octacarbonyl, $[Co(CO)_4]_2$, or cobalt hydrocarbonyl, $HCo(CO)_4$, functioning as the catalyst.[1]

In a third experiment, 300 p.s.i. of carbon monoxide was added ($8H_2$:1CO). The mixture was heated at 185° for 2 hours and at 200° for 1 hour, but no gas was absorbed. Distillation gave three fractions: a low-boiling portion containing unchanged butyraldehyde (83%); a middle fraction (1.4 g.) which infrared spectroscopy showed was free of butanol-1; and a residue (6.1 g.), part of which depolymerized to butyraldehyde on heating to 240–270°. In this case, sufficient carbon monoxide was present to poison the cobalt for the heterogeneous catalysis which was successfully conducted in the absence of carbon monoxide (first experiment), but insufficient carbon monoxide was present to permit the formation of $[Co(CO)_4]_2$ or $HCo(CO)_4$, which was a successful catalyst in the second experiment.

In a concluding experiment, butyraldehyde was treated with a clear benzene solution of $[Co(CO)_4]_2$ at 185° and 2000 p.s.i. of hydrogen. No hydrogenation occurred; the carbonyl was reduced to cobalt which did not function as a catalyst because of carbon monoxide poisoning. Distillation gave 39 g. (54%) of butyraldehyde; no butanol-1 was found in the residue (26 g.).

These experiments strongly indicate that the great variety of hydrogenations which occur in the presence of cobalt and a high partial pressure of carbon monoxide[1] probably proceed by homogeneous catalysis in which $[Co(CO)_4]_2$ or $HCo(CO)_4$ functions as the catalyst. Further confirmation was provided by four experiments with compounds containing sulfur. Under the conditions described, thiophenecarboxaldehyde and a solution of butyraldehyde containing small amounts of thiophene reacted rapidly with synthesis gas. With hydrogen alone, both hydrogenations were greatly retarded.

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STUDIES IN THE THEORY OF THE POLAROGRAPHIC DIFFUSION CURRENT. II. THE INSTANTANEOUS DIFFUSION CURRENT AND THE STREHLOW-VON STACKELBERG EQUATION

Sir:

In recent years a considerable body of information on the change of the instantaneous current at a dropping electrode during the life of a drop has become available.[1-4] These data show conclusively that the Ilkovič equation[5] is not an adequate representation of the phenomena occurring during the growth of a drop into a solution containing gelatin.

The subsequent appearance of a new equation for the average diffusion current[6] and its independent derivation by another method[7] have suggested its test with data secured by Taylor, Smith and Cooter[4] during the growth of two drops of t = 3.4 sec. into a 3 mM cadmium solution in 0.1 M potassium chloride containing 0.01% gelatin: these conditions are directly comparable with those used by Strehlow and von Stackelberg[6] in their study of the integrated average current.

The equation for the average current during the drop life

$$i_d/Cm^{2/3}t^{1/6} = 607nD^{1/2}[1 + 17D^{1/2}(t^{1/2}/m)^{1/3}] \quad (1)$$

becomes, on differentiation with respect to t

$$i_t = 708nD^{1/2}C[m^{2/3}t^{1/6} + 19.4D^{1/2}(m^{1/3}t^{1/3})] \quad (2)$$

Assuming m to be constant throughout the drop life, for the data of Taylor, Smith and Cooter we have

$$i_t = 7.46 \times 10^3D^{1/2}(t^{1/6} + 14.7D^{1/2}t^{1/3}) \quad (3)$$

or, taking the value of $D = 7.28 \times 10^{-6}$ cm.²/sec.

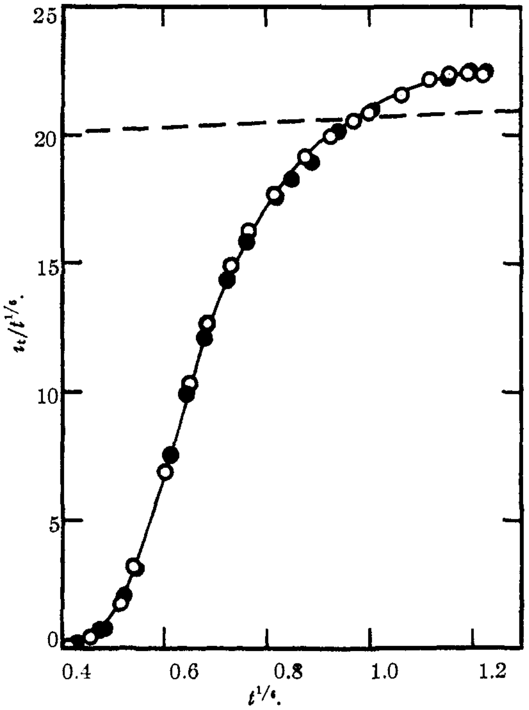

Fig. 1.—Plots of $i_t/t^{1/6}$ against $t^{1/6}$ for "drop one" (open circles) and "drop two" (solid circles): *cf.* ref. 4, p. 391. The dashed line represents the "theoretical" values according to equation (4).

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[1] J. H. Schulman, H. B. Battey and D. G. Jelatis, *Rev. Sci. Instruments*, **18**, 226 (1947).

[2] H. A. McKenzie, THIS JOURNAL, **70**, 3147 (1948).

[3] H. A. McKenzie, quoted by J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

[4] J. K. Taylor, R. E. Smith and I. L. Cooter, *J. Res. Natl. Bureau Standards*, **42**, 387 (1949).

