Estimation of Crotonaldehyde Carbonyl Stabilization Energy in Methanol

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WE have obtained an estimation of the crotonaldehyde carbonyl stabilization energy by comparing the extent of dimethyl acetal formation for crotonaldehyde and n-butyraldehyde.

Equilibrium constants for methyl hemiacetal and dimethyl acetal formation were obtained spectrophotometrically over a 25° temperature range. The thermodynamic data are summarized in the Table.

Thermodynamic parameters for the reaction

$$\mathrm{RCHO} + n\mathrm{MeOH} \rightarrow \mathrm{RCHXOMe} + (n - 1)\mathrm{H_2O}$$

R	n	X	ΔH(kcal./mole)	ΔS(e.u.)
$\mathrm{Pr^n}$	1	OH	− 7·6 ± 0·2	− 27 ± 1
$\mathrm{Pr^n}$	2	OMe	− 8·8 ± 0·3	− 29 ± 1
MeCH : CH[a]	1	OH	− 2·5 ± 0·2	− 23 ± 1
MeCH : CH	2	OMe	− 3·7 ± 0·2	− 25 ± 1

[a] Crotonaldehyde forms no detectable hemiacetal in neutral methanol. Thermodynamic values were calculated using the data for n-butyraldehyde and for crotonaldehyde dimethyl acetal.

The stabilization energy of the crotonaldehyde carbonyl group (in methanol) is calculated to be 5·1 ± 0·3 kcal./mole, which is the difference between the enthalpies of formation of the dimethyl acetyls of crotonaldehyde and n-butyraldehyde Inspection of molecular models suggests that steric contributions to this value are small, although because of repulsive interactions in n-butyraldehyde dimethyl acetal, 5·1 kcal./mole probably represents a minimum value.

Details of these experiments and of low-temperature n.m.r. detection of hemiacetals and hydrates will be published shortly.

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