polarization effect. It was found that an electrode either anodically or cathodically polarized in this fashion remained in its same condition after several hours of standing in 1 *M* sulfuric acid and was not changed even by several minutes in hot concentrated nitric acid. By "remaining in its same condition" is meant that the electrode would exhibit the same behavior in a subsequent electrolysis, which was the only criterion we could apply as to the state of the surface of the electrode.

Figure 1 shows the subsequent effect in an arsenic oxidation of prior hydrogen and oxygen pre-polarization treatment of the platinum anode. Figure 2 shows similar behavior in an iron oxidation.

It was further observed (Fig. 3) that if an oxygen pre-polarized electrode was allowed to stand for one hour in the arsenic solution before beginning the electrolysis the electrode slowly reverted to a condition similar to that of a hydrogen pre-polarized electrode. The most likely explanation is that the arsenic(III) reduces the platinum oxide (probably (PtO) and gives a clean platinum surface. A similar process occurs if the electrode stands in the iron solution before the electrolysis is begun but the reaction is quite rapid, about 10 to 20 seconds sufficing for the complete removal of the oxide. The speed of this reaction probably accounts for this effect not having been observed before in iron oxidations. However, it should be noted that, as Fig. 2 indicates, if the potential is applied and maintained, then the current remains low throughout the entire electrolysis. This means that the iron solution cannot reduce the oxide while the potential is applied and oxidation is occurring at the electrode.

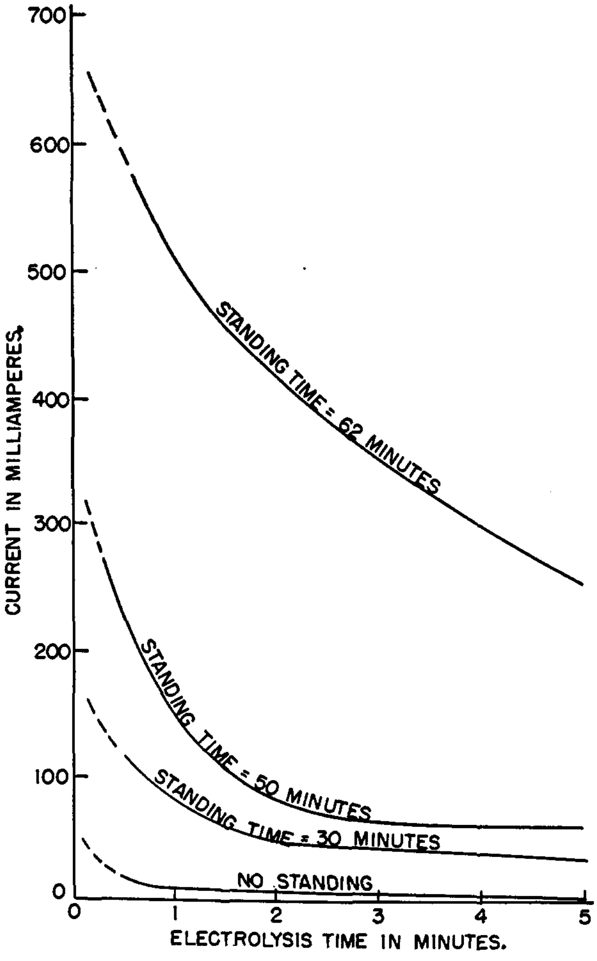

Fig. 3.—Effect of oxygen pre-polarized electrode standing in As(III) solution prior to electrolysis.

Acknowledgment.—This research was supported in part from funds granted by The Ohio State University Research Foundation to the University for aid in fundamental research and in part by a grant from the E. I. du Pont de Nemours and Company.

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X-Ray Examination of Polychlorotrifluoroethylene[1]

BY H. S. KAUFMAN

RECEIVED OCTOBER 24, 1952

The X-ray investigation of the structure of polychlorotrifluoroethylene has been undertaken in order to obtain an understanding of the behavior of the polymer in terms of its structural parameters. The polymer, known commercially as KEL-F, is of interest because of its chemical inertness, low solubility, high softening point, and satisfactory electrical and mechanical properties.

The development of crystallinity at temperatures below the first order transition temperature at 211° has been investigated by X-ray methods. The data supplement those obtained by Price[2] using optical methods.

