

TABLE VI

RELATIVE RATES OF REDUCTION OF ORGANIC HALIDES BY TRI-*n*-BUTYLTIN HYDRIDE AT 45°

Expt.	Competitor A	Competitor B	Solvent	$k_B/k_A$
1	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	2-BrC <sub>8</sub> H <sub>17</sub>	C <sub>6</sub> H <sub>6</sub> CH <sub>3</sub>	2.63
2	1-BrC <sub>8</sub> H <sub>17</sub>	2-BrC <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	2.72
3	<i>n</i> -BrC <sub>4</sub> H <sub>9</sub>	1-BrC <sub>8</sub> H <sub>17</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	1.10
4	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Br	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	7.56
5	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	<i>t</i> -C <sub>4</sub> H <sub>9</sub> Br	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	6.79
6	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	Cyclo-C <sub>6</sub> H <sub>11</sub> Br	Cyclo-C <sub>6</sub> H <sub>12</sub>	1.46
7	<i>n</i> -C <sub>4</sub> H <sub>9</sub> Br	Cyclo-C <sub>8</sub> H <sub>9</sub> Br	Cyclo-C <sub>8</sub> H <sub>12</sub>	2.37
8	BrCH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.30
9	BrCH <sub>2</sub> Cl	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.30
10	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	CCl <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> Cl	2.16
11	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	CCl <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> Br	2.38
12	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	CCl <sub>4</sub>	C <sub>6</sub> H <sub>5</sub> Br	2.14
13	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCHCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	3.18
14	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCHCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	3.50
15	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCHCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	3.30
16	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCHCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	3.26
17	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCHCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	3.42
18	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCHCl <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> Br	3.50
19	CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.15
20	CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.09
21	CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.04
22	CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.13
23	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCH <sub>2</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub> Cl	1.28
24	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	BrCH <sub>2</sub> CO <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	1.80
25	2-BrC <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	10.4
26	2-BrC <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	11.1
27	2-BrC <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	11.3
28	2-BrC <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	12.0
29	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	1-IC <sub>3</sub> H <sub>15</sub>	C <sub>6</sub> H <sub>5</sub> Br	1.95
30	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	1-IC <sub>3</sub> H <sub>15</sub>	C <sub>6</sub> H <sub>5</sub> Br	1.70
31	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2-BrC <sub>4</sub> H <sub>9</sub>	C <sub>6</sub> H <sub>5</sub> Br	54.6
32	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	CH <sub>2</sub> =CHCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.01
33	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.21
34	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	<i>m</i> -BrC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Cl	1.18
35	BrCHCl <sub>2</sub>	BrCCl <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	1.97
36	BrCHCl <sub>2</sub>	BrCCl <sub>3</sub>	C <sub>6</sub> H <sub>5</sub> Br	2.06
37	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	HC≡CCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	3.96
38	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	HC≡CCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	3.98
39	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	HC≡CCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	4.33
40	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Br	HC≡CCH <sub>2</sub> Br	C <sub>6</sub> H <sub>5</sub> Br	4.34

umn of 40% dimethyl sulfolane on firebrick (40 mesh) with results shown in Table II.

**Reduction of Optically Active  $\alpha$ -Phenylethyl Chloride by Triphenyltin Deuteride.**—To 17.5 mmoles of  $\alpha$ -phenylethyl chloride,  $\alpha^{27}\text{D} + 40.18^\circ$  (neat), was added 19.2 mmoles of triphenyltin deuteride, prepared by reduction of the chloride with lithium aluminum deuteride, and the mixture was allowed to stand at room temperature for 23 hr., during which time crystals of triphenyltin chloride formed in the flask. After heating on the steam bath for 4 hr. to ensure complete reaction the product was distilled yielding 1.41 g. of  $\alpha$ -deuteriophenylethane, b.p. 65–67° at 77–80 mm.,  $\alpha^{27}\text{D} 0.02^\circ \pm 0.03^\circ$  (neat). A control experiment showed no detectable racemization of the optically active chloride by the organotin chloride under the conditions of the reduction reaction.

**Determination of Relative Reactivities of Halides.**—The relative rate constants were determined by allowing the halides

TABLE VII

RELATIVE RATES OF REDUCTION BY TRI-*n*-BUTYLTIN HYDRIDE AT 80 ± 2° CATALYZED BY 1.6% AZOBISISOBUTYRONITRILE<sup>a</sup>

Expt.	Competitor A	Competitor B	$k_B/k_A$
41	C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	1.21
42	C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	1.26
43 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	1.48
44 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> Br	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	1.55
45	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2-BrC <sub>4</sub> H <sub>9</sub>	34.4
46	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2-BrC <sub>4</sub> H <sub>9</sub>	34.5
47 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2-BrC <sub>4</sub> H <sub>9</sub>	32.2
48 <sup>b</sup>	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	2-BrC <sub>4</sub> H <sub>9</sub>	32.0
49	CH <sub>2</sub> =CHCH <sub>2</sub> Cl	2-BrC <sub>8</sub> H <sub>17</sub>	15.4
50	CH <sub>2</sub> =CHCH <sub>2</sub> Cl	2-BrC <sub>8</sub> H <sub>17</sub>	17.3
51	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	CH <sub>2</sub> =CH <sub>2</sub> --CH <sub>2</sub> Cl	1.83
52	HC≡C--CH <sub>2</sub> Cl	2-BrC <sub>8</sub> H <sub>17</sub>	4.71
53	HC≡C--CH <sub>2</sub> Cl	2-BrC <sub>8</sub> H <sub>17</sub>	5.57
54	HC≡C--CH <sub>2</sub> Cl	2-BrC <sub>8</sub> H <sub>17</sub>	4.46
55	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	1.60
56	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> Cl	1.68
57	2-BrC <sub>8</sub> H <sub>17</sub>	BrCH <sub>2</sub> Cl	7.95
58 <sup>c</sup>	2-BrC <sub>8</sub> H <sub>17</sub>	BrCH <sub>2</sub> Cl	8.40
59 <sup>b</sup>	2-BrC <sub>8</sub> H <sub>17</sub>	BrCH <sub>2</sub> Cl	8.66

