

be obtained from the ratio of the intensity of the band attributed to the free carbonyl group to that of the band attributed to the enol-chelate structure. In 2-benzoylhydrindone this ratio is roughly 0.1:1; 2-benzoylcyclohexanone, 4:1; 2-acetylcyclohexanone, 0.4:1; 2-acetylcyclopentanone, 1:1. Apparently, in the compounds just mentioned no correlation exists. For example, 2-benzoylhydrindone is a stronger acid than 2-benzoylcyclohexanone but appears to have the lower enol content of the two compounds. On the other hand, 2-acetylcyclohexanone is the stronger acid and has a higher enol content than 2-benzoylcyclohexanone. The strongest acid of the β -diketones studied, *i.e.*, 2-acetylcyclopentanone, has a lower enol content than does 2-acetylcyclohexanone.

Among the straight-chain β -diketones in this study, a correlation appears to exist. The intensity ratios of these compounds are: dibenzoylmethyl bromide, 1.58:1; 3-allyl-2,4-pentanedione, 1.77:1; 3-*n*-butyl-2,4-pentanedione, 2.17:1. Dibenzoylmethyl bromide, the strongest acid, has the highest enol content; 3-*n*-butyl-2,4-pentanedione, the weakest acid, has the lowest enol content.

The ultraviolet absorption maxima of interest for the β -diketones studied are listed in Table IV. It will be seen from the table that, for these β -diketones, the logarithm of the extinction coefficient of a given peak remains essentially constant as the concentration is changed. This adherence to Beer's law usually is observed among β -diketones

TABLE IV

ULTRAVIOLET ABSORPTION SPECTRAL DATA OF β -DIKETONES

β -Diketone	Molarity $\times 10^3$	$m\mu$	l	$\log \epsilon_{\max}$
3- <i>n</i> -Butyl-2,4-pentanedione	4.88	291	0.258	3.42
	9.75	291	0.418	3.40
3-Allyl-2,4-pentanedione	18.7	288	1.34	3.56
	9.35	288	0.72	3.59
Dibenzoylmethyl bromide	4.23	232	1.39	4.21
	1.69	235	0.50	4.17
2-Acetylcyclopentanone	6.26	289	1.02	3.91
	5.01	289	0.77	3.89
	2.50	289	0.37	3.87
2-Benzoylhydrindone	4.62	249	1.30	4.15
	0.965	249	0.27	4.15
2-Acetylcyclohexanone		355	0.46	4.38
	11.3	290	2.01	3.95
2-Benzoylcyclohexanone	5.64	290	0.808	3.89
	5.05	315	0.56	3.71
		249	1.12	4.01
	11.0	315	1.04	3.68

and is interpreted to mean that the ratio of keto to enol forms is not changed with concentration.

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UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Carbonium Ions. VII. An Evaluation of the H_R Acidity Function in Aqueous Perchloric and Nitric Acids^{1,2}

BY N. C. DENO, HENRY E. BERKHEIMER, WILLIAM L. EVANS AND HENRY J. PETERSON

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The H_R acidity function (previously termed C_0 and J_0 as well as H_R) has been evaluated for 0–60% perchloric acid and 0–58% nitric acid. Values of $pK_R^+ + \log(c_{ROH}/c_R^+)$ are equal when determined in different aqueous mineral acids; and values of $d \log(c_{ROH}/c_R^+)/d \%$ acid are independent of the structure of R. The symbol c refers to the concentration in moles/l. These two facts demonstrate that a class of cation exists, the arylmethyl cations, for which the values of the activity coefficient (f_R^+) are equal in aqueous mineral acids. The structural characteristics of this class are discussed in light of solubility measurements on perchlorate salts in aqueous sulfuric acid. The equilibrium between HNO_2 and NO^+ follows the H_R function in aqueous perchloric acid.

Evaluation of H_R in Perchloric and Nitric Acids.

