Interaction of Quaternary Ammonium and Phosphonium Salts with Photosynthetic Membranes

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Distinct concentration ranges of selected quaternary ammonium and phosphonium salts were elaborated to induce stimulatory or inhibitory effects, respectively, on photosynthetic reactions. By means of fluorescence induction measurements 3 different effects of alkylbenzyldimethylammonium chloride (ABDAC; zephirol) in chloroplast preparations from Pisum sativum were observed. 60 μ M ABDAC produced a strong increase in $F_{\rm max}$ with concurrently improved Kautsky kinetics. Increased ABDAC concentration (500 µm) led to a strong fluorescence quenching - virtually indistinguishable from the conditions following the addition of photosystem II electron acceptors like K₃Fe[CN]₆. Further increase of ABDAC to 5 mm provoked a drastic increase in the fluorescence yield together with the complete loss of any detectable kinetics. We suggest a 3-step interaction of ABDAC with the thylakoid membranes of photosynthetic organisms similar to our earlier discussion (Bader and Höper (1993), Z. Naturforsch. 49 c, 87–94). We examined a series of derivatives with selectively modified side chains, central atoms and counter ions, respectively. Both an alkyl chain of the type ([-CH₂-]_n; $n \sim 10$) and effective polar components are indispensable for the adsorption and intercalation of the molecule onto and into the thylakoid membranes. The benzyl group could be replaced by a methyl residue without any loss of effectiveness; replacement of the central nitrogen (N) by phosphorus (P) and the counter ion Cl by Br did not modify the effects and the results were indistinguishable from the ABDAC effect proper. Shortening of the alkyl chain to $(-CH_2)_6$ resulted in a less effective interaction of e.g. tetraoctylammonium bromide with the photosynthetic membrane. Flash-induced oxygen evolution measurements with selected derivatives (15 µm) substantiated our interpretation of an improved OEC functioning by a substantial lowering of the miss parameter α and the exclusion of a chemical reduction as the standard S-state distribution was not affected. As evidenced by both SDS-PAGE and Western blot analyses the investigated molecules showed a direct interaction. The polypeptide patterns were characterized by a severe shift of the molecular weight components from high (20-67 kDa) to low (< 20 kDa) values.