[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarographic Wave Heights in Mixtures of Benzalacetone and Acetophenone

BY S. WAWZONEK[1] AND H. A. LAITINEN

In general, two or more substances can be determined simultaneously by the polarographic method, provided their reduction potentials are sufficiently different, by virtue of the fact that the diffusion currents of the individual components of the mixture are additive. Adkins and Cox[2] reported, however, that benzalacetone decreased the diffusion current of acetophenone so that the latter could not be determined in mixtures of the two ketones except by determining calibration curves for mixtures of similar composition. In an attempt to explain this anomalous behavior, we further investigated the reduction of acetophenone in the presence and absence of benzalacetone. In contrast to the one wave reported for acetophenone by Adkins and Cox, we obtained two waves in a 50% (by volume) isopropanol solution of 0.2 *N* tetramethylammonium hydroxide. The presence of benzalacetone affected the height of the first wave but the decrease was compensated for by an increase in the second wave as is shown in Fig. 1. The effect can be more clearly seen if the curves are corrected for the residual current as in Fig. 2. The sum of the total diffusion current of acetophenone and the diffusion current of benzalacetone was equal to the total diffusion current of a mixture for all concentrations of acetophenone tried.

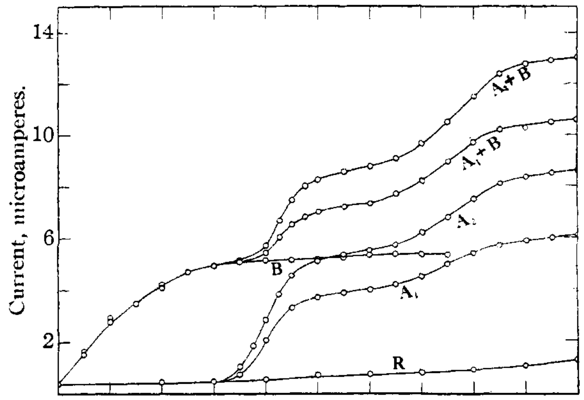

Fig. 1.—Curves in 0.2 *N* $(CH_3)_4NOH$-50% isopropanol: R, residual current; A_1, 0.001 *M* $CH_3COC_6H_5$; A_2, 0.0015 *M* $CH_3COC_6H_5$; B, 0.001 *M* $C_6H_5CH{=}CHCOCH_3$; A_1 + B, 0.001 *M* $CH_3COC_6H_5$ + 0.001 *M* $C_6H_5CH{=}CH{-}COCH_3$; A_2 + B, 0.0015 *M* $CH_3COC_6H_5$ + 0.001 *M* $C_6H_5CH{=}CHCOCH_3$.

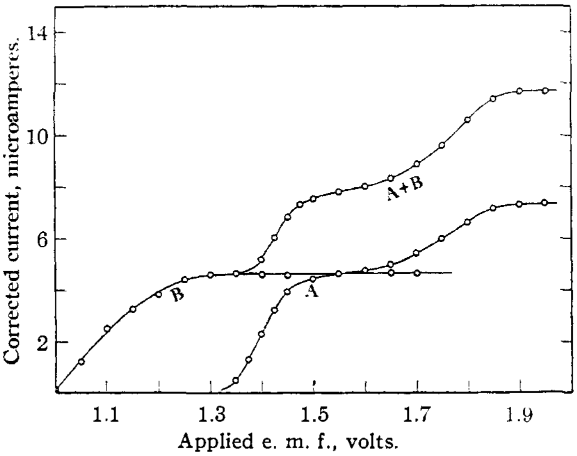

Fig. 2.—Corrected curves in 0.2 *N* $(CH_3)_4NOH$-50% isopropanol: A, 0.0015 *M* $CH_3COC_6H_5$; B, 0.001 *M* $C_6H_5CH{=}CHCOCH_3$; A + B, 0.0015 *M* $CH_3COC_6H_5$ + 0.001 *M* $C_6H_5CH{=}CHCOCH_3$.

