TABLE II: Kinetic Parameters of ZCH_2CH_2Cl at 440 °C

Z	$10^4 k_1$, s^{-1}	rel rate per H	E_a, kJ/mol	log A, s^{-1}	ref
H	1.34	1.0	241.8 (±4.2)	13.84 (±0.20)	16
C_6H_5	7.73	8.6	220.9 (±4.6)	13.07 (±0.35)	3
o-$CH_3C_6H_4$	6.44	7.2	231.4 (±3.6)	13.76 (±0.27)	this work
m-$CH_3C_6H_4$	6.07	6.7	219.2 (±3.5)	12.84 (±0.26)	this work
p-$CH_3C_6H_4$	7.60	8.4	234.1 (±2.5)	14.03 (±0.19)	this work
p-$CH_3OC_6H_4$	12.00	13.3	228.4 (±4.6)	13.81 (±0.34)	3

assists the elimination in each of these halides, the electron release of the methyl group, at the three isomeric positions of the benzene ring, is apparently ineffective on the rate of dehydrohalogenation when compared to the unsubstituted 2-phenylethyl chloride. Within the experimental error, the reaction velocities are the same. Therefore, the effect of the CH_3 substituent appears to be weak in order to reinforce the phenyl assistance in rate augmentation in some of these methyl 2-phenylethyl chlorides. However, in the case of the p-methoxy substituent, its electron delocalization (+R effect) toward the aromatic nuclei causes a significant increase in rates by participation of the p-anisyl when compared with ethyl chloride and 2-phenylethyl chloride as already described.[3]

Steric Acceleration in the Pyrolysis Kinetics of 2-Substituted Ethyl Acetates

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The rates of elimination of several cyclo and branched alkyl substituents at the β carbon of ethyl acetates have been determined in a static system over the temperature range of 360–420 °C and pressure range of 34–337 torr. The reactions are homogeneous in both clean and seasoned vessels, follow a first-order rate law, and are unimolecular. The rate coefficients are given by the following Arrhenius equations: for 2-cyclohexylethyl acetate, $\log k_1\ (s^{-1}) = (13.30 \pm 0.28) - (208.1 \pm 3.4)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; for 2-cyclopentylethyl acetate, $\log k_1\ (s^{-1}) = (13.20 \pm 0.26) - (207.4 \pm 3.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; for 3-methyl-1-pentyl acetate, $\log k_1\ (s^{-1}) = (13.62 \pm 0.09) - (211.9 \pm 1.2)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$; for 4-methyl-1-pentyl acetate, $\log k_1\ (s^{-1}) = (12.82 \pm 0.05) - (203.1 \pm 0.6)\ kJ\ mol^{-1}\ (2.303RT)^{-1}$. The present data together with those reported in the literature give a good correlation line only, when plotting $\log k/k_0$ against Hancock's E_s^c values ($r = 0.916$, $\delta = -0.121$, and intercept $= -0.020$ at 400 °C). This work ratifies that steric acceleration is responsible for the rate of elimination of alkyl and several polar substituents interposed by at least three methylene groups with respect to C_α–O bond of ethyl acetates. Unreported E_s^c values of several substituents are defined.

Introduction

Linear correlation for the gas-phase elimination of aliphatic β-substituted ethyl acetates have been reported only recently.[2,3] The compiled data and experimental results in these works revealed the various type of effects of Z in $ZC_\beta H_2C_\alpha H_2OAc$. Thus, we have group A where β-alkyl groups and several polar substituents interposed by at least three methylene groups with respect to the C_α–O bond of the acetate enhanced the rate of the reaction due to steric acceleration. Plotting $\log k/k_0$ vs. E_s values gave an approximate linear relationship ($r = 0.914$ at 400 °C). Steric acceleration has already been described for β-substituted ethyl acetates.[4] However, when the phenyl substituent in 2-phenylethyl acetate is considered an exception due to benzylic weakening of the C_β–H bond[2] and it is excluded from this graph, the above linear relationship will give an unsatisfactory correlation coefficient ($r = 0.800$ at 400 °C). This result suggests that additional data are needed for a better correlation. For group B, polar β substituents with a strong electron-withdrawing effect slowed the pyrolysis rates of these acetates.[3] In spite of small differences in effects, the greater the electronegativity of the substituent the slower is the pyrolysis. These groups gave a good linear relationship by plotting $\log k/k_0$ against σ^* values with $\rho^* = -0.19$ at 400 °C ($r = 0.961$). Likewise, plotting $\log k/k_0$ vs. σ_I values also yielded a good straight line with $\rho_I = -1.03$ at 400 °C ($r = 0.960$). The negative slopes indicated the formation of a partial positive carbon atom in the transition state and that electronic factors influenced the process of elimination. The only exception of the CH_3S substituent, which caused a significant acceleration, was attributed to the participation of the neighboring sulfur atom of the methylthio group. This consideration was derived by analogy with the anchimeric assistance of the said CH_3S group on the pyrolysis rate of 2-methylthioethyl chloride in the gas phase.[5] For group C, multiple-bonded or π-bonded substituents adjacent to the β carbon of ethyl acetate produce a strong activation in elimination rates due to the –M or –R effect. This phenomenon has already been

