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A Polarographic Study of Acetphenone and Benzalacetone

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One of the advantages of polarographic analysis is that, when a mixture of two or more substances is electrolyzed at a dropping electrode in the presence of an excess of supporting electrolyte, each substance will produce its own wave at a characteristic potential and the height of the wave will be proportional to its concentration. However, in the absence of a supporting electrolyte, the wave height for cations being reduced at the dropping electrode is dependent on the presence of another reducible substance. Heyrovsky and Bures (1), (2) first demonstrated that the limiting currents of potassium and sodium ions are increased or exalted by the preceding discharge of oxygen. Lingane and Kolthoff (3) also found a similar effect of thallous ions on the current-voltage curve of potassium ions. In a quantitative discussion of exaltation, Lingane and Kolthoff (3) assumed that the diffusion component of the limiting current is independent of the preceding discharge of a substance, and that it is only the migration component of the limiting current which is exalted.

Usually, in the presence of an excess of a supporting electrolyte, the component of the limiting current attributed to the migration of reducible cations, due to the potential gradient existing between the dropping electrode and the ions, is negligible; the limiting current is substantially equal to the diffusion current.

In almost all the electrolyses at the dropping electrode, the diffusion current of the substance was found to be independent of the presence of another reducible substance, provided there was an excess of supporting electrolyte. However, a few cases have been reported where the diffusion current was influenced by a preceding discharge of another substance. For example, while studying the relative oxidation-reduction potentials of various aldehydes and ketones, Adkins and Cox (4) found that the wave height of acetophenone was decreased by the preceding discharge of benzalacetone, as shown in Fig. 1. No explanation was offered.

In a supporting solution consisting of a 50% (by volume) mixture of ethanol and water which was 0.1 N in NH_4Cl as used by Adkins and Cox, current-voltage curves were obtained for individual ketones and their equimolecular mixtures. In contrast with the findings of Adkins and Cox, the results showed no interaction between the ketones.
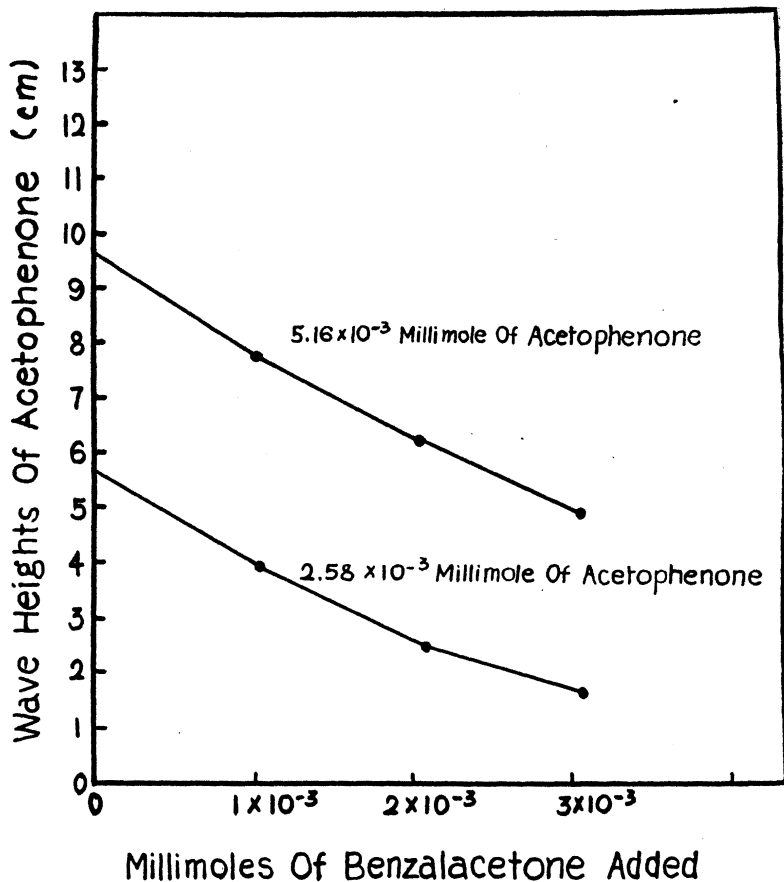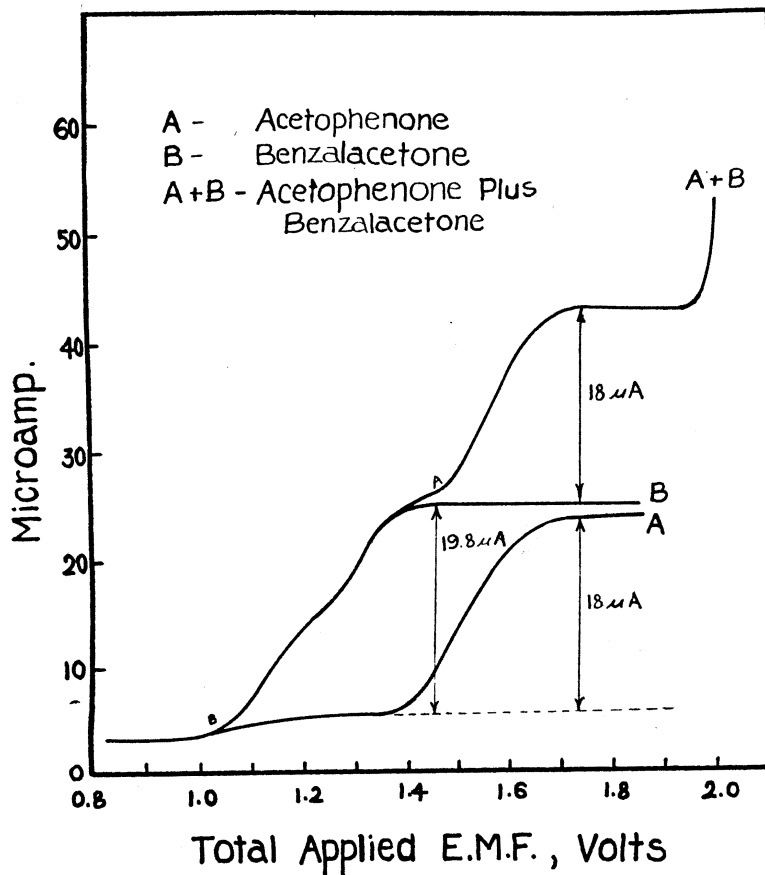
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Fig. 1. The Effect of Benzalacetone on the Wave Heights of Acetophenone (Adkins and Cox).

