ψ_1 and κ_1 given in Table V are subject to the uncertainty in C_M as evaluated from equation (4).[4]

In view of the inadequacy of our results on the dependence of K and of C_M on temperature, the uncertain accuracy of the intrinsic viscosities from the various sources of the data above, and the failure to correct to zero rate of shear (which may be important for the higher intrinsic viscosities), the ψ_1's and κ_1's given in Table V should be considered as provisional values only. Estimated uncertainties in ψ_1 and κ_1 are about 50%, aside from the absolute error which arises from the value of C_M. Likewise, the Θ's given may be incorrect by as much as ±50°, except in the case of the poor solvent, cyclohexane, where it is known within ±1°.

Notwithstanding the uncertainties in the results, definite conclusions are clearly indicated by the data of Table V. Thus the ψ_1's for the solvents possessing cyclic structures agree with each other within the experimental error and are in approximate agreement with the value of 0.15 obtained for polyisobutylene in the same solvents.[7] On the other hand, ψ_1's for methyl ethyl ketone and dichloroethane are lower, as were the ψ_1's for polyisobutylene in acyclic solvents. The κ_1 values are in qualitative agreement with predictions based on the cohesive energy densities of these solvents,[18] provided that the cohesive energy density of polystyrene is assumed to be equal to that for methyl ethyl ketone.

The low values found for the parameters for methyl ethyl ketone are in qualitative agreement with the osmotic results of Schick, Doty and Zimm.[19] They concluded, however, that the heat of dilution, though very small, is negative while the entropy of dilution is about zero, whereas our measurements lead to the conclusion that the heat is zero and the entropy, though unusually small, is nevertheless positive. Thus, methyl ethyl ketone appears to be a thermally neutral solvent for polystyrene; the small negative temperature coefficient of the intrinsic viscosity in this solvent we attribute to the decrease in K with temperature. It is a "configurationally poor" solvent as evidenced by the low magnitude of the intrinsic viscosity, which leads to the conclusion that ψ_1 is very low. Also in support of the low value of ψ_1 (in conjunction with a negligibly small heat of dilution) is the low value (0.58) found[11] for the exponent a in the empirical relationship $[\eta] = K'\bar{M}_v^a$ for this polymer-solvent combination.

Recent results of Bawn, Freeman and Kamaliddin[20] on vapor pressures of more concentrated solutions of polystyrene in toluene and methyl ethyl ketone show that the contrasting behavior of these solvents persists at high concentrations. Although neither shows a perceptible heat of mixing (*i. e.*, the activity is very nearly independent of temperature), the activity of methyl ethyl ketone is substantially greater than is that of toluene at the same concentration.

In order to arrive at more precise values for the parameters occurring in equations (1) and (2), the change in K with temperature should be established with greater certainty and viscosities should be determined over wide temperature ranges in each solvent. These latter determinations preferably should be made on polystyrene fractions of high molecular weight where corrections to zero shear rate doubtless will be required. The reliability of the absolute magnitudes of ψ_1 and κ_1 obtained in this manner depends on the validity of C_M as given by theory. This may be ascertained from independent determinations of ψ_1 and κ_1 through thermodynamic measurements on very dilute solutions.

Acknowledgment.—The authors wish to acknowledge the assistance of Miss Helen Bedon and Mr. Allan Shultz in carrying out the experimental work of this paper.

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[18] M. Magat, *J. Chim. Phys.*, **46**, 23 (1949).

[19] M. J. Schick, P. Doty and B. H. Zimm, This Journal, **72**, 530 (1950).

[20] C. E. H. Bawn, R. F. J. Freeman and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 677 (1950).

ITHACA, NEW YORK RECEIVED OCTOBER 23, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Racemization of Alkyl Hydrogen Sulfates in Sulfuric Acid[1]

BY N. C. DENO AND MELVIN S. NEWMAN

The racemization of *d*-*s*-butyl and *d*-pinacolyl hydrogen sulfates has been measured in several concentrations of sulfuric acid. The experimental results are best explained by an ionization (carbonium ion) mechanism.

The sulfation of *d*-2-butanol has been shown to yield mainly *d*-*s*-butyl hydrogen sulfate, which undergoes racemization in the sulfuric acid medium.[2] In order to obtain more evidence on the mechanism of this racemization, we have studied the behavior of *d*-*s*-butyl hydrogen sulfate in 45, 55 and 65% sulfuric acid solutions.

