

distillate was crystallized from petroleum ether to yield pale yellow needles of *o*-propionaminopropiophenone, m.p. 44–45°; $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 230 (log ϵ 4.37), 234 (log ϵ 4.37), 259 (log ϵ 4.02), 266 (log ϵ 3.94) and 324 $\mu\mu$ (log ϵ 3.61). The infrared spectrum in a KBr pellet had an NH absorption at 3120 cm^{-1} and carbonyl absorptions at 1682 (ketone) and 1650 cm^{-1} (amide).

Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 70.43; H, 7.40; N, 6.74.

2-Acetyl-3-ethylindole. (a) From 2,3-Diethyl-3-hydroperoxyindolenine.—(1) The indolenine III (0.5 g.) was dissolved in ethyl acetate (20 ml.) and evaporated to dryness on a steam-bath. The yellow residue was heated on the steam-bath for a further 30 min. The light brown viscous residue, which showed strong absorptions in the 1600–1700 cm^{-1} region of the infrared spectrum, was dissolved in benzene and chromatographed on alumina, eluting with benzene. A small amount of crystalline material (15 mg.) was obtained from the first fractions and was identical with *o*-propionaminopropiophenone (infrared and ultraviolet spectra). Later fractions yielded 2-acetyl-3-ethylindole (0.24 g.) which was obtained as colorless needles from petroleum ether, m.p. 117–118°; $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 212 (log ϵ 4.26), 238 (log ϵ 4.20), 314 (log ϵ 4.30). The infrared spectrum in a KBr pellet had an NH absorption at 3330 cm^{-1} and a carbonyl absorption at 1632 cm^{-1} .

Anal. Calcd. for $\text{C}_{12}\text{H}_{13}\text{NO}$: C, 76.97; H, 7.00; N, 7.48. Found: C, 77.17; H, 7.17; N, 7.41.

Continued elution of the column with benzene containing 1% methanol yielded viscous oils of unknown composition.

(2) The indolenine III (410 mg.) was dissolved in ethyl acetate (20 ml.), acetic acid (2 ml.) added, and the mixture allowed to stand at room temperature for 16 hr. During this time the solution became light brown. The solution was then evaporated *in vacuo* and the residue dissolved in benzene and chromatographed on alumina yielding 2-acetyl-3-ethylindole (0.22 g.). When the indolenine III was dissolved in acetic acid a pale yellow solution was obtained which became dark brown after 16 hr. Chromatography of the residue obtained after evaporation afforded a 44% yield of the ketone X.

(b) From 2,3-Diethylindole.—2,3-Diethylindole (1.0 g.) was exposed to air for several days. The brownish-yellow resinous mass was dissolved in benzene and chromatographed on alumina, eluting with benzene. The first fractions yielded

unchanged 2,3-diethylindole. Later fractions yielded crystalline 2-acetyl-3-ethylindole (yield varied from 0.1 to 0.3 g. in different experiments). In another experiment a freshly distilled, chromatographically pure sample of 2,3-diethylindole (1.0 g.) was exposed to the ultraviolet and visible light generated by a 125 watt Hanovia UV lamp. After 3 hr. the infrared spectrum of the reaction mixture indicated the presence of carbonyl compounds. After 6 hr. the yellow resinous material was chromatographed on alumina as before, yielding unchanged 2,3-diethylindole (0.17 g.) and 2-acetyl-3-ethylindole (0.22 g.).

(c) From 3-Ethylindole.—3-Ethylindole¹⁴ (4.0 g.) dissolved in ether (10 ml.) was added with stirring to a cooled solution of methylmagnesium iodide (prepared from methyl iodide (2 ml.) and magnesium (0.67 g.)) in ether (40 ml.). After 10 min. freshly distilled acetyl chloride (2 ml.) in ether (10 ml.) was added to this solution which was cooled to 0°. The yellow mixture was stirred for 2 hr. at room temperature and then water was added and the ether layer separated. The dried ether layer was evaporated and the residue chromatographed on alumina, eluting with a 1:1 mixture of benzene and petroleum ether. The first fractions were unchanged 3-ethylindole, then a series of liquid fractions which were apparently impure 1-acetyl-3-ethylindole. Final fractions yielded 2-acetyl-3-ethylindole (1.2 g.) identical (mixed m.p., infrared and ultraviolet spectra) with material obtained by the autooxidation of 2,3-diethylindole and by the action of heat on 2,3-diethyl-3-hydroperoxyindolenine.

Action of Heat on 2,3-Dimethyl-3-hydroperoxyindolenine.—2,3-Dimethyl-3-hydroperoxyindolenine⁷ (0.44 g.) was dissolved in ethyl acetate (20 ml.) and heated on the steam-bath for 15 min. The yellow residue was chromatographed on alumina yielding *o*-acetaminoacetophenone (0.17 g.) as fine pale yellow needles (from petroleum ether), m.p. 76–77° (lit.⁷ 77–78°); $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 230 (log ϵ 4.42), 235 (log ϵ 4.42), 258 (log ϵ 4.04), 265 (log ϵ 3.97) and 324 $\mu\mu$ (log ϵ 3.64).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_2$: C, 67.78; H, 6.26; N, 7.91. Found: C, 67.85; H, 6.48; N, 7.77.

No identifiable materials were obtained when the hydroperoxide was dissolved in acetic acid and maintained at room temperature for 24 hr. except *o*-acetaminoacetophenone. A similar result was observed when the hydroperoxide was added to a mixture of ethyl acetate and acetic acid.

(14) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON STATE UNIVERSITY, PULLMAN, WASH.]

