the +*I* electron release of the two methyl groups in $(C-H_3)_2C=CH$ 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. $^{\rm 12}$

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

Gabriel Chuchani,* Juana L. Triana, Alexandra Rotinov, and Dario F. Caraballo¹

Centro de Química, Instituto Venezolano de Investigaciones Científicas, Apartado 1827, Caracas 1010-A, Venezuela (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, $\log k(s^{-1}) = (12.70 \pm 0.50) - (197.0 \pm 6.1)$ kJ mol⁻¹ (2.303RT)⁻¹; for ethyl 3-chloropropionate, $\log k(s^{-1}) = (12.54 \pm 0.22) - (196.8 \pm 2.7)$ kJ mol⁻¹ (2.303RT)⁻¹; and for ethyl 4-chlorobutyrate, $\log k(s^{-1}) = (12.67 \pm 0.31) - (198.7 \pm 3.8)$ 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 substituents 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 3chloropropionate, 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 described⁶ (bp 47 °C at 20 torr; lit. bp 161 °C⁷). 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

⁽¹⁾ Visiting Professor, Facultad de la Salud, Universidad de Carabobo, Maracay, Aragua, Venezuela.

⁽²⁾ Taylor, R. J. Chem. Soc., Perkin Trans. 2 1978, 1255.
(3) Garcia de Sarmiento, M. A.; Dominguez, R. M.; Chuchani, G. J. Phys. Chem. 1980, 84, 2531.

⁽⁴⁾ Smith, G. G.; Mütter, L.; Peter Todd, G. J. Org. Chem. 1977, 42, 44.

⁽⁵⁾ Chuchani, G.; Martin, I.; Fraile, G.; Lingstuyl, O.; Díaz, M. J. Int. J. Chem. Kinet. 1978, 10, 893.

⁽⁶⁾ Vogel, A. I. "Practical Organic Chemistry", 3rd ed; Longmans: London, 1956; p 382.

⁽⁷⁾ Connant, J. B.; Kirner, W. R. J. Am. Chem. Soc. 1924, 46, 232.
(8) Maccoll, A. J. Chem. Soc. 1955, 965.

⁽⁹⁾ Maccoll, A.; Thomas, P. J. J. Chem. Soc. 1955, 979.

TABLE I: Variation of the Rate Coefficients with Temperature





Figure 1. Plot of percentage decomposition from pressure against the percentage decomposition by analysis: (•) ethyl acetate at 370.3 °C; (Δ) ethyl chloropropionate at 380.1 °C; (\Box) ethyl 4-chlorobutyrate at 370.1 °C.

vessel with a syringe through a silicon rubber septum.¹⁰

Results and Discussion

The gas-phase pyrolysis of ethyl chloroacetate, ethyl 3-chloropropionate, and ethyl 4-chlorobutyrate in a vessel seasoned with allyl bromide and in the presence of propene inhibitor yields ethylene and the corresponding carboxylic acid (eq 1).

$$ZCH_2COOCH_2CH_3 \rightarrow ZCH_2COOH + CH_2 = CH_2$$
(1)
$$Z = Cl, ClCH_2, ClCH_2CH_2$$

The stoichiometry based on eq 1 suggests that at long reaction time $P_f = 2P_0$, where P_f and P_0 are the final and initial pressures, respectively. The average experimental $P_{\rm f}/P_0$ values obtained at four different temperatures and ten half-lives are 3.04 for ethyl chloroacetate, 2.95 for ethyl 3-chloropropionate, and 2.06 for ethyl 4-chlorobutyrate. The observed departure from the theoretical stoichiometry is due to the fact that the halocarboxylic acid product fragments slowly into CO, CO_2 , and very small amounts of the corresponding ZCH_3 . Yet, the stoichiometry of reaction 1, up to 50% decomposition, was verified by comparing the percentage decomposition from pressure measurements with those obtained from the chromatographic analysis of ethylene (Figure 1).

The homogeneity of these reactions was examined by using a vessel with a surface-to-volume ratio 6.14 times greater than that of the unpacked vessel. Packing and unpacking has no significant effect on the rate coefficients



Figure 2. Gas-phase elimination of ethyl α -substituted acetates (ρ^* = 0.357, r = 0.903, and intercept = 0.048 at 400 °C).

if the vessels are seasoned with allyl bromide. The presence of different proportions of propene, a free-radical inhibitor, showed no effect on the rate of decomposition of these esters. No induction period was observed. The first-order rate coefficients of these esters calculated from $k_1 = (2.303/t) \log P_0/(2P_0 - P_t)$ has been found to be independent of their initial pressure. The plot of $\log (2P_0)$ $-P_t$) against time t gave a straight line up to 50% decomposition. The variation of the rates of elimination with temperature is given in Table I.

The results of Table I are expressed, when using the least-squares procedure and 0.8 confidence coefficient, by the following Arrhenius equations:

ethyl chloroacetate

$$\log k(s^{-1}) =$$

 $(12.70 \pm 0.50) - (197.0 \pm 6.1) \text{ kJ mol}^{-1} (2.303 RT)^{-1}$

ethyl 3-chloropropionate

$$\log k(s^{-1}) =$$

 $(12.54 \pm 0.22) - (196.8 \pm 2.7) \text{ kJ mol}^{-1} (2.303RT)^{-1}$

ethyl 4-chlorobutyrate

 $\log k(s^{-1}) =$

 $(12.67 \pm 0.31) - (198.7 \pm 3.8) \text{ kJ mol}^{-1} (2.303RT)^{-1}$

The data in the literature on the effect of substituents at the acyl carbon on the pyrolysis of ethyl esters are few. Table II is indicative of such a situation. However, these reported pyrolyses together with those of the present work are sufficient information in obtaining an approximate

⁽¹⁰⁾ Bridge, M. R.; Davies, D. H.; Maccoll, A.; Ross, R. A.; Banjoko, O. J. Chem. Soc. B 1968, 805.

