Summary

1. In acid solution the oxidation of cystine by iodine to cysteic acid is practically quantitative. The rate-determining step in the oxidation is the reaction between a molecule of cystine and a molecule of iodine (or substances whose concentrations are proportional to their concentrations).

2. Over a wide range of hydrogen-ion concentration (*P*H 1–5) the velocity constant remains almost constant.

3. In the range 0.01–0.06 *M* iodide, the velocity constant increases with increase in iodide concentration. This effect, together with the absence of pronounced effect of the hydrogen ion, makes it appear probable that the triiodide ion is the reactant.

4. In those solutions where the product of hydrogen-ion and iodide concentrations exceeds 0.003, the velocity constant increases with time during an experiment. It is not known whether this is due to the instability of the hydriodic acid, or to some other complication.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

The Ionization Constants of Certain Sulfur Derivatives of Phenylacetic Acid at 0 and 25°[1]

BY H. D. CROCKFORD AND T. B. DOUGLAS

The purpose of the work given in this paper was to study the effect produced on the ionization constant by successively attaching, in an organic acid, oxygen atoms to an atom capable of assuming higher valences. To this end the ionization constants of phenylthioglycolic acid, phenylsulfoacetic acid and phenylsulfoxyacetic acid were determined conductimetrically at 0 and 25°. From the data have been calculated the heat of ionization and the free energy of ionization of the compounds.

Behaghel[2] determined the ionization constants of the first two acids at 25° using the simple dilution law formula. We have employed for our calculations the Onsager equation used by MacInnes and Shedlovsky[3]

$$\log k = \log \frac{\alpha^2 m}{1 - \alpha} - A\sqrt{C_i}$$

in which $\alpha = \Lambda/\Lambda_e$ and Λ_e is the equivalent conductance of a mole of completely dissociated electrolyte at the concentration *m*. C_i is the ion concentration. The constant *A* has a value of 0.98 at 0 and 1.01 at 25°. Our results for the values determined by Behaghel differ from his in a manner that cannot be accounted for on the basis of the two different equations used in the calculations. We have therefore included these two data in this paper.

Experimental

Phenylthioglycolic Acid, $C_6H_5SCH_2COOH$.—This acid was prepared by the action of sodium thiophenylate on ethyl chloroacetate. After repeated crystallizations the acid was dried over phosphorus pentoxide for one and a half months, m. p. 63.0–63.5°.

Phenylsulfoxyacetic Acid, $C_6H_5SOCH_2COOH$.—Phenylthioglycolic acid was oxidized with 30% hydrogen peroxide and the product recrystallized from a mixture of ethyl acetate and benzene (1:3 by volume), m. p. 112.5–113°.

Phenylsulfonylacetic Acid, $C_6H_5SO_2CH_2COOH$.—The sodium salt of phenylthioglycolic acid was oxidized in alkaline solution with potassium permanganate at 0°. The acidified filtrate was extracted with ether and the acid recrystallized four times from benzene, m. p. 110.0–110.5°.

A Type 293-A General Radio Universal Bridge with a 1000-cycle oscillator was employed for the measurements. All measuring apparatus was properly calibrated. The conductance cell was frequently checked with potassium chloride solution. Temperatures were accurate to 0.02°. Due to the nature of the compounds studied the concentrations of the solutions involve an uncertainty of 0.1%.

Calculations and Results

Values for Λ_e as used in the Onsager equation were obtained from our values for the sodium salts of the acids used and the values of Λ given in the "International Critical Tables" for sodium chloride and hydrochloric acid. The usual method of approximation was employed. All experimental values were the average of at least four sets of conductivity data which showed a variation of less than 0.2%. Table I gives the values of the dissociation constants for the various concentrations of the three acids. Table II gives the average values of the constants, the free

[1] From the thesis of Mr. Douglas presented to the Graduate Faculty in partial fulfilment of the requirements for the degree of Master of Science.

[2] Behaghel, *J. prakt. Chem.*, **114**, 287 (1926).

