

## The Generation of *N*-Alkylformamides from Synthesis Gas and Ammonia

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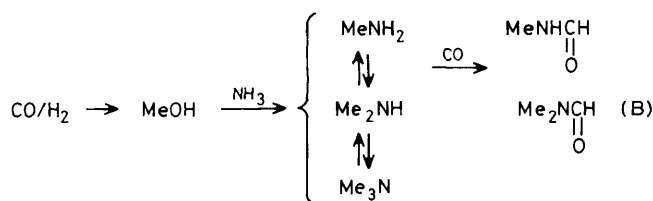
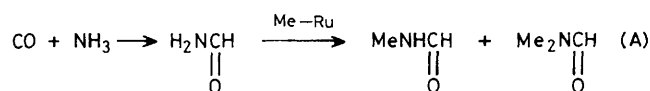
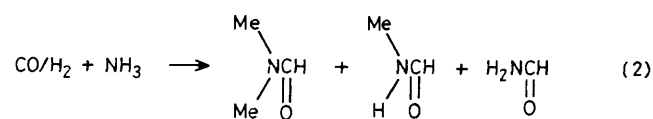
*N,N*-Dimethylformamide and *N*-methylformamide have been prepared from synthesis gas plus ammonia *via* ruthenium 'melt' catalysis.

There are already numerous disclosures in the literature illustrating the synthesis of *N*-substituted formamides, particularly *N,N*-dialkylformamides, from the corresponding alkylamines plus carbon monoxide (equation 1).<sup>1</sup> A range of catalysts may be employed, including metallic alkoxides,<sup>2</sup> cobalt,<sup>1a,3</sup> iron,<sup>1d</sup> and ruthenium-containing compounds,<sup>1b</sup> and reaction (1) is the basis of the Leonard process for producing *N,N*-dimethylformamide.<sup>4</sup>



Here we describe a new route to the synthesis of *N,N*-dimethylformamide using synthesis gas and ammonia as the only chemical building blocks (equation 2). The class of catalysts selected for this study are ruthenium 'melt' catalysts, comprising one or more ruthenium oxide, salt, and complex species, dispersed in various phosphonium salts. This class of 'melt' catalyst has been previously demonstrated by us to be particularly effective for the conversion of CO/H<sub>2</sub> into alkanols and diols<sup>5</sup> and for the generation of carboxylic acids.<sup>6</sup> In this communication, however, we describe our initial results on a new scheme (equation 2) for the selective production of formamide and its *N*-alkyl derivatives, but particularly *N,N*-dimethylformamide and *N*-methylformamide, by the reaction of synthesis gas with ammonia.

Table 1 illustrates the generation of *N,N*-dimethylformamide (DMF) and *N*-methylformamide (MMF), plus formamide, using different ruthenium catalyst precursors dispersed in tetrabutylphosphonium bromide and iodide. In the first entry, treatment of the Ru<sub>3</sub>(CO)<sub>12</sub>-Bu<sub>4</sub>PI dispersion with CO/H<sub>2</sub>/NH<sub>3</sub> at 220 °C for 4 h yielded a liquid product comprising 24% DMF and 43% MMF. The liquid yield increase was 112%. Entry 2 is for twice the quantity of ruthenium catalyst and ammonia coreactant, and here for-



Scheme 1

mamides constitute 84 wt% of the liquid product, with DMF providing 48 wt% of the formamide fraction. Further improvements in preparative technique are realized in entry 3 where DMF makes up 59% of the total liquid product, and in entry 5 where the overall selectivity to formamide derivatives is 96 wt%.

DMF synthesis (equation 2) may be realized over a broad range of operating conditions (180–280 °C, 100–430 atm), although improved selectivity to ΣNMF (DMF plus MMF) is generally favoured, relative to formamide itself (ΣF), by high partial pressures of syngas (< first order) and by operating temperatures of ≥180 °C (see Figure 1). Preferred temperature–pressure conditions are, in fact, somewhat analogous to those employed previously by us for ruthenium 'melt' catalysed methanol generation;<sup>5</sup> at 280 °C molar selectivity to ΣNMF (ΣNMF/ΣNMF + ΣF) exceeds 90 mole % and the ΣNMF/ΣF ratio is *ca.* 11 (Figure 1).

