hydrated electron was observed in ovalbumin solutions buffered from pH 8 to 12. In conclusion, the hydrated electron is a possible primary product in the ultraviolet-light photolysis of proteins containing aromatic amino acids. This species can act as a reducing agent when oxygen is unavailable, as a source of HO<sub>2</sub> radical in aerobic systems, and possibly as a charge carrier in natural proteins.

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# Polymorphism in Isopropyl Alcohol

Abstract. Evidence for two polymorphic forms of isopropyl alcohol is presented. Three transformation reactions were observed. The transformation temperatures for pure isopropanol were  $185.27_{7}^{\circ}K$  and  $183.65_{2}^{\circ}K$ . The purity of the alcohol was found to be 99.985 percent (calculated as moles).

Andon, Counsell, and Martin (1) recently described the thermodynamic properties of isopropyl alcohol from 10°K to 330°K. They stated that the graph of the temperature plotted against the reciprocal of the melted fraction was not a straight line, and hence it was not possible to calculate values for either the freezing point or for the purity of the sample. They were able to determine the heat of fusion which they reported as 1293 cal/mole. It was suggested that an abnormally large rise in heat capacity just below the melting point was due to a solid-solid transformation.

Several years ago F. L. Howard, T. W. Mears, and Philip Pomerantz (at the National Bureau of Standards) prepared a very pure sample of isopropyl alcohol. In order to avoid impurities that might have resulted from its preparation from refinery gases, the alcohol was synthesized by hydrogenation of

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purified acetone obtained from fermentation. The product was distilled from aluminum isopropylate through a fractionating column (15 m long and 2.5 cm in diameter) packed with 0.2-cm single-turn helices. The sample was degassed and sealed in ampoules. The final fractions contained from 0.002 to 0.008 percent water as determined by the Karl Fischer technique.

The purity of this alcohol has been recently determined by both calorimetric (2) and time-temperature freezing (thermometric) (3) methods. The calculated purity by both methods was approximately 99.985 percent (calculated as moles). When the calorimetric technique was used the melting point of the sample,  $T_t$ , was 185.246°K and the melting point of pure isopropanol,  $T_{t_0}$ , was calculated to be 185.258°K. The heat of fusion,  $\Delta H_t$ , was 1318 calories per mole. The graph of 1/Fplotted against T was linear, and there was no evidence of any polymorphism.

When this material was investigated by thermometric techniques the existence of two crystalline forms became apparent. Several portions of the sample were analyzed and all had the purity previously stated. All of these portions were transferred and analyzed under vacuum conditions. The freezing curves were not of good quality and only the melting curves were used in the analysis. The different portions of the isopropyl alcohol are herein referred to as samples 1, 2, 3, and 4. Three similar freezing-point cells were used, herein referred to as cells A, B, and C. The cells and the transfer manifolds were cleaned with chromic acid, followed by washing with distilled water. The cells were dried by heat and evacuation over an extended period of time.

We have now observed three transformation reactions. (1)  $L \rightleftharpoons S_1$ , (2)  $L \rightleftharpoons S_2$ , and (3)  $S_2 \rightarrow S_1 \rightarrow L$  or  $S_2 \rightarrow L$  $\rightarrow$  S<sub>1</sub>  $\rightarrow$  L. The symbols L, S<sub>1</sub>, and S<sub>2</sub> represent the liquid phase, the highermelting solid, and the lower-melting solid respectively.

When sample 1 was analyzed in cell A the first experimentally determined  $T_{t_0}$  was 185.65<sup>2</sup>°K, but four subsequent determinations yielded  $T_{t_0}$  values whose average was 183.24° K. Sample 1 was removed and sample 2 was analyzed still using cell A. Only the lower-melting form, S<sub>2</sub>, was found.

