but the saturated structure of all five carbonyl groups is attained not by all five sharing uniformly with the iron atom, but by four sharing, as in the $Fe(CO)_4^=$ ion, and the fifth bridging across two of the four. Similarly chromium hexacarbonyl[9] and molybdenum hexacarbonyl have two such bridges.

Cobalt trinitrosyl, $Co(NO)_3$, predicted by Reiff on the basis of the effective atomic number, should not be capable of existence if the symmetry of four groups attached to the central atom is an essential part of the stability of the electron distribution. Indeed, Blanchard, Rafter and Adams[10] failed completely to obtain such a substance under conditions that produced the nitrosyl tricarbonyl freely.

Summary

The existence of the hydrides of the carbonyls lends strong confirmation to the thesis that the electron pattern of nickel carbonyl is repeated in all the volatile carbonyls, the addition of hydrogen to the other carbonyls furnishing the number of electrons necessary to complete that pattern. In nitrosyl carbonyls and polymeric carbonyls the same electron pattern is completed.

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[9] Windsor has just determined the vapor density of chromium hexacarbonyl, and found that it corresponds to that of the single molecule $Cr(CO)_6$ [THIS JOURNAL, **56**, 823 (1934)].

[10] Blanchard, Rafter and Adams, *ibid.*, **56**, 16 (1934).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

A Series of Simple Basic Indicators. III. The Zero Point of the Acidity Function Scale

BY LOUIS P. HAMMETT AND MARTIN A. PAUL

In proposing an acidity function by means of which the "acidity in terms of a basic indicator" may be measured, Hammett and Deyrup[1] pointed out that the most desirable basis for a zero point of this scale would be one which would make the acidity function approach the *P*H in infinitely dilute aqueous solution. Because their work was concerned with acidities outside the range of the "dilute aqueous solution," they did not carry out the measurements necessary to establish this zero point and based their scale tentatively upon figures available in the literature for the base strengths of *p*-nitraniline and *o*-nitraniline. In the paper immediately following this it is shown that the transition range from "dilute aqueous solutions" to moderately concentrated solutions of strong acids is especially interesting for the problem of acid catalysis. It is therefore desirable to establish this zero point accurately and finally.

For this purpose we have extended the stepwise intercomparison method of Hammett and Deyrup by the addition of two stronger bases, benzeneazodiphenylamine and aminoazobenzene, whose ionization has been measured colorimetrically in solutions of hydrochloric acid so dilute that the activity of hydrogen ion may be set equal to the molarity of the acid, or, in the more concentrated solutions, to the mean ionic activity. The strength constants, pK', of the new stronger bases follow immediately from the measurement of their degree of ionization in the dilute acid solutions by the equation[1]

$$pK' = -\log (C_{\mathrm{OH_3^+}} C_{\mathrm{B}} / C_{\mathrm{BH^+}})$$

Since moreover the range of acidity in which they may be used overlaps that of *p*-nitraniline, a value for the pK' of the latter may be obtained by direct comparison of the strengths. The corrected value of pK' for *p*-nitraniline thus obtained serves as a basis for the correction of all of the pK' and H_0 values of Hammett and Deyrup to the new basis.

The present paper also contains measurements of the acidity functions of hydrochloric and nitric acids up to moderate concentrations and of other solutions of interest for the acid catalysis problem.

Materials and Method

For the work with the aminoazobenzene derivatives it was necessary to modify the method of Hammett and Deyrup because these are two color indicators and because of the low acidities in question. A measured number of drops, about 0.15 cc., of an ethyl alcoholic solution of the indicator was added to 25 cc. of the solution to be

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[1] Hammett and Deyrup, THIS JOURNAL, **54**, 2721 (1932).

tested. The final concentration of the indicator varied from 0.00002 to 0.00005 molar for aminoazobenzene and was about 0.000005 molar for benzeneazodiphenylamine. The reference solutions were 0.04 M sodium hydroxide and 0.3 M hydrochloric or nitric acid. The reproducibility of the value of $-\log C_{BH^+}/C_B$ is about ±0.02.

With the nitraniline derivatives, the method of Hammett and Deyrup was used without essential modification. In the experiments upon the effect of added salts and sugar, the same concentration of these non-acids was used in the reference solution by comparison with which the ionization ratio of the indicator was determined as in the solution under investigation. The effect of sucrose at 200 g. per liter upon the color intensity S_W[1] of *p*-nitraniline was 0.10 logarithmic units. The acids in the concentrations used did not affect the color intensity of the non-ionized form.

