ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM FULMER LABORATORY, DEPARTMENT OF CHEMISTRY, THE STATE COLLEGE OF WASHINGTON]

The Effect of Molecular Size and Structure on the Pyrolysis of Esters[1,2]

BY GRANT GILL SMITH AND WILLIAM H. WETZEL

RECEIVED AUGUST 27, 1956

The effect of molecular size on the ease of the pyrolysis of esters has been studied by pyrolyzing cyclohexyl formate and its homologs. Higher molecular weight esters decomposed at a lower temperature than the lower molecular weight homologs. The decrease, however, in the temperature of pyrolysis as the size of the esters increases in molecular size by one methylene group is not a regular decrease; rather, it decreases in a zig-zag fashion. Substituted cyclohexyl benzoates, with electronegative groups in the *meta* and *para* positions, pyrolyze more readily than do cyclohexyl benzoate or esters of aliphatic acids. The temperature of pyrolysis is directly related to the strength of the acid from which the ester is prepared and to the O–C stretching band in the infrared spectra of esters. *o*-Substituted esters tend to stabilize the esters toward heat.

The pyrolysis of esters was first observed in 1854[3] as a method for the preparation of olefins. In contrast to the dehydration of alcohols,[4–8] it has afforded a method of preparing pure olefins without carbon skeleton isomerization[9–11] and with little or no double bond shift.[8,12–15] Others have investigated the effects of changes in the structure of the alkyl portion in the pyrolysis of esters. Esters lacking β-hydrogens in the alkyl portion of the ester are quite stable and pyrolyze to a variety of products, presumably through free radical reactions.[16,17] Esters with β-hydrogens pyrolyze at lower temperatures than those without β-hydrogens producing only olefins and acids in essentially quantitative yields. Those from tertiary alcohols pyrolyze at lower temperatures than esters of isomeric primary and secondary alcohols.[16,18] β-Hydrogens in *cis*-positions are reported to be eliminated more easily than are *trans*-β-hydrogens.[19,20] Bailey and Hammond have found that this pyrolysis proceeds according to the Hofmann rule with primary β-hydrogens being selectively removed in competition with secondary and tertiary hydrogens.[21,22] Bailey has studied extensively the usefulness of ester pyrolysis in the synthesis of olefins which are difficult to obtain, for example, hydrocarbons with endocyclic double bonds,[23a] and of acids.[23b]

In general, higher molecular weight compounds undergo thermal decomposition more easily than their molecular weight homologs.[24] Although stearates and palmitates are reported to undergo pyrolysis at lower temperatures than acetates,[25] no comprehensive investigation has been reported in which each member of a homologous series had been studied relating the temperature of pyrolysis to chain length of the acyl portion; just recently the effects of *p*-substituents in the pyrolysis of benzoates was reported.[26]

A study has been made of the comparative temperatures of pyrolysis of cyclohexyl formate and of its homologs through cyclohexyl decanoate and of cyclohexyl octadecanoate. In order to relate pyrolysis to acid strengths (as measured by ionization constants of the acids corresponding to the acyl group of the esters) and to study the effects of proximity groups, the pyrolysis of *o*-, *m*- and *p*-substituted cyclohexyl benzoates are included. Pyrolysis temperatures are correlated to the O–C stretching band in the infrared spectra of esters.

Experimental

Synthesis of Esters.—Cyclohexyl esters of formic, acetic, propionic and butyric acids were prepared according to a method described by Senderens and Aboulenc.[27] Cyclohexyl octadecanoate was prepared from stearic acid after the method of Krafft.[25] A method described by Kirner[28] was used for the synthesis of all other esters. With a few exceptions, in which the esters were solids, the esters were purified by refractionation through a 13-cm. column of glass helix rings.[29] Physical constants and yields with their characteristic temperatures of pyrolysis are listed in Table I.

Pyrolysis.—The ester (3–13 g.) was introduced into the top of a vertical Pyrex tube (2 × 30 cm.), which was packed with short Pyrex rods, under an atmosphere of nitrogen.

