sulfides in a solution with such a sulfide ion concentration, but the complexes are precipitated instead probably because of their greater insolubility.

Summary

1. Dipotassium dioxalatothiometastannate was isolated for the first time and proved to have the formula $K_2SnS(C_2O_4)_2 \cdot 2H_2O$.

2. The compound was stable enough to permit removal of all of the water of hydration.

3. The solubilities of dipotassium dioxalatothiometastannate in water at 25 and 0° were determined.

4. The pH of water solutions of varying concentrations of dipotassium dioxalatothiometastannate was studied.

5. The reactions of a water solution of dipotassium dioxalatothiometastannate with various cations were studied.

6. E. m. f. measurements in solutions of dipotassium dioxalatothiometastannate with a silver–silver sulfide electrode were made in an attempt to determine the concentration of the sulfide ion.

The Reduction of Unsaturated Hydrocarbons at the Dropping Mercury Electrode. I. Phenyl Substituted Olefins and Acetylenes

BY H. A. LAITINEN AND S. WAWZONEK

Isolated ethylenic and acetylenic linkages are not reducible at the dropping mercury electrode. However, double bonds which are either conjugated with carbonyl groups or present in heterocyclic nuclei like pyridine and quinoline can be reduced.[1] We have found that other types of unsaturated linkage are electroreducible. In the present paper the results of a polarographic study of phenyl substituted olefins and acetylenes are reported. The reduction of other types of unsaturated hydrocarbons will be described in forthcoming publications.

Experimental

Dioxane–water mixtures containing 75% dioxane were used as a solvent, with 0.175 M tetrabutylammonium iodide as a supporting electrolyte. Since the half-wave potentials were unaffected by the pH of the solution (v. i.) unbuffered solutions were suitable for the measurements. Dioxane was found to be superior to acetone, isopropanol or methanol as a solvent in permitting the attainment of very negative potentials. In 50 to 85% dioxane solutions, using tetrabutylammonium iodide as the supporting electrolyte, the decomposition potential of the solvent was essentially constant at about −2.9 volts (vs. saturated calomel electrode), showing that the negative potential limit is determined by the discharge of the cation. Tetrabutylammonium salts were found to be superior to tetramethylammonium salts in having a more negative discharge potential.

The dropping mercury electrode had the following characteristics. At a pressure of 46.5 cm. of mercury, the drop time in the solvent used was 3.34 seconds (open circuit).

The value of m was 2.05 mg. sec.$^{-1}$, with a calculated value of $m^{2/3}t^{1/6}$ of 1.973 mg.$^{1/3}$ sec.$^{-1/3}$ (open circuit). Values of $m^{2/3}t^{1/6}$ at various potentials are given in Table II.

The electrolysis cell had a simple cylindrical shape with a mercury pool anode, and was provided with side arms for anode connection and for admission of nitrogen for the removal of dissolved oxygen. The anode potential was measured against a saturated calomel electrode (S. C. E.) by using a sintered glass salt bridge of the type described by Laitinen.[2] Its value was found to be reproducible at −0.452 volt in solutions of constant electrolyte concentration.

The current–voltage curves were determined with a Model XI Heyrovsky Polarograph having a current scale calibrated in microamperes. Data for the logarithmic analyses of the curves were obtained with a Fisher Elecdropode having specially calibrated current and voltage scales. The average resistance of the electrolytic cell was determined by the conventional Wheatstone bridge method, and found to be 2000 ohms. The half-wave potentials given in Table I are corrected for iR drop. All experiments were carried out at 25° in a water thermostat regulated to ±0.1°.

Materials.—The tetrabutylammonium iodide was prepared by a slight modification of the method used by Cox, Kraus and Fuoss.[3] Tri-n-butylamine (200 ml.) and n-butyl iodide (100 ml.) were heated together on a steambath for sixty-five hours. The resulting solid was filtered, washed with a small amount of ethyl acetate and then dissolved in the least amount of cold ethanol. The resulting solution was mixed with an equal volume of 10% potassium hydroxide in ethanol and poured into water. Removal of part of the alcohol under reduced pressure gave a crystalline precipitate of tetrabutylammonium iodide

(1) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers. New York, N. Y., 1941.