Capillary Characteristics: m = 0.890 mg/sec.;
t = 2.83 sec./drop (1.7 v.), 3.30 sec./drop (1.4 v.)

Fig. 2.   The Waves of Benzalacetone and Acetophenone.

The solutions were 0.005 molar in acetophenone, 0.0058 molar in benzalacetone, and contained 0.01% gelatine for the suppression of maxima. Their pH values were between 5.2 and 5.6. The electrolysis cell was maintained at 25°C. in a thermostat, and air was not excluded, since the waves of dissolved oxygen were negligibly small compared with those of the ketones. The same dropping electrode was used for all the measurements, and a saturated calomel electrode with an agar bridge served as reference electrode.
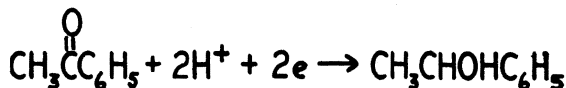
From the slope of the portion preceding a maximum, the resistances of the solutions were estimated to be 2000 ohms. Corrected for cell resistance, the half-wave potential of acetophenone was −1.48V. and the half-wave potentials of benzalacetone, which could not be de-

mated to be —1.15 V. and —1.30 V. Adkins and Cox found —1.52 V. for acetophenone (0.001 M) and —1.12 V. and —1.36 V. for benzalacetone (0.001 M), using a pool of mercury in the 0.1 N NH₄Cl solution as the internal anode. It seems probable that their values were not corrected for cell resistances. Assuming that the anode potential in 0.1 N NH₄Cl solution was equal to that of a 0.1 N calomel electrode, recalculation of their results with reference to a saturated calomel electrode yielded —1.43 V. for acetophenone and —1.03 V. and —1.27 V. for benzalacetone, with which the values obtained by the authors are in fair agreement.
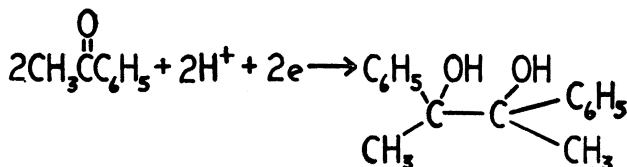
Next, in order to determine the effect of a lower hydrogen ion activity, the ketones were electrolyzed in the same supporting solution but with the pH adjusted to 7.7 by the addition of a 6 N NH₄OH solution. Again, benzalacetone was found to have no influence on the wave heights of acetophenone.