---

[1] Presented before the Division of Organic Chemistry, 128th Meeting of the American Chemical Society, Minneapolis, Minn., Sept. 12, 1955.

[2] Abstracted from a thesis presented to the Graduate School of the State College of Washington by William H. Wetzel in partial fulfillment of the requirements for the degree of Master of Science, July, 1956. Supported in part by a grant from the State College of Washington Research Fund.

[3] W. Heintz, *Pogg. Ann.*, **93**, 519 (1854).

[4] W. G. Young and J. J. Lucas, THIS JOURNAL, **52**, 1964 (1930).

[5] H. I. Waterman and Th. W. te Nuyl, *Rec. trav. chim.*, **51**, 533 (1932).

[6] F. C. Whitmore and J. M. Herndon, THIS JOURNAL, **55**, 3428 (1933).

[7] F. C. Whitmore, *ibid.*, **54**, 3274 (1932).

[8] L. I. Smith and G. F. Rouault, *ibid.*, **65**, 745 (1943).

[9] P. L. Cramer and M. J. Mulligan, *ibid.*, **58**, 373 (1936).

[10] J. P. Wibaut, A. J. van Pelt, Jr., A. Dias Santilhano and W. Beuskens, *Rec. trav. chim.*, **61**, 265 (1942).

[11] C. E. Rudy, Jr., and P. Fugassi, *J. Phys. Colloid Chem.*, **52**, 357 (1948).

[12] A. J. van Pelt, Jr., and J. P. Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

[13] R. Paul and S. Tchelitchoff, *Compt. rend.*, **233**, 1116 (1951).

[14] H. Gudgeon, R. Hill and E. Issacs, *J. Chem. Soc.*, 1926 (1951).

[15] W. J. Bailey and J. Rosenberg, THIS JOURNAL, **77**, 73 (1955).

[16] C. D. Hurd and F. H. Blunck, *ibid.*, **60**, 2419 (1938).

[17] E. M. Bilger and H. Hibbert, *ibid.*, **58**, 823 (1936).

[18] J. P. W. Houtman, J. van Steenis and P. M. Heartjes, *Rec. trav. chim.*, **65**, 781 (1946).

[19] R. T. Arnold, G. G. Smith and R. M. Dodson, *J. Org. Chem.*, **15**, 1256 (1950).

[20] E. R. Alexander and A. Mudrak, THIS JOURNAL, **73**, 59 (1951).

[21] W. J. Bailey and C. King, *ibid.*, **77**, 75 (1955).

[22] T. D. Nevitt and G. S. Hammond, *ibid.*, **76**, 4124 (1954).

[23] (a) W. J. Bailey and R. L. Hudson, *ibid.*, **78**, 2806 (1956); (b) W. J. Bailey and W. N. Turck, *J. Am. Oil Chem. Soc.*, **33**, 317 (1956).

[24] I. V. Obreimov, *Zhur. Eksptl. Teoret. Fiz.*, **19**, 396 (1949) [*C. A.*, **46**, 9906 (1952)].

[25] F. Krafft, *Ber.*, **16**, 3018 (1883).

[26] W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

[27] J. B. Senderens and Z. Aboulenc, *Compt. rend.*, **155**, 168, 1013 and 1014 (1912).

[28] W. R. Kirner, THIS JOURNAL, **48**, 1112 (1926).

[29] For more details on the syntheses of the esters, starting acids and acid chlorides, reference is made to footnote 2.