Kinetic Study of the Pyrolysis of 1,2-Diarylethyl Acetates. IV^{1,2}

BY GRANT GILL SMITH, FRANK D. BAGLEY^{3a} AND ROGER TAYLOR^{3b}

RECEIVED DECEMBER 12, 1960

A kinetic study of the thermal decomposition of eleven *meta* and *para* substituted 1,2-diphenylethyl acetates has been made; the energies and entropies of activation range from 40.6 to 43.8 kcal./mole and -0.215 to -2.54 e.u., respectively. The esters (both solids and liquids) were each pyrolyzed over a temperature range of 50° in a static system at reactant pressure of 15 to 150 mm. by use of a specially designed apparatus. The importance of the breaking of the carbon-hydrogen and carbon-oxygen single bonds and the formation of olefinic bond to the stability of the ester has been evaluated. Esters with strongly electron-releasing groups (*e.g.*, 4-OCH₃) in the 1-phenyl ring were very sensitive to surface reactions and could only be studied satisfactorily in the presence of an inhibitor.

Although much has been published recently about the pyrolysis of esters, no previous kinetic study

(1) (a) G. G. Smith and B. Kösters, *Chem. Ber.*, **93**, 2400 (1960). (b) Presented in part before the 138th National Meeting of the American Chemical Society, New York, N. Y., September, 1960. (c) Abstracted from a thesis presented to the Graduate School of the Washington State University by F. D. Bagley in partial fulfillment of the requirements for the Ph.D. degree, December, 1960.

(2) This work was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)616. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(3) (a) Dow Research Fellow, 1959–1960; (b) Postdoctoral Research Associate.

has been reported of the effect of substituents on the absolute reaction rate of pyrolysis of esters except for a study of the deuterium isotope effect.⁴ The thermal decomposition of esters with β -hydrogens lends itself to kinetic studies, since the reaction follows definite stoichiometry and side reactions are few. Rate studies have shown the reaction to follow first-order kinetics; it is unimolecular, homogeneous and generally has a negative entropy of activation.⁵ In comparative rate studies the sta-

(4) D. Y. Curtin and D. B. Kellom, *J. Am. Chem. Soc.*, **75**, 6011 (1953).

(5) (a) G. L. O'Conner and H. R. Nace, *ibid.*, **75**, 2118 (1953); (b)

bility of the esters has been shown to be a function of molecular weight⁶ and the nature of the acyl group of the ester.^{6a,6b,7} Where more than one olefin may arise because of elimination of a hydrogen from different β -carbon atoms, the direction of elimination is thought to be governed by the number of *cis*-hydrogens,⁸ crowding in the transition state,^{4,8c} thermodynamic stability^{8c,9} and the acidity of the β -hydrogen.^{8j,9,10}

Much has been written about the importance of thermodynamic stability and of β -hydrogen acidity, yet neither of these factors has been evaluated by a rate study in which there was only a single variant. Another known facet of the reaction shown to be important is the ease of cleavage of the carbon-oxygen bond, as indicated by the increasing rates of pyrolysis of primary, secondary and tertiary alkyl esters (Table I), although in this comparison other considerations such as molecular weight are involved.

TABLE I

RELATIVE RATES IN PYROLYSIS OF ESTERS OF PRIMARY, SECONDARY AND TERTIARY ALKYL GROUPS

Ester	Relative rate at 400°	
	Maccoll ^a	DePuy ^b
Ethyl acetate	1	1
Isopropyl acetate	26	19
<i>t</i> -Butyl acetate	1660 ^c	1170
Ethyl formate	0.76	0.76
Isopropyl formate	15.2	9.1
<i>t</i> -Butyl formate	547	

^a A. Maccoll, *J. Chem. Soc.*, 3398 (1958). ^b Reference 8m. ^c Maccoll, ref. 17a.

With the kinetic deuterium isotope effect indicating the importance of breaking the carbon-hydrogen bond, it is of interest that the relative rate of pyrolysis with reference to the carbon-oxygen bond is *tert.* > *sec.* > *prim.* irrespective of whether the β -H eliminated is *prim.*, *sec.* or *tert.* or whether the β -hydrogen is activated by a phenyl group. The relative rates of pyrolysis of several acetates (5-nonyl, α -phenylethyl, β -phenylethyl acetates and 2-acetoxycyclohexanone) have been compared to "show clearly that the amount of carbon-oxygen

C. E. Rudy, Jr., and P. Fugassi, *J. Phys. Colloid Chem.*, **52**, 357 (1948); (c) A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954); (d) D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 1715 (1953); (e) A. T. Blades, in C. H. DePuy and R. W. King, *Chem. Revs.*, **60**, 431 (1960).

(6) (a) F. Krafft, *Ber.*, **16**, 3018 (1883); (b) G. G. Smith and W. H. Wetzell, *J. Am. Chem. Soc.*, **79**, 875 (1957).

