

rate to give the free radicals necessary for initiation of polymerization. Apparently neither of these conditions produces a large concentration of radicals, for only easily polymerizable monomers seem to give polymers. It is of course known³ that aryl-diazonium salts initiate polymerizations of a variety of monomers in alkaline media, but they have apparently not been used for this purpose primarily in acid media.⁴

Experimental

Each of the polymerizations recorded in Table I was accomplished by either shaking (28 and 30° runs) or tumbling (0° and 50° runs) the indicated reaction mixture for the designated period, preliminary experiments having shown no differences in the products from these operations.

(3) J. M. Willis, G. Alliger, B. L. Johnson and W. M. Otto, Lecture before Division of Rubber Chemistry, American Chemical Society Meeting, Buffalo, New York, October 29, 1952.

(4) After this note had been accepted for publication W. Cooper published a note in *Chemistry and Industry*, No. 17, p. 407, April 25, 1953, describing the use of *p*-nitrobenzenediazonium *p*-chlorobenzene-sulfonate as an initiator for the polymerization of methyl acrylate and acrylonitrile in 2.5 *N* hydrochloric acid solution.

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N-Acetylimesatins and Related Compounds

BY FEDERICO PARISI

RECEIVED FEBRUARY 28, 1953

In the course of researches carried out some years ago at the University of Fribourg (Switzerland) on the constitution of the products of the reaction of indigo with benzoyl chloride,¹ it was supposed that imesatins were obtained by the degradation of the products of benzoylation with aromatic amines.

This supposition has since been found to be erroneous, although the possibility of the formation of an imesatin by the treatment of Dessoulay's compound with ammonia is still being studied.

This note will serve to record the preparation of several N-acetylimesatins and of two derivatives of N-chloroacetylisatin.

The N-acetylimesatins can be prepared by the action of the corresponding amines on N-acetylisatin (prepared according to J. Büchi²) in absolute alcohol without the use of catalysts.

For example: 0.01 mole of N-acetylisatin, 0.02 mole of amine and 30 ml. of absolute alcohol are heated under reflux on the water-bath for an hour, cooled and allowed to stand in the refrigerator to complete the separation of the solid. The product is collected, washed with cold alcohol and then with ether and recrystallized from an appropriate solvent (often glacial acetic acid). It may be necessary to allow the liquid to stand for some days in the refrigerator in order to complete the crystallization. In Table I are given the properties of the substances prepared.

Acetylation of imesatins with acetic anhydride does not produce the corresponding N-acetylimesatins but yields resinous substances.

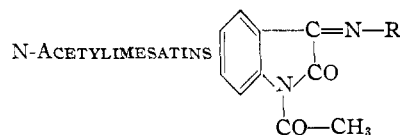
Derivatives of N-chloroacetylisatin have also been prepared using aniline according to Huntress.³ In absolute alcohol as for N-acetylimesatins, N-chloroacetylphenyli-

(1) H. de Deisbach and coll., *Helv. Chim. Acta*, **16**, 148 (1933); **17**, 113 (1934); **19**, 1213 (1936); **20**, 132 (1937); **23**, 469 (1940); **24**, 158 (1941); **26**, 1869 (1943); **31**, 724 (1948); **32**, 1214 (1949).

(2) J. Büchi and H. Humi, *Helv. Chim. Acta*, **32**, 1806 (1949).

(3) E. H. Huntress and J. Bornstein, *THIS JOURNAL*, **71**, 745 (1949).