—The H_R acidity function previously had been evaluated in 0–97% sulfuric acid using eq. 1 and a series of arylmethanols as indicators.³ It has now

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(2) The acidity function defined as equal to $pK_R^+ + \log(c_{ROH}/c_R^+)$ has been known as C_0 in our publications, J_0 in publications by V. Gold and co-workers, and H_R in publications by G. Williams and co-workers. The symbol H_R seems preferable since it indicates the close relationship to the H_0 acidity function. This fact coupled with its priority (A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3321 (1950)) has led us to abandon the symbol C_0 (and J_0) and to use H_R in all future publications.

(3) N. Deno, J. J. Jaruzelski and A. Schriesheim, *THIS JOURNAL*, **77**, 3044 (1955).

been evaluated in 0–60% perchloric acid and 0–58% nitric acid. The values of H_R as a function of % acid and moles/l. of acid are summarized in Table I.

$$H_R = pK_R^+ + \log(c_{ROH}/c_R^+) \quad (1)$$

It was found that values of $d \log(c_{ROH}/c_R^+)/d \%$ acid were independent of the structure of the arylmethyl group, R. The data in Table II show that pK_R^+ values are the same for a particular ROH even though measured in different aqueous mineral acids. Both of these results demonstrate that for arylmethanols, values of f_{ROH}/f_R^+ are independent of the arylmethyl group chosen. This generalization can be extended with perhaps some loss of precision to stating that f_R^+ is the same for different R groups at each acid concentration since it has al-

TABLE I

VALUES OF H_R IN AQUEOUS PERCHLORIC AND NITRIC ACIDS AT 25°

% HClO ₄	Moles/l.	$-H_R$	$-\frac{dH_R}{d}$ HClO ₄	$-H_0$	$-\frac{dH_0}{d}$ % HClO ₄
0.5	0.050	-1.30		-1.30	
.6	.060	-1.22		-1.22	
.7	.070	-1.16		-1.16	
.8	.080	-1.09			
1.0	.099	-0.97			
1.5	.149	-.74			
2.0	.198	-.54			
2.5	.246	-.38	0.31		
3.0	.295	-.23	.29		
4.0	.391	.03	.24		
5.0	.486	.24	.21		
6.0	.581	.43	.18		
7.0	.675	.59	.16	-0.44	
8.0	.768	.75	.15	-.34	0.10
10.0	.950	1.04	.14	-.16	.09
15.0	1.370	1.74	.14	.18	.06
20.0	1.780	2.43	.13	.47	.06
25.0	2.140	3.08	.13	.74	.06
30.0	2.485	3.79	.15	1.12	.07
35.0	2.80	4.61	.18	1.47	.08
40.0	3.08	5.54	.20	1.88	.10
42.0	3.18	5.95	.21	2.08	.10
44.0	3.28	6.38	.22	2.30	.11
46.0	3.37	6.82	.23	2.53	.12
48.0	3.46	7.31	.26	2.80	.14
50.0	3.55	7.86	.29	3.12	.16
52.0	3.63	8.45	.30	3.44	.16
54.0	3.70	9.05	.30	3.76	.16
56.0	3.77	9.68	.33	4.08	.16
58.0	3.84	10.37	.36	4.40	.17
60.0	3.91	11.14	.42	4.78	.17

% HNO ₃	Moles/l.	$-H_R$	$-\frac{dH_R}{d}$ HNO ₃	$-H_0$	$-\frac{dH_0}{d}$ % HNO ₃
0.2	0.032	-1.50		-1.50	
.3	.048	-1.32		-1.32	
.4	.064	-1.20		-1.20	
.5	.080	-1.10		-1.11	
1.0	.159	-0.74		-0.80	
1.5	.239	-.48		-.62	
2.0	.320	-.27		-.50	
2.5	.401	-.10	0.30	-.39	
3.0	.483	.04	.27	-.30	
3.5	.564	.16	.24	-.22	
4.0	.646	.28	.23	-.15	
5.0	.813	.49	.19	-.03	0.13
6.0	.980	.67	.17	.08	.11
8.0	1.323	1.00	.16	.23	.08
10.0	1.672	1.30	.14	.39	.07
15.0	2.57	2.00	.14	.72	.07
20.0	3.53	2.63	.12	.95	.05
25.0	4.55	3.23	.12	1.18	.05
30.0	5.60	3.83	.12	1.42	.05
35.0	6.72	4.45	.13	1.65	.05
40.0	7.90	5.07	.13	1.77	.04
45.0	9.10	5.70	.13	1.93	.02
50.0	10.35	6.40	.15		
55.0	11.65	7.17	.16		
56.0	11.91	7.32	.16		
58.0	12.43	7.18	.18		

