

Anal. Calcd. for $C_{12}H_{14}ON_2$: C, 71.25; H, 6.98; N, 13.86. Found: C, 70.96; H, 6.99; N, 13.84.

Summary

1. The preparation of pure ethyl formylbutyrate is described.
2. This aldo-ester reacted with phenylhydrazine, nitrophenylhydrazine and bromophenylhy-

drazine to give the corresponding pyrazolone compounds.

3. The aldo-ester reacted with hydroxylamine to give 4-ethylisoxazol-5-one.

4. The methylation of 1-phenyl-4-ethylpyrazol-5-one gave 1-phenyl-2-methyl-4-ethylpyrazol-5-one.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Kinetics of the Trivalent Vanadium-Iodine Reaction

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In oxidations by iodine in aqueous solutions, usually containing iodide, several possible oxidizing molecular species exist: namely, iodine molecules, triiodide ions, hypiodite ions and hypiodous acid molecules. That iodine atoms may be involved under ordinary conditions in the dark seems improbable, although such an interpretation is warranted in the photochemical oxidation of oxalate.¹ Iodine molecules have been shown to be a reacting species in several oxidations, among them, that of phosphorous acid,² of trivalent titanium³ and of ferrous iron.⁴ The oxidation of arsenious acid by iodine⁵ is an outstanding historical example of those reactions in which hypiodous acid molecules are involved in the rate determining step. Triiodide ion is at least one of the reacting molecular species in the oxidations of phosphorous acid,² of ferrous iron,⁴ and of hypophosphorous acid.⁶ It seems probable that some relation may be found between the molecular species of iodine involved and the nature of the reducing species or of its transformation, after a larger number of kinetic studies has been made.

The more immediate interest in this reaction is due to its possible importance in the interpretation of the induced catalysis of the autoxidation of hydriodic acid by vanadic acid.⁷ In a general qualitative survey of the reactions of vanadium in its different valence states Rutter⁸ observed that

(1) Griffith and McKeown, *Trans. Faraday Soc.*, **28**, 752 (1932).

(2) Mitchell, *J. Chem. Soc.*, **123**, 2241 (1923).

(3) Yost and Zabaró, *THIS JOURNAL*, **48**, 1181 (1926).

(4) Unpublished work of Bray and Hershey, presented at the San Francisco meeting of the American Chemical Society, Aug. 20, 1935.

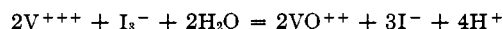
(5) (a) Roebuck, *J. Phys. Chem.*, **6**, 365 (1902); **9**, 727 (1905); (b) Liebhfafsky, *ibid.*, **95**, 1648 (1931).

(6) Mitchell, *J. Chem. Soc.*, **117**, 1322 (1920).

(7) Bray and Ramsey, *THIS JOURNAL*, **55**, 2279 (1933).

(8) Rutter, *Z. anorg. Chem.*, **52**, 368 (1907).

the trivalent vanadium-iodine reaction proceeded at a moderate rate. The stoichiometry of the reaction may be represented by the following equation.



Preparation and Standardization of Stock Solutions.—All chemicals were of C. P. grade. The sodium perchlorate and sodium iodide were shown free from possible impurities by methods recommended by Murray.⁹ Sodium oxalate from the Bureau of Standards was the primary standard. Known solutions of each of the following substances were obtained as indicated: potassium permanganate, with sodium oxalate; sodium thiosulfate, by the Volhard method, under conditions recommended by Bray and Miller;¹⁰ sodium triiodide and potassium iodate, with the sodium thiosulfate; perchloric acid, with potassium iodate by the method of Kolthoff;¹¹ sodium iodide and sodium perchlorate, from accurately weighed quantities which had been dried carefully (the former checked by the method of Andrews¹²); ammonium vanadate, iodometrically.¹³

The stock solutions of vanadic perchlorate, $V(ClO_4)_3$, were prepared by electrolytic reduction of vanadyl perchlorate, VO_2ClO_4 . The latter was formed by mixing vanadium pentoxide, from thermal decomposition of pure ammonium vanadate, with perchloric acid. The oxide dissolved as the reduction progressed. A platinized platinum cathode and a platinum anode were used. The reduction was followed analytically (by a method

(9) Murray, "Standards and Tests for Reagents and C. P. Chemicals," D. Van Nostrand Co., N. Y., 1927.