TABLE I



R	Crystallized from	M.p., °C.	Nitrogen, % Calcd.	Found
C ₆ H ₅	AcOH	177-178	10.61	10.59
1,2-C ₆ H ₄ CH ₃	AcOH	185-186	10.07	10.13
1,3-C ₆ H ₄ CH ₃	AcOH	169-170	10.07	9.91
1,4-C ₆ H ₄ CH ₃	AcOH	176-177	10.07	10.07
1,2-C ₆ H ₄ OH	<i>i</i> -Pr ₂ O	169-170	10.00	9.89
1,4-C ₆ H ₄ OH	Ph·CH ₃	194-195	10.00	9.83
1,4-C ₆ H ₄ COOH	AcOH	224 (dec.)	9.09	8.94
1-C ₁₀ H ₇	AcOH	170-171	8.92	9.01
2-C ₁₀ H ₇	AcOH	189-190	8.92	9.03
C ₅ H ₅ N ₂ ^a	AcOEt	169-170	20.00	19.82
C ₃ N ₂ NS ^b	AcOEt	184-185	15.50	15.41

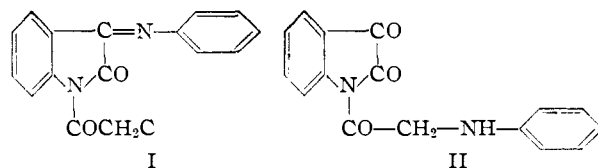
^a 4-Methylpyrimidyl. ^b 2-Thiazolyl.

mesatin (I) was obtained. After crystallization from acetic acid it has m.p. 146°.

Anal. Calcd. for C₁₆H₁₁N₂O₂Cl: N, 9.38; Cl, 11.88. Found: N, 9.57; Cl, 11.71.

On the other hand, 0.01 mole of chloroacetylisatin refluxed with 0.02 mole of aniline in 10 ml. of pyridine for five minutes yields after cooling and diluting with an equal volume of water, half a volume of acetic acid and 8 ml. of concentrated hydrochloric acid (without passing the change point of congo red) a resinous precipitate. When stirred for some time this precipitate redissolves in the liquid leaving only a small residue. The filtrate from this, made alkaline with ammonia, gives a yellow precipitate of phenylglycylisatin (II) soluble in mineral acids, in concentrated alkalies and in ethyl alcohol. Crystallized from acetic acid, it has m.p. 197°.

Anal. Calcd. for C₁₆H₁₂N₂O₃: N, 9.99; Cl, nil. Found: N, 10.16; Cl, absent.



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Polarography of Tripositive Antimony and Arsenic. Cathodic Reduction of Antimonous in Strong Hydrochloric Acid and Anodic Oxidation of Arsenite and Stibnite in Strong Sodium Hydroxide

BY G. P. HAIGHT, JR.¹

RECEIVED DECEMBER 17, 1952

The polarography of arsenic and antimony in acid solutions has been investigated by Lingane,² Kolthoff and Probst³ and Bambach⁴ who have shown that the tripositive state of each element is generally reducible while the pentavalent states are reduced only in very strong hydrochloric acid. Waves in 1.5 *M* HCl and in 1 *M* HCl plus 1 *M* tartaric acid have been found suitable for simultane-

(1) Chemistry Department, University of Kansas, Lawrence, Kansas.

(2) J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **16**, 583 (1943).

(3) I. M. Kolthoff and R. L. Probst, *Anal. Chem.*, **21**, 753 (1949).

(4) K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **14**, 265 (1942).

ous polarographic determination of these elements in the tripositive state by Bambach⁴ and the author.⁵ The antimony wave in hydrochloric acid has the general characteristics of a reversible 3-electron process and it has been generally assumed that the SbCl_4^- ion is the species being reduced. Pentavalent antimony is reduced prior to the anodic dissolution of mercury in 4 *M* or stronger HCl. Kolthoff and Probst³ have also reported anodic waves for the oxidation of the tripositive states to the pentavalent state in potassium hydroxide solutions. The object of this paper is to throw further light on the nature of the processes producing these anodic waves and to use polarographic data to determine the actual number of chloride ions associated with tripositive antimony in concentrated HCl.

Apparatus and Materials.—A Sargent Model XX recording polarograph was used for all measurements. A conventional mercury pool polarographic cell was used, the potential of the large mercury anode being determined separately at the end of each run. In basic media the pool had HgO in contact with it and was separated from the dropping electrode by a sintered glass disc. A potentiometer attached to the pool and to the dropping mercury electrode provided accurate measurements of e.m.f. All measurements were made at 30° except where indicated. Reagent grade chemicals were used throughout.

