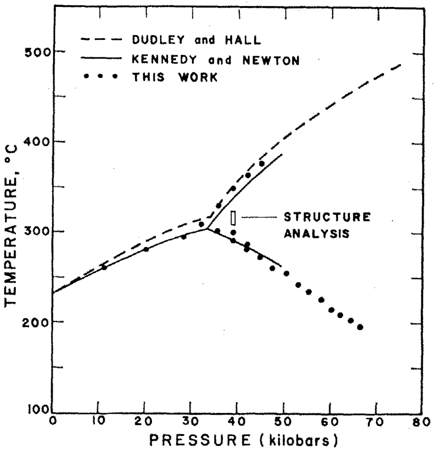

Fig. 1. Phase diagram for tin.

and considers the position of the atoms at the moment of maximum displacement. At this moment the atoms would have eight nearest neighbors. Musgrave then assumes that the more symmetrical bcc structure forms immediately from the bct structure.

This "virtual" bct structure would have lattice parameters of $a = 4.12$ Å and $c = 3.18$ Å, with $c/a = 0.77$ at 1 bar and 25°C. Our measurements indicate an incomplete movement of this virtual bct lattice toward the bcc lattice (the bcc lattice may be considered as a bct lattice with $c/a = 1.00$). Apparently at 39 kb and 314°C the bonds between second nearest neighbors located along the c axis are sufficiently important to prevent the complete movement to the bcc structure, as suggested by Musgrave.

In addition to the above elucidation of the tin II structure, we have used x-ray diffraction techniques to determine the phase diagram of tin. The melting curve was followed to 45 kb and the tin I-II phase boundary to 70 kb. Melting was followed to the triple point by observing the (200) and (101) lines of the tin I x-ray pattern as temperature was slowly increased at a fixed pressure. The temperature at which these lines disappeared into the background was taken to be the melting point. This temperature was reproducible to ± 4°C. Temperature was measured by a thermocouple located within an electrically heated graphite furnace used to heat the tin. The tin was centrally located within the furnace, and was surrounded by polyethylene. The x-ray beam was directed axially through the furnace. Melting beyond the triple point was similarly detected by observing the (110) and (101) lines of the tin II pattern.

The phase boundary between tin I-II was determined by the disappearance of the (200) and (101) lines of tin I and the appearance of the (110) and (101) lines of tin II. During temperature excursions of one particular sample, the presence of a small single crystal properly oriented for Bragg diffraction became evident in the form of a sharp, high-intensity peak. This peak, in a matter of seconds, would repeatedly disappear or reappear as the transition temperature was traversed. The rapidity of the transformation and the retention of the crystal orientation after passing to tin II and returning to tin I provide strong evidence for the nonreconstructive nature of this transition. It was possible to detect the occurrence of this transition within ± 2°C. A comparison of our determination of the tin phase diagram with that of Dudley and Hall and that of Kennedy and Newton is shown in Fig. 1 (*7*).

J. Dean Barnett
Roy B. Bennion
H. Tracy Hall*

Departments of Physics and Chemistry, Brigham Young University, Provo, Utah

References and Notes

1. J. D. Dudley and H. T. Hall, *Phys. Rev.* **118**, 1211 (1960).
2. G. C. Kennedy and R. C. Newton, in *Solids Under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill, New York, 1963), p. 163.
3. R. A. Stager, A. S. Balchan, H. G. Drickamer, *J. Chem. Phys.* **37**, 1154 (1962).
4. L. Kaufman, in *Solids Under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill, New York, 1963), p. 303.
5. J. C. Jamieson, Geol. Soc. Am., meeting, Houston (November 1962), abstr.
6. M. J. P. Musgrave, *Phys. Chem. Solids* **24**, 557 (1963).
7. Supported by U.S. Army Research Office, Durham.

* Alfred P. Sloan research fellow.

25 July 1963

Hydrated Electron: Production and Role in Photobiology

Abstract. *Many inorganic anions in aqueous solution either yield the hydrated electron on photolysis or they are strong scavengers. In neutral solution the hydrated electron is a primary photochemical product of aromatic amino acids.*

The hydrated electron is produced by ultraviolet-light flash photolysis of inorganic salts and aromatic compounds. Some anions that give the hydrated electron are Cl^-, Br^-, I^-, OH^-, $Fe(CN)_6^{4-}$, PO_4^{3-}, and CO_3^{2-} (*1, 2*). We obtained negative results with NO_3^-, BrO_3^-, and $CH_3CO_2^-$, although there was sufficient light absorption to induce photolysis. Figure 1 shows the hydrated-electron spectrum from Na_3PO_4 after correction for emulsion sensitivity. The fine structure on the uncorrected spectra obtained by Hart and Boag (*3*) with pulse radiolysis and by Grossweiner *et al.* (*2*) with flash photolysis is due to emulsion spectral sensitivity and nonlinearity; only a single broad band with a possible shoulder near 500 mμ is considered valid, in agreement with the work of Matheson *et al.* (*1*).