The nitric acid was redistilled in an all-Pyrex apparatus, the middle third being retained and used immediately, in order to prevent formation of nitrogen oxides. The hydrochloric acid was a reagent grade. Solutions were standardized by titration using potassium acid phthalate as primary standard. Aminoazobenzene was recrystallized from alcohol and water and melted at 125.7° corr. Benzeneazodiphenylamine after similar purification melted at 82.5°. The criteria of purity for the other indicators were the same as in the previous work.

Results

Table I contains the results on hydrochloric and nitric acid solutions. This contains the molal concentration of the acid m, and the logarithm of the observed ionization ratio $[BH^+]/[B]$.

For the more dilute solutions there is also given the logarithm of the mean ionic activity, $a_\pm$, taken from the Landolt–Börnstein "Tabellen" (1931 Suppl.) and a value of $pK' = \log [BH^+]/[B] - \log a_\pm$. From a large scale plot of these data the strengths of the indicators were calculated taking the average value of +2.80 for aminoazobenzene. As in the cases studied previously,[1] the parallelism of the lines on this plot for the different indicators demonstrated the lack of dependence upon acid concentration of the relative strengths of the indicators.

TABLE I

IONIZATION OF INDICATORS IN $HCl–H_2O$ SOLUTIONS

m	$\log [BH^+]/[B]$	$-\log a_\pm$	pK'
Aminoazobenzene			
0.00117	−0.14	+2.95	+2.81
.00154	− .04	2.83	2.79
.00188	+ .07	2.75	2.82
.00237	.18	2.65	2.83
.00355	.36	2.48	2.84
.00474	.46	2.36	2.82
.00710	.56	2.19	2.75
.00949	.72	2.07	2.79
.01183	.81	1.97	2.78
.01893	.99	1.78	2.77
.0213	1.03	1.73	2.76
.0237	1.13	1.69	2.82

m	$\log [BH^+]/[B]$
Benzeneazodiphenylamine	
0.00949	−0.56
.01900	− .31
.0285	− .16
.0381	+ .02
.0476	.06
.0570	.20
.0763	.32
.0859	.38
.0951	.45
.1141	.54
p-Nitroaniline	
0.0666	−0.14
.0859	− .04
.0951	+ .03
.1141	.08
.204	.42
.284	.61
.427	.76
.603	.88
0.761	1.07
.970	1.14
1.153	1.23
1.242	1.36
1.469	1.38
2.02	1.68
o-Nitroaniline	
0.767	−0.33
1.238	+ .03
1.782	.25
2.54	.54
3.66	.90
4.75	1.23
p-Chloro-*o*-nitroaniline	
2.34	−0.27
3.76	+ .20
4.56	.43
6.00	.85
6.88	1.08

IONIZATION OF INDICATORS IN NITRIC ACID–WATER SOLUTIONS

m	$\log [BH^+]/[B]$
p-Nitroaniline	
0.091	+0.01
.304	.57
.743	1.05
1.100	1.26
1.210	1.29
1.526	1.43
1.780	1.56
2.18	1.68
2.51	1.80
2.60	1.84
2.94	1.96
3.26	2.03
3.33	2.07
o-Nitroaniline	
1.420	+0.10
1.697	.21
2.12	0.35
2.44	.49
3.25	.69
3.55	.74
4.12	.89
4.69	1.02
5.33	1.18
5.80	1.32
6.65	1.37
7.14	1.51
p-Chloro-*o*-nitroaniline	
5.12	+0.34
6.42	.58
7.47	.74
8.65	.90
9.57	1.04

Table II contains the values of the base constants pK' for the four strong acid–water systems for which data are now available. These are based in the case of the other acids upon the