Debye–Scherrer diagrams of the polymer were obtained using crystal monochromatized CuKα radiation and a flat camera. The patterns of unoriented polycrystalline samples showed one strong line at about 5.5 Å. and several other relatively weak lines at smaller spacings. A high resolution Geiger counter spectrometer was used to study the fine structure that had been observed in some of the Debye–Scherrer patterns of highly crystalline samples.

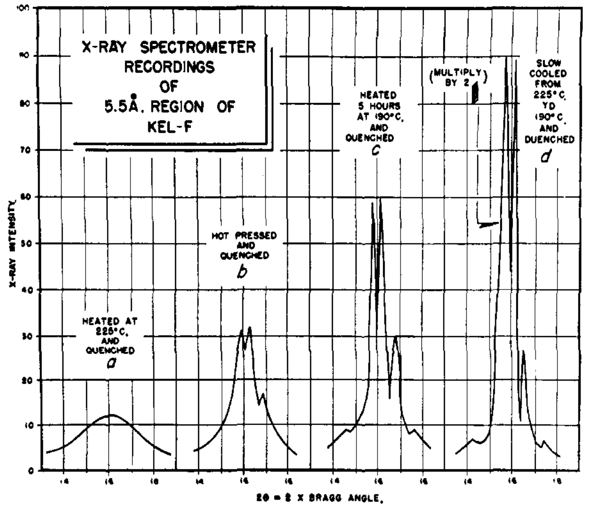

Fig. 1.

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[1] This paper was presented at the Diamond Jubilee Meeting of the American Chemical Society held in New York in September, 1951.

[2] F. P. Price, THIS JOURNAL, **74**, 311 (1952).

Typical spectrometer patterns of the 5.5 Å. region of samples of varying degrees of crystallinity are presented in Fig. 1. The quick quenching to a low temperature of polymer heated above its transition temperature results in a glass-clear sample which gives a low intensity, broad diffraction line characteristic of a relatively disordered amorphous structure (Fig. 1a). Extensive crystallinity with increasing opacity is developed by lengthening the residence time of the polymer at temperatures between 190° and the transition temperature. The increase in crystallinity is accompanied by a splitting of the broad amorphous line into two strong and relatively sharp lines with less intense lines at the side (Figs. 1b, c, d).

The influence of molecular weight on the development of crystallinity was investigated by studying the effect of the various thermal treatments noted in Fig. 1 on samples with molecular weights of 50,000, 75,000 and 100,000, respectively. For a given heat treatment, the degree of crystallinity developed varied inversely with molecular weight.

Fiber diagrams were obtained from highly crystallized and oriented fibers prepared by the hot drawing of the polymer. The fiber patterns varied with degree of orientation. Arcs which developed on slight orientation split in two at the equator as the extent of orientation was increased and finally, in the most oriented sample, sharp spots were formed. The spacings and relative intensities of these spots were in exact correspondence with the 5.5 Å. region lines observed in the spectrometer curves of the most crystalline sample.

Measurement of the lateral spacings along the row lines of the fiber diagrams and of the lines observed in the Debye–Scherrer patterns gave a series of spacings, beginning with 5.6 Å., which were in the inverse ratios of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$. These ratios, being characteristic of the hexagonal system, suggested that the polymer chains were packed in hexagonal unit cells. One dimension of the unit cell was calculated from these data and found to be 6.5 Å. The repeat distance along the fiber axis was determined to be 35 Å. from measurements of the layer-line separation of the spots. These data established the unit cell to be hexagonal, with the dimensions $A = 6.5$ Å. and $C = 35$ Å.

One structure which accounts for the extraordinarily long fiber spacing of 35 Å. is a spiral chain arranged so that the spiral starts to repeat itself after approximately 14 monomer units. This structure is similar to that which has been assigned to the spiral of polyisobutylene[3] and of Teflon.[4] A planar zig-zag chain such as in polyvinyl chloride or polyethylene is ruled out because it requires a fiber axis spacing of about 5 Å.

On the basis of this assumed structure, the density of the polymer may be calculated using the equation

$$d = \frac{1.65 \times M \times n}{V}$$

where

M = molecular weight of monomer unit = 116.5
n = no. of monomer units per unit cell = 14
V = volume of unit cell = 1290 Å.[3]

The calculated value is 2.10 g./cc, in agreement with the value of 2.12 g./cc. determined experimentally by the flotation method using a solution of *sym*-tetrabromoethane and diethyl phthalate.

