Proof of Structure of Isopropylthiophene.—The mono isopropyl thiophene obtained by the alkylation of thiophene by propylene and also by isopropyl alcohol showed constants in agreement with those given by Scheibler and Schmidt[5] for the 2-isomer. Two color tests, described by the same authors, indicated that our isopropylthiophene was the 2-isomer. More reliable evidence was obtained by converting it into its mono acetyl derivative, which was then converted into its known oxime (crystallized from Skellysolve B; m. p., 74–75° (cor.); lit., 74°) and *p*-nitrophenylhydrazone (crystallized from methyl alcohol; m. p., 193–194.5° (cor.); lit., 198°), both of which have been prepared by Scheibler and Schmidt from authentic 2-isopropylthiophene. The mixed melting point of the *p*-nitrophenylhydrazones showed that 2-isopropylthiophene was produced by both the propylene and the isopropyl alcohol alkylation of thiophene. This identity was confirmed by the color tests.

Anal. (oxime of 2-isopropyl-5-acetylthiophene). Calcd. for $C_9H_{13}NOS$: C, 59.0; H, 7.1; N, 7.6; S, 17.5. Found: C, 59.6; H, 7.5; N, 7.6; S, 17.7.

Anal. (*p*-nitrophenylhydrazone of 2-isopropyl-5-acetylthiophene). Calcd. for $C_{15}H_{17}N_3O_2S$: C, 59.4; H, 5.7; N, 13.9; S, 10.6. Found: C, 59.3; H, 5.5; N, 14.1; S, 10.4.

Acknowledgment.—The authors express their thanks to Patricia David and Elizabeth Depp for assistance in the experimental work.

Summary

Thiophene was alkylated by propylene, butylene-1, isobutylene, amylene, cyclohexene, isopropyl alcohol, and tertiary butyl alcohol. Several new mono and dialkyl thiophenes were prepared.

An alumina–silica type catalyst (Filtrol X-143) proved to be satisfactory for the alkylation of thiophene. Phosphoric acid can also be used, but other typical alkylation catalysts were found to be unsatisfactory, e. g., aluminum chloride, ferric chloride, stannic chloride, hydrogen fluoride, boron trifluoride–dimethyl ether complex, and sulfuric acid.

Suitable conditions were not found for the alkylation of thiophene by ethylene.

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(5) Scheibler and Schmidt, *Ber.*, **54**, 139 (1921).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Azidodithiocarbonic Acid. IX. Electrode Potential of the Azidocarbondisulfide-Azidodithiocarbonate Couple

BY ROBERT ULLMAN[1] AND G. B. L. SMITH

Previous studies on the azidodithiocarbonates described the preparation of azidocarbondisulfide by the addition of iodine to a solution of sodium azidodithiocarbonate.[2] This reaction indicated that the potential of the azidocarbondisulfide–azidodithiocarbonate couple was above that of the iodine–iodide couple in the electromotive series. The purpose of this research was to determine that potential.

Apparatus

The potential determinations were measured by a Leeds and Northrop hydrogen ion potentiometer, with a Leeds and Northrop no. 1230 box galvanometer as null-point indicator. Both normal and saturated calomel cells, used as standard electrodes, were prepared according to Clark.[3]

Preparation of Materials[1]

Six grams of sodium azide was dissolved in 25 ml. of distilled water, to which was added 7 ml. of carbon disulfide. The mixture was kept at 40° for forty-eight hours at which time the reaction was essentially complete.

$$NaN_3 + CS_2 \longrightarrow NaSCSN_3$$

Free azidocarbondisulfide was precipitated by concentrated hydrochloric acid at 0°. This was dried over phosphorus pentoxide and titrated with a standard solution of potassium hydroxide to form potassium azidodithiocarbonate.

Azidocarbondisulfide was precipitated by addition of a solution of iodine–potassium iodide to sodium azidodithiocarbonate.

$$2NaSCSN_3 + I_2 \longrightarrow 2NaI + (SCSN_3)_2$$

Experimental Procedure

The potential between a calomel half cell and a solution of potassium azidodithiocarbonate saturated with azidocarbondisulfide was measured at varying concentrations of potassium azidodithiocarbonate. The cell may be written

$$Hg \mid Hg_2Cl_2, KCl \parallel KSCSN_3, (SCSN_3)_2 \mid Pt$$

The potential is given by the Peters equation

$$E = E^0 - 0.059 \log c\gamma \qquad (1)$$

where E is the measured potential, E^0 the electrode potential, c the concentration of potassium azidodithiocarbonate, and γ its molar activity coefficient. Rewriting (1)

$$E^0 - 0.059 \log \gamma = E + 0.059 \log c$$

A plot of the right-hand side of (2) along the ordinate *vs.* the square root of c as abscissa was extrapolated to zero concentration. E^0, the intercept on the vertical axis, is equal to 0.275 volt (Fig. 1). All values were corrected to the normal hydrogen electrode.

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(1) An abstract of a thesis submitted in partial fulfillment for the degree of Master of Science in chemistry.

(2) Browne, Hoel, Smith and Swezey, THIS JOURNAL, **45**, 2541 (1923).

