which gives a quadratic equation, could, in general, be obviated by measurements of the temperature dependence of the Kerr effect or of rotational Raman intensities.

Acknowledgment. The award of University of Sydney Special

Project Research Scholarship (to P.B.L.) and financial support from the Australian Research Grants Scheme (to G.L.D.R.) are gratefully acknowledged.

Registry No. Fluorobenzene, 462-06-6.

# Correlation of Alkyl and Polar Substituents at the Alcoholic Side of Tertiary Acetates with the Rate of Pyrolyses in the Gas Phase

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The rate coefficients for the gas-phase pyrolysis of several tertiary acetates have been measured in a static system over the temperature range of 220-340 °C and pressure range of 40-186 torr. In seasoned vessels the reactions are homogeneous, follow a first-order rate law, and are unimolecular. The temperature dependence of the rate coefficients is given by the following Arrhenius equations: for 3,3,3-trichloro-2-methyl-2-propyl acetate, log  $k_1$  (s<sup>-1</sup>) = (13.86 ± 0.35) - (188.8 ± 3.8) kJ mol<sup>-1</sup> (2.303RT)<sup>-1</sup>; for methyl  $\alpha$ -acetoxyisobutyrate, log  $k_1$  (s<sup>-1</sup>) = (12.42 ± 0.28) - (174.6 ± 3.2) kJ mol<sup>-1</sup> (2.303RT)<sup>-1</sup>; for 2-methyl-2-hexyl acetate, log  $k_1$  (s<sup>-1</sup>) = (13.35 ± 0.33) - (166.1 ± 3.4) kJ mol<sup>-1</sup> (2.303RT)<sup>-1</sup>; for 2,4-dimethyl-2-pentyl acetate, log  $k_1$  (s<sup>-1</sup>) = (12.42 ± 0.19) - (154.1 ± 1.9) kJ mol<sup>-1</sup> (2.303RT)<sup>-1</sup>; for 2-methyl-2-acetoxy-4-phenylbutane, log  $k_1$  (s<sup>-1</sup>) = (11.97 ± 0.55) - (151.5 ± 5.6) kJ mol<sup>-1</sup> (2.303RT)<sup>-1</sup>. The effect of substituents in the gas-phase elimination of 2-substituted 2-propyl acetates may be either electronic or steric in nature. The linear correlations for electron-releasing groups and for electron-withdrawing groups are presented and discussed. The results of the present work together with those reported in the literature lead to the establishment of a possible generalization on the influence of substituents at the alcohols side of primary, secondary, and tertiary acetates pyrolyses in the gas phase.

#### Introduction

The rates of homogeneous gas-phase elimination of primary and secondary acetates with substituent Z at the  $\beta$ - (1, 2) and  $\alpha$ -carbon atoms (3, 4) are affected by various different effects.



Primary Acetates,  $C_{\beta}$ -Z Substituent (1). (a) Alkyl groups and polar substituents interposed by at least three methylene groups with respect to the  $C_{\alpha}$ -O bond enhanced the pyrolysis rates due to steric acceleration. The best approximate linear correlation obtained was possible by plotting log  $k/k_0$  vs. Hancock's  $E_s^{c}$  values ( $\delta = -0.121$ , r = 0.916, and intercept = -0.020 at 400 °C).<sup>2</sup>

(b) Electron-withdrawing polar substituents slowed the elimination rates according to their electronegativity. In this sense, plotting log  $k_{rel}$  against  $\sigma^*$  and  $\sigma_I$  values resulted in a good linear relationship ( $\rho^* = -0.19$ , r = 0.961;  $\rho_I = -1.03$ , r = 0.960 at 400 °C).<sup>3</sup>

(c) Multiple-bonded or  $\pi$ -bonded substituent Z attached directly to the  $\beta$ -carbon caused a significant augmentation in the rates due to the resonance effect.<sup>3</sup>

Secondary Acetates,  $C_{\beta}$ -Z Substituent (2). (a) The direction of elimination toward the formation of the 2-olefin in 2 indicated that polar substituent Z had the same effect as at the  $\beta$ -carbon in primary acetates (1). In this respect, when Z is a strong electron-withdrawing substituent, the rate of elimination tends to decrease. By plotting log  $k/k_0$  against  $\sigma^*$  and  $\sigma_I$  values very good linear correlation are obtained ( $\rho^* = -0.26$ , r = 0.996, and intercept = 0.019;  $\rho_I = -1.30$ , r = 0.995, and intercept = -0.05 at 320 °C).<sup>4</sup>

