(cor.), which is 5° higher than that recorded in the literature. The yield is about 50%. The compound is rather resistant to hydrolysis by water or alkali.

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Ferric Thiocyanate

BY H. I. SCHLESINGER

Recently Bent and French[1] indicated that they were unable to confirm the observation of Schlesinger and VanValkenburgh[2] that aqueous solutions of ferric thiocyanate contain a colored substance which migrates to the anode. Such solutions are complex, and observations of the phenomenon must be made under comparable conditions to be reproducible. Some years ago, M. Møller apparently encountered the same difficulty, but communicated with us before publication of his papers on this subject.[3] We were glad to furnish him the necessary information, and would have been glad to do so in the case of Bent and French. Since the matter has come up again, it seems desirable to publish some details concerning the original and some more recent experiments.

In the earlier work (carried out by Dr. VanValkenburgh at the University of Colorado) gelatin was used to decrease diffusion, and the results were later confirmed (with the aid of Dr. A. B. Burg) with solutions fixed with agar-agar. In most experiments the solutions were acidified. Bent and French state that the use of both gelatin and agar agar is out of the question since the thiocyanate solution was decolorized by these solutions. This difficulty is, however, easily overcome. Apparently the color is destroyed by impurities in gelatin or agar-agar. These impurities are rendered ineffective by addition of just enough ferric thiocyanate to produce a faint color, not deep enough to prevent observation of the migration effects.

To make sure that the gelatin or agar-agar had not been responsible for the migration toward the anode, observed in these experiments, Dr. H. C. Brown and I recently carried out additional ones in which these substances were not used. The electrolytic cell was a U-tube (25 mm. in width) to the bottom of which was sealed a narrower bent tube, fitted with a stopcock and storage bulb, from which ferric thiocyanate solution could be delivered into the U-tube. The latter contained a colorless solution. Slow introduction of the ferric thiocyanate resulted in the establishment of a fairly sharp boundary between the colored and colorless solutions, and diffusion across the boundary was very slow compared to the effects produced by the current (18 v., corresponding to a potential gradient of approximately 0.5 v./cm.). In some of the experiments the platinum electrodes were immersed directly in the colorless solution; in those marked* the electrodes were immersed in small secondary compartments (containing dilute sulfuric acid) which were in turn immersed in the colorless solution. This device, described by MacInnes,[4] not only prevents stirring but also avoids disturbing oxidation of thiocyanate ion to dithiocyanogen. Its use did not, however, materially alter the results. The details of the experiments are summarized in the table.

EXPERIMENTAL DATA

	Colored solution, *N*			Colorless solution, *N*	
Expt.	KCNS	Ferric salt	Acid	KCNS	Acid
1 and 2	4.0	0.1	0.1 H_2SO_4	2.0	0.02 H_2SO
3*	like Expt. 1			like Expt. 1 except*	
4	1.0	0.1	0.1 H_2SO_4	0.5	0.02 H_2SO_4
5*	like Expt. 4			like Expt. 4 except*	
6	4.0	0.1	0.1 H_2SO_4	...	0.3 HNO_3
7	4.0	0.1	0.1 HNO_3	2.0	0.1 HNO_3

The ferric salt was the sulfate in all experiments except the seventh in which the nitrate was used. In Expts. 1, 2, and 3, one colored boundary in ten minutes had advanced from 1.5 to 2.0 mm. toward the positive electrode, and the other boundary had receded from 1.0 to 1.5 mm. from the negative electrode. In Expts. 4 and 5 migration was in the same direction but seemed to be slightly slower. The difference was less than 0.5 mm. and is probably not significant; if real, it might be due to the difference in the character of the voltage distribution in the electrolytic column. The sixth experiment was continued for one hour, during which time one boundary moved nearly 5 mm. toward the anode, while the other remained nearly stationary. That the motion was not more extensive is probably due to the absence of thiocyanate ion in the colorless solutions; before a permanent color could persist, enough excess thi-

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(1) Bent and French, THIS JOURNAL, **63**, 568 (1941).

(2) Schlesinger and VanValkenburgh, *ibid.*, **53**, 1212 (1931).