Three types of kinetic experiments were conducted at 25°. (A) Lithium *d*-*s*-butyl sulfate was added to excess 45% sulfuric acid, and the optical rotation of the solution was measured at intervals. (B) Barium *d*-*s*-butyl sulfate was added to excess 45, 55 or 65% sulfuric acid and shaken well to effect the conversion to barium sulfate and *s*-butyl hydrogen sulfate. The acid sulfate was then isolated as the barium salt and the specific rotation and per cent. recovery were determined. (C) Lithium *d*-*s*-butyl sulfate was dissolved in 58% acid and recovered. The optical activity in the recovered salt was determined. It must be emphasized that owing to experimental difficulties all three

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[1] This work was made possible through the generous support of the Office of Naval Research.

[2] N. C. Deno and M. S. Newman, This Journal, **72**, 3852 (1950).

types of experiments were not precise, so that only qualitative kinetic results were obtained.

With experiments of type B and C, the rate of disappearance of optically active acid sulfate was determined by measuring the net loss of optical activity in the recovered barium or lithium *s*-butyl sulfate. In experiments of type A, this total disappearance was measured directly by the loss of optical activity. Although the disappearance of *d*-*s*-butyl hydrogen sulfate was the result of at least three reactions (racemization, hydrolysis and olefin formation), first order kinetics were anticipated for the total rate since the sulfuric acid was employed in large excess. This expectation was confirmed for experiments A and C. Those of type B showed a small departure which was due to difficulties in recovering the barium salts (*cf.* Experimental). The half-lives and rate constants for the total disappearance of *d*-*s*-butyl hydrogen sulfate are listed in Table I.

TABLE I

RACEMIZATION AND DISAPPEARANCE OF *d*-*s*-BUTYL AND *d*-PINACOLYL HYDROGEN SULFATES IN AQUEOUS SULFURIC ACIDS AT 25 ± 0.1°

Type A. Lithium *d*-*s*-butyl sulfate

Time, hr.	Optical rotation λ = 5200 Å.[a]
0	0.79
24	.63
98	.30
174	.15

$t_{1/2}$ = 66 hr. $k_1 = 2.9 \times 10^{-6}$ sec.$^{-1}$

Type B. Barium *d*-*s*-butyl sulfate

			Barium *s*-butyl sulfate	
H_2SO_4 concn., %	Time, hr.	Optical rotation	Recovery, %	% retention of[b] configuration
45	0	1.65		
	22	1.30	88	90
	112	.51	53	59
	209	.25	41	37
	$t_{1/2}$ = 66 hr.	$k_1 = 2.9 \times 10^{-6}$ sec.$^{-1}$		
55	0	1.65		
	6	.94	78	72
	12.5	.57	66	53
	18	.32	57	34
	24	.23	45	31
	$t_{1/2}$ = 6.5 hr.	$k_1 = 3.0 \times 10^{-5}$ sec.$^{-1}$		
65	0	1.65		
	1/6	1.18	87	82
	5/12	.84	78	62
	1	.45	65	42
	$t_{1/2}$ = 5/12 hr.	$k_1 = 4.6 \times 10^{-4}$ sec.$^{-1}$		

Type B. Barium *d*-pinacolyl sulfate

		Barium *d*-pinacolyl sulfate	
H_2SO_4 concn., %	Time, hr.	Recovery,[c] %	% retention of[b] configuration
45	68	25	89
55	6	27	73
65	1/4	26	64
65	1/2	7	35

Type C. Lithium *d*-*s*-butyl sulfate

H_2SO_4 concn., %	Time, hr.	Optical rotation
57.74	0	0.93
	1	.75
	2	.56
	3	.46

$t_{1/2}$ = 3.0 hr. $k_1 = 6.4 \times 10^{-5}$ sec.$^{-1}$

[a] Only a portion of the data is included. [b] The % retention of configuration is accurate to within 2 to 5%. [c] Data from blank experiments have shown that these values are too low.