Experimental Results. Chloro Complex of Tripositive Antimony.—It was confirmed that a plot of E vs. $\log i/(i_d - i)$ for the cathodic wave for tripositive antimony in strong HCl yielded a straight line with a slope of -0.020 , indicating reversible reduction. If the reversible character of the wave is accepted it follows that $E_{1/2} = C + 0.02 n \log (\text{Cl}^-)$ where $E_{1/2}$ is the half-wave potential, C a constant, and n is the number of chloride ions attached to antimony in the chloroantimonous complex. Figure 1 shows a plot of $E_{1/2}$ vs. $\log (\text{Cl}^-)$ in solutions which were 4 *M* in hydrogen ion.

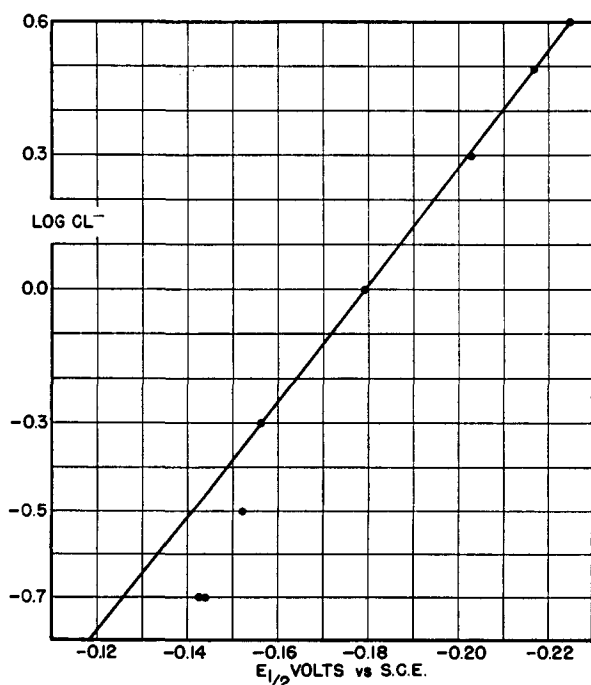


Fig. 1.—Variation of $E_{1/2}$ with (Cl^-) at constant (H^+) .

(5) G. P. Haight, Jr., unpublished work.

The result is a straight line with a slope of 0.077 indicating that 4 chloride ions are present in the complex as has been suspected all along. At 4 *M* Cl^- the half-wave potential is independent of hydrogen ion concentration. Figure 2 shows a plot of $E_{1/2}$ vs. the molal activity of hydrochloric acid for 1, 4 and 6 *M* solutions which yields a straight line plot of slope 0.079 which indicates good agreement with theory for a complex containing no hydrogen and four chloride ions.

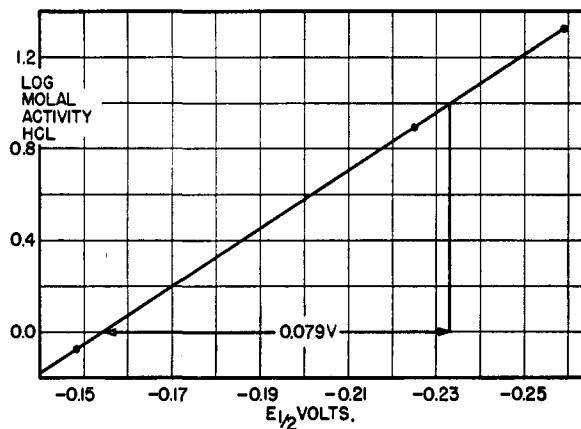


Fig. 2.—Reduction of Sb(III) to Sb^0 in HCl.

