larly, with benzene, at 10, 15 and 20°, values of 30.22, 29.56 and 28.92 were obtained as compared with the values of Young and Harkins[5] (p. 454), of 30.22, 29.55 and 28.88, respectively.

The pure dry nickel carbonyl was distilled at −2° into the apparatus which was connected with a mercury manometer. The apparatus was placed in a thermostat constant to ±0.025° and the surface tension determined under its own vapor pressure at different temperatures. Two independent sets of measurements were made on successive samples of the material. The results are given in Table I.

TABLE I

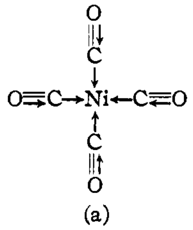
t, °C.....	8	14	20
γ.......	17.215	16.55	15.88
D^*......	1.34545	1.32446	1.31032
d^*......	0.00175	0.00238	0.00299
(P).....	258.75	260.40	260.65
Mean = 259.91.			

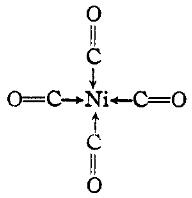
The densities D^* of the liquid were taken from the work of Mond and Nasini.[6] The vapor densities d^* were calculated from the vapor pressure measurements of Anderson,[7] assuming that the gas laws hold for nickel carbonyl vapor.

Discussion of Results

The value 259.9 for the parachor of nickel carbonyl is somewhat high compared to 250.8, the value calculated from the measurements of Ramsay and Shields.[1]

Experimental data[8] present strong evidence that (a) is the most probable structure for nickel carbonyl, though a resonance state between it and (b) is possible. Accepting (a) as the correct structure, the parachor of this should be four times that of CO plus that of Ni minus 4 × 1.6 for the four semi-polar links. Assuming that CO in the carbonyl has the same structure as free carbon monoxide, its parachor is 61.6 (the observed value for CO which presumably corresponds to resonance between C=O (P = 48.0) and $C \overset{\leftarrow}{\equiv} O$ (P = 69.6)), and that of the carbonyl is 240 + P_{Ni}. This gives (accepting 259.9 for Ni $(CO)_4$) the value 19.9 for P_{Ni}, which is possible but not in agreement with Sugden's value.


(a)


(b)

Summary

The surface tension of nickel carbonyl has been measured at 8, 14 and 20° and found to be 17.21, 16.55 and 15.88 dynes, respectively. Assuming the generally accepted structure for nickel carbonyl, a value of 19.9 for P_{Ni} is obtained from the experimentally determined mean parachor, 259.9.

ST. LOUIS, MO. RECEIVED OCTOBER 24, 1934

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(6) Mond and Nasini, *Z. physik. Chem.*, **8**, 150 (1891).

(7) Anderson, *J. Chem. Soc.*, p. 1655 (1930).

(8) Sutton and Bentley, *Nature*, **130**, 314 (1932); Sidgwick, "The Electronic Theory of Valency," Oxford University Press, London, 1929, p. 216.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Thickness of a Surface Film of Copper

BY M. L. NICHOLS

In 1887 Oberbeck[1] reported the results of his experiments on the thickness of a film of metal which will give the same electromotive force as the massive metal. Using a very small current, the metal was plated electrolytically on a sheet of platinum and the electromotive force between this and another sheet of platinum was measured. On standing, the plated metal dissolved and as soon as any platinum was exposed, there was a rapid decrease in the electromotive force. By making a number of such experiments, he was able to determine the current and the time necessary to plate out the metal required for this point of rapid decrease of electromotive force. Then from Faraday's law, and on the assumptions that the metal was plated out evenly and free from hydrogen, and that it had the same density as the massive metal, he calculated the thickness of the layer of metal. He found the values of 2.32–2.73 mμ for zinc, 1.57–1.91 mμ for cadmium and 0.69–0.73 mμ for copper.

Bancroft states[2] that "since the metal was

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(1) Oberbeck, *Ann. Physik*, [3] **31**, 337 (1887).

(2) Bancroft, "Applied Colloid Chemistry," 1932, p. 455.

probably porous and was not burnished, the figures are too high rather than too low. It is interesting to note that the lowest value is obtained with copper, the metal which gives the smallest crystals of the three."

