

From (5), (6) and (7), it follows that

$$K_I = K_{ROH} a_{H_2O} + K_{ROCH_3} \quad (8)$$

In the present study, we have determined the values of K_{ROH} , K_{ROCH_3} and k in methanol.

As will be evident from the experimentally determined value of k , the indicator equilibrium in anhydrous methanol may be represented by equation (7), if the total concentration of the indicator is small. The addition of water will tend to convert $ROCH_3$ into ROH , thus it will shift the color of the indicator in a buffer solution to the alkaline side.

If r denotes the ratio of alkaline to acid form of the indicator in pure methanol, we find

$$r = \frac{[ROCH_3]}{[R^+]} = \frac{K_{ROCH_3}}{a_{CH_3OH_2^+}} \quad (9)$$

where concentrations of the forms of the indicator are used instead of activities. In a previous study,⁴ it was demonstrated that, in buffered solutions, the indicator equilibria in methanol are unaffected by the addition of traces of water. In a given buffer then, K_{ROCH_3} and $a_{CH_3OH_2^+}$ are unchanged. Hence, in equation (9), r will remain constant even on addition of water. Starting with a given concentration of indicator, we determine experimentally the ratio

$$\frac{[ROCH_3] + [ROH]}{[R^+]} = r'$$

From equation (3) we see that

$$r' = r(1 + ka_{H_2O}) \quad (10)$$

Values of r' were determined experimentally at various concentrations of water. When these are plotted against the water concentration, the intercept will give the value of r and the slope, krf_{H_2O} , in which f_{H_2O} is the activity coefficient of water in methanol. In order to obtain a value of K_{ROH} in methanol which will correspond to its value in water, we have chosen pure water as the standard state of water. In dilute solution, f_{H_2O} is equal to 0.0751, according to Unmack.⁵ The activity coefficients of the other constituents may be considered to be unaffected by small amounts of water. Hence, by the above procedure, we find the value of k , and of r . From the latter and equation (9), K_{ROCH_3} can be calculated and, hence, K_{ROH} .

The indicator constants of penta- and hexamethoxytriphenylcarbinols were determined in pure methanol in the same manner as described in the previous paper,⁴ the extrapolation method

to zero ionic strength being used for finding the ratio of activities instead of concentrations.

It may be added that the values of the various constants do not require the use of entirely water-free methanol, as by extrapolation of the r' values obtained in the presence of larger excesses of water, the value of r at a water content of zero is found.

Experimental

The methods of purification of reagents already have been described.⁴ The indicators were samples furnished by H. Lund^{2,3} while working at the University of Michigan. Solutions of water in methanol were prepared by weighing the required amount of conductivity water in a calibrated volumetric flask of 50-ml. capacity and making up to the mark. Colorimetric comparisons were made with a Dubosq colorimeter.

Pentamethoxy Red.—The indicator equilibrium in water-free methanol was determined in trichloroacetate buffers, the concentration of the indicators in the buffers being $2 \times 10^{-6} M$. The results are given in Table I, and graphically represented in Fig. 1.

TABLE I
PENTAMETHOXY RED IN TRICHLOROACETATE BUFFER

$c_{Acetate}$	Salt added	c_{Salt}	$\sqrt{\mu}$	c_B/c_A	c_b/c_a	pK
0.0080			0.090	3.6	1.47	0.39
.0080			.090	2.5	0.91	.44
.0080			.090	1.96	.74	.43
.0080			.090	1.60	.55	.46
.0080			.090	1.35	.505	.43
.0080			.090	1.17	.43	.435
.008	LiCl	0.011	.14	2.5	.665	.57
.008	NaBr	.018	.16	2.5	.665	.57
.008	LiCl	.055	.25	2.5	.55	.66
.008	NaBr	.088	.31	2.5	.37	.83
.008	LiCl	.110	.345	2.5	.38	.82
.008	NaBr	.177	.43	2.5	.41	.74
.008	NaBr	.177	.43	6.2	.695	.95
.008	LiCl	.221	.48	2.5	.25	1.00
.008	LiCl	.331	.58	2.5	.22	1.06
.008	NaBr	.354	.60	6.2	.43	1.16
.008	LiCl	.442	.67	2.5	.183	1.13

The extrapolated value of pK' is 0.2. As pK_A of trichloroacetic acid is 4.9,⁶ we find for pK_{ROCH_3} a value of 5.1.

The effect of water up to a concentration of 1.8 M was determined in a buffer with ionic strength of 0.0080 ($c_B/c_A = 2.5$). The results are given in a graph in Fig. 2, in which r' is plotted against the concentration of water.

Hexamethoxy Red.—The indicator equilibrium in pure methanol was determined in salicylate buffers. The results are given in Table II and graphically in Fig. 3.

From the extrapolated value of pK' of 0.65 and pK_A of salicylic acid of 7.9,⁷ we find $pK_{ROCH_3} = 7.25$.

