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A Contribution to the Study of the Nature of the Interaction between Hydrous Oxides and Mordant Dyes.

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Reasons for Undertaking the Present Study

Some years ago, in the course of a study of the effect of hydrogen-ion concentration on the so-called adsorption of dyes by hydrous oxide gels, Gordon and Marker[1]

[1] Ind. Eng. Chem. 16, 1186 (1924).

remarked certain phenomena which were interpreted at that time as indicative of compound formation. The behavior of Orange II, applied to hydrous oxide gels of aluminum and iron at varying hydrogen-ion concentration, seemed to present particularly convincing evidence of chemical interaction between the dye and the adsorbent gel. Briefly summarized, the relevant observations made at that time were as follows:

Firstly, curves obtained by plotting pH values against milligrams of dye removed from solution per gram of gel, showed marked and rather sharp alterations in their slopes at low pH values. Secondly, it was found that solutions containing varying concentrations of dye,[2]

[2] Concentrations of 0.5 per cent, 0.75 per cent, and 1.16 per cent were employed.

but adjusted to the same pH value,[3]

[3] Unfortunately the actual pH value has not been recorded but the senior author has communicated to the present writer that it was somewhat below 3.0.

arrived at practically identical dye concentrations when allowed to come to equilibrium with aluminum and iron gels. Thirdly, analyses of samples of the supposed dye-metal compounds agreed with calculated values for those compounds within the limits of experimental error. At that time it was also noted that aluminum or ferric salts, either in solution or in the solid state, produced precipitates when added to solutions of Orange II. These precipitates were believed to be the slightly soluble dye salts of aluminum and ferric iron, respectively, although no analyses were made.

Some time later Weiser and Porter[4]

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[4] H. B. Weiser and E. E. Porter, J. Phys. Chem. 31, 1704 (1927). See also H. B. Weiser and E. E. Porter, "Colloid Symposium Monograph" Vol. V, 1928, p. 369, and H. B. Weiser, "A Survey of American Chemistry" Vol. III, 1928, pp 43-44.

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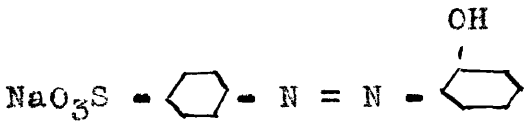
questioned these conclusions and criticized in detail certain portions of the experimental work upon which they were based, at the same time advancing other explanations to account for the phenomena observed. They furthermore recorded certain experimental observations of their own which were advanced as tending to disprove the theory of compound formation. Those criticisms and observations will be discussed in their appropriate connections in the present paper. Suffice it to say at this point that, while the remarks of Weiser and Porter cast doubt upon the original conclusions of Marker and Gordon, they involved certain obviously erroneous assumptions and failed in several particulars to account satisfactorily for

all of the phenomena of which the present writer had knowledge. On the whole it seemed highly desirable to re-examine the entire matter thoroughly.

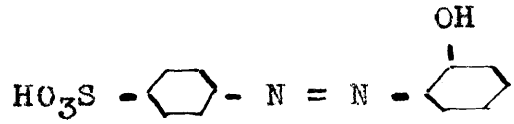
INTERACTION OF ORANGE II AND $AlCl_3$

One of the strongest indications of compound formation previously noted had been the constancy and equivalency of chemical composition of the product obtained. It was decided, therefore, to make a number of preparations under varying conditions in order to eliminate the possibility of hitting upon some one unfortunate coincidence of conditions which might lead to the formation of a heterogeneous product in which the dye radical and the metal ion might accidentally appear in equivalent quantities.

It may be well to preface an account of the procedures followed with the statement that Orange II is the sodium salt of 2-hydroxy-1-phenylazonaphthalin-1^4-sulfonic acid, to use the system of numbering employed by Richter. The respective structural formulae are as follows:



(Orange II)



(Free acid of Orange II)

For the purpose of this investigation Orange II may be regarded merely as the sodium salt of a substituted sulphonic acid. As a matter of convenience the dye radical or ion will occasionally be designated hereafter as X, the dye itself as NaX, and the free acid as HX.

It is common knowledge among organic chemists that the aromatic sulfonic acids are, as a group, strong acids. In

fact they are generally considered as comparable, in strength and in properties which involve their acid characteristics only, to the mineral acids -- at least to sulfuric acid. A priori there is all good reason to suppose that they would be capable of forming a wide range of metallic salts, including aluminum and ferric salts. As a matter of fact ferric and aluminum salts of several sulfonic acids have been prepared, analyzed, and studied by Dubsky.[5]

[5] J. V. Dubsky, J. prakt. Chem. 90, 61-118 (1914), $Fe(C_6H_5SO_3)_3.9H_2O$; ibid., 93, 142-161 (1916), $Al(C_6H_5.SO_3)_3.9H_2O$, $Al(C_6H_5.CH_2SO_3)_3.9H_2O$, $Al(HO.C_6H_4.-SO_3)_3.9H_2O$, $Al(C_{10}H_7.\alpha\text{-}SO_3)_3.9H_2O$, $Al(C_{10}H_7.\beta\text{-}SO_3)_3.9H_2O$.

On this basis one might anticipate the possibility of a metathetic reaction between aluminum chloride and the dye, according to the equation:

$$AlCl_3 + 3NaX \rightleftharpoons AlX_3 + 3NaCl,$$

with the equilibrium shifted almost completely to the right if the product, AlX_3, proved to be but slightly soluble.

This hypothetical reaction was investigated by preparing and analyzing three products. The first was obtained as follows. About[6] 13.5 grams of Orange II[7] ($C_{16}H_{11}O_4N_2SNa.5H_2O$) was dissolved in approximately one liter of distilled water and

[6] These quantities were weighed on a rough laboratory balance.

[7] The dye used was concentrated Orange II furnished by the du Pont Company through the courtesy of Mr. E. K. Bolton.

filtered. About 2.5 grams of $AlCl_3.6H_2O$ was dissolved in approximately 100 cc. of distilled water and filtered. The solutions were combined in the cold with stirring. The heavy, orange-yellow, apparently amorphous precipitate which remained suspended throughout the liquid was filtered off with the aid of suction, a perfectly clear filtrate being obtained. The filter cake was washed with 200 to 300 cc. of distilled water.

Preliminary experiments showed washing to be necessary, for the precipitate occludes and carries down some unchanged Orange II, as evidenced by the fact that sodium can be detected in the ignition residues. Since the product precipitated is pulverulent rather than gelatinous, the necessary washing is accomplished quite readily. The completion is indicated when the highly colored filtrate containing the excess of Orange II gives place to a faintly colored filtrate containing some of the product in solution and some dye acid arising from hydrolysis. The amount of water used in rinsing was so chosen that a small quantity, about 50 cc., of faintly colored filtrate passed from each sample.

The product was well drained and partially dried by suction and then allowed to air-dry for several days at room temperature. The cake which had then deepened in color to a reddish orange and had become hard and brittle was ground in a hand mortar and samples were taken for analysis.

The dye radical was determined by a slight modification of the $TiCl_3$ method outlined by Knecht and Hibbert[8] for Orange II.

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[8] "New Reduction Methods in Volumetric Analysis" Longmans, Green and Co., New York City, 1918. p. 76.

The deviation consisted in the fact that individual samples of 0.1 gram were analyzed instead of aliquot parts from a solution of one sample.

Aluminum was determined by igniting 0.5 gram samples of the product in covered platinum crucibles and blasting to constant weight.

Moisture content was determined by drying 0.5 gram samples to constant weight at 120°-125° C. in a Freas electric oven. The samples were dried in small glass-stoppered weighing bottles, the stoppers of course being removed while samples were in the oven but immediately replaced whenever they were withdrawn.

The results of our analyses on this product were as follows:

		Average
% H_2O	19.33 19.20	19.27
% Al	2.32 2.35	2.34
% X	78.30 78.42	78.36
		99.97

Reduced to a dry basis these figures give 2.88% of Al as compared with a calculated value of 2.67% for AlX_3, and 97.05% of X as compared with the calculated value of 97.33%.

