

for the values of K , and furnishes additional evidence of the trustworthiness of a higher value for the dissociation constant of water in the presence of sodium hydroxide than the one generally accepted.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

THE REACTION BETWEEN ALKALIES AND METOL AND HYDROCHINON IN PHOTOGRAPHIC DEVELOPERS.

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In our paper on the single potential of developers, we have mentioned noticing that the addition of hydrochinon caused a change of thirty millivolts in the hydrogen potential of a solution containing sodium carbonate and sodium sulfite. As this seemed to indicate a combination between the alkali and the reducing agent, it appeared possible to use these hydrogen potentials as a means of studying the reactions which take place when a developer is mixed. After determining the hydrogen potentials of pure solutions of sodium hydroxide and the hydrolysis constant of sodium carbonate, as described in our previous papers, we have the necessary information upon which to base our calculations of the reactions involved.

In this study we investigated four different hydrochinon developers, seven solutions of sodium hydroxide and hydrochinon, and one solution containing metol and sodium hydroxide. The composition of the developers is shown in Table I.

TABLE I.—COMPOSITION OF DEVELOPERS, GRAMS PER 1000 Cc. WATER.

Dev. No.	Hydrochinon.	Sodium sulfite.	Sodium carbonate.
1	11.1	7.8	141.7
2	7.0	50.0	150.0
3	7.0	50.0	75.0
4	7.0	None	75.0

The sulfite used was an analyzed anhydrous article, and the carbonate was prepared by drying the last c. p. salt at 300°. In making a determination the hydrogen potential of the solution containing all the constituents except the metol and hydrochinon was first found as described in our previous papers. Then the complete developer was tested in the same way. Where the solution contained only sodium hydroxide and hydrochinon (or metol), reference to the curve showing the hydrogen potentials of solutions of pure sodium hydroxide gave us directly the concentration of the sodium hydroxide before and after adding the reducing agent. From the difference between these two values the amount of sodium hydroxide used up could be readily calculated.

Where sodium carbonate was present, reference to the curves for the hydrogen potentials of sodium hydroxide solutions and for their dissociation gives us the hydroxyl-ion concentration corresponding to the potentials observed. It is next necessary to make corrections for the effect of the sodium carbonate and sulfite in repressing the dissociation of the hydroxide. Comparison of the data on the dissociation of these two salts showed that, over the range under consideration, sodium sulfite was about 10% more dissociated than the carbonate. The simplest way of obtaining the probable total sodium-ion concentration appeared to be to consider the sulfite equivalent to 10% more than its own molarity of the carbonate, add this quantity to the actual molarity of the carbonate, and from the curve determine the degree of dissociation of the carbonate at that dilution, and thus the total sodium-ion concentration. On the assumption, then, that in a solution of two salts having a common ion, each is dissociated to the same extent that it would be if it were present alone in a solution having the same concentration of this common ion, the degree of dissociation of the sodium hydroxide, as repressed by the carbonate and sulfite present, can be calculated as explained in the previous paper.

Having obtained the corrected concentration of the sodium hydroxide before and after the addition of the hydrochinon, it is evident that the sodium hydroxide which has been used up by the hydrochinon consists of two parts: one represented directly by the difference in the concentrations of the hydroxide before and after adding the hydrochinon, and the other corresponding to the amount of bicarbonate formed on the addition of the hydrochinon, due to the progressive hydrolysis as the sodium hydroxide concentration decreases. This formation of the bicarbonate furnishes the greater portion of the hydroxide used up, and is determined from the constant for the equilibrium

$$K = \frac{[\text{NaOH}] [\text{NaHCO}_3]}{[\text{Na}_2\text{CO}_3]}$$

for the given dilution. The values of this constant, as determined in the previous paper, were plotted as functions of the concentration, and formed a smooth curve. From this curve the value of K for any dilution can be determined by inspection. Substituting in this equation the net concentration of the carbonate and the corrected concentration of the sodium hydroxide at any time, we can find the amount of sodium bicarbonate present in the solution. The amount of hydroxide used up during the hydrolysis is evidently equivalent to the difference in the concentrations of the bicarbonate before and after adding the hydrochinon. By the net carbonate concentration, we understand the difference between the original concentration of carbonate and the amount hydrolyzed. By making a preliminary calculation from the corrected concentration

TABLE II.

