

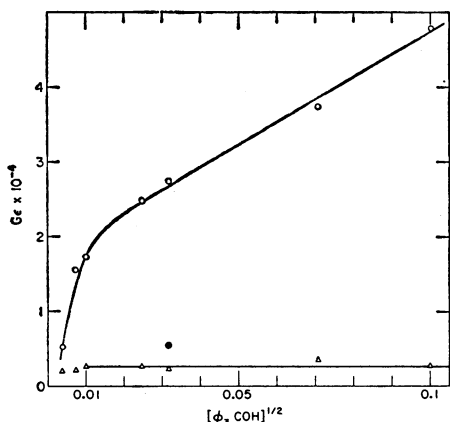


Fig. 2. Yields of triphenylmethyl radical (O) and ion (Δ) (multiplied by the respective peak extinction coefficients) in cyclohexane and of the ion in 2,2,4-trimethylpentane (●), versus the square root of the molarity of triphenylcarbinol. Each point is an average of four determinations.

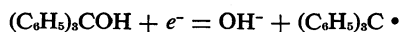
lute solutions in saturated hydrocarbons of triphenylcarbinol,  $(C_6H_5)_3COH$ . This alcohol forms triphenylmethyl-carbonium ion  $(C_6H_5)_3C^+$  by proton transfer from acidic solvents and is related to the unusually stable triphenylmethyl free radical  $(C_6H_5)_3C\cdot$ .

The spectrum of the transient absorption produced by an 8-μsec pulse of 2 Mev electrons (dose,  $0.5 \times 10^{17}$  ev/ml) in a  $10^{-3}M$  solution of triphenylcarbinol in cyclohexane, and the spectra of the ion  $(C_6H_5)_3C^+$  (a solution of the carbinol in  $H_2SO_4$ ) and of the radical in toluene (3) show (Fig. 1) that the radiation-produced absorption is the sum of absorptions due to the radical and the ion; no other components are of any importance.

From the maximum optical densities at the peaks of the radical and ion absorptions, and the energy input, we calculated the product  $G\epsilon$  (molecules formed per 100 ev input  $\times$  molar optical extinction coefficient) for the ion and radical separately (Fig. 2). Small corrections were made for decay during the pulse and for the absorption of light by the radical at the ion-peak wavelength. Both species show clean second-order decay; with a typical dose (1300 rad), the first half-life of the ion was  $3.0 \times 10^{-5}$  second. The radical was somewhat longer-lived.

The linear increase in radical yield with the square root of the carbinol concentration above  $10^{-4}M$  carbinol suggests that these radicals are produced in the initial recombination of ions

formed in pairs close together, if charge transfer from the solvent ion to the carbinol has occurred prior to neutralization. Approximate linear dependence on the square root of solute concentration is expected for this mechanism (4). The radical yield seen at lower concentrations arises from other processes, perhaps in part from electron capture by the carbinol:



The most striking feature is that the yield of the carbonium ion is independent of concentration down to  $10^{-4}M$ , and is almost as great at  $10^{-5}M$ . The ion presumably arises by proton transfer to the carbinol from the free solvent ions which escape initial recombination. This reaction is almost complete in a few microseconds at  $10^{-5}M$  carbinol, and therefore occurs at every or nearly every encounter between the reacting molecules. It is reasonable to assume that practically every ion of the solvent is converted to  $(C_6H_5)_3C^+$ .

The ratio of  $G\epsilon$  in 2,2,4-trimethylpentane and in cyclohexane should give the ratio of the ion yields, since the optical properties of the ion are expected to be the same in all nonpolar solvents. The ratio from Fig. 2 is 2.1, whereas the clearing-field method gave for the pure solvents an ion yield ratio of 2.2, identical within experimental error (5). This confirms one of the unexpected results obtained by the clearing-field method.

With  $G\epsilon$  in cyclohexane about 2760, if we take  $G$  from the clearing-field measurements as about 0.147, we find  $\epsilon$  about 18800. In  $H_2SO_4$  solution,  $\epsilon = 38000$ . The change by a factor of 2 is not surprising, since one solvent is extremely polar and acidic, while the other is entirely nonpolar.

C. CAPELLOS  
A. O. ALLEN

Chemistry Department,  
Brookhaven National Laboratory,  
Upton, New York 11973

#### References and Notes

1. J. P. Keene, E. J. Land, A. J. Swallow, *J. Amer. Chem. Soc.* **87**, 5284 (1965).
2. F. S. Dainton, T. J. Kemp, G. A. Salmon, J. P. Keene, *Nature* **203**, 1050 (1964).
3. T. L. Chu and S. I. Weissman, *J. Chem. Phys.* **22**, 21 (1954).
4. F. Williams, *J. Amer. Chem. Soc.* **86**, 3954 (1964).
5. W. F. Schmidt and A. O. Allen, *Science*, this issue.
6. Research performed under the auspices of AEC.