This agreement is interesting in view of the fact that individual ion activities are generally assumed to be different from average activity coefficients for salts and acids in aqueous solution. It suggests that the individual ion activity is either the same as or a linear function of the average activity coefficient of the dissolved ionic substance. If such is the case for other electrolytes, the technique illustrated in Fig. 2 might be useful in place of, or supplementary to, the technique of maintaining constant ion strength, which is exceedingly difficult to do in concentrated solutions of acids and bases. Also, in such solutions it is virtually impossible to find "inert" electrolytes which do not participate in complex formation. It was found impossible to use NaCl with NaOH in the arsenite study below, for instance. It should be noted that the points in Fig. 1 at Cl^- concentrations below 0.5 *M* show marked deviation from the other points. The H^+ concentration was maintained using HClO_4 . Compilations of Robinson and Stokes⁶ show that the HCl and HClO_4 activity coefficients are nearly the same up to 2 molal but begin to deviate sharply at 4 molal with the activity of HClO_4 increasing faster than HCl with increasing concentration. An increase in the activity coefficient of Cl^- due to promotion of their activity by high HClO_4 would cause the deviations observed in Fig. 1 as would change in number of Cl^- ions in the complex. The author feels that the straight line as far as is observed is rather fortuitously due to the near identity of activities of HCl and HClO_4 in this range. The technique of Fig. 2 has been applied to the study of the oxidation of tripositive antimony and arsenic in KOH solutions. Activities

(6) R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

of KOH solutions were obtained from the data of Akerlof and Bender.⁷

Anodic Oxidation of Tripositive Arsenic in Potassium Hydroxide Solution.—Figure 3 shows a typical polarogram of tripositive arsenic and antimony in 1 *M* potassium hydroxide. Both are anodically oxidized to the pentavalent state while antimony is reduced to the metal as well. A plot of *E* vs. log

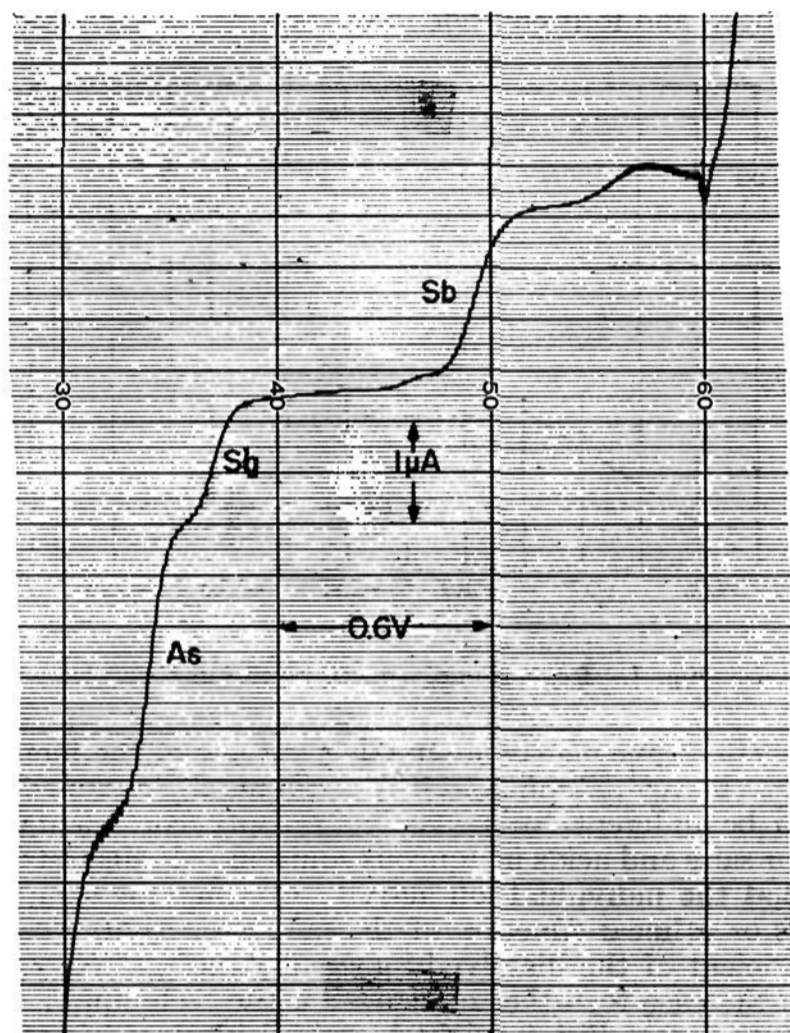


Fig. 3.—Polarogram of 4×10^{-4} *M* arsenite and 2×10^{-4} *M* stibnite in 1 *M* KOH, $m^{2/3}t^{1/6} = 1.74$ mg.^{2/3} sec.^{1/2}.

