and Jones, who found almost no inhibiting effect on ozone decomposition when they increased the concentration of oxygen by direct addition, is almost certainly to be accounted for by the presence of positive catalyst in their oxygen.

Summary

The foregoing article has led to the following conclusions.

1. The decrease in the specific second-order decomposition rate which accompanies increase in the total pressure of oxygen-ozone mixtures is due to the inhibiting effect of oxygen on the decomposition.

2. The result of Chapman and Jones, who found almost no inhibiting effect from the direct addition of oxygen to ozone mixtures, is to be explained on the basis of positive catalyst accidentally present in the oxygen which they added.

3. By electrolysis under suitable conditions from sulfuric acid, oxygen and ozone can be prepared which contain either no catalyst for ozone decomposition or at least a nearly constant amount.

4. Linde tank oxygen and oxygen freshly prepared by electrolysis from caustic solution may contain considerable amounts of catalyst for ozone decomposition. The amount of catalyst in oxygen from sodium hydroxide solutions is greatly reduced by passage through the silent discharge in a Siemen's ozonizer.

5. Different samples of oxygen show different degrees of ozonizability in the Siemen's ozonizer, and there is a tendency for high ozonizability to be correlated with low specific second-order decomposition rate.

PASADENA, CALIFORNIA

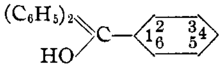
[CONTRIBUTION FROM THE PHARMACEUTICAL LABORATORY OF THE UNIVERSITY OF UTRECHT]

THE USE OF METHOXYTRIPHENYL CARBINOLS AS ONE-COLOR INDICATORS[1]

BY I. M. KOLTHOFF

RECEIVED MARCH 7, 1927 PUBLISHED MAY 10, 1927

The one-color indicators in use at the present time are colored in alkaline and colorless in acid solution. This work is a study of the constants and properties of a series of indicators which are colorless in alkaline and colored in acid solution. Triphenyl carbinol



is colored in sulfuric acid but the salt is hydrolyzed when diluted with

---

[1] The writer is indebted to Mr. H. Lund and Professor M. Gomberg, University of Michigan, for the preparations used in connection with this work. See H. Lund, THIS JOURNAL, **49**, 1346 (1927).

water. The basic character of the carbinol is, however, increased by the introduction of a sufficient number of methoxy groups so that these derivatives form colored salts which are stable in aqueous solution.

The use of an indicator to determine the P_{H} of a solution without using buffers necessitates a knowledge of its dissociation constant or hydrolysis constant.[2] The latter is preferable when dealing with basic indicators. From the equation $\text{BOH} + [\text{H}^+] \rightleftharpoons [\text{B}^+] + \text{H}_2\text{O}$, the following expression may be derived: $[\text{BOH}][\text{H}^+]/[\text{B}^+] = K_{\text{h}}$, where K_{h} is the hydrolysis constant (or indicator constant), [BOH] the concentration of undissociated or colorless indicator, and $[\text{B}^+]$ the concentration of the colored form. Then $[\text{H}^+] = ([\text{B}^+]/[\text{BOH}])K_{\text{h}}$. If K_{h} is known and a definite concentration of indicator is used, $[\text{B}^+]$ is determined by colorimetric measurement and $[\text{H}^+]$ can be calculated.

The dissociation constant of the base, K_{b}, is calculated from the equation $K_{\text{b}} = K_{\text{H}_2\text{O}}/K_{\text{h}} = 6.4 \times 10^{-15}/K_{\text{h}}$ (at 15°).

In determining K_{h}, to 10 cc. of freshly prepared phosphate or phthalate buffer solution was added 0.1 cc. of 0.1% alcoholic indicator solution and this was compared colorimetrically with standards prepared by diluting varying amounts of the indicator to 10 cc. with 0.1 *N* acetic acid or 0.1 to 0.2 *N* hydrochloric acid, depending on the P_{H} at which full color was developed. The P_{H} was varied over a range of about 1.5 units and the average of these seven or eight values for K_{h} was taken. This procedure is to be used in preparing solutions for the determination of P_{H} by the method of Michaelis.

The results are given in Table I.

TABLE I

HYDROLYSIS AND BASICITY CONSTANTS OF THE CARBINOLS

Scientific name	Proposed name	Range of color change, P_{H}		K_{h} 15°	$P_{K_{\text{h}}}$ 15°	$P_{K_{\text{h}}}$ 50% acetone and water	Temp. coeff. $P_{K_{\text{h}}}$ 15° 100°	K_{h} 100°	K_{b} 15°
2,4,6,2′,4′,2″,4″-Heptamethoxytriphenyl carbinol	Heptamethoxy red	7.0 colorless	5.0 red	1.4×10^{-6}	5.85	5.89			4.5×10^{-9}
2,4,2′,4′,2″,4″-Hexamethoxytriphenyl carbinol	Hexamethoxy red	4.6 colorless	2.6 pink-red	5.1×10^{-4}	3.29	2.86	0.007	1.27×10^{-4}	1.2×10^{-11}
2,4,2′.4′,2″-Pentamethoxytriphenyl carbinol	Pentamethoxy red	3.2 colorless	1.2 red-violet	1.52×10^{-2}	1.82	1.55	.008	3.2×10^{-3}	4.2×10^{-13}

---

[2] Michaelis and Gyemant, *Biochem. Z.*, **109**, 165 (1920). Michaelis and Krüger, *ibid.*, **119**, 307 (1921). Kolthoff, "Der Gebrauch von Farbenindikatoren," Julius Springer, Berlin, **1923**, 2nd ed., p. 130. Kolthoff and Furman, "Indicators," John Wiley and Sons, New York, **1926**, p. 14.