(3) W. M. Clark, "Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 1920.

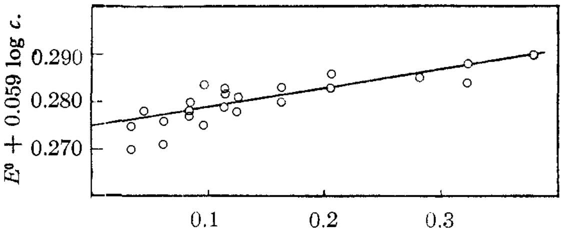

Fig. 1.—The square root of the concentration of potassium azidodithiocarbonate in (mole/liter).

Discussion

Since azidodithiocarbonic acid and azidocarbondisulfide decompose spontaneously,[1] the precision of the results is limited. For this reason it was considered unnecessary to use a thermostat to keep the temperature of the cell constant. Measurements were made at 25 ± 2.0°. The error thus introduced is of the order of magnitude of 0.001 volt, and not significant when compared to the errors brought about by the chemical instability of the above mentioned compounds.

The liquid junction potential between potassium azidodithiocarbonate and potassium chloride in the cell is unknown, but the use of a potassium chloride salt bridge very largely eliminates this effect.

Summary

1. The electrode potential of the azidocarbondisulfide–azidodithiocarbonate electrode was measured and found to be equal to 0.275 volt.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Viscosity–Molecular Weight Relation for Natural Rubber[1]

BY WALTER C. CARTER, ROBERT L. SCOTT AND MICHAEL MAGAT

Introduction

Houwink[2] and Flory[2] have shown that the Staudinger law in its simplest form, relating the intrinsic viscosity to the molecular weight deduced from thermodynamic properties of the polymer solutions through the equation

$$[\eta] = KM \qquad (1)$$

is not in agreement with experiment.

Both these authors agree that the correct relation is given by

$$[\eta] = KM^a \qquad (2)$$

where in the case of polyvinyl acetate compounds and polymethacrylate $a \cong 0.6$ (Houwink) and in the case of polybutene $a = 0.64$ (Flory). More recently Mark and Bartovics[3] found that a varies from 0.7 to 1.0 for polystyrene prepared at different temperatures in toluene and $a = 0.67$ for cellulose acetate in acetone. However, it seemed to us very important to check the validity of relations (1) or (2) on the very material for which Staudinger deduced his relation, *i.e.*, polyisoprene, (natural rubber), since in this case no argument of the type generally put forward by Staudinger and his co-workers that the deviations from eqn. 1 are due to the specific character of the polymer structure can be made.

Experimental

Molecular Weight Determination. Osmometer.—The molecular weight was determined from osmotic pressure measurements, using a cell identical with that described by Flory[2,4] so that no further description of it is necessary.

Membrane.—It was found, however, that the membranes described by Flory required long and slow measurements and became less and less permeable with time; this is probably due to the difference in solvents used—benzene and cyclohexane in the case of Flory, toluene in our case. It definitely appears that in toluene these denitrated collodion membranes are slowly dehydrated. Following a suggestion of Dr. R. M. Fuoss,[5] we have used collodion membranes without denitration. These membranes proved extremely satisfactory for polymers of molecular weight above 30–40,000 and hydrocarbon solvents. They allow fairly rapid measurements, about one to one and a half hours per solution, and the same membrane, if kept continuously in contact with toluene, can be used over a very long period of time. As a matter of fact, we are still using one of our membranes after twelve months of service. Since this type of membrane proves so successful it seems useful to include the details of its preparation, although it is similar to the one given by Fuoss and Mead.[6] Twenty cc. of solution containing 72% C. P. Merck collodion, 14% ether, 14% ethyl alcohol are poured into an iron ring about 10 cm. in diameter floating on a mercury surface and allowed to dry under a slow current of air. As soon as feasible (prolonged drying decreases the permeability) the film is transferred to water which precipitates the collodion and removes the solvent. The iron ring is disengaged and the membrane stands in water overnight and then is placed successively in water-alcohol, alcohol, alcohol-toluene, and toluene for two hours each. Before the membrane is used, however, it is necessary to age it, by letting it stand for about a week in pure toluene. This precaution is necessary because an unaged membrane was found to give erratic and irreproducible results.

Temperature.—The osmometer was placed in a large thermostat with extremely powerful agitation, controlled within ±0.1°. A better temperature control proved unnecessary, provided the temperature was uniform and the temperature variation in the course of a measurement (1 hour) did not exceed ±0.05°.

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(1) The major portion of this work was done on a grant from the Reconstruction Finance Corporation, Office of Rubber Reserve, for fundamental research in connection with the Government's synthetic rubber program.

(2) (a) R. Houwink, *J. prakt. Chem.*, **157**, 15 (1940–1941); (b) P. J. Flory, THIS JOURNAL, **65**, 372 (1943).

(3) A. Bartovics and H. Mark, *ibid.*, **65**, 1901 (1943).

(4) We wish to thank Dr. P. J. Flory for kindly lending us the blueprints of the cell prior to publication of this paper.

(5) Personal communication.

(6) R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).