$i/(i_d - i)$ for the arsenic wave yields a straight line of slope 0.029 corresponding to a reversible 2 electron change. Figure 4 shows a plot of $E_{1/2}$ vs. the logarithm of the molal activity of KOH for concentrations ranging from 0.5 to 10 *M*. The result is a straight line with a slope of 0.028, corresponding closely to a reversible two electron process involving one hydroxide ion.

$$E_{1/2} = -0.276 - 0.029 \log A_{\text{OH}^-} \text{ vs. S.C.E.}$$

Half-wave potentials are independent of arsenic concentration. Oxidation of solutions by air is quite rapid so no precise calculation of the diffusion current constant was made although a rough idea as to its value may be obtained from Fig. 1. The hydroxide medium is unsatisfactory for analytical use unless air-free KOH is employed and all operations are carried out in an inert atmosphere. In this study, air was not excluded until just prior to taking the polarograms. Since both ortho and meta forms exist in the case of arsenite and arsenate several possible reactions involving one hydroxide ion present themselves. Both ortho- and meta-arsenates yield identical solutions shortly

(7) G. Akerlof and P. Bender, *THIS JOURNAL*, **70**, 2366 (1948).

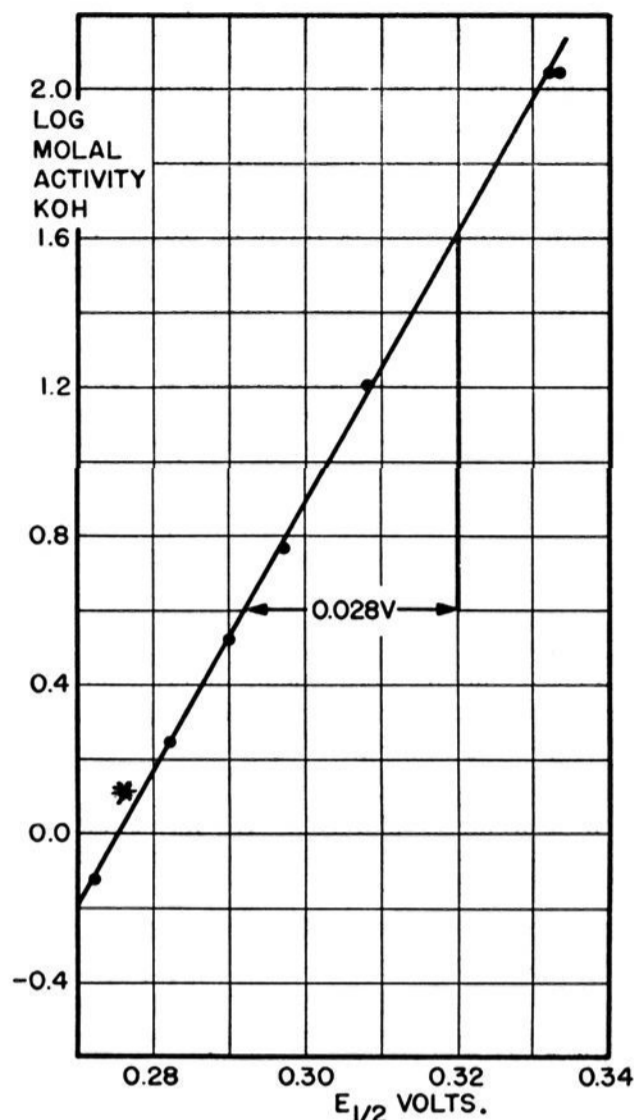
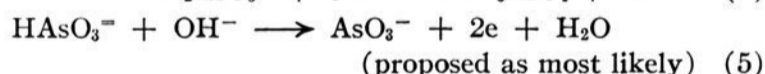
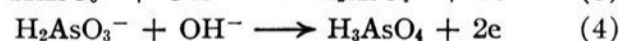
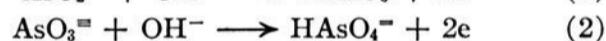


