

Terms & Conditions

Electronic Supporting Information files are available without a subscription to ACS Web Editions. The American Chemical Society holds a copyright ownership interest in any copyrightable Supporting Information. Files available from the ACS website may be downloaded for personal use only. Users are not otherwise permitted to reproduce, republish, redistribute, or sell any Supporting Information from the ACS website, either in whole or in part, in either machine-readable form or any other form without permission from the American Chemical Society. For permission to reproduce, republish and redistribute this material, requesters must process their own requests via the RightsLink permission system. Information about how to use the RightsLink permission system can be found at <http://pubs.acs.org/page/copyright/permissions.html>



ACS Publications

MOST TRUSTED. MOST CITED. MOST READ.

Copyright © 1997 American Chemical Society

Table 1S: First Order Rate Constant (k_{obs}) Measured at Various pH in Different Buffers ($\mu = 0.10$ M (KCl)) for Thio Esters **10-13** at 50^o C^a.

pH ^b	Buffer [Buffer]	10	11	12	13
		$k_{\text{obs}} \text{ s}^{-1}$	$k_{\text{obs}} \text{ s}^{-1}$	$k_{\text{obs}} \text{ s}^{-1}$	$k_{\text{obs}} \text{ s}^{-1}$
1.98	HCl 0.01		$(4.63 \pm 1.00) \times 10^{-6}$		
2.33	HCl 0.005		$(5.67 \pm 1.00) \times 10^{-6}$		
3.85	Acetate 0.05		$(1.60 \pm 0.08) \times 10^{-5}$		
3.83	Acetate 0.10		$(1.75 \pm 0.03) \times 10^{-5}$		
4.75	Acetate 0.05		$(2.23 \pm 0.07) \times 10^{-5}$		
4.77	Acetate 0.10		$(2.73 \pm 0.02) \times 10^{-5}$		
6.58	MES 0.05	$(2.88 \pm 0.22) \times 10^{-6}$	$(2.53 \pm 0.10) \times 10^{-5}$	$(6.05 \pm 0.25) \times 10^{-4}$	$(1.14 \pm 0.17) \times 10^{-5}$
6.61	MES 0.10	$(4.23 \pm 0.26) \times 10^{-6}$	$(2.78 \pm 0.13) \times 10^{-5}$	$(8.15 \pm 0.03) \times 10^{-4}$	$(1.54 \pm 0.10) \times 10^{-5}$
7.62	MOPS 0.05	$(3.95 \pm 0.07) \times 10^{-5}$	$(3.33 \pm 0.08) \times 10^{-5}$	$(4.05 \pm 0.10) \times 10^{-3}$	
7.59	MOPS 0.10	$(4.08 \pm 0.03) \times 10^{-5}$	$(3.57 \pm 0.08) \times 10^{-5}$	$(4.68 \pm 0.02) \times 10^{-3}$	
7.71	MOPS 0.05				$(6.69 \pm 0.09) \times 10^{-5}$
7.74	MOPS 0.10				$(7.18 \pm 0.01) \times 10^{-5}$
8.06	MOPS 0.05	$(8.72 \pm 0.07) \times 10^{-5}$		$(7.46 \pm 0.08) \times 10^{-3}$	$(1.38 \pm 0.02) \times 10^{-4}$
8.04	MOPS 0.10	$(9.02 \pm 0.11) \times 10^{-5}$		$(8.12 \pm 0.07) \times 10^{-3}$	$(1.45 \pm 0.02) \times 10^{-4}$
8.55	EPPS 0.05				$(5.06 \pm 0.04) \times 10^{-4}$
8.57	EPPS 0.10				$(5.18 \pm 0.03) \times 10^{-4}$
8.70	EPPS 0.05	$(2.60 \pm 0.05) \times 10^{-4}$	$(6.83 \pm 0.07) \times 10^{-5}$	$(1.53 \pm 0.13) \times 10^{-2}$	$(6.38 \pm 0.11) \times 10^{-4}$

8.68	<u>EPPS</u> 0.10	$(3.47 \pm 0.02) \times 10^{-4}$	$(7.77 \pm 0.03) \times 10^{-5}$	$(1.63 \pm 0.03) \times 10^{-2}$	$(6.63 \pm 0.10) \times 10^{-4}$
9.72	<u>Et₃N</u> 0.05				$(3.18 \pm 0.03) \times 10^{-3}$
9.70	<u>Et₃N</u> 0.10				$(3.36 \pm 0.10) \times 10^{-3}$
9.80	<u>Et₃N</u> 0.05	$(2.43 \pm 0.02) \times 10^{-3}$	$(5.48 \pm 0.05) \times 10^{-4}$	$(1.80 \pm 0.03) \times 10^{-2}$	
9.77	<u>Et₃N</u> 0.10	$(2.60 \pm 0.05) \times 10^{-3}$	$(5.98 \pm 0.05) \times 10^{-4}$	$(1.92 \pm 0.03) \times 10^{-2}$	
11.46	<u>NaOH</u> 0.003	$(8.30 \pm 0.23) \times 10^{-2c}$	$(1.37 \pm 0.03) \times 10^{-2}$	$(3.05 \pm 0.05) \times 10^{-2}$	

^a errors are standard errors of means of at least 2-4 replicates

^b The error in the pH readings is ± 0.04 for replicates

^c 46°C by stopped flow kinetics.

Table 2S. Second order rate constant for buffer catalysis for ester **10-13** at different pH, T = 50 °C, $\mu = 0.10$ M(KCl)

pH ^a	Buffer	10 $k_{2\text{buf}} (\text{M}^{-1} \text{s}^{-1})$	11 $k_{2\text{buf}} (\text{M}^{-1} \text{s}^{-1})$	12 $k_{2\text{buf}} (\text{M}^{-1} \text{s}^{-1})$	13 $k_{2\text{buf}} (\text{M}^{-1} \text{s}^{-1})$
3.83	Acetate		3.34×10^{-5}		
4.77	Acetate		9.98×10^{-5}		
6.60	MES	2.77×10^{-5}	6.67×10^{-5}	4.05×10^{-3}	8.60×10^{-5}
7.61	MOPS	2.51×10^{-5}	4.97×10^{-5}	1.53×10^{-2}	
7.72	MOPS				9.80×10^{-5}
8.04	MOPS	7.33×10^{-5}		1.14×10^{-2}	1.33×10^{-4}
8.55	EPPS				2.40×10^{-4}
8.70	EPPS	1.75×10^{-3}	1.92×10^{-4}	3.74×10^{-2}	5.00×10^{-4}
9.70	Et ₃ N				4.47×10^{-3}
9.78	Et ₃ N	3.67×10^{-3}	1.00×10^{-3}	3.81×10^{-2}	

^a The error in the pH readings for two different buffer concentration is ± 0.06