We observed a small amount of white powder which remained in the ampoules after the first two samples were distilled into the cell. Subsequently

it was found that invariably there were traces of this powder with the distilled alcohol. Only extremely minute amounts of this powder remained after distillation. No specific chemical analysis was obtained. By a cursory optical-microscopic examination particles were approximately a micron or less in diameter and probably not crystalline. Sample 3 was transferred to cell B and again only the freezing and melting behavior of S2 was observed. This sample was then removed, transferred to centrifuge tubes, and centrifuged at 25,000 rev/min. The top portion of the liquid was then transferred to cell C. Many experiments were made on this sample and the material always froze in the familiar high-melting form, S1. The residue from the centrifugation was then recombined with the above sample and, though many more experiments were run, only the lower melting modification was observed.

Cell A was thoroughly cleaned and the top portion of the centrifuged sample 4 was transferred to this cell and analyzed. It was now found that either modification could be produced, depending upon the rate at which the liquid was cooled, a fast rate producing the  $S_1$  form, a slower rate the  $S_2$  form. The appearance of either form did not seem to depend upon previous conditioning but only upon the cooling rate. Since this system produced either modification, it was used to determine experimentally the heat of fusion of the reaction  $L \rightleftharpoons S_2$ . A comparative technique (4) employing a correlation of the time necessary to freeze the sample in either form was used. By assuming that the value of 1318 cal/mole correctly represented the heat of fusion of the reaction  $L \rightleftharpoons S_1$ , the heat of fusion for the reaction  $L \rightleftharpoons S_2$  was calculated to be 1055 cal/mole. This value should not be in error by more than 10 percent.

Several peculiarities were observed. First the reaction,  $S_1 \rightarrow S_2$ , was not observed even when the sample, frozen as S1, remained for long periods of time below the transition temperature of  $S_2$ . Likewise the reverse reaction was not observed during the time that large amounts of S<sub>2</sub> remained in the cell. However, infrequently when S2 was nearly melted (more than 95 percent liquid) the temperature would rapidly rise to the melting range of the  $S_1$  modification. A short melting curve corresponding to this higher melting form would be observed prior to complete liquefaction. The silvering from the vacuum jacket of cell C was removed and the reaction,  $S_2 + L \rightarrow S_1 + L$ , was actually seen. The crystals of S<sub>2</sub> appeared to be quite small and grey in color. When the transformation to  $S_1$ began the crystals increased in number and size while the color changed from grey to a very pure white. Whether or not the transformation was  $S_2$  to  $S_1$  or L to S<sub>1</sub> could not be determined.

It is probable that a large percentage of organic compounds exhibit more than one crystalline form. In many cases the  $S_1 \rightleftharpoons S_2 \rightleftharpoons S_n$  transformations occur at equilibrium temperatures which are very much lower than the temperature of the  $L \rightleftharpoons S_1$  transformation. In such instances it is usually not difficult to establish the existence of the transformations. In other cases, however, the difference in temperature between the transformations  $L \rightleftharpoons S_1$  and the  $S_1 \rightleftharpoons S_2$  may be quite small, and the existence of the S<sub>2</sub> modification may not be conclusively established even though the compound has been extensively studied. This phenomenon has been observed with the isomers of dichloroethylbenzene. In this case it ap-

pears that nucleation of two or more forms may occur simultaneously during the initial supercooling. When this happens the calorimetric or thermometric experiments are extremely difficult to interpret. In the case of isopropyl alcohol we believe that the nucleation phenomenon of the S<sub>2</sub> form is a clear example of catalytic nucleation by a foreign body. However, whether this nucleation occurs through the liquid, vapor, or solid phase is not clearly established.

