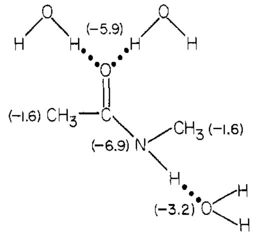
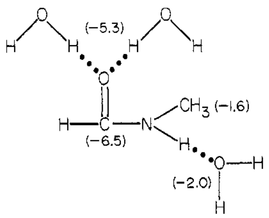
stabilizes the amide resonance form $^-O–C{=}N^+$ to a greater extent than does hydrogen. Thus the carbonyl of acetamides is more basic than the carbonyl of formamides. Similarly, the proton-donating ability of the acetamide N–H is enhanced over that of the formamide N–H.

When the interaction terms found in this work for the amides are used, the hydration enthalpy of a model peptide unit, NMA, in water may be found.



The numbers in parentheses give the NMA–water interaction in kcal mol^{-1}. The enthalpy terms at the methyl groups result principally from the energetically favorable restructuring of the water molecules about the methyl groups. For the water molecules at the carbonyl or N–H, a hydrogen bond can be formed, which may take the place of a water molecule previously hydrogen bonded to another water molecule. Consequently, the rearrangement of water molecules about the carbonyl and N–H groups is not significantly altered from normal structure.[1] The overall enthalpy of NMA in water is then found by summing all the interaction terms. This enthalpy is –19.2 kcal mol^{-1} as previously given. Similar calculations may be made for the amides in all solvents.

It is instructive to compare the hydration enthalpy of NMF in water with that of NMA.



The overall enthalpy of NMF is –15.4 kcal mol^{-1} as compared to –19.2 kcal mol^{-1} for NMA in water. The additional methyl group of NMA accounts for 1.6 kcal mol^{-1} of the 3.8 kcal mol^{-1} difference, but the remaining 2.2 kcal mol^{-1} come from the effect of the methyl group attached to the carbon on the functional group. The carbonyl of NMF is not as good a proton acceptor as that of NMA and the NMF proton is not as available for hydrogen bonding. In addition, the dipole of the functional group C=ON< is not as great for NMF as for NMA so that the VDW terms are less for NMF.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research and to the Research Corporation for funds for the purchase of the Tronac 450 calorimeter. The authors also acknowledge Project SEED for providing funds for one student (D.B.) to assist in this work.

Supplementary Material Available: Heats of solution and mmol quantities of solute used for NMF, DMF, NMA, and DMA in water; formamide and acetamide in DMF and DMA (3 pages). Ordering information is available on any current masthead page.

Gas-Phase Pyrolysis Kinetics of 5-Acetoxy-2-methylpent-2-ene

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(Received: October 6, 1980)

The kinetics of the gas-phase pyrolysis of 5-acetoxy-2-methylpent-2-ene has been measured over the temperature range 330–380 °C and pressure range 53–210 torr. The reaction, in a static system seasoned with allyl bromide, and in the presence of propene inhibitor, is homogeneous, obeys a first-order law, and is unimolecular. The rate constants are given by the Arrhenius equation $\log k(\mathrm{s}^{-1}) = (13.21 \pm 0.14) - (199.6 \pm 1.7)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$. The presence of the $(CH_3)_2C{=}CH$ group at the β-carbon atom of ethyl acetate does not provide anchimeric assistance in the elimination of this ester. A simultaneous effect of both steric acceleration and the allylic weakening of the β hydrogen appears to cause a slight rate enhancement of the Z = $(CH_3)_2C{=}CH$ group relative to Z = $CH_2{=}CH$ group in the pyrolysis of ZCH_2CH_2OAc.