2,4,2′,4′,4″- and 2,6,2′,6′,2″-Pentamethoxytriphenyl carbinol were found to have a range from colorless to pinkish-red and blue-violet, respectively, of 3.3 to 1.3 and 2.8 to 0.8. They offer no advantages, therefore, over the 2,4,2′,4′,2″ compound.

The decrease in value of K_h, at higher temperatures, corresponds to a large increase in K_b. K_{H_2O} at 100° is about 100 times as large as at 15°, whereas K_b for hexamethoxy red is only one-fourth as large. Hence, K_b at 100° must be 400 times as large. In none of the ordinary indicators does the dissociation constant increase so rapidly; it is always less than the increase for water, resulting, for basic indicators, in a decreased sensitivity toward the hydrogen ion at 100°. With these indicators, however, the sensitivity increases, and less acid is required to give the same color.

Table II shows the relative sensitivity of hydrochloric acid solutions in water as compared with solutions containing alcohol or sodium chloride.

Table II

Effect of Alcohol and Salt Solutions

Alcohol, %	Sensitivity ratio, water: alcohol	Solution	Sensitivity ratio, water: salt solution
30	4.7		
50	4.1	0.1 *N* NaCl	1.1
70	2.7	0.5 *N* NaCl	1.33
90	1.1	1.0 *N* NaCl	1.8
96	0.2		
100	0.1		

It is evident that the salt error of this indicator is very small; the salt and alcohol errors of the others are similar in this respect. Qualitatively, the salt error is in the same direction as with other basic indicators, such as methyl orange.

These indicators may also be used in the form of test paper.

The color change of the hepta compound is slow, requiring 15 minutes to reach a maximum. This renders it useless in titrations. The others, however, are very satisfactory in this respect.

In titrating sodium carbonate, 25.00 cc. of 0.1 *N* solution required 25.05 cc. and 25.03 cc. of 0.1 *N* hydrochloric acid using dimethyl yellow as indicator, and 25.00 cc. and 24.95 cc. using hexamethyl red, titrated to a barely visible pink. The addition of 0.10 cc. more of the acid gave a distinct pink, corresponding to the theoretical end-point, as shown by boiling off the carbon dioxide, which also made the color change sharper. One hundred cc. of water containing 0.25 cc. of 0.1% indicator solution required 0.04 cc. of 0.1 *N* hydrochloric acid to give a barely noticeable pink; 0.10 cc. gave a distinct pink, and this is the most satisfactory end-point (*P*H, 4.0). In titrating borax, the same results were obtained as with methyl red.

Phosphoric acid may be accurately titrated as a monobasic acid if a monobasic phosphate solution (*P*H, 4.5) containing the indicator is used for comparison. The end-point is a barely visible pink. The titration can then be continued, using phenolphthalein as indicator.

Using pure potassium dichromate solution containing the indicator for comparison, it was possible to detect 0.2–0.25% of free chromic acid in 1 g. of the salt in 25 cc. of water.

Ammonia and alkaloids may be satisfactorily titrated, using this indicator.

Pentamethoxy red may be used in determining the *P*H of gastric juice.

Summary

1. A number of triphenyl carbinol derivatives containing 5, 6 or 7 methoxy groups have been found to make excellent indicators which are unique in being colorless in alkaline and colored in acid solution.
2. Their constants and properties are given.
3. 2, 4, 6, 2′, 4′, 2″, 4″-Heptamethoxytriphenyl carbinol changes color so slowly as to be useless in titrations, but the others are satisfactory.

UTRECHT, HOLLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ARIZONA]

THE PREPARATION AND ANALYSIS OF PURE AURIC OXIDE[1]

BY W. E. ROSEVEARE WITH T. F. BUEHRER

RECEIVED MARCH 7, 1927 PUBLISHED MAY 10, 1927

In connection with the determination of the free energy of auric oxide from electromotive-force measurements, the results of which will be set forth in another paper by the authors,[2] it became necessary to prepare pure auric oxide which could be depended upon to give reproducible potentials. The present paper embodies the results of a critical study of existing methods of preparation as well as of certain analytical procedures which were devised and tested to determine the purity of the product obtained.

The various methods of preparing auric oxide have been summarized and discussed by Mellor[3] and by Abegg.[4] The method of Fremy[5] proved most satisfactory as a starting point in this preparation. It consists of three essential steps: (1) precipitation of the oxide from chloro-auric

---

[1] A paper presented by W. E. Roseveare, at the meeting of the Southwestern Division of the American Association for the Advancement of Science, Phoenix, Arizona, February 15–18, 1926.

[2] To be published by Buehrer and Roseveare in THIS JOURNAL.

[3] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., **1923**, vol. 3, p. 580.

[4] Abegg, "Handbuch der anorganischen Chemie," S. Hirzel, Leipzig, **1908**, vol. 2, pt. 1, p. 819.

[5] Fremy, *Ann. chim. phys.*, [3] **31**, 481 (1851). Ref. 3, p. 580.