ready been established that f_{ROH} values show relatively small variation with ROH structure in aqueous sulfuric acids.⁴

TABLE II

COMPARISON OF pK_{R^+} VALUES MEASURED AT 25° IN AQUEOUS SULFURIC, PERCHLORIC AND NITRIC ACIDS

Substituted triphenylmethanol	pK_{R^+}		
	H ₂ SO ₄	HClO ₄	HNO ₃
4,4',4''-Trimethoxy	0.82	0.82	0.80
4,4'-Dimethoxy	-1.24	-1.14	-1.11
4-Methoxy	-3.40	-3.59	-3.41
4-Methyl	-5.41	-5.67	
4-Trideuteriomethyl ^a	-5.43	-5.67	
3,3',3''-Trimethyl	-6.35	-5.95	
Unsubstituted	-6.63	-6.89	-6.60
4,4',4''-Trichloro	-7.74	-8.01	
4-Nitro	-9.15	-9.76	

^a A sample was kindly supplied by Dr. N. N. Lichtin who had obtained it from Dr. E. S. Lewis.

TABLE III

THE HNO₂-NO⁺ EQUILIBRIA AT 25°

% HClO ₄	Ref. 5 Log (cHNO ₂ /cNO ⁺)	$H_R - \log (cHNO_2/cNO^+)$ (pK_{R^+})
35.5	3.28	-7.98
38.5	2.62	-7.87
41.9	2.13	-8.06
45.0	1.55	-8.15
47.9	0.95	-8.23
50.4	0.18	-8.16
53.0	-0.49	-8.26
55.6	-1.33	-8.22
	Best value	-8.11

The data in Table V show that H_R equals pH in very dilute acid and demonstrates the precision to which pK_{R^+} for 4,4',4''-trimethoxytriphenylmethanol was obtained.

It can now be considered established that eq. 1 correlates the position of arylmethanol-arylmethyl cation equilibria with acidity for diaryl- and triarylmethanols. The situation with monoarylmethanols will be discussed in the next paper in this series.

The Equilibrium between HNO₂ and NO⁺.—The fact³ that the kinetics of oxidation of formic acid by nitrous acid in 20–32% sulfuric acid fit eq. 2

$$d \log k = -dH_R \quad (2)$$

suggested that (all derivatives in this paper are taken in respect to % acid) the equilibrium between HNO₂ and NO⁺ would fit eq. 1. It has now been possible to test this directly in perchloric acid solution since data on this equilibrium have appeared.⁵ The constancy of $H_R + \log (cNO^+/cHNO_2)$ is satisfactory as shown in Table III.

The above treatment correlates the data more precisely than the recent attempt⁶ to fit the data to $H_0 + \log a_{H_2O}$, a function whose applicability is questionable for this type of equilibrium, $ROH + H^+ = R^+ + H_2O$.³

(4) N. Deno and C. Perizzolo, *THIS JOURNAL*, **79**, 1345 (1957).

(5) K. Singer and P. A. Vamplew, *J. Chem. Soc.*, 3971 (1956).

(6) T. A. Turney and G. A. Wright, *ibid.*, 2417 (1958).

