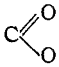
We have evaluated the relative values of the moments of the above forms by means of addition of the bond moment vectors and find that they have moments in the ratio of 1, 2.6, 3.7 and 4.8 for I *cis*, I *trans*, II *cis* and II *trans*, respectively. The carboxyl group has been considered as coplanar with the benzene ring in all calculations. The H atom tends to stay locked in the same plane as the  group because of the resonance in this group and, further, tends to stay in form I configuration because of the relatively large interaction energy between the O–H dipole and the C═O dipole. Form II of the above structures is not regarded as particularly probable except for the case of a highly electro-negative group at the ortho position which does not sterically hinder this configuration of the O–H group. It may be remarked that the small resonance energy between the carboxyl and phenyl group would probably not restrict the structures considered to only the coplanar ones; however, since our discussion is entirely qualitative, we have neglected other than planar configurations.

If fluorine is the X atom of the above structures, we might expect real contributions from form II *cis*. It is to be noted, however, that the presence of a hydrogen bonding solvent such as dioxane would probably prevent the existence of much of this form. As pointed out earlier, in the case of benzene solutions the situation might be entirely different.

In general then, we may conclude this section by stating that resonance, inductive and dipole interaction effects all probably contribute to the deviations we have observed and listed in Table II. It must be emphasized, however, that mere agreement between calculated values and observed values is very insufficient basis for attributing all effects to any one cause. It is equally hazardous to accept the agreement as evidence that no factors causing deviations are active.

Summary

The electric moments of *o*, *m* and *p*-fluorobenzoic acids and of *o*-chloro- and *o*-bromobenzoic acids have been determined in dioxane solutions. The values found were 2.10, 2.16, 1.99, 2.43 and 2.50, respectively. Calculation of the angle the carboxyl group moment makes with the *ϕ*–C axis gives a value of 74° if the moment of *p*-fluorobenzoic acid is used. This along with previously determined angle values from *p*-chloro- and *p*-bromobenzoic acid gives an average value of 74°. A discussion is given of factors which might contribute to deviations between observed values of moments and those calculated by vector addition of the component moments.

DURHAM, N. C. RECEIVED FEBRUARY 20, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RUTGERS UNIVERSITY]

The Solubility Product of Barium Chromate at Various Ionic Strengths

BY GEORGE L. BEYER AND WILLIAM RIEMAN III

The values previously reported for the solubility of barium chromate in water vary greatly. Schweitzer[1] in 1890 reported that at room temperature the ordinary salt had a solubility of 4 × 10^{-5} mole per liter of solution, while the ignited salt gave a solubility of 2.5 × 10^{-5} mole per liter. In 1908 Kohlrausch[2] reported that at 25° the solubility was 1.62 × 10^{-5} mole per liter, and in 1918 Waddell[3] reported a value of 3.1 × 10^{-5} mole per liter. In view of the importance of this precipitate in analytical chemistry, it is desirable to have accurate data regarding its solubility product.

Preparation of Reagents

Barium Chromate.—Solutions of recrystallized reagent-grade barium chloride and sodium chromate were prepared and used to precipitate barium chromate in the presence of an excess of barium chloride (Sample A) and in the presence of an excess of sodium chromate (Sample B). Sample A: Fifty millimoles of sodium chromate in 400 ml. of water was added in about thirty minutes to a mechanically stirred solution containing 60 millimoles of barium chloride in 1600 ml. of water. The mixture was then heated to 95–100° and digested for twenty-four hours at this temperature. After settling, the precipitate was washed in the beaker several times by decantation and was then washed in centrifuge tubes until the washings gave a negative chloride test. The preparation was mixed with water and stored in a Pyrex bottle. Sample B was prepared as follows. Fifty millimoles of barium chloride

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(1) Schweitzer, *Z. anal. Chem.*, **29**, 414 (1890).

(2) Kohlrausch, *Z. physik. Chem.*, **64**, 158 (1908).

(3) Waddell, *Analyst*, **43**, 288 (1918).

in 400 ml. of water was added as above to a solution containing 60 millimoles of sodium chromate in 1600 ml. of water. The digestion and washing were carried out as before.

Sodium Acetate, Sodium Chloride, Potassium Chloride.—These salts were tested and found to have no reducing action on ceric sulfate nor oxidizing action on ferrous sulfate. They were therefore used without further purification for the preparation of the solutions of known ionic strength.