(10) Bray and Miller, *THIS JOURNAL*, **46**, 2204 (1924).

(11) Kolthoff, *ibid.*, **48**, 1447 (1926).

(12) Andrews, *ibid.*, **25**, 756 (1903).

(13) Ramsey, *ibid.*, **49**, 1138 (1927).

to be described later) and stopped with a small quantity of vanadium still remaining in the tetravalent state. Washed carbon dioxide from a cylinder passed through the solution during the electrolysis and was kept over it during use. The resulting solutions were usually about 0.5 normal in perchloric acid.

The combined equivalent concentration of the tri- and tetravalent vanadium in this solution was obtained by adding a pipetted aliquot to an ammonium vanadate solution containing slightly more than enough vanadate to oxidize the trivalent vanadium, heating almost to boiling, and titrating with permanganate, thus oxidizing the tetravalent vanadium to the pentavalent state. That no oxygen error was involved during the oxidation of trivalent vanadium by the vanadate (which occurred instantaneously in these solutions) was shown by previously freeing the vanadate solution from air before adding the aliquot.

The concentration of the trivalent vanadium alone was found by adding a known volume of the solution to a measured quantity of known vanadate in excess, then determining the vanadate remaining by the iodometric method.¹⁸

Finally the concentration of the perchloric acid was found by adding a standard base in slight excess to a measured volume of the solution, filtering off the two hydroxides formed, and titrating with standard acid. The perchloric acid concentration may be calculated knowing that the trivalent and tetravalent vanadium are present as V^{+++} and VO^{++} , respectively.

These stock solutions of vanadic perchlorate were quite stable. Over a period of some three weeks the trivalent vanadium was converted to the tetravalent state to a slight extent, both by oxygen and by perchlorate. The extreme slowness of the latter oxidation was shown by tests for chloride during the period of use.

Rate Measurements.—The reaction was followed by determining the iodine present in measured aliquots (10 to 25 ml.), removed from the reacting mixture at suitable intervals. The following possible sources of error were considered: (1) loss of iodine by volatilization; (2) oxidation of trivalent vanadium by oxygen and perchlorate; and (3) oxidation of iodide by oxygen. Also the possibility of induction of one of these reactions by another or by the reaction being considered was not overlooked.

Experiments were carried out in the same man-

ner and under the same conditions as those finally adopted in the rate measurements but with vanadium absent. With the concentrations of iodine and iodide such as to give the maximum volatility existing in any experiment, the loss of iodine was found negligible. That none of the reactions listed under (2) and (3) above occurred to a measurable extent under the conditions adopted was proven by the fact that during several of the experiments the equivalents of trivalent vanadium oxidized were determined at intervals and found at all times to be precisely equivalent to the iodine reduced.

Prior to the addition of the triiodide solution, the last reagent added, the solution of the other reagents was freed from oxygen with carbon dioxide. In those runs requiring more than two or three hours, it was found necessary to maintain an atmosphere of carbon dioxide in the reaction flask. This was accomplished by providing that carbon dioxide passed through the flask above the solution only during the removal of aliquots, since a continuous stream of carbon dioxide caused an appreciable loss of iodine. In experiments requiring less time the maintenance of an atmosphere of carbon dioxide was found unnecessary. The initial time was taken as that at which one-half of the triiodide solution had been added.