(b) Alkyl groups at the  $\beta$ -carbon atom (2) give rise to alkylalkyl interactions in the cis conformation and alkyl-hydrogen interactions in the trans conformation. In the former, the rate tends to decrease due to steric hindrance, while in the later the rate increases because of steric acceleration.<sup>4</sup>

(c) If Z in 2 is a multiple-bonded or  $\pi$ -bonded substituent a strong activation in rates results from the resonance effect.<sup>4</sup>

Secondary Acetates,  $C_{\alpha}$ -Z Substituent (3). (a) Alkyl substituents at the  $\alpha$ -carbon atom enhanced the elimination rates of these esters by steric acceleration. However, poor correlations are obtained when plotting log  $k/k_0$  against the steric parameter  $E_s$  values of Taft ( $\delta = -0.206$ , r = 0.858, and intercept = -0.206 at 320 °C) and  $\nu$  values of Charton ( $\Psi = 0.460$ , r = 0.842, and intercept = 0.202 at 320 °C).<sup>4</sup>

(b) An electron-withdrawing substituent directly attached to the  $\alpha$ -carbon atom (3) influences the rates by electronic factors. Thus, plotting log  $k_{\rm rel}$  against  $\sigma^*$  and  $\sigma_{\rm I}$  values approximates straight lines which suggested that the greater the electronegative nature of substituent Z the slower the pyrolysis rates ( $\rho^* = -0.32$ , r = 0.878, and intercept = -0.151;  $\rho_{\rm I} = -2.18$ , r = 0.898, and intercept = -0.147 at 320 °C).<sup>4</sup>

Tertiary Acetates,  $C_{\alpha}$ -Z Substituent (4). (a) Alkyls and just one single polar group indicated steric acceleration in the elimination processes. An approximate straight line was obtained when plotting log  $k/k_0$  vs.  $E_s$  values ( $\delta = -1.19$ , r = 0.935, and intercept

Taken from the thesis of Neil González, submitted to the Faculty of the Department of Chemistry of Universidad del Zulia, 1984, in partial fulfillment for the requirements for the degree of Licenciate in Chemistry.
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= 1.822 at 300 °C).<sup>5</sup> A later work on the kinetically controlled direction of elimination of a few tertiary acetates showed, by plotting log  $k/k_0$  vs.  $E_s$  values, a good linear correlation ( $\delta = -0.63$ , r = 0.959, and intercept 0.070 at 240 °C).<sup>6</sup>

(b) Multiple-bonded or  $\pi$ -bonded substituents do not enhance significantly the rate of elimination which may be due to a simultaneous steric effect impeding copolanarity for maximum delocalization of electrons in the transition state.<sup>5</sup>

Since polar groups affect the elimination rates in primary (1)and secondary (2, 3) acetates by electronic factors, it seemed reasonable to believe that that type of substituents must exert a similar deactivation effect on tertiary acetates (4). Consequently, the present work was addressed to examine and to determine the pyrolysis kinetics of the esters (4) with some polar substituent Z attached to the  $\alpha$ -carbon. With this additional study, it is also intended, if possible, to establish a generalization of substituent effects in the gas-phase elimination of primary, secondary, and tertiary acetates of types 1-4.

#### Experimental Section

3,3,3-Trichloro-2-methyl-2-propyl Acetate. This compound was prepared by adding the corresponding alcohol to a mixture of anhydrous zinc chloride and acetyl chloride and then refluxed. The ester was distilled several times (bp 101 °C at 45 torr; lit. bp 196 °C at 760 torr<sup>7</sup>) and the fraction with 99.8% purity as determined by GLC (5% diisodecyl phthalate-Chromosorb W AW DMCS 60-80 mesh and 7% FFAP-Chromosorb W AW DMCS 80-100 mesh) was used. 3,3,3-Trichloro-2-methyl-1-propene and 1,1,3-trichloro-2-methyl-2-propene were unequivocally identified by NMR and mass spectrometry and analyzed in a column of 10% Dow Corning Silicone (200/100)-Chromosorb W AW DMCS 80–100 mesh.

Methyl  $\alpha$ -Acetoxyisobutyrate. Methyl  $\alpha$ -hydroxyisobutyrate was treated with ketene gas as described.<sup>8</sup> The product had a boiling point of 169-170 °C at 633 torr; lit. bp 76-77 °C at 18 torr.<sup>9</sup> It was fractionated several times, and the fraction of 99.1% purity (7% FFAP-Chromosorb W AW DMCS 80-100 mesh) was used. Methyl methacrylate (Merck Schuchardt) was analyzed in the same column.

