

were platinum coaxial helices or parallel pairs of platinum or gold foils. Isolated aqueous saturated calomel electrodes were used as reference electrodes. Qualitative experiments were done with 60 c.p.s. sine-wave alternating current, but measurements were made with square-wave alternating current.

In stirred solutions operating in the potentiodynamic mode with a.c. voltage of sufficient magnitude, bright DPA fluorescence is observed in the vicinity of the working electrode. In quiet solutions (electrodes separated by several centimeters), where the products of one electrode cannot be transported to the other electrode, luminescence originates within a few millimeters of the electrode surfaces. The intentional addition of water or molecular oxygen decreases the light intensity but does not entirely quench the process.

The variation of electroluminescence intensity with applied voltage and frequency was measured at λ_{\max} (identical with that of the normal fluorescence) with a monochromator and photometer. Intensity increased linearly with voltage up to a point⁷ but leveled off thereafter. At frequencies below 100 c.p.s. more than 95% of the light is modulated, while at 2 kc.p.s. at least 80% is modulated. The output frequency is *twice* that of the square-wave input, peaking on each half-cycle. Intensity decreases as the frequency is raised, and the upper limit (≥ 10 kc.) appears to be determined by the RC (resistance \times capacitance) time constant of the electrochemical cell. At a few cycles per second, discrete light pulses can be seen.

Cyclic voltammetry⁸ was used to study the anodic and cathodic processes of DPA in both DMF and AN. In agreement with earlier steady-state measurements,²⁻⁵ reduction in DMF yields a stable blue radical at a peak potential of -1.95 v. *vs.* s.c.e. without evidence of irreversibility up to sweep rates of 0.3 v./sec. Oxidation in DMF, with a peak potential of $+1.25$ v. *vs.* s.c.e., appears to be complicated by the simultaneous oxidation of the solvent (or possible impurities). There is an oxidation process proportional to the concentration of DPA, but repeated cycling also produces electroactive species identical with those observed when the solvent alone is electrolyzed. The products of oxidation in DMF are colorless, and no cathodic current corresponding to the reduction of an oxidized DPA species is observed on reversing the sweep. Potentiostatic experiments in both stirred and quiet solutions with separated, but not isolated, electrodes indicate that the colorless product of DPA oxidation in DMF is a relatively long-lived and sufficiently strong oxidizing agent to react with R^- in the chemiluminescent process.

In AN the blue anion radical can be observed visually at -1.8 to -2.0 v., but reduction occurs too close to solvent reduction for quantitative measurements. There are two well-defined one-electron oxidations in AN. The peak potential of $+1.22$ v. for the first process, invariant with sweep rate up to 1.4 v./sec., has a peak current proportional to the square root of the sweep rate. A cathodic process with current equal to that of the first anodic process is observed when the sweep direction is reversed. The electrochemical data⁸ and the observation of a blue product at the anode

(7) In the particular cell used, luminescence was observed at *ca.* 3.5 v. and tapered off above *ca.* 15 v.

(8) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

demonstrate that the electrochemical process is associated with the reversible $R^+ - R$ couple. The second anodic process at $+1.6$ v., of magnitude comparable to the first, is a further irreversible one-electron oxidation since the peak potential becomes more anodic with increasing sweep rate. The cyclic voltammograms in AN indicate that R^+ has a chemical lifetime of at least 10 sec.

By varying the midpoint of the triangular voltage program, it could be demonstrated (in AN) that R^+ and R^- are the reactants in the chemiluminescent reaction coupled with the electrochemical charge-transfer reactions. A discussion of the basis for chemiluminescence in the reactions



for this and other related systems is given elsewhere.⁹ The reaction of R^- with various oxidizing agents to form the excited singlet of R is compatible with our observation of luminescence in DMF even though these solutions do not appear to have any appreciable concentration of R^+ . The general requirement for chemiluminescence in these systems appears to be the reaction of a nonquenching oxidizing agent with R^- , which provides sufficient energy. For DPA this is 2.9-3.0 e.v., corresponding to the fluorescence peaks at 435 and 410 m μ . The chemiluminescent reaction of R^- with the oxidized form of DPA (which is *not* the radical cation) seems to satisfy these conditions. The difference in the standard potentials of the $R - R^-$ and $R^+ - R$ couples in AN is sufficient to provide the required energy.¹⁰

Acknowledgment.—We wish to thank Dr. J. W. Longworth for his assistance in making some of the photometric measurements.

(9) E. A. Chandross and F. I. Sonntag, *J. Am. Chem. Soc.*, **86**, 3179 (1964).

(10) NOTE ADDED IN PROOF.—Qualitative observations of electroluminescence have recently been reported by D. M. Hercules, *Science*, **145**, 808 (1964). Low-frequency alternating current (up to 10 c.p.s.) was utilized in some of the experiments.

BELL TELEPHONE LABORATORIES, INC. ROBERT E. VISCO
MURRAY HILL, NEW JERSEY EDWIN A. CHANDROSS

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Visible Absorption Spectra of Sodium in Molten Sodium Iodide

Sir:

In order to establish a possible correlation between the visible absorption of alkali metals in molten alkali halides and F center formation as observed in the solid, the visible absorption spectra of Na in molten NaI were obtained.

Quartz cuvettes, 1 cm. in diameter (i.d.), were used as containers. Although heated alkali metal vapors react with silicates, it was found that if the salts were anhydrous, the alkali metal would dissolve in the salt without discoloring that portion of the cell containing the melt. The cells were wrapped with inconel heating strips and placed in an insulating container. The steady-state temperatures were controlled by means of a Variac to within $\pm 5^\circ$. The temperature of the system was measured by means of a platinum-platinum-13% rhodium thermocouple.

