TECHNIQUES OF CHEMISTRY

VOLUME II

ORGANIC SOLVENTS

PHYSICAL PROPERTIES AND METHODS OF PURIFICATION

Fourth Edition

by

JOHN A. RIDDICK

Baton Rouge, Louisiana

WILLIAM B. BUNGER

Indiana State University
Terre Haute, Indiana

and

THEODORE K. SAKANO

Rose-Hulman Institute of Technology
Terre Haute, Indiana

On the basis of the First Edition
by ARNOLD WEISSBERGER and ERIC S. PROSKAUER
the completely revised Second Edition
by JOHN A. RIDDICK and EMORY E. TOOPS, JR.
and
the completely revised Third Edition
by JOHN A. RIDDICK and WILLIAM B. BUNGER

A Wiley-Interscience Publication
JOHN WILEY & SONS
New York • Chichester • Brisbane • Toronto • Singapore

Library of Congress Cataloging in Publication Data:

Riddick, John A. (John Allen), 1903–
Organic solvents.
(Techniques of chemistry; v. 2)
"On the basis of the first edition by Arnold Weissberger and Eric S. Proskauer, the completely revised second edition by John A. Riddick and Emory E. Toops, Jr., and the completely revised third edition by John A. Riddick and William B. Bunger."
"A Wiley-Interscience publication."
Bibliography: p.
Includes index.
1. Nonaqueous solvents. I. Bunger, William B., 1917– . II. Sakano, Theodore. III. Weissberger, Arnold, 1898– . Organic solvents. IV. Title. V. Series.
QD61.T4 vol. 2, 1986 542 s [547.1'3423] 86-15698
[QD544.5]
ISBN 0-471-08467-0

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

149. Methyl ether

Oxybismethane

$(CH_3)_2O$ 115-10-6 C_2H_6O

		cgs	SI	
mw		46.068	46.068	3468
bp	1 atm	-24.84	248.31	7289;122,1609,7623,3950,4726
dt/dp	1 atm	0.03012	0.2259	122;7289
dp/dt	1 atm	33.20	4.426	122
p	25	4450	593.3	122;1609,7623
eq 2.5	A	7.31646	6.44136	7293;3950
	B	1025.56	1025.56	
	C	256.05	256.05	
fp		-141.49	131.66	7289,3950;7623,1609,4726
d	-40	0.7538	753.8	2992;4856,4726
	-20	0.7174	717.4	1609;4856,2992,4726
	20(1)	0.6689	668.9	7289;5652,1609,7623
	25(1)	0.6612	661.2	
dd/dt	-60 - bp	0.00132	1.32	2992
n_D	-40	1.3438	1.3438	2992;1609
	20	1.3018	1.3018	2510;7289
	25	1.2984	1.2984	
dn/dt	-60 - bp	0.00050	0.00050	2992
γ	-42.0	21.3	0.0213	4762;1609
	-10.6	16.5	0.0165	
ΔH_v	20	4.443	18.59	1609
	bp	5.143	21.52	1609;3950,4762
ΔH_m		1.181	4.941	7290;3950,1609
ΔH°_f	25(g)	-43.99	-184.05	5856;7826,2036
ΔH°_c	25(g)	-349.04	-1460.38	5856;2036
C°_p	25	15.39	64.39	7826;7291,6553,3059,4042
C_p	-33	24.45	102.30	3950
	25	26.3	110.0	
t_c		126.9	400.1	122,7292;689,1349,4762
p_c		51.7	5.24	122;7292,1349,689
d_c		0.2714	271.4	1349;1609,7292
v_c		0.170	0.000170	7292
A	eq 2.72	0.03425	0.03425	7290
pK_a	aq H_2SO_4	-3.83	-3.83	434
pK_{BH^+}	25 aq H_2SO_4	-2.48	-2.48	5755;4556
ϵ	25(1)	5.02	5.02	1609;4904
μ/	25 in 38 (g)	1.35	1.35	7734;454,613
		1.28	1.28	3000;6373
δ		8.8	18.0	1271,4593