<sup>a</sup> In cumene as solvent. <sup>b</sup> Reactions conducted without the addition of azobisisobutyronitrile. <sup>c</sup> In bromobenzene as solvent.

to compete in pairs for an insufficient amount of hydride. Usually a half-mole of hydride was used per mole of halide. The competitors and an internal standard were placed in the reaction flask or ampoule followed by solvent and organotin hydride. The reaction vessel was kept in a constant temperature bath until all of the hydride was consumed as indicated by the absence of hydrogen evolution upon treatment with an ethereal solution of sulfuric acid. Analysis for unreacted halide and/or reduction product was made by gas chromatography using the internal standard method described by Keulemans.<sup>26</sup> A 4-ft. column packed with 20% paraffin oil on Chromosorb P (80–100 mesh) was used in most experiments. When *m*-trifluoromethylbenzyl chloride and benzyl chloride were the competitors a 4-ft. column packed with 17% silicone nitrile on Chromosorb P (60–80 mesh) was used. Relative rate constants were computed by the method of Ingold and Shaw.<sup>16</sup> In most cases the solvent was chlorobenzene or bromobenzene. For analytical convenience other solvents were used on occasion; these included toluene, cumene, cyclohexane, and 2,3-dimethylbutane. When using bromochloromethane and 2-bromooctane as competitors, the same relative rate constants were obtained with cumene and bromobenzene as solvents, indicating that the relative rates would vary little among the solvents used. Results of the individual competition experiments are given in Tables VI and VII.

(26) A. I. M. Keulemans, "Gas Chromatography," Reinhold Publishing Corp., New York, N. Y., 1957, p. 32.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8, CAN.]

## The Nature of Chromium(VI) in Acid Solution and Its Relation to Alcohol Oxidation<sup>1</sup>

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A spectroscopic investigation of the variation of the  $pK_a$  of chromic acid with changes in the identity of the mineral acid solvents has been made, and the results have been applied to explain observed variations in the rate of oxidation of isopropyl alcohol in solutions of different mineral acids. Protonation of the acid chromate ion is accompanied by incorporation of the mineral acid anion into the chromium(VI) species and this markedly affects the latter's oxidizing ability. The mechanism of the chromium(VI)-alcohol reaction in moderately concentrated aqueous solutions of mineral acid, HA, is believed to occur by a cyclic, unimolecular decomposition of the chromate ester, R<sub>2</sub>CHOCrO<sub>2</sub>AH<sup>+</sup>.

### Introduction

The mechanism of chromic acid oxidations of organic substrates has been extensively investigated by a large number of workers. Most commonly mechanistic

deductions have been drawn from the observation of changes in kinetic rate data that occurred when the

(1) From part of the Ph.D. Thesis of D. G. Lee, the University of British Columbia, 1963.

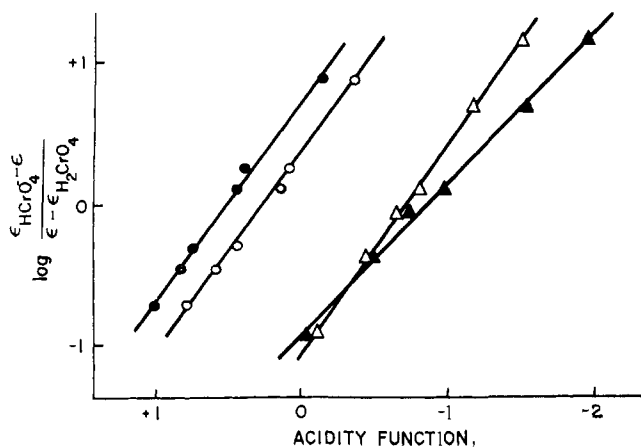


Fig. 1.—Ionization plots for chromic acid dissolved in (a) sulfuric acid (plotted against  $H_0$ ,  $\circ$ , and against  $H_-$ ,  $\bullet$ ) and (b) perchloric acid (plotted against  $H_0$ ,  $\Delta$ , and against  $H_-$ ,  $\blacktriangle$ ).

structure of the organic substrate was altered in some way.<sup>2</sup> Some attention has also been directed toward environmental influences on the nature of the chromium(VI) species present in solution. Cohen and Westheimer found that the chlorochromate ion, which is formed in 86.5% acetic acid solutions containing chromium(VI) and chloride ion, was a less active oxidizing agent than the chromium species which existed in this medium in the absence of chloride ion.<sup>3</sup> Holloway has also found spectroscopic evidence for the formation of a complex between chromic acid and phosphoric acid, and Chang and Westheimer have obtained similar evidence for  $\text{CrSO}_7^{2-}$  or its protonated analogs in sulfuric acid solutions containing chromium(VI).<sup>4</sup>

Since such environmental influences appear to affect the rate and perhaps even the mechanism of chromic acid oxidations, it was decided to carry out a systematic investigation of these effects. The present report describes the changes that occur in the structure and properties of the chromium(VI) species as its environment is changed by varying the identity of the mineral acid present with it in aqueous solution. The mineral acids used were phosphoric, sulfuric, hydrochloric, nitric, and perchloric. In addition, the effect of adding sodium perchlorate to some of these solutions was investigated.