Preliminary experiments had shown that the reaction rate decreased with increasing concentration of acid. It was found that adequate quenching was provided if the 10- to 25-ml. aliquots were added to approximately 100 ml. of ice-cooled 0.5 *N* sulfuric acid. The 0.01 *N* sodium thiosulfate was freshly prepared from the stock 0.1 *N* solution. A 10-ml. buret was used for the titrations; the end-point was determinable within 0.02 ml.

Order of the Reaction.—The ionic strength of the reaction mixture was maintained substantially constant at 1.00 by means of sodium perchlorate. At the same initial total iodide and iodine concentrations, variation in the quantity of the stock vanadic perchlorate-perchloric acid solution in a given volume of the reacting mixture caused no variation in the initial rate as determined by slopes. This shows the net order with respect to trivalent vanadium and acid to be zero. Other experiments in which the initial concentration of the acid alone was varied showed definitely that the rate was inversely proportional to the acid concentration. From these preliminary results

it followed that the reaction is first order with respect to trivalent vanadium. These conclusions were confirmed throughout the range of concentrations of vanadium and acid used. It is apparent from these results that the hydrolysis of both tri- and tetravalent vanadium must be negligible.

Results obtained by varying the triiodide and iodide concentrations indicated that iodine molecules might be the only oxidizing species; if this were the case, the rate equation would be

$$\frac{-d[\Sigma(I_2)]}{dt} = k \frac{(V^{+++})}{(H^+)} (I_2) \quad (1)$$

in which $\Sigma(I_2)$ represents the total iodine concentration. On account of the known equilibrium between triiodide, iodine and iodide this equation may be written

$$\frac{-d[\Sigma(I_2)]}{dt} = k' \frac{(V^{+++})(I_3^-)}{(H^+)(I^-)} \quad (2)$$

The results obtained by use of equation (2) are given in Table I. In experiments 1-9 and

TABLE I

KINETIC RESULTS AT $\mu = 1.00$ AND $T = 24.95 \pm 0.02^\circ$
Initial concentrations in moles/liter

Expt. ^a	(V ⁺⁺⁺)	(H ⁺)	$\Sigma(I^-)$	$\Sigma(I_2) \times 10^3$	(VO ⁺⁺⁺) $\times 10^3$	$k' \times 10^3$
1	0.0241	0.107	0.256	2.52	2.50	1.14
2	.0476	.214	.132	2.52	5.60	1.32
3	.0241	.107	.132	2.52	2.50	1.28
4	.0180	.0869	.501	2.50	3.40	1.04
5	.0658	.333	.105	2.00	19.4	1.30
6	.0217	.0590	.508	2.50	1.75	1.12
7	.0217	.0590	.258	2.50	1.75	1.14
8	.0217	.559	.158	2.56	1.75	1.20
9	.0217	.0590	.108	2.58	1.75	1.34
10	.00433	.0118	.158	2.52	0.350	1.25
11	.0362	.125	.00827	2.47	10.9	0.91
12	.0362	.125	.0283	2.48	10.9	1.07
13	.0347	.127	.0133	2.57	12.8	0.98
14	.0347	.127	.0337	2.57	12.8	.97
15	.0347	.127	.0483	2.47	12.8	1.15
16	.0347	.127	.208	2.83	12.8	1.14
17	.0317	.132	.0583	2.54	15.8	1.34

^a Numbered chronologically.

16-17, inclusive, the iodine and vanadic ion were the only substances involved whose concentrations changed appreciably during the experiment. Also the (I_2) was negligible relative to the (I_3^-) , which in turn was negligible relative to the (I^-) . In these experiments it was therefore convenient to determine k' from an integrated expression. In these cases equation (2) can be written

$$\frac{-d[\Sigma(I_2)]}{dt} = k' \frac{(I_3^-)}{(H^+)(I^-)} [(V^{+++})_0 - 2\{(I_3^-)_0 - (I_3^-)\}] \quad (3)$$

in which the subscript 0 indicates initial concentration. Letting $c = (I_3^-) \doteq (I_3^-) + (I_2)$, and $b = (V^{+++})_0 - 2(I_3^-)_0$, equation (3) becomes

$$\frac{-dc}{dt} = \frac{k'}{(H^+)(I^-)} \times c(2c + b) \quad (4)$$

which on integration gives

$$k' = \frac{2.303(H^+)(I^-)}{b(t - t_0)} \log_{10} \frac{(2c + b)(c_0)}{(2c_0 + b)(c)} \quad (5)$$

The values of k' given for each of these experiments are averages of those determined from at least five well distributed points on the best concentration-time curve.

