## Kinetics of the Hydrolysis of
p-Methoxybenzhydryl Benzoates[1]

Marc S. Silver and George C. Whitney
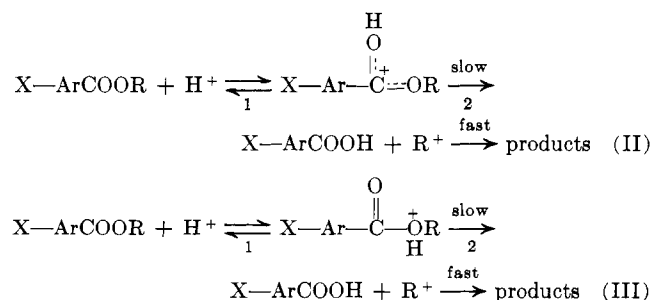
*Department of Chemistry, Amherst College,
Amherst, Massachusetts*

Resonance considerations, the investigations of Bender on O^{18} exchange,[2] and the study of Aksnes and Prue[3] on the hydrolysis of positively charged esters, all support the hypothesis that acid-catalyzed ester hydrolysis proceeds *via* carbonyl–oxygen protonation (I). The observation of Stewart and Yates,[4] that protonation of the carbonyl group in acetophenones, benzaldehydes, and benzoic acids correlates with the σ^+ parameter, suggested to us a possible further test of this hypothesis.

$$RCO_2R' + H^+ \quad \xrightarrow{\quad\quad}\quad \text{products} \quad (I)$$
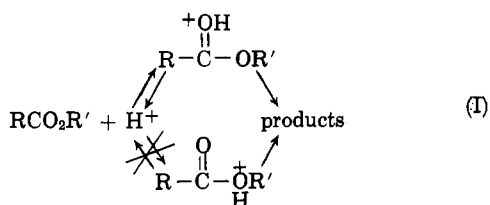
While the many-step $A_{AC}2$ hydrolysis (acyl–oxygen cleavage) appeared too complex for a σ^+ investigation, the two-step $A_{AL}1$ reaction (alkyl–oxygen cleavage) seemed potentially amenable to this approach (II and III). Mechanism II represents $A_{AL}1$ hydrolysis with carbonyl–oxygen protonation, and III, with ether–oxygen protonation. In II, both steps should correlate with σ^+ (because of the near symmetry of the protonated ester), the first step with negative, the second with positive ρ. The net reaction should correlate with σ^+, and a naive analysis suggests it will have a negative ρ, since step 1 represents development of the full difference in the resonance interaction between unprotonated and protonated ester, while in the transition state for step 2 this increased resonance interaction is only partially destroyed. Similar considerations predict a σ correlation for III and a probably negative ρ. The obtaining of meaningful data rests on there being an appreciable difference in ρ for steps 1 and 2, which in turn depends upon the nature of the transition state for step 2.

$$X\text{—ArCOOR} + H^+ \underset{1}{\overset{}{\rightleftharpoons}} X\text{—Ar—}\overset{\overset{H}{\overset{|}{O}}}{\underset{}{C}}\text{⁻OR} \xrightarrow[2]{\text{slow}}$$

$$X\text{—ArCOOH} + R^+ \xrightarrow{\text{fast}} \text{products} \quad (II)$$

$$X\text{—ArCOOR} + H^+ \underset{1}{\overset{}{\rightleftharpoons}} X\text{—Ar—}\overset{\overset{O}{\parallel}}{\underset{\overset{|}{H}}{C}}\text{—}\overset{+}{OR} \xrightarrow[2]{\text{slow}}$$

$$X\text{—ArCOOH} + R^+ \xrightarrow{\text{fast}} \text{products} \quad (III)$$

A series of p-methoxybenzhydryl benzoates was chosen for investigation, since the stability of the p-methoxybenzhydryl carbonium ion insures that alkyl–oxygen cleavage will occur.[5] The data in Table I reveal that the spread in reactivity for the acid-catalyzed hydrolysis is very small. The slightly negative ρ^6 (Table II) accords with either II or III. Hammett plots (*cf.* Table II) indicate that while the data are somewhat better correlated by σ^+ than by σ, the small difference between the two correlations precludes any conclusion about mechanism.[8]

Table I

Rates of Solvolysis of $(4\text{-}CH_3OC_6H_4)C_6H_5CHOOC_6H_4\text{-}X$ in 88.9% Acetone[a,b]

X	$10^5 k_{uncat}$ (90.5°)	$10^6 k_{uncat}$ (70.5°)	$10^4 k_H^+$ (90.5°)	$10^5 k_H^+$ (70.5°)
H	1.41	2.02	6.15	5.18
$m\text{-}NO_2$	39.0	57.7	2.96	3.38
$p\text{-}NO_2$	36.6	54.7	2.93	3.56
$m\text{-}Cl$	8.12	12.5	3.49	3.26
$m\text{-}CH_3$	1.32	1.93	6.05	5.80
$p\text{-}Cl$	4.88	6.92	4.13	3.95
$p\text{-}CH_3$	0.95	1.33	6.94	6.25
$p\text{-}CH_3O$	0.65	0.84	9.9	9.0

[a] All rate constants in sec.$^{-1}$. [b] For k_{uncat}, $[NaClO_4] = 0.0109$ at 25°; for k_H^+, $[HClO_4] = 0.0109$ at 25°.