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

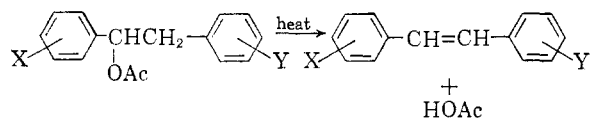
(8) (a) R. T. Arnold, G. G. Smith and R. M. Dodson, *ibid.*, **15**, 1256 (1950); (b) D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959); (c) E. E. Royals, *J. Org. Chem.*, **23**, 1822 (1958); (d) R. A. Benkeser and J. J. Hazdra, *J. Am. Chem. Soc.*, **81**, 228 (1959); (e) R. A. Benkeser, J. Hazdra and M. L. Burrous, *ibid.*, **81**, 5374 (1959); (f) G. Eglington and M. N. Rodger, *Chemistry & Industry*, 256 (1959); (g) W. O. Haag and H. Pines, *J. Org. Chem.*, **24**, 877 (1959); (h) W. J. Bailey and W. F. Hale, *J. Am. Chem. Soc.*, **81**, 647 (1959); (i) W. J. Bailey and W. F. Hale, *ibid.*, **81**, 651 (1959); (j) C. H. DePuy, R. W. King and D. H. Froemsdorf, *Tetrahedron*, **7**, 123 (1959); (k) E. W. Warnhoff and W. S. Johnson, *J. Am. Chem. Soc.*, **75**, 484 (1953); (l) H. C. Chitwood, U. S. Patent 2,251,983, Aug. 12, 1941; *C. A.*, **35**, 7416^g (1941); (m) for additional references see C. H. DePuy and R. W. King, ref. 5e.

(9) C. H. DePuy and R. E. Leary, *J. Am. Chem. Soc.*, **79**, 3705 (1957).

(10) (a) W. J. Bailey, F. E. Naylor and J. J. Hewitt, *J. Org. Chem.*, **22**, 1076 (1957); (b) T. D. Nevitt and G. S. Hammond, *J. Am. Chem. Soc.*, **76**, 4124 (1954); (c) J. G. Traynham and O. S. Pascual, *J. Org. Chem.*, **21**, 1362 (1956).

heterolytic bond-breaking must be very small" in the rate step.^{8j,11} In these cases the characteristics of both the carbon-oxygen and carbon-hydrogen bonds being broken were changed; the importance of changes in the individual bonds was indeterminate because the rates of pyrolysis of these esters were due to composite effects.

To clarify the relative importance on the ease of pyrolysis of esters of the three factors: olefin stability, β -hydrogen acidity and the nature of the carbon-oxygen bond, a kinetic study has been undertaken of the pyrolysis of a series of *meta* and *para* substituted 1,2-diphenylethyl acetates to the corresponding stilbenes (95% *trans*).



In this system the steric and statistical factors are held constant, and only one direction of elimination is possible. All are secondary alkyl acetates and the percentage change in molecular weight is small. In a 1,2-diarylethyl acetate, a 2-phenyl substituent has little effect upon the breaking of a carbon-oxygen bond,¹ and a 1-phenyl substituent has little effect upon the acidity of the β -hydrogen.

Comparison of pyrolysis rates of esters with 1-phenyl *versus* those with 2-phenyl substituents, where the products are identical, illustrates the importance of conjugation with the forming olefinic bond (thermodynamic stability) on the rate-controlling step of the reaction. Rate comparisons of esters with 2-phenyl substituents illustrate the effect of electronic changes around the β -carbon on the breaking of the carbon-hydrogen bond as a rate-controlling step. Rate comparisons of esters with substituents in the 1-phenyl ring illustrate the effect upon the rate-controlling reaction step of electronic changes in the breaking carbon-oxygen bond.

To make this kinetic study on the pyrolysis of high boiling 1,2-diarylethyl acetates in the gas phase, a new type of reactor was constructed that allowed rapid, easy introduction of either liquid or solid esters and permitted careful monitoring of pressure changes without the danger of condensing the reactant or products in a capillary side arm leading to a pressure-measuring device. Temperature control was accomplished with a large, well insulated aluminum thermostat. The details of this apparatus have been published elsewhere.¹²

Experimental

Ester Preparation.—The eleven 1,2-diarylethyl acetates were each prepared by several step syntheses. The methods involved have been described in the literature; therefore, the details are not given, but reference is made to footnote 1c. The physical properties of all the compounds prepared that have not been reported before and of all the esters are listed in Table II.

Method of Pyrolysis.—The apparatus used for determining the reaction kinetics has been described in detail.¹² It consists of a 185-ml. stainless steel reactor designed with a valve through which evacuation was attained and another metal to metal valve through which a small sample (100–

(11) J. L. R. Williams, K. R. Dunham and T. M. Laakso, *ibid.*, **28**, 676 (1958).

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

TABLE II
 1,2-DIARYLETHYL ACETATES AND SYNTHETIC INTERMEDIATES $\text{XC}_6\text{H}_4\text{CHCH}_2\text{C}_6\text{H}_4\text{Y}$

Ester number	X	Y	Yield, ^a %	M.p. ^b or b.p., °C. (mm.)	n_D^{20}	Carbon		Analyses, ^c %		Chlorine	
						Calcd.	Found	Hydrogen Calcd.	Found	Calcd.	Found
I	4-OCH ₃	4-Cl	73 ^d	75.5–76.0 ^d		67.00	67.05	5.62	5.61	11.63	11.66
II	4-OCH ₃	H	68.7	82.4–83.0 ^e							
III	4-CH ₃	H	73.2	44–45 ^f							
IV	H	3-Cl	56.9	143–145 (1)	1.5554	69.94	69.99	5.50	5.50	12.91	12.23
V	H	4-Cl	75.3	80.5–81.5 ^g		69.94	69.98	5.50	5.42	12.91	12.82
VI ^h	H	H	83	153.5–154 (10 ^h)	1.5480 ^h						
VII	H	4-CH ₃	75.1	155–157.5 (2.5)	1.5433	80.28	80.79	7.13	7.07		
VIII	H	4-OCH ₃	60.8	57.8–58.2 ⁱ							
IX ^j	4-Cl	H	87.2	89.2–89.8 ^k		69.94	70.18	5.50	5.60	12.91	12.86
X	4-Cl	4-OCH ₃	86.5	76–77 ^l		67.00	67.02	5.62	5.62	11.63	11.43
XI	3-Cl	H	84.6	141–143 (1)	1.5537	69.94	70.25	5.50	5.60	12.91	12.76
<i>p</i> -Chloro- α -(<i>p</i> -methoxyphenyl)-acetophenone ^m			17.2	108.5–109.0 ⁿ		69.10	69.09	5.03	5.11	13.60	13.27
1-(4-Chlorophenyl)-2-(4-methoxyphenyl)-ethanol ^o			95.4	83.5–85.0 ^p		68.60	68.45	5.76	5.81	13.50	13.26
2-(4-Chlorophenyl)-1-(4-methoxyphenyl)-ethanol ^q			80	84.0–85.5 ^r		68.60	71.59	5.76	5.37	13.50	13.70