TABLE I

PHYSICAL CONSTANTS OF ALIPHATIC AND AROMATIC CYCLOHEXYL ESTERS AND THEIR CHARACTERISTIC TEMPERATURES OF PYROLYSIS

Ester	Yield of ester, %	B.p.		n^{25}D	D$^{25}_{4}$	Formula	Analyses, %[a]				Characteristic temp., °C.	Yield of acid, %
		°C.	Mm.				Carbon		Hydrogen			
							Calcd.	Found	Calcd.	Found		
Formate[b]	60[c]	154–155[d]	701	1.4430		$C_7H_{10}O_2$					490	(97.0)[e]
Acetate	50[f]	168–169[g]	701	1.4405[g]		$C_8H_{12}O_2$					496	95.6
Propanoate	50[h]	72–73	10	1.4413	0.9698[i]	$C_9H_{14}O_2$					485	96.1
Butanoate	47[j]	202–203	700	1.4423[k]		$C_{10}H_{16}O_2$					490	97.6
Pentanoate	84	93	6	1.4439	0.9273	$C_{11}H_{18}O_2$	71.70	71.83	10.94	10.96	479	96.3
3-Methyl butanoate	65	215–216[l]	693	1.4418		$C_{11}H_{18}O_2$					471	95.2
Hexanoate	80	104–105	12	1.4460	0.9207	$C_{12}H_{22}O_2$	72.67	72.77	11.18	11.26	484	99.6
Heptanoate	81	117–118	6	1.4470	.9146	$C_{13}H_{24}O_2$	73.54	73.64	11.40	11.62	473	97.6
Octanoate	80	131–132	6	1.4490	.9089	$C_{14}H_{26}O_2$	74.33	74.43	11.58	11.64	478	98.2
Nonanoate	80	131–132	1	1.4482	.9091	$C_{15}H_{28}O_2$	74.94	74.84	11.74	11.80	471	(97.0)[e]
Decanoate	54	130–131	1	1.4479	.9032	$C_{16}H_{30}O_2$	75.52	75.78	11.89	11.91	478	(97.2)[e]
Octadecanoate[m]	76	.....	..	....	....	$C_{24}H_{46}O_2$	78.62	78.62	12.64	12.60	466	91.2
Benzoate	87	132[n]	1	1.5217[o]	1.0538	$C_{13}H_{16}O_2$					465	98.2
o-Fluorobenzoate	64	132–133	7	1.5083	1.1349	$C_{13}H_{15}O_2F$	70.25	69.97	6.80	6.66	450	92.0
o-Chlorobenzoate	89	159	6	1.5340[p]	1.1890[q]	$C_{13}H_{15}O_2Cl$	65.40	65.56	6.33	6.46	457	99.5
m-Chlorobenzoate	80	156–157	6	1.5309	1.1516	$C_{13}H_{15}O_2Cl$	65.40	65.56	6.33	6.46	444	94.0
p-Chlorobenzoate	90	153–154[r]	5		1.1395[s]	$C_{13}H_{15}O_2Cl$	65.40	65.18	6.33	6.58	448	95.0
o-Bromobenzoate	54	105–106	7	1.5486	1.3530	$C_{13}H_{15}O_2Br$	55.14	55.21	5.34	5.36	450	100.0
2,6-Dichloro-benzoate[t]	66					$C_{13}H_{14}O_2Cl_2$	57.16	57.17	5.12	5.29	433	86.2
o-Toluate	41	158	3	1.5230[u]	1.0436[u]	$C_{14}H_{18}O_2$	77.03	77.26	8.31	8.15	460	98.0
p-Toluate	76	158–159	12	1.5212[v]	1.0358[v]	$C_{14}H_{18}O_2$	77.03	76.95	8.31	8.23	464	98.7

[a] Elementary analyses were made by Galbraith Analytical Laboratories, Knoxville, Tenn. [b] Saponification equiv.: calcd. for $C_7H_{12}O_2$, 128.17; found, 128.7. [c] Senderens and Aboulenc reported quantitative yield.[27] [d] Senderens and Aboulenc reported b.p. 162.5° (750–753 mm.).[27] [e] The characteristic temperatures of these esters were based on the yields of olefin; all others were based on the yields of acids. [f] Simons and Meunier reported 90% yield (J. H. Simons and A. C. Meunier, THIS JOURNAL, **63**, 1921 (1941)). [g] Simons and Meunier reported b.p. 173.5° (735 mm.), $n^{19.6}$D 1.4405 (ref. *f*). [h] Senderens and Aboulenc reported 90% yield.[27] [i] Specific gravity in this case was determined at 0° with reference to water at 4°. Senderens and Aboulenc reported d^4_0 0.9718, b.p. 193° (750–753 mm.).[27] [j] Senderens and Aboulenc reported 90% yield.[27] [k] Simons and Meunier reported b.p. 207° (735 mm.), n^{22}D 1.4423 (ref. *f*). [l] Senderens and Aboulenc reported b.p. 223° (750–753 mm.), n^{18}D 1.444.[27] [m] Solid, m.p. 43°. [n] Sabatier and Mailhe reported b.p. 285°, no pressure was reported (P. Sabatier and A. Mailhe, *Compt. rend.*, **152**, 360 (1911)). [o] At 20.7°. [p] At 21°. [q] At 0°. [r] Solid, m.p. 36–37°. [s] At 41°. [t] Solid, m.p. 78.5–79.5°. [u] At 20°. [v] At 22.5°.

