[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA]

The Primary Dissociation Constant of Diphenylthiocarbazone

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Buch and Koroleff[1] and Irving and co-workers[2] have shown that diphenylthiocarbazone (dithizone) behaves as a monobasic acid, at least in aqueous solutions of moderate alkalinity (up to pH 12). Writing dithizone as HDz (since we are concerned here only with the ionization of the first hydrogen), the following equilibrium exists in water solutions:

$$\mathrm{HDz} \rightleftarrows \mathrm{H}^+ + \mathrm{Dz}^-$$

$$[\mathrm{H}^+][\mathrm{Dz}^-]_w/[\mathrm{HDz}]_w = K \qquad (1)$$

A value of approximately 3 × 10^{-6} for the ionization constant K has been reported by Irving and collaborators.[2] They applied two different methods. In one, the constant was obtained for a mixture composed of 20% water, 30% chloroform, and 50% alcohol by spectrophotometric measurement of the ratio of ionized and un-ionized dithizone at various acidities. The ionization constants of methyl red and brom thymol blue in the same mixed solvent were obtained spectrophotometrically, and from these and the known constants of the indicators in water a value 5.6 × 10^{-6} was interpolated for the ionization constant of dithizone in water. The second method involved determination of the partition coefficient of undissociated dithizone between carbon tetrachloride or chlorobenzene and 0.01 M hydrochloric acid. This ratio combined with other data (see below) afforded a value for the dissociation constant (average 2 × 10^{-6}). The results of the work reported here indicate that the value of the constant is slightly greater than 10^{-5}.

A possible method of obtaining K is to determine the concentration of undissociated dithizone in a saturated acidic aqueous solution in which the concentration of dithizonate ion is negligible. Dividing this value into the solubility product constant of dithizone in water, which can be determined from the solubility of dithizone in a basic medium, gives K directly. The present method is almost equivalent to this. For experimental reasons it is preferable to work with an organic solvent (carbon tetrachloride) almost saturated with dithizone, instead of with excess solid dithizone without organic solvent. In the latter case it is difficult to reach equilibrium, even from the supersaturated side. The method actually applied thus involves the determination of the partition coefficient of undissociated dithizone for carbon tetrachloride–water, and is similar to the second method employed by Irving and co-workers, who, however, used relatively dilute solutions of dithizone in carbon tetrachloride and chlorobenzene.

The partition coefficient of un-ionized dithizone between an immiscible organic solvent and an aqueous solution will be defined as

$$[\mathrm{HDz}]_o/[\mathrm{HDz}]_w = p \qquad (2)$$

The distribution of dithizone, in ionized and un-ionized forms, between the two solvents at a specified hydrogen ion concentration is given by the extraction coefficient E

$$E = \frac{[\mathrm{HDz}]_o}{[\mathrm{HDz}]_w + [\mathrm{Dz}^-]_w} = \frac{[\mathrm{H}^+]p}{[\mathrm{H}^+] + K} \text{ (from 1 and 2)} \qquad (3)$$

When $[\mathrm{H}^+]$ is small compared to K, the preceding expression becomes

$$E = [\mathrm{HDz}]_o/[\mathrm{Dz}^-]_p = [\mathrm{H}^+]p/K \qquad (4)$$

A number of workers have reported values for $E_{\mathrm{CHCl_3}}$ and $E_{\mathrm{CCl_4}}$ in basic medium, in which (4) holds, from which K/p can be calculated. Fairly good agreement has been obtained (Table I). It then remains to determine p to obtain the value of K. Apparently only one value of p for carbon tetrachloride–water has been reported, namely, 1.6 × 10^3 by Irving and collaborators. The present work leads to the value 1.1 × 10^4 for this constant.