At least two reaction pathways may be postulated for the formation of ΣNMF (MMF + DMF). The first (Scheme 1, path A) involves initial reaction of CO with ammonia to give formamide, followed by methylation with Me–Ru generated *via* ruthenium-catalysed CO hydrogenation.<sup>5</sup> An alternative pathway would proceed *via* initial formation of methanol from

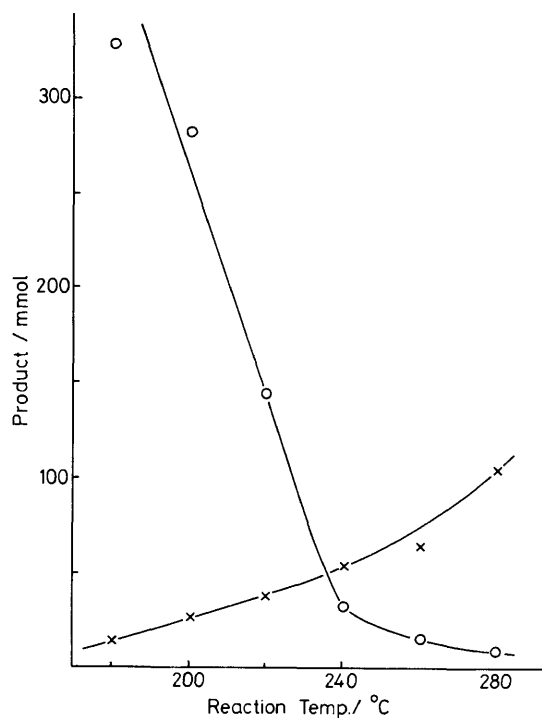


Figure 1. The effect of operating temperature on the synthesis of DMF, MMF, and formamide from CO/H<sub>2</sub>/NH<sub>3</sub>. ΣNMF, x; ΣF, o. Synthesis conditions as per Table 1. Catalyst composition: Ru<sub>3</sub>(CO)<sub>12</sub>, 2.0 mmol Ru; Bu<sub>4</sub>PBr, 10.0 g.

**Table 1.** Synthesis of formamides from synthesis gas and ammonia.<sup>a</sup>

Entry	Catalyst precursor	Ru (mmol)	NH <sub>3</sub> (mmol)	Time (h)	Liquid product composition (wt%) <sup>b,c,d,e</sup>			Liquid yield (wt%) <sup>f</sup>	Turnover frequency <sup>g</sup>
					ΣNMF		ΣF H <sub>2</sub> NCHO		
					Me <sub>2</sub> NCHO	MeNHCHO			
1	Ru <sub>3</sub> (CO) <sub>12</sub> -Bu <sub>4</sub> PI	2.0	400	4	23.9	42.7		112	15
2	Ru <sub>3</sub> (CO) <sub>12</sub> -Bu <sub>4</sub> PI	4.0	800	4	40.5	17.7	25.6	92	10
3	Ru <sub>3</sub> (CO) <sub>12</sub> -Bu <sub>4</sub> PBr	2.0	400	18	59.1	12.7	10.9	83	
4	Ru <sub>3</sub> (CO) <sub>12</sub> -Bu <sub>4</sub> PBr	2.0	400	4	13.6	21.1	59.6	105	7
5	RuCl <sub>3</sub> -Bu <sub>4</sub> PBr	2.0	400	4	25.0	28.5	42.5	109	12
6	Ru(acac) <sub>3</sub> -Bu <sub>4</sub> PBr <sup>h</sup>	2.0	400	4	22.3	14.4	53.2	101	8

<sup>a</sup> Standard catalyst charge: Ru, 2.0–4.0 mmol; Bu<sub>4</sub>PX, 10.0 g; operating conditions: 220 °C; 430 atm constant pressure; CO/H<sub>2</sub> (1:1).

<sup>b</sup> Analysis of crude liquid product by g.l.c. using a modified silicon column, programmed from 40–270 °C at 20 cm<sup>3</sup> min<sup>-1</sup> He flow.

<sup>c</sup> Formamide products were also identified by g.l.c. trapping, n.m.r. analysis, g.l.c.–mass spectra, and by g.l.c.–Fourier transform i.r.

<sup>d</sup> Other identified products include: H<sub>2</sub>O, Me<sub>3</sub>N, *N,N*-methylethylformamide, *N*-methylacetamide, *N,N*-dimethylacetamide, and CO<sub>2</sub>.

<sup>e</sup> Ammonium hydrogen carbonate and ammonium carbamate were isolated during product recovery and distillation. <sup>f</sup> Liquid yield (wt%) calculated on the basis of the total weight of catalyst charged. <sup>g</sup> Turnover frequency estimated on the basis of mmol of total *N*-alkylformamide products (ΣNMF)/g atom Ru/h. <sup>h</sup> acac = MeCOCHCOMe.

