with methylene radicals. Such a sequence of processes would build up a certain concentration of the intermediate methane which would then decrease as ketene is depleted. Actually the amount of methane increases as the reaction progresses.

Presence of Ethylene.—The experiments with initial ethylene confirm the findings of other workers in that the hydrocarbon deficiency indicative of higher polymer formation is considerably increased. Not only is this observed when ethylene is added to ketene alone (expts. 2 and 13) but a similar effect is obtained by adding ethylene to a ketene-hydrogen mixture (expts. 6 and 14), probably due in both cases to the greater concentration of the easily polymerized ethylene. However, it should be noted that when ethylene and hydrogen are added simultaneously (no. 14), the deficiency is less than when hydrogen is absent (expt. 13). This is comprehensible if one assumes that saturated hydrocarbons are more difficult to polymerize than unsaturates. Furthermore, the addition of ethylene (expt. 14) diminishes the quantity of methane resulting from interaction (expt. 6) of hydrogen and methylene, probably because the ethylene acts as a trap for methyl and methylene radicals.

Acknowledgments.—The writer wishes to thank Professor H. S. Taylor of this Laboratory for useful discussion and advice in connection with this research. He is grateful also to Mr. Robert B. Duffield for help in performing some of the analytical work, and to Mr. George G. Joris for the mass spectrographic analysis.

Summary

1. The extent of photodecomposition of ketene by ultraviolet light at about 45° appears to be independent of the nature of subsequent reactions, thus supporting the supposition that methylene radicals are produced as a result of light absorption.

2. In the presence of hydrogen the gaseous hydrocarbon is to a considerable degree saturated, the quantity of saturates increasing with time of exposure and higher initial hydrogen pressures. Simultaneously a saturated condensed polymeric product is formed. The hydrogen utilized is equivalent to the methane, higher saturated hydrocarbon and polymer present. The formation of saturates has been attributed to a reaction between hydrogen and methylenes to yield methyl radicals and hydrogen atoms, which is considered to proceed simultaneously with the recombination of methylenes to yield ethylene.

3. Saturates are formed also in the presence of methane, at the expense of the latter just as in the case of hydrogen. This is attributed to a reaction between methylene radicals and methane to form methyl radicals. The principal effect of ethylene is to increase the amount of condensed polymer.

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[CONTRIBUTION FROM THE COLLEGE OF ST. THOMAS]

The Activity Coefficients of the Undissociated Part of Weak Acids. II. Oxalic Acid

BY W. D. LARSON AND W. J. TOMSICEK

In the first paper[1] of this series, we showed that it is possible to determine the activity coefficients of undissociated molecules of weak acids by an e. m. f. method. It was found that there were only small changes in these coefficients up to an ionic strength of about 0.3.

The present study extends the method to a dibasic acid, which is considerably stronger as an acid than the acetic acid studied previously. In addition we have determined incidentally the standard e. m. f. of the mercury–mercurous oxalate electrode at 25°. For the purpose at hand, we have studied the e. m. f. at 25° of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2C_2O_4(s)},\ \mathrm{H_2C_2O_4}\ (c) \mid \mathrm{H_2} \qquad (1)$$

Materials and Apparatus.—Mercury, water, and hydrogen were treated as in the previous work.[1] Oxalic acid was a C. P. product, recrystallized twice from distilled water. Mercurous oxalate was prepared by precipitation from approximately 0.1 *N* solutions of mercurous nitrate and potassium oxalate. Oxalate was kept in excess. The precipitate was carefully washed by decantation and allowed to air-dry in a dark cupboard. It was then placed in a desiccator over calcium chloride for several weeks before use.

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[1] Larson and Tomsicek, THIS JOURNAL, **61**, 65 (1939).

This salt was extremely light sensitive, and was therefore stored in a dark place, and handled in a darkened room.

The cell vessels were those used before.[1] Air was removed from the oxalic acid solutions by boiling *in vacuo*, and then storing under nitrogen. In the preparation of mercurous oxalate half-cells, it was necessary to allow the cell solution to become thoroughly equilibrated with the mercurous oxalate if cells were to come to constant e. m. f. in a reasonable length of time. This was accomplished by placing mercury–mercurous oxalate, and oxalic acid solution in a flask, from which the air had been removed, and allowing it to stand for about twenty-four hours before filling the cell. The room temperature was always near 25° during the equilibration.

