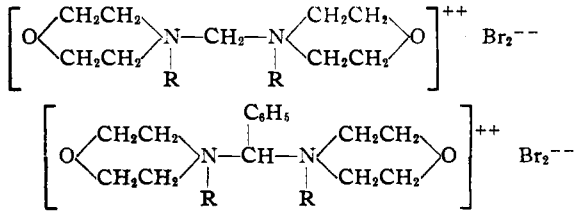
zal-di-morpholine, prepared according to M. Zief and J. P. Mason,[2] were condensed with a variety of alkyl bromides, such as *n*-butyl, *n*-heptyl, *n*-octyl, tetradecyl and hexadecyl bromides, to yield the corresponding symmetrical di-morpholinium di-bromides possessing the following structures



R: *n*-C_4H_9-, *n*-C_7H_{15}-, *n*-C_8H_{17}-, *n*-$C_{14}H_{29}$-, *n*-$C_{16}H_{33}$-

Procedure

To 0.01 mole of methylene- or benzal-di-morpholine was added 0.02 mole of the respective alkyl bromide and 11 ml. of 95% ethyl alcohol. The mixture was then gently refluxed for four hours. The reaction material when solid, or otherwise after removal of the alcohol by evaporation under reduced pressure, was crystallized from ethyl acetate; yields, 50–70%.

TABLE I

Compounds	Formulas	M. p., °C. (uncor.)	Analyses, % N Calcd.	Found
4,4′-Methylenedimorpholinium di-bromides				
4,4′-Di-*n*-butyl	$C_{17}H_{36}N_2O_2Br_2$	144 (dec.)	6.08	6.22
4,4′-Di-*n*-heptyl	$C_{23}H_{48}N_2O_2Br_2$	141 (dec.)	5.14	5.17
4,4′-Di-*n*-octyl	$C_{25}H_{52}N_2O_2Br_2$	143 (dec.)	4.89	4.95
4,4′-Di-tetradecyl	$C_{37}H_{76}N_2O_2Br_2$	165 (dec.)	3.78	3.90
4,4′-Di-hexadecyl	$C_{41}H_{84}N_2O_2Br_2$	180 (dec.)	3.52	3.31
4,4′-Benzaldimorpholinium di-bromides				
4,4′-Di-*n*-butyl	$C_{23}H_{40}N_2O_2Br_2$	174	5.22	5.34
4,4′-Di-*n*-heptyl	$C_{29}H_{52}N_2O_2Br_2$	153	4.51	4.63
4,4′-Di-*n*-octyl	$C_{31}H_{56}N_2O_2Br_2$	156	4.32	4.39
4,4′-Di-tetradecyl	$C_{43}H_{80}N_2O_2Br_2$	175	3.43	3.72
4,4′-Di-hexadecyl	$C_{47}H_{88}N_2O_2Br_2$	178	3.21	3.10

(2) M. Zief and J. P. Mason, *J. Org. Chem.*, **8**, 1 (1943).

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The System Sulfur Dioxide–Acetic Acid

BY W. H. SCHEUB AND C. R. MCCROSKY

To find out whether a definite compound of sulfur dioxide and acetic acid exists, the melting points of a series of mixtures of these two substances have been measured.

The acetic acid was dehydrated by successive treatments of glacial acetic acid with triacetyl borate and 20% oleum. In each treatment the mixture was first refluxed and then fractionally distilled. The mixtures were prepared by dissolving previously dried sulfur dioxide in the anhydrous acetic acid and were then frozen in a bath of solid carbon dioxide and acetone, or of liquid air. The melting points were determined by means of a chromel–alumel thermocouple and were accurate to well within ±0.1°. Melting points rather than freezing points were measured since the mixtures were found to supercool to a marked degree.

TABLE I

MELTING POINT DATA OF THE SYSTEM SULFUR DIOXIDE–ACETIC ACID

Mole % SO_2	M. p., °C.	Mole % SO_2	M. p., °C.
0.0	16.6	33.5	−40.4
7.7	11.5	46.4	−38.0
9.6	8.3	59.6	−38.7
13.1	−44.1	63.3	−39.2
18.0	−44.2	78.3	−75.6
24.7	−41.9	100.0	−72.7

The observations are collected in Table I and are represented graphically in Fig. 1.

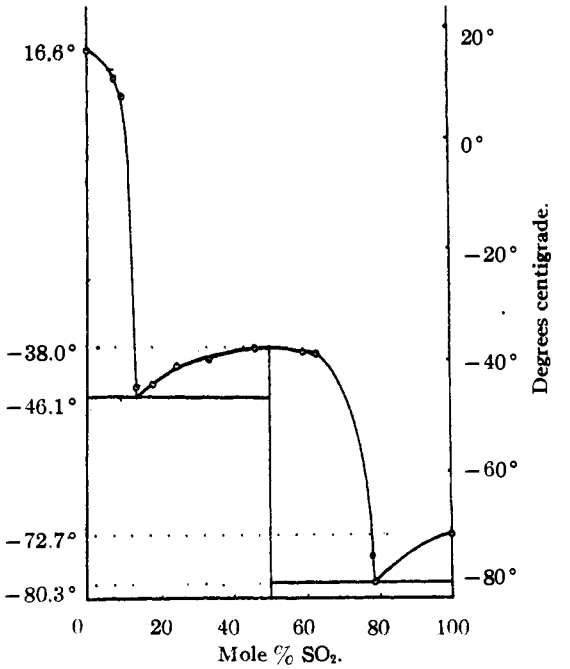

Fig. 1.

It can be seen that the melting point curve shows a maximum at 50 mole % sulfur dioxide and a temperature of −38°. The indicated compound, $HSO_2C_2H_3O_2$, solidifies in the form of thin, colorless flakes which show a tendency to sublime. The lower eutectic was established by a definite melting point at −80.3°; the upper eutectic at −46.1° was derived by extrapolation. These eutectic mixtures contained, respectively, 78.4 and 13.2 mole % of sulfur dioxide.

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