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[1] Taken from the thesis of Ignacio Martín, submitted to the Faculty of IVIC, January 1981, in partial fulfillment of the requirements for the Degree of Magister Scientiarum.

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TABLE I: Temperature Dependence of the Rate Coefficients

2-Cyclohexylethyl Acetate							
temp, °C	360.2	370.1	380.1	390.1	400.1	410.1	420.1
$10^4 k_1$, s^{-1}	1.37	2.56	4.63	8.49	14.44	25.69	40.56
2-Cyclopentylethyl Acetate							
temp, °C	360.1	370.2	380.1	390.1	400.1	410.1	420.1
$10^4 k_1$, s^{-1}	1.22	2.36	4.30	7.45	13.30	22.28	37.15
3-Methyl-1-pentyl Acetate							
temp, °C	360.2	370.1	380.1	390.1	400.1	410.1	420.1
$10^4 k_1$, s^{-1}	1.43	2.62	5.04	8.86	15.31	26.66	46.72
4-Methyl-1-pentyl Acetate							
temp, °C	360.1	370.1	380.1	390.1	400.1	410.1	420.1
$10^4 k_1$, s^{-1}	1.22	2.15	3.86	6.89	11.86	20.25	33.68

put forward[4] with the CH_3CO group in acetylethyl acetate pyrolysis.[6] The hydrogen atom of C_β–H bond being more loose or acidic assists the leaving acetoxy group, even though the polarization of the C_α–O bond is determinant.

The correlation for group A, as described above, is rather poor ($r = 0.800$ at 400 °C) when the phenyl substituent is properly defined in Group C. This unsatisfactory correlation coefficient obligates us to revise and add more data to obtain a better relationship concerning the effect of alkyl substituents at the β carbon of ethyl acetate. Consequently, the present work is an attempt to determine the gas-phase pyrolysis kinetics of these type of esters with cyclic and branched groups such as 2-cyclohexylethyl acetate, 2-cyclopentylethyl acetate, 3-methyl-1-pentyl acetate, and 4-methyl-1-pentyl acetate.

Experimental Section

The reagent 2-cyclohexylethyl acetate was acquired from Aldrich. The remaining substrates were prepared by treating the corresponding alcohol in pyridine with acetyl chloride as described.[7] 2-cyclopentylethyl acetate (bp 114–5 °C at 50 torr; lit. bp 75 °C at 14–15 torr[8]); 3-methyl-1-pentyl acetate (bp 90 °C at 60 torr; lit. bp 164–5 °C at 760 torr[9]); and 4-methyl-1-pentyl acetate (bp 87 °C at 60 torr; lit. bp 159 °C at 755 torr[10]). These primary esters were distilled several times and the fraction with at least 99.7% purity (gas–liquid chromatography) was used. Vinylcyclohexene, vinylcyclopentene, 3-methyl-1-pentene, and 4-methyl-1-pentene were acquired from Aldrich. These olefins were at least 99% pure and used as standard references. The columns for quantitative analyses were a 6-ft FFAP–7% Chromosorb G AW DMCS 80-100 mesh for cyclohexylethyl acetate, cyclopentylethyl acetate, vinylcyclopentene, and vinylcyclohexene; while a 6-ft diisodecyl phthalate–5% Chromosorb G AW DMCS 60–80 mesh for 3-methyl-1-pentyl acetate, 4-methyl-1-pentyl acetate, 3-methyl-1-pentene, and 4-methyl-1-pentene. A column of 12 ft of bis(2-methoxyethyl) adipate–20% Chromosorb P 80-100 mesh was employed to detect the formation of any other isomeric olefin products. Nevertheless, the pyrolysis of these substrates only gave normal elimination products.