^a Yields are expressed as percentages of recrystallized or distilled products. ^b Melting points were determined by the capillary method and are uncorrected. ^c Analyses are by A. Bernhardt, Mikroanalytisches Laboratorium im Max-Planck-Institut, Mülheim (Ruhr), Germany. ^d Upon discovery that the alcohol from which this ester was prepared was unstable, the crude alcohol was immediately acetylated and recrystallized from ethanol-ethyl acetate and then from ethanol; the yield of I from the crude alcohol was 21%. ^e R. Huisgen and C. Ruchardt, *Ann. Chem. Liebigs*, 601, 1 (1956). ^f Two recrystallizations each from petroleum ether and absolute ethanol. ^g Recrystallized twice from cyclohexane. ^h This ester was prepared by the method of Curtin and Kellom⁴ who reported b.p. 121–123° (0.8 mm.), n_D^{20} 1.5478; refractive index taken at 20°. ⁱ R. Huisgen and C. Ruchardt, footnote *e*, reported m.p. 58.5–59°. ^j Compound II and all of the ensuing alcohols were acetylated by a modification of the method of W. R. Kirner, *J. Am. Chem. Soc.*, 48, 1112 (1926). ^k Recrystallization from benzene-petroleum ether. ^l Recrystallized once from benzene-petroleum ether and twice from ethanol. ^m This ketone was prepared from the addition of *p*-chlorophenylmagnesium bromide to *p*-methoxyphenylacetonitrile followed by hydrolysis. The 2,4-dinitrophenylhydrazone was prepared, m.p. 207.5–209.5°. ⁿ Twice recrystallized from ethanol. ^o This alcohol was prepared by a sodium borohydride reduction in ethanol. ^p Twice recrystallized from benzene-petroleum ether. ^q This alcohol was prepared by treatment of *p*-chlorobenzylmagnesium chloride with anisaldehyde. The alcohol was found to be unstable and to dehydrate at room temperature, as indicated also by the analysis. ^r Twice recrystallized from ethanol.

200 μ l.) was introduced with a 5-inch needle and microsyringe. Samples were injected either as liquids or as solutions in chlorobenzene, or cyclohexane or a mixture of these solvents. These solvents were shown not to decompose or polymerize under the reaction conditions. Cyclohexane was used to dissolve those compounds which showed a tendency toward surface reactions, *i.e.*, those compounds containing 1-(4-methoxyphenyl) substituents. The addition of these solvents to the esters not containing a 1-(4-methoxyphenyl) substituent had no effect on the rate. Although the low melting esters could be studied as melts, it was more convenient to inject them as solutions. Pressure changes were measured by a null point gauge consisting of a 0.005 inch thick stainless steel diaphragm which served as one end of the reactor. The reactor, including the valves, sample injection port and diaphragm gauge were all maintained at the reaction temperature in a well insulated 135 lb. aluminum block. Pressure changes were measured to within 0.2 mm. and temperature control was within 0.2°.

For a product analysis study, the esters were pyrolyzed by sealing small amounts in an evacuated glass tube and immersing them in a molten metal bath at the desired temperature. Products were analyzed by infrared analysis for extent of pyrolysis and for identity of products from isomeric esters.

Nuclear Magnetic Resonance Analysis.—Solutions of 100 mg. of ester dissolved in 0.5 ml. of 2% tetramethylsilane in carbon tetrachloride were degassed and sealed in 5 × 150 mm. glass tubes for n.m.r. analysis. The spectra were taken on a Varian Associates 60 Mc. spectrometer.

Results

The kinetics data for the pyrolysis of the 1,2-diarylethyl acetates are shown in Table III. For each ester $\log(P_\infty - P_t)$ vs. time plots were linear to beyond 95% reaction which indicated that all the

reactions followed first-order kinetics. A typical plot for the pyrolysis of ester V at two different initial pressures is shown in Fig. 1.¹³ Rates could

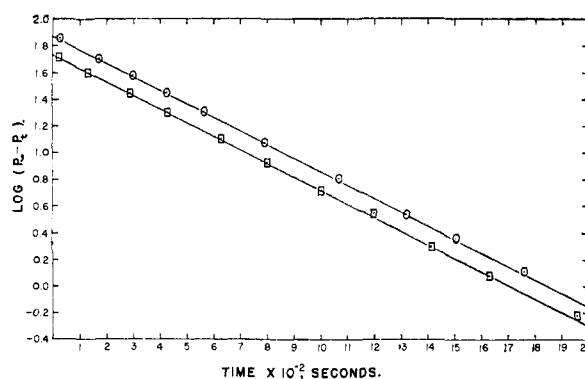


Fig. 1.—Pyrolysis of ester V at 322.6° at two different initial pressures.

be duplicated to within $\pm 2\%$; the errors resulting from calculating the energy and entropy of activation from data obtained over a 50° range are, therefore, ± 0.6 kcal. and ± 1.0 e.u., respectively.