The quantities of dye and $AlCl_3.6H_2O$ used in the preparation of the product just described represent an equivalent ratio of 1:1. Two other preparations were made and analyzed in

the same manner except that equivalent ratios of 2:1 and 1:2, respectively, were used. The actual quantities employed were 27.0 grams of dye to 2.5 grams of $AlCl_3.6H_2O$ in the first case, and 13.5 grams of dye to 5.0 grams of $AlCl_3.6H_2O$ in the second case. The analyses were as follows:

	2 Dye: 1 $AlCl_3$			1 Dye: 2 $AlCl_3$		
	#1	#2	Avge.	#1	#2	Avge.
% H_2O	19.11	18.95	19.03	17.73	17.73	17.73
% Al	2.25	2.24	2.25	2.40	2.39	2.40
% X	78.87	78.99	78.93	79.14	79.36	79.25
	100.23	100.18	100.21	99.27	99.48	99.38

The average analyses for all three products, reduced to a dry basis are summarized in Table I.

TABLE I.

	Calc. for AlX_3	1 Dye:1 $AlCl_3$	2 Dye:1 $AlCl_3$	1 Dye: 2 $AlCl_3$
% Al	2.67	2.88	2.77	2.91
% X	97.33	97.05	97.48	96.33
	100.00	99.93	100.25	99.24

The agreement between observed and calculated values is not perfect, yet it is on the whole rather good when one considers that the rinsing of the precipitate might be expected to hydrolyze the salt, giving a product too low in dye and too high in aluminum. At any rate it seems safe to assume that the figures just quoted indicate a relationship other than coincidental between the quantities of dye radical and aluminum present in the products so formed.

Weiser and Porter[4] accounted for the precipitate

formed when a solution of aluminum chloride is added to a solution of Orange II by calling it "a mixture of the hydrous alumina gel and Orange II acid", "due to the simultaneous hydrolysis of the two salts, one of a weak, slightly soluble acid with a strong base, and the other of a slightly soluble base with a strong acid." This explanation is founded upon two erroneous assumptions. The free acid of Orange II is neither a weak acid nor is it slightly soluble. We shall deal with both these points more specifically in a moment. It is sufficient to remark now that the free acid is considerably more soluble than the dye itself and that in the experiments just discussed the dye solutions employed were far from saturated. Even had these assumptions been correct it is difficult to see how equivalent quantities of dye acid and alumina gel could have been carried down under all three sets of conditions described.

THE FREE ACID OF ORANGE II

The free acid of Orange II used in the experiments which will be described hereafter was prepared and purified according to the method of Sisley.[9] Briefly described the

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[9] P. Sisley, Bull. Soc. Chem. 3 25, 962 (1910)

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method consists essentially in refluxing Orange II with a large excess of strong mineral acid and filtering off the precipitated dye acid which is still contaminated with some of the dye. After drying to remove HCl the precipitate is extracted with a mixture of alcohol and ether and reprecipitated by the addition of a large excess of ether. When dry, the new

precipitate is again extracted, but this time with ethyl alcohol. The dye acid is finally precipitated with a large excess of ether, filtered off after standing over night, rinsed with ether, and air-dryed. It is thus obtained in the form of minute reddish-brown, needle-like crystals carrying four molecules of water of crystallization.

It may be well to discuss at this point several of the properties of the dye acid, for we have already had occasion to refer to them and shall do so again hereafter.

Sisley[9] determined the solubility of the dye acid in water and in varying concentrations of hydrochloric acid at 19° C. His figures are reproduced in Table II. The first two columns are Sisley's; the other two columns have been calculated by the writer for convenience in reference.

TABLE II

Solubility of $HX.4H_2O$ in Water and Hydrochloric Acid at 19° C.

Conc. of HCl gm. per l.	Sol. of $HX.4H_2O$ gm. per l.	Normality HCl	HX gms. per l.
0	174.4	0.0	142.8
1	140.6	0.027	115.2
5	88.7	0.137	72.6
10	69.7	0.274	57.1
20	9.7	0.548	7.9
30	1.89	0.822	1.55
40	0.42	1.096	0.33
50	0.27	1.37	0.22

Working at a room temperature of 25°C. the writer attempted an approximate check on Sisley's figures by preparing

saturated solutions of dye acid in distilled water and in tenth normal hydrochloric acid. With distilled water we were unable to obtain a solution in equilibrium with the solid acid. The acid behaved very much like sugar, continuing to dissolve until a solution of sirupy consistency was obtained. The solution could actually be drawn into a thread with a glass rod. After about 25 grams of acid had been added to approximately 60 cc. of water the project was abandoned. With tenth normal hydrochloric acid a saturated solution was obtained. Ten cubic centimeters of the solution were made up to one liter and 20 cc. aliquots were titrated with $TiCl_3$. The HX content was found to be 57.1 grams per liter. The figure obtained by plotting Sisley's first four values, drawing a smooth curve through them, and dropping perpendiculars at a tenth-normal concentration of HCl is 82.7 grams of HX per liter.

It is rather difficult to account plausibly for the considerable discrepancy between the results of Sisley and those of the writer. Sisley records one phenomenon which may or may not throw light on the first point of difference. He prepared Orange II in three forms -- anhydrous NaX, NaX.2 $1/2H_2O$, and $NaX.5H_2O$. In determining the solubility of the salt he noted that the hydrates appeared rather stable even in the presence of water, and he records three solubilities for the three respective forms of the salt. All forms in time reached the solubility ascribed to $NaX.5H_2O$. Whether the dye acid behaves in a similar fashion is a question. The writer has not observed anything to indicate that it does. The difference in temperatures (19° and 25° C.) might also account for a considerable difference in the solubility of the acid.

Neither of these possibilities, however, seems to account adequately for the lesser solubility observed in 0.1 hydrochloric acid. Unfortunately Sisley does not describe the method whereby he determined the amount of acid present in solution. It is certain, however, that he did not titrate with $TiCl_3$.

Since these points are irrelevant to the main purpose of this investigation they have not been pursued to a solution. The significant fact established is that the dye acid is extremely soluble in pure water solution and quite soluble even in tenth-normal hydrochloric acid.

We have not succeeded in crystallizing the dye acid from water nor from dilute hydrochloric acid solutions, although it did crystallize from 20% HCl solution.

Sisley[8] also remarked the apparent strength of the dye acid, as evidenced by the comparatively large excess of mineral acid necessary to free it from its sodium salt. His figures are presented in Table III.

TABLE III

Conc HCl %	Equivalents HCl per equiv. NaX	Orange II Decomposed %	Orange II Undecomposed %
0.4	1.07	no ppt	no ppt
1	2.14	"	"
2	4.28	"	"
2.5	5.35	46.2	53.8
3	6.42	58.5	41.5
4	8.56	78.1	21.9
5	10.70	79.4	20.6
10	21.40	80.9	19.4
15	32.10	87.5	12.5
20	42.80	97.4	2.6

As a further check upon this point small quantities of dye acid and of dye were carefully purified for the purpose of preparing solutions to be investigated potentiometrically. The dye acid prepared as already described, was dissolved in warm alcohol. Ether was then carefully added little by little in such manner that any dye acid precipitated was redissolved before the addition of more ether. When it seemed probable that further addition of ether would cause a permanent precipitate the flask containing the mixture was loosely stoppered with a cork stopper and allowed to stand for several days. The dye acid crystallized in large, nearly black needles which reflected a greenish sheen. Some of the crystals were over a centimeter in length and about half the diameter of a pencil lead. After being washed with ether and air-dried they were analyzed, yielding a moisture content of 9.92% and an HX content of 90.13%. These figures agree well with the theoretical values for $HX.2H_2O$.

	Calc. for $HX.2H_2O$	Found
% HX	90.11	90.13
% H_2O	9.89	9.92
	100.00	100.05

The dye itself was crystallized, first from NaCl solution and then from alcohol.

Solutions of the dye and dye acid were made up and carefully adjusted to a normality of exactly 0.01. The concentrations were checked by titration against $TiCl_3$.

The solutions were then placed in Bureau of Standards

burets and mixtures were prepared for hydrogen-ion measurement.

The hydrogen-ion readings were made with a Leeds-Northrup student-type potentiometer outfit, using a quinhydrone electrode and a saturated calomel cell. The quinhydrone electrode was chosen because of the convenience and rapidity with which it can be handled and with the idea of avoiding any effect which might be produced by the reduction of dye at the hydrogen electrode.[10]

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[10] A comparative study of the results obtained with the hydrogen and quinhydrone electrodes on Orange II solutions has now been completed and is reported in this paper.

The quinhydrone was prepared according to the method of Billmann and Lund[11] and twice recrystallized from distilled water slightly

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[11] Ann. Chem. (9), 16, 321 (1921)

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acidified with acetic acid. At the time the readings were made the outfit was checked against an M/20 solution of carefully purified acid potassium phthallate. The pH value of 3.96 obtained agreed well with the value of 3.974 reported by Clark and Lubs.[12] All pH values were calculated by means of the

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[12] J. Biol. Chem. 25, 479 (1916)

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factors and cell constants tabulated by Clark.[13] The results

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[13] "The Determination of Hydrogen Ions". The Williams & Wilkins Co., Baltimore. Third Edition. 1928. pp 672 and 674.