Determination of Solubility

Suspensions of barium chromate were prepared to contain about one millimole of preparation A or B in a liter of standard salt solution. The salt concentrations were varied to give different ionic strengths. Before dilution to one liter, 10 ml. of 0.01 *N* ammonia was added to give a *p*H of 8.5 to 9.0, thus preventing appreciable hydrolysis of the chromate ion. These suspensions were agitated in a thermostat at 25.2 ± 0.5° for several hours. It was found that equilibrium was established in two hours or less in all cases.

These suspensions were filtered through a porcelain micro filter stick, and 200 ml. of each filtrate was pipetted into a flask. Twenty ml. of 12 *N* hydrochloric acid and 5.00 ml. of 0.01 *N* ferrous sulfate were added, and the solution was titrated with 0.01 *N* ceric sulfate. Two drops of 0.025 *M* ferroin were used as the indicator. Blanks were run with 200 ml. of water instead of the chromate solution in order to standardize the ferrous sulfate solution, which contained ferric sulfate to stabilize it.

This method for the determination of chromate was tested by using samples of 0.000400 *N* potassium dichromate. The maximum error over the range of quantities used in the determination of solubility was found to be ±0.3 microequivalent.

Results

The mean solubility of Sample A in the absence of foreign salts, determined from three different suspensions, was found to be 1.17×10^{-5} mole per liter, that of Sample B, 1.13×10^{-5} mole per liter, the mean for the two samples being 1.15×10^{-5} mole per liter. The close agreement between these results is evidence for the purity of both preparations.

In order to make sure that equilibrium had been attained, its approach in the absence of foreign salts was made both from undersaturation and from supersaturation with barium chromate Sample B. The approach from supersaturation was accomplished by keeping a suspension at 40 ± 0.5° for several hours and then at 25.2 ± 0.5°, samples being taken at each temperature. The values for the concentrations obtained in this manner are given in Table I.

The values for the solubility of Sample A at 25° in the presence of foreign salts are given in Table II.

Table I

Approach to Equilibrium of Barium Chromate Suspensions

Time in bath, hours	Temperature of bath, °C.	Concentration, molarity $\times 10^5$
0.5	25	1.06
1.0	25	1.16
1.5	25	1.12
2.0	25	1.16
2.5	25	1.12
3.0	25	1.16
4.0	25	1.14
18.0	25	1.12
3.0	40	1.47
15.0	40	1.51
17.0	40	1.49
20.0	25	....
20.5	25	1.27
21.0	25	1.14
22.0	25	1.20
23.0	25	1.14
29.0	25	1.14
35.0	25	1.12

Table II

The Effect of Ionic Strength on the Solubility Product of Barium Chromate

Foreign salt	Molarity of foreign salt	Solubility, molarity $\times 10^5$	$\sqrt{\mu}$	*pS'*	*pS*
None	0.0000	1.15	0.007	9.88	9.91
$NaC_2H_3O_2$	.0025	1.40	.051	9.71	9.93
$NaC_2H_3O_2$	.0100	1.81	.10	9.48	9.91
$NaC_2H_3O_2$	.0225	2.12	.15	9.35	9.95
$NaC_2H_3O_2$	.0400	2.51	.20	9.20	9.93
$NaC_2H_3O_2$	.0625	2.85	.25	9.09	9.94
$NaC_2H_3O_2$	.0900	3.25	.30	8.98	9.93
$NaC_2H_3O_2$	.1225	3.62	.35	8.88	9.92
$NaC_2H_3O_2$	.1600	4.02	.40	8.79	9.91
$NaC_2H_3O_2$	.2025	4.25	.45	8.74	9.93
$NaC_2H_3O_2$	.2500	4.74	.50	8.65	9.91
NaCl	.0625	2.80	.25	9.11	9.96
NaCl	.2500	4.47	.50	8.70	9.96
KCl	.0625	2.83	.25	9.09	9.94
KCl	.2500	4.57	.50	8.67	9.93
				Mean	9.93

The solubility of Sample B in the absence of foreign salts at 18 ± 0.5° was found to be 0.98×10^{-5} mole per liter.