Fig. 4.—Oxidation of arsenite in KOH: *, in NaOH at 27°.

after dissolution in water with the meta form probably being converted to the ortho form. Precipitation reactions yield ortho-arsenites as a rule indicating that that form is predominant in solution. Some possible electrode reactions involving one hydroxide are



Since "ic" acids are generally much stronger than "ous" acids it would seem unlikely that the product would contain more protons than the arsenite species originally present in strongly alkaline solution. This would rule out equations 1 to 4. The fact that ordinary arsenate solutions are not reducible would rule out the products in equations 2 to 4. Equation 5 seems the most likely description of the electrode process, the AsO_3^- produced being converted to AsO_4^- after diffusing away from the electrode. The first dissociation constant of arsenious acid is 6×10^{-10} which would indicate the presence of at least one hydrogen in the ortho form even in strongly basic solutions. Equation (5) represents a simple electrical change with the same spatial configuration of oxygen about arsenic and should be easier to accomplish electrically than conversion of ortho-arsenite to ortho-arsenate.

Anodic Oxidation of Tripositive Antimony in Potassium Hydroxide.—The analysis of the anodic

wave for tripositive antimony reveals a somewhat more complicated situation than with arsenic. The slope of the E vs. $\log i/(i_d - i)$ plot gives a straight line in all cases with a slope which varies from 0.047 to 0.037 as the hydroxide ion concentration increases from 1.0 to 10.0 moles/l. These slopes are high compared to 0.030 characteristic of a reversible 2 electron change. Raising the temperature to 40° failed to alter the slope beyond the limits of experimental error, indicating the spread wave does not result from a high activation energy for the reaction. The half-wave potential varies with the molal activity of potassium hydroxide in manner characteristic of a reversible 2 electron change involving two hydroxide ions as shown in Fig. 5. Also shown in Fig. 5 is the effect of a 10° rise in temperature on the half-wave potentials in 1 M and 10 M KOH. At 30°

$$E_{1/2} = -0.453 - 0.060 \log a_{\text{OH}^-} \text{ vs. S.C.E.}$$

The small negative shift with increasing temperature is characteristic of a reversible process. Whitney and Davidson⁸ have shown that the complexes SbCl_4^- and SbCl_6^- interact to give a colored complex in strong hydrochloric acid. It would seem possible then that the corresponding hydroxy complexes, if formed, would interact. Such interaction would serve to decrease the concentrations of $\text{Sb}(\text{OH})_4^-$ and $\text{Sb}(\text{OH})_6^-$ at the surface of the mercury drop in such a way as to spread the wave out, increasing the slope of the E vs. $\log i/(i_d - i)$ plot as observed. Solutions of high ionic strength might be expected to cut down interaction and the plot should show a trend toward a reversible slope with increasing ion strength as it does. The reaction $2\text{OH}^- + \text{Sb}(\text{OH})_4^- \rightarrow \text{Sb}(\text{OH})_6^- + 2e$ satisfies the dependence of $E_{1/2}$ on hydroxide ion activity. Since pentavalent antimony is not reduced under these conditions it would seem likely that the form produced by the oxidation would be an unusual form not normally encountered in solution. Pauling⁹ and Beintema¹⁰ have shown the existence of salts of $\text{Sb}(\text{OH})_6^-$ but the species has not heretofore been identified in solution where it may polymerize to an irreducible form. Many other equations involving two hydroxide ions and two electrons are of course possible, but the correlation of the reaction given with other known phenomena of antimony complexes seems to favor it in the author's opinion. This proposed mechanism is very tentative and confirmation or rejection must wait on data from other types of experiments if such are possible.

