(dec. sharply at 182°). Further crystallization from ethanol–benzene produced yellow plates, m.p. 182.2–183.6°; reported m.p. 185°.[8]

4-Acetyl-7-methoxybenzofuran.—By the quinoline–copper decarboxylation procedure above, 1.81 g. of the coumarilic acid gave 1 g. of the benzofuran, m.p. 87–95°. Repeated sublimation, finally at 80–100° (0.35 mm.) (bath temp.) gave colorless material, m.p. 92.8–95.2°; $\lambda_{\max}^{\text{alc}}$ 235, 293.5 mμ (ε 17,500, 16,100).

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.69; H, 5.31.

2-(?)Chloro-7-methoxybenzofuran-4-carboxylic Acid.—One-half gram of the sublimed benzofuran above (m.p. 94–97°) and 60 ml. of dioxane were added to 180 ml. of alkaline commercial bleach solution and treated as described above. The dioxane was distilled, the cooled solution was treated with a small portion of sodium bisulfite and acidified. The colorless product weighed 0.51 g., m.p. 236–240°. By sublimation at 150–170° (0.06 mm.) long thin colorless prisms were obtained, m.p. 249.0–252.5° (Kofl.). The presence of chlorine was shown by a sodium fusion test; $\lambda_{\max}^{\text{alc}}$ 228, 273 mμ (ε 31,300, 12,300).

Anal. Calcd. for $C_{10}H_7ClO_4$: C, 53.00; H, 3.11. Found: C, 52.74; H, 3.18.

Methyl 4-Ethyl-7-methoxycoumarilate (XXI).—One gram of XX was hydrogenated using 200 mg. of 10% palladium–carbon in 25 ml. of acetic acid containing 1 drop of 70% perchloric acid. In 65 min., 254 ml. of hydrogen was absorbed. Dilution with water gave 0.7 g. of product which was brought to a melting point of 74.3–74.5° by crystallization from aqueous ethanol; $\lambda_{\max}^{\text{alc}}$ 238.5, 283 mμ (ε 22,600, 16,400), $\lambda_{\text{infl}}^{\text{alc}}$ 311 mμ (ε 3860).

Anal. Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.90; H, 6.11.

Saponification gave the acid, crystallized from benzene, m.p. 187.3–188.1°; $\lambda_{\max}^{\text{alc}}$ 235, 276 mμ (ε 24,700, 16,500).

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.50. Found: C, 65.23; H, 5.23.

5-Ethyl-2-hydroxy-3-methoxybenzaldehyde.—Clemmensen reduction of acetovanillone, m.p. 97–112°, gave 4-ethyl-2-methoxyphenol (64%), b.p. 140–146° (46 mm.).

The benzoate melted at 57–60° after crystallization from alcohol; reported[25] m.p. 58–59°.

The 2,4-dinitrophenyl ether from alcohol melted at 87.0–88.6°.

Anal. Calcd. for $C_{15}H_{14}N_2O_6$: C, 56.60: H, 4.43. Found: C, 56.21; H, 4.30.

The Duff reaction[7] on 20 g. of the above phenol with steam distillation and extraction of the distillate with ether gave 5-ethyl-2-hydroxy-3-methoxybenzaldehyde, a light yellow oil (9.3 g. 39%), b.p. 98° (0.37 mm.). The sample submitted for analysis boiled at 120° (2 mm.); $\lambda_{\max}^{\text{alc}}$ 224, 269, 351 mμ (ε 21,000, 11,200, 2830).

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.72. Found: C, 66.73; H, 6.75.

The semicarbazone formed fluffy, pale yellow, microscopic prisms from 1:1 aqueous ethanol, m.p. 186–189° (Kofl.).

Anal. Calcd. for $C_{11}H_{15}N_3O_3$: C, 55.68; H, 6.37. Found: C, 55.57; H, 6.68.

The aldehyde (7.2 g.) was treated with malonic acid and aniline[26] to produce 6.51 g. (66%) of 6-ethyl-8-methoxycoumarin-3-carboxylic acid, m.p. 156–170°. Five crystallizations from alcohol gave light yellow crystals, m.p. 175.6–177.8°; $\lambda_{\max}^{\text{alc}}$ 208, 254.5, 307.5 mμ (ε 34,300, 8750, 14,700).

Anal. Calcd. for $C_{13}H_{12}O_5$: C, 62.90; H, 4.88. Found: C, 62.75; H, 4.93.

