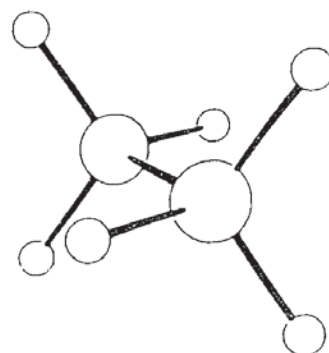


ANDREW STREITWIESER, JR.
CLAYTON H. HEATHCOCK

INTRODUCTION TO ORGANIC CHEMISTRY

THIRD EDITION



THIRD EDITION

Introduction to Organic Chemistry

Andrew Streitwieser, Jr.

Clayton H. Heathcock

UNIVERSITY OF CALIFORNIA, BERKELEY

Macmillan Publishing Company *New York*

Collier Macmillan Publishers *London*

Copyright © 1985 Macmillan Publishing Company, a division of Macmillan, Inc.

Printed in the United States of America

All rights reserved. No part of this book may be reproduced or transmitted in any form or by any means, electronic or mechanical, including photocopying, recording, or any information storage and retrieval system, without permission in writing from the Publisher.

Earlier editions, copyright © 1976 and 1981 by Macmillan Publishing Co., Inc. Selected illustrations have been reprinted from *Orbital and Electron Density Diagrams: An Application of Computer Graphics*, by Andrew Streitwieser, Jr., and Peter H. Owens, copyright © 1973 by Macmillan Publishing Co., Inc.

Macmillan Publishing Company
866 Third Avenue, New York, New York 10022

Collier Macmillan Canada, Inc.

Library of Congress Cataloging in Publication Data

Streitwieser, Andrew,
Introduction to organic chemistry.

Includes index.

I. Chemistry, Organic. I. Heathcock, Clayton H.

II. Title.

QD251.2.S76 1985 547 84-15399

ISBN 0-02-418140-4 (Hardcover Edition)

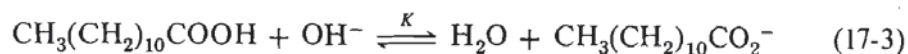
ISBN 0-02-946720-9 (International Edition)

Printing: 1 2 3 4 5 6 7 8 Year: 5 6 7 8 9 0 1 2 3

ISBN 0-02-418140-4

Chap. 17
Carboxylic
Acids

becomes less important than the nonpolar hydrocarbon tail (R). Consider the reaction of a carboxylic acid such as dodecanoic acid with hydroxide ion.



The equilibrium constant for reaction (17-3) may be derived as follows.

$$K_a = \frac{[\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2^-][\text{H}^+]}{[\text{CH}_3(\text{CH}_2)_{10}\text{COOH}]} = 1.3 \times 10^{-5} M \quad (17-4)$$

$$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14} M^2 \quad (17-5)$$

Rearranging (17-5), we have

$$[\text{H}^+] = \frac{10^{-14}}{[\text{OH}^-]} M \quad (17-6)$$

Substituting (17-6) into (17-4) and expanding, we have

$$K = \frac{[\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2^-]}{[\text{CH}_3(\text{CH}_2)_{10}\text{COOH}][\text{OH}^-]} = 1.3 \times 10^9 M^{-1} \quad (17-7)$$

Equation (17-7) is merely the equilibrium expression for reaction (17-3). The large value of K shows that the reaction proceeds to completion; dodecanoic acid is converted by aqueous sodium hydroxide completely into the salt, sodium dodecanoate. Note that the anions of carboxylic acids are named by dropping *-ic* from the name of the parent acid and adding the suffix *-ate*. Although dodecanoic acid is a neutral molecule, sodium dodecanoate is a salt. Dissolution of this salt gives an anion and a cation, which can be solvated by water. It is not surprising that the solubility of sodium dodecanoate (1.2 g per 100 mL) is much greater than that of dodecanoic acid itself (0.0055 g per 100 mL).

EXERCISE 17.5 Equation (17-7) can be used to calculate the ratio of ionized and nonionized dodecanoic acid at a given pH, by inserting the proper value for $[\text{OH}^-]$. Calculate this ratio for $\text{pH} = 2, 4, 6,$ and 8 .

D. Soaps

The sodium and potassium salts of long-chain carboxylic acids ("fatty acids") are obtained by the reaction of natural fats with sodium or potassium hydroxide. These salts, referred to as soaps, have the interesting and useful ability to solubilize nonpolar organic substances. This phenomenon can easily be understood if one considers the structure of such a salt.



The molecule has a polar ionic region and a large nonpolar hydrocarbon region. In aqueous solution a number of carboxylate ions tend to cluster together so that the hydrocarbon tails are close to each other, thus reducing their energy by the attractive van der Waals forces enjoyed by normal hydrocarbons. The surface of the sphere-like cluster is then occupied by the highly polar CO_2^- groups. These polar groups face the medium, where they may be solvated by H_2O or paired with a cation. The resulting spherical structure, called a **micelle**, is depicted in cross section in Figure 17.3. The wavy lines in the figure represent the long hydrocarbon chains of the salt molecules.