Figure 3 shows that the 2nd antimony wave which is cathodic is 3/2 the height of the first as found by Kolthoff and Probst. The plot of E vs. $i/(i_d - i)$ for this wave gives a straight line with a slope of 0.076—nearly four times the value for a reversible 3 electron change. The small wave following may be partial reduction to stibine.

Summary.—This paper describes the nature of the chloroantimonous complex and the participation of hydroxide in the polarographic oxidation of arsenite and antimonite solutions. In addition it

(8) J. Whitney and N. Davidson, *THIS JOURNAL*, **71**, 3809 (1949).

(9) L. Pauling, *ibid.*, **55**, 1895 (1933).

(10) J. Beintema, *Rec. trav. chim.*, **56**, 931 (1937).

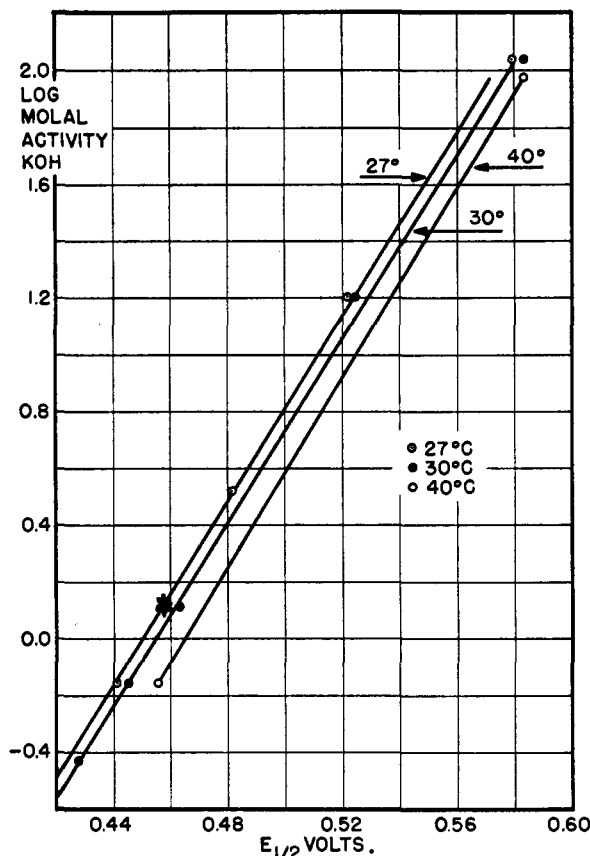


Fig. 5.—Oxidation of stibnite in KOH: *, in NaOH at 27°.

introduces a new technique of plotting $E_{1/2}$ vs. molal activities of ions involved in the reaction as a means for studying complexes in solutions of strong acids and bases at concentrations above 1 molal.

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The Reaction of Methanesulfonyl Chloride with Alcohols in the Presence of Pyridine

BY C. R. NOLLER, C. A. LUCHETTI, E. M. ACTON AND R. A. BERNHARD

RECEIVED FEBRUARY 2, 1953

The reaction of methanesulfonyl chloride with an alcohol in the presence of pyridine might be expected to yield either the alkyl methanesulfonate or the alkyl chloride. As subsequent reactions the pyridine may remove methanesulfonic acid from the ester or hydrogen chloride from the alkyl chloride to give the olefin, or may form alkylpyridinium salts.

The reaction of methanesulfonyl chloride with an alcohol in the presence of pyridine at room temperature or below is the usual method for preparing alkyl methanesulfonates.¹ 1-Hydroxy-2-octyne does not yield the ester by this procedure, but a

(1) V. C. Sekera and C. S. Marvel, *THIS JOURNAL*, **55**, 345 (1933); M. Zief, H. G. Fletcher and H. R. Kirshen, *ibid.*, **68**, 2743 (1946); M. F. Clarke and L. N. Owen, *J. Chem. Soc.*, 315 (1949); 2103, 2108 (1950).