Introduction

The neighboring olefinic double bond has been found to assist anchimerically the gas-phase dehydrohalogenation of $CH_2{=}CHCH_2CH_2Cl$[1] and $(CH_3)_2C{=}CHCH_2CH_2Cl$.[2] These studies were associated with the π-bond participation during solvolysis of their corresponding tosylates.[3,4] However, the vinyl group in 3-buten-1-yl acetate does not participate in the rate of pyrolysis of this ester; it only increases the elimination rate due to an allylic weakening of the C_β–H bond.[5] The loosening of C_β–H has also been found to be caused by other π-bonds adjacent to the β-carbon atom in ethyl acetates, where the sequence in py-

TABLE I: Temperature Dependence of the Rate Constants

temp, °C	330.2	340.3	350.1	355.1	360.2	370.1	380.1
10^4k_1, s^{-1}	0.84	1.63	2.95	3.99	5.62	9.84	17.62

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0022-3654/81/2085-1241$01.25/0

TABLE II: Influence of Z = π Bond in ZCH_2CH_2OAc Pyrolyses at 360 °C

Z	10^4k_1, s^{-1}	10^4k_H, s^{-1}	rel rate/H	E_a, kJ mol^{-1}	log A, s^{-1}	ref
H	1.02	0.34	1.0	200.5(±3.8)	12.55(±0.30)	11
CH_3CH_2	1.15	0.58	1.7	199.3(±4.6)	12.50(±0.36)	11
$CH_2{=}CH$	4.27	2.14	6.3	200.8(±2.1)	13.20(±0.17)	5
$CH{\equiv}C$	6.92	3.46	10.2	197.3(±1.6)	13.12(±0.13)	6
$(CH_3)_2CH^a$	1.05	0.53	1.6	202.5(±3.8)	12.73(±0.19)	12
C_6H_5	4.68	2.34	6.9	191.6	12.48	11
$CH_3CH_2CH_2{}^a$	1.51	0.76	2.2	194.1	12.20	13
$(CH_3)_2C{=}CH$	5.50	2.75	8.1	199.6(±1.7)	13.21(±0.14)	this work

[a] This compound is the closest saturated ester reported in the literature for comparative purpose.

rolysis rates $CH{\equiv}C > Ph > CH_2{=}CH$[6] is in accord with their effect on the acidity of C_β–H.[7]

Since the rate of acetolysis of 4-methyl-3-penten-1-yl tosylate is 1200 times faster than ethyl tosylate at 45 °C[4] and the rate of pyrolysis of 5-chloro-2-methylpent-2-ene is 53 times faster than ethyl chloride at 440 °C,[2] it seemed desirable to examine if the neighboring $(CH_3)_2C{=}CH$ group assists the gas-phase elimination of 5-acetoxy-2-methylpent-2-ene.

Experimental Section

5-Acetoxy-2-methylpent-2-ene was prepared from dimethylcyclopropylcarbinol according to the method of Julia et al.[8] (bp 104–105 °C (85 torr)). This ester was distilled several times and the fraction with over 99.8% purity (gas–liquid chromatography) was used. The olefins 2-methylpenta-1,4-diene, 4-methylpenta-1,3-diene, and *trans*-2-methylpenta-1,3-diene were acquired from K & K Labs Inc. The column for quantitative analyses was diisodecyl phthalate–5% Chromosorb G AW DMCS 60–80 mesh (length, 6 ft; temp, 130 °C). The purity and identity of the acetate and dienes were further verified with a mass spectrometer, by infrared spectroscopy, and by nuclear magnetic resonance.

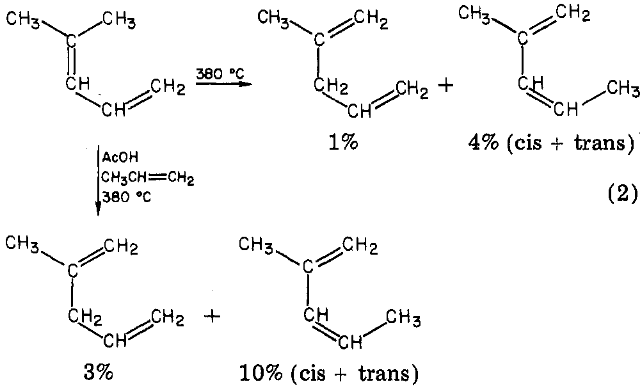
The ester was pyrolyzed in a static reaction vessel seasoned by the decomposition product of allyl bromide.[9,10] The reactions were always carried out in the presence of the inhibitor propene and kinetic measurements were obtained manometrically. The temperature was kept constant to better than ±0.2 °C.