The half-life of *d*-*s*-butyl hydrogen sulfate at different acidities was plotted against Hammett's H_0 function[3] (Table II). The slope of unity indicates that the hydrogen ion activity enters into the rate law as the first power. Since the acid sulfate is presumably completely ionized in 45–65% sulfuric acid, the entrance of the hydrogen ion activity as the first power can be interpreted to mean that *s*-butyl hydrogen sulfate enters into reaction rather than its anion or conjugate acid. Since the racemization reaction accounts for a large share of the disappearance, the above interpretation will hold for the racemization mechanism.

TABLE II

DEPENDENCE OF RATE OF DISAPPEARANCE OF *d*-*s*-BUTYL HYDROGEN SULFATE ON THE ACIDITY FUNCTION H_0

H_2SO_4 concn., %	H_0	$k_1 \times 10^6$	6 + log k_1	$\frac{\log k_1}{H_0}$
45	−2.09	2.9	0.46 >	
55	−3.24	30	1.48 >	0.89
57.74	−3.55	64	1.81 >	1.07
65	−4.33	460	2.66	1.09
			Over-all value	1.02

Under the conditions studied, the rate of sulfation is very slow[2] so that the racemization of the acid sulfate demonstrated by experiments of type B cannot be attributed to hydrolysis and resulfation. Three mechanisms were considered for the racemization: successive inversions by the bisulfate anion (S_N2); ionization into the alkyl carbonium ion plus bisulfate ion followed by reassociation (S_N1); and formation of 2-butene followed by reconversion to the acid sulfate. The possibility of 2-butene being an intermediate is unlikely in view of the failure of 2-butene to react rapidly with 65% sulfuric acid.[4]

In order to obtain some indication as to which of the two remaining mechanisms, S_N1 or S_N2, was operating, barium *d*-pinacolyl sulfate was studied in 45, 55 and 65% acids with experiments of type B. The pinacolyl derivative was chosen because of its resistance to S_N2 type reactions.[5] Thus, if *d*-pinacolyl hydrogen sulfate racemized at a rate comparable to that of *d*-*s*-butyl hydrogen sulfate, it would indicate that the S_N1 mechanism operated in the racemization of the pinacolyl derivative, and probably also with the *s*-butyl analog. Although the data obtained were erratic, in all cases racemization occurred at rates which were of the same order of magnitude as those with *d*-*s*-butyl hydrogen sulfate (the four most consistent runs are recorded in

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[3] L. P. Hammett, *et al.*, THIS JOURNAL, **54**, 2721 (1932); *ibid.*, **56**, 827 (1934).

[4] A. T. King, *J. Chem. Soc.*, 1404 (1919); R. M. Taveau, U. S. Patent 1,810,192; *C. A.*, **25**, 4557 (1931); A. Dobrjanski, *Neft. Khoz.*, **9**, 565 (1925); *Chem. Zentr.*, **97**, I, 2220 (1926); H. S. Davis and R. Schuler, THIS JOURNAL, **52**, 721 (1930).

[5] E. D. Hughes, *Trans. Faraday Soc.*, **37**, 620 (1941); F. C. Whitmore, E. L. Wittle and A. H. Popkin, THIS JOURNAL, **61**, 1586 (1939).

Table I). This result can be most easily seen by comparing the per cent. retention of configuration for the two barium alkyl sulfates at comparable times in the same strength acid (Table I). For example after six hours in 55% acid, the recovered barium *s*-butyl sulfate had 72% retention of configuration while the pinacolyl derivative had 73% retention. However, the recovery of pinacolyl hydrogen sulfate was less, 27% compared with 78% for the butyl derivative, indicating a more rapid disappearance rate. The possibility of racemization taking place through the olefin, *t*-butylethylene, was eliminated by showing that when this olefin was stirred with 65% sulfuric acid at 25° for twenty minutes, no barium alkyl sulfate could be isolated.

Thus, the most probable mechanism for the racemization involves ionization to carbonium and bisulfate ions (S_N1) followed by reassociation to alkyl hydrogen sulfate.

$$d\text{-ROSO}_3\text{H} \longrightarrow \text{R}^+ + \text{HSO}_4^- \rightleftarrows dl\text{-ROSO}_3\text{H}$$

Although reactions involving the methyl-*t*-butyl carbonium ion usually result in rearrangement, in this case, a considerable portion of this carbonium ion evidently recombines with bisulfate ion without rearrangement. Recently, it has been shown that pinacolyl chloride results from the addition of hydrogen chloride to *t*-butylethylene.[6]

