec.$^{-1}$
No catalyst	1.45	Manganous sulfate	0.672
Aluminum chloride	1.25	Manganous chloride	0.587
Ammonium molybdate	0.843	Magnesium phosphate	1.25
Beryllium sulfate	1.13	Molybdic acid	1.44
Boric acid	1.44	Nickel chloride	1.37
Cobalt chloride	1.40	Titanium oxide	1.47
Cadmium chloride	1.28	Zirconium sulfate	1.52
Cerous nitrate	0.707		

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[17] W. M. Cumming, I. V. Hopper and T. S. Wheeler, "Systematic Organic Chemistry, Modern Methods of Preparation and Estimation," Constable and Co., Ltd., London, 1950, p. 492.

[18] F. Feigl, "Qualitative Analysis by Spot Tests—Inorganic and Organic Applications" (translated by R. E. Oesper), Elsevier Publ. Co., Amsterdam, 1947, p. 395.

[19] *Cf.* "Organic Analysis," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1954, pp. 1–6.

[20] V. Antony and A. C. Chatterji, *Proc. Nat. Acad. Sciences, India*, **23A**, 20 (1954); *Z. anorg. allgem. Chem.*, **280**, 110 (1955); *Z. physik. Chem.*, in press.

Effect of Formic Acid.—Rate constants with respect to chromic acid have been calculated for the reaction in the absence and in the presence of various amounts of formic acid. It increases the rate slightly (Table IV). This may be partly due to its oxidation and partly due to its contribution of a small amount of hydrogen ions, which accelerate the reaction.

TABLE IV

EFFECT OF ADDING FORMIC ACID ON THE OXIDATION RATE AT 35°

Formaldehyde, 0.0827 *M*; chromic acid, 0.002 *M*; perchloric acid, 0.2175 *M*

Init. concn. of formic acid, *M*	0.0000	0.0850	0.1699	0.3398
$k \times 10^4$, sec.$^{-1}$	1.26	1.34	1.36	1.45

Induction Factor.—Definite amounts of formaldehyde, chromic acid, manganous sulfate and perchloric acid were pipetted into erlenmeyer flasks. The reaction was allowed to proceed to completion at room temperature (2 to 4 days). It was noticed that a small amount of manganese dioxide, formed during the reaction, dissolves gradually as the reaction proceeds further. The reaction mixture was, therefore, filtered and the chromic acid content in the filtrate was estimated iodometrically. The amount of formaldehyde oxidized is known directly from the amount of formaldehyde added. The amount of manganous sulfate oxidized is known from the amount of chromic acid reduced after making allowance for the oxidation of formaldehyde.

$$\text{I.F.} = \frac{\text{cc. of } 0.1\ N\ \text{Mn}^{++}\ \text{oxidized}}{\text{cc. of } 0.1\ N\ \text{HCHO oxidized}}$$

TABLE V

INDUCED OXIDATION OF MANGANOUS SULFATE TO MANGANESE DIOXIDE: INDUCTION FACTOR

10 cc. of 0.1000 *N* chromic acid, 10 cc. of 0.5000 *N* $MnSO_4$, 10 cc. of 0.5800 *N* $HClO_4$; final volume in each case was 35 cc.; time = 100 hours, strength of formaldehyde = 0.1149 *N*, strength of thiosulfate = 0.1026 *N*.

Vol., cc., of formaldehyde	Vol., cc., of thiosulfate	Equiv. of Mn^{++} oxidized	Equiv. of HCHO oxidized	Induction factor
5.0	3.30	0.870	5.745	0.15
4.0	4.40	.891	4.596	.19
3.0	5.60	.809	3.447	.23
2.0	6.75	.779	2.298	.34
1.0	8.05	.603	1.149	.51

Discussion

The order of the reaction has been found to be fourth at all hydrogen ion concentrations. The results are in conformity with the previous work on the oxidation of monohydric[20,21] and dihydric[22] alcohols by chromic acid. As we increase the concentration of chromic acid from 0.0005 to 0.01 *M*, the values of velocity constants decrease (Table I). This effect may be correlated with the hydrolysis of the dichromate ion represented by the equation

$$Cr_2O_7^{=} + H_2O \rightleftarrows 2HCrO_4^-$$

The explanation given by Westheimer and Novick[21] is probably the correct one here also.