Since in experiments 10-15 inclusive the concentrations of the acid and/or iodide, as well as those of the vanadium and iodine, were so low that their concentrations changed appreciably during a run, the graphical slope method was employed to evaluate k' from equation (2). In each experiment slopes were obtained at not less than five well distributed points by use of both the Latshaw tangentimeter¹⁴ and the Richards-Roope Tangent Meter.¹⁵ Application of this method to a few of the experiments in which the "integration" method had been used, gave in each case satisfactory agreement in the values of k' . The value 0.00140 for the triiodide equilibrium constant at 25° was considered sufficiently accurate for the purpose of calculating the ratios of $(I_3^-)/(I^-)$.¹⁶

In none of the experiments was the average deviation of the values of k' from that given greater than 5%, and in most, less than 3%. Also there was no trend in the values of k' in any particular experiment. Several of the experiments were run in duplicate, and such pairs gave values of k' agreeing within these limits. The small variation in the values of k' over the wide range of concentrations used establishes equation (2) as the rate law.

Among the factors which may be effective in producing the small variation in the values of k' obtained are (1) the possibility of formation of vanadic-iodide complexes, and (2) the inadequacy of "ionic strength" alone as a criterion of constant ionic environment in solutions of such high concentrations of mixed electrolytes.

That the presence of tetravalent vanadium had no effect on the rate is shown by the results of experiment 5, in which the vanadyl perchlorate

(14) Latshaw, *THIS JOURNAL*, **47**, 793 (1925).

(15) Richards and Roope, *Science*, **71**, 290 (1930).

(16) (a) Jones and Kaplan, *THIS JOURNAL*, **50**, 1845 (1928); (b) La Mer and Lewinsohn, *J. Phys. Chem.*, **38**, 171 (1934).

was purposely made initially greater than that finally produced in any other experiment.

The Salt Effect.—Several experiments were carried out at various ionic strengths between 0.31 and 1.76, and at a constant iodide concentration of 0.108 molal. The large negative non-linear salt effect is shown in Fig. 1.

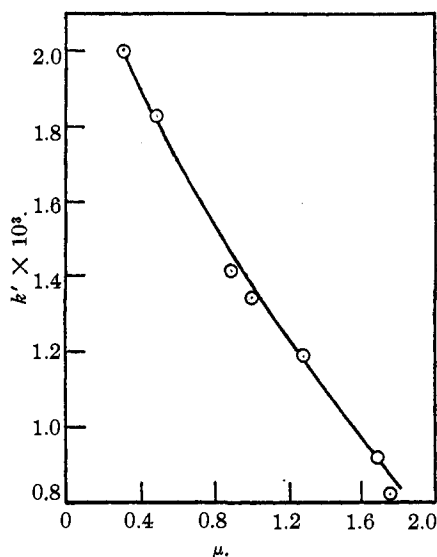


Fig. 1.—The salt effect.

Discussion.—The rate law established at constant ionic strength may be interpreted as meaning that the sole rate-determining step is a bimolecular one between iodine molecules and hydrolyzed vanadium ions, VOH^{++} . $(\text{VOH}^{++}) = K_2(\text{V}^{+++})/(\text{H}^+) = K_2(\text{total trivalent vanadium})/(\text{H}^+)$, since the (VOH^{++}) is negligible compared to the (V^{+++}) .

