[Contribution from the Department of Chemistry of the University of North Dakota]

STUDIES IN AZO INDICATORS[1]

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Received March 17, 1930 Published June 6, 1930

Since Sørensen's studies using indicators for the determination of hydrogen-ion concentrations, there has been a constantly widening use of indicators for the measurements in various fields. One of the difficulties has been that it required several different types of indicators having entirely different color changes to cover the *P*H range from 1.0 to 14.0. Each of these has individual characteristics which make knowledge gained from the use of one useless when it is necessary to use another. If a satisfactory series of indicators with the same color change could be prepared which would cover the whole *P*H range, their use would be greatly simplified. Certain groups are known to affect the color of dyes and should alter the color change of indicators. This paper is the report of a study made to determine the effect of substitution in the benzene nucleus and the position of this substitution on indicators of the methyl orange and methyl red type. Published work of this nature has been given in the paper of A. Thiel,[2] this deals with substitutions in naphthylamino-azobenzene. Several compounds which contribute to such a study are included in the work of Clark.[3]

Studies in Derivatives of Methyl Orange

Methyl orange has long been used as an indicator and several theories have been proposed for its color changes.[4] The following work is to determine the effect of changing the position of the "diazo" group relative to the sulfonic acid group about the benzene ring on the ease of the electron shift, and also to determine the effect, if any, when substituent groups are introduced into either the benzene sulfonic acid part of the molecule or the dimethylaniline part, on this electron shift.

The method which was used for preparing the various diazo compounds was a modification of the one described in Gattermann.[5] The hydrogen-ion concentration at which color change took place was determined by a modification of the method of Fales and Mudge.[6]

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[1] This communication is an abstract of theses submitted by Harold W. Haugen and B. Elwood Fahl in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at the University of North Dakota.

[2] A. Thiel, *C. A.*, **18**, 3568 (1924); *Z. anorg. allgem. Chem.*, **136**, 393–405 (1924).

[3] Value given in Clark, "The Determination of Hydrogen Ions," p. 78, 3.1–4.4.

[4] Ostwald, *Z. physik. Chem.*, **9**, 579 (1892); Stieglitz, This Journal, **25**, 1112 (1903); Vorländer, *Ber.*, **36**, 1485 (1903); Hantzsch, *ibid.*, **41**, 1187 (1908); **46**, 1537 (1913); **48**, 158 (1915); Thiel, *C. A.*, **18**, 56 (1924); *Ber.*, **56B**, 1667–1671 (1923).

[5] Gattermann, "Practical Methods of Organic Chemistry," The Macmillan Co., New York, **1925**.

[6] Fales and Mudge, This Journal, **42**, 2447 (1920).

Experimental Part

OBSERVATIONS

Diazo compound	PH between which color change took place
Methyl orange	2.8–4.1
p-Dimethylamino-azobenzene-*o*-sulfonic acid	2.8–4.1[8]
Ethyl orange	2.8–4.5[9]
p-Dimethylamino-azobenzene-2-sulfonic acid	3.5–4.47
p-Dimethylaminobenzene-azo-4-methyl-benzene-2-sulfonic acid	2.8–4.4[7]
p-Dimethylaminobenzene-azo-4-methylbenzene-2-sulfonic acid	2.9–4.1
p-Dimethylaminobenzene-azo-4-nitrobenzene-2-sulfonic acid	2.5–4.0
p-Dimethylaminobenzene-azo-4-methylbenzene-3-sulfonic acid	2.8–4.1
p-Dimethylaminobenzene-azo-4-aminobenzene-3-sulfonic acid	2.2–2.5

Studies in Derivatives of Methyl Red

It appears that methyl red undergoes two color changes while changing colors. This has been accounted for in the color theories of Stieglitz, Thiel[4] and Hantzsch. There are several references[10] in the literature for the preparation of methyl red but the method given by Clark and Kirner[11] seemed the best to follow. In many of the derivatives several modifications were necessary.