TABLE II

BASIC STRENGTH OF INDICATORS

Indicator	HCl	HNO_3	H_2SO_4	$HClO_4$
Aminoazobenzene	+2.80			
Benzeneazodiphenylamine	+1.52			
p-Nitroaniline	+1.11	[+1.11]	[+1.11]	[+1.11]
o-Nitroaniline	−0.17	−0.20	−0.13	−0.19
p-Chloro-*o*-nitroaniline	− .91	− .97	− .85	− .91
p-Nitrodiphenylamine			−2.38	
2,4-Dichloro-6-nitroaniline			−3.22	−3.18
p-Nitroazobenzene			−3.35	−3.35
2,6-Dinitro-4-methylaniline			−4.32	
2,4-Dinitroaniline			−4.38	−4.43
N,N-Dimethyl-2,4,6-trinitroaniline			−4.69	
Benzalacetophenone			−5.61	
β-Benzoylnaphthalene			−5.92	
p-Benzoyldiphenyl			−6.19	
6-Bromo-2,4-dinitroaniline			−6.59	
Anthraquinone			−8.15	
2,4,6-Trinitroaniline			−9.29	

TABLE III

IONIZATION OF *o*-NITROANILINE IN $CCl_3COOH–H_2O$ MIXTURES

Moles acid/liter soln.	0.5	2.0	4.0
log $[BH^+]/[B]$	− .81	−0.73	−0.73

value of +1.11 which we derive for *p*-nitraniline from hydrochloric acid solutions. This value incidentally is in agreement with the directly determined one for the most dilute nitric acid solutions.

The new value for *p*-nitraniline is 0.29 unit lower than the value of +1.40 provisionally adopted by Hammett and Deyrup. It follows that all values of pK' and H_0 given in the previous work should be corrected to the new scale by subtraction of 0.29 unit. The corrected figures are included in Table II.

TABLE IV

EFFECT OF NEUTRAL SUBSTANCES ON ACIDITY FUNCTION H_0; INDICATOR, *p*-NITROANILINE

Moles per liter of soln. at 25°			
HCl		KCl	log $[BH^+]/[B]$
0.100		0.00	+0.06
.100		1.00	.23
.100		2.00	.36
.100		3.00	.51
HCl	Sugar	KCl	
0.100	200 g.	0.00	+0.09
.100	200 g.	3.00	.51
HCl	Sugar	$BaCl_2$	
0.100	200 g.	0.00	+0.09
.100	200 g.	.50	.30
.100	200 g.	1.00	.42
.100	200 g.	1.30	.49
HNO_3		KNO_3	
0.25		0.00	+0.48
.25		1.35	.66
.25		2.70	.82

Values of H_0 on this scale for the five acids studied in this or the previous[1] work are plotted against molal concentration in Fig. 1.[2]

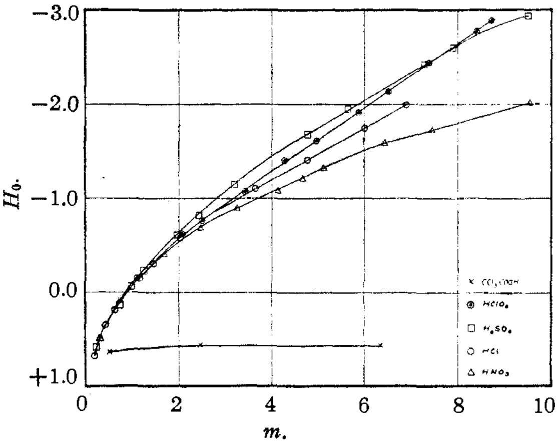

Fig. 1.

Table IV shows the effect of sucrose and of salts upon the acidity function of some acid solutions. The negligible effect of the sucrose justifies the comparison of reaction rates obtained in solutions containing 200 g. per liter of sucrose with acidity functions obtained in sucrose free solutions.

Summary

By measurements of the ionization in dilute hydrochloric acid solutions of some azobenzene indicators the zero of the scale of acidity functions, H_0, is established.

For correction to the new scale 0.29 unit should be subtracted from the values based upon the zero provisionally adopted by Hammett and Deyrup.

Acidity functions have been determined for hydrochloric and nitric solutions up to 7 and 9.5 molar, respectively, and for certain other solutions of interest for studies of acid catalysis.

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(2) The first application of indicators to the estimation of the relative acidities of concentrated aqueous solutions of strong acids seems to be that of Proszt, "Mitt. berg. Huttenmann. Abt. kgl. Hochschule Bergforstwesen Sopron," Ungarn, 1929, p. 211. In so far as a comparison is possible, there is agreement between his results and ours, in spite of the fact that his indicators were not of the simple basic type.