A similar normal additive behavior was observed in the following 50% isopropanol solutions: 0.1 *N* ammonium chloride, Fig. 3; 0.1 *N* lithium chloride, Fig. 4; and 0.01 *N* tetramethylammonium hydroxide, 0.1 *N* tetramethylammonium bromide, Fig. 5. The diffusion currents obtained,

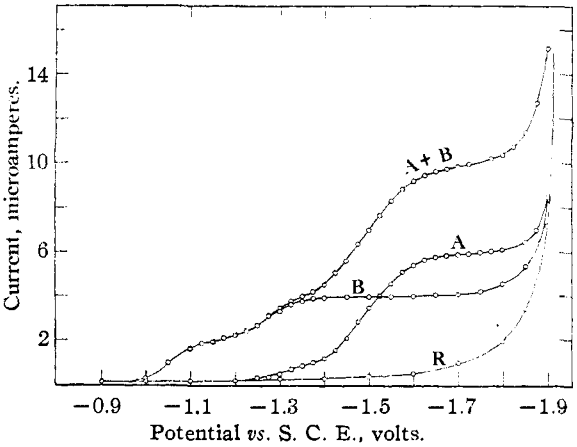

Fig. 3.—Curves in 0.1 *N* NH_4Cl-50% isopropanol: R, residual current; A, 0.001326 *M* $CH_3COC_6H_5$; B, 0.00096 *M* $C_6H_5CH{=}CHCOCH_3$; A + B, 0.001326 *M* $CH_3COC_6H_5$ + 0.00096 *M* $C_6H_5CH{=}CHCOCH_3$.

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[1] National Research Council Fellow, 1940–41.

[2] H. Adkins and F. W. Cox, THIS JOURNAL, 60 1151 (1938).

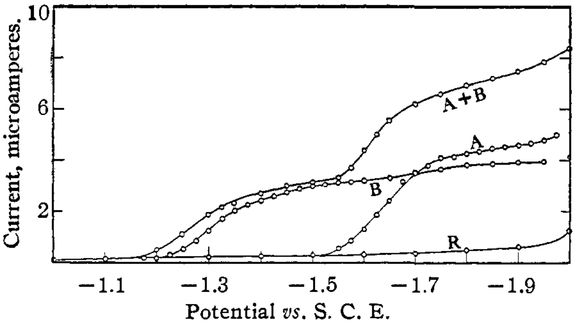

Fig. 4.—Curves in 0.1 *N* LiCl–50% isopropanol: R, residual current; A, 0.001326 *M* $CH_3COC_6H_5$; B, 0.00096 *M* $C_6H_5CH{=}CHCOCH_3$; A + B, 0.001326 *M* $CH_3COC_6H_5$ + 0.00096 *M* $C_6H_5CH{=}CHCOCH_3$.

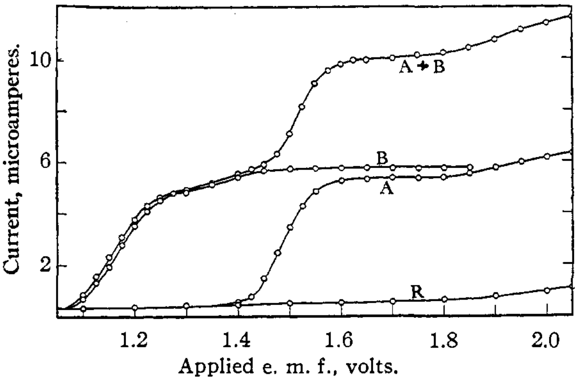

Fig. 5.—Curves in 0.001 *M* $(CH_3)_4NOH$–0.1 *N* $(CH_3)_4NBr$–50% isopropanol: R, residual current; A, 0.001 *M* $CH_3COC_6H_5$; B, 0.001 *M* $C_6H_5CH{=}CHCOCH_3$; A + B, 0.001 *M* $CH_3COC_6H_5$ + 0.001 *M* $C_6H_5CH{=}CHCOCH_3$.