(13) Studies have indicated that the partial pressure of acetic acid would not be reduced significantly because of acid dimerization in the vapor state under the experimental conditions (D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 1715 (1953); H. L. Ritter and J. H. Simons, *J. Am. Chem. Soc.*, 67, 757 (1945); F. H. MacDougall, *ibid.*, 58, 2585 (1936)).

TABLE III
 PYROLYSIS RATES OF 1,2-DIARYLETHYL ACETATES^a

Ester no.	X	Y	Temp., °C.	10 ³ k, sec. ⁻¹
I	4-MeO	4-Cl	343.5	15.1
			330.5	6.83
			313.2	2.63
			293.8	0.794
II	4-MeO	H	344.4	15.0
			330.2	6.36
			315.7	2.94
			296.7	0.993
III	4-Me	H	344.4	7.70
			330.4	3.48
			315.6	1.46
IV	H	3-Cl	297.7	0.464
			362.4	15.2
			342.7	4.85
			331.9	2.63
V	H	4-Cl	314.6	0.904
			365.0	16.4(5)
			344.7	5.37
			333.9	2.81
VI	H	H	314.6	0.867
			362.4	14.5
			342.7	4.67
			331.9	2.45
VII	H	4-Me	314.6	0.854
			365.0	15.6
			345.0	4.98
			333.9	2.70
VIII	H	4-MeO	315.2	0.866
			365.0	13.3(5)
			345.0	4.68
			333.9	2.45
IX	4-Cl	H	315.0	0.801
			365.0	12.5
			345.9	4.56
			333.9	2.35
X	4-Cl	4-MeO	314.9	0.770
			362.7	10.3
			343.5	3.68
			331.9	1.76
XI	3-Cl	H	315.4	0.671
			365.0	9.20
			346.0	3.38
			334.2	1.56(5)
			315.6	0.532

^a Esters IV, VI, VII and XI were introduced into the reactor as liquids. Esters III, V, VIII, IX and X were introduced as solution in chlorobenzene. Esters I and II were injected as solutions in cyclohexene or cyclohexene-chlorobenzene to inhibit a heterogeneous reaction.

Esters I and II [both containing a 1-(4-methoxy) group] were markedly more sensitive to reaction conditions and until cyclohexene was used as an inhibitor it appeared that the 4-methoxy substituent in the 1-aryl ring caused a different type of a reaction to occur. However, after long seasoning of the stainless steel reactor (following two or three hundred reactions) and by using cyclohexene as an inhibitor reproducible results were obtained. (Toluene was first used; however, toluene was found to decompose under the reaction conditions.¹⁴) Al-

(14) Toluene under the experimental conditions decomposed to a significant amount during the hour or two needed to carry out some of the runs. Therefore, it was not considered satisfactory as a solvent.

though the 1-(4-methoxy)-phenyl esters were still the most reactive esters, their rates were of the order expected. Furthermore, the rates could be easily duplicated from day to day which had previously not been possible. The cause of the erratic results was not fully determined, but most likely was due to a heterogeneous reaction on the reactor surface. For example, esters I and II were completely pyrolyzed when heated for as little as 10 minutes at 245° and 0.75 minute at 355° in an unseasoned sealed glass tube, whereas 2-(4-methoxyphenyl)-1-phenylethyl acetate (VIII), the isomer of II, did not decompose by a detectable amount when heated for 58 minutes at 245° and was not completely decomposed when heated for 10 minutes at 340°. The same olefin products were obtained from the pyrolysis of isomers II and VIII.

To establish that olefin and acetic acid were the only products of the reaction under study, all of the 1,2-diarylethyl acetates were pyrolyzed in evacuated sealed glass tubes immersed in a molten metal-bath at 350–355° for 1 hour. The low boiling fraction was removed by distillation and was shown to be acetic acid. Infrared spectra taken of the residue indicated: complete decomposition of the ester, formation of the expected *trans*-stilbene¹⁵ and complete removal of the acetic acid by distillation.

At sufficiently high temperatures alkyl aryl ethers are known to cleave to phenols and alkenes.¹⁶ In order to find whether ether cleavage was a complicating side reaction of importance in the methoxy substituted esters, anisole, 4-methoxystilbene and 4-chloro-4'-methoxystilbene were injected into the apparatus used for the kinetic experiments at the experimental temperature. There was no significant pressure increase during the time of a typical ester half-life. To further establish the lack of ether cleavage, the products from the sealed tube pyrolysis of ester II were washed with sodium carbonate solution to remove the acetic acid and any phenol that may have formed. The infrared spectrum of the washed product was identical to that of the residue after removal of only the low-boiling fraction (acetic acid) by distillation; the probability of ether cleavage being a complicating reaction was thereby eliminated.

Figures 2 and 3 are Arrhenius diagrams of the data; from them, energies and entropies of activation and relative reaction rates at 600°K. were calculated; Table IV.

The chemical shift values, δ , from the nuclear magnetic resonance spectra of esters II, IV, VI, VIII and XI for the methylene hydrogens, are shown in Table IV. The frequency of the single bond carbon-oxygen stretch, as measured by the infrared spectra of the esters, were all the same (1235 cm.⁻¹) within experimental error and are not tabulated.

At higher temperatures in a flow system when the contact time is only a fraction of a second toluene is reported to decompose; M. Takahaki, *Bull. Chem. Soc. Japan*, **33**, 801, 808 (1960); G. M. Badger and T. M. Spotswood, *J. Chem. Soc.*, 4420 (1960).