TABLE IV

SOLUBILITY OF THE PERCHLORATE SALTS I AND II AT 25° IN DIFFERENT CONCENTRATIONS OF SULFURIC ACID

% H ₂ SO ₄	Moles/l. ^a × 10 ²		-Log <i>f</i> ±		d log <i>f</i> / d % H ₂ SO ₄		d log <i>f</i> / d % H ₂ SO ₄
	I ^c	II ^c	I	II	I	II	
0	2.76	42.3	2.56	1.374	-0.027	-0.026	-0.018
4.84	3.48	54.8	2.46	1.292	- .010	- .013	- .006
9.82	3.54	60.6	2.45	1.215	+ .009	- .006	+ .007
19.55	3.39	64.9	2.47	1.186	- .004	.000	.000
29.59	3.77	72.5	2.42	1.140	- .007	- .011	- .010
40.52	4.87	106.0	2.31	0.975	- .013	- .018	- .021
50.83	7.56		2.12		- .025		- .030
60.24	14.3		1.84		- .037		- .042

^a Determined from the absorption spectra of the saturated solutions. The values of log *e* for I were 2.531 at 350, 2.363 at 360, 2.179 at 370 and 1.953 at 380 mμ. The values of log *e* for II were 1.337 at 330, 0.940 at 340, 0.523 at 350 and 0.107 at 360 mμ. With II, the values of *e* increased from 0-50% sulfuric acid and corrections were made for this effect in calculating the solubility. The details of these spectral shifts will be published in the Ph.D. thesis of Henry J. Peterson. ^b An average value for tetraphenylphosphonium and tetrabutylammonium perchlorates (ref. 4). ^c I is 2'-(N,N-diethylamino)-1'-phenylethyl 4-nitrobenzoate perchlorate and II is bis-(1-naphthylmethyl)-ammonium perchlorate.

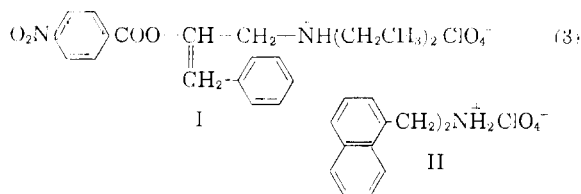
TABLE V

LOG (*c*_{R⁺}/*c*_{I,II}) FOR 4,4',4''-TRIMETHOXYTRIPHENYLMETHANOL AT 25°

% HClO ₄	log (<i>c</i> _{R⁺} / <i>c</i> _{OH})	pH + log (<i>c</i> _{R⁺} / <i>c</i> _{OH})	% HNO ₃	log (<i>c</i> _{R⁺} / <i>c</i> _{OH})	pH + log (<i>c</i> _{R⁺} / <i>c</i> _{OH})
0.5	-0.48	0.82	0.2	-0.70	0.80
.6	- .41	.81	.3	- .53	.79
.7	- .34	.82	.4	- .40	.80
.8	- .27		.5	- .30	.80
1.0	- .15		1.0	.06	
1.5	.08		1.5	.32	
2.0	.28		2.0	.53	
2.5	.44		2.5	.70	
3.0	.59		3.0	.84	
4.0	.85		3.5	.96	
5.0	1.07		4.0	1.08	
6.0	1.28		4.5	1.19	

Activity Coefficient Behavior of Cations in Aqueous Sulfuric Acids.—It was found^{3,4} that the activity coefficients of arylmethyl cations (*f*_{R⁺}) did not equal the activity coefficients of the protonated oxygen and nitrogen bases (*f*_{BH⁺}) used to evaluate the *H*₀ acidity function. In an effort to understand the basis of this difference, the solubility of three perchlorate salts were studied as a function of sulfuric acid concentration.⁴ This work has been extended to two more perchlorate salts.

The solubility of 2'-(N,N-diethylamino)-1'-phenylethyl 4-nitrobenzoate perchlorate (I) and bis-(1-naphthylmethyl)-ammonium perchlorate (II) in



0-60% sulfuric acid are recorded in Table IV. These two salts are protonated amines and thus should follow eq. 3 and the activity coefficient of the cations would equal *f*_{BH⁺}. It is also true that the activity coefficients of these two cations equal

the activity coefficients of the tetraphenylphosphonium ion and the tetrabutylammonium ion since d log *f* ± values for all four perchlorates are similar from 0-60% sulfuric acid (cf. Table IV).

