a small concentration for the cryptozoon formations. The overlying shale, however, does not differ appreciably from that normally present in rocks of this type.

TABLE I

| Source | Per cent. total K | Abundance ratio | Per cent. $K^{41}$ |
|---|---|---|---|
| Mineral Water | | | |
| Geyser | 3.40 | 13.85 ± 0.1 | 6.76 |
| Coesa | 3.73 | 13.85 ± .1 | 6.76 |
| Hathorn | 6.03 | 13.85 ± .1 | 6.76 |
| Cryptozoon | | | |
| *Undulatum* | Small | 13.95 ± 0.1 | 6.69 |
| *Proliferum* | | 13.95 ± .1 | 6.69 |
| Trenton limestone | Trace | 14.00 ± .1 | 6.67 |
| Shale overlying | ? | 14.20 ± .03 | 6.58 |

The abundance ratio for the isotopes of lithium in the Saratoga mineral waters and cryptozoon was $Li^7/Li^6 = 11.8 \pm 0.1$. In comparison the abundance ratio for the majority of other lithium sources tested ranged between 11.6 and 11.8. The lithium isotope ratio in Saratoga water, therefore, does not differ appreciably from normal. The amount of rubidium present was so small that an accurate abundance ratio could not be obtained, although the results showed that the ratio did not differ appreciably from normal, which is $Rb^{85}/Rb^{87} = 2.6$.

The results just described are of interest in that they represent the only inorganic source so far discovered in which the $K^{41}$ content is appreciably higher than normal. It is significant that the lithium isotope ratio does not deviate correspondingly. It would appear, in consequence, that the process which concentrated $K^{41}$ does not concentrate $Li^7$; this precludes most physical mechanisms [Brewer, *J. Chem. Phys.*, **4**, 350 (1936)] for the isotope effect since they would be expected to result in larger deviations for lithium than for potassium. The simplest interpretation for these results is, therefore, that the salt deposits from which the water arises are of marine plant origin rather than that any isotope effect is occurring at the present time which would result in an abnormal abundance ratio for potassium.

BUREAU OF CHEMISTRY AND SOILS A. KEITH BREWER
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

NEW YORK STATE RESEARCH OSKAR BAUDISCH
INSTITUTE FOR HYDROTHERAPY
SARATOGA SPRINGS, N. Y.

RECEIVED JUNE 14, 1937

## POLAR GROUP ORIENTATION IN LINEAR POLYMERIC MOLECULES. THE OMEGA-HYDROXYDECANOIC ACIDS

*Sir:*

From dielectric constant–frequency data obtained with dilute solutions the average times of relaxation and molecular weights of zein, gliadin, lignin, hemoglobin, etc., have been determined. In these cases the molecular weight values so obtained agree with figures which have been obtained by the application of the classical diffusion, sedimentation and osmotic pressure methods, and the identity of the electrical and molecular kinetic units is established.

However, there is a class of high molecular weight polymeric substances which at least in dilute solutions did not give a measurable dispersion of dielectric constant in a frequency interval where an effect of this kind would be expected if electrical and kinetic or chemical units are assumed to be equivalent, but the data do show a definite and constant orientation contribution of the solute molecules to the dielectric constant of the solution over a considerable range of frequency.

The ω-hydroxydecanoic acid polymers are typical of substances of this class. Their dielectric behavior in dilute solution can be explained if it is assumed that in the long molecules there are polar groups at regularly recurring intervals which can orient in the applied field. Since there are nine C–C bonds between each pair of polar ester groups, free rotation of the latter seems probable. In this event the mean square sum of *n* group moments is approximately equal to the sum of the squares of the several individual moments; thus

$$\mu^2 = \mu^2_{\mathrm{OH}} + \mu^2_{\mathrm{COOH}} + (n - 1)\,\mu^2_{\mathrm{COOC}}$$

In this equation, $\mu$ is the average dipole moment of the polymeric molecules. Since, in Debye units, $\mu_{\mathrm{OH}} \cong 1.7$; $\mu_{\mathrm{COOH}} \cong 1.4$; $\mu_{\mathrm{COOC}} \cong 1.8$, this equation reduces to $\mu^2 = 4.85 + (n - 1)\,3.24$. We give in tabular form below electric moment data for six polymeric ω-hydroxydecanoic acids. The observed moments have been calculated from dielectric constant, density and refractive index data for dilute benzene solutions obtained in this Laboratory. Dielectric constant measurements were made at wave lengths $\lambda = 79$ m. and $\lambda = 180$ m.