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obtained are summarized in Table IV.

TABLE IV

pH Values of HX Solutions and HX-NaX Mixtures 32.5° C.

Composition of Solution			pH	$[HX]$ x 10^{-2}	$[H^+]$ [a] x 10^{-2}
cc. 0.01 N HX	cc. 0.01 N NaX	cc. H_2O			
10	-	-	2.05	1.0	.891
8	2	-	2.14	0.8	.725
5	5	-	2.31	0.5	.490
2	8	-	2.75	0.2	.178
8	-	2	2.15	0.8	.708
5	-	5	2.32	0.5	.479
2	-	8	2.66	0.2	.219

[a] On the assumption that pH = $\log \frac{1}{[H^+]}$

The results on the water dilutions are not strictly comparable to those obtained with the NaX-HX mixtures, for in the one case we are considering solutions of varying ionic strength and in the other, of constant ionic strength. Another factor which might affect the results is the possibility that at high dilutions the hydroxy of the napthol group may come into play. Nevertheless we can conclude with some certainty that Orange II is a practically neutral salt -- a fact which supports the contention that the dye acid is

a strong acid.

Interaction of HX with $AlCl_3.6H_2O$

It had already been noted in our laboratory, though not previously recorded in the literature, that aluminum chloride solution forms a precipitate when added to a solution of the free dye acid. It seemed that this phenomenon might be reasonably accounted for by the equation:

$$AlCl_3 + 3HX \rightleftharpoons AlX_3 + 3HCl$$

where the product AlX_3 is but slightly soluble. As a test of that hypothesis the present investigator prepared two products.

Quantities of reagents and volumes employed were approximately equivalent to those used in examining the NaX-$AlCl_3$ interaction. The equivalent ratios employed were 2 $AlCl_3$: 1HX and 1 $AlCl_3$: 1.5 HX. The procedure was varied as follows. The dye acid solution was heated to boiling and the aluminum chloride solution added slowly with stirring. The solution was filtered hot and the product began to crystallize as soon as the liquid began to cool. Almost the entire product crystallized in minute, orange-yellow needles, although a few leaflets could be seen. The crystals were filtered out by means of suction and then allowed to air-dry. The dry filter cakes had the appearance of felt. Analyses of these products are presented in Table V.

TABLE V

	2 $AlCl_3$: 1 HX			1 $AlCl_3$: 1.5 HX		
	#1	#2	Avge.	#1	#2	Avge.
% H_2O	20.36	20.26	20.31	16.88	16.94	16.91
% Al	2.13	lost	2.13	2.24	2.20	2.22
% X	77.62	76.66	77.64	80.82	80.73	80.78
	100.11		100.08	99.94	99.87	99.91

In Table VI the average values are reduced to a dry basis and compared with the calculated values for AlX_3. The agreement is rather good.

TABLE VI

	2 $AlCl_3$: 1 HX	1 $AlCl_3$: 1.5 HX	Calc. for AlX_3
% Al	2.67	2.66	2.67
% X	97.42	97.15	97.33
	100.09	99.81	100.00

Interaction of HX with Hydrous Alumina Gel

Marker and Gordon[1] reported the preparation of a product containing equivalent quantities of aluminum and dye radical through the interaction of dye acid and alumina gel. Unfortunately the exact procedure followed was not described.

Weiser and Porter[4] have contended that the product obtained was a mixture of dye acid and gel and have accounted for the equivalency of components by assuming that equivalent quantities of dye acid and gel had been suspended in water

and boiled, and that on cooling the solid matter had been filtered off and analyzed. They say:

> "If the alleged compound is merely a mixture of gel with the Orange II acid crystals, why does the composition correspond to that of a chemical compound? The answer is that it does not unless the two insoluble substances, the gel and the insoluble acid, are mixed in the theoretical ratio and the analysis made for that ratio. We are forced to the conclusion that this unfortunate procedure was followed by Marker and Gordon."

Weiser and Porter, however, offer no analyses to substantiate their assertions, although they do report some qualitative experimental work. They say:

> "In every case, the presence of crystals was observed in accord with the statements of Marker and Gordon. However, the crystals were not an aluminum salt but were merely the free acid of Orange II. A particularly striking crop of crystals was obtained by heating and cooling the mixture. .... There is no doubt whatsoever that the crystals formed in the presence of the gel are the free acid ...."

In this connection they discuss some qualitative observations on the behavior of the crystals which will be discussed presently.

As a matter of fact the product previously investigated by Marker and Gordon had been prepared as follows.[14]

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[14] Private communication.

A quantity of hydrous aluminum gel was added to a solution containing dye acid in considerable excess of the quantity calculated as necessary for reaction with the aluminum. The mixture was boiled and then filtered hot. As the clear filtrate cooled, needle-like crystals separated from it. These crystals, which Weiser and Porter designate as crystals of dye acid, constitute the product analyzed by Marker and found to contain equivalent

quantities of dye radical and aluminum.

As a check upon this previous experiment, the writer repeated the preparation, employing a small excess of dye acid over that calculated as equivalent to the alumina gel used. The mixture was filtered hot and the crystals which separated from the clear filtrate upon cooling were filtered with suction, air-dried for several days, and analyzed. The results were as follows.

	Found				
	#1	#2	Avge.	Reduced to dry basis	Calc. for AlX_3
% H_2O	19.62	19.64	19.63	-	-
% Al	2.21	2.19	2.20	2.74	2.67
% X	78.03	78.03	78.03	97.20	97.33
	99.86	99.86	99.86	99.94	100.00

Taken in conjunction with the already presented data bearing upon the solubility and strength of the dye acid, these facts seem to furnish adequate comment upon the remark of Weiser and Porter[4] that, "Since Marker and Gordon assume an appreciable solubility of the alleged salts, a simple consideration of well-established laws of the kinetics of chemical reactions should have suggested the improbability of forming a salt from the much less soluble gel and a weak, slightly soluble acid."

Observations upon the Behavior of the Supposed Al Compound

It will be noted that in none of the preceding tabulations has a definite degree of hydration been assigned to the

crystals obtained. Two considerations prompt this omission. Firstly, the indications are that the product obtained by allowing a boiling solution of AlX_3 to cool and crystallize, consists of a mixture of hydrates. The product usually consists almost entirely of fine needle-like crystals, but these crystals vary in size and color depending upon the concentration and temperature of the solution from which they separate. Often a few leaflets may also be seen, especially if the mother liquor is highly concentrated and rather acid.

Secondly it is evident that the hydrates which precipitate from solution are not stable in contact with air at room temperature. As an example Table VII presents two series of determinations made upon samples prepared under the same conditions, but exposed to the air for different intervals. The first was made after the product had been air-dried for three days; the second after about six weeks. Calculated values for two hypothetical hydrates are included for purposes of comparison only.

TABLE VII

	Exposed to air 3 days	Calc. for $AlX_3.14H_2O$	Exposed to air 6 weeks	Calc. for $AlX_3.10H_2O$
% H_2O	20.31	20.01	15.07	15.16
% Al	2.13	2.14	2.28	2.26
% X	77.64	77.85	82.61	82.58
	100.08	100.00	99.96	100.00

Our experience with moisture determinations on these salts leads us to doubt whether there is any distinct hydrate, stable over the usual range of atmospheric temperature

and humidity. We have not, however, investigated this point carefully.

The crystals of AlX_3, like those of the dye acid retain their form under drying to constant weight at 120° - 125° C. The color, however, changes to a dark, reddish brown. The anhydrous crystals are hygroscopic and change color as they regain moisture, through red to reddish orange. The compound decomposes somewhere between 145° and 155° C. Sisley[9] noted that the dye acid also decomposes at about 150° C.

The crystals cannot be <u>totally</u> redissolved in pure water nor in 95% ethyl alcohol in the cold. The liquid takes on the characteristic color of the dye, the crystalline form disappears and a pulverulent, orange-yellow solid phase remains. If a small amount of HCl or dye acid or a rather larger amount of $AlCl_3$ are added to the liquid, considerable quantities of crystals will dissolve without residue upon heating. If a moderate quantity of the salt is added to boiling water it will dissolve almost without residue. The salt is considerably more soluble in ethyl alcohol than in water.