The effect of salts on the indicator equilibrium was also

(6) H. Goldschmidt and H. Aarfott, *Z. physik. Chem.*, **117**, 317 (1925).

(7) H. Goldschmidt and F. Aas, *ibid.*, **112**, 429 (1924)

(5) A. Unmack, *Z. physik. Chem.*, **129**, 349 (1937).

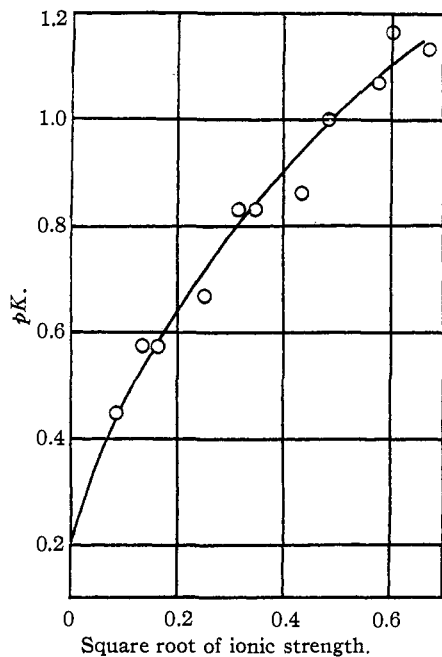


Fig. 1.—Pentamethoxy red in trichloroacetate buffer.

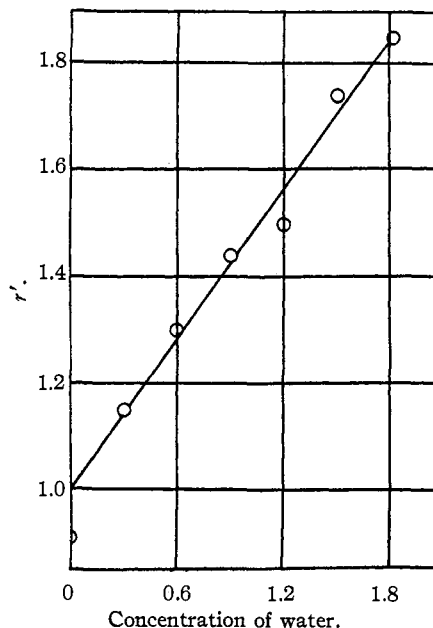


Fig. 2.—Effect of water on the indicator ratio of pentamethoxy red in trichloroacetate buffer.

determined in *m*- and *p*-nitrobenzoate buffers and was found almost identical with that in salicylate buffers. The effect of water up to a concentration of 1.8 molar was determined in a salicylate buffer and also in a *m*-nitrobenzoate buffer, the two determinations giving an average value of *k* in satisfactory agreement. The data obtained in the salicylate buffers are plotted in Fig. 4.

The methoxytriphenylcarbinols act as basic indicators and their behavior should be similar to that of methyl yellow or neutral red. From the general equation

$$pK = pK' - \log f_{1a} + \log f_{1b} - \log f_B + \log f_A \quad (11)$$

we see that the slope of the curve obtained on plotting *pK* against the square root of the ionic

TABLE II
HEXAMETHOXY RED IN SALICYLATE BUFFER

<i>c</i> _{Salicylate}	Salt added	<i>c</i> _{Salt}	$\sqrt{\mu}$	<i>c</i> _B / <i>c</i> _A	<i>c</i> _{1b} / <i>c</i> _{1a}	<i>pK</i>
0.0060			0.078	0.415	1.06	-0.41
.0060			.078	.48	1.15	-.38
.0060			.078	.575	1.3	-.35
.010			.10	.95	1.82	-.28
.006	LiCl	0.011	.13	.415	0.87	-.32
.006	NaBr	.022	.195	.415	.60	-.16
.006	LiCl	.055	.25	.415	.515	-.09
.006	NaBr	.062	.26	.415	.48	-.07
.006	LiCl	.110	.34	.415	.41	.01
.006	NaBr	.122	.36	.415	.41	.01
.006	LiCl	.221	.48	.415	.31	.13
.006	NaBr	.182	.435	.415	.34	.08
.006	LiCl	.331	.58	.415	.265	.19

A summary of the values of the various constants calculated from the results is given in Table III.