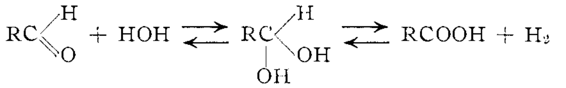
The temperature coefficient of the reaction between 25 and 35° has been found to be 1.65. This value corresponds fairly well with the value for a quadrimolecular reaction.[23] The induction factor has been found to be 0.5, indicating that Cr^{4+} ion is the active oxidizing agent.[24,25] Cerous salt also retards the reaction. Since the only known valence states of cerium are 3 and 4, the valence of cerium must be increased by one during the reaction. Hence the Ce^{3+} salt probably reacts with a compound containing Cr^{4+}. This conclusion is consistent with the general mechanism.[26]

The stoichiometry for the oxidation of formaldehyde by chromic acid in acid solution may be expressed by the equation

$$2HCrO_4^- + 3HCHO + 8H^+ \longrightarrow 2Cr^{+++} + 3HCOOH + 5H_2O$$

The results obtained both from chemical kinetics and temperature coefficients show that in the oxidation of formaldehyde studied here, one molecule of acid chromate ion, one molecule of formaldehyde and two ions of hydrogen are involved in the rate-determining step.

Wieland[27] pointed out that the majority of oxidation reactions of organic compounds are dehydrogenations. He observed that the oxidations of aldehydes are in reality dehydrogenation of aldehyde hydrate[28] and the function of the oxidizing agent is to act as a hydrogen acceptor



$$RC\begin{smallmatrix}H\\O\end{smallmatrix} + HOH \rightleftarrows RC\begin{smallmatrix}H\\OH\\OH\end{smallmatrix} \rightleftarrows RCOOH + H_2$$

It is known that water adds to aldehydes and sometimes stable hydrates were detected.[29,30] During the course of the study on the oxidation of formaldehyde by hydrogen peroxide, Wieland and Wingler[1] found that a peroxide, dihydroxymethyl peroxide, is formed as an intermediate product, also obtained by Legler.[31] Results of Wirtz and Bonhoeffer[2] also support the Wieland–Wingler mechanism; by use of the deuteriohydrogen peroxide they found that the evolved gas was hydrogen and not deuterium. Merz and Waters[32] also found that the aldehydes react in their hydrated form, $R{-}CH(OH)_2$.

It was found by Bieber and Trümpler[33] that aqueous formaldehyde solutions in concentrations less than 1 *M* consist almost entirely of $CH_2(OH)_2$. The mechanism of oxidation of formaldehyde by chromic acid may, therefore, be represented as

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(21) *Cf.* F. H. Westheimer and A. Novick, *J. Chem. Phys.*, **11**, 506 (1943).

(22) A. C. Chatterji and S. K. Mukherjee, *Z. physik. Chem.*, **207**, 372 (1957); *ibid.*, in press.

(23) N. R. Dhar, *Z. anorg. allgem. Chem.*, **128**, 218 (1923).

(24) F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949); Errata, June (1950).

(25) W. Watanabe and F. H. Westheimer, *J. Chem. Phys.*, **17**, 61 (1949).

(26) F. H. Westheimer, J. Hampton and A. Leo, THIS JOURNAL, **78**, 306 (1956).

(27) H. Wieland, *Ber.*, **54**, 2353 (1921); **55**, 3639 (1922); *J. Chem. Soc.*, 1055 (1931).

(28) H. Wieland and D. Richter, *Ann.*, **495**, 284 (1932).

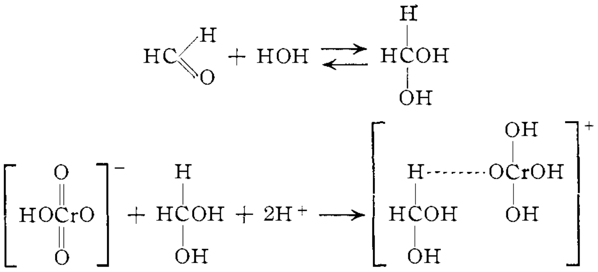
(29) R. P. Bell and co-workers, *Trans. Faraday Soc.*, **46**, 34 (1950); **48**, 439 (1952); **52**, 1093 (1956); *Bull. soc. chim.*, **115**, 115 (1955).

(30) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 366.

(31) L. Legler, *Ann.*, **217**, 381 (1883).

(32) J. H. Merz and W. A. Waters, *Disc. Faraday Soc.*, **No. 2**, 186 (1947).