[3] MacInnes and Shedlovsky, THIS JOURNAL, **54**, 1429 (1932); Shedlovsky, *ibid.*, **54**, 1411 (1932).

energy of ionization and the heats of ionization. The latter are calculated on the very doubtful assumption that this magnitude remains constant between 0 and 25°.

TABLE I

Molality	—S— acid K (0°)	 K (25°)	—SO— acid K (0°)	 K (25°)	—SO_2 acid— K (0°)	 K (25°)
0.00201	0.000297	0.000269	0.00261	0.00220	0.00444	0.00357
.00401	.000306	.000279	.00263	.00221	.00449	.00365
.0100	.000301	.000277	.00254	.00219	.00451	.00365
.0201	.000302	.000278	.00255	.00219	.00440	.00364

TABLE II

Acid	K (0°)	K (25°)	$\Delta F°$ (0°), cal.	ΔF (25°), cal.	ΔH, cal.
—S—	0.000302	0.000276	4400	4860	− 600
—SO—	.00258	.00220	3240	3630	−1000
—SO_2—	.00446	.00363	2940	3330	−1300

Table III gives the values for Λ_e for the acids at 25° for certain concentrations. This table is included to show the comparative values for the ion mobilities in the acids. It is to be noted that the —SO— ion has a decidedly lower mobility than either of the other ions. This may perhaps be due to hydration of the —SO— group.

TABLE III

Molality	—S—	—SO—	—SO_2—
0.001	375.8	373.2	375.1
.0025	372.3	370.2	372.2
.004	371.0	368.4	370.7

For the —S— and —SO— acids at 25° Behaghel obtained ionization constants of 0.0002971 and 0.002148. These are averages for three concentrations. His individual values differ more widely than ours.

It is seen that the addition of the oxygen atom to the —S— acid decreases the free energy of ionization far more than the addition of the oxygen atom to the —SO— acid. The heat of ionization is increased with the addition of oxygen.

Summary

1. The ionization constants in aqueous solutions at 0 and 25° of phenylthioglycolic acid, phenylsulfoacetic acid and phenylsulfonylacetic acid have been determined conductimetrically at 0 and 25°.
2. From the values obtained have been calculated the free energies and heats of ionization.

CHAPEL HILL, N. C.

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The Photochlorination and the Chlorine-Sensitized Photo-oxidation of Gaseous Tetrachloroethylene

BY ROSCOE G. DICKINSON AND JAMES L. CARRICO

In the absence of oxygen, the illumination of a carbon tetrachloride solution of chlorine and tetrachloroethylene with blue light has been found to bring about chlorination which proceeds[1] as a chain reaction with a large quantum yield and at a rate proportional to the square root of the intensity of illumination. In the presence of oxygen, the chlorination is strongly inhibited and instead there occurs a chlorine-sensitized oxidation to trichloroacetyl chloride and phosgene; this reaction proceeds in solution with a comparatively small quantum yield and at a rate proportional to the first power of the light intensity.[2] It was found possible to account for the kinetics of the chlorination by either of two simple and plausible reaction schemes, one involving C_2Cl_5 and the other Cl_3.

In extension of this work we have found these reactions to occur in the gas phase and have made some preliminary observations on their kinetics. In order not to be too seriously involved with purely thermal reaction, the temperatures have been kept at 40° or below. The oxidation products are about as volatile as the reactants; but the solid chlorination product, hexachloroethane, has at 40° a vapor pressure of only 1 mm. Its precipitation on the vessel walls during an illumination might be expected to render satisfactory radiation measurements impossible. However, under the conditions of our experiments, the crystals formed were comparatively few and large; moreover, a very slight temperature difference prevented this formation on the part of the vessel through which illumination occurred. It was thus possible to carry on chlorination experiments without complication from this source.

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(1) J. A. Leermakers and R. G. Dickinson, THIS JOURNAL, **54**, 4648 (1932).

(2) R. G. Dickinson and J. A. Leermakers, *ibid.*, **54**, 3852 (1932).