This should not be taken to mean that none of the salt dissolves in pure water or in 95% alcohol. If either of these liquids is heated with an excess of the crystals and filtered hot, crystals will again separate from the clear filtrate upon cooling. No doubt these phenomena form the basis for the statement of Weiser and Porter[4] that the crystals (which they believed to be crystals of the dye acid) can be dissolved from the gel with hot water or alcohol, as well as for their further assertion that, "If the (water) solution is filtered while hot the needle crystals of the free acid

separate from the filtrate on cooling."

It is a rather tedious matter to prepare in this manner sufficient salt for a complete analysis, but the simple expedient of igniting a few of the crystals and noting the residue of Al_2O_3 remaining would have revealed to them their error. An analysis performed by us upon a sample obtained in this way gave the following results:

	Found			Avge. reduced to Dry Basis	Calc. for AlX_3
	#1	#2	Avge.		
% H_2O	19.67	19.59	19.63	-	-
% Al	2.03	2.04	2.04	2.54	2.67
% X	78.26	78.38	78.32	97.45	97.33
	99.97	100.01	99.99	99.99	100.00

The needle-like crystals obtained from alcoholic solution are larger than those which separate from water and deep red in color. On this account the writer considered the possibility that the liquid of hydration might in this case be alcohol. A sample crystallized from alcohol containing a small amount of $AlCl_3.6H_2O$ in solution was analyzed with the following results.

(Average of duplicate determinations)

	Found	Reduced to Dry Basis	Calc. for AlX_3
% Loss of Weight on Drying	17.52	-	-
% Al	2.21	2.68	2.67
% X	80.34	97.40	97.33
	100.07	100.08	100.00

About three drops of the liquid of hydration was distilled from a small sample of the crystals into a receiver

containing about 0.5 cc. of distilled water. When submitted to the iodoform test after the manner recommended by Mulliken,[15]

[15] "Identification of Pure Organic Compounds." John Wiley & Sons, Inc. New York. First edition. 1914, Vol. I, p. 166.

the liquid gave a decided test for alcohol.

Unfortunately the entire lot of crystals was exhausted in other tests before the writer had an opportunity to make a refractometric reading upon the liquid of hydration. Another sample of somewhat smaller crystals was prepared from alcohol containing a slight excess of HX in solution. The analysis was as follows:

(Average of duplicate determinations)

	Found	Reduced to Dry Basis	Calc. for AlX_3
% Loss of wt. on drying	15.60	-	-
% Al	2.23	2.64	2.67
% X	82.13	97.31	97.33
	99.96	99.95	100.00

A few drops of the liquid of hydration examined in an Abbe refractometer at 27° C. gave a reading of 1.338. Since at 28° water has an index of 1.33219 and ethyl alcohol an index of 1.35721, it seems that the liquid of hydration must be largely water.

The explanation which seems to us to account most plausibly for the phenomena just discussed is that in pure water or in 95% alcohol the salt partially hydrolyzes, due to its slight solubility in the cold. If, however, some substance which might be expected to prevent hydrolysis or to dissolve

the hydrous alumina so formed is added, complete solution results upon heating.

Under these circumstances it seemed to us useless to attempt any exact solubility determinations, and we have contented ourselves with the qualitative observations just made. It is obvious from what we have already said that the solubility of the salt increases greatly with increasing temperature. It is also evident that the previous assumption of Marker and Gordon that the true solubility of the salt could be calculated from the amount of dye radical present in a solution in equilibrium with the solid phase was erroneous.

This was one of the mistaken preconceived notions with which the writer entered upon the investigation of the present problem. Out of it grew the plan for a method of attack which yielded experimental results quite different from those anticipated. For reasons which will develop as we proceed it became evident that a strictly quantitative study could yield results which would be valid for one specific set of conditions only -- a set of conditions which, by the way, could not be completely defined, or even reproduced at will. Hence these particular experiments were not pushed to a quantitative conclusion, but they furnish the basis for a rather interesting qualitative discussion which may be worthy of introduction here.

The idea originally entertained by the writer was that a check upon the solubility figure of Marker as well as further evidence upon the question of compound formation could be obtained by allowing varying quantities of solid AlX_3 to come to solution equilibrium in a fixed volume of water.

(The quantities of salt were to be so chosen that all were in excess of the amount necessary to saturate the solution.) One would, of course, anticipate that a salt of what we may term simple, normal behavior would yield in all cases solutions of the same concentration (as measured by titration of the dye radical with $TiCl_3$). Since aluminum salts are invariably hydrolyzed, one might also anticipate that one saturated solution would display the same degree of hydrolysis as another saturated solution (as indicated by measurement of the hydrogen-ion concentration). Furthermore one might predict that a quantity of dye acid allowed to come to equilibrium with an excess of alumina gel in a volume of water small enough to be saturated by the AlX_3 formed would produce a liquid phase of the same dye-ion and hydrogen-ion concentrations as that obtained by allowing solid salt to come to solution equilibrium with water.

Although the observations already recorded indicate that the salt (AlX_3) is not one of "simple, normal" behavior, it might appear at first thought that this line of reasoning would still apply. A little consideration, however, makes obvious the fallacy of this expectation. Let us begin by analyzing in some detail the behavior of AlX_3 in the presence of water.

It may be well to preface that analysis with a notation that the experiments of Heyrovsky[16] on $AlCl_3$, indicate

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16 J. Chem. Soc. 117, 11-26 (1920)

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that the hydrolysis occurs in three stages as might be expected. There has been some disagreement over the details of transition

from one stage to another, but two points seem to be generally accepted: first, that the third stage of hydrolysis is reached only in very high dilutions, and second, that precipitation takes place only when hydrolysis has reached the third stage.

It is always questionable as to how far one is justified in reasoning by analogy, and it must remain somewhat speculative in the case of AlX_3 whether or not the earlier stages of hydrolysis may not give rise to insoluble products. The fact that no basic salts were encountered in the present study is indicative, though perhaps not conclusive, evidence in the negative. However, the general principles employed in the discussion we are about to undertake would not be greatly altered by this point and it would be desirable in any case, for the sake of simplicity, to confine our consideration to the third stage of hydrolysis. One assumption we are fairly safe in making, it would seem. Although the dye acid (HX) has been shown to be a strong acid it can hardly be considered the equal in this respect of HCl. Hence, one would naturally expect that the third stage of hydrolysis would be reached in higher equivalent concentrations of AlX_3 than of $AlCl_3$.

With these preliminary observations disposed of let us return to a contemplation of the behavior of AlX_3 in contact with water. The first point to be noted is that it would be a mistake to take a saturated solution of AlX_3 as our point of departure in this instance. The solubility of AlX_3 is very low at room temperatures and it may well be that a saturated solution would be sufficiently dilute to experience the third degree of hydrolysis. However, we do not begin with a saturated solution and it is unnecessary to make any assumptions on this point.

When a quantity of AlX_3 is introduced into water we may suppose that a small increment of AlX_3 immediately goes into solution. In the extremely dilute solution so produced we may safely assume that the salt immediately undergoes the third degree of hydrolysis. The reactions involved may be indicated as follows:

(1) AlX_3 (solid) $\longrightarrow$ AlX_3 (sol'n)

(2) AlX_3 (sol'n) $\rightleftharpoons$ $Al^{+++} + 3X^-$

(3) $H_2O \rightleftharpoons H^+ + OH^-$

(4) $Al^{+++} + 3OH^- \rightleftharpoons Al(OH)_3$

(5) $H^+ + X^- \rightleftharpoons HX$

Upon the basis of the newer ionization theories there is valid objection to the inclusion of (5) but the point is unimportant in this connection. It will be noted that all reactions except (1) are written in the form of equilibria. At the outset (1) should not represent an equilibrium, though it may or may not finally attain that status. In consideration of the extremely low basic solubility product[17] of $Al(OH)_3$ it is evident that equilibrium (4) is located very far toward the right. For all practical purposes we would ordinarily write the summation equation:

(6) $Al^{+++} + 3X^- + 3H^+ + 3OH^- \longrightarrow Al(OH)_3 + 3H^+ + 3X^-$,

which would lead to practically complete hydrolysis. However, in addition to the opposed reactions involved in the ionic equilibrium between Al^{+++}, X^-, H^+, and OH^-, there is another reaction which combats complete hydrolysis, and this is the

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[17] Heyrovsky calculates it to be 1.06×10^{-33}.

reaction which introduces an indeterminate factor.