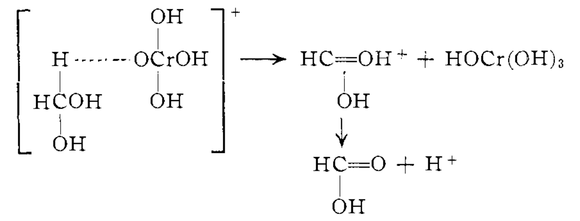
(33) R. Bieber and G. Trümpler, *Helv. Chim. Acta*, **30**, 1860 (1947); *C. A.*, **43**, 940e (1949).



$$HC\begin{smallmatrix}H\\O\end{smallmatrix} + HOH \rightleftarrows H\overset{H}{\underset{OH}{C}}OH$$

$$\left[HO\overset{O}{\underset{O}{Cr}}O\right]^- + H\overset{H}{\underset{OH}{C}}OH + 2H^+ \longrightarrow \left[\begin{array}{ll} H\cdots\cdots & O\overset{OH}{\underset{OH}{Cr}}OH \\ H\underset{OH}{C}OH & \end{array}\right]^+$$

The intermediate complex then decomposes through the oxonium compound



$$\left[\begin{array}{ll} H\cdots\cdots & O\overset{OH}{\underset{OH}{Cr}}OH \\ H\underset{OH}{C}OH & \end{array}\right]^+ \longrightarrow H\underset{OH}{C}{=}OH^+ + HOCr(OH)_3$$

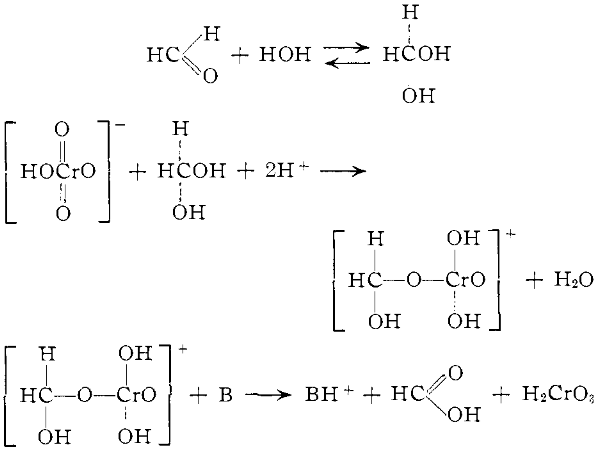
$$\downarrow$$

$$H\underset{OH}{C}{=}O + H^+$$

Since the oxidation of an aldehyde to an acid may be accomplished by the same reagents which convert alcohols to aldehydes, it is expected that both the mechanisms are probably similar. This hydride abstraction mechanism is similar to that suggested for the oxidation of monohydric alcohols by chromic acid.[20,24]

Recently Westheimer and co-workers,[34] during the course of their study on the oxidation of isopropyl alcohol by chromic acid, postulated that an ester of the alcohol and chromic acid is an essential intermediate in that oxidation reaction. They arrived at this conclusion from the important observations: 1. A chromic acid ester of isopropyl alcohol can be prepared in benzene or toluene solutions. 2. In aqueous solution the reaction is catalyzed by pyridine.

Taking their view to be correct, Wiberg and Stewart[11,35] have suggested an ester formation mechanism for the oxidation of benzaldehyde by chromic acid and of substituted benzaldehydes by potassium permanganate. If this view be accepted then the mechanism of oxidation of formaldehyde by chromic acid may also be represented as



$$HC\begin{smallmatrix}H\\O\end{smallmatrix} + HOH \rightleftarrows H\overset{H}{\underset{OH}{C}}OH$$

$$\left[HO\overset{O}{\underset{O}{Cr}}O\right]^- + H\overset{H}{\underset{OH}{C}}OH + 2H^+ \longrightarrow \left[H\overset{H}{\underset{OH}{C}}{-}O{-}\overset{OH}{\underset{OH}{Cr}}O\right]^+ + H_2O$$

$$\left[H\overset{H}{\underset{OH}{C}}{-}O{-}\overset{OH}{\underset{OH}{Cr}}O\right]^+ + B \longrightarrow BH^+ + HC\begin{smallmatrix}O\\OH\end{smallmatrix} + H_2CrO_3$$

This mechanism is slightly different from that proposed by Wiberg and Stewart. Here the ester is formed by utilizing the oxygen of aldehyde, whereas in their case the oxygen of the oxidizing agent forms the ester bond.