Organic material such as butter or motor oil that is not normally soluble in water may "dissolve" in the hydrocarbon interior of a micelle. The overall process of soap

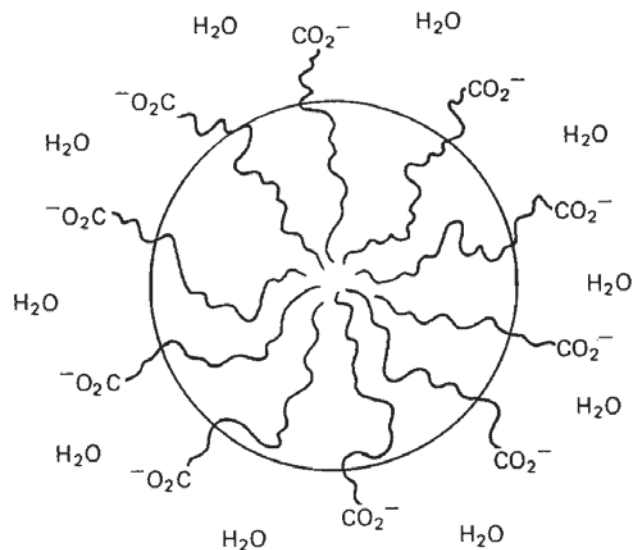


FIGURE 17.3 Cross section of a micelle.

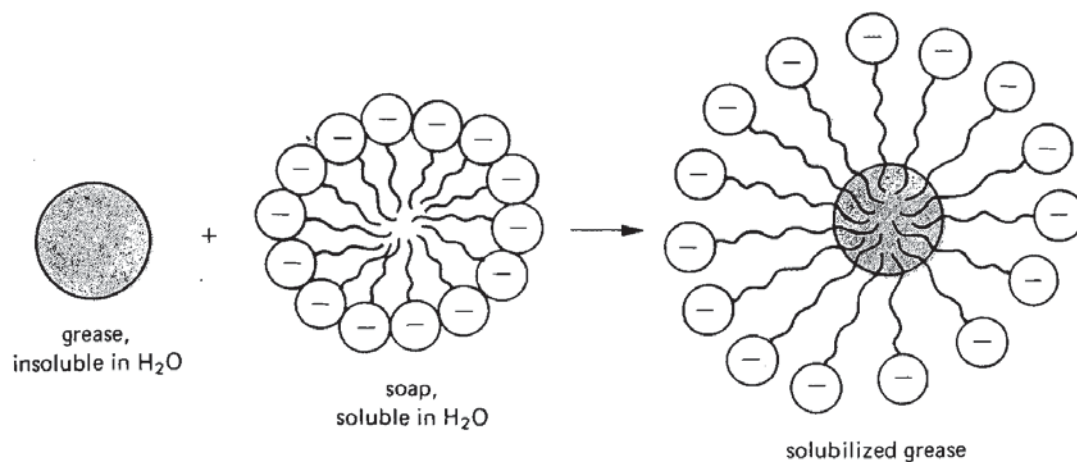
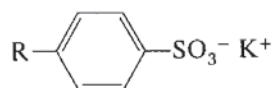


FIGURE 17.4 Schematic diagram of soap solubilization.

Certain bacteria can metabolize soaps. This degradation is most rapid when there are no branches in the hydrocarbon chain of the soap molecule. Since the naturally occurring fatty acids are all unbranched compounds, soaps derived from natural fats are said to be **biodegradable**. Before 1933 all cleaning materials were soaps. In that year the first synthetic detergents were marketed. Detergents have the useful property of not forming the hard "scum" that often results from the use of a soap with hard water. This scum is actually the insoluble magnesium and calcium salts of the fatty acid. The first detergents were alkylbenzenesulfonates. Like soaps, they had a large nonpolar hydrocarbon tail and a polar end.



R = branched alkyl chain

However, being branched compounds, these early detergents were not rapidly biodegradable. Since the materials could not be completely metabolized by the bacteria that operate in sewage treatment plants, they were passed into natural waterways with the treated

Explore Litigation Insights

Docket Alarm provides insights to develop a more informed litigation strategy and the peace of mind of knowing you're on top of things.

Real-Time Litigation Alerts



Keep your litigation team up-to-date with **real-time alerts** and advanced team management tools built for the enterprise, all while greatly reducing PACER spend.

Our comprehensive service means we can handle Federal, State, and Administrative courts across the country.

Advanced Docket Research



With over 230 million records, Docket Alarm's cloud-native docket research platform finds what other services can't. Coverage includes Federal, State, plus PTAB, TTAB, ITC and NLRB decisions, all in one place.

Identify arguments that have been successful in the past with full text, pinpoint searching. Link to case law cited within any court document via Fastcase.

Analytics At Your Fingertips



Learn what happened the last time a particular judge, opposing counsel or company faced cases similar to yours.

Advanced out-of-the-box PTAB and TTAB analytics are always at your fingertips.

API

Docket Alarm offers a powerful API (application programming interface) to developers that want to integrate case filings into their apps.

LAW FIRMS

Build custom dashboards for your attorneys and clients with live data direct from the court.

Automate many repetitive legal tasks like conflict checks, document management, and marketing.

FINANCIAL INSTITUTIONS

Litigation and bankruptcy checks for companies and debtors.

E-DISCOVERY AND LEGAL VENDORS

Sync your system to PACER to automate legal marketing.