Table II

Correlation of the Rates of Solvolysis of p-Methoxybenzhydryl Benzoates in 88.9% Acetone with the Hammett Equation

Temp., °C.	Rate constant	Parameter[d]	ρ	r^a	s^b	n^c
90.5	k_{uncat}	σ	1.77	0.996	0.064	8
	k_H^+	σ	-0.47	.960	.057	8
	k_H^+	σ^+	-0.36	.975	.047	8
	k_H^+	σ^n	-0.41	.974	.042	5
70.5	k_{uncat}	σ	1.81	.997	.061	8
	k_H^+	σ	-0.35	.885	.079	8
	k_H^+	σ^+	-0.28	.938	.050	8
	k_H^+	σ^n	-0.26	.867	.065	5

[a] The correlation coefficient. [b] The standard deviation of experimental measurements from the regression line. [c] The number of compounds used in the calculation of ρ. [d] σ^n as defined by H. Van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. trav. chim.*, **78**, 815 (1959).

A different series of compounds would probably not circumvent the difficulty here encountered. For step 1, ρ should be[4] about -1.5 in any example. To obtain a larger net ρ, one must diminish ρ for step 2, which means that the transition state for step 2 should occur earlier in the reaction coordinate. This in turn would result from increasing the stability of the carbonium ion being produced,[9] but the stability of the p-methoxy-

(1) (a) Supported by a Frederick Gardner Cottrell grant from the Research Corporation; (b) from the B.A. thesis of G. C. Whitney.

(2) For a summary, see J. Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, Chap. 12.

(3) G. Aksnes and J. E. Prue, *J. Chem. Soc.*, 103 (1959).

(4) R. Stewart and K. Yates, *J. Am. Chem. Soc.*, **82**, 4059 (1960), and preceding papers.

(5) S. R. Johns and V. R. Stimson, *J. Chem. Soc.*, 467 (1960).

(6) In contrast, hydrolysis by the $A_{AC}2$ mechanism has a small positive ρ.[7b]

(7) (a) H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953) (Table II); (b) reactions 48a and 48b; (c) reactions 1k–1r.

(8) Some possible reasons for such poor correlations are discussed by J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(9) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

TABLE III

MELTING POINTS AND ANALYSES[a] OF $(4\text{-}CH_3OC_6H_4)C_6H_5CHOOC_6H_4\text{-}X$

X	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	% Nitrogen or Chlorine Calcd.	% Nitrogen or Chlorine Found
H	56–59[b]	79.22	79.36	5.70	5.71		
m-NO₂	104–106	69.41	69.11	4.72	4.74	3.86	3.80
p-NO₂	81–82	69.41	69.33	4.72	4.84	3.86	3.74
m-Cl	Oil	71.49	71.81	4.86	5.21	10.05	9.78
p-Cl	66–67	71.49	71.48	4.86	4.72	10.05	9.92
m-CH₃	Oil	79.50	79.69	6.06	6.31		
p-CH₃	46–49	79.50	79.62	6.06	6.19		
p-CH₃O	57–60	75.84	75.96	5.78	5.84		

[a] Analyses by Dr. Weiler and Dr. Strauss, Oxford, England. [b] A. G. Davies and J. Kenyon, *Quart. Rev.*, **9**, 203 (1955), report 58°.

TABLE IV

RATE OF HYDROLYSIS OF $0.0226\ M$ p-METHOXYBENZHYDRYL m-NITROBENZOATE IN 88.9% ACETONE AT 90.5°, $[NaClO_4] = 0.0106\ M$

Time, sec.	$0.01127M$ NaOH, ml.[a]	$10^4\ k$, sec.$^{-1}$
0[b]	0.68	...
400	2.02	3.80
800	3.20	3.87
1200	4.21	3.90
1600	5.06	3.87
2000	5.79	3.88
2400	6.40	4.01
3200	7.47	3.94
	Av.	3.90 ± 0.05

[a] Amount of base to titrate a 5.0-ml. aliquot. [b] Zero time represents 200 sec. after a sample was immersed in the bath.

benzhydryl carbonium ion is such that improvement along this line does not appear worth pursuing.

The uncatalyzed hydrolysis of the p-methoxybenzhydryl esters by the B_{AL}[1] mechanism (IV) appears closely

$$X\text{—ArCOOR} \xrightarrow{\text{slow}} X\text{—ArCOO}^- + R^+ \xrightarrow{\text{fast}} \text{products} \quad (IV)$$
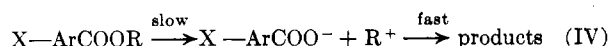
analogous to the ionization of benzoic acids. It is, therefore, not surprising that the hydrolysis shows a good σ correlation (Table II) and that ρ, for the hydrolysis (1.8), is comparable to ρ for benzoic acid ionization[7c] in ethanol-water.