The tube was heated with a Hoskins electric furnace (Type FD 303). The temperature of the tube was controlled and recorded with a two point Brown electronic recorder-controller. Two iron–constantan thermocouples, encased in a glass tube, were centered one-fourth and one-half way down from the top in the tube. Introduction of esters caused the temperature in the top portion of the tube to drop; however, the temperature in the middle part of the tube was maintained nearly constant (±2°) during each experiment. The rate of addition of an ester was 0.38 g. per minute, and the ester remained in the tube seven seconds.[30] Oil-pumped nitrogen was introduced into the top of the Pyrex tube at the rate of 46 bubbles (11.1 ml.) per minute. Care was exercised that identical conditions were maintained, except for a change in the temperature, during each pyrolysis. Each ester was pyrolyzed at six to eight different temperatures ranging from 380 to 520°. Carbon formed very slowly in the tube and was removed periodically by heating the system to 520° in the presence of air. The acid, olefin and unreacted ester were condensed in an ice-cooled receiver located directly below the pyrolysis zone. This receiver was also attached to a Dry Ice trap. No appreciable amounts of volatile organic materials were collected. An Ascarite tube, attached in series, absorbed the liberated carbon dioxide.

Analytical Determinations.—The extent of pyrolysis was determined by quantitatively analyzing the acid or olefin obtained in the receivers. The pyrolysate was diluted with carbon tetrachloride or ethanol in a 250-ml. volumetric flask. To determine amounts of acids, aliquots were titrated with standard alkali using phenolphthalein as indicator; the amount of cyclohexane was determined from the same volumetric solution using an indirect bromination procedure described by Siggia.[31] This method was found to be very sensitive to concentration; therefore, it had to be followed with care in order to obtain reproducible results. To test these methods, a mixture of known quantities of cyclohexene and propanoic acid was prepared and subjected to analysis; the bromination method resulted in an error of ±1%, and the acid titration gave a ±0.5% error.

Discussion of the Experimental Results

From the initial analytical results by which the extent of pyrolysis at any given temperature was determined, attempts were made to find a method for comparing the effects of size and structure of the acyl portions of esters on the temperature of pyrolysis. Since the alkoxide part of the ester was constant throughout this study, only the influences of the acyl groups could affect the results. Little correlation was obtained by attempting to relate the sizes and structures of esters to the temperatures of pyrolysis where maximum yields were produced. It did prove successful to relate the size and structure of an ester to a "characteristic temperature." This is defined as the temperature at which a maximum is obtained from a plot of per-

---

[30] Since esters were introduced on a gram basis, tests were made to determine if operation on a mole basis would alter the results. Little, if any, difference was observed in the yield obtained when the temperature was maintained constant; however, it was more difficult to control the temperature when operationg on a mole basis.