Without attempting to characterize it in detail we may designate this reaction as the action of free dye acid on solid $Al(OH)_3$ to re-form the salt AlX_3 or its component ions. The rate of this opposing reaction depends only incidentally and partially on the total amount of $Al(OH)_3$ present. It is actually determined by two factors: first, the effective concentration of free dye acid present in solution, and secondly, the area of the interface between the solution and the solid $Al(OH)_3$. To a certain extent it may also be affected by the nature of the solid side of the interface.

Now the tendency of $Al(OH)_3$ precipitates to alter with time and under the influence of temperature changes and other factors is well-known. The general trend of the alteration is: first, the aggregation of individual particles with diminution of total surface, followed by crystallization with probable further change in surface extent and ~~certain changes~~ in the nature of the surface.

As the condition of the solid $Al(OH)_3$ changes, the rate of the reaction between HX and $Al(OH)_3$ also changes, with consequent shift in the equilibrium point of the entire system. It is difficult to say how long a time might be required to attain final equilibrium. Our knowledge of the behavior of $Al(OH)_3$ is far from complete but the indications are that the final state attained may depend to a considerable extent upon the history of the system. The detailed influence of all the significant factors entering into that history is not known -- perhaps we do not even recognize <u>all</u> the significant factors. At any rate it seems dubious at the present time whether we

can even exactly reproduce AlX_3 - H_2O equilibria at will.

In the light of the foregoing considerations, however, two facts emerge from the fog. One is that the equilibrium point attained between solid AlX_3 and a fixed volume of water is neither independent of the exact quantity of AlX_3 employed nor can it be predicted upon the basis of any direct proportionality between the amount of AlX_3 originally present and the dye-ion or hydrogen-ion concentrations of the final solution. It is also evident that the solution obtained by bringing dye acid to equilibrium in the presence of excess $Al(OH)_3$ cannot be expected to duplicate a solution obtained by bringing AlX_3 to equilibrium with water except by coincidence.[18]

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[18] This point will be further discussed in the present paper.

The writer has been unable to find in the literature on hydrolysis, heterogeneous equilibria, or velocities of heterogeneous reactions anything which bears very directly upon the foregoing discussion, although paper of A. Tian[19]

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[19] J. Chim. Phys. 19, 190-216 (1921)

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on "The Slow Hydrolysis of Salts" contains some suggestive ideas. The theoretical discussion here presented, it must be admitted, is, therefore, cut largely from whole cloth. It is, nevertheless, supported by experimental observations. To speak more frankly, it has been fabricated (as the reader may have already surmised) to explain experimental results which were at first thought to be anomalous.

In the first experiment varying quantities of AlX_3

were introduced into 100 cc. volumetric flasks and distilled water was added up to the mark. The flasks were allowed to stand for about a week, with occasional hand shaking, before pH measurements were made. Salt #1 had been crystallized from aqueous solution containing an excess of $AlCl_3$ together with some free HCl. Salt #2 had been crystallized from an alcoholic solution containing free $AlCl_3$ and free HCl. Salt #3 was crystallized from an aqueous solution containing a slight excess of HX. All flasks had been kept at a room temperature which varied but little from 20° C. and all pH measurements were made at that temperature. The results are presented in Table VIII.

TABLE VIII

Salt	Gms. AlX_3 in 100 cc. volume	pH
#1	0.05	3.99
#1	0.10	3.96
#1	0.20	3.83
#1	0.50	3.73
#2	0.10	4.18
#2	0,20	4.09
#3	0.10	4.24
#3	0.20	4.22
#3	0.50	4.14

The writer was at first inclined to attribute the pH variations here noted to free acid contamination. Consequently, a salt which might be expected to display greater electrometric purity was selected for the next experiment.

This salt (designated as #5) had been prepared by extracting crystalline AlX_3 with boiling water and allowing new crystals to form from the clear filtrate on cooling. In this case the salt was allowed to stand in contact with water for two days and a night with frequent hand shaking during the daytimes and the one evening. In this case the dye radical concentration was determined by titration with $TiCl_3$. The room temperature throughout was in the vicinity of 30° C. The results led the writer to doubt that equilibrium had been attained. Unfortunately the small amount of salt #5 available had been exhausted in this experiment. For a repetition, salt #6, which had been obtained by treating $Al(OH)_3$ with a slight excess of HX, was adopted. In this case the flasks were placed in a water bath and kept at a temperature near 100° C. with frequent hand shaking for about 8 hours. They were then allowed to stand overnight and for about half the next day, being frequently shaken by hand in the daytime. The titrations were made at a room temperature of about 30° C. The results are presented in Table IX.

TABLE IX

Salt	Gms. AlX_3 in 100 cc. volume	Mgms. X per liter in solution
#5	0.10	367.57
#5	0.20	403.39
#5	0.50	449.60
#6	0.05	310.94
#6	0.10	355.99
#6	0.20	392.98
#6	0.50	439.20

The writer at last began to suspect that which should have been evident from the first -- namely, that his original assumptions were in error. The revision of ideas which followed has already been outlined.

It is evident that the pH measurements and the X-ion titrations here presented are not concordant. They were not obtained upon solutions derived from the same specimens of salt, and they were not obtained at the same temperature. Temperature increase, of course, affects the hydrolysis equilibrium in two opposite ways. First, it would be expected to follow the general rule of increasing the hydrolysis of a salt of a strong acid and a weak base. Second, it considerably increases the solubility of this particular salt, which would have the opposite effect of decreasing hydrolysis. It is doubtful that these two effects exactly compensate each other in this case. Certainly, the latter effect is, in general, much the greater (for AlX_3). One may also question whether, in any of the cases examined, the true final equilibrium state had been attained. It is highly improbable, however, that any deviation from true equilibrium which existed could have affected the results materially -- certainly it could not have altered their general trend.

For the reasons already set forth it seemed unprofitable to pursue the study further by obtaining a set of concordant pH and X-ion determinations.

In the hope of discovering a suitable solvent for cryoscopic determinations we tested the solubility of the aluminum salt in a number of organic liquids. In none of the following liquids was the compound sufficiently soluble to impart an

appreciable tint: benzene, toluene, petroleum ether, hexane, acetone, carbon tetrachloride, carbon disulfide, acetone. Methyl alcohol acts similarly to ethyl alcohol.

To dry ethyl ether, the anhydrous salt imparts no tint. Both the aluminum salt and the dye acid are precipitated from alcoholic solution by the addition of an excess of ether. The method of Sisley for the preparation of the dye acid makes use of this fact. We also found that the anhydrous dye acid is insufficiently soluble in dry ether to color it. Wet ether is faintly colored by the crystalline salt. This partially confirms the statement of Weiser and Porter[4] that, "on shaking with ether the crystals dissolve, leaving the gel in the water layer and the ether layer is colored yellow." We found, however, that if a small portion of the wet ether layer which has been colored in this manner is drawn off and shaken with a comparatively large quantity of distilled water the color is extracted by the water layer, leaving the ether layer water-white. There is no basis for the implication that ether will extract dye acid from the aluminum salt or even from a mixture of dye acid and alumina gel.

The HX - $Al(OH)_3$ Equilibrium

If we throw into reverse the reasoning which we have already applied to the AlX_3 - H_2O equilibrium it becomes evident that varying quantities of dye acid brought to equilibrium with excess of $Al(OH)_3$ in a fixed volume of H_2O will not produce solutions of constant dye-ion concentration.

It also appears highly improbable that exact repetitions of procedure employed upon different gel samples will precisely reproduce results.

The first point is well illustrated by an experiment performed by the writer. An alumina gel which had been purified by repeated washing and decantation until the decanted liquid showed no test for chlorides and the gel had begun to peptize was employed. The gel was allowed to settle as much as it would in a cylindrical battery jar, when it formed a layer about three or four inches deep at the bottom. The water above this layer was siphoned off and after the thinly suspended gel had been thoroughly stirred, 50 cc. volumes were drawn with a pipette and placed in 250 cc. glass-stoppered bottles.[20] To the series of bottles varying volumes of approximately 0.01N HX were added. To each bottle was then added the number of cubic centimeters of water calculated as necessary to bring the total volume of the system to 200 cc.

After the stoppered bottles had stood, with occasional hand shaking for about three months it was still obvious to the eye that there was considerable variation in the dye-ion con-

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[20] Samples of gel were also drawn at this time for determination of the Al_2O_3 content. Maturer consideration showed that nothing significant could be calculated from a knowledge of the exact quantities of reactants present, so this determination was never made. There is no doubt, however, that throughout the series the gel was in equivalent excess of the dye acid added to it.

centrations of the supernatant solutions. The bottles were then placed with loosened stoppers in a water bath and digested at near 100° C. for about a day and a half. During this time they were frequently shaken by hand. Upon cooling to room temperature it was found that the solution in bottle #1 was the only one which could be distinguished by eye from the others of the series. The results of the $TiCl_3$ titrations are presented in Table X.