5-Ethyl-7-methoxycoumarilic Acid.—The sodium ethoxide condensation of the above aldehyde (4.1 g.) with methyl bromoacetate followed by saponification as previously described gave 4.12 g. of tacky brown solid soluble in sodium bicarbonate. Sublimation at 150° (0.13 mm.) gave 1.24 g. of colorless crystals contaminated with a yellow oil. Three crystallizations from methanol–water gave colorless needles, m.p. 205.4–206.6°; $\lambda_{\max}^{\text{alc}}$ 234.5, 274 mμ (ε 21,800, 16,800).

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.30; H, 5.36.

The amide melted at 182.0–183.6° after crystallization from aqueous methanol.

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98. Found: C, 65.72; H, 6.19.

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[25] C. E. Coulthard, J. Marshall, and F. L. Pyman, *J. Chem. Soc.*, 280 (1930).

[26] W. Borsche and P. Hahn-Weinheimer, *Chem. Ber.*, **85**, 198 (1952).

Pyrolysis Studies. VII.[1,2] Rates of Thermal Decomposition of Substituted Ethyl Benzoates

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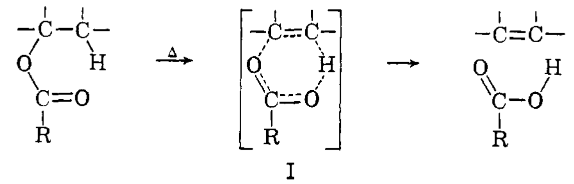
Relative rates of elimination in the pyrolysis of a series of *meta-* and *para-*substituted ethyl benzoates together with infrared data are shown to confirm that heterolytic breakage of the alkoxy C—O bond is of paramount importance in ester pyrolysis. The relative rates are best correlated using Taft's σ^0 values.

The pyrolytic decomposition of esters containing at least one β-hydrogen atom to olefins and acids is generally considered to proceed *via* a cyclic concerted mechanism.

In the transition state (I), the C—H bond and the alkoxy C—O bond are partially broken, and the olefinic C=C bond and the O—H bond are partially formed.[4]



I

Previous work[5] has shown that the C—O bond breakage is *heterolytic* and that the α-carbon atom develops some carbonium ion character in the transition state. Thus relative rate data for the vapor phase pyrolysis of a series of *meta-* and *para-* substituted 1-phenylethyl acetates show a σ^+ correlation.[5] It also appears that for a given ester at a fixed temperature, the rate of decomposition is determined more by the stability of the

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[1] Part VI: R. Taylor and G. G. Smith, *Tetrahedron*, submitted for publication.

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[4] (a) C. H. DePuy, R. W. King, and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959); (b) C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960) and references therein.

[5] R. Taylor, G. G. Smith, and W. H. Wetzel, *J. Am. Chem. Soc.*, **84**, 4817 (1962).

breaking alkoxy C—O bond than by that of the breaking C—H bond or the forming C=C bond.[6]

Additional information about the charge separation in the transition state and about the mechanism of the reaction can be obtained by studying a series of esters in which the electron availability at the carbonyl group varies. In particular, Maccoll's proposal[7] that the reaction is pseudo E2, involving nucleophilic attack of the carbonyl oxygen atom on the β-hydrogen atom can be directly evaluated. Accordingly, we now report relative rate data for the vapor phase pyrolysis of a series of substituted ethyl benzoates. Some advantages of using systems of this type to study ester pyrolysis have been detailed previously.[6] We have also measured the frequency of the infrared band in the 1100–1200-cm.$^{-1}$ region for twelve of the seventeen esters studied. This band is known to be associated with carbon–oxygen single bond stretching[8] and should therefore vary with the strength of the alkoxy C—O bond and hence correlate with the rate of decomposition.

Experimental

Ester Preparation.—Esters were prepared from commercially available acids and ethanol using either sulfuric acid or dry hydrogen chloride as catalyst. Liquid esters were purified by careful fractionation, and solid esters were purified by crystallization to constant melting point. The physical constants of the pure esters were found to agree with the best literature values.

Methods of Pyrolysis.—Two methods, both of which have been described in detail previously, were used in the present study.

The first was a continuous flow dynamic method[9] in which a fixed volume of ester was injected into a stream of helium flowing through the pyrolysis apparatus at a constant rate. After passing through a cold trap to remove the substituted benzoic acid, the mixture of gases was passed through a gas chromatograph where the amount of ethylene produced was measured. The furnace temperature was 515°, the rate of helium flow was 72 ml./min., and the gases were separated on a 15-ft. 40–60-mesh silica gel column at 56°. Liquid esters were injected into the system using a 10 μl. microsyringe fitted with a Chaney adapter. Solid esters were injected using a heated syringe and needle, or in some cases as solutions in 1,4-dioxane.