A similar study was made, using a McIlvaine standard buffer solution which had been diluted with ethanol until the alcohol concentration was 50% by volume. Since the ethanol-water solution of NH₄Cl used in the preceding experiments had pH values ranging from 5.2 to 5.6, the pH of the ethanol-buffer solution was adjusted to 5.4, in order to obtain comparable results. As in the NH₄Cl solution, benzalacetone was reduced in two steps. The total wave heights of the ketone in the two supporting solutions were about equal. On the other hand, the diffusion current of acetophenone was about one-half of that found in the NH₄Cl solution and the half-wave potential was intermediate in value with respect to those of the first and the second reduction waves of benzalacetone. In the NH₄Cl solution, the reduction wave of acetophenone was preceded by the waves of benzalacetone (Fig. 2). These facts led to the conclusion that the waves in the two supporting solutions correspond to two different courses of reduction of acetophenone.

I. In NH₄Cl solution:

$$CH_3\overset{O}{\underset{}{C}}C_6H_5 + 2H^+ + 2e \rightarrow CH_3CHOHC_6H_5$$

II. In ethanol-buffer solution:

$$2CH_3\overset{O}{\underset{}{C}}C_6H_5 + 2H^+ + 2e \rightarrow \underset{CH_3}{\overset{C_6H_5\ \ OH}{C}}-\underset{CH_3}{\overset{OH}{C}}-C_6H_5$$

An accurate measurement of the diffusion current of acetophenone from the current-voltage curve of a mixture of this ketone and benzalacetone was not possible because of the proximity of the second wave of benzalacetone to the wave of acetophenone.

Figures 3 and 4 show polarograms of the ketones in McIlvaine's standard buffer solutions (without ethanol) of various pH values.

The solutions were prepared by adding 2.5 ml. of 0.2% gelatin solution to 10 ml. of 0.08 M alcoholic solution of a ketone and diluting the mixture to 50 ml. with the buffer. The pH was determined with a Coleman pH Electrometer.
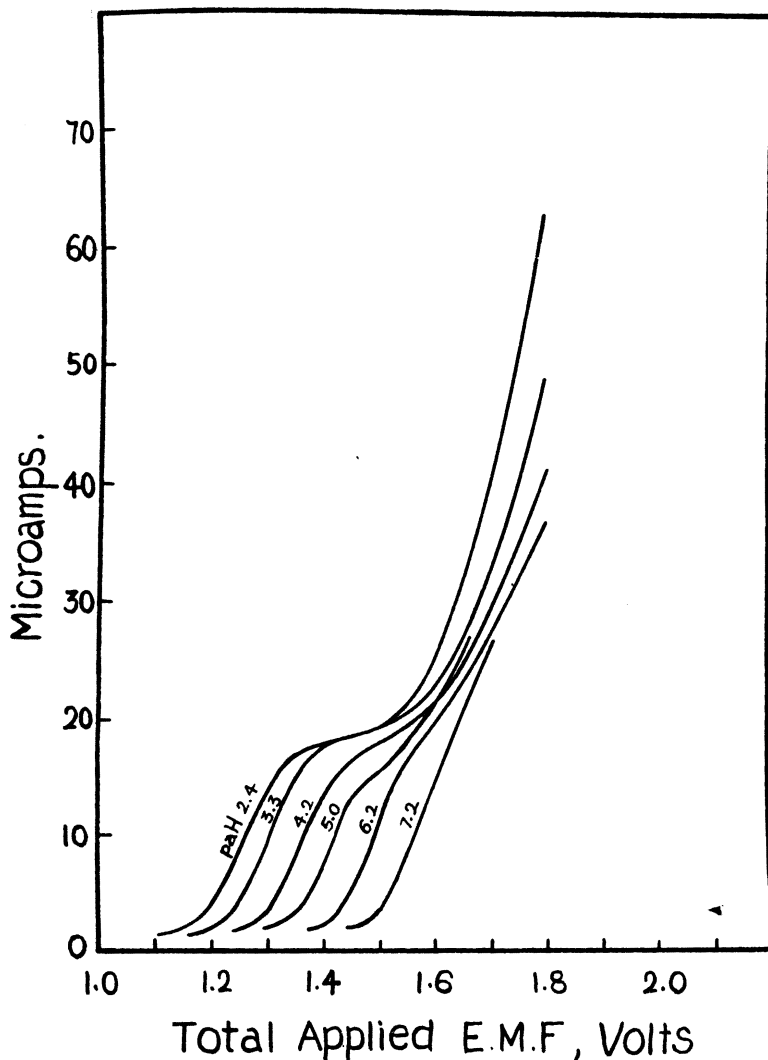

