follow reaction yields mainly chlorine dioxide and accounts for the observed stoichiometry.

We have performed experiments to establish whether for the catalyzed reaction the chlorine atoms in the chloride ion remain distinct from those appearing in the product ClO_2. On the basis of the mechanism proposed above for the change, it is expected that they do remain distinct, since very little transfer of activity from HCl^*O or Cl_2^* to ClO_2 takes place in the reaction of these with ClO_2^-.

The experiments are outlined below, and show that in fact little mixing of activity between Cl^- and ClO_2^- is observed when the former acts as catalyst for the disproportionation of chlorite ion. The slight amount of exchange, about the same in extent as in the oxidation of chlorite by chlorine or hypochlorite, supports the view that the same intermediate is involved in both reactions.

Experiment.—The concentration of hydrochloride in each experiment was 0.58 *M*. The chloride ion was radioactive and its specific activity was determined before the reaction. After considerable chlorine dioxide had been formed, it was separated from other species as described above, and its specific activity determined. In one of the experiments, the specific activity of the chlorine dioxide formed was 4 ± 4, that expected if exchange with the halogen in the system were complete 50; in a second, these numbers were 27 ± 15 and 336. The results in the second experiment correspond to 8 ± 5% exchange. Thus the amount of exchange which takes place is about the same as in the oxidation of chlorite by chlorine or HOCl. Since the mechanism proposed includes as a step the oxidation of chlorite by HOCl or chlorine, slight transfer of activity to the product ClO_2 is expected.

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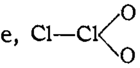
Summary

By experiments using radioactive chlorine as a tracer, the following observations have been made. (a) The oxidation of chlorite by chlorate in acid is much slower than the disproportionation of chlorite. (b) In the reaction of chlorite with chlorine (or hypochlorous acid) to form chlorine dioxide or chlorate and chloride ion, most of the chlorine atoms in the chlorine dioxide or chlorate are derived from the chlorite. (c) In the reaction of chloride ion with chlorate ion in acid to produce chlorine and chlorine dioxide, the chlorine atoms in the chlorine dioxide are for the most part derived from the chlorate. (d) In the disproportionation of chlorite in acid catalyzed by chloride ion, the chlorine atoms in the chlorine dioxide are for the most part derived from the chlorite. (e) In each of the changes under (b), (c) and (d), a small but definite degree of mixing of the chlorine atoms in the products has taken place. (f) The reverse reaction in the system (c) near its equilibrium composition is very slow. (g) The exchange of chlorine activity between ClO^- and ClO_2^- in base is very slow. (h) The exchange of chlorine with chlorate ion in acid at room temperature and at elevated temperatures is very slow.

The significance of these observations in relation to other published observations and in relation to reasonable mechanisms for the reactions has been discussed. An unsymmetrical intermediate,  $Cl{-}Cl\langle^{O}_{O}$ (or Cl—O—Cl—O), common to the systems (b), (c) and (d) is postulated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, FRESNO STATE COLLEGE]

The Apparent and Partial Molal Volume of Copper Sulfamate in Aqueous Solutions

BY ELTON M. BAKER

The object of this investigation was to determine the apparent and partial molal volume of copper sulfamate at 25° for various concentrations of solutions from accurate density measurements. At infinite dilution the apparent molal volume becomes the partial molal volume. The literature contains limited data for salts of the type contained in this study.

Experimental

The experimental procedure consisted of determining densities of aqueous solutions of copper sulfamate in calibrated weld precision pycnometers of approximately 25 ml. capacity. These were calibrated using distilled water. The deviation was less than 0.005%. The density obtained for each concentration is the average of three determinations. The maximum deviation between values in any series was 0.005%. The densities were determined at 25 ± 0.02°. The temperatures were determined by a long mercurial thermometer of short range, calibrated by the National Bureau of Standards. Calibrated weights were used and weighings could be reproduced to ±0.05 mg. All weights were corrected to vacuum. Weighing was done in a room at 25 ± 1°.

Copper sulfamate was prepared by the interaction of C. P. sulfamic acid and basic copper carbonate. The blue copper sulfamate was recrystallized three times from distilled water. The copper content was determined by allowing an excess of potassium iodide to reduce weighed samples of the stock solution of copper sulfamate in an acid buffer. The released iodine was titrated using standard thiosulfate solution with potassium thiocyanate added near the end-point. The accepted value was the average of three analyses in which the maximum deviation between analytical results for any concentration was less than 0.07%.

Molal concentrations were then obtained and molar concentrations were calculated with the use of densities.

A saturated solution was prepared by allowing a warm concentrated copper sulfamate solution to cool to 25°, then permitting it to come to equilibrium with the solid phase which separated. Weighed samples of the supernatant liquid were analyzed as before. The solubility was found to be 74.73 (±0.05) g. per 100 g. of water.