Cells were run at least in duplicate. They agreed to within 0.15 mv., and were constant for as long as five days. They attained their constant value in about thirty minutes after starting the hydrogen.

The oxalic acid solutions were analyzed with standard permanganate solution. The precision of the analyses was such that the concentrations are known to within 0.1%. All concentrations are expressed in moles per liter of solution.

Cells were thermostated in a water-bath at 25°. The temperature was constant within 0.03°. The temperature was read from a thermometer certified by the U. S. Bureau of Standards.

E. m. f. measurements were made with a L. & N. type K potentiometer, and a type R galvanometer from the same makers. The standard cell was an Eppley unsaturated cadmium cell, certified by the manufacturers.

Results

Twenty-two cells were prepared and measured in the final work. The data are presented in Table I.

TABLE I

E. M. F. AT 25° OF THE CELLS: Hg | $Hg_2C_2O_4$(s), $H_2C_2O_4$ (c) | H_2 (1 ATM.)

c	$-E$, v.	$-E^0$, v.
0.05380	0.6315	0.4173
.1022	.6200	.4173
.2054	.6085	.4174
.3043	.6023	.4174
.3987	.5981	.4173
.4778	.5953	.4172
.6127	.5917	.4173

The e. m. f. of cell (1) at 25° is given by equation (2)

$$E = E^0 - 0.02957 \log_{10} a^2_{H^+} a_{C_2O_4^=} \qquad (2)$$

where E is the observed e. m. f., E^0 is the standard e. m. f. of the mercurous oxalate electrode, and a_{H^+} and $a_{C_2O_4^=}$ represent the activities of hydrogen and oxalate ions. In order to evaluate the last term in equation (2), we make use of the relation

$$K_1K_2 = a^2_{H^+} a_{C_2O_4^=} / a_{H_2C_2O_4} \qquad (3)$$

in which K_1 and K_2 are the primary and secondary ionization constants of oxalic acid, and the a's are the activities of the species denoted by the subscripts. If we further assume that $a_{H_2C_2O_4}$ is equal to the molar concentration of undissociated $H_2C_2O_4$ in the solution, $c_{H_2C_2O_4}$, we are able to find a numerical value of $a^2_{H^+} a_{C_2O_4^=}$ for a given solution of oxalic acid by well known methods, since the $c_{H_2C_2O_4} = c(1 - \alpha)$ where α is the degree of ionization for the first step. This procedure leads to the equation

$$E^0 = E - 0.02957 \log_{10} K_1K_2\left(1 - \frac{-K_1 + \sqrt{K_1^2 + 4K_1c}}{2c}\right) \qquad (4)$$

where c is the molarity of the oxalic acid solution. The values of E^0 listed in Table I were calculated by means of equation (4). In these calculations, we have used the values $K_1 = 0.0536$[2] and $K_2 = 5.18 \times 10^{-5}$.[3]

Discussion

From the data of Table I we take -0.4173 ± 0.0001 v. as the best value for the standard e. m. f. of the Hg | $Hg_2C_2O_4$(s), $C_2O_4^=$ electrode at 25°. To be compared with this is the value -0.41 v. given by Latimer[4] calculated from a value of the solubility product given by Brodsky.[5] Our value of the standard e. m. f. leads to 1.27×10^{-13} for the activity product of $Hg_2C_2O_4$. Our assumption that $c_{H_2C_2O_4} = a_{H_2C_2O_4}$ is the same as assigning a value of unity to the activity coefficients of undissociated oxalic acid in all of the solutions. This assumption seems to be justified, for if there were a change in the activity coefficient, there would be a change in the calculated E^0.[6] The range of ionic strengths studied corresponds approximately to 0.03 to 0.17.

Clayton and Vosburgh[7] have measured the e. m. f. of the cells

Cd(Hg) | $CdC_2O_4 \cdot 3H_2O$(s), $H_2C_2O_4$ (m), quinhydrone | (Pt)

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(2) Darken, THIS JOURNAL, **63**, 1007 (1941).

(3) Harned and Fallon, *ibid.*, **61**, 3111 (1939).

(4) Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, p. 164.

(5) Brodsky, *Z. Elektrochem.*, **35**, 833 (1929).

(6) The method of calculation is given in more detail in reference 1.