If a slow reaction between HIO and V^{+++} occurs to any measurable extent, a second term, $k''(\text{V}^{+++})(\text{I}_3^-)/(\text{H}^+)(\text{I}^-)^2$ (considering the mass-action expression for the small hydrolysis of iodine, $\text{I}_2 + \text{H}_2\text{O} = \text{H}^+ + \text{I}^- + \text{HIO}$), would have appeared in the rate equation. The constancy of k' over the eighty-fold range of iodide concentration is conclusive evidence that this reaction is not measurably involved.

Several rapid follow-up reaction mechanisms are possible. (1) The $\text{VOH} \cdot \text{I}_2^{++}$ critical complex¹⁷ may break down directly to vanadyl vanadium and I_2^- , the latter immediately oxidizing trivalent vanadium or reacting with another of its own kind to form iodine and iodide ions. Diiodide ion has been previously assumed as an intermediate by

(17) Brönsted, *Z. physik. Chem.*, **102**, 169 (1922).

Wagner.¹⁸ (2) The complex may decompose into iodide and pentavalent vanadium, the latter immediately reacting with trivalent vanadium. (3) VOH^{++} may react rapidly with the complex to form vanadyl vanadium and iodide. This last mechanism is similar to that proposed by Yost and Zabaro³ in their kinetic study of the entirely analogous trivalent titanium-iodine reaction.

Application of Brönsted's theory¹⁷ to this reaction results in the expression

$$\text{rate} = k_B K_1 \frac{(\text{I}_3^-)}{(\text{I}^-)} K_2 \frac{(\text{V}^{+++})}{(\text{H}^+)} \frac{\gamma_{\text{VOH}^{++}} \gamma_{\text{I}_2}}{\gamma_{\text{VOH} \cdot \text{I}_2^{++}}} \quad (6)$$

in which k_B is the Brönsted specific reaction rate, K_1 and K_2 are the mass action "constants" for the triiodide equilibrium and the vanadium hydrolysis, respectively, and the γ 's are activity coefficients. It is evident that at constant ionic strength the above equation reduces to the experimentally found rate law.

It is possible to draw certain rather qualitative conclusions regarding K_2 if the assumption is made that the large negative salt effect found is principally due to changes in the activity coefficients of the chemical species as the ionic strength is varied, rather than to a solvent effect brought about by this variation. The ratio $\gamma_{\text{VOH}^{++}}/\gamma_{\text{VOH} \cdot \text{I}_2^{++}}$ may be assumed not to change to any great extent over the range of salt concentrations considered; both K_1 and γ_{I_2} are known to be substantially constant over the range of ionic strength of 0.0 to 2.0.^{16b} According to this theory, the assumptions made, and the facts stated, it follows that this large negative salt effect is due to a rapid decrease of K_2 as the salt concentration is increased. This is equivalent to stating that the quotient, $\gamma_{\text{V}^{+++}}/\gamma_{\text{H}^+} \gamma_{\text{VOH}^{++}}$, decreases rapidly as the ionic strength increases. That this be so does not require that these ion activity coefficients individually decrease over the range of ionic strength used. In fact, from the well known variation in the activity coefficients of the univalent strong acids over this range of ionic strength, it seems probable that the activity coefficient of the hydrogen ion does pass through a minimum at some ionic strength between 0.3 and 1.8.

Summary

The rate of the reaction at 24.95° between iodine and trivalent vanadium in perchloric acid solutions has been measured, and found to be, at constant ionic strength, directly proportional to

(18) Wagner, *ibid.*, **113**, 261 (1924).

the concentrations of triiodide and vanadic ions, and inversely proportional to the concentrations of the hydrogen and iodide ions. This result is in agreement with the postulation that the single rate determining step is one between hydrolyzed vanadic ions, VOH^{++} , and iodine molecules.

Several possible rapid follow-up mechanisms have been suggested. The salt effect has been measured over the range of ionic strengths from 0.31 to 1.76, and a possible explanation for its large negative magnitude has been advanced.