(3) (a) Thesis, "Studies on Aqueous Solutions of the Iron Thiocyanates." Copenhagen, 1937; (b) *Kem. Maanedsblad*, **18**, 138 (1937); (c) *Chem. Abst.*, **33**, 9179 (1939).

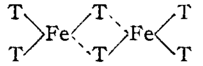
(4) MacInnes, "The Principles of Electrochemistry." Reinhold Publishing Corporation, New York, N. Y., 1939, p. 73.

ocyanate ion would have to accumulate to prevent dissociation of any complex ion which might migrate into the colorless portion. The seventh experiment was carried out because it had been suggested that migration of ferric ion toward the anode might have been caused by the presence of polyvalent sulfate ion. In this experiment the only negative ion, aside from the thiocyanate, was the nitrate ion. The latter was chosen, rather than some other univalent ion, in part because it does not affect the ferric thiocyanate color even when present in much higher concentrations than those here employed, and because it is an ion commonly present in qualitative analyses for ferric ion. The results were practically identical with those of the other experiments, showing that the migration observed is not dependent on the presence of sulfate ion. In all of the experiments the boundaries remained remarkably sharp; in Expt. 6 which continued during one hour, the boundaries were definitely sharper at the end of that period than at the start of the experiment.

In most of these experiments thiocyanate ion was used in both colorless portions to decrease dissociation of any complex ion (positive or negative) which might migrate into these solutions. It was expected that migration of ferric ion into the cathode compartment would produce red color there, and cause an apparent migration toward the cathode, but this phenomenon was not observed. Several explanations might be offered, for example, that ferric ion, encountering a great excess of thiocyanate ion in the cathode compartment, is converted completely into a negative complex thiocyanate ion, which is immediately driven away from the negative electrode. No check of this or any other explanation was attempted.[5]

On the basis of work in part similar to that of Bent and French, Møller had already reached the conclusion, now proposed by the former, to the effect that solutions of ferric thiocyanate contain $Fe(CNS)^{++}$ and $Fe(CNS)_2^+$ ions, and had given values for their stability constants. He ascribes the migration of the red color to the anode, observed by us, to the presence of a negatively charged, colloidal basic ferric thiocyanate. This explanation seems improbable in view of the fact that most of all the older and all of the recent migration experiments herein described, were carried out in solutions containing considerable concentrations of acid.[6]

Møller's studies on the autoreduction of ferric thiocyanate, on ferrothiocyanate ions and on complex compounds containing dithiocyanogen, led him to emphasize the fact that solutions of ferric thiocyanate are far more complex than is generally realized. He admits that in high concentrations of thiocyanate ions, small amounts of a negative ion, $Fe(CNS)_4^-$ may be present. Although our migration experiments lead us to believe that he may overestimate the amount of excess thiocyanate ion required and may underestimate the amount of the negative complex ion present, we are inclined to favor the formula he assigns to the latter. It will be recalled that the major purpose of Schlesinger and VanValkenburgh's work was to show that, in non-aqueous solutions, ferric thiocyanate is dimeric, and that this dimeric substance has the same absorption spectrum as do aqueous solutions. At the time (1931), analogy with cupric and cadmium salts suggested $Fe(Fe(CNS_6))$ as the most likely constitution of the dimer. Since then studies on other dimeric compounds of trivalent elements make the following bridged structure for the dimer in question seem very possible (T represents thiocyanate ion in the formula)



In such a compound, iron has the coördination number 4; consequently the dissociation of the dimer into two $Fe(CNS)_4^-$ ions seems reasonable in aqueous solutions containing an excess of thiocyanate ions. Such an excess was used in the experiments herein described, and is characteristic of the conditions under which the thiocyanate test for iron is made. The larger concentrations of iron employed by us in the migration experiments might readily be counterbalanced by the still larger excess of thiocyanate ion which would inevitably be used in testing for small amounts of iron. But it is also clear that any negative ferri-

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(5) In several experiments carried out before those just described, migration toward both anode and cathode was observed. But in these experiments a sintered glass plate had been sealed into the U-tube in a position about 1 cm. above the point at which the boundary was to be established. We have little confidence in the significance of these observations, since the boundaries did not remain sharp, as they did in the simpler apparatus later used, thus indicating that the resistance of the glass plates introduced secondary effects (*e. g.*, convection due to local heating). Unfortunately we could not reproduce the conditions of Bent and French's experiments because the latter do not make clear what concentration of ferric ion they employed. Presumably it was much smaller than in our work.