**Table 2.** Formamides from synthesis gas.<sup>a</sup>

Entry	Catalyst precursor	Added reactants	Product composition (mmol)			Reaction rate ΣNMF/ g atom Ru/h	Ratio ΣNMF/ΣF
			Me <sub>2</sub> NCHO	MeNHCHO	H <sub>2</sub> NCHO		
7	Ru <sub>3</sub> (CO) <sub>12</sub> -Bu <sub>4</sub> PBr	NH <sub>3</sub>	20.3	38.9	144	7.4	0.41
8	" "	NH <sub>3</sub> + MeOH <sup>b</sup>	41.3	152	63.8	24.2	3.0
9	" "	NH <sub>3</sub> + [ <sup>13</sup> C]MeOH <sup>c</sup>	12.4 <sup>d</sup>	54.1 <sup>d</sup>	127	8.3	0.53
10	" "	NH <sub>3</sub> + H <sub>2</sub> NCHO <sup>e</sup>	1.8	11.8	72.6 <sup>f</sup>	1.7	0.19
11	" "	Me <sub>3</sub> N	3.2	2.2			

<sup>a</sup> Catalyst charge: Ru, 2.0 mmol; Bu<sub>4</sub>PBr, 10.0 g; operating conditions as in Table 1. <sup>b</sup> Added MeOH, 200 mmol. <sup>c</sup> Added [<sup>13</sup>C]MeOH, 31 mmol.

<sup>d</sup> <sup>13</sup>C-enrichment at the methyl positions only. <sup>e</sup> Added H<sub>2</sub>NCHO, 100 mmol, <sup>f</sup> Represents the additional H<sub>2</sub>NCHO formed, beyond that charged.

CO/H<sub>2</sub>,<sup>5</sup> to be followed by the production of methylamines and subsequent carbonylation (Scheme 1, path B).

Consistent with path A, Hieber *et al.* have reported that ammonia and ruthenium carbonyl iodide react to produce free and co-ordinated formamide under extremely mild conditions (> -30 °C).<sup>7</sup> However, our experimental data appear more in keeping with ΣNMF formation *via* path B. We find, for example, that the addition of methanol in entry 8, Table 2, brings about a three-fold increase in the rate of ΣNMF formation and significantly improves the selectivity to ΣNMF (*e.g.* ΣNMF/ΣF ratio, 0.4 → 3.0). Furthermore, the introduction of [<sup>13</sup>C]MeOH (entry 9) produces both DMF and MMF with <sup>13</sup>C-enrichment only at the methyl positions. Selectivity to ΣNMF may also be improved as a function of reaction time (*cf.* entries 3 and 4); these and similar data may be interpreted in terms of two or more consecutive steps to the formation of ΣNMF. However, the presence of added formamide (entry 10) dramatically reduces the rate of ΣNMF formation (by a factor of *ca.* four), as well as lowering the ΣNMF selectivity. No liquid product is observed in the absence of ruthenium.

Homogeneous ruthenium-catalysed transalkylation of amines is well documented in the literature,<sup>8</sup> and it is likely that the three methylamines of path B are in dynamic equilibrium under the conditions of Table 1. We can, in fact, generate some DMF from syngas plus Me<sub>3</sub>N alone, as seen in

entry 11, Table 2. Trimethylamine is consistently detected as the principal organic by-product (Table 1). This tertiary amine could originate both from ammonia methylation (as depicted in path B), or through ruthenium-catalysed hydrogenation of the DMF fraction in the presence of syngas.<sup>9</sup> Only trace quantities of another by-product, CO<sub>2</sub>, are normally detected, but a competing ruthenium-catalysed water-gas shift reaction<sup>5</sup> is evidently occurring in view of the formation of substantial quantities of ammonium hydrogen carbonate (Table 1).

The ligand spatial arrangement around ruthenium during this catalysis has not yet been fully defined. Spectral data suggest the presence of the anionic ruthenium carbonyl halides [Ru(CO)<sub>3</sub>Br<sub>3</sub>]<sup>-</sup> and [Ru(CO)<sub>2</sub>Br<sub>4</sub>]<sup>2-</sup>. However, there are no dramatic improvements in either formamide productivity or ΣNMF selectivity upon the addition of monodentate or chelating N- or P-donor ligands, *e.g.* 2,2'-bipyridyl, Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>, and PBu<sub>3</sub>, to the ruthenium catalyst component, or upon the use of bimetallic systems such as Ru in combination with Co, Fe, Rh, and Mn (added as their carbonyls or carbonyl derivatives). We see no evidence of isocyanate by-products<sup>10</sup> under the conditions of Table 1 and no direct evidence for the formation of coupling products such as ureas or oxamides.<sup>1b</sup>

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