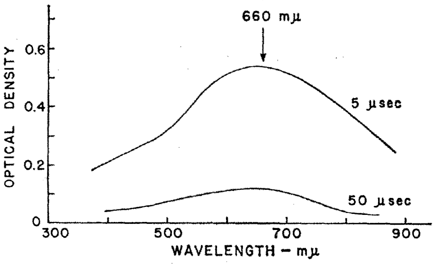

Fig. 1. Transient spectra from the flash photolysis of air-free 0.05*M* Na_3PO_4 at *p*H 11.8. The data were taken on Kodak 103-F and I-N plates and corrected for spectral sensitivity.

There is evidence that some of the anions that do not yield hydrated-electron spectra react rapidly with it, so that the hydrated electron could have been produced in those cases also. For example, the addition of 0.01*M* $NaNO_3$ or $KBrO_3$ to 0.001*M* *p*-cresol at *p*H 11.7 (Na_3PO_4 buffer) suppresses the hydrated electron, although the production of *p*-methylphenoxyl radical is not altered. Again, the photolysis of 0.0002*M* KI in 0.5*M* phosphate buffer at *p*H 9 gives the I_2^- absorption and only a very weak hydrated-electron band, indicating that $H_2PO_4^-$ or HPO_4^{2-} is a scavenger. However, $CH_3CO_2^-$ neither gives the hydrated electron on photolysis nor scavenges. The photochemical scavenging experiments are in agreement with rate constants, measured by pulse radiolysis, which show that NO_3^- reacts very rapidly with the hydrated electron and that $CH_3CO_2^-$ reacts very slowly (*4*).

Noting that hydrogen phosphate buffer scavenges the hydrated electron, we reinvestigated the photolysis of aromatic amino acids in air-free, neutral solution. Under such conditions, positive results were obtained with phenylalanine, tyrosine, and tryptophan. The earlier negative results at *p*H 4 to 5 were due to scavenging by buffer as well as hydrogen ion (*2*). Furthermore, the hydrated electron was observed in ovalbumin solutions buffered from *p*H 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_2 radical in aerobic systems, and possibly as a charge carrier in natural proteins.

GEORGE W. SWENSON
EARL F. ZWICKER
LEONARD I. GROSSWEINER
Department of Physics, Illinois Institute of Technology, Chicago 16

References and Notes

1. M. S. Matheson, W. A. Mulac, J. Rabani, *J. Phys. Chem.*, in press.
2. L. I. Grossweiner, G. W. Swenson, E. F. Zwicker, *Science* **141**, 805 (1963).
3. E. J. Hart and J. W. Boag, *J. Am. Chem. Soc.* **84**, 4090 (1962).
4. S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, J. K. Thomas, presented at Faraday Society Discussion No. 36, Notre Dame, Ind.
5. Supported by research grant GM 10038-01 from the National Institutes of Health.

20 August 1963

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*°K and* 183.65_2*°K. The purity of the alcohol was found to be* 99.98_5 *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 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 99.98_5 percent (calculated as moles). When the calorimetric technique was used the melting point of the sample, T_f, was 185.246°K and the melting point of pure isopropanol, T_{f_0}, was calculated to be 185.258°K. The heat of fusion, ΔH_f, was 1318 calories per mole. The graph of $1/F$ plotted 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 $S_2 \rightarrow L \rightarrow S_1 \rightarrow L$. The symbols L, S_1, and S_2 represent the liquid phase, the higher-melting solid, and the lower-melting solid respectively.

When sample 1 was analyzed in cell A the first experimentally determined T_{f_0} was 185.65_2°K, but four subsequent determinations yielded T_{f_0} values whose average was 183.24_0°K. Sample 1 was removed and sample 2 was analyzed still using cell A. Only the lower-melting form, S_2, 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 S_2 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, S_1. 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 S_1, 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_2 remained in the cell. However, infrequently when S_2 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