(2) H. A. Laitinen, *Ind. Eng. Chem.*, *Anal. Ed.*, 13, 393 (1941).

(3) N. L. Cox, C. A. Kraus and R. M. Fuoss, *Trans. Faraday Soc.*, 31, 749 (1935).

which, after three recrystallizations from anhydrous ethyl acetate, melted at 141–142°; yield 150 g.

The dioxane was purified by refluxing with sodium for ten hours and distilling.

Stilbene, triphenylethylene, diphenylbutadiene, heptyne-1, o-allylanisole, and phenylacetylene were obtained from stock and were purified before using. The styrene was first treated with K_2HgI_4 and then freshly distilled.

1,1-Diphenylethylene,[4] β-methylstyrene[5] and tetraphenylethylene[6] were prepared by appropriate methods given in the literature.

Diphenylacetylene was prepared by a modification of the method used by Limpricht and Schwanert.[7] Stilbene dibromide was refluxed with 200 ml. of 30% potassium hydroxide in methanol for twelve hours. The potassium bromide formed was filtered off while hot and washed with ether. Water was next added to the filtrate, the methanol removed by distillation and the resulting solution extracted with ether. Removal of the ether followed by distillation under reduced pressure gave 14.6 g. of diphenylacetylene; b. p. 111–112° (1 mm.).

Results

All of the hydrocarbons investigated showed a single well-defined reduction wave. Tracings of typical polarograms are shown in Fig. 1 for styrene and in Fig. 2 for triphenylethylene. Only a slight tendency toward the appearance of maxima was observed. With low concentrations of hydrocarbons no maxima were found, whereas slight maxima were obtained in most cases with increasing
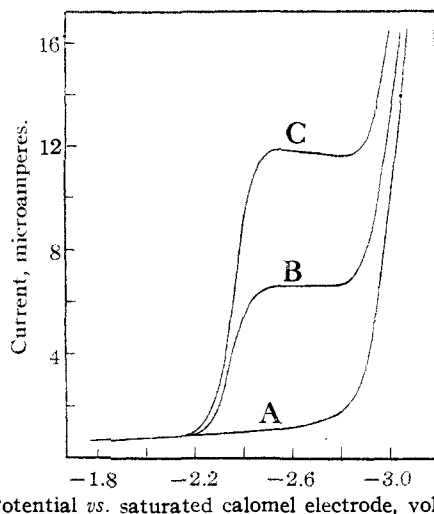

Potential vs. saturated calomel electrode, volts.

Fig. 1.—Polarogram of styrene in 75% dioxane, 0.175 M, tetrabutylammonium iodide: Curve A, residual current; curve B, 1.095 × 10⁻³ M styrene; curve C, 2.19 × 10⁻³ M styrene.

(4) C. F. H. Allen and S. Converse, "Organic Syntheses," Collective Vol. I, 2nd ed., p. 226.

(5) J. Levy and M. Dvoleitzka-Gombinska, Bull. soc. chim., 49, 1765 (1931).

(6) J. F. Norris, R. Thomas and B. M. Brown, Ber., 43, 2958 (1910).
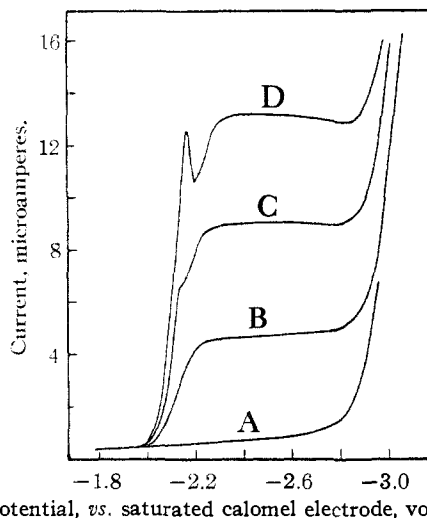
(7) H. Limpricht and H. Schwanert, Ann., 145, 347 (1868).