Experimental

The esters were prepared by conventional means[10] from readily available starting materials. The properties of the esters are given in Table III. The 88.9% acetone was prepared by mixing 250 ml. of redistilled water, which contained either perchloric acid or sodium perchlorate, with 2000 ml. of pure acetone[11] at 25°. The kinetic procedure involved standard ampoule technique, with titration of the acid present by standard base.[12] Very small corrections had to be supplied for solvent decomposition in a few runs. All runs were followed to at least 70% reaction, except for the p-methoxy (to 25%) and the unsubstituted, m-methyl and p-methyl esters (to 50%) in the uncatalyzed reactions at 70.5°. Good first-order plots were obtained and Table IV shows a typical example.

(10) H. L. Goering and J. P. Blanchard, *J. Am. Chem. Soc.*, **76**, 5405 (1954).

(11) J. K. Kochi and G. S. Hammond, *ibid.*, **75**, 3445 (1953).

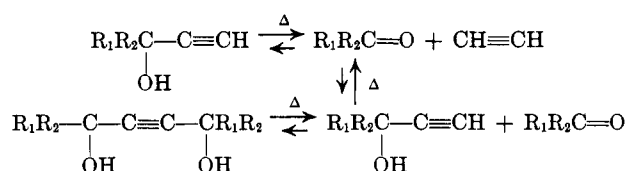(12) H. L. Goering and E. F. Silversmith, *ibid.*, **77**, 6249 (1955).

The Reaction of Alkali Metal Hydroxides with Tertiary Acetylenic Carbinols and Glycols

R. J. TEDESCHI, M. F. WILSON, J. SCANLON, M. PAWLAK, AND V. CUNICELLA

Central Research Laboratories, Air Reduction Company, Inc., Murray Hill, New Jersey

The base-catalyzed cleavage of tertiary acetylenic carbinols[1-3] and glycols[4,5] to ketones and acetylene has been extensively studied. The cleavage is generally irreversible above 100° and diol cleavage proceeds through the intermediate formation of carbinol. The reverse reaction (ethynylation) also is well documented and is known as the Favorskiĭ synthesis.[2,6]

$$R_1R_2C\text{—}C\equiv CH \underset{\Delta}{\overset{\Delta}{\rightleftarrows}} R_1R_2C\text{=}O + CH\equiv CH$$

$$R_1R_2\text{—}C\text{—}C\equiv C\text{—}CR_1R_2 \xrightarrow{\Delta} R_1R_2C\text{—}C\equiv CH + R_1R_2C\text{=}O$$

However, the direct, stoichiometric reaction of pure alkali metal hydroxides with tertiary acetylenic carbinols and glycols followed by isolation and characterization of the reaction products has never been reported. The closest analogy has been the preparation of potassium derivatives[7,8] using potassium metal in which reaction with the tertiary hydroxyl groups was claimed.

Work at this laboratory now has shown that the heterogeneous reaction of essentially anhydrous, finely divided potassium hydroxide with either 3-methyl-1-butyn-3-ol (I) or 2,5-dimethyl-3-hexyne-2,5-diol (II) takes place rapidly and in high conversion in inert solvents under mild reaction conditions.

(1) L. Henry, *Ber.*, **8**, 398 (1875).

(2) A. E. Favorskiĭ and M. Skossarewskii, *Zh. Fiz. Khim. Obshchestva*, **32**, 652 (1900); *Bull. soc. chim.*, **26**, 284 (1901).

(3) Farbenfabriken Vorm. Friedr. Bayer and Co., German Patent 285,770; *Chem. Zentr.*, II, 508 (1915).

(4) G. Arbuzov, *Zh. Fiz. Khim. Obshchestva*, **53**, 288 (1921); *Chem. Abstr.*, **18**, 2327 (1924).

(5) G. Arbuzov and T. Temnikova, *Zh. Fiz. Khim. Obshchestva*, **54**, 219 (1922); *Chem. Abstr.*, **18**, 2514 (1924).

(6) A. W. Johnson, "Acetylenic Compounds," Vol. I, "The Acetylenic Alcohols," Edward Arnold Co., London, 1946, pp. 14, 137, 147.

(7) P. L. Salzberg and C. S. Marvel, *J. Am. Chem. Soc.*, **50**, 1737 (1928).

(8) G. Arbuzov, *et al.*, *Zh. Fiz. Khim. Obshchestva*, **53**, 288 (1921); *Chem. Abstr.*, **18**, 2327 (1924); *Zh. Fiz. Khim. Obshchestva*, **54**, 219 (1922); *Chem. Abstr.*, **18**, 2514 (1924).