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The Mechanism of Substitution Reactions. Substitution of Bromine and Chlorine in Phenylbromo and Phenylchloroacetic Acids by Chloride and Bromide Ions in Aqueous Solution

BY M. J. YOUNG AND A. R. OLSON

When an optically active bromo compound is treated with chloride ion, a whole system of reactions is initiated. By making a kinetic study of the system of reactions which occurs when *l*-bromosuccinic acid is treated with chloride ion in aqueous solution, Olson and Long¹ were able to prove the correctness of the theory of the mechanism of substitution reactions advanced by Olson,² and by Bergmann, Polanyi and Szabo,³ according to which configurational inversion accompanies every single-step substitution.

The present study deals with the kinetics of the corresponding system of reactions produced by treating *l*-phenylbromoacetic acid with chloride ion in aqueous solution. The results provide additional confirmation of the above-mentioned theory.

The relations between the heats of activation of the various reactions in the succinic system, studied by Olson and Long,⁴ are again apparent in this system. The same is true of the temperature independent factors.

Preparation of Materials

Phenylbromoacetic acid and phenylchloroacetic acid were prepared from mandelic acid (phenylhydroxyacetic acid) by treatment with the corresponding phosphorus pentahalides, following the procedure given by Walden and Bischoff.⁵ The acids were resolved by fractional crystallization of their morphine salts from methyl alcohol, following the procedure of McKenzie and Clough.⁶ The products were shown to be chemically pure by the usual analyses. Complete resolution was not obtained in all

cases but as is shown by the rate laws, optical purity is in no way essential. It is essential that the assumption that *l*-phenylchloroacetic acid and *l*-phenylbromoacetic acid have the same configuration be correct. This assumption is in accord with the opinion of those who have worked with such compounds.

Apparatus

For all measurements of optical activity a laboratory constructed polarimeter of the Lippich type was used, with monochromatic light (λ 5461) obtained from a mercury arc and suitable filters. The angle of rotation was determined from the deflection of the image of an illuminated scale, four meters distant, produced in a small plane mirror mounted nearly on the axis of the analyser, and reflected into a telescope parallel to the optic axis by means of a periscope arrangement. This device enabled rotations to be read directly to 0.007° (1 mm. of scale) and estimated to 0.001° . A given setting can be duplicated to 0.005° . A thermostat provided with glass windows was mounted directly on the polarimeter so that tubes did not have to be removed for observation.

Experimental Procedure

Due to the slowness with which the phenylhalogenoacetic acids dissolve in water, the following procedure was adopted. A weighed amount of the active acid was dissolved in 0.4 cc. of methyl alcohol. To this solution was added the required amount of 2.00 *N* perchloric acid (about 10 cc.) followed, after re-solution had occurred, by the required amount of 2.00 *N* halogen acid (about 10 cc.). The addition of so small an amount of methyl alcohol has no observable effect on the reaction rates. All solutions were prepared at the temperature of the experiment. After the solution process, the material was transferred rapidly to a 30-cm. polarimeter tube and placed in the thermostat. Zero time was taken as the moment of addition of halide ion. The time interval between this addition and the first reading was never more than four minutes. In all experiments the concentrations are: active acid 0.015 *M*, halide ion 1.00 *M*, hydrogen ion 2.00 *M*, unless otherwise specified.

The Formation of Mandelic Acid from Phenylhalogenoacetic Acids.—The detailed mechanism

(1) A. R. Olson and F. A. Long, *THIS JOURNAL*, **56**, 1294 (1934).

(2) A. R. Olson, *J. Chem. Phys.*, **1**, 418 (1933).

(3) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

(4) A. R. Olson and F. A. Long, *THIS JOURNAL*, **58**, 393 (1936).

(5) Walden and Bischoff, *Ann.*, **279**, 122 (1894).

(6) McKenzie and Clough, *J. Chem. Soc.*, **93**, 818 (1908).