2-Methyl-2-hexyl Acetate. Acetyl chloride was added to 2methyl-2-hexanol in dimethylaniline as described.<sup>10</sup> The acetate (bp 92 °C at 60 torr; lit. bp 159-160 °C at 760 torr<sup>11</sup>) was distilled several times and the fraction of 97.5% purity as determined by GLC (7% FFAP-Chromosorb W AW DMCS 80-100 mesh) was used. Commercial samples of 2-methyl-1-hexene (Aldrich) and 2-methyl-2-hexene (K&K Labs.) were analyzed in a 7-m column of 20% bis(2-methoxyethyl) adipate-Chromosorb P AW 80-100 mesh.

2,4-Dimethyl-2-pentyl Acetate. 2,4-Dimethyl-2-pentanol with ketene gas8 yielded the corresponding acetate. Several distillations of this product gave a boiling point of 54-55 °C at 16 torr and a purity of 98.8% when analyzed by GLC (10% Dow Corning Silicone (200/100)-Chromosorb W AW DMCS 80-100 mesh and 7% FFAP-Chromosorb W AW DMCS 80-100 mesh). 2,4-Dimethyl-1-pentene (K&K Labs) and 2,4-dimethyl-2-pentene (K&K Labs) were analyzed in a 0.19% picric acid-Carbopack C 80–100 mesh column.

2-Methyl-2-acetoxy-4-phenylbutane. This ester was prepared by adding the corresponding alcohol to a acetic anhydride-sodium acetate mixture and refluxed for 3 h. The acetate (bp 73 °C at 0.05 torr; lit. bp 125-126 °C at 12 torr<sup>12</sup>) was distilled to 97.8% purity as determined by GLC (10% Dow Corning Silicone

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The Journal of Physical Chemistry, Vol. 89, No. 7, 1985 1315

## Temperatures<sup>a,b</sup>

3,3,3-Trichloro-2-methyl-2-propyl Acetate						
temp, °C	3,3,3-trichloro- 2-methyl- 1-propene	1,1,3-trichloro- 2-methyl- 2-propene				
289.9	98.7	1.2				
310.0	98.6	1.2				
330.1	98.2	1.6				
	2-Methyl-2-hexyl Ace	tate				
temp, °C	2-methyl-1-hexene	2-methyl-2-hexene				
240.2	69.5	30.4				
260.0	69.2	30.9				
270.1	70.1	29.7				
2,4	4-Dimethyl-2-pentyl A	cetate				
2.4-dimethyl- 2.4-dimethyl-						
temp, °C	1-pentene	2-pentene				
220.1	69.5	30.6				
239.7	69.0	30.9				
250.0	69.2	30.9				
2-Me	thyl-2-acetoxy-4-phen	vlbutane				
	2-methyl-4-	2-methyl-4-				
temp, °C	phenyl-1-butene	phenyl-2-butene				
230.1	66.3	33.8				
250.1	66.8	33.0				
280.0	66.4	33.3				

<sup>a</sup> Vessel S/V = 1 and seasoned with allyl bromide. <sup>b</sup> Methyl  $\alpha$ -acetoxyisobutyrate is not included in this table, because it yields only methyl methacrylate.

(200/100)-Chromosorb W AW DMCS 80-100 mesh). 2-Methyl-4-phenyl-1-butene (K&K Labs) and 2-methyl-4phenyl-2-butene (identified by NMR and mass spectrometry) were analyzed in the same Silicone column.

The pyrolysis experiments were carried out in a static system,<sup>13</sup> and the reaction vessel was at all times seasoned with allyl bromide.13 The kinetic measurements were obtained manometrically and the temperature was maintained to better than  $\pm 0.2$ °C with a calibrated platinum—platinum-13% rhodium thermocouple. The acetic acid product was quantitatively determined when titrated with a solution of 0.05 N sodium hydroxide.

