Greek Letters

γ	activity coefficient
ϕ	fugacity coefficient

Subscripts

1	more volatile component
2	less volatile component

Superscripts

E	excess property
L	liquid-phase property
V	vapor-phase property
^	mixture component property
'	vapor pressure

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Solubility of Sodium Formate in Aqueous Hydroxide Solutions

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Measurements were made of the solubility of sodium formate at 21, 60, and 120 °C in aqueous solutions of sodium hydroxide. The concentration of sodium hydroxide ranges from 0 to 40% w/w. The results are combined with data of binary systems to give a semiquantitative description of the total phase diagram HCOONa–NaOH–H_2O.

Today sodium formate is industrially made by contacting gaseous carbon monoxide with a warm solution of sodium hydroxide.

We are investigating the possibility of continuously separating the product from the reacting mixture. The initial concentration of sodium hydroxide and the reaction temperature suitable to precipitate sodium formate have been investigated.

As a part of this ongoing study, it is necessary to know the solubility of sodium formate in aqueous solutions of sodium hydroxide.

Experimental Section

Weighed amounts of NaOH and HCOONa ("Carlo Erba" pure reagents) were dissolved in deionized water and stored in a 250-cm^3 closed flask to prevent any evaporation; the flask was placed in an oil bath (±0.5 °C). After 6 h, no changes in concentrations could be observed. The results are based on samples taken 24 h after the preparation.

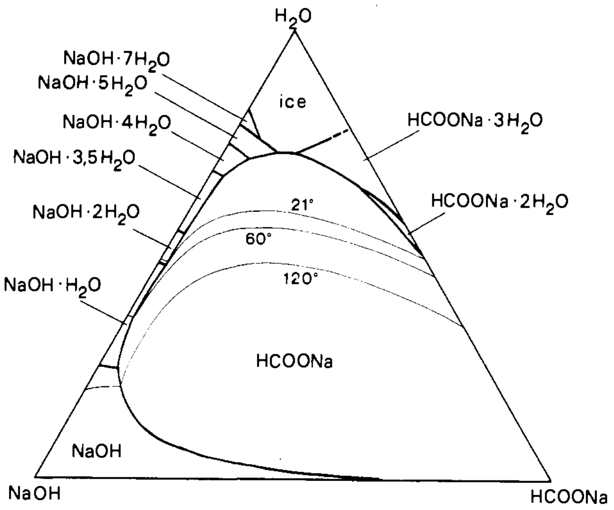

Figure 1. The phase diagram HCOONa–NaOH–H_2O (w/w).

The analysis of sodium formate was made on weighed samples of the supernatant liquid by potassium permanganate oxidation and by iodometric titration of permanganate excess. The analysis of sodium hydroxide was made by titration with newly titrated HCOOH solution (phenolphthalein indicator).

Table I. Liquid-Phase Composition (wt %) of Saturated Solutions of Sodium Formate[a]

T = 21 °C			T = 60 °C			T = 120 °C		
NaOH	HCOONa	H_2O	NaOH	HCOONa	H_2O	NaOH	HCOONa	H_2O
0.0	50.3	49.7	0.0	54.7	45.3	0.0	65.6	34.4
1.7	47.9	50.4	3.3	50.0	46.7	12.6	44.8	42.6
3.7	45.4	50.9	7.3	44.2	48.5	15.9	35.7	48.4
8.8	36.9	54.3	11.8	37.2	51.0	36.6	18.0	45.4
9.9	35.5	54.6	16.2	30.9	52.9	37.3	15.6	47.1
12.0	31.6	56.4	21.4	25.1	53.5	79.2	0.0	20.8
16.0	26.3	57.7	32.8	11.1	56.1			
18.6	22.2	59.2	40.6	5.1	54.3			
21.5	19.2	59.3	63.6	0.0	34.6			
24.1	16.0	59.9						
32.4	8.2	59.4						
35.5	5.6	58.9						
52.1	0.0	47.9						

[a] Error ±0.05.

Results and Discussion

The results are given in Table I. The liquid-phase composition is expressed in terms of weight percent; the solid phase is, in any investigated condition, anhydrous sodium formate. Three determinations were made at least for each data point and we have reported the significant digits of the averages.