⁽¹¹⁾ Taft, Jr.; R. W. "Steric Effects in Organic Chemistry"; Newman,

^{1976, 280.}

⁽¹³⁾ Blades, A. T.; Gilderson, P. W. Can. J. Chem. 1960, 38, 1412.

 ⁽¹⁴⁾ Kairitis, D. A.; Stimson, V. R. Aust. J. Chem. 1968, 21, 1349.
 (15) Cross, J. T. D.; Stimson, V. R. Aust. J. Chem. 1967, 20, 177.

⁽¹⁶⁾ Taylor, R. J. Chem. Soc., Perkin Trans. 2 1975, 1025.

TABLE II: Kinetic Parameters for ZCOOCH₂CH₃ at 400 °C

Z	$10^4 k_1, s^{-1}$	$E_{\rm a}$, kJ/mol	$\log A$, s ⁻¹	$\log k/k_o$	ref
CH,	9.93	200.4 ± 3.8	12.55 ± 0.30	0.000	12
CH ₃ CH,	9.40	202.9 ± 1.5	12.72 ± 0.08	-0.024	13
CH, CH, CH,	9.27	207.1 ± 6.7	13.04 ± 0.54	-0.030	14
(CH ₁),Č	8.96	184.1	11.24	-0.045	15
Č, H,	16.48	199.5 ± 2.1	12.70 ± 0.20	0.220	16
C,H,CH,	11.97	200.0 ± 2.5	12.60 ± 0.20	0.081	16
trans-CH ₃ CH=CH	11.12	195.9	12.25	0.049	14
ClCH,	25.75	197.0 ± 6.1	12.70 ± 0.50	0.414	this work ^{a}
ClCH,CH,	18.47	196.8 ± 2.7	12.54 ± 0.22	0.269	this work ^a
ClCH ₂ CH ₂ CH ₂ CH ₂	17.74	198.7 ± 3.8	12.67 ± 0.31	0.252	this work a

^a The Arrhenius parameters were calculated by the least-squares procedure. The 80% confidence limits are quoted.

linear relationship when plotting $\log k/k_0 \text{ vs. } \sigma^*(z)$ (Figure 1, $\rho^* = 0.357$, r = 0.903, and intercept = 0.048 at 400 °C). Even though the Cl substituent interposed by one or two methylene groups with respect to the acyl carbon tends to decrease the rate of elimination, its effect is still significant relative to ethyl acetate (Table II). The positive ρ^* value implies the formation of a very discrete negatively charged carbon atom in the transition state. This means that elongation and polarization of the C_β-H bond, in the sense C_{β}^{b} -...H^b+, determine the rate (1). Consequently, the



more the electron withdrawal of substituent Z, the faster is the C_{α} -O bond breaking and the greater is the delocalization of the p electrons of the oxygen atom toward the carbonyl carbon atom. The C=O bond is therefore more basic or nucleophilic for β -hydrogen abstraction and a faster rate of decomposition results. Otherwise, the greater the electron-releasing effect of Z, such as the +I effect of alkyls, the more difficult the stabilization of the p electrons of the oxygen atom. Hence, the carbonyl oxygen is less basic or nucleophilic for bond formation with the β hydrogen, thus causing the rate of elimination to slow down. The present argument finds support from a previous work on the pyrolysis of *tert*-butyl esters of substituted acetates.² The approximate correlation of log $k_{\rm rel}$ vs. $\sigma_{\rm I}$ constants ($\rho_{\rm I}$ = 1.4 at 600 K), implied that electron-withdrawing substituents speed the elimination rates, and electron-releasing substituents decrease it.

In view of the conclusions arrived at with respect to ethyl and *tert*-butyl α -substituted acetates, recent work regarding the effect of alkyl branching in isopropyl α -substituted acetates pyrolyses³ must be reconsidered. Even though a good linear relationship of log $k_{\rm rel}$ vs. $\sigma^*_{(Z)}$ ($\rho^* =$ 0.464, r = 0.963, and intercept = 0.044 at 330 °C) was obtained, the effect of alkyl branching may not necessarily be steric as reported,³⁻⁵ but rather, by supplying electrons, be a +I inductive effect. A careful analysis of the abovementioned investigations,3 wherein compounds with alkyl substituents were studied in detail over a wide range of temperatures, gives k values that lie on the correlation line. Yet, those points for alkyls which are above the line were determined at a single temperature.⁴ Since alkyls, within the experimental errors, yield values very close in rates, perhaps a detailed wider range of working temperature of the corresponding isopropyl esters could well give k values more in accord to their +I electron-releasing effect.

The present work together with that described above^{3,4} may imply, in general, that electron-withdrawing substituents at the acyl portion of ethyl, isopropyl, and *tert*-butyl esters enhance the elimination rates, whereas electron-releasing groups retard the rate of decomposition.