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floors known as tablazos. These de-

posits extend inland as nearly level

plains for many miles, particularly

from the Sechura Desert northward

into Ecuador. The tablazo deposits

show evidence of regional uplift and

warping of Pleistocene and post-

Pleistocene age. The tablazos are

especially well developed in the region

of Talara, and have been studied by

Bosworth (1), Lemon and Churcher

(2), and Richards (3). The following

three principal levels have been recog-

nized (after Bosworth): (i) Lobitos

tablazo, altitude 15 to 33 m (50 to

110 ft), thickness 1.5 to 4.5 m (5 to

15 ft); (ii) Talara tablazo, altitude 45

to 105 m (150 to 350 ft), thickness

2.4 to 7.5 m (8 to 25 ft); (iii) Mancora

tablazo, altitude 60 to 370 m (200 to

1200 ft), thickness 23 to 75 m (75 to

250 ft).

20 August 1963

Earlier workers such as Suter (4)and Daly (5) attempted to correlate the various tablazos with high interglacial stands of the sea, whereas more recent workers explain the elevation of the land on tectonic grounds.

In addition to the three easily recognized tablazos, there are conspicuous shell ridges left by a still more recent uplift. These, known as the Salina deposits, are especially conspicuous near Puerto Chuelo, 32 km south of Talara. These shell ridges parallel the present beach, extend some 8 km inland, and reach more than 9 m (30 ft) in elevation. Shells of Donax peruviana Deshayes, Tivela hians Philippi, and Thais chocolata Duclos are the most common.

A specimen of Donax peruviana from the Salina beds north of Puerto Chuelo at an elevation of about 4.5 m (15 ft) has given a radiocarbon date of  $3000 \pm 200$  years B.P. (L-703-D), while a shell of Turritella gonostoma Val. from the Lobitos tablazo at approximate altitude of 23 m (75 ft), 16 km north of Talara, has given an age greater than 30,000 vears (L-703-A).

Uplift and warping of the coast of Peru is obvious. That it is still going on is suggested by the very recent date of the shell from the Salina beds near Puerto Chuelo. The "dead" date of the shell from the Lobitos tablazo places the submergence at least as old as the Wisconsin. Unfortunately, present methods cannot be used to date the older, higher tablazos.

Colombia. Anderson (6) reported horizontal Pleistocene marine terraces with corals and mollusks along the Caribbean coast of Colombia to an elevation of 18 m (60 ft). More recently, dePorta and dePorta (7) described two Pleistocene terraces on the island of Tierrabomba (near Cartagena) at 20 and 3 m, respectively. They suggested a possible correlation of the higher terrace with the Penhalloway terrace of the Southern Atlantic Coastal Plain, and the lower one with the Silver Bluff of Florida. The age of the Silver Bluff is not known. Some, such as MacNeil (8) and Fairbridge (9), regard it as dating from a Holocene high stand of the sea, while others, such as Price (10) and Richards (3), suggest that it might represent a regression of the Pamlico (Sangamon) sea.

One of us (H.G.R.) visited the island in June 1962 with Jaime dePorta, and an extensive molluscan fauna was ob-

## **Emerged Holocene South American Shorelines**

Abstract. A pelecypod from the Salina beds of northern Peru at elevation 4.5 m (15 ft) shows a date of about 3000 years B.P., while a gastropod from elevation 22.5 m (75 ft) was older than 30,000 years B.P. A pelecypod from the island of Tierrabomba, near Cartagena, Colombia, at elevation 2.7 m (9 ft) gave a date of about 2850 years, while a pelecypod from Comodoro Rividavia, Argentina, at elevation 9 m (30 ft) gave a date of 5350 years B.P.

It has been generally recognized that the western coast of South America is unstable, and has been so throughout much of the Cenozoic. Opinion differs regarding the eastern coast. Some workers believe that the eastern coast has been stable throughout much of the Pleistocene with the various shorelines having been caused by eustatic changes of sea level; others believe that the eastern coast is unstable tectonically, the movements being largely of an epeirogenic nature.

Recent field work in Peru, Colombia, and Argentina by Richards has afforded the opportunity for radiocarbon dating of mollusks by Broecker at the Lamont Geological Observatory. These studies suggest at least local Holocene uplift in the three areas studied.

Peru. The coast of northern Peru is marked by a series of elevated sea