As the two hydrogen ions attach themselves to the oxygen atoms of the acid-chromate ion, the removal of a hydrogen atom with an electron pair from the aldehyde molecule is facilitated.[21] Waters[36] observed that chromic acid is essentially a dehydrogenator that abstracts uncharged hydrogen atoms from the organic molecules.

Wiberg[35] observed that in the oxidation of benzaldehyde by chromic acid, the rate-determining step involves the cleavage of C–H bond of the carbonyl group, as indicated by the deuterium isotope effect; the aldehyde in which the aldehyde hydrogen had been replaced by deuterium was found to be oxidized at a much slower rate than the unlabeled compound. A similar deuterium isotope effect was also observed in the case of oxidation of acetaldehyde by chromic acid[37] and in the case neutral and acid-catalyzed oxidation of aromatic aldehydes by potassium permanganate.[11] It has been assumed, therefore, that in the case of oxidation of formaldehyde by chromic acid also the rate-determining step involves the cleavage of aldehyde C–H bond.

Preliminary experiments failed to detect any formation of chromic acid ester of formaldehyde hydrate in benzene or carbon tetrachloride solutions. Although the chromic acid ester (of the hemiacetal type) could not be isolated, it cannot be concluded that such compounds are not formed. The study on the effect of pyridine in buffered solutions on the oxidation rate is in progress. Preliminary observations reveal that pyridine accelerates the reaction, showing thereby the ester mechanism is more probable.

The following general scheme for the mechanism of oxidation of formaldehyde by chromic acid may be formulated as

$$HCrO_4^- + CH_2(OH)_2 \longrightarrow Cr^{4+} + HCOOH$$
$$Cr^{4-} + Cr^{6+} \longrightarrow 2Cr^{5+}$$

and

$$Cr^{5+} + CH_2(OH)_2 \longrightarrow Cr^{3+} + HCOOH$$

or

$$2Cr^{4+} + CH_2(OH)_2 \longrightarrow 2Cr^{3+} + HCOOH$$

or

$$Cr^{4+} + CH_2(OH)_2 \longrightarrow Cr^{2+} + HCOOH$$
$$Cr^{2+} + Cr^{6+} \longrightarrow Cr^{5+} + Cr^{3+}$$
$$Cr^{5+} + CH_2(OH)_2 \longrightarrow Cr^{3+} + HCOOH$$

In presence of manganous sulfate the reaction may take place as

$$HCrO_4^- + CH_2(OH)_2 \longrightarrow Cr^{4-} + HCOOH$$
$$Cr^{4+} + Mn^{2+} \longrightarrow Cr^{3+} + Mn^{3+}$$
$$2Mn^{3+} + 2H_2O \longrightarrow MnO_2 + Mn^{2+} + 4H^+$$

In presence of cerous salts the following mechanism is suggested

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(34) F. Holloway, M. Cohen and F. H. Westheimer, THIS JOURNAL, **73**, 65 (1951).

(35) K. B. Wiberg, *ibid.*, **76**, 5371 (1954).

(36) W. A. Waters, *Trans. Faraday Soc.*, **42**, 184 (1946).

(37) J. W. Cornforth and G. Popjäk, *Nature*, **164**, 1053 (1949); K. B. Wiberg, *Chem. Revs.*, **55**, 728 (1955).

$$HCrO_4^- + CH_2(OH)_2 \longrightarrow Cr^{4+} + HCOOH$$

$$Cr^{4+} + Ce^{3+} \longrightarrow Cr^{3+} + Ce^{4+}$$

The hydrogen ions, which act as a catalyst, are omitted for the sake of convenience. These are almost similar to that proposed in the case of oxidation of monohydric alcohols.[20,24,25]

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Fluorocarbon Nitrogen Compounds. III.[1] Some Reactions of Bis-(trifluoromethyl)-amine, $(CF_3)_2NH$[2]

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Because of the reduction in base strength caused by the two CF_3 groups, bis-(trifluoromethyl)-amine, $(CF_3)_2NH$, does not react normally with the usual amine reagents. In most reactions it tends to reverse the method of synthesis and revert to $CF_3N{=}CF_2$ and HF; however, it can be nitrated to give $(CF_3)_2N{\cdot}NO_2$. Reaction of the mercury derivative, $(CF_3)_2NHgN(CF_3)_2$, which is made indirectly by addition of HgF_2 to $CF_3CF{=}CF_2$, with chlorine or bromine gives the corresponding $(CF_3)_2NX$ derivatives. These cannot be made by direct halogenation. $(CF_3)_2NBr$ adds easily across the double bond of $CF_3CF{=}CF_2$. With inorganic halides of the type MCl_3, the products are HCl, MF_3 and $CF_3N{=}CCl_2$.

