

REACTION OF BETA-CAROTENE WITH METAL IONS

K.A. Crouse, Kamaliah Sirat, M.H.T. Tarafder, M.W. Yii, M. Badri and M.A. Rahim Khan

Faculty of Science and Environmental Studies
Universiti Putra Malaysia, 43400 UPM, Serdang, Selangor,
Malaysia

Keywords: beta-carotene, beta-carotene-metal complexes, beta-carotene stability, organometallic, kinetics.

Introduction

Beta-carotene is naturally present in palm oil and many other vegetables and vegetable oils. Beta-carotene is known to be a precursor of vitamin A and is proposed to be a free radical scavenger playing an important role as an anti-cancer agent. Metals/ metal ions are known to play a role in the degradation of crude palm oil but the mode of action is to date undetermined. It has also been proposed that oxidation of beta-carotene is one of the reasons for off-flavours sometimes found in palm oil. Carotenes have been found to react with strong acid in non-aqueous media to produce cations which were found to be unstable and were said to possibly undergo isomerization and oxidation. The objectives were to study the kinetics and mechanism of reaction of beta-carotene with different metal ions in various solvent systems. It is expected that the outcome of this research will be an understanding of the role of metals in their reaction with beta-carotene. Such an understanding could lead to modification in the methods of production, storage and use of palm oil and beta-carotene if necessary/beneficial.

Materials and Methods

The study of the kinetics of the reaction of beta-carotene with different metal ions including Co, Fe, Sn, Cr, Mo, W and Cu in non-aqueous solvent systems are carried out using the standard methodology for reaction kinetics. The variation in concentration of beta-carotene is followed using uv/vis spec-

troscopy. Intermediates produced, which are sufficiently stable to enable isolation are characterised by elemental analysis, uv/visible and infrared spectroscopy and thermal degradation. Final degradation products are separated using extraction and precipitation and are to be analysed using chromatographic procedures.

Results and Discussion

Pi-complexes of beta-carotene with Cr, Mo and W carbonyls and Cu and Fe nitrates have been characterised. To date no complexes have been isolated containing Ni, Sb, Sn or Co. The formula proposed for the carbonyl complexes is $M_4L(CO)_4$, while that for the Cu and Fe complexes are $Cu_4L(NO_3)_8 \cdot 4H_2O$ and $Fe(NO_3)_3 \cdot 2CH_2Cl_2$ where L= carotene and M=metals. Kinetic studies of the reactions of Cr and Mo carbonyls with beta-carotene have been done in CCl_4 while the Cu, Fe and Co nitrates were reacted in mixed ethanol- CCl_4 solvents and Sn(II) and Sn(III) chlorides were investigated in acetone and ethanol. In all cases (except Sn(II) where reaction did not take place) the reactions were found to be pseudo first order in beta-carotene. The enthalpies and entropies of activation have been determined. Negative entropies of activation indicate that the transition states are more ordered than the initial states. Investigation of the Co system using aquated $Co(NO_3)_2$ and $CoCl_2$ in ethanol/ CCl_4 indicate that the immediate coordination environment at the Co center plays a crucial role in the formation and decomposition of the Co-carotene complex.

Conclusions

The presence of metals accelerates the decomposition of beta-carotene in all solvent systems studied. The reaction most certainly involves a metal-carotene intermediate. The complexes do not undergo simple dissociation but the beta-carotene is decomposed in the reaction. The rates of reaction are most likely highly sensitive to the immediate coordination environment at the metal centres. Most intermediates seem to be very unstable and therefore elusive. Complexes of metal carbonyls are more readily isolated than others.