TABLE III

LATTICE SPACINGS FROM X-RAY DIFFRACTION PHOTOGRAPHS OF BARIUM *dl*-PINACOLYL SULFATE DIHYDRATE[a]

Qual. intensity[b]		Lattice spacing: Starting material	Lattice spacing: Material recovered from 30-min. contact with 65% H_2SO_4
Very strong (diffuse)	band	5.070	5.068
Very strong (diffuse)		4.703	4.745
Strong		4.122	4.135
Weak		3.867	3.860
Very strong		3.472	3.477
Medium		3.130	3.131
Medium		2.940	2.940
Medium		2.741	2.745
Very weak		2.613	2.619
Weak		2.497	2.500
Weak	band	2.316	2.316
Medium		2.151	2.153
Medium	band	2.111	2.110
Weak		2.001	2.002
Medium		1.923	1.927
Medium (distinct)		1.771	1.779
Weak		1.549	1.548
Weak		1.499	1.499
Weak		1.443	1.444
Weak		1.329	1.326
(The remaining lines were very weak)		1.224	1.222
		1.1390	
		1.0787	
		1.0519	
		0.8890	
		.8501	
		.8136	
		.7955	
		.7848	

[a] The photographs were taken on a Straumanis type camera with radius of 5.73 cm. The target material was Cu, the wave length used was the average of K_{α_1} and K_{α_2}, λ = 1.9373 Å. The *d*-spacings were obtained from the tables of G. Switzer, J. M. Axelrod, M. L. Lindberg and E. S. Larsen (circular 29, U. S. Dept. of Interior, Geological Survey, Aug., 1948). [b] The qualitative intensities of both photographs were the same.

In the work with *d*-pinacolyl hydrogen sulfate, it was necessary to show that the recovered barium salt of the alkyl acid sulfate was barium pinacolyl sulfate. Accordingly, barium *dl*-pinacolyl sulfate was equilibrated with 65% sulfuric acid at 25° and recovered after ten, twenty and thirty minutes. X-Ray diffraction photographs were taken of the recovered barium salt. All photographs had identical spacings and qualitative intensities of which those from the starting material and the thirty-minute run are given as representative (Table III). The diffraction data showed that even after thirty minutes (when *d*-pinacolyl hydrogen sulfate would have been over half racemized) the reisolated barium salt was still principally barium *dl*-pinacolyl sulfate.

Incidental to this investigation, it was found that pinacolyl alcohol in dilute aqueous solution can be converted into pinacolone with bromine water. Subsequent conversion of the pinacolone into its 2,4-dinitrophenylhydrazone in 75% over-all yield from the alcohol provides a means of establishing the presence of pinacolyl alcohol in dilute aqueous solution.

Experimental

The following descriptions are typical of the experiments of type A, B and C.

Type A.—A solution of 0.64 g. of lithium *d*-*s*-butyl sulfate in 25 cc. of 45% sulfuric acid was filtered through fine filter paper and thermostated at 25 ± 0.1°. The optical rotation was periodically observed.

Type B.—A mixture of 2.09 g. of barium *d*-*s*-butyl sulfate trihydrate and 10 cc. of aqueous sulfuric acid at 25° was vigorously shaken and thermostated at 25 ± 0.1°. After the prescribed time, the mixture was diluted with 100 cc. of water and an excess of barium carbonate was added. The barium sulfate was removed by filtration with the aid of diatomaceous earth (Super-cel), previously washed with distilled water. The filtrate was evaporated to dryness in a current of air. The residue was dissolved in 5 cc. of distilled water, and filtered through fine filter paper. The filtrate was brought to 15 cc. by washings. The optical rotation of this solution was measured. The concentration of barium alkyl sulfate was determined on a 5-cc. aliquot by evaporation and ignition to barium sulfate.[7] In this manner, we could measure both per cent. recovery of barium alkyl sulfate and the per cent. retention of configuration (assuming that all barium was present in sample as expected salt). The experiments with barium *d*-pinacolyl sulfate were identical except that 2.00 g. of the barium salt was shaken with 20 cc. of acid.

Although precautions were taken to make all transfers quantitative, blank experiments showed that recovery was as low as 80% due to solute held by the bulky barium sulfate precipitate. This is the probable reason that these experiments showed a departure from first order kinetics.