TABLE I

50% Isopropanol solution	Acetophenone concn., millimolar	Acetophenone i_d, microamperes	Benzalacetone concn., millimolar	Benzalacetone i_d, microamperes	Mixture i_d, microamperes
0.2 *N* $(CH_3)_4NOH$	1.00	4.84	1.00	4.60	9.29
	1.50	7.34	1.00	4.60	11.70
.1 *N* NH_4Cl	1.326	5.13	0.950	3.66	8.96
.1 *N* LiCl	1.326	4.08	.950	3.33	7.14
.01 *N* $(CH_3)_4NOH$ .1 *N* $(CH_3)_4NBr$	1.00	5.22	1.00	5.25	10.50

corrected for the residual currents, are given in Table I. The shape of the acetophenone and the benzalacetone waves was, however, affected by the solutions used. In alkaline solutions acetophenone exhibited two waves while in neutral or slightly acid media only one wave was obtained. The reverse was true with benzalacetone, two waves appearing in ammonium chloride, lithium chloride and 0.01 *N* $(CH_3)_4NOH$–0.1 *N* $(CH_3)_4NBr$ solutions and only one in 0.2 *N* tetramethylammonium hydroxide solution. That *p*H was the factor influencing the height of the second wave and not the concentration of the tetramethylammonium ion was shown by the fact that increasing the concentration of tetramethylammonium bromide from tenth normal to two tenths normal in a hundredth molar tetramethylammonium hydroxide solution did not affect the results in any way.

The reason for the two waves for acetophenone is probably the direct reduction to acetophenone pinacol and to phenylmethylcarbinol. The possibility that the second wave represents the further reduction of acetophenone pinacol was eliminated since this compound did not give a wave in a 50% isopropanol solution of 0.2 *N* tetramethylammonium hydroxide. This result also rules out any slow alkaline cleavage of acetophenone pinacol to acetophenone and phenylmethylcarbinol, one possibility in view of the instability of benzophenone pinacol and other pinacols toward alkali observed by Bachmann.[3] Similarly the waves for benzalacetone are due to the reduction of benzalacetone itself since benzylacetone and 4,5-diphenyloctanedione-2,7, two possible reduction products, showed no reduction in a 50% isopropanol solution of tenth normal ammonium chloride.

The function of the benzalacetone in the reduction of acetophenone is not as yet clear. Benzylacetone and 4,5-diphenyloctanedione-2,7, two possible reduction products of benzalacetone, had no effect on the polarographic waves of acetophenone. The possibility that benzalacetone and acetophenone underwent a Michael reaction followed by condensation in alkaline medium to form 3,5-diphenylcyclohexen-2-one was eliminated since the wave obtained for this compound was entirely different from that obtained for a mixture of acetophenone and benzalacetone in alkaline medium. The effect of benzalacetone upon the acetophenone waves may be considered comparable to that of calcium and strontium ions and tetramethylammonium hydroxide upon the benzaldehyde wave observed by Tokuoka.[4] In this case benzaldehyde gave one wave at a *p*H greater than six. In solutions of salts of calcium and strontium and tetramethylammonium hydroxide, however, two waves of equal heights were obtained. No explanation was offered for the phenomenon.

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[3] W. E. Bachmann, THIS JOURNAL, **55**, 1179 (1933).

[4] M. Tokuoka, *Coll. Czech. Chem. Comm.*, **7**, 392 (1935).

Experimental

The current–voltage curves were determined manually by means of a Fisher Elecdropode after removing dissolved air in the usual way with tank nitrogen. All solutions were made up in 50% isopropanol by volume. For the ammonium chloride and lithium chloride solutions an electrolysis cell of the type described by Lingane and Laitinen[5] was used with a saturated calomel reference electrode. In these experiments the m and t values of the dropping electrode were, respectively, 1.931 mg./sec. and 4.10 seconds with the capillary dipping into distilled water at 25° and an open electrical circuit.