Potential, vs. saturated calomel electrode, volts.

Fig. 2.—Polarogram of triphenylethylene in 75% dioxane, 0.175 M tetrabutylammonium iodide: Curve A, residual current; curve B, 1.178 × 10⁻³ M; curve C, 2.36 × 10⁻³ M; curve D, 3.54 × 10⁻³ M triphenylethylene.

hydrocarbon concentration. The most prominent maxima are shown in Fig. 2, and never were found to interfere with diffusion current measurements. The maxima were not suppressed by methyl red. Hence half-wave potential measurements were made only on curves having no maxima.

TABLE I

HALF-WAVE POTENTIALS AND DIFFUSION CURRENT CONSTANTS OF VARIOUS COMPOUNDS IN 0.175 M TETRABUTYLAMMONIUM IODIDE, 75% DIOXANE

Compound	$\pi_{1/2}$ vs. S. C. E., volts	i_d, micro- amperes	C, milli- moles/ liter	i_d/C, micro- amperes/ millimole/ liter
$C_6H_5CH=CH_2$ (I)	2.343	5.63	1.095	5.25
	2.351	11.00	2.190	5.03
$C_6H_5CH=CHCH_3$ (II)	2.537	5.26	1.176	4.48
	2.539	13.00	2.940	4.42
$(C_6H_5)_2C=CH_2$ (III)	2.258	3.62	0.947	3.82
	2.270	9.03	2.365	3.98
$C_6H_5CH=CHC_6H_5$ (IV)	2.140	2.38	0.597	3.99
	2.137	4.83	1.194	4.05
	2.157	7.20	1.790	4.02
	2.136[a]	4.60[a]	1.127[a]	4.08[a]
$C_6H_5—CH=CH—$ $CH=CHC_6H_5$ (V)	1.981	3.18	0.810	3.92
	1.978	6.40	1.620	3.85
$(C_6H_5)_2C=CHC_6H_5$ (VI)	2.118	4.19	1.178	3.56
	2.113	8.68	2.36	3.53
	...[b]	12.83	3.54	3.62
$(C_6H_5)_2C=C(C_6H_5)_2$ (VII)	2.046	6.87	1.95	3.52
$C_6H_5C≡CH$ (VIII)	2.370	12.85	1.395	9.20
	...[b]	25.12	2.790	9.00
$C_6H_5C≡CC_6H_5$ (IX)	2.195	12.10	1.595	7.59
	...[b]	23.88	3.190	7.48

[a] In 0.175 M tetrabutylammonium iodide, 0.052 M tetrabutylammonium hydroxide; anode potential −0.440 volt (vs. S. C. E.). [b] Slight maximum, half-wave potential not determined.

Table I shows a summary of the observed half-wave potentials and diffusion current constants.

The half-wave potential was found quite generally to be independent of the concentration of hydrocarbon even in unbuffered solution. Since the solution at the electrode surface becomes more alkaline at the half-wave point with increasing hydrocarbon concentration it may be inferred that the half-wave potential is independent of the pH of the solution. Actually it was shown (Table I) that stilbene has the same half-wave potential in alkaline solution as in neutral solution when proper correction for anode potential is made.

The diffusion current showed a proportionality with concentration in every case studied. It is evident that the polarographic method offers a possible quantitative procedure for the determination of these hydrocarbons in the absence of more readily reducible substances.

A comparison of the half-wave potentials of the series of phenyl ethylenes (I, III, IV, VI, VII in Table I) shows the increasing ease of electroreduction with increasing substitution. The comparison between stilbene and 1,1-diphenylethylene (compounds III and IV) clearly demonstrates the increased activation of the double bond in stilbene. Styrene (I) was found to be distinctly more readily reduced than β-methylstyrene (II).

1,4-Diphenylbutadiene-1,3 (V) was shown to undergo a 1,4-reduction, because a comparison of its diffusion current constant with those of ethylenic hydrocarbons of similar molecular weight (III and IV) showed that only two electrons per molecule are involved in the reduction. No indication of a second reduction step was found.