[31] S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 33.

centage yield divided by the pyrolysis temperature *vs.* the pyrolysis temperature. In effect, the characteristic temperature is that temperature at which the most efficient pyrolysis takes place when the rate of flow is constant. The effect of attempting to increase the yield by increasing the temperature above the characteristic temperature is negligibly small. The characteristic temperature is a measure of the ease of the pyrolysis of esters. The significance of relating ease of pyrolysis to this characteristic temperature is demonstrated in subsequent discussions. In Table I the characteristic temperatures of pyrolysis of the 21 esters studied are listed. The total yields of acid and olefin (in those experiments where both could be determined accurately) were 95–100% at the characteristic temperature except in a few instances. In most cases the amount of acid or the amount of olefin could be used to determine the extent of pyrolysis. In the cases of the substituted benzoates, the characteristic temperatures were determined from the results of titrations of the acids; attempts to determine characteristic temperatures from yields of the olefin led to useless results, probably because of ring bromination during the titration step.

As was expected, higher characteristic temperatures were obtained for the lower molecular weight esters than for the higher molecular weight ones. The characteristic temperature for cyclohexyl acetate was 496°; that for cyclohexyl octadecanoate was 466°. The decrease in the characteristic temperatures as the esters increase in molecular size by one methylene group is not a regular decrease; rather, it decreases in a zig-zag fashion as shown in Table I. Those esters with an even number of carbon atoms in the acyl group appear to be more stable than those with an odd number of carbons in that portion of the molecule. This is analogous to the relationships among the melting points of the related acids. Such is perhaps only fortuitous, for in the pyrolysis of esters chemical bonds are broken and formed, whereas in the melting of the acids intermolecular crystalline forces are destroyed.

However, a similar zig-zag plot is obtained when the number of carbon atoms in the acyl portion of the ester is plotted as a function of the wave number for the O–C stretch of the esters. Those esters most stable to heat proved also to have the highest wave number. This, of course, is as would be expected since the wave number is related to the stability of the bond.

To investigate the effect of structure on the temperature of the pyrolysis of esters, eight aromatic esters were pyrolyzed under conditions identical except for temperatures. By using esters with approximately the same molecular weight, the effect of a change in molecular weight was eliminated. With the exception of two esters, cyclohexyl *o*-bromobenzoate and cyclohexyl 2,6-dichlorobenzoate, the molecular weight range was ±7%. It was noted that the characteristic temperature was directly proportional to the strengths of the *m*- and *p*-substituted acids to which the esters were related. This linear relationship is illustrated in Fig. 1. It is possible that the same forces which induce breaking of the O–H bond in strong acids may be responsible for the facile cleavage of the O–R bond in esters during pyrolysis, and if such is the case, it explains—at least in part—the observed ease of pyrolysis with esters of strong acids. Since, however, the ionization of acids takes place under entirely different conditions (with solvents at moderate temperatures) from the pyrolysis of esters (a homogeneous, high temperature reaction), the correlation can, at best, be only qualitative. Esters of mono-*o*-substituted acids, however, show deviations from such linear relationships. The influence of the *o*-methyl group causes only a slight deviation from the linear relationship; this might be interpreted as a mild stabilizing influence. The deviations of the *o*-halogen esters were very marked. The characteristic temperature of the *o*-chlorobenzoate was even higher than that of the *p*-chloro isomer. There seems little question but that the *o*-chloro group does stabilize the ester toward pyrolysis. If the ease of pyrolysis of an ester is strictly a linear function of the strength of the acid (as measured by ionization constant) to which the ester is related, the *o*-substituted benzoates should pyrolyze at lower temperatures than the *m*- and *p*-substituted ones. The marked deviation from linearity in the plot (Fig. 1) could be due partly to the stabilization of the *ortho* group in the ester pyrolysis but very likely is due primarily to the large deviation in the ionization constant of the *o*-substituted acids. The *o*-substituted acids are considerably stronger than