30 January 1968; revised 12 March 1968

#### Proton Radiography

**Abstract.** Energetic protons from an accelerator may be used to produce radiographs showing unusually high contrast but relatively poor spatial resolution.

Energetic protons from an accelerator may be used to produce radiographs showing unusually high contrast but relatively poor spatial resolution. Figure 1 is a proton radiograph of a stack of aluminum absorbers, 18 g/cm<sup>2</sup> in thickness, with a piece of aluminum foil 0.035 g/cm<sup>2</sup> thick inserted at a depth of 9 g/cm<sup>2</sup>. Although the foil represents an increment of only 0.2 percent in the total thickness of aluminum, its outlines are quite clear. The fuzziness of the edges, caused by multiple small-angle scattering of protons in the aluminum, is estimated to extend 0.15 cm from each side of the true edge.

In order to produce a wide, uniform proton beam to illuminate the object to be radiographed, I have used a scatterer of lead, 7.4 g/cm<sup>2</sup> thick, in the external beam of the Harvard cyclotron (1). The beam striking the lead scatterer has a diameter of approximately 2 cm. Protons are reduced in energy from 160 to 137 Mev by the lead, but 3 m downstream, at the point where the radiographs are made, the proton flux is nearly uniform to a radius of 10 cm from the beam line. The measured percentage of this proton flux penetrating to various depths in aluminum is shown

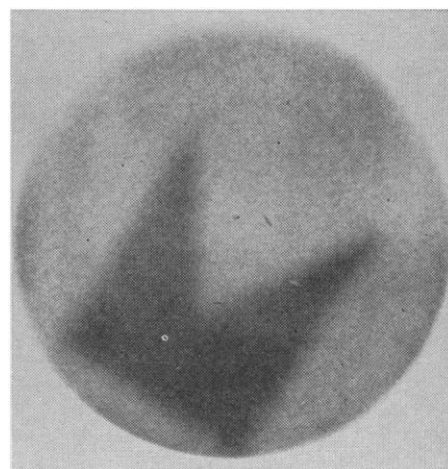


Fig. 1. Proton radiograph of aluminum absorber 7 cm in diameter and 18 g/cm<sup>2</sup> thick, with an additional thickness of 0.035-g/cm<sup>2</sup> aluminum foil, cut in the shape of a pennant, inserted at a depth of 9 g/cm<sup>2</sup>. The addition of 0.2 percent to the total thickness produces a substantially darker area on the film.

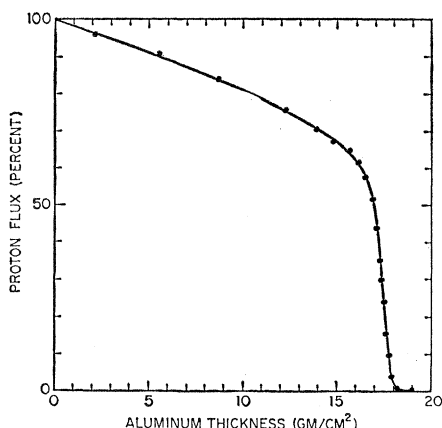


Fig. 2. Proton flux as a function of depth in aluminum. The steeply falling portion of the curve near 18 g/cm<sup>2</sup> is used to obtain the high contrast of Fig. 1.

in Fig. 2. Near total thickness of 18 g/cm<sup>2</sup> the flux is changed rapidly by small changes in thickness. A test object with average thickness equivalent to 18 g/cm<sup>2</sup> of aluminum, but with local voids, transmits a greater flux through the portion containing the voids; this variation can be recorded on photographic film pressed against the exit face of the test object. A thin object can be built up to equivalence to 18 g/cm<sup>2</sup> by placement of additional absorber ahead of it. Irregular objects can be radiographed by immersing them in an appropriate fluid contained in a parallel-sided box.

The proton exposure required to produce a radiograph depends on the photographic film and the thickness of the

absorber used. A surface exposure of  $2 \times 10^9$  proton/cm<sup>2</sup> was required for Fig. 1, with relatively insensitive Polaroid type-52 film (2). Induced radioactivity has not been a problem at such low exposures. Substantially lower exposures are sufficient if more-sensitive film is used in contact with an intensifying screen.