The method used for determining the indicator constant was by colorimeter[12] for that concentration when half of the indicator had changed.

EXPERIMENTAL OBSERVATIONS

Indicator	Approximate indicator constant
Methyl red[13]	6.05×10^{-6}
2-Carboxybenzene-azo-dimethyltoluidine	6.19×10^{-6}
5-Nitro-2-carboxybenzene-azodimethylaniline	3.04×10^{-5}
4-Nitro-2-carboxybenzene-azodimethylaniline	3.07×10^{-5}
m-Carboxybenzene-azodimethylaniline	2.32×10^{-3}
p-Carboxybenzene-azodimethylaniline	4.5×10^{-3}
p-Dimethylamino-azobenzene-*p*-phenylacetic acid	1.07×10^{-3}
p-Dimethylamino-azobenzene-*p*-bromo-*p*-phenylacetic acid	4.37×10^{-4}

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[7] The value of the mid-point as determined by a modification of the Gillespie colorimeter as described in Clark, Ref. 3, p. 69, was 3.31, C. S. Slater, Master's "Thesis," University of North Dakota (unpublished).

[8] This compound seems to have many advantages over methyl orange for clear-cut color changes as an indicator for the same range.

[9] Value 3.5–4.5, given in Clark, Ref. 3, p. 86.

[10] Rupp and Loose, *C. A.*, **3**, 523 (1909); Tizard, *C. A.*, **5**, 1222 (1911); Rupp, *C. A.*, **10**, 2214 (1912).

[11] Clark and Kirner, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1922**, Vol. II.

[12] This colorimeter was for two-color indicators as designed by G. A. Abbott of North Dakota and constructed by Bausch and Lomb.

[13] This value agrees with that of Clark, *C. A.*, **11**, 1443 (1918); THIS JOURNAL, **46**, 581 (1924), but is much higher than the value obtained in a different manner by Theil and Dassler, *C. A.*, **18**, 56 (1924).

Conclusions

1. Substitution of methyl groups produces very little effect on the hydrogen-ion concentration at which the indicator changes color.
2. The position of the acid group produces the greatest change in indicator properties. When in the ortho position the change takes place at the higher *P*H, when in para lower and lowest in meta.
3. The introduction of strongly negative groups such as the nitro group causes a change at a lower *P*H.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE CHAIN CHARACTERISTICS OF THE ETHYLENE-OXYGEN REACTION

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RECEIVED MARCH 21, 1930 PUBLISHED JUNE 6, 1930

It is now well known that many reactions once thought to be of the simple classical type actually occur by a chain mechanism. Generally speaking, the existence of these chains has been demonstrated in one or more of three ways, by measuring the quantum yield in photochemical experiments, by studying the unusual kinetics of gaseous reactions, or by introducing some active material or "trigger" to start the chains. In the case of hydrocarbon oxidations, the photochemical method is not very convenient experimentally. Before making a study of the kinetics of these reactions it was considered advisable to demonstrate their chain character in a direct manner by the last of the methods mentioned above. The use of ozone as a "trigger" in gaseous reactions was first developed by Semenoff and Rjabinin[2] in the combustion of sulfur. An attempt has been made to apply ozone as a "trigger" to the ethylene-oxygen system at temperatures where sufficient reaction takes place to be measurable but well below the ignition point. Under these conditions ozone has an extremely short life, so that the actual amount employed in starting chains may be very much smaller than the amounts actually introduced into the gas stream. We would therefore obtain only a lower limit of ozone efficiency and of chain length in this manner.

Ethylene and oxygen (from cylinders), at measured rates of flow, and dried over phosphorus pentoxide, were passed through a reaction vessel maintained at a definite temperature in a furnace, then through a weighed tube of phosphorus pentoxide for a given time, the increase in weight being noted. With everything else constant, the oxygen was then partially

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[1] Commonwealth Fund Fellow.

[2] Semenoff and Rjabinin, *Z. physik. Chem.*, 1B, 193 (1928).