### Experimental

**Materials.**—Chromic acid stock solutions were prepared by dissolving weighed amounts of potassium dichromate in definite volumes of distilled water. Mineral acid solutions were prepared from commercially available reagent grade acids. The concentrations of these solutions were determined by titrating with standardized sodium hydroxide solutions. Isopropyl alcohol was refluxed over calcium oxide for 2 hr. and then distilled. A

(2) (a) R. Brownell, A. Leo, Y. W. Chang, and F. H. Westheimer, *J. Am. Chem. Soc.*, **82**, 406 (1960); (b) Y. W. Chang and F. H. Westheimer, *ibid.*, **82**, 1401 (1960); (c) J. Rocek and F. H. Westheimer, *ibid.*, **84**, 2241 (1962); (d) F. Mares and J. Rocek, *Coll. Czech. Chem. Commun.*, **26**, 2389 (1961); (e) J. Rocek, *ibid.*, **25**, 1052 (1960); (f) J. Rocek, *Tetrahedron Letters*, **5**, 1 (1959); (g) K. B. Wiberg and W. H. Richardson, *J. Am. Chem. Soc.*, **84**, 2800 (1962); (h) K. B. Wiberg and R. J. Evans, *Tetrahedron*, **8**, 313 (1960); (i) H. Kwart, J. A. Ford, and G. C. Corey, *J. Am. Chem. Soc.*, **84**, 1252 (1962); (j) H. Kwart, *Suomen Kemi.*, **34A**, 173 (1961); (k) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, **81**, 2116 (1959); (l) H. Kwart and P. S. Francis, *ibid.*, **77**, 4907 (1955); (m) H. Kwart, *Chem. Ind. (London)*, 610 (1962); (n) J. C. Richer, L. A. Pilato, and E. L. Eliel, *ibid.*, 2007 (1961); (o) P. A. Best, J. S. Littler, and W. A. Waters, *J. Chem. Soc.*, 822 (1962); (p) J. Schreiber and A. Eschenmoser, *Helv. Chim. Acta*, **38**, 1529 (1955); (q) H. G. Kuivola and W. J. Becker, *J. Am. Chem. Soc.*, **74**, 5329 (1952).

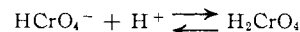
(3) M. Cohen and F. H. Westheimer, *ibid.*, **74**, 4387 (1952).

(4) F. Holloway, *ibid.*, **74**, 224 (1952), and F. H. Westheimer, private communication.

middle fraction boiling at 81.5–82.0° was collected and used for the kinetic experiments.

**Kinetic Method.**—The disappearance of chromium(VI) was followed spectrophotometrically. In each run 3.0 ml. of a chromic acid solution was pipetted into a 1.0-cm. silica cell and thermostated at  $25.0 \pm 0.1^\circ$  in the cell compartment of a Beckman model DU spectrophotometer. A large excess of isopropyl alcohol was then added from a microliter syringe fitted with a Chaney adapter. The solution was mixed thoroughly and the optical density at 444  $m\mu$  was determined at intervals. The optical density at this wave length was corrected for chromium(III) absorption by use of a previously prepared calibration curve and a plot of the logarithm of chromium(VI) concentration against time was prepared. (For oxidations where the chromium(VI) concentration was sufficiently low the peak at 349  $m\mu$  was used and no correction to the optical density was required.)

**Determination of Apparent  $pK_a$  values for  $\text{H}_2\text{CrO}_4$ .**—For the equilibrium



the  $pK_a$  is defined

$$K_a = \frac{a_{\text{HCrO}_4^-} a_{\text{H}^+}}{a_{\text{H}_2\text{CrO}_4}} = \frac{C_{\text{HCrO}_4^-} C_{\text{H}^+} f_{\text{HCrO}_4^-} f_{\text{H}^+}}{C_{\text{H}_2\text{CrO}_4} f_{\text{H}_2\text{CrO}_4}}$$

$$pK_a = \log \frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}} - \log \frac{a_{\text{H}^+} f_{\text{HCrO}_4^-}}{f_{\text{H}_2\text{CrO}_4}}$$

In dilute solutions the last term on the right becomes pH. In more concentrated acid solutions it is commonly denoted as  $H_-^5$ ; i.e.

$$-H_- = \log \frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}} - pK_a$$

From this equation it can be seen that a plot of  $\log (C_{\text{H}_2\text{CrO}_4}/C_{\text{HCrO}_4^-})$  against  $-H_-$  should give a straight line of unit slope and an intercept at the  $pK_a$ . The ratio  $C_{\text{H}_2\text{CrO}_4}/C_{\text{HCrO}_4^-}$  was determined, following the method of Symons, *et al.*,<sup>6</sup> by measuring the extinction coefficient of  $\text{Cr}^{VI}$  at one or more wave lengths over a wide range of acidities. (The term  $C_{\text{H}_2\text{CrO}_4}$  is used to designate the concentration of the chromium species formed when  $\text{HCrO}_4^-$  reacts with acid.) Then if  $\epsilon_{\text{H}_2\text{CrO}_4}$  is the extinction coefficient of a solution of  $\text{H}_2\text{CrO}_4$  at a particular wave length and  $\epsilon_{\text{HCrO}_4^-}$  is the extinction coefficient of a solution of  $\text{HCrO}_4^-$  at the same wave length

$$\frac{C_{\text{H}_2\text{CrO}_4}}{C_{\text{HCrO}_4^-}} = \frac{\epsilon_{\text{HCrO}_4^-} - \epsilon}{\epsilon - \epsilon_{\text{H}_2\text{CrO}_4}}$$

where  $\epsilon$  is the extinction coefficient of a solution containing both  $\text{H}_2\text{CrO}_4$  and  $\text{HCrO}_4^-$ . The particular wave length at which measurements were made was chosen from a comparison of the spectra of the two species such that a maximum change in the extinction coefficient was obtained.

For sulfuric acid, perchloric acid, and hydrochloric acid solutions a plot of

$$\log \frac{\epsilon_{\text{HCrO}_4^-} - \epsilon}{\epsilon - \epsilon_{\text{H}_2\text{CrO}_4}}$$

against  $H_-$  was then prepared and the apparent  $pK_a$  was obtained from the zero intercept (Fig. 1). For solutions of phosphoric acid and nitric acid, where no  $H_-$  functions are available,  $H_0$  was used. The use of  $H_0$  instead of  $H_-$  will introduce some error, since in the cases where both the  $H_-$  and  $H_0$  functions are known, for a particular medium there is a deviation, although this is not great in reasonably dilute solutions. The slopes of the ionization plots were 1.38 for  $\text{H}_2\text{SO}_4$  ( $H_-$ ), 1.04 for  $\text{HClO}_4$  ( $H_-$ ), 1.68 for  $\text{HCl}$  ( $H_-$ ), 0.83 for  $\text{HNO}_3$  ( $H_0$ ), and 1.11 for  $\text{H}_3\text{PO}_4\text{-NaClO}_4$  ( $H_0$ ).