For the tetramethylammonium hydroxide solutions a cylindrical cell with a mercury pool anode was used. The m and t values of the dropping electrode in these experiments were, respectively, 3.296 mg./sec. and 2.23 seconds. The potential of the mercury anode in 0.2 N tetramethylammonium hydroxide was −0.250 volt (*vs.* saturated calomel electrode). In all of the above cases the temperature was 25°. In the experiments in 0.01 M tetramethylammonium hydroxide, 0.1 M tetramethylammonium bromide solution the potential was −0.150 volt and the temperature was 28°.

The acetophenone, benzalacetone and benzylacetone were purified by distillation before using. The sample of acetophenone pinacol used melted at 124–5°. 4,5-Diphenyloctanedione-2,7 and 3,5-diphenylcyclohexen-2-one were prepared according to directions given by Harries[6] and Kohler,[7] respectively.

Summary

1. Benzalacetone has no effect on the total diffusion current of acetophenone but affects the shape of the acetophenone wave.

2. The relative height of the first wave of acetophenone decreases with increasing alkalinity. In ammonium chloride and lithium chloride solutions, only one wave is observed.

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[5] J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

[6] C. Harries and G. Eschenbach, *Ber.*, **29**, 383 (1896).

[7] E. P. Kohler, *Am. Chem. J.*, **37**, 386 (1907).

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Heat Capacity and Entropy, Heats of Fusion and Vaporization and the Vapor Pressure of Silicon Tetramethyl

BY J. G. ASTON, R. M. KENNEDY AND G. H. MESSERLY

A preliminary value[1] for the entropy of gaseous silicon tetramethyl has shown that the potential hindering internal rotation of the methyl groups is about 1280 cal. This value was based on a heat of vaporization obtained from the vapor pressure equation and approximate state data. This paper presents a final value obtained using the measured heat of vaporization, and the complete thermal data down to 11.8°K. on which it is based.

Preparation and Purification of Silicon Tetramethyl.—The silicon tetramethyl was prepared from a Grignard reagent according to the procedure of Krause,[2] modified by the use of n-butyl ether as a solvent. The silicon tetrachloride and methyl iodide were purified by fractional distillation before use.

The silicon tetrachloride was added to the methylmagnesium iodide in n-butyl ether. After completion of the reaction, the solution was refluxed at 125° under a condenser kept at 30° until no more condensate formed in the carbon dioxide-snow trap attached to the outlet of the reflux condenser. The condensate was purified by distilling it into a solution of two moles of methylmagnesium iodide in one liter of n-butyl ether, stirring for five hours at room temperature and removing the product in the same manner. The gas was passed through two concentrated sulfuric acid traps, a potassium hydroxide tube and a phosphorus pentoxide drying tube before introduction into the laboratory low-temperature column. A middle cut of about 44 cc., boiling range 0.1°, was taken and put into gold calorimeter C in the usual manner.

The melting range of this sample (freezing point 171.78° K.) indicated 0.10 mole per cent. of solid-insoluble liquid-soluble impurity. However, the heat capacities of the liquid showed a peak 7° below the melting point of methyl iodide (207°K.). Qualitative examination of the sample showed the presence of an iodide; and gas density measurements showed that 20.1 mole per cent. of methyl iodide[3] was present. The failure to detect this in the melting point examination could be due only to the fact that the minimum boiling mixture (b. p. 26.1°) obtained in the fractionation was very close to the eutectic composition.

Thus 171.78°K. is the eutectic temperature of this binary system.

The methyl iodide was removed by formation of the methiodide of pyridine. A 100% excess of purified pyridine (based on the methyl iodide) was introduced with the sample into a glass bulb which was sealed and heated to 80°. The methylpyridinium iodide was separated by filtration and the silicon tetramethyl by distillation. The distillate was dried by passage over potassium hydroxide

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[1] Aston and Kennedy, THIS JOURNAL, **62**, 2567 (1940).

[2] Krause and v. Grosse, "Die Chemie der metall-organischen Verbindungen," Gebr. Borntraeger, Berlin, 1937, p. 258.

[3] In computing the number of moles per cc. the mixed gas was assumed to obey the modified Berthelot equation with the same critical constants that are assumed for pure silicon tetramethyl—see subsequent paragraphs.