Reactions between sodium carbonate, sodium sulfite, and hydrochinon. Salt concentrations expressed in mols per liter, ionic concentrations in gram-ions per liter.

Developer.	Composition.				Total Na ⁺ .	Corresp. NaOH.	α for this NaOH conc.	Obs. OH ⁻ .	Corr. NaOH.	K × 10 ⁶ .	On adding hydrochinon.			Conc. hydrochinon.	Mols NaOH per mol hydrochinon.
	Na ₂ CO ₃ .	Na ₂ SO ₃ .	Total equiv. Na ₂ CO ₃ .	α for this Na ₂ CO ₃ .							Decrease NaOH.	Increase NaHCO ₃ .	Total NaOH consumed.		
1 (before)	1.337	0.062	1.40	0.25	0.70	0.95	0.735	0.00109	0.00148	3.7	0.0010	0.0624	0.0634	0.101	0.63
1 (after)	1.337	0.062	1.40	0.25	0.70	0.95	0.735	0.00033	0.00045						
2 (before)	1.415	0.40	1.85	0.20	0.74	1.02	0.725	0.00669	0.00922	3.7	0.0081	0.0438	0.0519	0.064	0.81
2 (after)	1.415	0.40	1.85	0.20	0.74	1.02	0.725	0.00081	0.00112						
3 (before)	0.708	0.40	1.15	0.29	0.667	0.89	0.745	0.00360	0.00483	4.3	0.0040	0.0274	0.0314	0.064	0.49
3 (after)	0.708	0.40	1.15	0.29	0.667	0.89	0.745	0.00061	0.00082						
4 (before)	0.708	None	0.708	0.555	0.503	0.64	0.784	0.00437	0.00558	4.3	0.0042	0.0469	0.0511	0.064	0.92
4 (after)	0.708	None	0.708	0.355	0.503	0.64	0.784	0.00050	0.00063						

of the sodium hydroxide, using the figure for the original concentration of the carbonate, the approximate amount (molarity) of bicarbonate formed can be determined. Subtracting this from the original carbonate value gives a very close approximation of the net carbonate, from which a final figure for the bicarbonate can usually be obtained.

From the total bicarbonate formed during the hydrolysis, plus the direct loss of the hydroxide concentration, the total amount of sodium hydroxide which has combined with the hydrochinon is easily determined, and can be compared with the amount of hydrochinon present.

We have carried out this determination on the four developers shown in Table I, with the results shown in Table II. It will be noticed, that, strictly speaking, No. 4 is not a developer since it contains no sulfite. It was included for the purpose of showing more clearly the effect of the sulfite.

Since Sheppard and Mees,¹ in their work on hydrochinon developers, used sodium hydroxide instead of the carbonate, and found that the velocity of development was a maximum when approximately two molecules of the hydroxide were present for one molecule of hydrochinon, and thus concluded that the active developing agent was the anion of the diquinolate,—we undertook a series of measurements on mixtures of various proportions of hydrochinon and sodium hydroxide, without sulfite, in order to determine whether under other conditions the diquinolate was formed. These results are presented in Table III.

TABLE III.

Reaction between hydrochinon and metol and sodium hydroxide. Concentrations all expressed as gram-molecules per liter. Determination below dotted line is metol and sodium hydroxide, without hydrochinon.