The  $H_0$  and  $H_-$  functions used were those reported by Paul and Long<sup>5</sup> and Boyd,<sup>7</sup> respectively. The acidity function for phos-

(5) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957).

(6) N. Bailey, A. Carrington, K. A. Lott, and M. C. R. Symons, *J. Chem. Soc.*, 290 (1960).

(7) R. H. Boyd, *J. Am. Chem. Soc.*, **83**, 4288 (1961); *J. Phys. Chem.*, **67**, 737 (1963).

phoric acid containing a 1:1 molar ratio of sodium perchlorate was determined in these laboratories.<sup>8</sup>

### Results

The apparent  $pK_a$  of chromic acid determined by plotting  $\log \frac{\epsilon_{\text{HCrO}_4^-} - \epsilon}{\epsilon - \epsilon_{\text{H}_2\text{CrO}_4}}$  against the  $H_-$  function for perchloric acid gave a value of  $-1.01$  which is in good agreement with the value of  $-0.98$  previously determined by Bailey, Carrington, Lott, and Symons.<sup>6</sup> However, the apparent  $pK_a$  varies from one acid medium to another (Table I) and the variation is so large that it cannot merely be a consequence of experimental error. Furthermore, the slope deviation from unity is also considerably greater than that found for simple protonation processes.

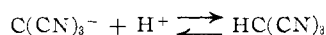
TABLE I

COMPARISON OF THE  $pK_a$  OF CHROMIC ACID IN AQUEOUS SOLUTIONS OF VARIOUS MINERAL ACIDS AND THE POINT OF SLOPE CHANGE IN A PLOT OF  $\log k$  vs.  $H_0$  FOR THESE ACIDS

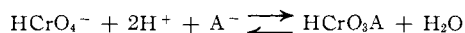
Acid	$pK_a$ , $H_-$ scale	$pK_a$ , $H_0$ scale	$H_0$ value of slope change
HNO <sub>3</sub>		-1.91	-2.45
HClO <sub>4</sub>	-1.10	-0.83	-1.25
H <sub>2</sub> SO <sub>4</sub>	+0.51	+ .34	+0.02
HCl	+0.76	+ .52	+0.59
H <sub>3</sub> PO <sub>4</sub>		+1.74 <sup>a</sup>	+1.10
H <sub>3</sub> PO <sub>4</sub> -NaClO <sub>4</sub> (1:1 molar ratio)		+1.38	+1.35

<sup>a</sup> This value was determined in these laboratories by Miss Min-Min Wei.

The protonation of organic indicators such as the cyanocarbon anions is known to occur by means of a conventional equilibrium step involving a cyanocarbon anion, the corresponding cyanocarbon acid, and a proton.<sup>7</sup>

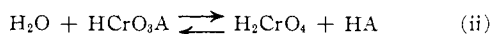
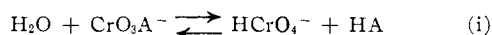


However, the results presented in Table I indicate that in the protonation of an inorganic indicator such as chromate anion some consideration must also be given to the proton source, *i.e.*, the equilibrium appears to be established in such a way that there is a direct involvement of the mineral acid which furnishes the protons.



It is observed that at acidities below the apparent  $pK_a$  of chromic acid the spectral character of chromium(VI) solutions is independent of the proton source. In dilute solutions chromium(VI) shows the same ultraviolet and visible spectrum irrespective of the mineral acid present. However in more concentrated solutions beyond the apparent  $pK_a$  of chromic acid, small but significant differences appear (Fig. 2).

This evidence would seem to indicate that the ion  $\text{CrO}_3\text{A}^-$  is not present in significant concentrations under conditions where the monoanion is the dominant species but that  $\text{HCrO}_3\text{A}$  is the major neutral  $\text{Cr}^{\text{VI}}$



species, *i.e.*, equilibrium i would seem to be to the right but equilibrium ii to the left.<sup>9</sup>

(8) D. G. Lee and R. Stewart, *Can. J. Chem.*, **42**, 486 (1964).

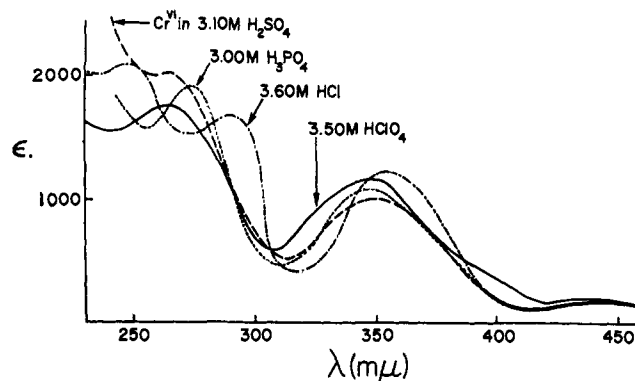
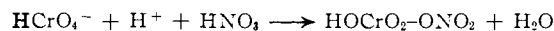
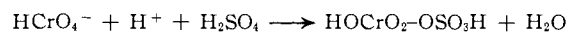
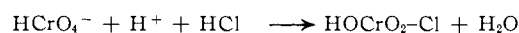
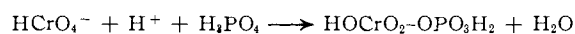


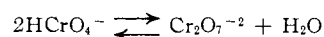
Fig. 2.—Ultraviolet spectrum of chromium(VI) in various aqueous acids: —, 3.50 M HClO<sub>4</sub>; ----, 3.10 M H<sub>2</sub>SO<sub>4</sub>; - · - ·, 3.60 M HCl; · · · ·, 3.00 M H<sub>3</sub>PO<sub>4</sub>.