(15) Curtin and Kellom⁴ pyrolyzed deuterated 1,2-diphenylethyl acetate and determined the yields to be 95% *trans*- and 5% *cis*-stilbene.

(16) C. D. Hurd, "The Pyrolysis of Organic Compounds," The Chemical Catalog Co., Inc. (Reinhold Publ. Corp.), New York, N. Y., 1929, p. 201.

TABLE IV
KINETIC DATA FROM PYROLYSIS OF 1,2-DIARYLETHYL ACETATES^a

Ester no.	X	Y	E_a , kcal./mole	log A	ΔS^\ddagger , e.u., 600°K.	Relative rates at 600°K.	TMS ^b δ_{int} , p.p.m. -CH ₂ -
I	4-MeO	4-Cl	40.6	12.56	-2.45	3.20	
II	4-MeO	H	40.6	12.54	-2.54	3.02	-3.01
III	4-Me	H	41.7(5)	12.67	-1.95(5)	1.57	
IV	H	3-Cl	43.3	13.07(5)	-0.105	1.06	-3.06
V	H	4-Cl	43.3	13.06	-.169	1.02(5)	
VI	H	H	43.3	13.05	-.215	1.00	-3.03
VII	H	4-Me	43.0	12.94(5)	-.695	0.955	
VIII	H	4-MeO	42.1(5)	12.58	-2.36	.881	-2.97
IX	4-Cl	H	42.1(5)	12.56(5)	-2.43	.851	
X	4-Cl	4-MeO	43.2	12.87	-1.04	.724	
XI	3-Cl	H	43.8	12.96	-0.627	.582	-2.99

^a Rate data calculated for the temperature listed from the data in Table III. ^b Chemical shift from n.m.r. ($H_s - H_r$)/ $H_r \times 10^6$, spectra using tetramethylsilane as an internal standard.

Discussion

A study of the reaction rates and energies and entropies of activation of the 1,2-diarylethyl acetates will evaluate the importance of the β -hydrogen acidity, carbon-to-carbon double bond formation

not eliminate the possible effect of olefin stability on the transition state. This is true. However, if olefin stability were important the opposite order of reactivity would result, unless, of course, the two factors are operating in an almost equal and opposite direction.

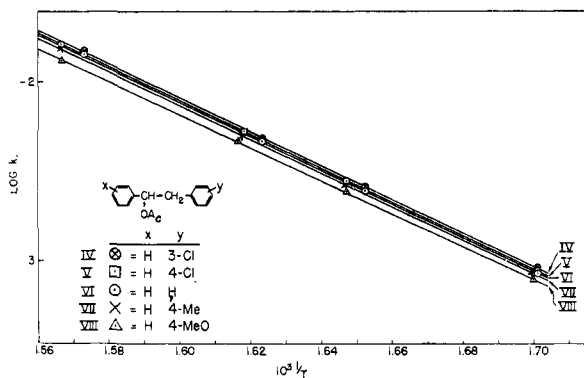


Fig. 2.—Arrhenius diagrams for esters IV–VIII.

and carbon-oxygen single bond character on the stability of esters. The steric, statistical, direction of elimination and molecular factors are fixed and, therefore, constant in these ester pyrolyses. It is convenient to discuss separately the stability of esters with regard to these three facets: β -hydrogen acidity, olefinic stability and carbon-oxygen bond character.

β -Hydrogen Acidity.—The acidity of the β -hydrogen and the importance of the cleavage of the carbon-hydrogen bond can be evaluated by comparing the rates of the 2-phenyl substituted esters, IV, V, VI, VII, VIII and X, Table IV, Figs. 2 and 4. In these esters the strength of the carbon-oxygen bond remains essentially constant. Substituents that increase the acidity of the β -hydrogens, such as *m*-chloro (IV), cause a very minor increase in the rate, and those that decrease the β -hydrogen acidity, such as *p*-methoxy (VIII), cause a slight decrease in the rate. The direction is as predicted from the acidity of the β -hydrogen; however, the change in rate is very minor. A Hammett plot of $\log(k/k_0)$ vs. σ , Fig. 4 (reaction constant, $\rho = 0.08$), clearly indicates almost a negligible effect upon the rate by β -substituents of the type studied. One might argue that this system does

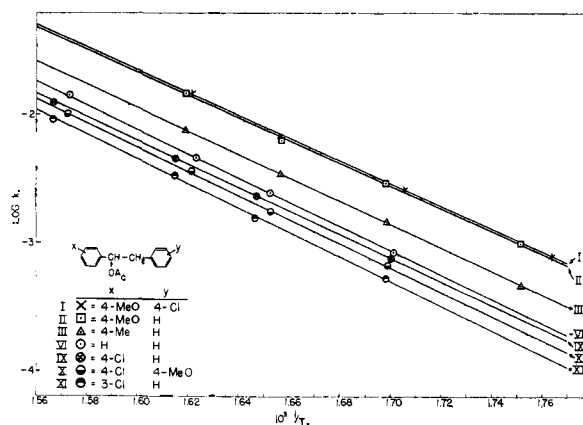


Fig. 3.—Arrhenius diagrams for esters I–III, VI, IX–XI.

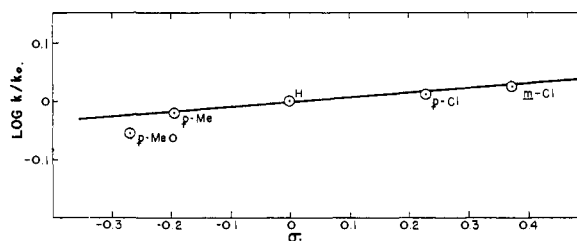


Fig. 4.—Hammett σ - ρ plot of 1-phenyl-2-arylethyl acetates (esters IV–VIII) at 600°K.