TABLE X

Bottle	Cc. HX sol'n added	X conc. of final sol'n. Mgms. per l.
#1	20	314.13
#2	50	621.89
#3	100	629.95
#4	150	668.11

CONCLUSIONS FROM THE PRESENT STUDY OF ALUMINUM - ORANGE II PRODUCTS.

The facts which have been here set forth seem to leave no room for doubt that the compound which, for convenience, we have designated AlX_3 actually exists. In view of the fact that the dye itself has been shown to be a practically neutral salt, and the dye acid to be a strong acid, it is more than improbable that the addition of Orange II solution to a solution of $AlCl_3$ could give rise to hydrolysis which would result in a heavy precipitate of hydrous alumina. Even if such a precipitation did take place, the high solubility of the dye acid forbids the assumption that it is also precipitated. If it be contended that hydrous alumina <u>is</u> precipitated and that it carries down the dye acid by adsorption, there still remains

the phenomenon of dye radical and aluminum equivalents obtained under a wide variation of proportions between the original reactants. If adsorption is assumed, it is necessary to assume adsorption of equivalents - which differs from compound formation only in nomenclature.

None of the other products which we have prepared was obtained under conditions which by any possibility admit an explanation involving the assumption of hydrous alumina precipitation.

There is, then, firstly, the impossibility of accounting for all the facts on the basis of any hypothesis other than that of compound formation. Secondly, there is the fact that nine products prepared under varying conditions and reported in this paper, as well as a few duplications in procedure unreported here, all showed upon analysis equivalent quantities of aluminum and dye radical. Thirdly, there is the fact that these products can be crystallized both from aqueous and from alcoholic solution - crystallization being one of the ancient and honorable criteria of the true chemical compound.

Our experiments indicate that the reactions represented by the equations:

$$3\ NaX + AlCl_3 \longrightarrow AlX_3 + 3\ NaCl$$

and

$$3\ HX + AlCl_3 \longrightarrow AlX_3 + 3\ HCl$$

take place either in cold or in hot solution. There is no reason to believe that the reaction:

$$3\ HX + Al(OH)_3 \longrightarrow AlX_3 + 3H_2O$$

does not also take place in the cold. We have conducted it in

the hot because of the much greater solubility of AlX_3 in hot solution, which affords an opportunity to obtain a relatively concentrated, absolutely gel-free filtrate from which the product can be crystallized by cooling.

It is obvious, therefore, that the earlier experiments of Marker and Gordon[4] were conducted under conditions which afforded ample opportunity for compound formation. (In those experiments portions of alumina gel were treated with Orange II solutions, to which had been added varying quantities of mineral acid. The systems were then digested at 100° C. for several hours with frequent shaking.)

It is probable that, in the cold, compound formation may be limited by the formation of a coating of slightly soluble AlX_3 over the gel particles so that true equilibrium is not attained or is attained but slowly. This point has not been thoroughly investigated. Such a phenomenon does not, however, constitute adsorption within the true meaning of the term.

Even under the conditions employed by Marker and Gordon the chemical equilibrium obtained is exceedingly complex and, for reasons which have already been pointed out, almost impossible to reproduce. The solutions investigated by them must have contained at equilibrium the following ions: Al^{+++}, X^-, H^+, OH^-, SO_4^{--}, Na^+, as well as the molecules AlX_3 and H_2O. They possibly contained, also, the ions, AlX_2^- and AlX^{--}. The solid phase must have contained $Al(OH)_3$ and it conceivably contained also some such compounds as AlX_2OH and $AlX(OH)_2$. The equilibrium point would have been affected by the purity and previous history of the alumina gel employed and by the treatment

imposed upon the system in the attempt to bring it to equilibrium. In addition to all this there still remains the possibility that some adsorption phenomena still further complicate the system.

Non-reproducability does not, however, demonstrate that adsorption exists here, and it seems fairly evident that the essential phenomena are strictly chemical. At any rate it is obvious that such studies are less than meaningless as studies of adsorption.

The Interaction of NaX and HX with Ferric Compounds.

In the investigation of the interaction of Orange II and its free acid with ferric compounds, several complications must be taken into account. These will be discussed in their appropriate connections as we proceed.

A clue to the first difficulty to be surmounted is found in the previously cited paper by Sisley.[9] This investigator prepared the ferrous salt of HX but stated that the ferric salt does not exist. According to him, the addition of a ferric salt to a solution of the dye or its acid results in the reduction of the ferric ion, accompanied by the decomposition of the dye radical with the evolution of N_2 and of a strong odor of β-naphtho quinone -- the process resulting in the precipitation of the ferrous salt of HX.

Sisley does not describe the conditions under which this experiment was carried out nor does he offer any analyses in substantiation of the composition assigned to the precipitate. It seems, however, that his general procedure for the preparation of salts of HX was to add a solution of a metallic chloride or sulfate

to a boiling solution of HX and to allow the less soluble metallic-dye salt to crystallize from solution on cooling.

Under these conditions the writer found that there was unmistakable evidence of the decomposition of the dye. However, $TiCl_3$ titrations of known mixtures of ferric sulfate solution and dye acid solution which had been boiled for varying lengths of time showed that the mutual destruction of the ferric ion and the dye radical takes place but slowly, even at boiling temperatures. When ferric salt solutions were added to solutions of HX at room temperatures there was no visible evidence of decomposition and no apparent odor. Subsequent titrations of mixtures which had been allowed to stand at room temperature for periods up to twenty-four hours indicated that this decomposition either does not take place in the cold or proceeds so slowly as to be negligible.

While these observations held forth a promise of the possibility of harmonizing Sisley's statements with the report of Marker and Gordon[1] that a product of the composition FeX_3 had been obtained, they clearly indicated that the method of analysis employed for NaX and AlX_3 could not be relied upon for the investigation of ferric-dye products. The difficulty to be surmounted arises in the necessity of titrating the dye radical in the presence of ferric ion. Unfortunately the dye radical can be titrated with $TiCl_3$ only at temperatures near the boiling point, and at these temperatures the dye radical and the ferric ion destroy each other. Furthermore the oxidation of the dye radical results in an irreversible decomposition. Finally, the reduction of this dye by $TiCl_3$ is rapid enough for titration

purposes only in the presence of Rochelle salts, which interfere with ferric ion titration, probably because of complex formation.

Determination of X in Presence of Fe^{+++}.

It is perhaps unnecessary to describe here the schemes of analysis which were tried and found wanting. The scheme finally adopted avoids the three sources of error which are most inimical to the reliability of this determination: (1) the dye is not heated in the presence of Fe^{+++}; (2) Rochelle salts are not introduced in the presence of Fe^{+++}; (3) the solution to be titrated is kept practically free of dissolved O_2.

The procedure is as follows. A 0.1 gram sample of the finely ground ferric-dye product is brushed into a 250-cc. Erlenmeyer titration flask. Fifty cubic centimeters of ethyl alcohol and 10cc. of concentrated HCl are added.[21] The flask is

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[21] The ethyl alcohol is previously distilled from $TiCl_3$ solution. Just before the determinations are to be made the alcohol and the HCl are both boiled for about twenty minutes and cooled under the tap in stoppered flasks.

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then closed with a three-hole rubber stopper[22] and swept out with

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[22] One hole is provided for the CO_2 inlet tube, one fits the buret, and the third serves for the escape of excess CO_2.

CO_2. A stream of CO_2 is maintained through the flask from this point onward. An excess of standardized $TiCl_3$ solution is then run into the flask. It is highly important that the sample be totally dissolved at this point. Some time may be lost in effecting complete solution, but impatience will result only in the ruin

of the determination.[23] The flask is then detached from the $TiCl_3$

[23] $TiCl_3$ reduces Fe^{+++} in the cold, but it can do so only if the iron is in solution. It is essential that all Fe^{+++} be removed before the titration mixture is heated.

buret and transferred to a hot plate or an asbestos pad over a small gas flame, where it is allowed to remain until the color of the dye is totally destroyed and only the faint purplish tinge of excess $TiCl_3$ remains. (This usually involves gently simmering the titration solution for several minutes). The flask is then carefully cooled under the tap and 10 cc. of 10% KSCN solution is introduced through a hole in the stopper by means of a pipet. A back titration is then performed, using standard ferric sulfate solution containing about 3.639 grams Fe^{+++} per liter.[24] The end-point is indicated when a faint but permanent orange-brown tint

[24] One cubic centimeter of ferric solution of this concentration is equivalent to about 2.5 cc. of the standard $TiCl_3$ solution. This is unfortunate, but the indicator does not operate satisfactorily in the volume of titration solution present if a more dilute ferric solution is employed.

is attained. This titration is best performed by daylight.