#### **Results and Discussion**

The experimental stoichiometry for the gas-phase elimination of the tertiary chlorides, as described by eq 1 and 2, in a static

 $CH_3COOC(CH_3)_2Z \rightarrow ZC(CH_3) = CH_2 + CH_3COOH$ (1)

$$Z = Cl_3C, CH_3OCO$$

$$CH_{3}COOC(CH_{3})_{2}CH_{2}Z \rightarrow ZCH_{2}CH(CH_{3})=CH_{2} + ZCH=C(CH_{3})_{2} + CH_{3}COOH$$
(2)

$$Z = CH_3CH_2CH_2, (CH_3)_2CH, C_6H_5CH_2$$

system with vessel seasoned with allyl bromide, implies  $P_f/P_0 =$ 2, where  $P_{\rm f}$  and  $P_0$  are final and initial pressures, respectively.

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TABLE II:	Variatio	i of Olefin	Formation	from	Percentage
Decompositi	on of the	Tertiary 2	Acetates at	One 7	[emperature <sup>a</sup>

3,3,3-Trichloro-2-methyl-2-propyl Acetate at 319.9 °C						
	3,3,3-trichloro-	1,1,3-trichloro-				
	2-methyl-	2-methyl-				
% decomp	1-propene	2-propene				
16	98.1	0.8				
27	97.8	1.1				
41	98.2	1.4				
63	98.0	1.1				
2-Me	thyl-2-hexyl Acetate a	at 270.1 °C				
	2-methyl-1-hexene	2-methyl-2-hexene				
% decomp						
27	68.6	30.3				
50	70.0	30.1				
73	70.4	29.4				
87	69.6	30.2				
2, <b>4-D</b> in	nethyl-2-pentyl Acetat	e at 260.0 °C				
	2,4-dimethyl-	2,4-dimethyl-				
% decomp	1-pentene	2-pentene				
18	68.3	31.5				
32	69.2	30.0				
54	69.9	29.8				
77	69.6	30.6				
2-Methyl-	2-acetoxy-4-phenylbut	ane at 270.0 °C				
	2-methyl-4-	2-methyl-4-				
	phenyl-1-butene	phenyl-2-butene				
% decomp	· · · · · · · · · · · · · · · · · · ·					
22	66.1	33.2				
36	66.9	32.8				
58	66.1	34.0				
74	66.3	33.5				

<sup>a</sup> Methyl  $\alpha$ -acetoxyisobutyrate yielded exclusively methyl methacrylate.

The average experimental  $P_f/P_0$  values obtained at four different temperatures and ten half-lives were as follows: 2.03 for 3,3,3-trichloro-2-methyl-2-propyl acetate, 1.97 for methyl  $\alpha$ acetoxyisobutyrate, 1.91 for 2-methyl-2-hexyl acetate, 1.79 for 2,4-dimethyl-2-pentyl acetate, and 1.95 for 2-methyl-2-acetoxy-4-phenylbutane. The small departure found in 2,4-dimethyl-2pentyl acetate was due to polymerization of the olefinic products. Confirmation of the above stoichiometry, up to 70–80% reaction, was possible by comparing the titration of acetic acid product and/or the chromatographic analyses of the unreacted ester to pressure increase.

The homogeneity of these elimination was examined by using vessels with a surface-to-volume ratio factor of 6.0 greater than that of the normal vessel. The packed and unpacked vessels when seasoned with allyl bromide gave no changes in rate coefficients. However, the packed and unpacked clean Pyrex vessel showed some heterogeneous effect.

The analyses of the decomposition product of these esters, up to 70-80% reaction, are given in Table I. The olefin ratios have been found to be about the same at three different temperatures. Further examination of whether the formation of these olefinic products is invariable as the reaction progresses at a given temperature was carried out (Table II). The results of Table II confirm the results of Table I, which indicate that product formation from the gas-phase elimination of these tertiary acetates proceeds by kinetic control.

The presence of cyclohexene, a free radical inhibitor, showed no significant effect on the rate coefficients. No induction period was observed. Cyclohexene was at all times used as an inhibitor during the pyrolysis of 2,4-dimethyl-2-pentyl acetate, since the olefinic products tend to polymerize slightly.