If two electrodes of copper and platinum are placed in a copper solution and connected, copper should plate out on the platinum until a film, thick enough to act as the massive metal, is obtained. Then, by determining quantitatively this amount of copper, the thickness of the film can be calculated. By this method, the obvious errors of Oberbeck's method can be eliminated. He calculated his results from the current and the time by means of Faraday's law and, if some of the cuprous salt formed during electrolysis diffused away from the cathode or if any hydrogen was liberated, his results are necessarily too high. Also his deposit probably was not uniform, which would also give a high result while the method used here must give a uniform and non-porous deposit. Since Oberbeck's results are obviously wrong and too high, the above method was used to determine the thickness of such a layer of copper.

A copper coulometer solution was prepared according to the directions of Findlay.[3] Two 5 × 7.5 cm. sheet copper electrodes were cleaned with nitric acid and a layer of copper was plated out on these by placing each in some of the copper coulometer solution, between two platinum electrodes, and electrolyzing for ten hours at a current of 0.1 ampere. The solution was stirred continuously during the electrolysis.

The copper electrodes were then placed in a cell, containing some of the copper coulometer solution, and short circuited to a sheet platinum electrode, placed between the two copper electrodes and about 1 cm. from each. The sheet platinum electrode was approximately 5 × 6 cm., having an actual immersed area of 60.968 sq. cm. The cell was allowed to stand and the electromotive force between the copper and platinum electrode was measured at intervals, using a Type K potentiometer and a galvanometer. The copper should plate out on the platinum until the electromotive force between the two becomes zero. The actual results obtained were

Time, hrs.	0	4	20	24
Voltage	0.2649	0.0267	0.0126	0.0066
Time, hrs.	26.5	28	44	45.5
Voltage	0.0121	0.0044	0.0156	0.0056

The electromotive force between the two similar copper electrodes was measured also and found to be 0.0008 volt.

As a result of this preliminary experiment, the following procedure was adopted. The electrodes were immersed in the copper coulometer solution, connected and allowed to stand for at least twenty-four hours. (The actual times varied between twenty-four and forty-six hours.) The platinum electrode was then removed and washed thoroughly with water. The electrode had the appearance of a platinum electrode except on examination at an oblique angle, when it showed a reddish luster. The electrode was immersed in a cell containing 50 ml. of 1:1 nitric acid and after ten minutes the electrode was removed and the adhering solution rinsed off. The rinsings were collected in a platinum dish and evaporated to dryness. After this was repeated ten times, the nitric acid was also transferred to the platinum dish and evaporated to dryness. The total residue was dissolved in a small amount of water containing two drops of 1:5 sulfuric acid. The copper was determined[4] by electrolyzing the hot solution for thirty minutes at 2 volts and 0.013 ampere. In weighing the electrode, the weights were corrected for any change in zero point and sensitivity of the balance. A blank run was made in the same manner as the previous experiments, except that the platinum sheet was not connected to the copper electrodes, and this was deducted from the weight of copper obtained.

Two series of experiments of this type gave 0.192 and 0.228 mg. of copper. For ten experiments the total area of the platinum electrode is 609.68 sq. cm. and assuming the density of the deposited copper to be 8.89, the thickness of the film of copper is 0.35×10^{-6} mm. and 0.42×10^{-6} mm. or an average value of 0.39 mμ.

The thickness of a surface film of copper is therefore approximately one-half the thickness as determined by Oberbeck, which is what one would expect since, as was pointed out previously, his method must give values which are too high. The method used here could be used also for a metal such as zinc, even though a little hydrogen may be liberated during the deposition of the zinc. It could be used also, though with less accuracy, for nickel, which may contain some hydrogen since the weight of the hydrogen is relatively small. This would be impossible by Oberbeck's

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(3) Findlay, "Practical Physical Chemistry," 1932, p. 186.

(4) Pregl, "Quantitative Organic Microanalysis," 1930, p. 167.

method since the error introduced by the liberation of hydrogen on the calculation of the weight of the metal from Faraday's law would be very large.

Summary

A direct method for the determination of the thickness of a surface film of metal, which corrects for the obvious errors of Oberbeck's method, has been devised.

The thickness of a surface film of copper is about 0.39 mμ instead of 0.69–0.73 mμ, as given by Oberbeck.