Orig. conc. NaOH.	Conc. hydrochinon added.	NaOH: hydrochinon as mixed.	Final conc. NaOH.	Loss of conc. NaOH.	Mols NaOH comb. one mol hydrochinon.
0.102	0.0273	3.74	0.0432	0.059	2.14
0.0103	0.00364	2.83	0.00278	0.0075	2.06
0.103	0.0509	2.02	0.0144	0.0884	1.73
0.103	0.0545	1.89	0.01087	0.0920	1.72
0.0103	0.00636	1.62	0.00148	0.0088	1.38
0.0103	0.01	1.03	0.000495	0.0098	0.98
0.0103	0.0109	0.945	0.00046	0.0098	0.90
...
	(Metol)	(Metol)			(Metol)
0.0103	0.0029	3.56	0.0016	0.0087	3.00

It will be noticed from this table that, by varying the proportions of hydrochinon and alkali, either the mono- or diquinolate or mixtures of the two can be formed, as would be expected; and that in both cases the solution is still alkaline; even though, in the last solution in the table

¹ "Investigations of the Photographic Process," p. 176.

(above the dotted line), there is an excess of hydrochinon over the amount required to form the monoquinolate. As would be expected, the ratio of the constituents, the alkalinity of the final solution, and the dilution seem to be the factors which decide the extent to which the two substances combine; in other words, there is the expected tendency toward hydrolysis of both the mono- and diquinolates, and the tendency of the diquinolate to hydrolyze is evidently greater than that of the monoquinolate. The last two results are especially interesting, as it will be noticed that the alkalinity of the final solution is about the same as that found in the carbonate solution (Developer No. 4, Table II). The proportion of the hydrochinon combined with the alkali in the two cases checks as well as could be expected, considering the difference in the concentration of the hydrochinon, and bears out the theory that in ordinary hydrochinon developers, made up with sodium carbonate, the anion of the monoquinolate is probably the principal developing agent.

Another very interesting conclusion which can be drawn from Table II relates to the role of the sulfite. A study of the number of mols of sodium hydroxide consumed per mol of hydrochinon, makes it appear very probable that the sulfite combines with some of the hydrochinon, and that the sulfite and hydroxide divide the hydrochinon between them, according to some definite law. It will be noted that Developers 3 and 4 are the same, except that the sulfite is omitted in No. 4. In the latter, apparently 92% of the hydrochinon has combined with the alkali (assuming the formation of the monoquinolate), and 8% is free. Upon now adding sulfite so that the concentration of the latter is 0.40 molar (Developer No. 3), we find that only 49% of the hydrochinon remains combined with the hydroxide, although the developer is now more alkaline than it was before adding the sulfite (0.00082 *N* in free sodium hydroxide as compared with 0.00063). Upon doubling the concentration of the carbonate (Developer No. 2) the proportion of the hydrochinon combined with the alkali rises to 81%, but does not reach the value for Developer No. 4, where the sulfite is absent, although the final alkali concentration of the developer has nearly doubled (0.00112 as compared with 0.00063). Developer No. 1 has nearly twice the hydrochinon concentration of the others, about the same carbonate as No. 2, but only about one-sixth as much sulfite. The final alkalinity is the lowest of all, the developer being only 0.00033 *N* in hydroxyl ion and 0.00045 *N* in sodium hydroxide; the larger proportion of the hydrochinon increases the proportion of this substance which does not combine with the hydroxide, but which at least partly combines with the sulfite. The phenomena are easily explained upon the basis of the following equations showing the probable equilibria:

$$K_1 = \frac{[\text{C}_6\text{H}_4(\text{OH})_2][\text{NaOH}]}{[\text{C}_6\text{H}_4\text{OHONa}]}$$

$$K_2 = \frac{[\text{C}_6\text{H}_4\text{OHONa}][\text{NaOH}]}{[\text{C}_6\text{H}_4(\text{ONa})_2]}$$

$$K_3 = \frac{[\text{C}_6\text{H}_4(\text{OH})_2][\text{Na}_2\text{SO}_3]}{[\text{C}_6\text{H}_4(\text{OH})_2 \cdot \text{Na}_2\text{SO}_3]}$$

The formula for the addition compound with sodium sulfite is not known, but is assumed for purposes of illustration. From our result it would appear that K_2 is greater than K_3 , and this in turn much greater than K_1 , which would make the monoquinolate the most stable substance of the three.