Acknowledgments.—The author is grateful to Drs. E. Solomon, I. Fankuchen and D. Harker for their helpful comments and suggestions.

M. W. KELLOGG CO.
NEW YORK, N. Y.

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[3] C. S. Fuller, C. J. Frosch and N. R. Pape, THIS JOURNAL, **62**, 1909 (1940).

[4] R. H. H. Pierce, W. M. D. Bryant and J. F. Whitney, presented at National A. C. S. Meeting, Buffalo, N. Y., March, 1952

Dissociation Constants of Substituted Ethylenediamines[1]

BY FRED BASOLO, R. KENT MURMANN AND YUN TI CHEN

RECEIVED NOVEMBER 6, 1952

In the course of investigating the stepwise formation constants of numerous metal ammines, it was necessary to determine the acid–base dissociation constants or "hydrolysis" constants of the amines. These dissociation constants have been reported for the N-alkylethylenediamines[2] and this paper gives an account of analogous determinations for several NN'-dialkylethylenediamines and C-substituted ethylenediamines.

Experimental

Reagents.—NN'-diMeen, NN'-diEten, NN'-di-*n*-Pren and NN'-di-*n*-Buen[3] were prepared by the method of Schneider.[4] NN'-di-*i*-Pren was prepared by a modification of the procedure of Zienty,[5] using ethylene dibromide and isopropylamine. One mole of ethylene dibromide was refluxed with five moles of isopropylamine for 24 hours. The mixture became almost solid with crystals. An excess of 20% sodium hydroxide solution was added and the mixture distilled over solid sodium hydroxide. The amine was then distilled over sodium; yield 60%.

Both *dl*-bn and *m*-bn were prepared by reduction of dimethylglyoxime with platinum and hydrogen in a Parr bomb (80% yield)[6] and also by reduction with Raney nickel–aluminum alloy and aqueous alkali (41% yield).[7] The second method was found to be the most convenient in spite of the low yield because it could be carried out on a larger scale. The *meso* and *racemic* bn's were separated by fractional crystallization of the dihydrochlorides from methyl alcohol. The *racemic* form is about eight times more soluble than the *meso* form at room temperature. The free amines were liberated by the reaction of the calculated amount of sodium methoxide with the dihydrochlorides in absolute alcohol, followed by distillation under reduced pressure.

iso-Bn was prepared by the reduction of α-aminobutyronitrile with lithium aluminum hydride in anhydrous ether. Eighty-four grams of α-aminoisobutyronitrile in 200 ml. of anhydrous ether was added dropwise, over a period of two hours, to a well-stirred slurry of 76 g. of $LiAlH_4$ and 2 l. of

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[1] This investigation was supported by a grant-in-aid from the National Institutes of Health; Grant No. G-3239.

[2] F. Basolo and R. K. Murmann, THIS JOURNAL, **74**, 2373 (1952).

[3] The diamines discussed here are designated as follows: NN'-diMeen = N,N'-dimethylethylenediamine; NN'-diEten = N,N'-diethylethylenediamine; NN'-di-*n*-Pren = N,N'-di-*n*-propylethylenediamine; NN'-di-*i*-Pren = N,N'-di-*i*-propylethylenediamine; NN'-di-*n*-Buen = N,N'-di-*n*-butylethylenediamine; pn = 1,2-diaminopropane (propylenediamine); *dl*-bn = *rac*-2,3-diaminobutane; *m*-bn = *meso*-2,3-diaminobutane; *iso*-bn = 1,2-diaminoisobutane; TetraMeen = 2,3-diamino-2,3-dimethylbutane; *dl*-stien = *rac*-1,2-diphenylethylenediamine; *m*-stien = *meso*-1,2-diphenylethylenediamine.

[4] P. Schneider, *Ber.*, **28**, 3074 (1895).

[5] F. B. Zienty, THIS JOURNAL, **68**, 1388 (1946).

[6] L. B. Clapp, Ph.D. Thesis, University of Illinois, 1941.

[7] F. H. Dickey, W. Fickett and H. J. Lucas, THIS JOURNAL, **74**, 944 (1952)