solvent effects on the dehydrochl orination of 1.1.1- trichloro- 2.2- diary lethanes and on the hydrolysis of trichlorome thylbenene

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The kinitics of dehydrochlorination of trichloro-2,2-diaryleth-anes (trichloro-2,2-diphenylethane, 1,1,1-trichloro-2,2-bis-p-chloro-phenylethane and 1,1,1-trichloro-2,2-bis-p-methylphenylethane) by methoxide and propoxide ions in methanol-carbontetrachloride and methanol / i-propanol mixed solvents were studied in solvent composi-tions from 0.1 to 1.0 and from 0.0 to 1.0 methanol mole fraction respectivity, at the temperature range 25 to 55°C .The rate of the dehydrochlorination of 1,1,1-trichloro-2,2-diaryleth-anes are gaverned by EL cB mechanism in which the rate of reaction is first order with respect to 1,1,1-trichloro-2,2-diarylethanes and to the base ion concentration in each case. The dehydrochlorination of 1,1,1-trichloro-2,2-diarylethanes followed a second-order rate law. The mechanism of reaction involve two steps, the initial formation of the carbanion which is turn eliminate chloride ion to yield 1,1,1- trichloro-2,2-diaryleth ylenes.In the dehydrochlorination of 1,1,1-trichloro-2,2-diarylethanes, the rate -increases with increasing the methanol content in solutions in case of methanol carbontetrachloride, but the rate increases as the i-propanol content of solution increaese in case of methanol/i-prop-anol solutions.The results were discussed on the basis of the simple electrostatic theory of medium effect and the changing of solvent structure. The plot of In k versus 1/D in case of the dehydrochlorination of 1,1,1- trichloro-2,2-diarylethanes in methanol-carbontetrachloride and in methanol / i-propanol gave no stright line relationship. This is not in occordance with electrostatic theory of medium effects.In spit of large difference of the activation parameters for the 1,1,1-trichloro -2,2-diarylethanes, it was found that the activation parameters (Ea, H* and S) have maximum and minimum values at different solvent compositions.In the dehydrochlorination of trichloro-2,2-diarylethanes in methanol-carbontetrachloride mixed solvents, it can be show that the activation parameters for the dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane have miximum and minimum values at 0.7 and -0.4 methanol mole fraction, respectively, but in case of both 1,1,1- trichloro-2,2-bis p-chlorophenylethane and 1,1,1-trichloro-2,2-bis-p-methylphenyethane the activation parameters have a miximum value at about 0.2 methanolornOle fraction and then decreases with increasing the methanol content.In the -dehydrochlorination reaction of 1,1,1-trichloro-2,2-diarylet-hanes in methanol/i propanol mixed solvents, it can be shown that the activation parameters for the

dehydrochlorination of 1,1,1-trichloro-2,2-diphenylethane, . frist decrease to a minimum values at about0.2 methanol mole fraction and then increases with -increasing the methanol content. However, the activation parameters for the dehyd rochlorination of 1,1 ,1-trichloro-2,2-bis-p-chlorophenylethane have two maxima, one at about 0.8 and other at about 0.1 methanol mole fraction. Also, the -activation parameters for the dehydrochlorination of 1,1,1-trichloro-2,2-bis-p methylphenylethane have two mixima values at about 0.2 and 0.9 methanol mole fractions and minimum value at about 0.4 methanol mole fraction.The hydrolysis of trichloromethylbenzene is studied in water-acetone solution covering solvent composition range from 0.1 to 0.7 water mole fraction at the temperature range 25 to 45°C the rate of hy-drolysis decreases by increasing the water content in solution up to 0.5 water mole and then increases. The result were discussed on the basis of the simple electrostatic theory of medium effect and the changing of solvent structure. The plot of Ink versus (D-1)(2D+1)-I gave no stright line.The activation parameters for the hydrolysis of trichloromethylben-zene have minimum values at about 0.23 water mole fraction.The calculated values of the free energy of activation A G*do not change much with solvent composition and the plot of A I-1* versus A S* gave a stright line in all substrates (1,1,1-trichloro-2,2-diaryl-ethanes and trichloromethylbenzene) this is due to the linear compen-sation between A H and AS .