Results and Discussion

The pyrolysis of 5-acetoxy-2-methylpent-2-ene, in a static system seasoned with allyl bromide and in the presence of propene inhibitor, was studied in the temperature range 330–380 °C and pressure range 53–210 torr. The stoichiometry of reaction 1 requires the final pressure,

$$(CH_3)_2C{=}CHCH_2CH_2OAc \rightarrow C_6H_{10} + AcOH \quad (1)$$

P_f, to be twice the initial pressure, P_0. The average experimental P_f/P_0 values at four different temperatures and ten half-lives was 2.17. The departure of $P_f = 2P_0$ is due to a small decomposition of the acetic product. The above stoichiometry was verified by comparing the percentage decomposition of the substrate from pressure measurements with those obtained by chromatographic analysis of the diene products. The ester (1) yielded largely 4-methylpenta-1,3-diene, *cis*- and *trans*-2-methylpenta-1,3-diene, and a very small amount of 2-methylpenta-1,4-diene. Traces of 4-methyl-1-pentene and 1-butene were also detected. The formation of isomers of the normal elimination product 4-methylpenta-1,3-diene has suggested that this olefin must undergo an isomerization process. To check this fact, pure olefin (eq 2) alone produced 5% isomerization, whereas in the presence of AcOH and propene inhibitor the yield was 13% isomerization in 2 min at 380 °C. These processes were found to be too fast, even at the lowest working temperature of 330 °C, in order to estimate the rates of isomerizations.



(2)

The homogeneity of this reaction was studied by using a vessel with a surface-to-volume ratio of 6.14 relative to the normal vessel. The rates were unaffected in the packed and unpacked seasoned vessels, but a small heterogeneous effect was found in the clean packed and unpacked vessels. The presence of different ratios of propene, a free-radical inhibitor, had no effect on the rates, and no induction period was observed.

The rate constants for elimination showed no significant variation with change of initial pressure and the first-order plots are linear up to 60% decomposition. The variation of the rate constants with temperature (Table I) was fitted to the following Arrhenius equation obtained by the least-squares procedure (0.8 confidence coefficient): $\log k(s^{-1}) = (13.21 \pm 0.14) - (199.6 \pm 1.7)$ kJ mol^{-1} $(2.303RT)^{-1}$.

Apparently, from the data listed in Table II the $(CH_3)_2C{=}CH$ group does not anchimerically assist the elimination of 5-acetoxy-2-methylpent-2-ene, because its rate ratios with respect to ethyl acetate of 8.1 and to the closest saturated ester *n*-pentyl acetate of 3.7 are not very significant.

The sequence of the substituents adjacent to the β carbon of ethyl acetate, $CH{\equiv}C > C_6H_5 > CH_2{=}CH$,[6] shown in Table II is similar to their effect on the acidity of the C_β–H bond.[7] However, it is interesting to note that

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the $+I$ electron release of the two methyl groups in $(CH_3)_2C{=}CH$ which ought to weaken the C_β–H less than the $CH_2{=}CH$ group, promotes a small increase in rate. This departure in k values may be attributed to the simultaneous effect of both steric acceleration by the two methyl groups and the allylic weakening of the β hydrogen. Branched alkyl substituents adjacent to the β carbon atom of ethyl acetate are known to slightly enhance steric acceleration.[12]

The present results confirm that esters are semipolar or semiconcerted in the transition state and less heterolytic in nature than alkyl chlorides.[14] Consequently, the occurrence of neighboring group participation in gas-phase pyrolysis of esters is uncommon.