Phenylacetylene (VIII) and diphenylacetylene (IX) were found to have slightly more negative half-wave potentials than the corresponding ethylenic compounds (I and IV). A complete reduction involving four electrons per molecule, giving rise to a single polarographic wave, was found in each case by a comparison of the observed diffusion current constants.

Heptyne-1 and o-allylanisole did not give polarographic waves under these conditions, showing that isolated double or triple bonds are not electroreducible.

Mechanism of the Reduction.—Logarithmic analyses of the reduction waves of stilbene and diphenylacetylene were made by plotting the quantity $\log i/(i_d - i)$ against the potential. The results are shown in Fig. 3. In each case a

straight line was obtained. The slopes of the lines were 0.062 and 0.069 volt for stilbene and diphenylacetylene, respectively. These results are in essential agreement with the theoretical slope of 0.059 volt (25°) for a reversible, potential-determining reaction involving one electron.
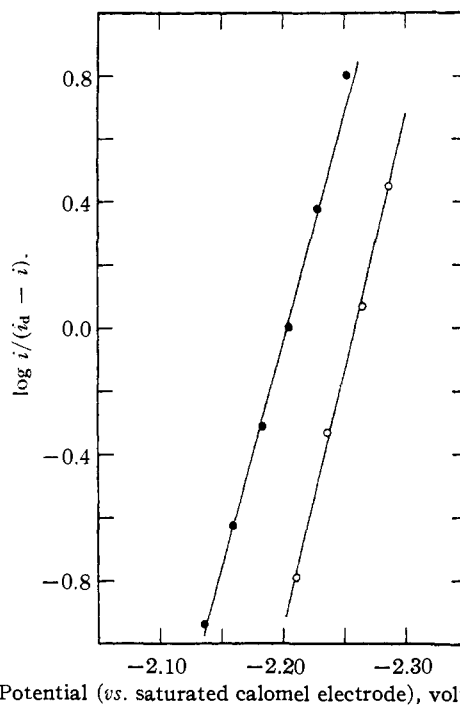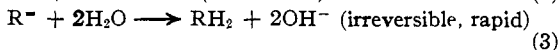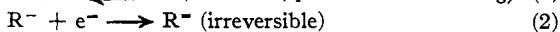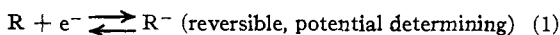

Fig. 3.—Analysis of current–voltage curves: O, C_6H_5-$CH{=}CHC_6H_5$; ●, $C_6H_5C{\equiv}CC_6H_5$; in 75% dioxane, 0.175 M tetrabutylammonium iodide.

Considering the fact that the half-wave potential is independent of the pH, the following mechanism is suggested for the electroreduction of olefins in neutral or alkaline solution.

$$R + e^- \rightleftarrows R^- \text{ (reversible, potential determining)} \quad (1)$$
$$R^- + e^- \longrightarrow R^= \text{ (irreversible)} \quad (2)$$
$$R^= + 2H_2O \longrightarrow RH_2 + 2OH^- \text{ (irreversible, rapid)} \quad (3)$$

The first reversible reaction would yield a univalent negative ion, the surface concentration of which would be proportional to the current, i. The concentration of the original hydrocarbon is porportional to the quantity $i_d - i$, where i_d is the diffusion current. The potential π would be determined by the ratio $C^0_R/C^0_{R^-}$ of the surface concentrations of R and R^-. Then

$$\pi = \text{const} + \frac{RT}{F} \ln \frac{C^0_R}{C^0_{R^-}} = \pi^{1/2} + \frac{RT}{F} \ln \frac{i_d - i}{i} \quad (4)$$

Equation 4 is the observed current–voltage relationship, with the theoretical slope of the logarithmic plot equal to 0.059 volt at 25°.