The solubility of brucine and antipyrine perchlorates also were studied but the absorption spectra in the 220-320 mμ region were varying at 10% sulfuric acid indicating that further protonation was occurring.

The situation at present is as follows. There are three categories of cations. Within each category, the value of *f* in aqueous mineral acids is independent of the cation structure. The three categories are the protonated oxygen and nitrogen bases (BH⁺) used by Hammett to evaluate the *H*₀ acidity function, the arylmethyl cations (R⁺) used³ to evaluate *H*_R, and certain cation transition states which appear to contain a water molecule as a common feature.

The BH⁺ category contains such diverse structures as conjugate acids of the substituted anilines, the substituted acetophenones, aliphatic alcohols, aliphatic ketones, as well as tetraphenylphosphonium ion, tetrabutylammonium ion, ion I, ion II, etc.

The R⁺ category includes mono-, di- and triaryl-methyl cations as well as the NO⁺ ion. These examples seem to have only one feature in common and that is the presence of an open sextet of electrons. As a hypothesis, we propose that a weak orbital overlap occurs with the oxygen of the water (oxygen-bonding) and that this weak bonding is a different function of acidity from the usual cation-solvent interaction.

There is a less likely possibility that the R⁺ category is characterized by extensive delocalization of charge in the cation. This possibility is unattractive because of the smallness of the NO⁺ ion and because the classical coulombic interaction of a charged ion with a homogeneous dielectric (Born eq.) would indicate that delocalization or non-delocalization of charge in a given sphere would have small effect.

A third category is indicated by the fact that the kinetics of certain reactions follow eq. 4

$$d \log k = d \log c_{\text{H}_2\text{O}} \quad (4)$$

These reactions have transition states containing a water molecule and a +1 charge.⁷ It can be shown that the fit with eq. 4 is equivalent to having the activity coefficient of the transition state (f^*) equal to $f_{\text{H}_2\text{O}^+}$. As a provisional hypothesis, we propose that this category is characterized by cations in which the charge is centered on a H₂O⁺ moiety which is rather loosely held so that the interaction with solvent is much like that of H₃O⁺ itself and thus $f^* = f_{\text{H}_3\text{O}^+}$.

Fortunately, literature data indicate that the f behavior of most cations closely approach that of one of the three limiting categories.

Activity Coefficient Behavior of Neutral Molecules in Aqueous Sulfuric Acid.—Earlier it had been found⁴ that $d \log f$ behavior in water-sulfuric acid was similar for a wide variety of neutral molecules. To that list can now be added salicylic acid,

(7) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1, 935 (1957); R. W. Taft, Jr., N. C. Deno and P. A. Skell, *Ann. Rev. Phys. Chem.*, **9**, 306 (1958).

a difunctional compound with internal hydrogen bonding. The actual values of % sulfuric acid, solubility in (moles/l.) $\times 10^3$, and $d \log f$ were 0, 16.1, 0.014; 4.84, 11.6, 0.014; 9.82, 8.3, 0.018; 19.55, 6.3, 0.023, 29.59, 4.1, 0.23; 40.52, 2.0, 0.013; 50.83, 1.7, 0.0; 60.24, 4.0. The values of e increased with increasing concn. of sulfuric acid and the details of this change will appear in the Ph.D. thesis of Henry J. Peterson.

Experimental

The data used to calculate H_R appear in the Ph.D. Thesis of H. E. Berkheimer, Pennsylvania State Univ., 1959. The indicators that were used are listed in Table II. In all cases, values of $d \log (c_{\text{ROH}}/c_{\text{R}^+})/d c_{\text{H}_2\text{SO}_4}$ were independent of the indicator used.

The data on 4,4',4''-trimethoxytriphenylmethanol are presented in detail (Table V) to show that measurements were made in acids sufficiently dilute so that $H_R = pH$. Thus, H_R values in sulfuric, nitric and perchloric acids are all based on the same standard state assignment, namely, that $f = 1$ for all species in dilute aqueous solution.