149. Methyl ether

(Continued)

		cgs	SI	
soly	in aq,24 aq in,24	35.3%w 7.0%w	35.3%w 7.0%w	1609
fl pt	TOC	-41	232	1609;6402
Beil	19,281			
uv	6428,3189,7430			
ir	5754,5845,6894,3845,4943,5849,1712,3059			
Raman	3845,4943,7200,6772,4100			
ms	4784,7199			
nmr	98			

150. Ethyl vinyl ether

Ethoxyethene

$CH_2{=}CHOC_2H_5$ 109-92-2 C_4H_8O

		cgs	SI	
mw		72.107	72.107	3468
bp	1 atm	35.72	308.87	2035,8161,7795;4091,8116,122
dt/dp	1 atm	0.0372	0.279	122;7615
dp/dt	1 atm	26.9	3.58	122
p	25	515	68.7	122;7615,4091
eq 2.4	A B	7.41783 1400.44	6.5427 1400.44	7615
fp		-115.8	157.4	2035;7615
d	9.2 20	0.7723 0.7531	772.3 753.1	1408;8116 8161;7795
dd/dt		0.00117	1.17	7615
n_D	20 25	1.37542 1.37288	1.37542 1.37288	4091;2035,8161,7795,7615
dn/dt	25	0.00051	0.00051	4091
η	20	0.2	0.0002	7615

and so forth, include α, β-conjugated unsaturates such as acrolein, isoprene, and sorbic acid.

Inhibition of Peroxide Formation. Bailey and Roy [552] found that peroxide formation can best be inhibited by storing ethers over sodium amalgam in brown bottles.

In France, du Pont has patented a stabilizer for cyclic ethers, 4,4′-thiobis(6-*tert*-butyl-*m*-cresol) effective in concentrations of 0.01–1% [2145].

Hamstead and Van Delinder [3128] present an excellent discussion of autoxidation and inhibition of peroxides in ethers. They studied the inhibition of isopropyl ether and present information that should be valuable for the storage of all ethers.

Robertson and Jones [6200] state that aldehydes, ethers, and esters of unsaturated acids are stabilized from peroxide formation by the addition of 0.0001–1% of 2,5-bis(dimethylaminomethyl)hydroquinone.

Jones [3747] found 3,3′,5,5′-tetralkylstilbenequinone to be a stabilizer for aldehydes, ethers, and esters of unsaturated acids.

N-Benzyl-*p*-aminophenol, 16 ppm; diethylenetriamine, 50 ppm; triethylenetetramine, 50 ppm; tetraethylenepentamine, 50 ppm; morpholine, 300 ppm; and ethylenediamine, 50 ppm were found effective for peroxide inhibition in isopropyl ether [1518]. The last two amines were the least effective.

Aliphatic Open-Chain Ethers (149–164)

149. Methyl Ether

Erlenmeyer and Kriechbaumer [2284] prepared methyl ether in 1874 by heating 1.3 parts of methanol with 2 parts of concentrated sulfuric acid solution at 140°. Similar preparations with methanol and concentrated acid solutions are given in Newth [5476] and Senderens [6573].

Kennedy and coworkers [3950] prepared methyl ether for *calorimetric studies* by adding methyl iodide to a solution of sodium in aldehyde-free methanol. The gas was dried over activated alumina and then the ether was distilled in a low-temperature column of 12 theoretical plates. Impurities were determined from a freezing point determination as 1 ppm.

SAFETY

Anesthesia is caused when the ether concentration is 65%v in air; profound anesthesia occurs at 85%v concentration [1174]. The LC_{50} in mice was reported as 494.4 ppm for a 15-min inhalation [1347].

The *flammable limits* in air are 3.3 and 27.3%v [2456]; see also [6402, 1609]. The *minimum ignition temperature* in air is 350° [5415, 6402].

150. Ethyl Vinyl Ether

Dolliver and coworkers [2035] passed acetal over 5% platinized asbestos at 280–290°. Repeated fractional distillation, followed by drying with calcium chloride, gave a pure ethyl vinyl ether.

Böhme and Bentler [943] prepared ethyl vinyl ether in 49% yield by refluxing 21.7 grams of 2-ethoxy-2-chloroethane with 36 grams of *N*,*N*-dimethylaniline on a water bath until the reaction starts and fractionally distilling the upper layer.