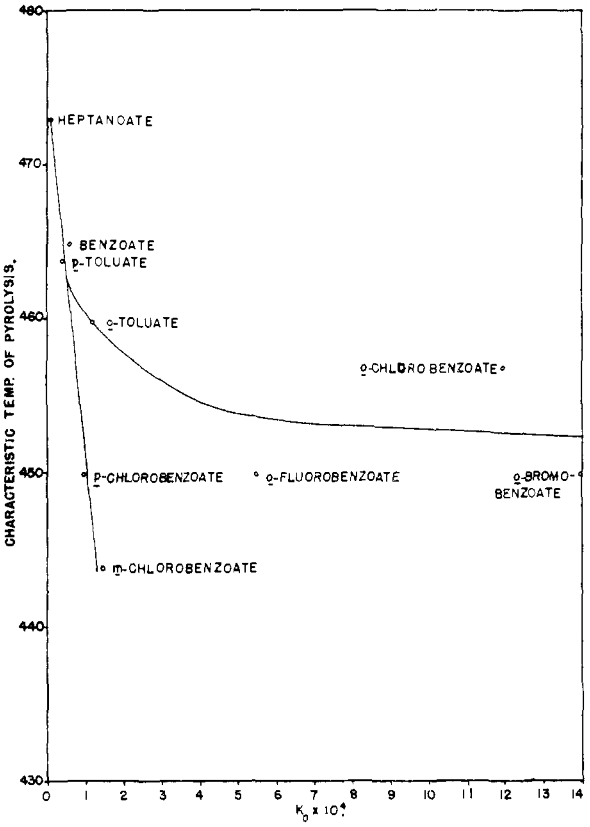


Fig. 1.—Characteristic temperatures *vs.* the ionization constants of the acids related to the acyl group of the esters.

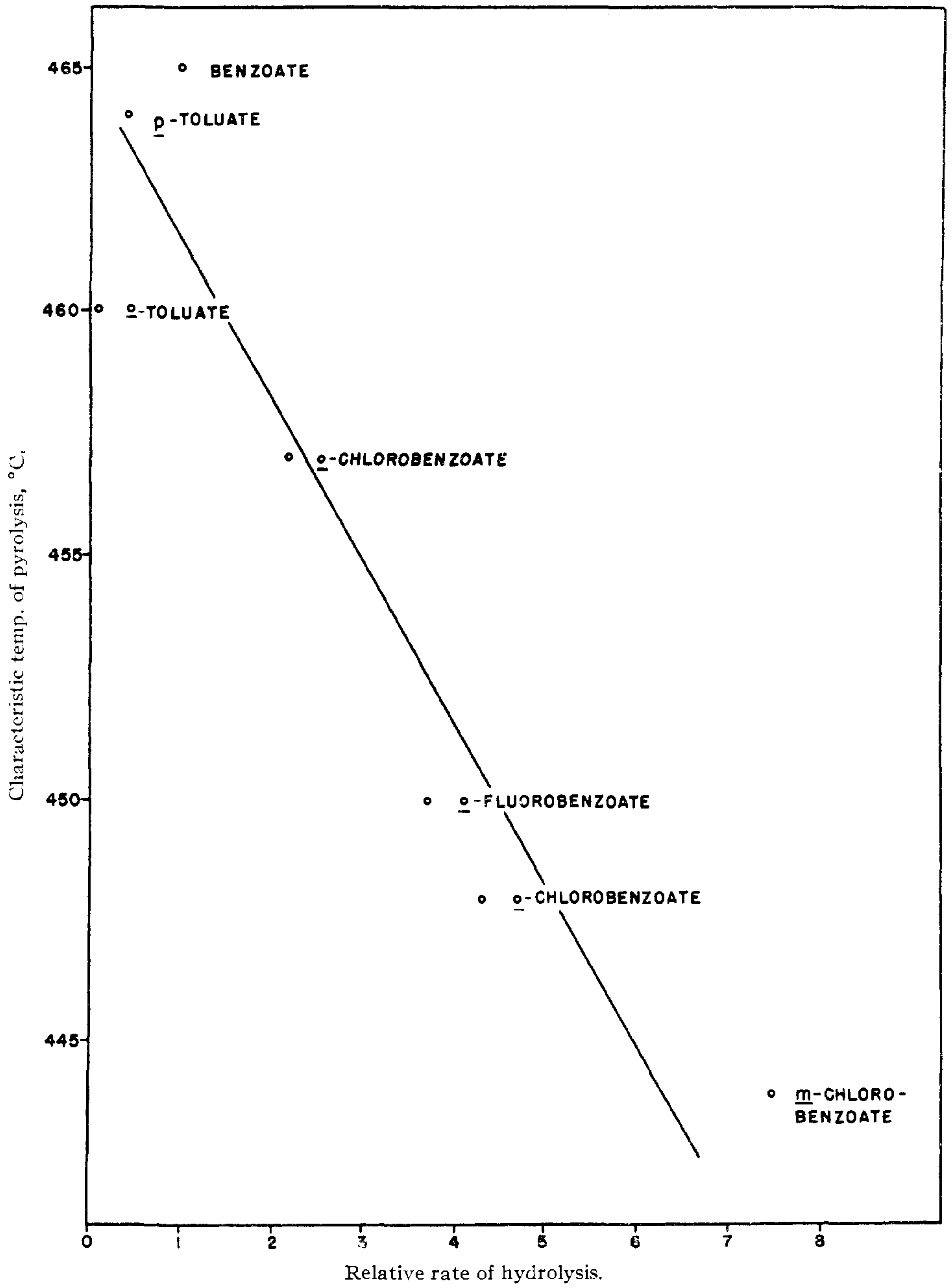
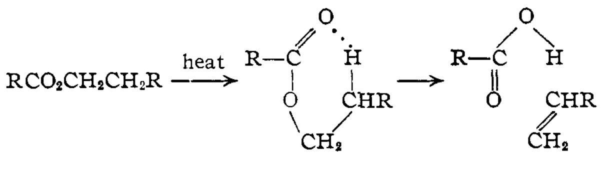