[5] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 30–39.

[6] H. Strehlow and M. v. Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

[7] J. J. Lingane and B. A. Loveridge, THIS JOURNAL, **72**, 438 (1950).

given by Strehlow and von Stackelberg for cadmium in this supporting electrolyte

$$i_t/t^{1/6} = 20.12 + 0.798t^{1/6} \qquad (4)$$

Figure 1 shows a plot of $i_t/t^{1/6}$ against $t^{1/6}$ for the two drops reported,[4] together with the straight line predicted by equation (4). Below $t = 1$ sec., the relatively high back pressure decreases m, and therefore the diffusion current calculated on the assumption that m is invariant with time. However, the experimental values are much too low to be accounted for by any reasonable modification of the theory. Above $t = 1$ sec. the experimental values are too large by as much as 8%, and the "theoretical" slope appears to be attained only as a limit with increasing drop age.

It has been shown[1–4] that, under conditions similar to those prevailing in these experiments, the average current is, very closely, 0.80 times the maximum current instead of the 0.857 predicted by the Ilkovič equation. Equations (1) and (3) yield for the average and maximum currents the values 22.10 and 25.92 microamp., respectively, and the ratio of these figures is 0.853.

From these considerations we conclude that the Strehlow–von Stackelberg equation does not provide a significantly more satisfactory representation than does the Ilkovič equation of the change of instantaneous current with drop age.[8]

Acknowledgment.—This work has been supported by Contract Number AT (30-1)-842 between the Atomic Energy Commission and Yale University.

[8] NOTE ADDED IN PROOF: On the basis of experiments with 1 mM cadmium in 0.5 M potassium chloride–0.01% gelatin, Airey and Smales (*Analyst*, **75**, 287 (1950)) recently concluded that the $i_t/t^{1/6}$ prediction of the Ilkovič equation was obeyed to ±2.5% at drop ages between 0.75 and 3.9 sec. Their values show an ill-defined trend in accord with the experimental curve of Fig. 1, but they do not give sufficient data to allow comparison with the results of Taylor, Smith, and Cooter at very small values of t.

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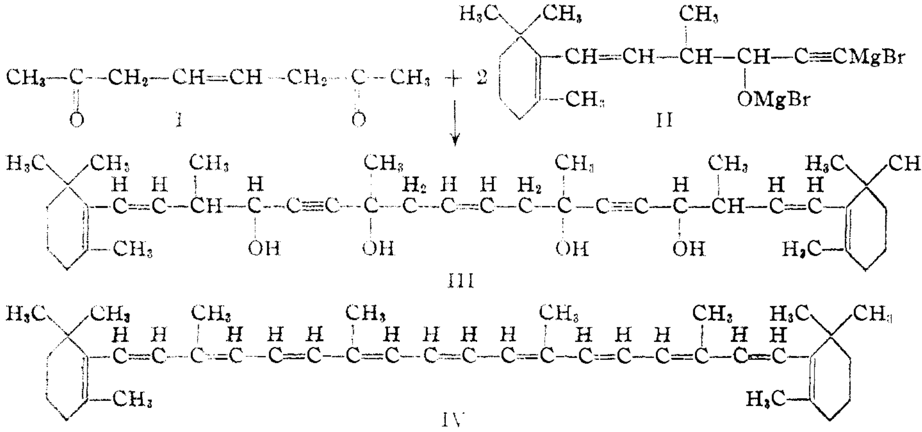
SYNTHESIS OF β-CAROTENE

Sir:

The recent preliminary announcements[1] in Europe of the synthesis of β-carotene prompted us to publish our own synthesis of this carotenoid. In our synthesis the ketone (I)[2] was allowed to react, via the Grignard reaction, with two moles of the acetylene carbinol (II) prepared from the C_{14}-aldehyde[3] to form the tetrol (III). This tetrol was selectively hydrogenated with two moles of hydrogen in the presence of palladium deposited on calcium carbonate, and the resulting product dehydrated with four mole-equivalents of pyridine hydrobromide in boiling pyridine.[4] The crude deep red product was recovered and chromatographed through a calcium hydroxide column. Typical carotene zones were formed and from these was isolated a product which upon two crystallizations from a benzene–methanol mixture gave red hexagonal and rhombic plates typical of β-carotene, m. p. 179–181°. A mixed m. p. with an authentic sample of natural β-carotene gave no depression. No mixed chromatogram tests were carried out. Our synthetic β-carotene gives a deep blue color with antimony trichloride in chloroform and an absorption spectrum in benzene identical with that of the natural β-carotene. It showed maxima (Beckman Model DU) at 429 (inflection), 454, and 484 mμ, respectively. The principal maximum at 454 mμ had an $E^{1\%}_{1\,\text{cm.}}$ value of about 2000. This work is being actively continued and detailed results will be reported elsewhere.



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[1] (a) Karrer and Eugster, *Compt. rend.*, **230**, 1920 (May 31, 1950); (b) Inhoffen, Bohlmann, Bartram and Pommer, *Chemiker-Ztg.*, **74**, 285 (1950); (c) Inhoffen, Pommer and Bohlmann, *ibid.*, **74**, 309 (1950).

[2] This ketone was first synthesized in this Laboratory by E. E. Mange, B.S. Thesis, M. I. T., 1948.

[3] Milas, *et al.*, THIS JOURNAL, **70**, 1587 (1948).

[4] Milas, *et al.*, *ibid.*, **70**, 1597 (1948).