The reliability of the procedure described was tested by titrating mixtures made up of known volumes of standard ferric and HX solutions which had been separately boiled to remove oxygen and cooled. The use of alcohol and HCl was, of course, unnecessary in this case. A typical series of titrations is recorded in Table XI.

Table XI

Cc. Standard Fe^{+++} Sol'n.	Cc. Standard HX Sol'n.	Net $TiCl_3$ titer (cc.).
10	-	15.58
		15.55
		15.57
		15.60
-	10	16.16
		16.19
		16.16
		16.18
10	10	32.74
		32.72
		32.77
		32.75
		32.72
		32.74
		32.75
		32.77

It will be noted that the sum of the averages of the separate HX and Fe^{+++} titrations (32.747 cc.) agrees almost exactly with the average of the combined titrations (32.745 cc.)

It is, of course, obvious that the net titer obtained in the procedure outlined for iron-dye products represents the summation of the Fe^{+++} and the X contents. The actual X content must be obtained by difference after the execution of an in-

dependent Fe^{+++} determination.

Determination of Fe^{+++} in Iron-Dye Products.

The writer at first supposed that it might be possible to estimate the Fe^{+++} content conveniently by destroying the dye with "Superoxol" (30% H_2O_2) and titrating the remaining Fe^{+++} with $TiCl_3$. Experiments on mixtures of known composition, however, demonstrated that the results obtained by this method are invariably much too low. The addition of bromine resulted in but little improvement. Apparently the oxidation products of the dye are able to form very stable complexes with the Fe^{+++} ion.

The method finally adopted was the well-known one of igniting to Fe_2O_3. In dealing with these products, however, certain unusual precautions as to heating are necessary. It was found that the best procedure was to ignite 0.5 gram samples in covered platinum crucibles over a very small Bunsen flame, so adjusted that only the very bottom of the crucible was heated to a dull red glow. The ignition is continued until the ash assumes a bright reddish brown color, when the crucibles are cooled and weighed. Further heating and weighing until constant weight is attained is carried out.

Stronger heating of the crucibles than has been indicated results in the formation of a coke-like mass from which it is difficult or impossible to burn off all the carbonaceous material at low temperatures. At high temperatures there is, of course, danger of Fe_3O_4 formation.

The ignition determinations may be checked by dissolving the ash in HCl, boiling with a few drops of bromine to insure

complete oxidation, and titrating the cooled solution with $TiCl_3$, using KSCN as indicator. In the experience of the writer, the titrations usually check the weighings quite closely.

Preliminary experiments on a number of iron-dye products indicated that moisture content cannot be determined by drying at 120°-125° C. Evidently the small amount of water present is quite sufficient to make possible the oxidation of the dye radical by the ferric ion. The analyses hereafter recorded, are therefore expressed in terms of equivalent ratios of iron to dye and no attempt has been made to state the absolute compositions of the respective products.

Interaction of NaX with $FeCl_3$ (Cold)

Since it seemed desirable to avoid the mutually destructive action of the ferric ion and the dye radical it was decided to carry out these reactions in the cold, which precluded the possibility of obtaining a crystalline product. Unfortunately, the precipitate obtained by adding $FeCl_3$ solution to a solution of dye or dye acid is much more finely divided than that which results when $AlCl_3$ is used, and it is, moreover, gelatinous in nature rather than pulverulent. Consequently its occlusive (or adsorptive) properties might be expected to be more marked. Furthermore, the iron-dye product appears to be hydrolyze more readily when washed with cold water than does the aluminum product. Nevertheless the same procedure was followed as was employed in investigating the NaX-$AlCl_3$ reaction. Equivalent quantities and equal volumes were used. Results are tabulated in Table XII, all ratios being expressed in terms of ~~equivalents~~ ions.

Table XII

Fe:X Ionic Ratio of Original Reactants	% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
2:3	6.72	77.72	1:1.89
1:6	6.33	77.10	1:2.08

The experiment was repeated, employing one liter of 0.1 N HCl as the reaction medium instead of one liter of H_2O. The results are recorded in Table XIII.

Table XIII

Fe:X Ionic Ratio of Original Reactants	% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
2:3	3.95	79.50	1:3.41
1:6	3.85	79.11	1:3.53

In the preparation of a third pair of products, two liters of 0.05 N HCl constituted the reaction medium. (See Table XIV).

Table XIV

Fe:X Ionic Ratio of Original Reactants	% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
2:3	4.90	80.24	1:2.80
1:6	4.67	80.08	1:2.94

Interaction of HX with $FeCl_3$ (Cold)

Products were similarly prepared by the interaction of HX with $FeCl_3$, using one liter of H_2O as the reaction medium. Table

XV records the results.

Table XV

Fe:X Ionic Ratio of Original Reactants	% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
2:3	5.01	79.51	1:2.70
(1:3)	(4.63)	(77.47)	(1:2.86)
1:4.5	4.47	78.58	1:3.00

The figures in parenthesis are data on a sample prepared and analyzed by Mr. George Seidel. These will be mentioned again later.

Interaction of HX with Hydrous Ferric Oxide

In effecting the interaction of HX with hydrous ferric oxide it was, of course, impossible to proceed in the cold, for the product cannot be separated from the gel save by solution, filtration, and precipitation on cooling. Experiments conducted in the course of evolving a system of analysis for the dye in the presence of Fe^{+++} ion, however, demonstrated that the oxidation-reduction reaction between the dye and ferric iron proceeds rather slowly even at the boiling point. Nevertheless the preparation was made in such manner that the reactants were heated in the presence of each other for as short a time as possible.

Ferric chloride equivalent to one part as employed in previous preparations was dissolved in a small amount of water and precipitated with an excess of ammonium hydroxide. After boiling to remove excess ammonia, the precipitated hydrous ferric oxide was filtered out on a small Buchner funnel. Gel and paper

were then added to one liter of boiling solution containing double the amount of HX calculated as equivalent to the amount of Fe^{+++} taken. The mixture was thoroughly stirred and then filtered through a large Buchner filter. The filtrate was quickly chilled and the fine crystals which separated constituted the product. Analytical data are recorded in Table XVI.

Table XVI

% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
6.12	69.91	1:1.95

The results thus far obtained seemed capable of rational interpretation but it was deemed advisable to supplement them with further investigations before drawing other than tentative conclusions. The additional preparations to be described were all made and analyzed by Mr. George Seidel under the direction of the writer.

Interaction of HX with $FeCl_3$ (Hot)

The procedure in this and in the following preparations was again designed to minimize the oxidation-reduction between dye and ferric iron. The dye acid was dissolved in a little less than a liter of water and brought to boiling. The ferric chloride was separately dissolved in a small amount of water and also brought to boiling. The solutions were then mixed and rapidly filtered hot through a large Buchner funnel. The filtrate was rapidly chilled and the crystalline precipitate was separated and air-dried.

Table XVII

Fe:X Ionic Ratio of Original Reactants	% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
2:3	6.45	68.78	1:1.22
1:4.5	6.36	70.16	1:1.26
2:3	6.24	69.25	1:1.20
1:4.5	6.17	69.72	1:1.28

This preparation was repeated because the results were not what had been anticipated. At the same time Mr. Seidel prepared and analyzed the sample recorded in Table XV as a check upon the previous preparations of the writer in the cold.

Additional Experiments

Two further preparations were repeated following the respective procedures already outlined. The filtrates obtained were each divided into two equal portions, A and B. Portions A were chilled and the products were immediately isolated and analyzed. Portions B were also chilled but the products were allowed to stand in the presence of the mother liquor at room temperature for a week. Both were stirred electrically throughout that time. Results are recorded in Table XVIII.

Table XVIII

Reactants		% Fe in Product	% X in Product	Fe:X Ionic Ratio in Product
1 $FeCl_3$ + 4.5 HX	A	6.04	67.84	1:1.27
	B	6.09	67.35	1:1.26
1 $Fe(OH)_3$+6 HX	A	5.88	69.03	1:2.00
	B	3.05	73.18	1:4.09

Discussion of Results

The writer does not advance the following conclusions as definitely proved in all particulars. They are, however, consistent with the data recorded and with known chemical phenomena.