Type C.—A solution of 0.5 g. of lithium *d*-*s*-butyl sulfate in 10 cc. of 57.74% sulfuric acid was thermostated for the requisite time and then diluted with water. The remainder of these experiments were carried out in a manner analogous to those of type B, except that the aliquots were ignited to lithium sulfate rather than barium sulfate.

***d*-2-Butanol.**—The ratio of $[\alpha]^{25}_{5160}$ to $[\alpha]^{25}_{5893}$ was determined. From this ratio $[\alpha]^{25}_{5160}$ +18.67° was calculated assuming $[\alpha]^{25}_{5893}$ +13.87° for completely resolved *d*-2-butanol.[8]

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(6) G. G. Ecke, N. C. Cook and F. C. Whitmore, THIS JOURNAL, **72**, 1511 (1950).

(7) It was necessary to reignite the barium sulfate after moistening with sulfuric acid in order to convert any barium sulfide to the sulfate.

(8) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 49 (1911).

d-**Pinacolyl Alcohol.**—Two crystallizations of brucine pinacolyl phthalate[9] from acetone gave pure brucine *d*-pinacolyl phthalate (m.p. 148–151°). The success of the resolution lay in adding a pure seed crystal to a concentrated solution (about 40%) of the brucine salt in acetone at 25°. This non-equilibrium crystallization is aided by the fact that the brucine salt of the *l*-isomer crystallizes much more slowly than that of the *d*-isomer. After two hours about 80% of the salt of the *d*-isomer had precipitated in nearly pure form. The brucine salt from two such crystallizations gave *d*-pinacolyl alcohol, $[\alpha]^{25}_{5160}$ +7.97° and $[\alpha]^{25}_{5160}$ +9.44° (using 0.81 for the density of *d*-pinacolyl alcohol). This value is somewhat higher than the $[\alpha]^{25}_{5893}$ +7.71° previously reported.[9]

The *l*-pinacolyl alcohol recovered from the filtrate had $[\alpha]^{25}_{5893}$ −4.41°.

Barium *d*-*s*-Butyl Sulfate.—This sulfate was prepared as described.[2] The barium *d*-*s*-butyl sulfate was analyzed after drying at 25° and 1 mm. to constant weight (several hours required).

Anal. Calcd. for $(C_4H_9OSO_3)_2Ba\cdot 3H_2O$: Ba, 27.6. Found: Ba, 27.7.

Barium *d*- and *dl*-Pinacolyl Sulfates.—A mixture of 25 g. (0.157 mole) of pyridine–sulfur trioxide and 20 cc. (16 g., 0.157 mole) of *d*-pinacolyl alcohol ($[\alpha]^{25}_{5893}$ +7.97°) was vigorously shaken in a stoppered flask immediately after mixing. The mixture warmed up to about 70° and nearly liquefied. The vigorous shaking was continued until the contents of the flask solidified (about five minutes). After standing several days, the solid was dissolved in 200 cc. of distilled water and 30 g. of finely ground barium hydroxide octahydrate was slowly added with good stirring. After several hours an additional 10 g. of barium hydroxide octahydrate was added. After 18 hours, excess carbon dioxide was passed in and the mixture decolorized with charcoal (Darco G-60) and filtered with the aid of Super-cel (previously washed with distilled water). The colorless solution was evaporated to dryness in a current of air. The white crystalline residue was dried at 25° and 1 mm. to constant weight (six hours). The barium *d*-pinacolyl sulfate trihydrate weighed 36 g. (83%).

Anal. Calcd. for $(C_6H_{13}OSO_3)_2Ba\cdot 3H_2O$: Ba, 24.8. Found: Ba, 24.8, 24.7, 24.7.

dl-Pinacolyl sulfate was prepared in a manner identical to barium *d*-pinacolyl sulfate. The barium salts of the *d*- and *dl*-sulfates were hydrated to different degrees when dried under the same conditions.

Anal. Calcd. for $(C_6H_{13}OSO_3)_2Ba\cdot 2H_2O$: Ba, 25.7. Found: Ba, 25.6, 25.6, 25.7.

The products varied in stability. Some samples, by the odor of olefins and failure to dissolve completely in water, showed evidence of decomposition within several days.