In connection with the hydrochinon developer, a very interesting observation was made and is mentioned in our paper on the single potentials of developers. The hydrogen potential of a part of a sample of Developer No. 1 was taken, air was then bubbled through the rest of the sample for three hours and it was allowed to stand exposed to the air for four hours more. Upon taking the hydrogen potential of this oxidized developer (now deep brown in color), it was found to be identical with the original value. This developer was then allowed to stand exposed to the air all night, and the potential again taken. The value was still the same as that of the original fresh developer. It would appear then, that the oxidation of such a developer, even though carried as far as it could be, does not change its alkalinity, *i. e.*, does not form any new compounds of an acidic nature.

One experiment was made with some of Hauff's metol, and is shown at the bottom of Table III, separated from the hydrochinon results by a dotted line. Assuming the formula, $\text{HO} \cdot \text{C}_6\text{H}_4 - \text{NHCH}_3 \cdot \frac{1}{2}\text{H}_2\text{SO}_4$, as stated by Sheppard and Mees¹ with a molecular weight of 172, the surprising result is obtained that three molecules of sodium hydroxide can combine with one molecule of metol. One of these apparently removes the half molecule of sulfuric acid, another unites with the OH group, while the third may have replaced the sulfuric acid in its combination with the $\text{CH}_3\text{NH}-$ group. Further work of this sort on developing agents should produce much valuable information, and we believe that the results presented herewith indicate a suitable method for such work.

Summary and Conclusions.

1. It is possible by electrometric measurements to determine the reactions between some of the constituents of a developer, using our values for the hydrogen potentials of pure sodium hydroxide solutions and for the hydrolysis constant of sodium carbonate.
2. Such studies indicate that sodium hydroxide and hydrochinon can form either mono- or diquinolates, according to the conditions.
3. It appears that with sodium carbonate and hydrochinon, in the

¹ "Investigations of the Photographic Process," p. 187.

concentrations usually used for developers, most of the hydrochinon would unite with the alkali to form the monoquinolate if the sulfite were not present.

4. When sulfite and carbonate are both present, they appear to divide the hydrochinon between them.

5. Complete oxidation of a hydrochinon developer may be accomplished without changing its alkalinity.

6. One molecule of metol appears to be capable of combining with three molecules of sodium hydroxide, in the absence of a sulfite.

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REACTIONS IN LIQUID AMMONIA. II.

1. THE ACTION OF ACID AMIDES ON THE AMIDES, IMIDES AND NITRIDES OF CERTAIN HEAVY METALS. 2. METALLIC SALTS OF ACID AMMONO ESTERS.

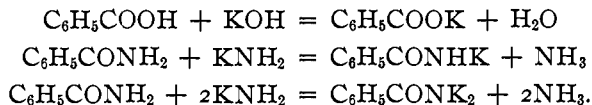
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Introduction.

Some years ago Franklin and Stafford¹ found that certain acid amides and potassium amide react with each other, when dissolved in liquid ammonia, in a manner strikingly similar to the familiar interaction of acids and bases in aqueous solutions.

Typical examples of such analogous reactions are represented by the equations,



The first equation represents the action of an aquo acid on an aquo base to form an aquo salt, the second and third, the action of an ammono acid on an ammono base to form ammono salts.

In view of the analogies thus indicated, and of others given in detail elsewhere,² the writer has long had in mind attempts to prepare ammono salts of some of the heavier metals by the action of liquid ammonia solutions of ammono acids on the insoluble amides, imides or nitrides of the metals. Such reactions are, of course, in principle not different from those studied by Franklin and Stafford referred to above, but at the same time it is interesting and important to show that salts of the heavy metals may be prepared in this way.

The amide of silver,³ the imides of lead¹ and copper⁴ and the nitride of

¹ *Am. Chem. J.*, **28**, 95 (1902).

² *Ibid.*, **47**, 285 (1912).

³ *THIS JOURNAL*, **27**, 833 (1905).

⁴ *Ibid.*, **29**, 656 (1907).