Treatment of Results.—The apparent molal volumes were calculated from the observed densities by means of the equation proposed by Gucker[1]

$$\phi(V_2) = 1000/c - 1/d_1[1000d/c - M_2] \qquad (1)$$

where $\phi(V_2)$ is the apparent molal volume, M_2 is the molecular weight of the copper sulfamate, d_1 and d are the densities of the solvent and solution, respectively, and c is the concentration (moles of solute per liter of solution). The absolute density of water was used as 0.99707 g./ml. The densities and the corresponding values of concentration and apparent and partial molal volumes are shown in Table I.

TABLE I

Density	Concentration Molal	Concentration Molar	$\overline{V}_2$	$\phi(V_2)$	$d\phi(V_2)$
1.01340	0.08348	0.08283	59.86	58.77	−0.30
1.02316	.13394	.13250	60.40	59.00	− .10
1.10238	.56471	.54394	65.33	62.31	+ .02
1.18428	1.0484	.97910	68.86	64.72	+ .18
1.22814	1.3315	1.2199	71.14	66.51	− .27
1.28484	1.7130	1.5304	73.09	67.90	− .13
1.36007	2.2627	1.9495	75.54	69.74	− .05
1.44351	2.9221	2.4140	77.36	71.01	+ .38

From the data a second order equation expressing $\phi(V_2)$ as a function of c was found. The value of the coefficients was obtained by the method of averages[2]

$$\phi(V_2) = 56.08 + 7.07c^{1/2} + 1.92c \qquad (2)$$

In Column 6 are shown the deviations, $d\phi(V_2)$, of the observed values from those calculated from the equation.

Partial molal volumes were obtained using concentrations and calculated apparent molal volumes by the relation proposed by Gucker[1]

$$\overline{V}_2 = \phi(V_2) + c^{1/2}\left[\frac{1000 - c\,\phi(V_2)}{2000 + c^{3/2}\dfrac{\partial\phi(V_2)}{\partial c^{1/2}}}\right]\frac{\partial\phi(V_2)}{\partial c^{1/2}} \qquad (3)$$

where $\phi(V_2)$ is the apparent molal volume and

$$\partial\phi(V_2)/\partial c^{1/2} = 7.07 + 3.84c^{1/2} \qquad (4)$$

as obtained from equation (2).

The partial molal volume of copper sulfamate at zero concentration was determined as 56.08 ml. per gram molecular weight by the evaluation of the first constant in equation (2).

Summary

1. Densities at 25 ± 0.02° of copper sulfamate solutions ranging from 0.08 to 2.4 molar have been determined.

2. The solubility of copper sulfamate at 25° was determined: 74.73 g. per 100 g. of solvent.

3. The apparent and partial molal volumes of the solute have been calculated.

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[1] Gucker, *J. Phys. Chem.*, **38**, 307 (1934).

[2] Lipka, "Graphical and Mechanical Computation," John Wiley and Sons, Inc., New York, N. Y., 1921, pp. 126, 145.

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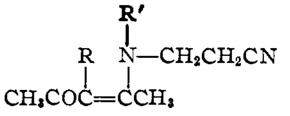
[JOINT CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Infrared Spectra of Amino-substituted α,β-Unsaturated Ketones

BY NORMAN H. CROMWELL, FOIL A. MILLER,[1] AGATHA R. JOHNSON, ROBERT L. FRANK AND DAVID J. WALLACE

A recent study of some cyclizations involved the preparation of 4-(2′-cyanoethyl)-amino-3-penten-2-one (I), 4-(2′-cyanoethyl)-amino-3-methyl-3-penten-2-one (II) and 4-N-(2′-cyanoethyl)-methylamino-3-penten-2-one (III) and the possibility of their ring closure by the aldol condensation. The properties of these substances



$$\begin{array}{l} \qquad\quad\;\; R' \\ \qquad\quad\;\; | \\ \quad R \quad N\text{—}CH_2CH_2CN \\ \quad | \quad\;\; | \\ CH_3COC{=}CCH_3 \end{array}$$

I, R = R′ = H
II, R = CH_3, R′ = H
III, R = H, R′ = CH_3

have proved to be unusual and have prompted us to undertake a study of their infrared absorption spectra and those of a number of previously reported related compounds.

Preparation and Properties

Compounds I, II and III were readily prepared by condensation of the appropriate β-aminopropionitrile with acetylacetone or 3-methylacetylacetone. Assignment of the double bond in these structures to the position α,β to the carbonyl rather than β,γ between the carbon and nitrogen atoms, is based on their ultraviolet absorption maxima in the region characteristic of α,β-unsaturated carbonyl compounds and on a comparison of their infrared spectra with those of compounds VII through IX of known structure.

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