The kinetic isotope effect study^{4,8j} indicates that the carbon-hydrogen bond is broken in the rate-determining step. From this one would expect to find a measurable effect upon the reaction rate by a 2-phenyl substituent. From the nuclear magnetic resonance spectra of the esters used in this study it is evident that the 2-phenyl substituents cause only small decreases in shielding of the methylene protons (see δ -values in Table IV). As this is a measure of acidity, this particular study does not adequately demonstrate the effect of strongly acidic β -hydrogens on the rate.

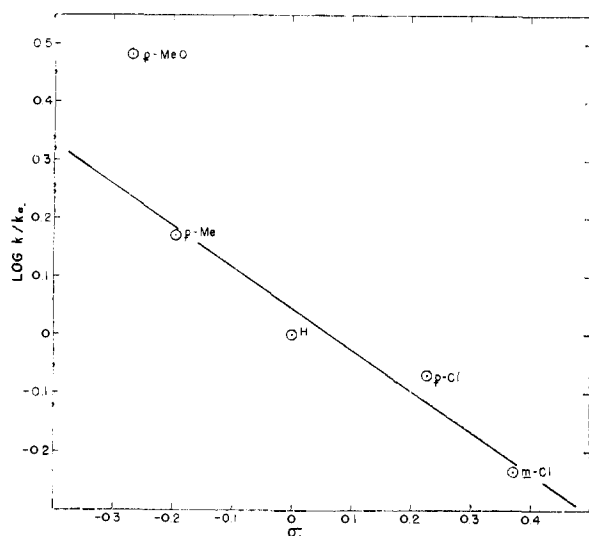


Fig. 5.—Hammett σ - ρ plot of 1-aryl-2-phenylethyl acetates (esters I-III, VI, IX-XI) at 600°K.

There is evidence that strongly activating groups do influence the rate more significantly. It is reported by Maccoll^{17a} that a β -carbonyl increased the rate 100-fold, an effect that must be attributed to the β -hydrogen acidity rather than to increased olefin stability; see below. The effect of a β -carbonyl has been demonstrated by the pyrolysis of methyl *trans*-2-acetoxycyclohexanecarboxylate in which the product was almost exclusively methyl 1-cyclohexenecarboxylate^{17b}; the increased specificity in direction of elimination can best be attributed to the influence of the carboxy group on the acidity of the β -hydrogen. Furthermore, 1-phenyl-2-propyl acetate yields 75% 1-phenylpropene, and 1,1-diphenyl-2-propyl acetate produces 1,1-diphenylpropene exclusively.¹⁸ Although olefin stability may serve to explain the former result, steric requirements preclude the coplanarity of both phenyl groups with the forming double bond in the transition state, a condition necessary if olefin stability were important. Again, the increased specificity in the direction of elimination is best explained by the increased β -hydrogen acidity caused here by the phenyl inductive effect. However, as this work shows, stability of the ester is not markedly changed by changes in the acidity of the β -hydrogens.

Olefin Stability.—To evaluate the importance of conjugation with the forming carbon-carbon double bond, esters VI, IV and XI, III and VII, and II and VIII are compared; Table IV. In this comparison isomeric ester pairs yield the same olefin; however, the rates are significantly different. The effect is greatest with the methoxy substituted esters II and VIII. As shown by this comparison, it is doubtful that olefin stability is of any appreciable significance in controlling the reaction rate though it may determine the direction of elimination where other directing factors are not present.⁹

(17) (a) A. Maccoll, in "Theoretical Organic Chemistry," papers presented to the Kekulé Symposium, London, 1958, Butterworth's Scientific Publications, London, 1959, p. 230. (b) W. J. Bailey and R. A. Baylouny, *J. Am. Chem. Soc.*, **81**, 2126 (1959).

(18) W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

Carbon-Oxygen Single Bond Character.—From a comparison of esters I, II, III, VI, IX and XI, Table IV, Figs. 3 and 5, the effect of a 1-phenyl substituent can be evaluated. Because olefin stability does not appear to be significant and the electron density around the β -hydrogens of these esters is nearly constant (as indicated by n.m.r. δ -values), any change in the rate must logically be attributed to the effect of the 1-phenyl substituents on the carbon-oxygen cleavage and in turn on the rate of pyrolysis. A substituent change from electronegative (3-Cl) to electropositive (4-MeO) increases the rate and is consistent with the postulate of carbon-oxygen bond cleavage being important in the rate-controlling step. This is graphically illustrated by a Hammett plot, Fig. 5. The deviations from the Hammett equation are discussed in a subsequent paper dealing with the effect of substituents on the pyrolysis of α - and β -arylethyl acetates. By ignoring the 4-MeO group the ρ factor is -0.71 , which demonstrates the importance of carbon-oxygen single bond character on stability. The negative ρ -value demonstrates that the reaction rate is sensitive to marked changes in electron availability at the reaction site to facilitate carbon-oxygen single bond breaking. Whether the electron-releasing substituents in the 1-phenyl ring decreased the transition state energy level or raises the ground state energy of the reacting ester (over the unsubstituted ester) is, of course, not known, but there is no question that the energy of activation is the least with those esters with the most electron releasing substituent. The differences in the ΔS^* are not outside experimental error and are not thought to be significant.