(6) Sulfates in excess destroy the red ferric thiocyanate color. The amount of sulfuric acid used in the experiments described was, however, too small to cause interference with the observations.

thiocyanate ion must be more or less dissociated in solution, and we do not wish to deny that ions of the type postulated by Møller and by Bent and French play an important role in this test.

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Dicyclopentadiene: Preparation from the Monomer; Dielectric Constants of Dimer at Several Temperatures

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The usual method of preparing dicyclopentadiene is to fractionally distill the crude, impure dimer, and allow it to polymerize at room temperature overnight. This procedure is repeated a number of times, depending upon the purity of the original material, until a fraction is obtained that distills over at 41.5°—the boiling point of pure cyclopentadiene. When this latter material polymerizes, it yields a white, crystalline solid. The accepted values for the melting point and refractive index of dicyclopentadiene are given as 31.5° and 1.5120 (20°), respectively.

In an attempt to shorten the preparation of the dimer, we have adopted a slightly different procedure. Dicyclopentadiene obtained through the courtesy of the Research Laboratory of the United Gas Improvement Co. of Philadelphia was a faint straw-colored liquid containing 98% dimer. It was fractionally distilled once, and the distillate which came over between 40 and 44° was collected. This was allowed to stand overnight at 15°. The incompletely polymerized liquid was then placed under vacuum to remove the last traces of monomer and any other volatile impurities. Crystallization took place suddenly. The melting point of this crystalline solid was 27.8°, corrected, but the refractive index of the melt was identical with that of the solid which melted at 31.5°. After resolidification, the melting point was 31.5°, the same as that of the dicyclopentadiene prepared by the previous method.

It was found that low temperature (15–20°) was essential to the formation of the above crystals which we shall call an isomer of dicyclopentadiene. This form of the dimer was readily reproducible, the melting point being 27.8° for each preparation. The melting point and freezing point after resolidification was always 31.5°. When polymerization was carried out at slightly higher temperatures and when polymerization was not hastened by pumping off the more volatile monomer, the solid produced melted at 31.5° and possessed a strong, camphor-like odor. The isomer, on the other hand, had only a slight odor. Microscopic examination showed the crystalline forms to be quite different.

This evidence seems to indicate that a polymorph or an isomer of dicyclopentadiene has been obtained. From the accepted formula of this compound, *cis* and *trans* isomers are possible. It is reasonable to assume that these two forms exist as dynamic isomerides, since any operation which changes the form of the crystals melting at 27.8° leads, upon resolidification, to the more stable form having a melting and freezing point of 31.5°.

Experimental.—The dielectric constants were measured with a parallel resistance bridge previously described.[1] The beat frequency was set at 1000 cycles. A small multiple plate variable condenser inserted in a small Pyrex tube was used as the cell. About 25 ml. of liquid sample was required to completely immerse the plates of the condenser. The cell assembly was placed in a thermoregulated oven which was controlled to ±0.05°. The capacitance of the cell in air did not change over the temperature range employed. The time allowed for the temperature of the cell to reach equilibrium with the oven was forty-five minutes for each 10°.

No difference in dielectric measurements was observed when a frequency of 21,000 cycles was used instead of 1000. The values of the dielectric constant of dicyclopentadiene thus obtained were

t° C.	40	50	60	70	80	90	100
ϵ	2.43	2.41	2.39	2.37	2.35	2.33	2.31

These data indicate that over this temperature range dicyclopentadiene does not possess a very high dipole moment.

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(1) American Society for Testing Materials, Specification D150 36T.

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NEW COMPOUNDS

Phenacyl, *p*-Phenyl- and *p*-Bromophenacyl, and *p*-Nitrobenzyl Esters of Certain α-Hydroxy Fatty Acids

The authors recently had occasion to synthesize a series of α-hydroxy fatty acids, of which, among other derivatives, the following new esters were prepared. The procedures for their preparation and for the determination of