It appears, then, that the following species are formed in the protonation of  $\text{HCrO}_4^-$  by the various mineral acids.<sup>3,4</sup>

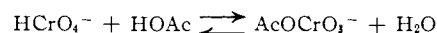


In agreement with these ideas Carrington<sup>10</sup> and Symons<sup>10</sup> have interpreted the spectrum of  $\text{Cr}^{\text{VI}}$  in sulfuric acid solutions as that of a mixture of species including  $\text{HOCrO}_2(\text{OSO}_3\text{H})$ . These authors have also presented evidence that the monosulfate  $\text{MnO}_3(\text{OSO}_3\text{H})$  is formed when  $\text{MnO}_4^-$  is dissolved in sulfuric acid. Hence it appears possible that the oxyanions of several transition metals may, when dissolved in strong acids, become bonded to the corresponding conjugate base.

The well known case of complex formation between two acid chromate anions to give a dichromate anion can be considered as another example of this general reaction.



It has also been suggested that  $\text{Cr}^{\text{VI}}$  dissolved in acetic acid solutions may exist in the form of an acetylchromate ion<sup>3,11</sup>



A partial explanation of the enhanced rates of oxidation observed in acetic acid solutions may be found in this suggestion since the acetyl group would increase the electron-accepting power of chromium.<sup>3</sup>

Further, if this is a correct picture, one would expect the  $pK_a$  values of these species to increase with decreasing electron-withdrawing power of the A groups. For example, since the bisulfate group probably has a greater electron-withdrawing power than chloride, one would expect the  $pK_a$  for  $\text{H}_2\text{CrSO}_7$  to be more negative than the  $pK_a$  of  $\text{HCrO}_3\text{Cl}$ . That is, the greater the

(9) The spectra shown in Fig. 2 for chromium(VI) in aqueous phosphoric and hydrochloric acids are very similar to those reported by Holloway (for aqueous phosphoric acid)<sup>4</sup> and by Cohen and Westheimer (for acetic acid-chloride solutions).<sup>3</sup> However, the states of protonation assigned to these complexes herein are different. In the case of a polyprotic acid like phosphoric acid it is possible that the protonated chromium(VI) entity is  $\text{H}_2\text{CrPO}_7^-$ .

(10) A. Carrington and M. C. R. Symons, *Chem. Rev.*, **63**, 443 (1963); see also H. C. Mishra and M. C. R. Symons, *J. Chem. Soc.*, 4411 (1962).

(11) M. C. R. Symons, *ibid.*, 4331 (1963).

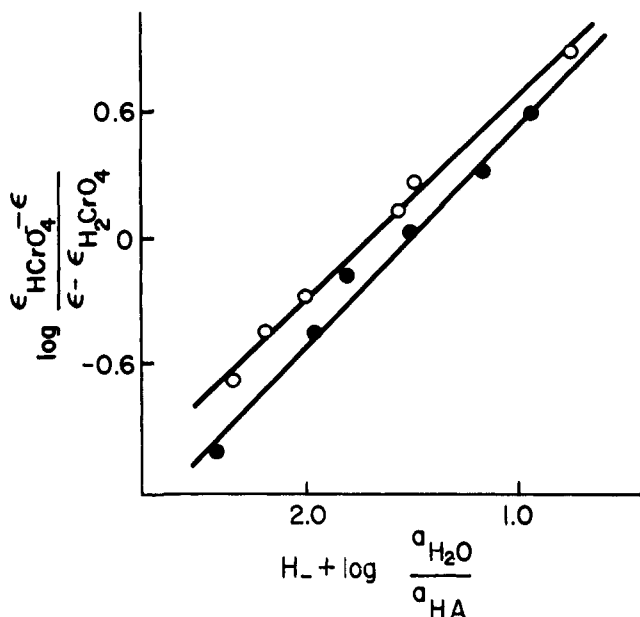


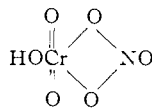
Fig. 3.—Modified ionization plots for chromic acid dissolved in sulfuric acid, O (slope 0.97), and in hydrochloric acid, ● (slope 1.03).

electron-withdrawing power of the A group the less available for protonation will be the electrons associated with the oxygen atom attached to chromium. Since the strengths of the mineral acids, HA, also vary in a similar way with electron-withdrawing power of the A groups, one might expect a correlation to exist between the strengths of the mineral acids and the corresponding  $\text{HCrO}_3\text{A}$  species. Such a correlation is seen for all the mineral acids investigated with the exception of  $\text{HNO}_3$ ; *i.e.*, the strengths of these acids increase in the order  $\text{H}_3\text{PO}_4 < \text{HNO}_3 < \text{HCl} < \text{H}_2\text{SO}_4 < \text{HClO}_4$  while the  $-\text{p}K_a$  values increase in the order  $\text{H}_3\text{CrPO}_7 < \text{HCrO}_3\text{Cl} < \text{H}_2\text{CrSO}_7 < \text{HCrClO}_7 < \text{HCrNO}_6$ .<sup>12</sup>

The spectra of chromic acid in  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$  are all similar, as would be expected if all of these species contained chromium–oxygen bonds. The spectrum of chromic acid in  $\text{HCl}$ , on the other hand, shows a greater variation from the spectra obtained in  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$  (Fig. 2), presumably because in this particular case a chromium–chloride bond is substituted for a chromium–oxygen bond.

The bonding in these species could be considered to be mostly covalent in analogy with the bonding in chromium compounds such as chromyl chloride,<sup>13a</sup> chromyl bromide,<sup>13b</sup> and chromyl acetate.<sup>14</sup> While some covalent perchlorate compounds have recently been prepared<sup>15,16</sup> it is probable that the bonding in  $\text{HCrClO}_7$  is

(12) The apparent anomaly of the  $\text{HCrNO}_6$  species in this respect is not as yet completely understood. It is possible, however, that the bonding in this species is different from the bonding in the other cases. For example,  $\text{HCrNO}_6$  may exist as an oxygen-bridged compound



If this is so it would be expected that  $\text{Cr}^{\text{VI}}$  would have a considerably different ultraviolet spectrum in  $\text{HNO}_3$  as compared to other mineral acids. However, nitric acid itself has an absorption band at 350  $\text{m}\mu$  blanking out the most interesting part of this spectrum.