The second procedure was a static method[6,10] and used a stainless steel reactor fitted with a null-point gauge and an exterior pressure measuring system. A small sample (75–200 μl.) of the ester was injected, the reactor was sealed and the reaction followed by noting the increase in pressure with time. The furnace temperature was 414 ± 0.5°.

Spectra.—Infrared spectra were taken in 3% carbon disulfide solution using a Beckman IR-4 spectrometer fitted with sodium chloride optics.

Results

In the continuous flow method, the amount of ethylene produced by a given ester was directly proportional to the rate of decomposition, since the stoichiometry of ester to olefin is one. Throughout the series the reaction temperature, time, and the volume of the reactant were constant so that the ratio of the amount of ethylene produced to that produced by unsubstituted ethyl benzoate when multiplied by the ratio of the molar volumes[11] gave the relative rate of decomposition. The results are given in Table I together with the frequencies of the C—O stretching vibrations in the 1100–1150-cm.$^{-1}$ region. The relative rates are mean values, as multiple samples were pyrolyzed to minimize errors in sampling and in integration of the curves and the reference compound, ethyl benzoate, was pyrolyzed immediately before and afterwards in each case to minimize errors due to slight changes in furnace temperature and to check reproducibility. For the relative rates the average deviation was within ±3% for all esters except ethyl *m*- and *p*-hydroxybenzoates and ethyl *p*-aminobenzoate (±3.5%) which were injected in 1,4-dioxane solution,[12] and ethyl *m*- and *p*-nitrobenzoates (±4%) which were injected as melts.

TABLE I

RELATIVE RATE DATA FOR PYROLYSIS OF SUBSTITUTED ETHYL BENZOATES AT 515°

Substituent	Relative rate	C—O frequency, cm.$^{-1}$
p-NH_2	0.86	...
p-OH	.91	...
p-OMe	.96	1175
m-OH	.98	...
H	1.00	1170
m-NH_2	1.01	1164
p-Me	1.03	1170
m-OMe	1.07	1175
m-Me	1.08	1162
p-Br	1.25	1107
m-Br	1.27	1117
m-Cl	1.28	1123
p-Cl	1.28	1117
m-I	1.32	1106
p-I	1.32	1106
p-NO_2	1.42	...
m-NO_2	1.50	...

In all cases the gas chromatograms showed additional peaks, indicating that the reaction was not entirely clean. Carbon dioxide, which presumably arises from decarboxylation of the substituted benzoic acid, was identified as a secondary decomposition product in all cases, a greater amount being formed when electron withdrawing substituents were present. Other secondary decomposition products obtained in some cases where carbon monoxide and ethane, and oxides of nitrogen in the case of the nitro esters. It should be emphasized that these secondary reactions do not affect the validity of the relative rate data.

In the static method, although the pyrolysis temperature was 100° lower, it was evident that secondary decomposition was still occurring as the reaction continued past the theoretical P_∞. The rate constants were therefore obtained from the initial slopes of the log $(2P_0 - P_t)$ against time plots. Each ester was pyrolyzed several times, the mean values of the rate constants are given in Table II together with the "linearity," the percentage reaction for which the log $(2P_0 - P_t)$ against time plot was linear. For the rate constants the average deviation was within ±2% except for ethyl *p*-methyl- (±8%), and ethyl *m*-methyl benzoates (±5%). The cause of the big deviation in the case of the *p*-methyl compound is not known. However, the linearity is only 50%, a lower figure than that for the other compounds. It was not possible to study all seventeen esters by this method. In the case of solid esters, the heated syringe

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[6] G. G. Smith, F. D. Bagley, and R. Taylor, *J. Am. Chem. Soc.* **83**, 3647 (1961).

[7] A. Maccoll, *J. Chem. Soc.*, 3398 (1958).

[8] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, chap. 11.

[9] G. G. Smith, W. H. Wetzel, and B. Kösters, *Analyst*, **86**, 480 (1961).

[10] G. G. Smith and F. D. Bagley, *Rev. Sci. Instr.*, **32**, 703 (1961).

[11] This correction was necessary as equal *volumes* rather than equimolar quantities of esters were pyrolyzed.

[12] A small correction had to be applied in these cases as, under the experimental conditions, 1,4-dioxane decomposed slightly to give ethylene.

Table II

Rates of Decomposition of Substituted Ethyl Benzoates at 414°

Substituent	10^3k, sec.$^{-1}$	Linearity, %
p-Me	1.74	~50
H	1.97	68
m-Me	2.12	58
m-OMe	2.41	64
p-Cl	2.42	65
p-Br	2.63	66
m-Cl	2.77	68
m-Br	2.95	75

and needle technique used in the flow method was unsuccessful; in other cases, the secondary reaction was so fast that it was impossible to obtain the initial slope of the log $(2P_0 - P_t)$ against time plot.