The pyrolysis experiments were carried out in a static system, with the vessel clean or seasoned with allyl bromide.[11,12] The kinetics were followed by pressure increases and the temperature was constant within ±0.2 °C with a calibrated platinum—platinum–13% rhodium thermocouple. The reaction vessel showed no temperature at different points, and the reagents were injected directly into the reaction vessel with a syringe through a silicone septum.[13]

TABLE II: Arrhenius Parameters of the Esters

ester	log A, s^{-1}	E_a, kJ/mol
$c\text{-}C_6H_{11}CH_2CH_2OAc$	13.30 ± 0.28	208.1 ± 3.4
$c\text{-}C_5H_9CH_2CH_2OAc$	13.20 ± 0.26	207.4 ± 3.2
$CH_3CH_2CH(CH_3)CH_2CH_2OAc$	13.62 ± 0.09	211.9 ± 1.2
$(CH_3)_2CHCH_2CH_2CH_2OAc$	12.82 ± 0.05	203.1 ± 0.6

Results and Discussion

The stoichiometry of reaction 1 showed good agreement between the percentage decomposition of the substrate from pressure measurements with those obtained by the chromatographic analysis of the olefin product.

$$CH_3COOCH_2CH_2R \rightarrow RCH{=}CH_2 + CH_3COOH \qquad (1)$$

$$R = c\text{-}C_6H_{11},\ c\text{-}C_5H_9,\ s\text{-}C_4H_9,\ i\text{-}C_4H_9$$

Additional evidence of the above stoichiometry is the relationship between the final pressure, P_f, and the initial pressure, P_0, which should theoretically be equal to 2. The experimental results of P_f/P_0 at five different temperatures and ten half-lives are 2.02 for 2-cyclohexylethyl acetate, 2.09 for cyclopentylethyl acetate, 2.08 for 3-methyl-1-pentyl acetate, and 2.09 for 4-methyl-1-pentyl acetate. The small departure from theoretical stoichiometry is due to the slight decomposition of the acetic acid product.

The gas-phase elimination of the acetates has been observed to be first order. In plotting log $(2P_0 - P_t)$ against time, a satisfactory straight line to about 86% is obtained. The rates were unaffected by a sixfold increase in surface-to-volume ratio, by the presence of propene, a radical-chain inhibitor, and by an initial pressure above 30 torr. The variation of the rate coefficients with temperature is shown in Table I.

Table II shows the Arrhenius parameters of the esters obtained by using the least-squares procedure. The errors were estimated to 80% confidence limits.

When the log k_{rel} of the substituents listed in Table III is plotted against the steric parameters, E_s values of Taft[14] ($r = 0.800$ at 400 °C), ν values of Charton[14] ($r = 0.842$ at 400 °C), and E_s' values of Dubois et al.[14] ($r = 0.878$ at 400 °C), unsatisfactory linear correlations are still obtained. These results are found to be the consequence of two facts: (a) the point for the CH_3COCH_2 substituent is way above

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TABLE III: Kinetic Parameters of RCH_2CH_2OAc at 400 °C

R	10^4k_1, s^{-1}	10^4k_H, s^{-1}	E_a, kJ/mol	log A, s^{-1}	log k/k_0	E_s^c	ref
H	10.00	3.33	200.4 (±3.8)	12.55 (±0.30)	0.000	0.00	4[a]
CH_3	8.51	4.26	204.1 (±3.8)	12.77 (±0.30)	0.107	−1.24	4[a]
C_2H_5	10.47	5.24	199.5 (±4.6)	12.50 (±0.36)	0.197	−1.62	4[a]
n-C_3H_7	13.80	6.90	194.1	12.20	0.316	−1.91	6[b]
i-C_3H_7	10.23	5.12	202.5 (±3.8)	12.73 (±0.29)	0.187	−2.32	2[a]
n-C_4H_9	9.12	4.56	200.8	12.54	0.137	−1.94	16[b]
t-C_4H_9	19.05	9.53	194.1 (±4.2)	12.34 (±0.35)	0.457	−3.70	2[a]
s-C_4H_9	15.31	7.66	211.9 (±1.2)	13.62 (±0.09)	0.362	−2.98	this work
i-C_4H_9	11.86	5.93	203.1 (±0.6)	12.82 (±0.05)	0.251	−2.48	this work
c-C_6H_{11}	14.44	7.22	207.4 (±3.2)	13.20 (±0.26)	0.336	(−2.95)[c]	this work
c-C_5H_9	13.30	6.65	208.1 (±3.4)	13.30 (±0.28)	0.300	−2.64	this work
CH_3OCH_2	8.13	4.07	203.3 (±1.3)	12.69 (±0.10)	0.087	(−0.89)[c]	4[a]
$C_6H_5OCH_2$	14.22	7.11	198.0 (±3.5)	12.52 (±0.28)	0.330	(−2.90)[c]	4[a]
$C_6H_5CH_2$	10.91	5.46	203.1 (±2.3)	12.80 (±0.18)	0.215	−1.93	4[a]
CH_3COCH_2	20.14	10.07	198.9 (±2.9)	12.74 (±0.23)	0.480		4[a]
$CH_3OCH_2CH_2$	12.88	6.44	209.5 (±2.9)	13.37 (±0.30)	0.286	(−2.53)[c]	17[a]