Fig. 2.—Characteristic temperatures *vs.* relative rates of alkaline hydrolysis of aromatic carboxylic esters.

the *m*- and *p*-isomers; their ionization constants are five to fifteen times greater.

Probably, however, the characteristic temperatures are affected by a number of factors. It has been demonstrated that the molecular weight of the ester affects the temperature of pyrolysis. Because *o*-substituents increase the dissociation of the acids, they could also weaken the O–R bonds in the esters and permit them to pyrolyze more readily than esters from weaker acids. Since they do not, however, it appears that *o*-substituents have some other influence which retards pyrolysis.

Hurd and Blunck[16] proposed the concept that alkyl esters pyrolyze by the simultaneous breaking of the O–R bond and formation of an O–H bond between the carbonyl oxygen and the hydrogen of the alkyl portion of the ester



Results from kinetic studies show that this reaction is first order, homogeneous, and has a negative entropy of activation.[32-34] These are all compatible with a mechanism involving a quasi-cyclic intermediate as shown above. It is reasonable to assume that *o*-substituents of the types involved in these studies may retard the formation of such an O–H bond and, in so doing, stabilize these esters by preventing the formation of the postulated six-membered cyclic intermediate.

It is not particularly surprising, however, that the *o*-chloro and *o*-bromo groups actually affect this reaction in an anomalous fashion, for there are many examples of the well known proximity effect.[35] It is more surprising that the small *o*-fluoro group also demonstrates this same stabilization of the ester toward heat. The influence of an *o*-halogen may be caused by depolarization of the carbonyl group by the halogen, thus decreasing the attraction of a β-hydrogen to the carbonyl oxygen. A steric factor may explain the slight stabilizing influence of the *o*-methyl group.

When the characteristic temperatures of pyrolysis of esters were plotted as a function of their rates of hydrolysis in 85% ethanol, as shown in Fig. 2, a linear relationship was obtained for nearly all the benzoates including those substituted *ortho*. The relative rates of hydrolysis are reported by Ingold.[36] Apparently the proximity effect on the pyrolysis of esters is of the same order of magnitude as is the proximity effect on the rate of hydrolysis of esters.

As would be expected, esters with the greatest vibrational energy required higher temperatures to bring about their pyrolysis. This correlation is shown in Fig. 3. Although there is not ideal correlation between the characteristic temperature of pyrolysis and the O–C stretching of the infrared spectra of the esters, there is general agreement.