(7) Clayton and Vosburgh, THIS JOURNAL, **59**, 2414 (1937).

over a concentration range of 0.003 to 0.025 molal. Their solutions contained also potassium oxalate and potassium acid oxalate so that it is not possible to calculate a standard e. m. f. from their data without certain assumptions concerning the activity coefficients of the ions involved. It is interesting to note that these authors obtained values for the *activity product* of cadmium oxalate which vary with the ionic strength. Since the method of calculation used by them appears to be entirely reasonable, it seemed likely to us that they had made an unfortunate choice of activity coefficients for use in equation (5) of their paper. It seems unlikely that the activity coefficient for undissociated oxalic acid could vary appreciably at the ionic strengths they used. We have recalculated values of the logarithm of the activity product of cadmium oxalate from their data, and by their method, but using different activity coefficients for the ions concerned.

According to the Debye–Hückel limiting law, the mean activity coefficient for a 1–2 electrolyte is equal to the square of the mean activity coefficient for a 1–1 electrolyte at the same ionic strength. Instead of the activity coefficients of Randall and Scott[8] for sodium sulfate we have used the square of the activity coefficients for HCl, taken from Harned and Ehlers.[9] We also used the more recent value of Harned and Fallon[3] for K_2 for oxalic acid. These recalculations lead to a value of the logarithm of the activity product, $\log_{10} K$, of -7.785 ± 0.005, which shows no trend with changes in ionic strength.

Since the activity product of $CdC_2O_4 \cdot 3H_2O$ is a constant, we can obtain a constant value for the standard e. m. f. of the Cd (Hg) | $CdC_2O_4 \cdot 3H_2O(s)$, $C_2O_4^=$ electrode since $E^0_{Cd/CdC_2O_4} = E_{Cd/Cd^{++}} - 0.02957 \log_{10} K$. Again, since this standard e. m. f. is constant over a range of ionic strengths from 0.025 to 0.33, it appears that these changes in ionic strength do not produce any variation in the activity coefficient of un-ionized oxalic acid over the same range.

Summary

1. From measurements of the cell Hg | $Hg_2C_2O_4(s)$, $H_2C_2O_4$ (*c*) | H_2, we find the standard e. m. f. of the Hg | $Hg_2C_2O_4(s)$, $C_2O_4^=$ electrode to be -0.4173 ± 0.0001 v. These measurements also indicate that the activity coefficient of the undissociated oxalic acid does not change in value over an ionic strength range of 0.02 to 0.17.

2. Recalculation of the e. m. f. data of Clayton and Vosburgh[7] for the cell Cd (Hg) | $CdC_2O_4 \cdot 3H_2O(s)$, $H_2C_2O_4$ (*m*), quinhydrone | (Pt) indicates that the activity product of cadmium oxalate is a true constant over the ionic strength range from 0.025 to 0.33. This result leads to the conclusion that the activity coefficient of undissociated oxalic acid over the same ionic strength range does not change.

ST. PAUL, MINN. RECEIVED SEPTEMBER 19, 1941

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[8] Randall and Scott, THIS JOURNAL, **49**, 654 (1927).

[9] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RHODE ISLAND STATE COLLEGE]

The Viscosity of Formamide–Dioxane Solutions at 5, 25 and 40°

BY W. GEORGE PARKS,[1] I. MILTON LEBARON[2] AND EVERETT W. MOLLOY[1]

Introduction

The viscosity of binary liquid solutions has been measured by several investigators[3] in an attempt to correlate the viscosity with diverse physical properties such as migration of ions, conductivity, chemical constitution, association and hydration. In addition, attempts have been made to find mathematical expressions relating the viscosity of a solution to that of the components and their ratio; also to deduce changes in a solution such as alterations in the degree of association, or the formation of complexes or compounds, from peculiarities in the viscosity–concentration curves.[4] Any liquid or solution with marked anomalies from the point of view of one property is particularly desirable for such a study. Since pure formamide is an associated liquid[5] with a high dielectric constant and 1,4-dioxane has a relatively low dielectric constant the viscosity–concentration curves for such a binary solution might show

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[2] Present address, Colorado School of Mines, Golden, Colorado.

[3] Dunstan and Mussell, *J. Chem. Soc.*, **97**, 1935 (1910). Lemonde, *Ann. phys.*, **9**, 539 (1938). Merry and Turner, *J. Chem. Soc.*, **105**, 748 (1914).

[4] Spells, *Trans. Faraday Soc.*, **32**, 530 (1936).

[5] Turner and Merry, *J. Chem. Soc.*, **97**, 2069 (1910). Walden, *Z. physik. Chem.*, **75**, 555 (1910).