One might argue that a ρ -value of -0.71 is not particularly significant in contrast to ρ -values found in solution for electrophilic reactions. When the reaction site is not directly attached to the ring ρ -values of 2-3 are common and even greater than 10 when ring reactions are considered. One could not expect a polar transition state in the gas phase of the same magnitude as found in solution. Although the ρ -value is small (-0.71) in the pyrolysis of 1-aryl-2-phenylethyl acetates, it is significant in demonstrating that substituents in the 1-aryl ring have greater influence on the reaction rate than the same substituents do in the 2-aryl ring where the ρ -value is only $+0.08$ even when the 4-methoxy substituent is present. A 4-methoxy substituent in the 2-aryl ring by the argument of DePuy and Leary⁹ should cause stabilization through π -overlap with the forming double bond and in so doing increase the ease of pyrolysis. The aryl substituents would seem to act, therefore, not by stabilizing the forming double bond but more logically by effecting the carbon-oxygen bond.

The data reported by DePuy, King and Froemsdorf^{8j} (relative rates of pyrolysis: 5-nonyl acetate > α -phenylethyl acetate > β -phenylethyl acetate > 2-acetoxycyclohexanone) given as support of their hypothesis for a *small* amount of carbon-oxygen bond breaking as rate determining, is, in fact, good evidence for this. As illustrated in Table IV, electron release in the aryl ring increases

the rate of pyrolysis demonstrating that the character of the C-O bond affects stability. Hence the work of DePuy, *et al.*, can be explained logically in this manner. With α -phenylethyl acetate^{8j} the phenyl group withdraws electrons causing the ester to react slower than 5-nonyl acetate; 2-acetoxycyclohexanone reacts the slowest of these three secondary acetates, which is expected on the basis of strong electron withdrawing of the carbonyl group from the reaction site.

Furthermore, DePuy and Leary⁹ reported that 1-(4-methoxyphenyl)-3-phenyl-1-propyl acetate pyrolyzes three times more rapidly than 3-(4-methoxyphenyl)-1-phenyl-1-propyl acetate under identical conditions. The present work supports this relative reactivity (see ester II, Table IV). They submitted these data as support for the hypothesis that olefin stability is of major importance in the stability of esters. These data could equally well be explained by the influence of a 1-(4-methoxyphenyl) on the breaking C-O bond and in view of the present study we believe these data are better explained in this way.

The kinetic effect of β -hydrogen acidity and the rates reported in Table IV appear to be at variance with the pyrolysis of 1-(4-methoxyphenyl)-3-phenyl-2-propyl acetate and 1-(4-chlorophenyl)-3-(4-methoxyphenyl)-2-propyl acetate.⁹ In these pyrolyses the major olefinic product was the isomer in which the double bond was conjugated with the methoxyphenyl group; this isomer has been shown to be the more stable of the two. These results are not those that would be predicted based on the acidity of the β -hydrogen and should be reinvestigated. Perhaps the method of analysis was not fully reliable. In the pyrolysis of the sterically similar 1-methoxy-2-propyl acetate and 2-butyl acetate the former yielded more of the internal olefin than did the latter^{8j}; this was attributed to greater olefin stability. DePuy, *et al.*,^{8j} state the methoxy group stabilizes the transition state leading to the formation of the olefin in the same manner as it stabilizes the vinyl ether being formed. It may be that the small shift in product ratio was caused by the inductive effect rather than the resonance effect of the methoxy group dominating in the transition state. In view of the present study this explanation appears to be more logical.

Maccoll¹⁹ concluded that the pyrolysis of esters

(19) A. Maccoll, *J. Chem. Soc.*, 3398 (1958).

can best be considered as a nucleophilic attack of the acyl-oxygen atom on the β -hydrogen atom, *i.e.*, the forming O-H bond primarily determines the rate and not the breaking alkyl-oxygen bond; and, furthermore, the mechanism for the pyrolysis of esters is in marked contrast with that postulated for halides, where the dominating factor is the *breaking* C-X bond. With a knowledge of the data in Table IV and Fig. 5 it is evidence that the character (and hence the breaking) of the carbon-oxygen bond principally determines the stability of the ester. The doubtful influence of a nucleophilic attack on stability has been clearly shown by a study of the relative rates of pyrolysis on twenty six substituted ethyl benzoates.²⁰ Those substituents that reduced the electron density at the carboxyl position increased the rate and those that increased the electron density decreased the rate.

The mechanism of the pyrolysis of esters can now be discussed in light of these points: the reaction is stereospecific in the *cis* sense, unimolecular, homogeneous, shows a deuterium isotope effect and generally has a negative entropy of activation. Its rate is influenced by electron release to the carbon-oxygen single bond and by strong electron withdrawal from the β -hydrogen. The character of the bonds being *broken*, particularly the carbon-oxygen bond (and not those being formed), are principally responsible for the stability of the esters. Olefin stability is of little importance in determining the stability of the esters in contrast to the character of the C-O bond but apparently explains the slight changes in olefin distribution that are not accounted for by the statistical factor. Esters with substituents which markedly release electrons to the carbon-oxygen single bond, *e.g.*, 1-(4-methoxyphenyl), are very sensitive to surface reactions and can only be properly studied in the presence of a suitable inhibitor and in a very well seasoned reactor. Under properly controlled conditions the pyrolysis of carboxylic esters proceeds *via* a highly concerted mechanism with simultaneous carbon-oxygen and carbon-hydrogen bond breaking in the transition state.

Acknowledgments.—The authors wish to thank Dr. Kenneth Wiberg for taking the nuclear magnetic resonance spectra, and the Air Force Office of Scientific Research and the Dow Chemical Co. for financial support.

(20) G. G. Smith and D. F. Brown, unpublished work.