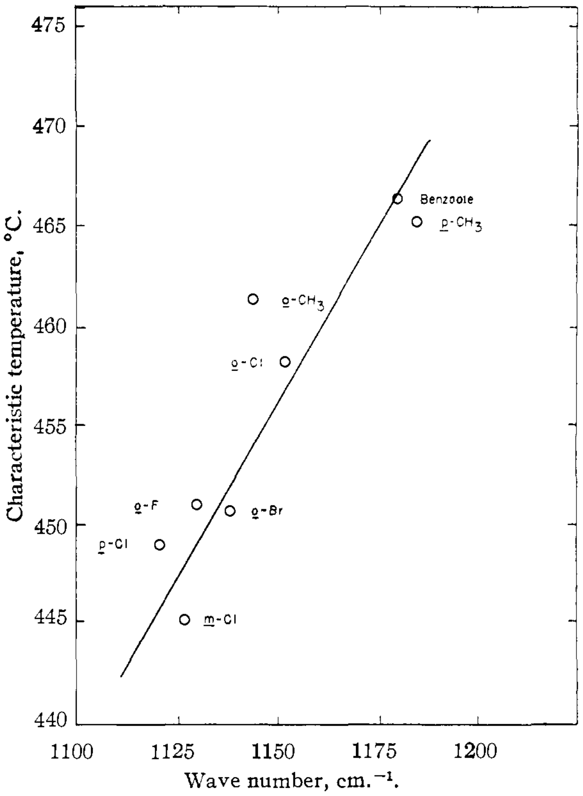


Fig. 3.—Plot of characteristic temperature *vs.* O–C stretching band in the infrared spectra of substituted cyclohexyl benzoates.

The esters with the highest wave numbers also show the greatest stability to heat.

In order to relate the effect (if any) of *o*-substituents more quantitatively to the ease of ester pyrolysis, it will be necessary to determine the thermodynamic properties (energy and entropy of activation) by appropriate kinetic studies of various substituted benzoates. This method of relating entropy of activation to the *ortho*-effect is well known and will aid in the future study of the mechanism of the pyrolysis of esters.

PULLMAN, WASHINGTON

[32] A. T. Blades, *Can. J. Chem.*, **32**, 366 (1954).

[33] E. E. Sommers and T. I. Crowell, THIS JOURNAL, **77**, 5443 (1955).

[34] D. H. R. Barton, A. J. Head and R. J. Williams, *J. Chem. Soc.*, 1715 (1953).

[35] L. P. Hammett, "Physical Organic Chemistry," McGraw–Hill Book Co., Inc., New York, N. Y., 1940, p. 204.

[36] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," George Banta Publishing Co., 1st Ed., Menasha, Wisconsin, 1953, p. 759.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Stereochemical Course in the Alkylation of Phenylacetonitrile and Phenylacetic Acid with Optically Active α-Phenylethyl Chloride[1]

BY WILLIAM J. CHAMBERS, WALLACE R. BRASEN AND CHARLES R. HAUSER

RECEIVED AUGUST 6, 1956

Phenylacetonitrile and phenylacetic acid were alkylated with L(+)-α-phenylethyl chloride (I) to give *erythro*-D(+)-2,3-diphenylbutyronitrile (II) and *erythro*-D(−)-2,3-diphenylbutyric acid (III), respectively. In both alkylations an optically active asymmetric center has been produced. The effect of temperature on the observed rotation of optically active α-phenylethyl chloride has been measured.

Recently potassiophenylacetonitrile prepared by means of potassium amide in liquid ammonia was alkylated with racemic α-phenylethyl chloride to give a 99% yield of the higher melting diastereomeric pair of 2,3-diphenylbutyronitrile (equation 1).[2] This racemic modification has been shown to be the *erythro* form.[3]

[1] Supported by the National Science Foundation.

[2] C. R. Hauser and W. R. Brasen, THIS JOURNAL, **78**, 494 (1956).

[3] W. R. Brasen and C. R. Hauser, *ibid.*, **79**, 395 (1957).