At any of the working temperatures, the rate coefficients were invariable with changes in the initial pressure of the tertiary esters (Table III) and the first-order plots are satisfactorily linear up

TABLE III: Invariability of Rate Coefficients with Initial Pressure

	-							
3,3,3-Trichloro-2-methyl-2-propyl Acetate at 330.1 °C								
$P_0$ , torr	84.5	96.0	135.0	168.5	186.0			
$10^4 k_1, s^{-1}$	30.43	30.67	31.04	30.31	30.91			
M	ethyl $\alpha$ -Ao	etoxyisob	utyrate at	330.8 °C				
$P_0$ , torr	51.0	74.5	94.0	122.0	148.5			
$10^4 k_1$ , s <sup>-1</sup>	20.76	20.93	21.01	20.70	20.96			
2	2-Methyl-2	2-hexyl Ac	etate at 26	50.2 °C				
$P_0$ , torr	78.7	97.5	112.5	126.0	145.0			
$10^4 k_1$ , s <sup>-1</sup>	11.83	11.86	11.59	11.71	11.70			
2,4	-Dimethyl	-2-pentyl	Acetate at	239.7 °C				
P <sub>0</sub> , torr	69.0	95.0	106.5	125.5	161.0			
$10^4 k_1$ , s <sup>-1</sup>	5.54	5.49	5.45	5.34	5.39			
2-Ace	2-Acetoxy-2-methyl-4-phenylbutane at 250.0 °C							
$P_0$ , torr	40.5	64.5	70.5	91.0	122.0			
$10^4 k_1$ , s <sup>-1</sup>	7.61	7.78	7.56	7.41	6.93			

#### **TABLE IV: Temperature Dependence of Rate Coefficients**

	2.1.2 Trichland 2 monthal 2 monthal								
	5,5,5-1 FR	:moro-2-1	netnyi-2-	propyl A	cetate				
temp, °C	280.1	289.9	300.2	310.0	319.9	330.1			
$10^4 k_1$ , s <sup>-1</sup>	1.06	2.18	4.53	9.30	17.57	30.74			
	Me	thyl α-A	cetoxyiso	butyrate					
temp, °C	290.2	300.5	310.5	320.1	330.8	340.0			
$10^4 k_1$ , s <sup>-1</sup>	1.68	3.55	6.17	11.16	20.89	35.52			
17									
	2	-Methyl-	2-hexyl A	Acetate					
temp, °C	240.2	250.0	260.2	270.1	280.1				
$10^4 k_1, s^{-1}$	2.79	6.13	11.74	23.85	46.69				
17									
	2,4-	Dimethy	l-2-penty	l Acetate					
temp, °C	220.1	229.8	239.7	250.0	260.0	270.1			
$10^4 k_1$ , s <sup>-1</sup>	1.23	2.60	5.44	10.60	20.69	39.15			
•									
	2-Acet	oxy-2-me	ethyl-4-pl	henylbuta	ne				
temp, °C	230.1	240.0	250.0	259.8	270.0	280.0			
$10^4 k_1$ , s <sup>-1</sup>	1.60	3.67	7.51	13.57	24.30	43.91			

**TABLE V: Arrhenius Parameters of the Tertiary Acetates** 

ester	$\log A$ , s <sup>-1</sup>	$E_{\rm a}$ , kJ/mol
CH <sub>3</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> CCl <sub>3</sub>	$13.86 \pm 0.35$	188.8 ± 3.8
CH <sub>3</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> COOCH <sub>3</sub>	$12.42 \pm 0.28$	$174.6 \pm 3.2$
CH <sub>3</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	$13.35 \pm 0.33$	$166.1 \pm 3.4$
CH <sub>3</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	$12.42 \pm 0.19$	$154.5 \pm 1.9$
CH <sub>3</sub> COOC(CH <sub>3</sub> ) <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	$11.97 \pm 0.55$	$151.5 \pm 5.6$



Figure 1. log  $k/k_0$  vs.  $E_s$  values of alkyl substituents at 280 °C ( $\delta = -0.55$ , r = 0.956, and intercept = 0.114).

to about 70% decomposition. The variation of the rate coefficients of these reactions with temperature is given in Table IV.

Table V lists the Arrhenius parameters for elimination of these acetates obtained by using the least-squares procedure, and the errors were estimated to 80% confidence coefficients.

Table VI lists a sufficient number of pyrolyzed tertiary acetates which make it possible to assess adequately the substituent effect of Z at the oxymethine carbon atom (4). In this respect, the data of Table VII from Table VI appears to indicate that various types of effects are determinant in the rates of the reaction. Apparently,

TABLE VI: Kinetic Parameters for CH<sub>3</sub>COOC(CH<sub>3</sub>)<sub>2</sub>Z Pyrolysis at 280 °C<sup>a</sup>