To begin with, there can be no doubt that the products investigated result from true chemical interactions. All of the preparations described were made in acid media [25]; hence there is no question of initial $Fe(OH)_3$ precipitation. The precipitates are all copious and immediate -- not at all of the character which could result from "slow hydrolysis" of dilute ferric solutions. If $Fe(OH)_3$ is precipitated at all, the precipitation must result from hydrolysis of the product initially formed.

The products reported here are probably nearly all mixtures of two or more of the following compounds: FeX_3, $Fe(OH)X_2$, $Fe(OH)_2X$, $Fe(OH)_3$, and $FeX_3 \cdot \underline{n}\ HX$. The composition of the product obtained depends upon the actual and relative concentrations of the reactants, the acidity of the reaction medium, and the temperature. These factors all operate as might be predicted from the known principles of hydrolysis.

The compounds, $Fe(OH)X_2$ and $Fe(OH)_2X$, which are of a disputed type, are included in the list of probable products because the samples recorded in Tables XVI, XVII, and XVIII were all obtained in crystalline form.

The high ratios recorded in Table XIII might be attributed

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[25] This holds true even for the $FeCl_3$ - NaX interaction. NaX solutions are neutral or faintly acid. Repeated pH determinations of 0.01 M NaX solutions gave values of the order of 6.5. The ferric chloride used also contained some free HCl.

to adsorption of HX by the apparently amorphous product but such an explanation could not account for the composition of the B portion of the $Fe(OH)_3$ - HX product recorded in Table XVIII, for the initial product which was allowed to stand in the presence of the mother liquor was crystalline. Hence the rather indefinite hypothetical compound, $FeX_3.\underline{n}$ HX, is listed as a probable product. The formation of a product of this nature would seem to be favored both by high acidity of the reaction medium and by a high absolute and relative X-ion concentration. As a matter of fact this supposed compound might equally well be represented as a neutral salt containing a complex ferric-dye ion. Iron is noted for its tendency to form complexes with organic ions.

Apparently hydrolysis of the normal salt increases rapidly with rise in temperature even though solubility also increases markedly. Subsequent cooling apparently results in precipitation of a basic salt or mixture of basic salts before the normal salt has a chance to form. (Compare Tables XV and XVII.)

One may well inquire why a product with the ionic ratio, Fe:X = 1:2.00, formed in the hot, should increase its ratio to Fe:X = 1:4.09 when allowed to stand in the presence of the mother liquor in the cold, when a similar product with a ratio of Fe:X = 1:1.27 does not alter within the limits of analytical error under the same treatment. (See Table XVIII). In the opinion of the writer the most plausible explanation is as follows.

In the first place one must take into consideration the fact that the mother liquor in the former case is ~~much~~ more acid and much more concentrated in X-ion than the mother liquor in the latter case. When $Fe(OH)_3$ is treated with HX solution in the manner previously described only a very small portion of the iron

present reacts. Most of it is removed in the initial filtration. The filtrate from which the product separates on cooling contains most of the HX originally present, but only a small quantity of iron. The conditions are favorable, therefore, for the formation of a compound containing an abnormal proportion of X-ion when the system is allowed to stand in the cold.

In the case of the $FeCl_3$ - HX product the respective concentrations of Fe and X in the system are substantially those of the original reactants, which are just about correct for the formation of normal FeX_3. The normal salt is, itself, so insoluble, however, that it either does not form from the basic product in the cold or it forms an insoluble, adherent coating over the basic particles and the reaction speedily comes to a stop.

The acid or complex salt is either more soluble or it forms a loosely adherent coating which is removed by the agitation of stirring, allowing the reaction to proceed.

It is quite possible that the product reported as FeX_3 by Marker and Gordon [1] was a product containing an excess of X, for the ordinary method of analysis presumably employed by them would almost inevitably have given a result somewhat too low for X-ion. Even so it is a remarkable coincidence that their preparation should have led to so exact a balancing of errors.

There can be no doubt that Sisley [9] was mistaken in asserting that the ferrous salt is precipitated when ferric chloride or sulfate is added to NaX solution! He must have obtained a product approximating $Fe(OH)X_2$ in composition -- which would have given an Fe:X ratio very close to that calculated for FeX_2. Observing evidences of oxidation-reduction when dye is heated in presence of ferric ion he evidently added two and two to get five.

Behavior of Quinhydrone and Hydrogen Electrodes in Presence of Orange II.

As has already been stated the quinhydrone electrode was adopted for use in the present study chiefly because the writer doubted that reliable hydrogen-electrode readings could be made in the presence of a substance so readily reducible as Orange II. The ease and rapidity with which the quinhydrone electrode can be manipulated are further advantages sufficient in themselves to recommend its use within the acid range. It seemed desirable, however, to compare the results obtained by use of the two electrodes in acid solutions containing Orange II.

A new Bailey electrode vessel was used for the first comparisons. The electrode was thoroughly cleansed and rinsed and was given a very light coating of platinum black [26]. Initial saturation was accomplished by electrolysis (using two dry cells in series), first in a dilute H_2SO_4 solution and then in dilute KOH solution. After thorough rinsing the electrode was checked against M/20 acid potassium phthalate buffer. Electrolytic hydrogen from a steel tank, washed successively in alkaline pyrogallol, alkaline potassium permanganate, and concentrated sulfuric acid, was employed. The pH value calculated by means

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[26] According to some investigators, [Cf. Graves and Tartar, J. Amer. Chem. Soc. 47, 1226, (1925)] a heavy coating favors reduction reactions at the electrode. Clark ["The Determination of Hydrogen Ions." 1928. pp. 286-9] prefers a light coating for all purposes.

of the constants tabulated by Clark [13] was 3.96, as compared with the quinhydrone electrode reading, 3.97, and the value, 3.974, reported by Clark and Lubs. [12]

A solution containing 90 cc. of approximately 0.01 M Orange II and 10 cc. of exactly 0.1 M HCl was then submitted to examination. The pH value calculated from the quinhydrone electrode reading was 2.06. No strictly comparable values are recorded in the literature, but a solution which should have a pH value of approximately the same order of magnitude has been reported several times, namely a solution 0.01 N in HCl and 0.09 N in KCl. Values quoted by Clark [27] are as follows:

Sørensen and Linderstrøm-Lang (1924)	2.037
Cullen, Keeler and Robinson (1925)	2.04
Biilman (1927)	2.029
Kolthoff and Tekelenberg (1927)	2.038
Gjaldbaek (1925)	2.063
Clark (calculated)	2.076
Larsson (1922)	2.093

With the Bailey hydrogen electrode no readings would be obtained at all until the cell was reversed and then the readings were subject to drift and non-reproducible. Average E. M. F. values were of the order of -.0020 volts. To ascertain whether the electrode had been "poisoned" by adsorption of the dye, it was rinsed thoroughly with distilled water and again checked against the buffer solution, when the pH value calculated was

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[27] "The Determination of Hydrogen Ions." 1928. p. 477.

3.97. Repeated alternate checks against the buffer and attempts to obtain intelligible readings on dye solutions gave no different results.

It seems fairly evident, therefore, that the hydrogen electrode is unreliable in the presence of Orange II. Clark[28] reports, however, that he has made reasonable qualitative measures of the pH values of solutions of ferric iron by plunging a previously saturated electrode into the solution and making a quick reading. This apparently was the method adopted by White and Gordon[29] to obtain pH values for Orange II solutions. Obviously, only roughly approximate values could be expected from this method when applied to solutions so unadapted to hydrogen-electrode investigation. Nevertheless the writer prepared a Wilson electrode[30] and checked it against the buffer solution, obtaining a pH value of 3.95. When applied to acid solutions of Orange II in the manner described it gave readings invariably much too low and impossible of exact

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[28] "The Determination of Hydrogen Ions." 1928. p. 437-8. See also F. L. Browne, J. Amer. Chem. Soc. 45, 297, (1923)

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[29] J. Phys. Chem. 32, 380-400 (1928).

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[30] The Wilson electrode is a slight modification of the Hildebrand electrode, employing a plain piece of platinum wire instead of a platinum foil.

reproduction. For example, the dye solution already mentioned should give an E. M. F. in the vicinity of 0.3700 volt. Actually the readings were slightly over 0.2000 volt. The writer does not claim that better results cannot be obtained by this method but admits that he was unable to improve upon those reported here.

The conclusion to be drawn is that there is no excuse for using the hydrogen electrode to investigate acid solutions of Orange II and little prospect of obtaining strictly accurate readings in the alkaline range.