Discussion

The results from both studies show that the decomposition is accelerated by electronegative substituents attached to the carbonyl group and correspondingly retarded by electropositive substituents. The findings of Bailey and Hewitt,[13] who measured the extent of pyrolysis in several methylisobutylcarbinyl benzoates and of Smith and Wetzel[14] who determined the characteristic temperatures of pyrolysis for several cyclohexyl benzoates support this observation. DePuy and co-workers also noted recently[15] that esters with electronegative groups attached to the carbonyl carbon atom tend to pyrolyze at lower temperatures.

The experimental evidence is in accord with the previously proposed view of the transition state in which the alkoxy C—O bond breakage is heterolytic.[5] Electronegative substituents attached to the carbonyl group increase the rate because they stabilize the partially formed oxygen anion.

Maccoll's conclusion[7] that the elimination is pseudo E2 involving nucleophilic attack of the carbonyl oxygen atom on the β-hydrogen atom is questionable as the observed effects of substituents are exactly opposite to what his mechanism predicts. Electronegative substituents will decrease the basicity of the carbonyl oxygen and should *reduce* the rate according to Maccoll's mechanism, whereas these studies show that they increase the rate.

The results in Table I show that the C—O absorption in the 1100–1200-cm.$^{-1}$ region tends to occur at progressively lower frequencies as the rate of reaction increases.[16] This is in good agreement with the proposed relationship[6] between the stability of the ester and the strength of the alkoxy C—O bond, for although the 1100–1250-cm.$^{-1}$ absorption is not a pure C—O stretching band[8] its position will be influenced by changes in the stability of the alkoxy C—O bond and it is likely to occur at a lower frequency if this bond is weakened.

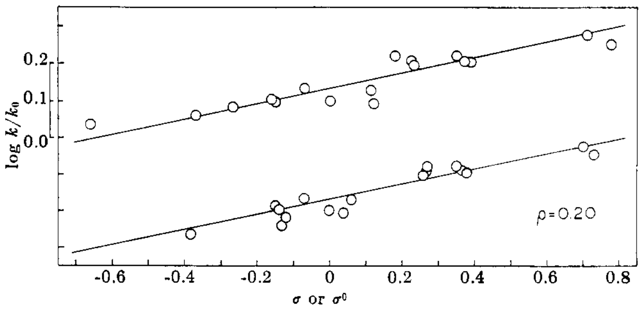

Fig. 1.—Hammett σ plot (top) and Taft σ^0 plot (bottom) for pyrolysis of substituted ethyl benzoates at 515°.[18]

It is of interest to correlate relative rates of this type with the acidity of the eliminated acid. In previous studies Smith and Wetzel[14] related pK_a to the characteristic temperature and Bailey and Hewitt[13] related pK_a to the extent of pyrolysis. Both groups of workers noted that esters of strong acids decomposed more readily, acidity and ease of pyrolysis being enhanced by electronegative substituents attached to the carbonyl group. With relative rate data for esters of aromatic acids it is possible to use the well known Hammett substituent constants. Fig. 1 shows a plot of log relative rate against σ and also against Taft's σ^0 for pyrolysis of substituted ethyl benzoates at 515°.[17] It is noticeable that the linearity is improved if the σ^0 values are used. Such relations are observed when the resonance stabilization of the reaction site by the aryl groups in the initial and transition states is similar.[18b,19] A σ^0 correlation rather than the usual σ correlation is not unexpected as the difference in negative charge on the alkoxy C—O oxygen atoms in the initial and transition states in ester pyrolysis will be much less than the corresponding charge difference in the ionization of benzoic acids. This and other σ^0 relations will be discussed in more detail in Paper VIII of this series.

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(13) W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

(14) G. G. Smith and W. H. Wetzel, *J. Am. Chem. Soc.*, **79**, 875 (1957).

(15) C. H. DePuy, C. A. Bishop, and C. N. Goeders, *ibid.*, **83**, 2151 (1961).

(16) Smith and Wetzel[14] observed a similar relationship between C—O frequency and characteristic temperature in the cyclohexyl benzoate series.

(17) The rate data at 414° are not plotted because relatively few substituents were studied and none for which the σ and σ^0 values are radically different.

(18) (a) σ values are from D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958); (b) σ^0 values are from R. W. Taft, Jr., *J. Phys. Chem.*, **64**, 1805 (1960).

(19) (a) H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959); (b) J. Hine, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 91.