The smallest change in thickness that can be detected depends on the steepness of the flux-depth curve and on the characteristics of the photographic film. With Polaroid type-52 film and the proton beam just described, the minimum detectable change is now 0.01 g/cm<sup>2</sup>, or about 0.05 percent of the total thickness examined. Since the spatial resolution is so poor by comparison, the technique is best suited to detection of thin cracks or inclusions having considerable extent transverse to the beam, or to detection of density changes as small as 0.01 g/cm<sup>3</sup> extending over a volume of 1 cm in diameter, or greater, within a nearly homogeneous object. Applications to detection of flaws in technical materials and to medical radiography are possible.

A. M. KOEHLER

Cyclotron Laboratory,  
Harvard University,  
Cambridge, Massachusetts

#### References and Notes

1. G. Calame *et al.*, *Nucl. Instr.* **1**, 169 (1957).
2. Polaroid Corp., Cambridge, Mass.
3. Aided by ONR contract NONR 1866(56) and NASA grant NsG 262-63.

15 January 1968

## Sodium Ion Influences on Phosphorylations Associated with Oxidation of Succinate by Turnip Root Mitochondria

**Abstract.** Sodium ions ( $10^{-3}$  mole/liter) cause a marked increase in the ratio of phosphate esterified to oxygen utilized when turnip root mitochondria oxidize succinate. Separate study of the two phosphorylation sites associated with succinate oxidation indicates that the observed effect is a summation of differential responses of these sites to sodium ions. The activity of the first site, that associated with the reduction of cytochrome *c*, is stimulated about threefold by  $10^{-3}$  molar NaCl, whereas phosphorylation at the second site, coupled with the oxidation of ferrocytochrome *c*, is slightly inhibited by the same concentration of NaCl.

Although the yield of certain crops is increased as a result of the application of sodium salts (1) and although *Atriplex vesicaria* has a specific requirement for sodium when cultured in water carefully purified of Na<sup>+</sup> (2), sodium is more commonly considered to be either not required by plants or specifically toxic to them. The search for explana-

tions of the variety of responses elicited from plants by Na<sup>+</sup> has only recently turned to study of the effects of this ion on cell-free systems. Pea seedlings grown 6 days in  $75 \times 10^{-3}M$  NaCl produce mitochondria which have a higher rate of oxidation but the same P/O ratios [phosphate esterified (micromoles per hour) to oxygen utilized (microatoms

per hour)] as mitochondria from untreated seedlings (3). However, NaCl added to mitochondria during and after preparation has no effects on either oxidation or phosphorylation (3), but the experimental procedures indicate the presence of substantial concentrations of K<sup>+</sup>, which in our experiments can mask the effects of added Na<sup>+</sup>.

We have tried to determine the effects of Na<sup>+</sup> in a wide range of concentrations on the oxidation of succinate by plant mitochondria and the phosphorylations which accompany this oxidation.

Fresh turnips (*Brassica rapa*, L.) were obtained from a local market. Mitochondria were prepared from 200 g of root tissue by the method of Wedding and Black (4), the mitochondrial pellet being suspended after the second wash in 2 ml of 0.4M sucrose in 0.05M tris-Cl buffer [tris(hydroxymethyl)aminomethane] at pH 7.0.

The oxidative and phosphorylative capacity of mitochondria is usually measured in experiments where no particular effort is made to eliminate or restrict monovalent cations. In addition to the endogenous ions contributed by the tissues from which mitochondria are prepared, many substrates and cofactors are available only as Na or K salts. To provide for a minimum concentration of monovalent cations in the reaction mixture, we used all substrates and cofactors as tris or magnesium salts as indicated in the legends for the figure and tables. These salts were prepared either by neutralization of commercially available free-acid preparations, or by passage of Na or K salts of commercial products through Dowex 50 (8 percent cross-linkage, 400 mesh) ion-exchange resin followed by adjustment of the pH with tris base or MgO. The Na<sup>+</sup> content of flasks receiving no added NaCl was  $5 \times 10^{-5}M$ .

The oxidation of succinate was measured in a Warburg respirometer at 27°C. At the end of a 10-minute equilibration period, the system was closed and the mitochondria were tipped in from a side arm. Oxygen uptake was measured for the subsequent 30 minutes, after which the flasks were removed and placed in an ice bath. For measurement of phosphate esterification, 0.5 ml of the reaction mixture was pipetted into 2.0 ml of 10 percent trichloroacetic acid and centrifuged at 500g, and 0.2-ml samples of the clear supernate were used for determination of residual inorganic phosphate (4).

The "P/O" ratios relating to the re-