Discussion

The error in the determination of chromate in the 200-ml. portion of filtrate (0.3 microequivalent) corresponds to an error of 0.04 unit in the value of the classical solubility exponent, *pS'*, for the solution containing no foreign salt. In the presence of foreign salts, the solubility is greater, and the error in terms of *pS'* units is less. The effect of sodium or potassium chloride as solvent salt is seen to differ slightly from the effect of sodium acetate.

The thermodynamic solubility exponent, pS, can be obtained by extrapolation to zero ionic strength of the graph of pS' against $\sqrt{\mu}$. However, this extrapolation gives the greatest weight to the least accurate determinations, *i. e.*, those at low ionic strength. A better method of finding pS involves the use of the equation

$$pS = pS' - 2 \log f_{\pm}$$

where $f_{\pm}$ denotes the mean activity coefficient of the ions of the barium chromate. Values of $f_{\pm}$ may be calculated by the use of the equation of Gronwall, LaMer and Sandved.[4] The last column in Table I shows the pS values thus calculated on the assumption that a = 4.3 Å. This radius was chosen because it yields the most consistent pS values for sodium acetate as the solvent salt. It is in good agreement with the mean value (4.5 Å.) of the effective radii of the barium and chromate ions as given by Kielland.[5]

Barium chromate differs markedly from strontium chromate in the time required to establish solubility equilibrium. Whereas two hours suffice for barium chromate, it is reported[6] that over a year is required for strontium chromate.

In the separation of barium from strontium by the standard method[7] of precipitating barium chromate, it was found that the pH is about 5.7. From the data presented in this paper along with the values[8] for the equilibrium constants of the reactions

$$HCrO_4^- \rightleftharpoons H^+ + CrO_4^=$$
$$2HCrO_4^- \rightleftharpoons Cr_2O_7^= + H_2O$$

it can be calculated that a quantitative precipitation of barium should occur at a much lower pH, about 4.6. The application of this lower pH should give a precipitate with much less coprecipitated strontium, thus improving the separation. This point is now under investigation.

Summary

The solubility product of barium chromate at ionic strengths up to 0.25 has been determined. The results are in good agreement with the extended Debye–Hückel equation.

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[4] Gronwall, LaMer and Sandved, *Physik. Z.*, **29**, 358 (1928).

[5] Kielland, THIS JOURNAL, **59**, 1675 (1937).

[6] T. W. Davis, *Ind. Eng. Chem., Anal. Ed.*, **14**, 709 (1942).

[7] Hillebrand and Lundell, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1929, p. 492.

[8] Neuss and Rieman, THIS JOURNAL, **56**, 2238 (1934).

NEW BRUNSWICK, N. J. RECEIVED OCTOBER 19, 1942

[CONTRIBUTION FROM THE BUREAU OF ANIMAL INDUSTRY, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Absorption of Light by 1,5-Dien-3-ynes in the Region 2300–2900 Å.[1]

BY HARRY BASTRON, RUSSELL E. DAVIS AND LEWIS W. BUTZ

The characteristic ultraviolet absorption curves of 1,5-dien-3-ynes have not yet been reported. Determination of the curves of certain polycyclic adducts of these hydrocarbons has yielded valuable information concerning the structure of the adducts.[2] The latter are obtained mixed with byproducts which are quantitatively important and the composition of which, if known, might suggest something about the dienyne addition reactions. Conceivably, adducts might be formed which contain the 1,5-dien-3-yne system as part of their structure. For this reason the absorption of a series of dienynes has been determined. The group examined consisted of one open-chain, two monocyclic, and four bicyclic dienynes.

Six of the dienynes were prepared in our own Laboratory by the dehydration of the corresponding ethynylenediols with hot aqueous mineral acid. The seventh, a methoxy dienyne, was given to us by Dr. C. S. Marvel whose generosity it is a pleasure to acknowledge.

The dienynes, prepared according to the published procedures (see table), are yellow liquids. The yellow cyclohexenylcyclopentenylacetylene was refluxed with potassium hydroxide in ethanol, and in this way a colorless preparation was obtained.[3] The curve of this colorless sample is very similar to the curve of a yellow sample of the closely related methoxy derivative (Curves 5 and

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[1] This work was supported in part by an allotment from the Special Research Fund (Bankhead-Jones Act of June 29, 1935). Not subject to copyright.

[2] Butz and Joshel, THIS JOURNAL, **64**, 1311 (1942), and earlier papers.

[3] By Dr. L. M. Joshel.