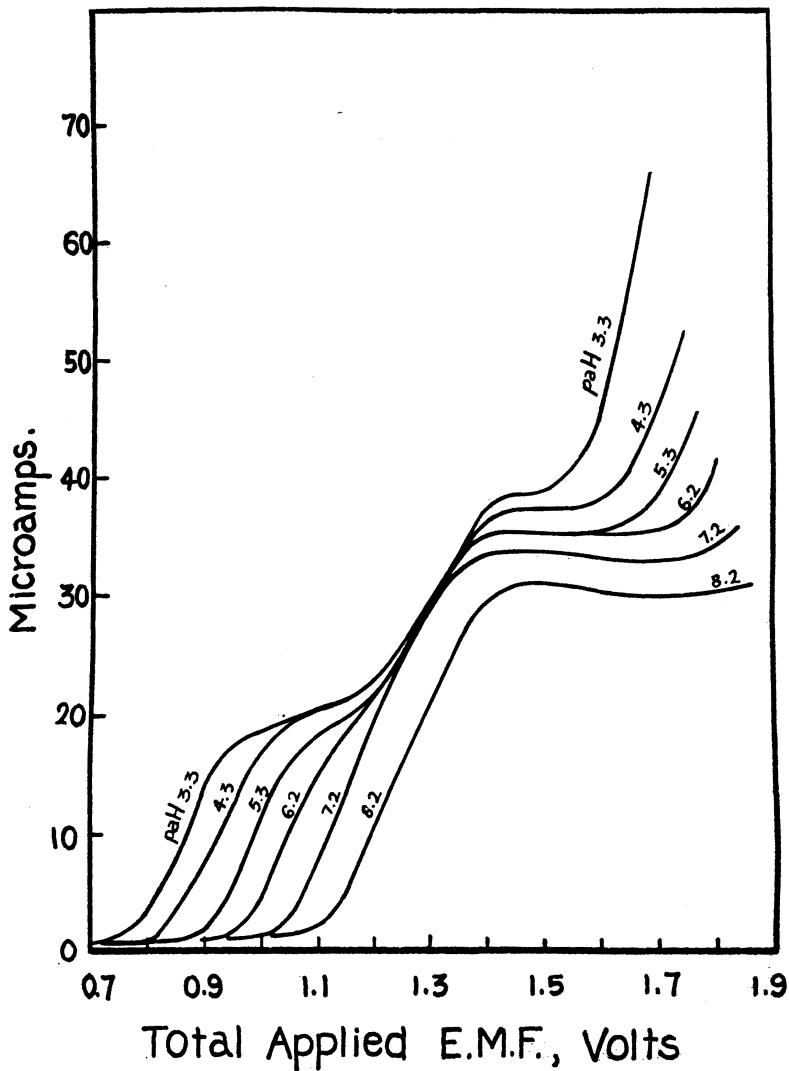Fig. 3.   Current-Voltage Curves of Acetophenone in McIlvaine's Buffer Solutions.

Fig. 4.   Current-Voltage Curves of Benzalacetone in
McIlvane's Buffer Solutions.

The ketones produced strong maxima in all the supporting solutions that were used. These maxima were completely suppressed by gelatin. Although KSCN suppresses a negative maximum in the case of zinc, it proved ineffective here.

SUMMARY

1. In contrast with the findings of Adkins and Cox, benzalacetone was found to have no depressive effect on the wave height of aceto-phenone within the range of concentrations studied (0.001 M to 0.005 M), which includes the concentrations used by them.

2. In an NH_4Cl supporting solution, acetophenone was reduced at the dropping electrode to an alcohol, but in McIlvaine's buffer solutions, the reduction wave found corresponded to its partial reduction to a glycol.

3. The current-voltage curves of benzalacetone and acetophenone in McIlvaine's buffer solutions of various pH values showed that the reduction wave of acetophenone and the first reduction wave of ben-zalacetone were, as expected, shifted to more negative potentials as the pH was increased. The second wave of benzalacetone was little affected by the change in pH.

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