Distillation of Ammonium Formates

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It was found that cyclohexylammonium formate and *tert*-butyl-ammonium formate precipitate easily from a chilled solution of excess amine and 89% formic acid. These solids were distilled under vacuum without noticeable decomposition. With diethylamine, triethylamine or *N,N*-dimethylpropyldiamine, azeotropes were obtained containing the appropriate ammonium formate and formic acid. Under the same reaction conditions *n*-butylamine and isobutylamine gave constant boiling ternary mixtures of the corresponding butylammonium formate, butylformamide and formic acid. 3-Dimethylammoniumpropylformamide formate was isolated as a liquid.

FORMATES OF organic bases have been used variously, for example, as components of drilling fluids, as buffers in paper ionophoresis and ion exchange chromatography, as activators in rubber and plastics formulations, and as reagents in the Leuckhart reaction. However, only a few references could be found describing their synthesis. Data are reported on the synthesis and distillation of ammonium formates as an aid to studies requiring authentic samples.

It was found that cyclohexylammonium formate and *tert*-butylammonium formate each precipitate easily from a chilled solution of 89% formic acid and a twofold excess of amine. These solids were distilled under vacuum without noticeable decomposition. *Tert*-butylammonium formate sublimed slowly at 60° C. and 0.5 mm. When diethylamine, triethylamine or *N,N*-dimethylpropyldiamine were used azeotropes were obtained containing the appropriate ammonium formate and formic acid, Table I. Under the same reaction conditions *n*-butylamine and isobutylamine gave constant boiling mixtures of the corresponding butylammonium formate, butylformamide and formic acid. In the latter two cases dehydration of the ammonium formate to give a formamide occurs very readily and appears quite sensitive to reaction conditions. It was found that a distillation of excess isobutylamine from its mixture with formic acid performed at atmospheric pressure rather than under the vacuum of a water aspirator and keeping the rest of the procedure constant gave primarily isobutylformamide instead of the azeotrope.

In the vacuum distillation experiments using diethylamine or *N,N*-diethylpropanediamine and formic acid, the possibility that the azeotropes collected are ternary mixtures of formic acid, water and a formamide was eliminated on the basis of a comparison of the indices of refraction of the azeotropes with mixtures of authentic formamide, water and formic acid. Furthermore, vacuum distillation of equimolar mixtures of formic acid, water and 3-dimethylaminopropylformamide did not yield the previously isolated azeotrope but gave 3-dimethylammoniumpropylformamide formate.

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Table I. Ammonium Formates and Their Azeotropes

Ammonium Formates and Their Azeotropes	Formula	M.P.,[a] °C.	B.P.,[a] °C./Mm.	n^{t}_{D}	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Formic Acid, %[b] Calcd.	Formic Acid, %[b] Found
n-Butylammonium formate, *n*-butylformamide, formic acid	$7C_5H_{13}NO_2 \cdot 2C_5H_{11}NO \cdot 2CH_2O_2$	...	77/0.5	1.4370^{23}	50.0	49.9	10.3	10.2	8.2	7.6
Iso-butylammonium formate *iso*-butylformamide, formic acid	$5C_5H_{13}NO_2 \cdot 3C_5H_{11}NO \cdot 2CH_2O_2$	...	75/1.4	$1.4350^{24.5}$	51.0	51.6	10.3	10.3	9.3	9.1
tert-Butylammonium formate	$C_5H_{13}NO_2$	93	78/0.6	...	50.4	49.9	11.0	10.9	0	0
Cyclohexylammonium formate	$C_7H_{15}NO_2$	101	77/0.45	...	57.9	58.4	10.4	10.5	0	0
N,N-Dimethylpropane-diammonium formate, formic acid	$3C_7H_{18}N_2O_4 \cdot CH_2O_2$	...	96/0.6	$1.4750^{24.5}$	42.0	42.2	9.0	9.2	7.3	6.4
Diethylammonium formate, formic acid	$3C_5H_{13}NO_2 \cdot 2CH_2O_2$	...	61/0.55	$1.4240^{25.5}$	45.5	45.4	9.7	9.5	20.3	19.6
Triethylammonium formate formic acid	$5C_7H_{17}NO_2 \cdot 6CH_2O_2$	...	49/0.45	1.4279^{25}	48.7	48.7	9.7	9.5	27.3	28.3
3-Dimethylammonium-propylformamide formate	$C_7H_{15}N_2O_3$	...	91/0.65	1.4768^{23}	48.0	47.7	8.6	8.8	0	0

[a] Melting and boiling points are uncorrected. [b] Based on a calculation from potentiometric titration using a standard sodium hydroxide solution. The portion of the curve corresponding to undissociated formic acid was used in the calculation.