					10 <b>*</b> k	i, s <sup>-1</sup>				
	Z	1-olefin, %	2-olefin, %	$10^4 k_1$ , s <sup>-1</sup>	1-olefin	2-olefin	$E_{\rm a}$ , kJ/mol	$\log A$ , s <sup>-1</sup>	ref	
	CH <sub>3</sub>	100		21.88	14.59 <sup>b</sup>		$167.2 \pm 2.3$	$13.13 \pm 0.23$	14	
	CH <sub>3</sub> CH <sub>2</sub>	72.6	27.4	33.88	24.60	9.28	$168.7 \pm 0.6$	$13.46 \pm 0.06$	14	
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	63.8	36.2	64.57	41.20	23.37	169.8	13.85	15	
	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	69.6	30.3	45.97	32.00	13.93	$166.1 \pm 3.4$	$13.35 \pm 0.33$	this work	
	(CH <sub>3</sub> ) <sub>2</sub> CH	92.0			32.33 <sup>c</sup>		170.2	13.59°	16	
			8.0							
	$(CH_3)_3C$	100		162.18	162.18		$172.0 \pm 4.6$	$14.45 \pm 0.47$	5	
	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	69.2	30.8	73.42	50.81	22.61	$154.1 \pm 1.9$	$12.42 \pm 0.19$	this work	
	C <sub>6</sub> H,	100		37.15	37.15		$170.2 \pm 3.8$	13.64	16	
	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	66.6	33.4	45.85	30.54	15.31	$151.5 \pm 5.6$	11.97 ± 0.55	this work	
	CH <sub>2</sub> =CH	100		35.48	35.48		$169.8 \pm 3.8$	13.59	16	
	$CH_2 = CHCH_2$	54	46	34.67	18.72	15.95	$171.0 \pm 2.9$	$13.69 \pm 0.28$	17	
	c-C <sub>3</sub> H,	100		67.61	67.61		$170.7 \pm 3.8$	13.95	16	
2	CH <sub>3</sub> COCH <sub>2</sub>	5			13.49		$160.6 \pm 6.3$	$12.30 \pm 0.60$	18	
	· ·		95			302.0	$134.7 \pm 4.2$	$11.20 \pm 0.40$		
	CH <sub>3</sub> CO	100		2.40	2.40		180.9 ± 1.8	$13.47 \pm 0.17$	19	
	CH <sub>3</sub> OOC <sup>d</sup>	100		0.85	0.85		$174.6 \pm 3.2$	$12.42 \pm 0.28$	this work	
	NC	100		0.49	0.49		198.6 ± 8.8	$14.45 \pm 0.82$	5	
	Cl <sub>3</sub> C	98.5		1.07	1.05		$188.8 \pm 3.8$	$13.86 \pm 0.35$	this work	

<sup>*a*</sup> The Arrhenius parameters were, whenever possible, recalculated from reported data of the cited reference by the least-squares procedure. The confidence coefficient used to determine the errors was 0.8. <sup>*b*</sup> This value corresponds to the elimination toward two methyl, thus allowing a determination of the effect of the third methyl substituent. <sup>*c*</sup> Calculated from data of ref 16. <sup>*d*</sup> This ester was redetermined, see ref 5.

TABLE VII: Linear Correlation for CH<sub>3</sub>COOC(CH<sub>3</sub>)<sub>2</sub>Z at 280 °C<sup>a</sup>

Z	$\frac{\log k_{\rm Z}/k_0}{(1-{\rm olefin})}$	σ*	$\sigma_{\mathrm{I}}$	$E_{s}$	$E_s^{\ c}$
CH,	0.000	0.00	-0.04	0.00	0.00
CH <sub>3</sub> CH <sub>2</sub>	0.227	-0.10	-0.05	-0.07	-0.38
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	0.451	-0.115	-0.01	-0.36	-0.67
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	0.341	-0.13	-0.04	-0.39	-0.70
(CH <sub>3</sub> ) <sub>2</sub> CH	0.346	-0.19	-0.06	-0.47	-1.08
$(CH_3)_3C$	1.046	-0.30	-0.07	-1.54	-2.46
$(CH_3)_2CHCH_2$	0.542	-0.125	-0.03	-0.93	-1.24
C <sub>6</sub> H <sub>5</sub>	0.406	0.60	0.10		
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub>	0.321	0.08	0.02	-0.38	-0.69
$CH_2 = CH$	0.386	0.52	0.09		
$CH_2 = CHCH_2$	0.108	0.23	0.00		
c-C <sub>3</sub> H <sub>5</sub>	0.666	-0.15	-0.08	$-1.16^{b}$	-1.77°
CH <sub>3</sub> COCH <sub>2</sub>	-0.034	0.60	0.10 <sup>d</sup>	-0.75	-1.06
CH <sub>3</sub> CO	-0.784	1.65	0.29		
CH <sub>3</sub> OCO	-1.234	2.00	0.34		
NC	-1.474	3.64	0.48	0.63	-0.29°
Cl <sub>3</sub> C	-1.143	2.65	0.40	-2.06	-2.98°