[a] The Arrhenius parameters were recalculated from data of the cited references by the least-squares procedure, the 80% confidence limits being quoted. [b] The kinetic parameters are only reported. [c] The new defined E_s^c values are in parentheses.

slope of the lines, and (b) the difference in the elimination velocities obtained in the experimental part of this work $CH_3CH_2(CH_3)CH$ > c-C_6H_{11} > c-C_5H_9 > $(CH_3)_2CHCH_2$ is dissimilar to the sequence by Taft's E_s values $CH_3CH_2(CH_3)CH$ (−2.37) > $(CH_3)_2CHCH_2$ (−2.17) > c-C_6H_{11} (−2.03) > c-C_5H_9 (−1.75), Charton's ν values $CH_3CH_2(CH_3)CH$ (1.02) > $(CH_3)_2CHCH_2$ (0.98) > c-C_6H_{11} (0.87) > c-C_5H_9 (0.71), and Dubois' E_s' values $CH_3CH_2(CH_3)CH$ (−1.00) > $(CH_3)_2CHCH_2$ (−0.93) > c-C_6H_{11} (−0.69) > c-C_5H_9 (−0.41). This apparent discrepancy appears to be cleared up in considering Hancock's et al. steric parameters E_s^c values,[14,15] where a correction factor pertaining to the hyperconjugation effect of the alkyl groups has been considered. Both sequences, the E_s^c values and the rate differences obtained in this work, are similar (see Table III). Therefore plotting log k/k_0 against the reported E_s^c values in the literature[14] gives a good straight line (Figure 1, r = 0.916, δ = −0.121, and intercept −0.020 at 400 °C). By extrapolation of this straight line, the following E_s^c values of some of the substituents listed in Table III are approximately defined: c-C_6H_{11}, −2.95; $PhOCH_2$, −2.90; $CH_3OCH_2CH_2$, −2.53; and CH_3OCH_2, −0.89. The acetonyl substituent, CH_3COCH_2, is not defined because its point of relative rate, as explained before, is way above the slope of the line. Also, the bulkiness of the CH_3COCH_2 can not be greater than the $(CH_3)_3C$ group (see Dreiding scale models). This high rate of elimination of 2-acetylpropyl acetate may well be due to difficulties in experimental condition[4] or to some other factor. In considering this new defined E_s^c values (Table III, seventh column with values in parentheses), the plot of log k/k_0 vs. E_s^c yields, as expected, a better straight line (Figure 1, r = 0.935, δ = −0.121, and intercept = −0.020 at 400 °C).

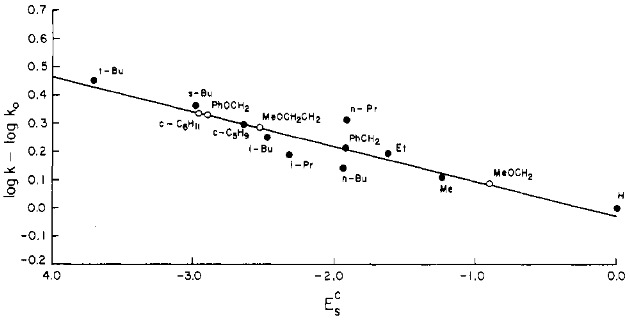

Figure 1. Plot of log k/k_0 for the pyrolysis of $CH_3COOCH_2CH_2R$ at 400 °C against the reported E_s^c values (filled circles). The new approximately defined E_s^c values are the open circles.

Within the experimental error of this work, the linear correlation shown in Figure 1 confirms that the unimolecular elimination of these acetates of group A is subject to steric acceleration.[2,3] The greater the bulkiness of the substituent at the β carbon of ethyl acetate, the greater the pyrolysis rate. This means that, in the transition state, the hybridization at both C_α and C_β atoms ($CH_3COOC_\alpha H_2C_\beta H_2R$) from sp^3 to sp^2 relieves the strain between the substituents on these carbon atoms.

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