Materials

Dithizone (Eastman Kodak Co.) was recrystallized by evaporating a filtered chloroform solution in a stream of air at about 40° until one-third to one-half of the dithizone had recrystallized out. The crystals were collected in a sintered glass filter crucible and washed with a few portions of carbon tetrachloride, in which dithizone is much less soluble than in chloroform. Extractive titration of a solution of the purified dithizone against silver nitrate in dilute nitric acid showed the air-dried product to contain 98% of the active reagent. The unpurified material contained 94% dithizone.

The carbon tetrachloride was reagent grade, and the water was redistilled.

Experimental

In one series of experiments, the distribution coefficient of undissociated dithizone between carbon tetrachloride and water was obtained by vigorously shaking 10 to 25 ml. of approximately 0.05% (weight/volume) carbon tetrachloride solution of dithizone with 125 to 200 ml. of 0.1 or 0.01 N hydrochloric acid. After various periods of shaking the aqueous solution was filtered through paper which had been well washed with the same solution. Dithizone was determined in the filtrate by shaking 25 or 50 ml. of the solution with 5 ml. of carbon tetrachloride, and measuring the transmittancy of the latter with the aid of a 610 mμ filter. At the same time the concentration of dithizone in the carbon tetrachloride phase was determined by withdrawing a small portion, diluting to 125 times its volume with pure carbon tetrachloride, and measuring the transmittancy of the solution. A calibration curve was established, which showed that the extinction was directly proportional to the dithizone concentration in the carbon tetrachloride.

The carbon tetrachloride extract of the aqueous solution gave an extinction of about 0.05 in a 1-cm. cell when 50 ml. of solution was taken, so that the photometric error was of secondary importance.

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[1] K. Buch and F. Koroleff, *Finska Kemistsamfundets Medd.*, **54**, 98 (1945).

[2] H. Irving, S. J. H. Cooke, S. C. Woodger and R. J. P. Williams, *J. Chem. Soc.*, 1847 (1949).

In another series of experiments to determine the partition coefficient of undissociated dithizone, extraction equilibrium was approached from the supersaturated side in the aqueous phase. This was done by adding a drop of concentrated ammonium hydroxide to 200 ml. of water and shaking the latter for one minute with 25 ml. of an almost saturated (0.05%) dithizone solution in carbon tetrachloride. The aqueous solution became yellow from dithizone present as dithizonate ion. Hydrochloric acid was then added to produced a final concentration of 0.1 or 0.01 *N*. Dithizone was thus precipitated in finely divided form. This mixture was then shaken in the presence of the carbon tetrachloride solution of dithizone, and the aqueous solution was analyzed for dithizone after filtration. In this series, as in the preceding one, a mechanical shaker (240 cycles per minute) was used.

The *p*H of the aqueous solutions was determined after shaking by means of a glass electrode, with Bureau of Standards potassium biphthalate as reference substance.

TABLE I

VALUES OF K/p FOR DITHIZONE IN CARBON TETRACHLORIDE–WATER

Reference	$K/p = [H^+][Dz^-]/[HDz]_{CCl_4}$
Clifford and Wichmann[a]	1.9×10^{-9} (31°)
Buch and Koroleff[b]	1.6×10^{-9}
Irving, *et al.*[c]	1.4×10^{-9} (*ca.* 20°)
This work[d]	1.4×10^{-9} (25°)

[a] *J. Assoc. Official Agr. Chem.*, 19, 130 (1936). A single determination at *p*H 10. [b] Average of 7 determinations, *p*H 7–9. [c] Average of 9 values in the *p*H range 7.85–10. [d] Determined at *p*H 8 and 9.