Gas-Phase Elimination Kinetics of Ethyl Esters of Chloroacetate, 3-Chloropropionate, and 4-Chlorobutyrate. The Electronic Effects of Substituents at the Acyl Carbon

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(Received: October 9, 1980)

Several ethyl chloroesters were pyrolyzed in a static reactor in the presence of a propene inhibitor at temperatures between 360 and 420 °C and pressures between 49 and 209 torr. The reactions are homogeneous, unimolecular, and follow a first-order rate law. The temperature dependence of the rate coefficients is given by the following Arrhenius equations: for ethyl chloroacetate, $\log k(\mathrm{s}^{-1}) = (12.70 \pm 0.50) - (197.0 \pm 6.1)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$; for ethyl 3-chloropropionate, $\log k(\mathrm{s}^{-1}) = (12.54 \pm 0.22) - (196.8 \pm 2.7)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$; and for ethyl 4-chlorobutyrate, $\log k(\mathrm{s}^{-1}) = (12.67 \pm 0.31) - (198.7 \pm 3.8)\ \mathrm{kJ\ mol^{-1}}\ (2.303RT)^{-1}$. The data from the rate coefficients give an approximate correlation only with σ^* values ($\rho^* = 0.357$, $r = 0.903$, and intercept = 0.048 at 400 °C). The present work together with those reported in the literature suggests, in general, that electron-withdrawing substituents at the acyl carbon of ethyl, isopropyl, and *tert*-butyl esters of substituted acetates enhance the rate of elimination, whereas electron-releasing substitutents decrease it.

Introduction

Two recent works on the effect of substituents at the acyl carbon in the gas-phase pyrolysis of esters obtained approximate linear correlations. Thus, for *tert*-butyl α-substituted acetates, the plot of $\log k/k_0$ vs. σ_I gave a $\rho_I = \sim 1.4$ at 600 K,[2] whereas for isopropyl α-substituted acetates, plotting $\log k/k_0$ vs. σ^* yielded $\rho^* = 0.464$, $r = 0.963$, and intercept = 0.044 at 330 °C.[3] The former work reached the conclusion that electron-withdrawing substituents enhance the rate of elimination, while electron-supplying substituents decrease it. In the latter work, polar substituents affect the elimination by electronic transmission, where the reaction rate is faster the greater the electron withdrawal of the substituent. However, for alkyls the rate of decomposition was believed to be influenced by steric factors as reported in earlier investigations.[4,5]

In connection with the above-described works,[2,3] a careful appraisal of the literature of the substituent effect at the acyl carbon of ethyl esters shows few pyrolysis studies for comparison. Because of this fact, the aim of the present work is to study along this line the effect of a polar substituents at the α carbon. Moreover, it is also intended to insulate this polar group with methylene groups with respect to the acyl carbon in order to decrease its electronic effect and to increase the alkyl nature of the substituent. This gradual increase in alkyl nature should determine whether steric and/or polar factors are determinant at the acetate portion of esters. To meet this end, the gas-phase pyrolyses of ethyl chloroacetate, ethyl 3-chloropropionate, and ethyl 4-chlorobutyrate were undertaken.

Experimental Section

Ethyl 3-chloropropionate and ethyl 4-chlorobutyrate were acquired from Aldrich. However, ethyl chloroacetate was prepared when chloroacetic acid was treated with ethanol as described[6] (bp 47 °C at 20 torr; lit. bp 161 °C[7]). These esters were distilled several times and the fraction with over 99.8% purity (gas–liquid chromatography) was used. A column of FFAP 7%-Chromosorb A AW DMCS 80–100 mesh was used for the analysis of the esters, whereas a 6-ft column of Porapak R 80–100 mesh was used to quantitatively determine the olefin product ethylene.

The substrates were pyrolyzed in vessels which had been seasoned by decomposition of allyl bromide[8,9] and the kinetics were followed manometrically. No temperature gradient was found along the reaction vessel. The temperature was found to be stable within ±0.2 °C with a calibrated platinum–platinum—13% rhodium thermocouple. The ethyl esters were injected into the reaction

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