THE OXIDATION-REDUCTION POTENTIAL OF DIPHOSPHOPYRIDINE NUCLEOTIDE

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The generally-accepted value for the oxidation-reduction potential of diphosphopyridine nucleotide (DPN) is that reported by BORSOOK[1]; $E'_0 = -0.282$ V at pH 7.0 and 30°. This value differs from the value of −0.320 V (pH 7.0 and 25°), obtained by combining data[2,3] for the ethanol-DPN-acetaldehyde equilibrium with reliable values for the free energy of formation of aqueous ethanol (−43,390 cal.)[4] and acetaldehyde (−33,710 cal.). The latter value is obtained from data for the gaseous substance[4] and the partial vapour pressure[5] in solution.

To obtain an independent value for the DPN potential, the reaction between oxidised and reduced DPN, *iso*propanol and acetone has been studied. This was found to be catalysed by crystalline alcohol dehydrogenase prepared according to RACKER[3]. The equilibrium constant is as follows (25°):

$$K = \frac{[\text{acetone}] \cdot [\text{DPN.H}] \cdot [\text{H}^+]}{[\textit{iso}\text{propanol}] \cdot [\text{DPN}^+]} = 7.3 \cdot 10^{-9}\, M$$

Thermal data for acetone and *iso*propanol[6,7,8] are in excellent agreement with entirely independent equilibrium data for the catalytic dissociation of gaseous *iso*propanol into gaseous acetone and hydrogen[9,10]; the two ΔF° values thus obtained for this reaction differ by only 65 cal. The mean value together with vapour pressure data[11,12] gives at 25°:

*iso*propanol (aq) = acetone (aq) + $2H^+ + 2\varepsilon$; $\Delta F^\circ = 5{,}890$ cal.*

and hence:

DPN.H = $DPN^+ + H^+ + 2\varepsilon$; $\Delta F^\circ = -5{,}200$ cal.*

This corresponds to $E'_0 = -0.320$ V (pH 7.0; 25°) which is identical with the value from the ethanol-acetaldehyde system. In view of this agreement and the reliability of the free energy data, especially those for the *iso*propanol system, this value of E'_0 is estimated to be correct to ± 0.005 V. Full experimental and theoretical details will be submitted for publication in the *Biochemical Journal*.

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* The standard state for dissolved reactants, including the hydrogen ion, is unit activity (1 *M*). Although these are hypothetical conditions for many biological reactions, their use in free energy calculations is both valid and convenient.