Since the spinach extracts contain pentose phosphate isomerase, the immediate precursor for carbon fixation may be ribose-5-phosphate or ribulose-phosphate. ATP may enter the reaction either before or after pentose phosphate is cleaved. The formation of PGA from carbon atoms 1 and 2 of pentose phosphate and carbon dioxide requires a reductive step which may be linked by TPN to the oxidation of glyceraldehyde-3-phosphate arising from carbon atoms 3, 4 and 5. The green parts of plants have been shown to contain a triose phosphate dehydrogenase which is active with TPN.[6]

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(6) M. Gibbs, *Nature*, **170**, 164 (1952).

(7) Aided by a fellowship from the National Foundation for Infantile Paralysis.

ELECTRON TRANSFER BETWEEN NAPHTHALENE NEGATIVE ION AND NAPHTHALENE[1]

Sir:

We have investigated the electron transfer reaction between naphthalene negative ion and naphthalene dissolved in tetrahydrofuran by a spectroscopic method.

Naphthalene negative ion, in dilute solution in tetrahydrofuran, possesses a complex paramagnetic resonance absorption spectrum of twenty-eight lines.[2] The lines are hyperfine components arising from interaction between the magnetic moment of the unpaired electron and the magnetic moments of the protons in the naphthalene negative ion.

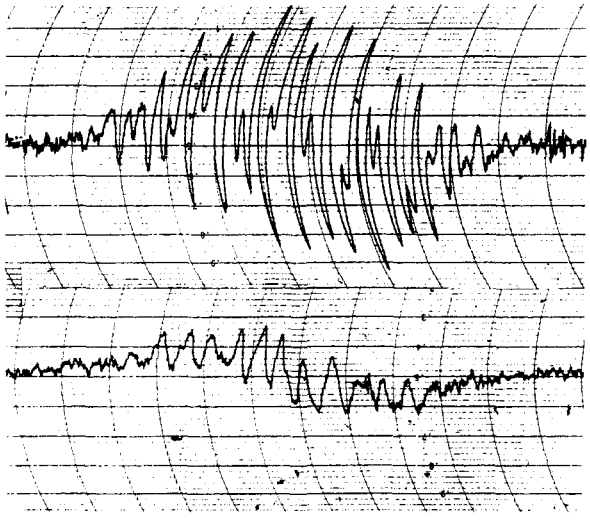

Fig. 1.—First derivative with respect to magnetic field *versus* magnetic field of the paramagnetic resonance absorption of naphthalene negative ion: upper curve ($C_{10}H_8^-$) = 5×10^{-4} *M*, ($C_{10}H_8$) = 0.0; lower curve ($C_{10}H_8^-$) = 5×10^{-4} M, ($C_{10}H_8$) = 0.35 *M*.

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For our purposes it is convenient to describe the spectrum by means of the reciprocal line breadths and reciprocal intervals. The reciprocal breadth of the individual lines, in dilute solutions of the sodium salt of naphthalene negative ion, is 6×10^{-7} seconds; the reciprocal intervals are in the neighborhood of 3×10^{-7} seconds.

When naphthalene is added to a dilute solution of naphthalene negative ion, the paramagnetic resonance spectrum of the latter is altered. Addition of a small amount of naphthalene leads to broadening of the individual hyperfine components. As larger amounts of naphthalene are added the hyperfine components merge into a single peak with broad tails extending beyond the region encompassed by the original hyperfine pattern.

A representative pair of spectra taken at 30°, one with the naphthalene negative ion at a concentration of 5×10^{-4} *M* and with no added naphthalene, the other with naphthalene negative ion at 5×10^{-4} *M* and naphthalene at 0.35 *M* are given in Fig. 1. (The spectra are displayed as first derivative of absorption with respect to magnetic field versus field.) The broadening of the individual lines may be observed by direct measurement, by the merging together of close components, and by the decrease in amplitude between maxima and minima.[3]

The line broadening in the presence of naphthalene we ascribe to the transfer of electrons from naphthalene negative ions to naphthalene molecules. Such transfer limits the lifetimes of the quantum states responsible for the hyperfine pattern and consequently broadens the lines. According to this interpretation of the line broadening the mean lifetime of an individual naphthalene negative ion in the presence of 0.8 *M* naphthalene is 1.2×10^{-6} second. Under the assumption that the electron transfer follows a second order rate law, the rate constant at 30° is 1.0×10^6 liter mole^{-1} sec.$^{-1}$.

The method here described does not depend, as do most rate determinations, on some method of distinguishing reactants from products. The observations reveal directly the quantity of interest—the mean time during which a particular configuration persists undisturbed.

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(2) D. Lipkin, D. E. Paul, J. Townsend and S. I. Weissman, *Science*, **117**, 534–535 (1953); S. I. Weissman, J. Townsend, D. E. Paul and G. E. Pake, *J. Chem. Phys.*, **21**, 2227 (1953); D. E. Paul, Ph.D. Thesis, Washington University, 1954.

(3) Under the conditions prevailing in this experiment the amplitude is proportional to the square of the reciprocal line breadth.