(13) (a) W. H. Hartford and M. Darrin, *Chem. Rev.*, **58**, 1 (1958); (b) V. H. L. Krause and K. Starke, *Z. Naturforsch.*, **17b**, 1 (1962).

(14) P. Lepse, Ph.D. Thesis, University of Washington, 1961.

(15) B. J. Hathaway and A. E. Underhill, *J. Chem. Soc.*, 3705 (1960).

(16) H. C. Clark and R. J. O'Brien, *Inorg. Chem.*, **2**, 740 (1963).

considerably ionic. Note that the slope of the ionization curve (Fig. 1) is almost unity for perchloric acid suggesting that the  $\text{Cr}^{\text{VI}}$  is behaving in a "normal" fashion and that the departure from unity of the slopes of the ionization curves of the other acids is due to covalent bond formation between chromium and the A groups. In this connection it should be noted that addition of sodium perchlorate to solutions of phosphoric and nitric acid did not greatly affect the observed  $\text{p}K_a$  of chromic acid in these solutions. This indicates that perchlorate will not replace either phosphate or nitrate in these compounds.

In addition to the above considerations it follows that if the protonation equilibrium involves a molecule of mineral acid a plot of  $\log(\epsilon_{\text{HCrO}_4^-} - \epsilon)/(\epsilon - \epsilon_{\text{H}_2\text{CrO}_4})$  against either a simple  $H_0$  or  $H_-$  function should not necessarily give a straight line of unit slope. The function that should give rise to a linear plot of unit slope can be derived



$$K = \frac{(\epsilon_{\text{HCrO}_3\text{A}})(a_{\text{H}^+})(a_{\text{HA}})}{(\epsilon_{\text{HCrO}_4^-})(a_{\text{H}_2\text{O}})}$$

$$\text{p}K = \log \frac{C_{\text{HCrO}_3\text{A}}}{C_{\text{HCrO}_4^-}} - \log \frac{a_{\text{H}^+} \cdot f_{\text{HCrO}_4^-}}{f_{\text{HCrO}_3\text{A}}} - \log \frac{a_{\text{HA}}}{a_{\text{H}_2\text{O}}}$$

$$\text{p}K = \log \frac{C_{\text{HCrO}_3\text{A}}}{C_{\text{HCrO}_4^-}} + H_- + \log \frac{a_{\text{H}_2\text{O}}}{a_{\text{HA}}}$$

Hence a plot of  $\log(\epsilon_{\text{HCrO}_4^-} - \epsilon)/(\epsilon - \epsilon_{\text{H}_2\text{CrO}_4})$  against the function  $H_- + \log(a_{\text{H}_2\text{O}}/a_{\text{HA}})$  should yield a straight line of unit slope. Such functions have been calculated for  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$  and are presented in Table II. The plots for  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$  illustrated in Fig. 3

TABLE II

THE  $H_- + \text{LOG } a_{\text{H}_2\text{O}}/a_{\text{HA}}$  FUNCTIONS FOR  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , AND  $\text{HClO}_4$

Molarity	$\text{HCl}^a$	$\text{H}_2\text{SO}_4^b$	$\text{HClO}_4^c$
0.1	2.10	2.35	2.05
0.5	0.70	1.30	0.95
1.0	-.05	0.60	.10
1.5	-.44	.10	-.48
2.0	-.83	-.35	-.97
2.5	-1.08	-.85	-1.42
3.0	-1.27	-1.30	-1.84
3.5	-1.43	-1.70	-2.26
4.0	-1.57	-2.10	-2.62
4.5	-1.70	-2.60	-2.97
5.0	-1.82	-3.00	-3.28
5.5	-1.96	-3.40	-3.55
6.0	-2.06	-3.80	-3.81
6.5	-2.21	-4.20	-4.07
7.0		-4.60	-4.30
7.5		-5.15	
8.0		-5.50	

<sup>a</sup>  $H_-$  values for this acid are available only up to 2.0  $M$ ;  $H_0$  values were used beyond this point.  $H_-$  values from Professor R. H. Boyd, personal communication;  $H_0$  values from ref. 5; activity coefficients and activity of water from J. N. Pearce and A. F. Nelson, *J. Am. Chem. Soc.*, **55**, 3075 (1933). <sup>b</sup>  $H_-$  values from ref. 7; activity coefficients from H. S. Harned and W. J. Hamer, *J. Am. Chem. Soc.*, **57**, 27 (1935); activity of  $\text{H}_2\text{O}$  from J. F. Bunnett, *ibid.*, **83**, 4956 (1961). <sup>c</sup>  $H_-$  values from ref. 7; activity coefficients and activity of water obtained as in note a.

indicate that good straight line plots with near unit slopes are obtained when these functions are used. By comparing these plots with those in Fig. 1 where the simple  $H_0$  and  $H_-$  functions are used, it is evident that the

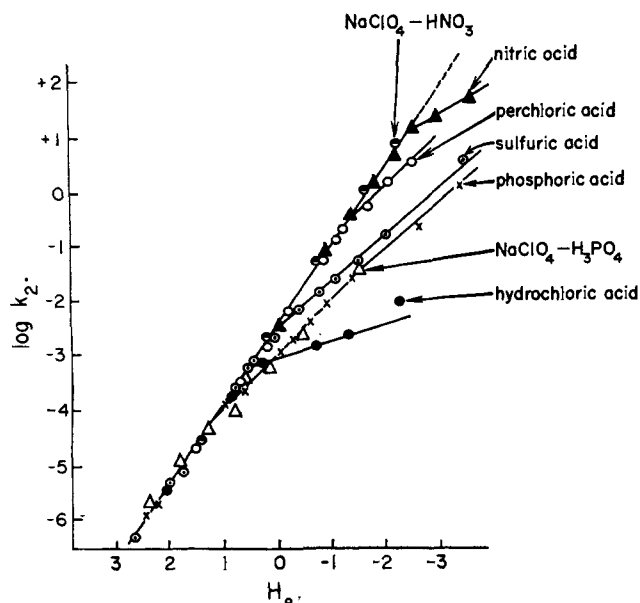


Fig. 4.—Variation of rate with acidity for the chromium(VI) oxidation of isopropyl alcohol in aqueous solutions of mineral acids.

slopes obtained when this new function is used are much closer to unity. This result serves to justify further the previous assumption that there is a distinct difference between the protonation reaction of organic indicator bases and the acid chromate ion. In the latter case a molecule of the proton-supplying mineral acid is evidently incorporated into the species when protonation occurs.