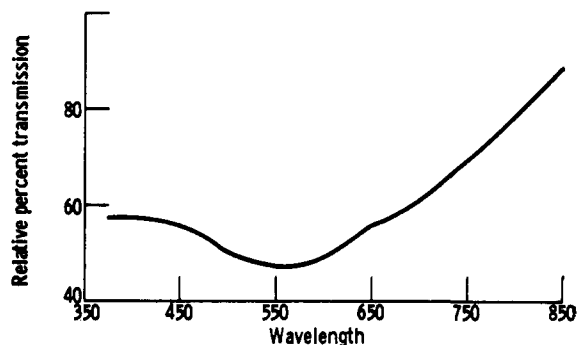


Fig. 1.—Visible absorption spectra of saturated solution of Na in NaI at 675°.

The spectra were obtained by means of a Beckman DK, double-beam, recording spectrophotometer. Each metal-salt mixture was compared to air in the reference compartment. In order to balance the instrument, the reference beam was attenuated. The results as shown are therefore reported as relative per cent transmission.

Removal of water from reagent grade NaI was done by repeated washings with dry liquid ammonia. Additions of sodium metal were made by carrying the sodium metal over in a diffusion stream of ammonia into the salt. The residual ammonia was removed from the metal-salt mixture by pumping. This method of preparing a mixture of sodium and sodium iodide is identical with the previously described procedure for preparing a mixture of lithium metal with the eutectic LiCl-KCl.¹ This procedure has the advantage of introducing an excess of metal into the salt in order that a concentrated solution be formed upon melting of the salt. In this work the most stringent vacuum conditions were maintained analogous to the work of Dewald and Lepoutre.²

The visible absorption spectra of a saturated solution of Na in NaI at 675° are shown in Fig. 1. The fact that the solution was saturated was indicated by the presence of excess sodium at the bottom of the cuvette upon freezing and by the fact that, as the temperature was raised above 700°, the solution became completely absorbing and no peak structure was observed. Prior to the melting of the salt, the appearance of liquid sodium at the bottom of the cuvette was observed. As the heating was continued, the solid NaI melted at approximately 650° yielding a more transparent region resembling a dark blue solution of sodium in liquid ammonia. In the cell, the monochromatic beam passed through this more transparent region. We arbitrarily chose to make our measurements of this system at 675°. As the temperature was raised above 700°, the system became completely absorbing. When the temperature was lowered to 675°, the band initially observed was reproduced. Upon lowering the temperature still further to 650°, where the NaI began to freeze, the system became opaque.

No discoloration of the glass was observed at the glass-liquid interface. However, in the space above the liquid, the glass was discolored to a dark brown, presumably owing to sodium metal attack.

The location of the F center band in crystalline NaI

- (1) J. Greenberg and I. Warshawsky, *J. Am. Chem. Soc.*, **86**, 3572 (1964).
 (2) J. F. Dewald and G. Lepoutre, *ibid.*, **76**, 3369 (1954).

has been reported to be at both 6090 and 5880 Å.³ Since increasing temperatures cause the peak of the band to shift to lower energies,⁴ the theoretical position of an F band in molten NaI would be at longer wave lengths. The presence of a band with a peak approximately at 570 m μ for a saturated solution of Na in NaI at 675° does not, therefore, appear to be a function of F center formation. Sodium atoms and molecules, however, do absorb in the region of the observed band. Since the position of the peak is close to that of the observed transition for sodium atoms, it is likely that the primary absorbing species are sodium atoms. The absorption at shorter wave lengths may be due to sodium molecules.⁵ The presence of dimers (molecules) in solutions of alkali metals in their molten halides has already been suggested to explain a minimum in the electrical conductances of these systems.⁶

It appears that the alkali metal can be present in three forms in the melt. In the case of dilute solutions (10⁻³ mole % metal) there is a possible interaction of the alkali metal with the melt to form an F center. This has been suggested by Bredig⁷ and can be inferred from the fact that the spectra of such dilute solutions are independent of the metal that has been added. As the concentration of the metal is increased, the spectra can be interpreted in terms of atomic and molecular species of the metal as has been done here for the saturated solution at 675°. Upon further increasing the metal concentration, the solution becomes optically opaque in the visible and typical of the metallic state above the consolute temperature.⁶

(3) H. F. Ivey, *Phys. Rev.*, **72**, 341 (1947).

(4) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals," Clarendon Press, London, 1948, p. 116.

(5) G. H. Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1950.

(6) H. R. Bronstein and M. A. Bredig, *J. Am. Chem. Soc.*, **80**, 2077 (1958).

(7) M. Blander, "Molten Salt Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p. 382.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

LEWIS RESEARCH CENTER

CLEVELAND, OHIO

J. GREENBERG

I. WARSHAWSKY

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Synthesis of L-Ribofuranose and L-Adenosine¹

Sir:

Nucleosides of L-ribose would be enantiomorphic with the natural RNA components, and consequently are of great interest for studying physical and biological properties of nucleic acids. Furthermore, L-ribosides of fraudulent heterocyclic bases, *e.g.*, 6-mercaptapurine or 6-thioguanine, might be free of some of the biological properties, *e.g.*, enzymatic cleavage, which lessen the therapeutic value of the widely studied D-ribonucleosides² of these bases. An efficient preparation of L-ribose in the furanose form is essential for the synthesis of L-nucleosides. We now report two new and convenient syntheses of the L-ribofuranose derivative X by application of the sodium benzoate-dimethylformamide (DMF) inversion^{3,4} of sugar sulfonates, and the use of

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(2) G. A. LePage and I. G. Junga, *Cancer Res.*, **23**, 739 (1963), and leading references cited therein.

(3) E. J. Reist, L. Goodman, and B. R. Baker, *J. Am. Chem. Soc.*, **80**, 5775 (1958).