Figure 1 is a semiquantitative description of the total phase diagram HCOONa–NaOH–H_2O based on the knowledge of binary systems (*1*, *2*). It is a triangle diagram in which the compositions on the coordinates are taken from literature data and the compositions at 21, 60, and 120 °C are experimental values. Similar to other phase diagrams (salt–strong base–water), a large range of pure solid HCOONa existence can be predicted.

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NEW COMPOUNDS

Hydrazinophosphorus Compounds. 2. Mass Spectra of Diphenylphosphino- and Diarylphosphorohydrazides

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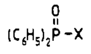
The mass spectra of diphenylphosphino- and diarylphosphorohydrazides have been examined. Diphenylphosphinohydrazide (Ia) behaves in a manner comparable to derivatives having the diphenylphosphinyl moiety (Ib–e). The molecular ion of diarylphosphorohydrazides (IIa,b), on the other hand, undergos fragmentation to give the corresponding phenol as a base peak.

Whereas the behavior of organophosphorus compounds under electron impact has been extensively investigated, this is clearly reflected in the recent review published by Granoth in this field (*3*), a general study on the hydrazinophosphorus compounds has not been reported hitherto.

As a corollary to our interest in the reactivity of hydrazinophosphorus compounds (*2*), we wish to report the behavior of diphenylphosphino- and diarylphosphorohydrazides under electron impact.

It has been well established (*4*) that although the phosphine oxides (Ib,c) and the phosphinate (Id) give ions of mass 201 as base peak, arising by the loss of group X (I), the spectrum of benzylphosphinate (Ie) has ions of mass 202 as base peak, arising by the elimination of benzaldehyde from the molecular ion and the 201 ion is of rather low intensity (15%).



$$(C_6H_5)_2P(=O)-X$$

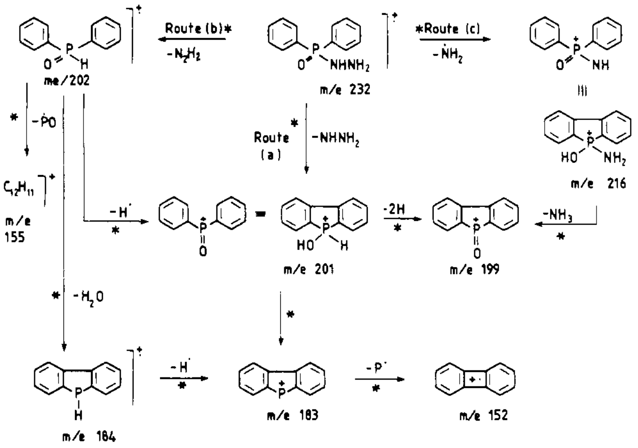
(I)

a; X = $NHNH_2$
b; X = H d; X = OC_6H_5
c; X = $CH_2C_6H_5$ e; X = $OCH_2C_6H_5$

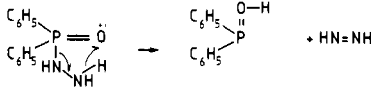
The most interesting feature of the mass spectrum of diphenylphosphinohydrazide (Ia) (Figure 1) is that it shows both ions 201 and 202, the former ions being the base peak and the latter the next most abundant (90%). Most of the peaks observed at the lower mass result from fragmentation of these two species (*7*).

A common feature between the hydrazide (Ia) and the ester (Ie) is the presence of hydrogens on an atom β to phosphorus.

Scheme I



Both yield the *m*/*q* 202 ion as a base peak. Compounds without β hydrogens do not behave similarly. A possible mechanism for the formation of *m*/*q* 202 ion might be through a hydrogen transfer in the molecular ion via a five-membered cyclic transition state as follows:



The molecular ion of the hydrazide (Ia) undergoes fragmentation via three routes; the decomposition pathways which account for all the abundant ions and metastable transitions (marked with an *) are summarized in Scheme I.

Route (a) involves the formation of the phosphacylium ion (M − 31) by the loss of the hydrazine moiety. In this case it behaves like the benzylphosphine oxide (Ic) and the phenoxyphosphinate (Id). This route is supported by the appearance of a weak metastable peak at *m*/*q* 174.5. Route (b) involves the formation of 202 ion (M − 30), similar to the behavior of the benzyloxy ester (Ie). The appearance of a strong metastable ion at *m*/*q* 176.1 supports this route. This indicates that both 201 and 202 ions