In the case of perchloric acid the slope obtained with the simple  $H_-$  function is only slightly greater than unity (Fig. 1) and application of the new function lowered the slope by approximately 0.2 unit.

### Discussion

If the picture of the chromic acid equilibrium presented in the preceding section is correct, one would expect that the physical and chemical properties of chromic acid would vary somewhat with the identity of the mineral acid solvent. It has previously been pointed out that while the acid chromate spectrum is identical for all the mineral acids investigated, the spectrum of chromic acid itself varied somewhat from acid to acid (Fig. 2). Similarly, it was found that the rate of oxidation of isopropyl alcohol by the acid chromate anion depended only on the acidity of the medium and not on the nature of the proton-supplying mineral acid. On the other hand, it has been observed that the rate of oxidation by chromic acid depends not only on the acidity of the medium, but also on the identity of the mineral acid. These observations are illustrated in Fig. 4 where the logarithm of the rate constant for oxidation of isopropyl alcohol by chromium(VI) is plotted against  $H_0$  for  $H_3PO_4$ ,  $HCl$ ,  $H_2SO_4$ ,  $HClO_4$ , and  $HNO_3$ . In addition, points are plotted for solutions of  $H_3PO_4$  and  $HNO_3$  containing a 1:1 molar ratio of sodium perchlorate. It can be seen that addition of sodium perchlorate to these solutions had no effect on the rate of oxidation outside of its effect on the acidity of the medium.

It is interesting to note that a sharp change in slope is observed for each particular mineral acid solution very near to the apparent  $pK_a$  of chromic acid in that

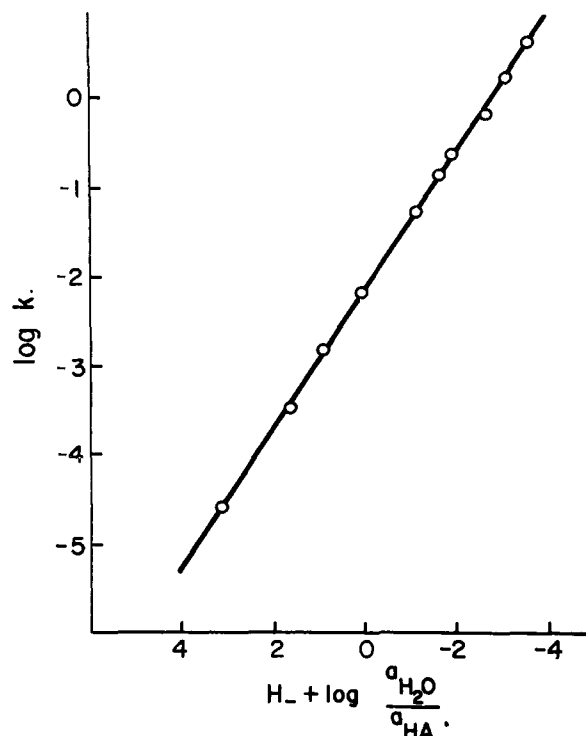


Fig. 5.—Variation of rate with a modified acidity function for the chromium(VI) oxidation of isopropyl alcohol in aqueous perchloric acid.

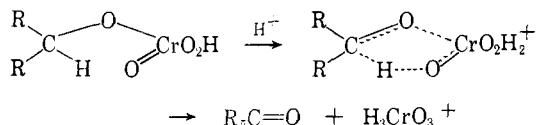
medium (Table I). Apparently the rate of oxidation by the protonated species of chromium(VI) varies with the acidity of the solution (as determined by  $H_0$ ) in a different manner than does the rate of oxidation by the unprotonated acid chromate anion. The observation that the variation in oxidation rate does not appear until after the apparent  $pK_a$  of the  $Cr^{VI}$  species is reached supports the suggestion that this equilibrium is such that a molecule of mineral acid does not become incorporated in the monoanion.

The oxidizing ability of the protonated species,  $HCrO_3A$ , increases in the order  $H_3CrPO_7 < HCrClO_3 < H_2CrSO_7 < HCrClO_7 < HCrNO_6$  for a given  $H_0$  value. This is the same order in which the apparent  $pK_a$  values of these species vary. Such a correlation is not unexpected since A groups which are electron withdrawing will decrease the ease of protonation of the species but increase the tendency of the chromium species to accept electrons from a reducing agent (the position of  $HCrNO_6$  is again anomalous.)

Although the new function,  $H_- + \log (a_{H_2O}/a_{HA})$ , gives a much better fit to the ionization data in hydrochloric and sulfuric acids than do the simple acidity functions  $H_0$  and  $H_-$ , it gives a linear correlation with the oxidation rate data only in the case of perchloric acid. The deviation from linearity apparent in Fig. 4 for perchloric acid systems vanishes when the new function is used as can be seen in Fig. 5. (The slope is 0.8 in this case as opposed to 1.5 for the linear portion of the perchloric acid curve in Fig. 4.) In the case of hydrochloric and sulfuric acids, however, there is little alteration in the shape of the curves from those shown in Fig. 4.