ITHACA, N. Y. RECEIVED OCTOBER 29, 1934

[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Kinetics of Thermal Cis–Trans Isomerization. IV

BY G. B. KISTIAKOWSKY AND WALTER R. SMITH

The rates of isomerization of several *cis–trans* isomers in the gas phase have been dealt with in previous contributions.[1] The present paper describes experiments with the methyl esters of the *cis* and *trans* cinnamic acids.

Experimental Details

Preparation of *Cis*-methyl Cinnamate.—Phenylpropiolic acid was prepared by bromination of the ethyl ester of *trans* cinnamic acid and subsequent elimination with alcoholic potassium hydroxide. Treatment with a cold saturated aqueous solution of hydrogen bromide yielded a mixture of β-bromocinnamic and allo-β-bromocinnamic acid.[2] Separation of these two acids was largely effected through the barium salt, the barium salt of the *trans* modification being much less soluble in water than that of the *cis-β*-bromo acid. By treating the acid with zinc dust in alcohol[3] a mixture of about 80% *cis*-cinnamic acid and 20% *trans* cinnamic acid was obtained. A first separation of the acid was carried out by converting the acids to the calcium salts, the salt of the *trans* acid being much less soluble than that of the *cis* form. Final separation was achieved by means of the aniline salt.[4]

Two recrystallizations gave a product melting 82–83°. Treatment with dilute aqueous sodium hydroxide yielded pure isocinnamic acid. The acid was esterified by treating an ether suspension of the silver salt with methyl iodide. The ester was washed with sodium bisulfite, sodium bicarbonate and finally with water. After drying and sucking off all the ether, the ester was twice distilled at reduced pressure; melting point −3.5°; n^{20}_{D} 1.5528.

Preparation of the *Trans* Ester.—The *trans* methyl cinnamate was obtained by treating Kahlbaum cinnamic acid with methyl alcohol in the presence of concentrated sulfuric acid according to the method of Fischer and Speier.[5] The ester had the melting point 34°.

Method of Analysis.—The method of analysis was essentially the same as that described in an earlier paper,[1c] except that the sample was placed in a jacketed tube which was immersed in an unsilvered Dewar flask containing ether chilled to a few degrees below the melting point of the sample. The bath warmed very gradually and the temperature at which the last crystal disappeared was noted by means of a single junction copper–constantan thermocouple. Calibration was effected by following the same procedure with known mixtures of the isomers. Figure 1 is a reproduction of the calibration curve.

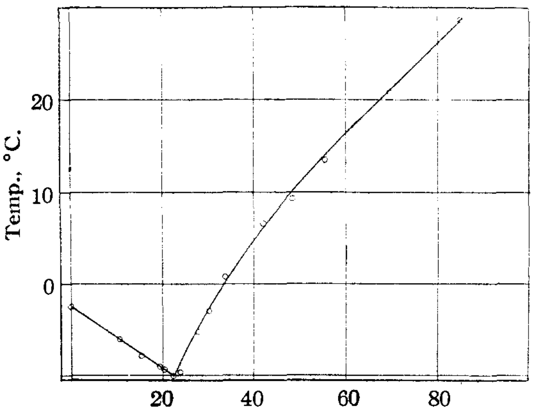

Fig. 1.—Freezing points of *cis* and *trans* methylcinnamic esters.

Experimental Procedure.—The apparatus employed was the low pressure static system described elsewhere.[1b] The technique of starting and stopping runs also has been described adequately in the earlier papers.[1]

Experimental Results and Discussion

The runs with the *cis* isomer proceeded without any appreciable decomposition. On freezing out the product at the end of the run, crystals identical in appearance with the *trans* ester were obtained. Some of the crystals were dried and their melting point determined as 34°, identical with that of the previously prepared *trans* ester. The mixed melting point was unchanged.

Tables I and II present the data accumulated in

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[1] (a) G. B. Kistiakowsky and M. Nelles, *Z. physik. Chem.*, **152**, 369 (1931); (b) M. Nelles and G. B. Kistiakowsky, THIS JOURNAL, **54**, 2208 (1932); (c) G. B. Kistiakowsky and Walter R. Smith, *ibid.*, **56**, 638 (1934).

[2] Sudborough and Thompson, *J. Chem. Soc.*, **83**, 1158 (1903).

[3] Liebermann and Scholz, *Ber.*, **25**, 950 (1892).

[4] Liebermann, *ibid.*, **24**, 1102 (1891).

[5] Fischer and Speier, *ibid.*, **28**, 3254 (1895).