The second step of the reduction cannot involve the addition of a proton to form a free radical RH unless the rate of the reaction $R^- + H_2O \rightarrow$ RH + OH$^-$ would be independent of the pH, because the surface concentration $C^0_{R^-}$, and hence the half-wave potential, would be a function of the pH. Hence the simplest assumption is made, namely, that the second step involves the irreversible addition of a second electron to form a divalent negative ion of the type postulated as a product of sodium addition to unsaturated hydrocarbons in liquid ammonia.[8] The subsequent addition of two protons to the divalent ion could not affect the concentration of the potential-determining system; hence the reduction potential would not depend on the pH.

For acetylenic hydrocarbons, a similar two-step electron addition is postulated as the first stage. Since the half-wave potential of an acetylenic hydrocarbon is in general more negative than that of the corresponding ethylenic compound, it is readily understood that a single reduction wave must be obtained. The reduction potential, according to the proposed mechanism, is determined by the ease of addition of the first electron. The corresponding ethylenic compound at this potential would be rapidly reduced completely to the substituted ethane.

Diffusion Coefficients.—A knowledge of the relative diffusion coefficients of organic compounds as a function of the molecular weight is helpful in determining the number of electrons involved per molecule in the electrode reaction. For an accurate calculation it is necessary to correct the observed values of the diffusion current constants for the change of drop time with potential, particularly at extremely negative values of the potential.[9] At potentials more negative than -2 volts ($vs.$ S. C. E.) the drop time becomes so small that a direct measurement no longer is convenient. Hence the relative value of $m^{2/3}t^{1/6}$ as a function of potential was measured by determining the diffusion current of nitrobenzene over a wide range of potentials (-1.4 to -2.8 volts). From the relative values, the absolute values of $m^{2/3}t^{1/6}$ were easily caluulated.

Table II gives the values of $m^{2/3}t^{1/6}$ at the potentials, π_d, at which the diffusion currents were measured, together with the relative values of the

(8) W. C. Fernelius and G. W. Watt, *Chem. Rev.*, **20**, 216 (1937).
(9) I. M. Kolthoff and E. F. Orlemann, THIS JOURNAL, **63**, 2085 (1941).

diffusion coefficient taking that of styrene as unity. The absolute values in the last column were calculated from the Ilkovic equation,[1,10] using average values of the diffusion current constants from Table I. The decrease in the diffusion coefficients with increasing molecular weight is evident. Although there may be some question as to the accuracy of the Ilkovic equation at very negative potentials because of the rapid drop rate, the results given are certainly sufficiently exact to be useful in interpreting diffusion current data in 75% dioxane in unknown cases.

TABLE II

COMPARISON OF DIFFUSION COEFFICIENTS OF HYDRO-CARBONS IN 75% DIOXANE

Com-pound	π_d	$m^{2/3}t^{1/6}$, mg.$^{2/3}$sec.$^{-1/2}$	D, rel.	D_1 cm.^{2} sec.$^{-1}$ $\times 10^6$
I	2.51	1.792	1.000	0.562
II	2.75	1.702	0.832	.468
III	2.45	1.800	.579	.325
IV	2.31	1.828	.593	.333
V	2.15	1.869	.526	.296
VI	2.28	1.836	.461	.260
VII	2.21	1.852	.440	.248
VIII	2.55	1.782	.793	.440
IX	2.35	1.820	.521	.293

Summary

The polarographic reduction of a series of phenyl substituted olefins and acetylenes has been studied. The most suitable solvent medium was found to be a dioxane–water mixture containing 75% dioxane, with tetrabutylammonium iodide as a supporting electrolyte.

Each compound was found to give a single reduction wave in neutral or alkaline medium with a half-wave potential which is independent of the pH. The diffusion current was found to be proportional to the hydrocarbon concentration. The polarographic method has been shown to be useful in the detection and determination of olefins and acetylenes with activated double or triple bonds.

The half-wave potential is suggested as a measure of the relative activation of ethylenic and acetylenic linkages by substituent groups.

The equations of the rising portions of the waves have been determined for an olefin and an acetylenic hydrocarbon, and a reduction mechanism is suggested.

The diffusion coefficients of the hydrocarbons have been calculated from diffusion current data.

(10) D. Ilkovic, *Coll. Czech. Chem. Commun.*, **6**, 498 (1934).