**Mechanism of the Chromic Acid Oxidation of Alcohols.**—Current evidence indicates that the mechanism of this reaction involves formation of a chromate

ester intermediate which probably decomposes unimolecularly to products.<sup>2k,17-19</sup>



Protonation of the chromate part of the ester increases the electron-attracting properties of the chromium, but the exact mode of electron transfer would depend on the amount of orbital overlap between the developing H-O and the separating O-Cr bonds in the transition state and could well vary with changes in

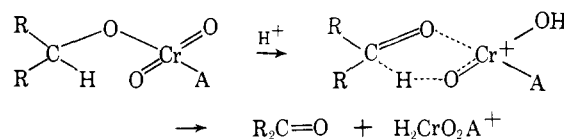
(17) J. Rocek, F. H. Westheimer, A. Eschenmoser, I. Moldovanyi, and J. Schreiber, *Helv. Chim. Acta*, **45**, 2554 (1962).

(18) R. Stewart, "Oxidation Mechanisms: Applications to Organic Chemistry," W. A. Benjamin, Inc., New York, N. Y., 1963.

(19) R. Stewart and D. C. Lee, *Can. J. Chem.*, **42**, 439 (1964).

the nature of the reactants and the conditions employed.

In light of the results presented in the present paper this mechanism would have to be modified in moderately concentrated acid regions to allow for participation by the conjugate base of the proton source used in the reaction.



The present results show that the identity of the conjugate base has a profound effect on the rate of reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZONA]

## Metal Ion Induced Rearrangements of Bisbenzthiazolines to Schiff-Base Chelates

BY HANS JADAMUS, QUINTUS FERNANDO, AND HENRY FREISER

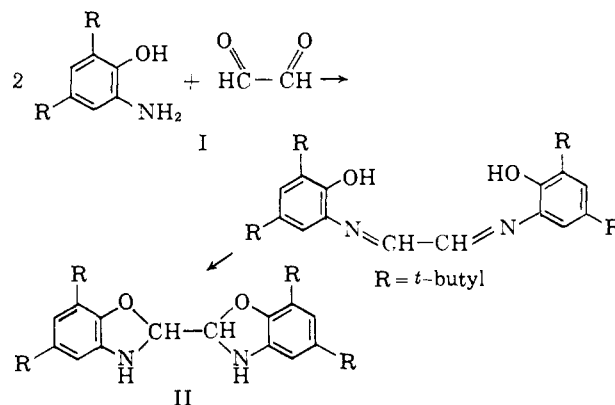
RECEIVED JUNE 5, 1964<sup>1</sup>

The condensation products of *o*-aminobenzenethiol with glyoxal, diacetyl, and benzil were prepared and their reactions with zinc(II), cadmium(II), and mercury(II) have been studied. 2,2'-Bisbenzthiazoline and its 2,2'-dimethyl homolog were found to rearrange under the influence of these metal ions to give the corresponding Schiff-base chelates. A kinetic study was carried out to help explain the nature of the reactions.

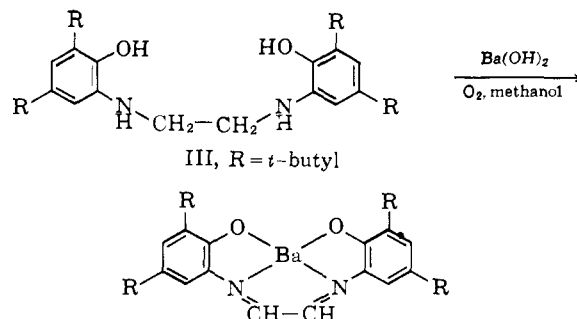
Schiff bases constitute an important class of polydentate ligands. The direct approach in synthesizing a Schiff base from the condensation of an *o*-hydroxy-, *o*-amino-, or *o*-mercaptoamine with a carbonyl compound often results in the undesirable side reaction involving ring closure with the formation of a heterocyclic compound. The solution to this problem, first used by Schiff in 1869,<sup>2</sup> is to prepare the Schiff base in the form of its metal chelate by reacting the metal complex of one of the starting materials with the other. For example, bis-salicylaldehyde-copper(II) reacts with 4-methyl-1,2-phenylenediamine to give the Schiff base chelate. This technique of avoiding the formation of the heterocyclic compound has been widely used by P. Pfeiffer<sup>3</sup> and others.<sup>4</sup>

In some restricted cases, it is possible to isolate the intermediate Schiff base before it is isomerized to the heterocycle, *e.g.*, if a substituent on one of the reactants provides steric hindrance to ring closure. An example is the reaction of 4,6-di-*t*-butyl-2-aminophenol and glyoxal which gives the intermediate yellow glyoxal bis(2-hydroxy-3,5-di-*t*-butylanil) (I)<sup>5</sup> as well as the colorless 5,7,5',7'-tetra-*t*-butyl-2,2'-bisbenzoxazoline (II). As might be expected, this Schiff base forms chelates with a number of metal ions.

Another route to these chelates is to start from a reduced form of the ligand such as N,N'-bis(2-hydroxy-3,5-di-*t*-butylphenyl)ethylenediamine (III),<sup>6</sup> which is



itself a chelating agent, and to oxidize it in the presence of a suitable metal ion to the Schiff base chelate.



Although most workers have attempted to avoid the formation of the heterocyclic compound, Bayer and Schenk have recently shown that in the presence of

(1) A preliminary account of this work was received on Sept. 3, 1963.

(2) H. Schiff, *Ann. Chem. Pharm.*, **150**, 193 (1869).

(3) P. Pfeiffer, W. Offermann, and A. Werner, *J. prakt. Chem.*, **159**, 313, (1942).

(4) (a) H. S. Verter and A. E. Frost, *J. Am. Chem. Soc.*, **82**, 85, (1960);

(b) M. S. Thompson and D. H. Busch, *ibid.*, **84**, 1962, (1962).

(5) H. Haussler and H. Jadamus, *Ber.*, in press.

(6) F. Lober and K. Ley, German Patent 1,104,552; *Chem. Abstr.*, **56**, 5887a, (1962).