Irving and co-workers particularly have obtained a series of closely agreeing values for K/p in the *p*H range 8 to 10. Since the values reported have been obtained in alkaline medium and with dilute solutions of dithizone in carbon tetrachloride, it was thought desirable to attempt a determination of this constant in acidic medium and with a strong, almost saturated solution of dithizone in carbon tetrachloride, *i. e.*, under conditions comparable to those under which the partition coefficient p was determined. For this purpose, the carbon tetrachloride solution of dithizone was shaken mechanically with Clark and Lubs buffers of *p*H 5 and 6, and dithizone was determined in both phases after various times of shaking. It was found that in most runs the concentration of dithizone in the aqueous phase was still increasing after 30 or even 60 minutes. An average value of 1.9×10^{-9} for K/p was obtained in these experiments (account was taken of the presence of un-ionized dithizone), but this value cannot be regarded as very satisfactory because of the uncertainty in attainment of equilibrium and the possibility of side reactions (instability of dithizone) when the shaking time becomes long. At any rate this approximate value shows that K/p remains substantially constant over the *p*H range 5 to 10.

Irving's value of K/p was verified by a number of experiments at *p*H 8 and 9 (Clark and Lubs buffers), in which range equilibrium is attained by shaking for a few minutes only. Dithizone was determined in both phases. The original concentration of dithizone in the carbon tetrachloride was 0.01%. The average value obtained was 1.4×10^{-9}, or the same within experimental limits of error, as Irving's.

Discussion

The values obtained for $[HDz]_{CCl_4}/[HDz]_{H_2O}$ are listed in Table II. The average value for the series in which equilibrium was approached from undersaturation in the aqueous phase is 1.0×10^4. **The same value is obtained for 0.01 as for 0.1** *N* hydrochloric acid. Equilibrium is attained slowly. Approximately one hour appears to be needed for reaching equilibrium under the conditions of the present work.

TABLE II

PARTITION COEFFICIENT OF UNDISSOCIATED DITHIZONE BETWEEN CARBON TETRACHLORIDE AND WATER

Concentration of HCl, *M*	Temp., °C.	$p = [HDz]_{CCl_4}/[HDz]_{H_2O} \times 10^{-4}$ Time of shaking, hr. 1/4	1/2	1	1 1/2
0.1	25–26	1.1			
.1	27		1.2	1.0	1.0
.1	27		1.2		1.0[c]
.1[a]	24–26		1.2	1.15	
.1[a]	25–26	1.3[b]	1.2		
.01	25	1.4	1.3	1.0–	
.01	27	1.5		1.0	1.0
.01[a]	26	1.2[b]		1.15	

[a] Equilibrium approached from initial supersaturation in aqueous phase instead of undersaturation as in others. [b] Shaken two minutes. [c] Allowed to stand overnight and shaken three hours more.

Equilibrium is attained much more rapidly when the aqueous phase is supersaturated with dithizone before shaking with carbon tetrachloride. A few minutes appear to be sufficient. (This is in accord with predictions based on the value of the partition coefficient; the rate constant for the passage of dithizone molecules from the water phase into carbon tetrachloride should be p times that in the opposite direction.) An average value of approximately 1.2×10^4 is obtained for the partition coefficient when equilibrium is approached from supersaturation in the aqueous phase. Perhaps greater weight should be given to this average than the one from the first series. However, since the difference between the two sets is small, 1.1×10^4 will be taken as the value of p.

The calculated value of the dissociation constant of dithizone then is $1.4 \times 10^{-9} \times 1.1 \times 10^4 = 1.5 \times 10^{-5}$. The constant has not been determined with sufficient accuracy to warrant the use of activity coefficients. The value may be taken as holding in solutions of about 0.1 ionic strength.

The approximate values of some other constants can be derived from the above figures. Taking the solubility of dithizone in carbon tetrachloride to be 0.055% (w/v) or 2.1×10^{-3} *M* at 25° the calculated solubility of undissociated dithizone in water at room temperature is 0.05 mg. per liter or 2×10^{-7} *M*. The solubility product of dithizone is 3×10^{-12}.

Summary

From the value 1.1×10^4 found for $[HDz]_{CCl_4}/[HDz]_{H_2O}$ and 1.4×10^{-9} for $[H^+][Dz^-]/[HDz]_{CCl_4}$, the value 1.5×10^{-5} is calculated for the primary dissociation constant of diphenylthiocarbazone in water at room temperature.

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