The following specific rotations were calculated on the basis of *anhydrous* barium *d*-pinacolyl sulfate: $[\alpha]^{25}_{5893}$ +6.39°, $[\alpha]^{25}_{5461}$ +7.63° and $[\alpha]^{25}_{5160}$ +8.68°. It was assumed that no racemization took place in converting the *d*-pinacolyl alcohol ($[\alpha]^{25}_{5893}$ +7.97°) to the sulfate.[10]

Bromine Oxidation of Pinacolyl Alcohol.—To a solution of 0.406 g. of pinacolyl alcohol in 100 cc. of ice-water was added a solution of 0.65 g. of bromine dissolved in 100 cc. of ice water. The solution was allowed to warm up to 25° over one hour and then stand three hours at 25°. An excess of 2,4-dinitrophenylhydrazine dissolved in dilute sulfuric acid was added and the precipitate collected after one hour. The yield was 0.85 g. (75%) m.p. 119–124°. One recrystallization from methanol raised the m.p. to 126.1–126.5° (undepressed when mixed with authentic dinitrophenylhydrazone of pinacolone) with little loss. This was the best way we found for establishing the presence of pinacolyl alcohol in dilute aqueous solution.

The barium pinacolyl sulfate was resistant to the action of bromine water at 25° as well as to alkaline permanganate and dichromate in dilute sulfuric acid.

α-Naphthylurethan of Pinacolyl Alcohol.—The α-naphthylurethan, m.p. 126.8–127.6°, was obtained in 72% yield by heating the components for ten minutes at 100° and crystallizing from 60–70° alkanes.

Anal.[11] Calcd. for $C_{17}H_{21}O_2N$: C, 75.3; H, 7.8. Found: C, 75.5; H, 8.0.

COLUMBUS 10, OHIO RECEIVED AUGUST 25, 1950

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[9] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, 1120 (1914).

[10] *Cf.* R. L. Burwell, THIS JOURNAL, **71**, 1769 (1949); R. L. Burwell and H. E. Holmquist, *ibid.*, **70**, 878 (1948).

[11] Clark Microanalytical Lab., Urbana, Ill.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY, SCHOOL OF MEDICINE]

Apparent Ionization Exponents of 4-Hydroxyquinoline, 4-Methoxyquinoline and N-Methyl-4-quinolone; Evaluation of Lactam–Lactim Tautomerism[1]

BY GABRIEL F. TUCKER, JR.,[2] AND J. LOGAN IRVIN[3]

Apparent ionization exponents for 4-hydroxyquinoline (4-quinolone), 4-methoxyquinoline and N-methyl-4-quinolone have been determined by combined spectrophotometry and potentiometry. These data are applied in the calculation of the microscopic ionization constants and of the equilibrium constant for the lactam–lactim tautomerism of 4-hydroxyquinoline. This compound in aqueous solution at *p*H 7 exists predominantly in the lactam form (4-quinolone), and some evidence is presented which suggests that this form also predominates in solvents of low dielectric constant.

Ewing and Steck[4] have presented absorption spectra for 4-hydroxyquinoline in 0.01 *N* hydrochloric acid, 0.01 *N* sodium hydroxide, aqueous buffer at *p*H 7, and 95% ethanol. In comparing the properties of this compound with those of other hydroxyquinolines, these authors suggested that their data and other observations in the literature were consistent with the existence of a 4-quinolinol: 4-quinolone tautomerism, but no quantitative data were presented for the evaluation of the tautomeric equilibrium.

An examination of the spectrophotometric data of Ewing and Steck and a review of the older literature suggested that quantitative data for the ionization exponents of 4-hydroxyquinoline would be particularly useful in evaluating the contributions of tautomerism and resonance to the properties of this compound. In the present paper the ionization exponents of 4-hydroxyquinoline, N-methyl-4-quinolone and 4-methoxyquinoline are reported from spectrophotometric measurements, and from these the status of the 4-hydroxyquinoline:4-quinolone tautomerism is deduced. These studies are of biochemical interest inasmuch as certain derivatives of 4-hydroxyquinoline are products of the metabolism of the amino acid tryptophan. Also any investigation of lactam–lactim tautomerism has biochemical implication

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[2] Henry Strong Denison Scholar for 1949–1950; 1950–1951.

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[4] G. W. Ewing and E. A. Steck, THIS JOURNAL, **68**, 2181 (1946); **71**, 238 (1949).