<sup>a</sup>Reference 20. <sup>b</sup>Previously estimated value, see ref 4. <sup>c</sup>Estimated from equation  $E_s^c = E_s + 0.306(n-3)$ , see ref 21. <sup>d</sup>Estimated from the equation  $\sigma_{I(2)} = 0.45\sigma^*(ZCH_2)$  where  $\sigma^*$  value of CH<sub>3</sub>COCH<sub>2</sub>CH<sub>2</sub> is 0.23, see ref 20.



Figure 2. log  $k/k_0$  vs.  $E_s^{\circ}$  values for alkyl substituents at 280 °C ( $\delta = -0.38$ , r = 0.964, and intercept = 0.055).

alkyl groups affect the elimination rates by steric acceleration. That is, plotting log  $k_Z/k_0$  against the steric parameter  $E_s$  values of Taft<sup>20</sup> (Figure 1,  $\delta = -0.55$ , r = 0.956, and intercept = 0.114 at 280 °C) gives a good straight line. Since a better correlation of alkyl substituents at the  $\beta$ -carbon atom of primary acetates



Figure 3. log  $k/k_{CH_3}$  vs.  $\sigma^*$  values for polar substituents at 280 °C ( $\rho^* = -0.45$ , r = 0.950, and intercept = 0.012).



**Figure 4.** log  $k/k_{CH_3}$  vs.  $\sigma_1$  values for polar substituents at 280 °C ( $\rho_1 = -3.11$ , r = 0.964, and intercept = 0.035).

pyrolyses (1) with Hancock's steric parameter  $E_s^c$  was obtained,<sup>2</sup> the plot of log  $k_{rel}$  of the alkyls of Table VII vs.  $E_s^c$  values<sup>20</sup> yields also a slightly improved straight line (Figure 2,  $\delta = -0.38$ , r = 0.964, and intercept = 0.055 at 280 °C).

Considering the polar groups (Table VII) attached directly to the  $\alpha$ -carbon in 4, their effects are electronic in nature. This consideration derives by plotting log  $k_Z/k_0$  against  $\sigma^*$  values<sup>20</sup> (Figure 3,  $\rho^* = -0.45$ , r = 0.950, and intercept = 0.012 at 280 °C) and log  $k_Z/k_0$  vs.  $\sigma_1$  values<sup>20</sup> (Figure 4,  $\sigma_1 = -3.11$ , r = 0.964, and intercept = 0.035 at 280 °C). These results also imply that the greater the electron-withdrawing character or electronegativity of the polar substituent, the slower is the pyrolysis rate of the tertiary ester.

Multiple-bonded or  $\pi$ -bonded substituents CH<sub>2</sub>=CH and C<sub>6</sub>H<sub>5</sub> (Table VI) as Z in 4 affect the rates as has already been described

<sup>(20)</sup> Hansch, C.; Leo, A. "Substituent Constants for Correlation Analysis in Chemistry and Biology"; Wiley: New York, 1979.

<sup>(21)</sup> Hancock, C. K.; Meyers, E. A.; Yager, B. J. J. Am. Chem. Soc. 1961, 83, 4211.

in the introductory part of this work, i.e., through the simultaneous steric and resonance effect.

In conclusion, the present work appears to confirm previous results on the substituent effects of primary  $(1)^{2,3}$  and secondary acetates (2, 3).<sup>4</sup> Therefore, it is plausible to establish a generalization, even if a few eventual exceptions may appear, about the influence of Z in the gas-phase elimination of esters of type 1-4.

(1) Alkyl groups at the  $\alpha$ - and  $\beta$ -carbon atoms affect the decomposition velocity through steric factor. The alkyl-hydrogen interactions give a rate increase due to steric acceleration, while alkyl-alkyl interactions decrease it because of steric hindrance.

(2) Strong polar groups at the  $\alpha$ - and  $\beta$ -carbon deactivate the elimination in the sense that the greater the electron-withdrawing effect or electronegativity of the substituent the slower is the rate of the reaction.

