ABSTRACTS

Effect of Adjacent Groups on the Symmetrical CD$_3$ Deformation Frequencies

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The symmetrical CD$_3$ deformation frequencies δ_{CD_3} of deuterated methyl compounds CD$_3$XH$_{m-1}$, CD$_3$XD$_{m-1}$, (CD$_3$)$_2$XH$_{m-2}$, (CD$_3$)$_2$XD$_{m-2}$,...... (CD$_3$)$_m$X are studied in relation to the type of X atom in groups IV~VII of the periodic table, where m is the valence of X atom.   The frequency variations are ascribed to changes in the deformation force constants, and can be expressed as

$$\delta_{CD_3} = 317 \log\left(\frac{x_X}{r_{CX}^2}\right) + 1046$$

for almost every molecule examined.   Here x_X represents the electronegativity of X atom and r_{CX} the C–X bond length.   This equation is in good agreements with the theoretical one which was derived from the results previously proposed by the author for the symmetrical CH$_3$ deformation frequencies of undeuterated methyl compounds, and which was obtained by taking into consideration the change of G matrix on deuteration of methyl group.   Discrepancies between observed and calculated frequencies for some molecules may be attributed to the coupling of the vibration with the other modes of vibrations in the molecule.

High Pressure Synthesis of Acetic Acid from Methanol and Carbon Monoxide

Kinetic Studies on the Reaction Catalized by Phosphoric Acid

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Kinetic studies have been made on the synthesis of acetic acid from methanol and carbon monoxide in the presence of phosphoric acid :

$$CH_3OH + CO \xrightarrow{H_3PO_4} CH_3COOH \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(1)$$
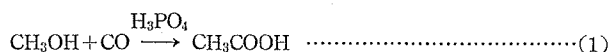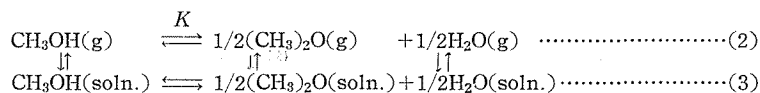
Following results have been found out :
1) Equilibrium data :
Methanol is in equilibrium with the dehydration products *i.e.*, Me$_2$O and H$_2$O,

in the autoclave above 300°C, and each gaseous component is also in equilibrium with each dissolved in the phosphoric acid medium.

Following equilibrium constants have been obtained :

$$CH_3OH(g) \overset{K}{\rightleftharpoons} 1/2(CH_3)_2O(g) +1/2H_2O(g) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(2)$$
$$\updownarrow \qquad\qquad \Updownarrow \qquad\qquad \downarrow\uparrow$$
$$CH_3OH(soln.) \rightleftharpoons 1/2(CH_3)_2O(soln.)+1/2H_2O(soln.)\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

dehydration equilib. : $K = P_e^{1/2} P_w^{1/2} P_m^{-1}$ $\qquad (K=2.1$ at 350°C, 2.3 at 370°C)

methanol vapor equilib. : $P_m N_p N_{ml}^{-1} = 2.9 P_m + 106$ $\qquad$ (350°, 370°C)

ether vapor equilib. : $N_{el} N_p^{-1} = 0.001 P_e$ $\qquad$ (350°, 370°C)

water vapor equilib. : $P_w = 30 N_w N_p^{-1}$ $\qquad$ (350°, 370°C)

where, suffixes w, m, e and p stand for H_2O, MeOH, Me_2O and H_3PO_4 respectively, and l stands for the liquid. N and P denote the mole of each component and pressure, respectively.

2) Effect of temperature (330°~390°C, CO 700 atm., MeOH 0.25M, 85 wt% H_3PO_4 0.25M) :

Initial velocity $(dy/dt)_0 \times 10^{-3}$ is 1.20 at 330°C, 3.58 at 350°C, 7.04 at 370°C and 16.8 at 390°C, respectively.

3) Effect of pressure (370°C, CO 500~1000 atm., MeOH 0.25M, 85 wt% H_3PO_4 0.25M) :

Forty mol% yield is attained at 500 atm. of CO pressure and 80 mol% yield at 1000 atm., both after 3 hrs.

Initial velocity is of the first order with respect to the fugacity of CO.

4) Effect of the charged amount of MeOH and H_3PO_4 (370°C, CO 600 atm., 85 wt% H_3PO_4 0.125~0.526M, MeOH 0.125~0.526M) :

Initial velocity is expressed to be the first order with respect to the dissolved MeOH, which can be calculated by eq. (8).

$$N_{ml} N_{m0}^{-1} = (2a_0 f_1 N_{m0})^{-1}\{ -(a_0 f_0 N_{m0}+b_0 - a_0 f_2 - f_1)$$
$$+[(a_0 f_0 N_{m0}+b_0 - a_0 f_2 - f_1)^2 - 4a_0 f_1 (f_2 - f_0 N_{m0})]^{1/2}\}\cdots\cdots\cdots(8)$$

where, $a_0 = 2.9 N_p$, $b_0 = 106 V_f (N_p RT)^{-1}$, $G = 2(0.001 RT N_p V_f^{-1}+1)$,

$\qquad H = (1+2R'GN_{m0}^{-1}+R'KN_{m0}^{-1})^{1/2}$, $R' = N_{m0}(N_p AG)^{-1}$, $K = K_p^2 RT V_f^{-1}$,

$\qquad f_0 = (GHK^{1/2}-1)B^{-1}$, $f_1 = (1-GK^{1/2}PH)B^{-1}$, $f_2 = R'GB^{-1}$, $B = G^2 K - 1$,

$\qquad V_f =$ free volume of autoclave, $N_{m0} =$ charged MeOH (mol.).

All values can be derived from the relations (4), (5), (6) and (7).

5) From the above results, next rate equation can be derived for the initial stage of the reaction.

$$(dy/dt)_0 = k f_{c0} (N_{ml}/N_{m0}) \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots(9)$$

where, $y =$ produced AcOH/chared MeOH (M/M)

$\qquad f_{c0} =$ fugacity of CO, $(N_{ml}/N_{m0}) =$ eq. (8)

Rate constants k's have been calculated to be 1.76×10^{-5} at 330°C, 4.47×10^{-5} at 350°C, $7,50 \times 10^{-5}$ at 370°C. The activation energy of 27 Kcal./mole has been obtained.