Although hydrocarbon alkyls of nitrogen form only one series of compounds, the amines (RNH_2, R_2NH, R_3N), perfluoroalkyls of nitrogen form two series, the nitrides (R_FNF_2, $(R_F)_2NF$, $(R_F)_3N$) and the amines (R_FNH_2, $(R_F)_2NH$, $(R_F)_3N$). The tertiary compounds in the two fluorocarbon series are obviously identical and are properly classed with the inert nitrides, while the primary amines apparently lose HF so easily that none has yet been isolated as such. Of the true fluorocarbon amines, therefore, only the secondary compounds are available for study. Although fluorocarbon secondary amines have been known since 1940, when Ruff inadvertently prepared $(CF_3)_2NH$,[4] very little has been published concerning their chemistry. This paper describes some reactions and derivatives of the first member of the series, $(CF_3)_2NH$.

Bis-(trifluoromethyl)-amine (I), which was prepared easily by addition of HF to perfluoro-2-azapropene, $CF_3N{=}CF_2$ (II), boils at −6°, twelve degrees lower than dimethylamine. This boiling point lowering is presumably due to decreased hydrogen bonding; the reduced basicity of the nitrogen atom, of which this is one indication, is a chief cause of the wide chemical dissimilarity between the two compounds. Compound I did not form a hydrohalide with HCl and did not give a solid addition product with boron trifluoride, being in the latter respect even less basic than II. It did not react under normally mild conditions with the acid chloride or anhydride of trifluoroacetic acid and could be distilled unchanged from its solution in anhydrous CF_3COOH, although in the last case it became necessary to heat the solution considerably above room temperature in order to drive off the amine completely.

In contrast to its unreactivity toward the usual amine reagents, compound I was entirely destroyed by exposure to water and aqueous acids or bases. The decomposition probably proceeds by initial loss of HF and subsequent hydrolysis of the II so formed, according to equation 1.

$$(CF_3)_2NH \xrightarrow{-HF} CF_3N{=}CF_2 \xrightarrow{H_2O} CF_3N{=}C{=}O \xrightarrow{H_2O} F^-, CO_2, NH_3 \quad (1)$$

There is considerable evidence in support of this sequence,[5] which includes intermediate isocyanate formation, rather than that originally proposed by Barr and Haszeldine,[6] in which $CF_3N{=}CF_2$ was thought to be converted by water directly to CF_3NH_2 and COF_2. In the present work, if conditions were not completely anhydrous during nitration, formation of II from I could be observed (step 1). Furthermore, II could be converted to the isocyanate by careful treatment with water (step 2), either by reaction in the vapor phase at low pressure[5] or, better, by heating II with a slowly acting source of water such as a hydrated metallic fluoride.[7] The first two steps of this hydrolysis mechanism therefore can be considered to be experimentally verified. Its further course is less well established, but may involve either degradation through a carbamic acid structure,[5] or antecedent hydrolytic attack on fluorine.[8] All the fluorine is eventually converted to fluoride ion.

Related to this series is perfluorodimethyl carbamyl fluoride, which is thought to decompose by way of the same intermediates, as in reactions 2 and 3.

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(1) For the preceding paper in this series, see J. A. Young and R. D. Dresdner, THIS JOURNAL, **80**, 1889 (1958).

(2) Presented before the Southeast Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14–16, 1957. This work was supported by a grant from the Office of Naval Research, and reproduction in whole or in part is permitted for any purposes of the United States Government.

(3) This paper includes work done by Skevos N. Tsoukalas in partial fulfillment of the requirements for the M.S. degree, University of Florida

(4) O. Ruff and W. Willenberg, *Ber.*, **73**, 724 (1940).

(5) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956).

(6) D. A. Barr and R. N. Haszeldine, *ibid.*, 1881, 2532 (1955).

(7) Details of this preparation will be presented in a forthcoming paper.

(8) R. L. Dannley and R. G. Taborsky, *J. Org. Chem.*, **22**, 77 (1957).