TABLE III
CALCULATION OF CONSTANTS OF METHOXYTRIPHENYL-CARBINOLS

Indicator	Intercept	Slope	<i>k</i>	<i>pK</i> _{ROCH₃}	<i>pK</i> _{ROH}
Pentamethoxy red	1.0	0.48	6.4	5.1	4.3
Hexamethoxy red	1.17	1.10	12.5	7.25	6.15

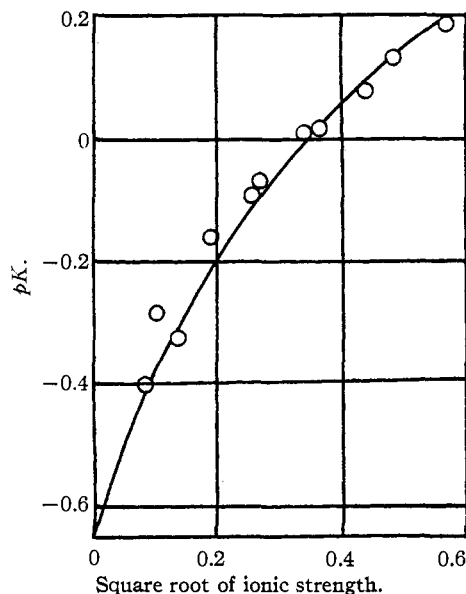


Fig. 3.—Hexamethoxy red in salicylate buffer.

strength should approach +4, as the ionic strength approaches zero. That this is the case is seen from Figs. 1 and 3.

From the values of k , it is seen that in mixtures of methanol and water, containing a large amount of the latter component, the methoxytriphenylcarbinols are largely present in the ROH form.

From the practical point of view, the values of the constant

$$k' = \frac{[\text{ROH}]}{[\text{ROCH}_3]c_{\text{H}_2\text{O}}}$$

are more interesting than the k values. For the pentamethoxy indicator, k' is equal to 0.48, and for the hexamethoxy indicator, 0.94.

Finally, it may be mentioned that pK_{ROH} increases more when going from water to methanol as a solvent than that of other cation acids. The pK of the latter increases by about one unit.¹ In water, the pK values of penta- and hexamethoxy red are 1.85 and 3.3,⁸ respectively. In methanol, the pK values increase by 2.45 and 2.85, respectively.

Summary

1. The effect of salts upon the color of penta- and hexamethoxytriphenylcarbinols in methanol corresponds to that of a system of uncharged base-cation acid.

2. In pure methanol, the carbinols are present

(8) I. M. Kolthoff, *THIS JOURNAL*, **49**, 1218 (1927).

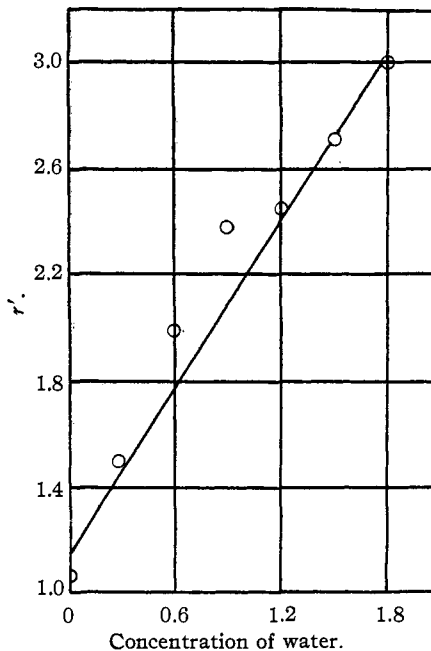


Fig. 4.—Effect of water on the indicator ratio of hexamethoxy red in salicylate buffer.

mainly in the form of the methyl ether. The equilibrium constant of the reaction between the methyl ether and water has been evaluated.

3. The values of pK_{ROCH_3} and pK_{ROH} of the carbinols in methanol have been determined.

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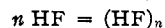
[CONTRIBUTION FROM THE LABORATORIES OF THE PENNSYLVANIA STATE COLLEGE AND PRINCETON UNIVERSITY]

The Molecular Structure of Hydrogen Fluoride¹

BY S. H. BAUER, J. Y. BEACH² AND J. H. SIMONS

Structural studies of hydrogen fluoride may be traced back for more than half a century.³ That the compound is polymerized in the vapor phase has been known since the early work of Mallet.⁴ Simons and Hildebrand demonstrated that some of the polymers are of an order higher than tetramers,⁵ for they obtained apparent molecular weights for the gas as large as 87.4. Further, they showed that *one* way of interpreting the available

vapor density data (over the pressure range 56 to 760 mm. and temperature range -39 to 88°) rests on the assumption of the single equilibrium



with $n = 6$ and

$$\log K_6 = \frac{+40,000}{4.597T} - 43.145$$

Although the data could be correlated with the existence of a larger number of species in equilibrium, the simpler hypothesis seemed reasonable in view of the fact that the molecular weight apparently approached 120 as the temperature was lowered and that within the experimental error agreement was found with the even whole number six for the degree of polymerization. Latimer

(1) Part of these results were presented to the American Chemical Society at Milwaukee, September, 1938.

(2) National Research Fellow in Chemistry.

(3) Two reviews have appeared: J. H. Simons, *Chem. Rev.*, **8**, 213 (1931); K. Fredenhagen, *Z. Elektrochem.*, **37**, 684 (1931).

(4) Mallet, *Am. Chem. J.*, **3**, 189 (1881).

(5) J. H. Simons and J. H. Hildebrand, *THIS JOURNAL*, **46**, 2183 (1924).