UNIVERSITY PARK, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Reaction of Chlorohydrins and Hydroxide Ion in the Solvents H₂O and D₂O^{1,2}

BY PETER BALLINGER AND F. A. LONG

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The reaction between chlorohydrins and sodium hydroxide or tetramethylammonium hydroxide has been studied by combined kinetic and equilibrium measurements in the solvents H₂O and D₂O. The mechanism is known to involve specific hydroxide ion catalysis *via* a two-step mechanism and data are given for both the slow step and the prior equilibrium. Conductivity studies confirm the earlier conclusion of Twigg and co-workers that measurable amounts of the intermediate alkoxide ion are present. Some of the observed variation of second-order rate coefficients with concentration of reactants is due to this but there is also evidence that much of the variation is due to kinetic salt effects. The over-all rate coefficients in D₂O relative to H₂O are $k^D/k^H = 1.54$ for 2-chloroethanol and $k^D/k^H = 1.58$ for 2-chloropropanol. These values are in substantial agreement with the k^D/k^H ratio of 1.45 reported for the base-catalyzed decomposition of diacetone alcohol, a reaction which also involves specific hydroxide ion catalysis. Measurements of relative rates have been made for several mixtures of H₂O and D₂O and the dependence of rate on atom fraction of D agrees excellently with the revised Nelson-Butler equation, in contrast to the results for diacetone alcohol. The conductivity measurements lead to values of 4.9×10^{-16} and 1×10^{-15} for the acid ionization constant of 2-chloroethanol in the solvents H₂O and D₂O, respectively. From these values and the observed kinetic effect of D₂O, it is concluded that the unimolecular reaction of a 2-chloroalkoxide ion to give an epoxide goes about 15% faster in D₂O than in H₂O. Finally, the observed kinetic effects of D₂O are compared with the available data for other mechanisms of base catalysis. Relative rates in D₂O will probably distinguish between specific hydroxide ion catalysis and general base catalysis with a pre-equilibrium proton transfer but will probably not distinguish between specific catalysis and a one-step, slow proton transfer.

Introduction

Data on relative rates of reaction in D₂O and H₂O frequently have been used as a criterion of mechanism for acid catalysis and the behavior to be expected for various mechanisms is fairly well understood.^{3,4} Much less is known about base-catalyzed reactions. Some early work is available for the case of general base catalysis⁵⁻⁷ and Long and Watson recently have reported on a fairly complete study of the base-catalyzed keto-enol reaction.⁸

However, for the case of specific hydroxide ion catalysis there appears to have been only one investigation, that of Nelson and Butler on diacetone alcohol.⁹ Unfortunately these investigators found for mixtures of H₂O and D₂O that the relative rate was linear in the atom fraction of D and they interpreted this as evidence that the reaction did not involve a prior equilibrium, *i.e.*, did not go by specific hydroxide ion catalysis.¹⁰ In view of these facts it seemed useful to study the effect of D₂O as solvent for a reaction whose mechanism fairly surely involved specific base catalysis. The reaction chosen was the formation of an epoxide from a chlorohydrin. There were several reasons for this choice.

(1) Work supported by a grant from the Atomic Energy Commission.

(2) Presented in part at 133rd Meeting of the American Chemical Society, San Francisco, California, April 1958.

(3) R. P. Bell, "Acid-Base Catalysis," Oxford Press, 1941, Chap. V11.

(4) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(5) O. Reitz and J. Kopp, *Z. physik. Chem.*, **A184**, 429 (1939).

(6) O. Reitz, *ibid.*, **A176**, 363 (1936).

(7) S. K. March and V. K. LaMer, *This Journal*, **60**, 2588 (1938).

(8) F. A. Long and D. Watson, *J. Chem. Soc.*, 2019 (1958).

(9) W. E. Nelson and J. A. V. Butler, *ibid.*, 957 (1938).

(10) On the basis of the presently available evidence it seems fairly certain that the diacetone alcohol reaction does in fact proceed by specific hydroxide ion catalysis. An excellent summary of the situation is to be found in A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 283-296.