(3) A multiple-bonded or  $\pi$ -bonded substituent attached directly to the  $\alpha$ -carbon tends to stabilize the polarization of the C<sub> $\alpha$ </sub>-O bond in the transition state through a resonance effect. Consequently, the rate of elimination is, most of the time, significantly increased. When these substituents are attached directly to the  $\beta$ -carbon atom, the rates are also increased through the resonance effect. The hydrogen of the  $C_{\beta}$ -H bond becomes more acidic and thus assists the leaving acetoxy group in the transition state.

Acknowledgment. We are grateful to the Consejo Nacional de Investigaciones Científicas y Tecnológicas (CONICIT) for their support (Project No. 51.78.31, S1-1072).

**Registry No.** 4 ( $Z = CCl_3$ ), 597-37-5; 4 (Z = (O)OMe), 57865-37-9; 4 (Z = Bu), 34650-24-3; 4 (Z = (CH<sub>3</sub>)<sub>2</sub>CHCH<sub>2</sub>), 34856-44-5; 4 (Z = PhCH<sub>2</sub>CH<sub>2</sub>), 103-07-1.

## Ionization of Multiply Substituted Methylbenzoic Acids in Water: Conductance and Thermodynamics

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Experimental conductance data over the temperature range from 0 to 100 °C are presented for three tetramethyl- and two trimethylbenzoic acids in water. Analyses of the data as a function of concentration and of temperature provide not only  $\Lambda_0$  values and ionization constants but also standard-state changes in enthalpy, entropy, and heat capacity for ionization and their temperature dependence. Fifteen methylbenzoic acids listed in order of increasing  $\Delta S^{\circ}$  for ionization at 25 °C form three sets classified according to whether there are two, one, or no ortho substituents. Within each of these sets  $\Delta S^{\circ}$ is more negative the larger the number of methyl groups present on the aromatic ring. Heat capacity changes for these five acids, as for some but not all other methylbenzoic acids, show maxima around 50 °C at about -30 cal K<sup>-1</sup> mol<sup>-1</sup>. Walden products for those anions without a para substituent increase from 0 °C to maxima at about 30 °C while those containing para substituents also show marked increases between 70 and 100 °C. It is suggested that the observed behavior can be seen as a consequence of the ability of the substituted aromatic ring to sweep out in the water a low dielectric constant cavity adjacent to the carboxyl group.

#### Introduction

There has been little published on the acidities of substituted benzoic acids with more than two substituents and nothing on the thermodynamics of the ionization of multiply substituted methylbenzoic acids. Some years ago Crawford and Magill<sup>1</sup> pointed out that 2,3-dimethylbenzoic acid is a stronger acid than 2methylbenzoic acid although 3-methylbenzoic acid is less acidic than benzoic acid. Dippy and Hughes<sup>2</sup> and other authors have referred to this high acidity of 2,3-dimethylbenzoic acid as evidence for a "buttressing" effect of a meta group when adjacent to an ortho group. Crawford and Magill<sup>1</sup> expected duroic acid (2,3,5,6-tetramethylbenzoic acid) to be more acidic than the 2,6acid but found it to be less acidic, in contrast to the behavior of the 2,3- acid. Subsequent reports<sup>3</sup> from Crawford and his students showed the same type of effect with various other more bulky alkyl groups. They attributed this "low acidity" of duroic and similar acids with two ortho groups to steric effects and referred to acids like duroic acid as "highly hindered" acids.

Work in this laboratory<sup>4</sup> has confirmed the high acidity of 2,3-dimethylbenzoic acid compared to the 2-methyl acid not only at 25 °C but also for temperatures from 0 to 100 °C. Thermodynamic changes for acid ionization indicate that for the 2,3- acid

the high acidity results from  $\Delta H^{\circ}$  being more negative than it is for the ionization of o-toluic acid which more than outweighs the small decrease in standard entropy. These thermodynamic changes differ markedly from those for 3-methylbenzoic acid and benzoic acid where the small decrease in acidity attending substitution at the 3-position is the result of a negative  $\Delta S^{\circ}$  with almost no change in  $\Delta H^{\circ}$ .

We now report on a number of tri- and tetra-substituted methylbenzoic acids that we have examined as part of a continuing study of the effects of various substituents on the ionization behavior of derivatives of benzoic acid in water solution. The results provide data on enthalpy, entropy, and heat capacity changes as a function of temperature. These together with limiting conductances for the various acids make it possible to draw some general conclusions about the effect of methyl substituents on the ionization of benzoic acid.

#### **Experimental Section**

Acid ionization constants were determined by precision con-

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