It appears that the individual polar ester groups spaced in regular fashion along the length

TABLE I

POLARITY OF $\omega$-HYDROXYDECANOIC ACID POLYMERS

| Molecular weight | $n$ (monomeric units) | $\mu_{\text{calcd.}} \times 10^{18}$ | $\mu_{\text{obsd.}} \times 10^{18}$ |
|---|---|---|---|
| 905 | 5 | 4.2 | 5.0 |
| 2,120 | 12 | 6.6 | 6.7 |
| 4,140 | 24 | 9.1 | 10.2 |
| 7,780 | 46 | 12.4 | 12.4 |
| 9,070 | 53 | 13.3 | 15.7 |
| 13,900 | 82 | 16.4 | 19.0 |

of the molecule are rotating in the electrical field and are the main source of the observed orientation polarization. Consistent with this explanation, polarization per gram for these polymers is found to be independent of molecular weight and dipole moment varies with the square root of molecular weight. The dielectric behavior suggests that these polymeric molecules have the form of flexible chains.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WISCONSIN
MADISON, WISCONSIN

WILBUR B. BRIDGMAN
J. W. WILLIAMS

RECEIVED JULY 9, 1937

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## THE ADDITION OF THIOCYANIC ACID TO OLEFINIC DOUBLE BONDS

*Sir:*

In pursuance of a general plan of research on the reactions of olefinic double bonds being carried out in this Laboratory, we were led by the absence of work on the addition of thiocyanic acid to simple olefins to examine the behavior of this substance. We have succeeded in adding thiocyanic acid to a number of olefins.

An ether solution of thiocyanic acid prepared according to Klason [*J. prakt. Chem.*, [2] **35,** 407 (1887)] with an equimolar amount of isobutylene yielded after four hours at room temperature an oil boiling at 51–54° at 25 mm.

*Anal.* Calcd. for $C_5H_9NS$: C, 52.17; H, 7.82. Found: C, 52.08; H, 7.81.

This product we have characterized as a mixture of *t*-butyl thiocyanate and *t*-butyl isothiocyanate through their derivatives, *t*-butyl-N-acetyldithiocarbamate of m. p. 113° [Wheeler and Merriam, THIS JOURNAL, **24,** 680 (1902)] and *t*-butylthiourea of m. p. (decomp.) 168° [Rudneff, *Ber.*, **12,** 1023 (1879)], respectively. When our product was treated in aqueous alcohol with silver nitrate for two, five, or ten minutes, the amount of silver thiocyanate formed by both volumetric and gravimetric determinations corresponded to 32% of *t*-butyl thiocyanate in our mixture, assuming that this compound was the sole source of the precipitate. Upon allowing our product to stand for thirty-six hours at room temperature with excess ammoniacal silver nitrate in aqueous alcohol [Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," J. Springer, Berlin, 1931, p. 633], the amount of silver precipitated as the sulfide (determined volumetrically after proper deduction for the amount present as silver thiocyanate) corresponded to 62% *t*-butyl isothiocyanate in our product. We have not yet accounted for the remaining 6% and the possibility exists that isobutyl compounds may be present in small amount. We have modified the directions of Wheeler and Merriam for the preparation of *t*-butyl thiocyanate by keeping the reaction mixture at 0°, and found that the product boiled at 53–54° at 25 mm. and contained 42% *t*-butyl thiocyanate, determined as described above.

In similar fashion we found that trimethylethylene, styrene, 2-pentene and camphene add thiocyanic acid. The latter compound recalls the work of Challenger, Smith and Paton [*J. Chem. Soc.*, **123,** 1055 (1923)] who observed that pinene reacts with thiocyanic acid to yield "a substance...containing nitrogen and sulfur." Since this substance was never further identified, we assume that these authors have abandoned the investigation.

We propose to study the addition of thiocyanic acid to olefinic double bonds both intensively and extensively with emphasis on the effect of peroxides and other catalysts on addition and rearrangement.

GEORGE HERBERT JONES LABORATORY
UNIVERSITY OF CHICAGO
CHICAGO, ILLINOIS

M. S. KHARASCH
ERNEST M. MAY
FRANK R. MAYO

RECEIVED JULY 19, 1937

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## ISOLATION OF ERYTHROIDINE, AN ALKALOID OF CURARE ACTION, FROM ERYTHRINA AMERICANA MILL.

*Sir:*

It was known long ago by Altamirano [*Gaceta Medica De Mexico*, **23,** 369 (1888)] that extracts of the seeds of *Erythrina americana* Mill. produce a strong curare action, *i. e.*, a selective paralyzing action on motor nerve endings of striated muscle. Thus, the use of such an extract was suggested as a substitute for curare, which has been used therapeutically against tetanus and other con-