# Catalytic Aminomethylation of Alkenes in a Dimethylformamide Medium

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**Abstract**—The hydroaminomethylation of alkenes with dimethylamine catalyzed by rhodium and ruthenium complexes in a dimethylformamide medium under synthesis-gas pressures of 2 MPa has been studied. It has been shown that the combined use of these metals leads to a significant increase in the rate of formation of amines and selectivity for *n*-alkyldimethylamine. It has been found that the reaction can proceed with dimethylformamide used as an aminating agent without the addition of dimethylamine.

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Dimethylalkylamines with ten or more atoms in the hydrocarbon chain are the main type of feedstock for the synthesis of cationic and nonionic surfactants based on N-oxides. Conventional manufacturing routes for these amines involve either high-temperature transformations of alcohols and dimethylamine on heterogeneous catalysts or the production of monochlorinated derivatives via the radical hydrochlorination of olefins [1]. In the latter case, the second stage of the process includes the reaction with dimethylamine, which gives hydrochloride, and the isolation of dimethylalkylamine. The multistage nature of the processes and their noncompliance with the current environmental protection requirements necessitate a search for new methods of manufacturing these products from the basic petrochemical feedstock, i.e., olefins. One of these methods is hydroaminomethylation.

This process is a sequence of reactions that includes the hydroformylation of an unsaturated compound and the subsequent reductive amination of the resulting aldehydes. The general reaction scheme, which covers the formation of both the main products (amines) and byproducts, can be represented as follows:



General scheme of the hydroaminomethylation of alkenes.

Hydroaminomethylation is mediated by transition metal complexes with phosphorus-containing ligands, mostly alkyl and aryl phosphines. Rhodium-containing catalyst systems are most widely used; they make it possible to implement hydroaminomethylation for terminal alkenes with a short and long carbon chain, aliphatic unsaturated compounds with different functional groups in their structure, styrenes, diphenylethylenes, and internal olefins [2-4]. The process was conducted in various solvents (THF, toluene, methanol) in order to increase the homogeneity of the system. The tandem hydroaminomethylation of higher terminal alkenes with the participation of an aqueous solution of dimethylamine under conditions of a twophase catalysis was also studied in [5-9]. It was shown that the formation of amines can proceed at a high rate and with a high selectivity.

It should be noted that in all these cases, one of the main limitations to the implementation of the reaction was a low solubility of dimethylamine in nonpolar media and, accordingly, a low efficiency of mass transfer between the aqueous solution of dimethylamine and alkene in two-phase systems. The use of toluene or methanol as solvents requires significant energy consumption for the isolation of reaction products.

In this study, we propose a modified hydroaminomethylation system that involves a dimethylamine solution in dimethylformamide (DMF) as a reagent. This solvent provides an easy mixing of reagents and is the product of the carbon monoxide reaction with dimethylamine. During the course of the hydroaminomethylation reaction, equilibrium between dimethylamine, DMF, and synthesis gas is established in the system and, as such, can significantly increase the efficiency and adaptability of the proposed process.

#### **EXPERIMENTAL**

(Acetylacetonato)dicarbonylrhodium(I) (Rh(acac)  $(CO)_2$ ) synthesized as described in [10] was used as a source of rhodium. Triruthenium dodecacarbonyl Ru<sub>3</sub>(CO)<sub>12</sub> was prepared according to [11]. Nonene-1, octene-1, decene-1, dodecene-1, and triphenyl phosphite were distilled under vacuum in an argon stream. DMF was dried over calcinated molecular sieves 3A and then distilled in an argon stream.

The hydroaminomethylation reaction was run in a Parr Instrument autoclave (volume of 0.1 L) equipped with a turbine stirrer (1500 rpm), a pressure sensor, and temperature control devices under a synthesis gas pressure of 0.6 to 4 MPa ( $H_2/CO = 1$ ) at a temperature of 80–170°C. The reaction was conducted under constant stirring for a predetermined time (0.5 to 6 h).

Gas-liquid chromatographic analysis was performed using the internal standard method with a Hewlett Packard chromatograph with a FID and a 30-m capillary column coated with the SE-30 phase with a temperature program of  $100-230^{\circ}$ C and helium as a carrier gas. The products were identified by mass spectrometry using a Finnigan MAT ITDS GC–MS instrument. The ionization energy was 70 eV; the source temperature was 220°C. The mixture components were separated on a 30-m SE-30 capillary column with an inner diameter of 0.25 mm using temperature programming from 100 to 300°C.

# **RESULTS AND DISCUSSION**

Hydroaminomethylation Mediated by Rhodium-Containing Catalyst Systems

The hydroaminomethylation was carried out using a dimethylamine solution in DMF under synthesis gas pressures of up to 4 MPa at a temperature of 80-160°C with  $Rh(acac)(CO)_2$  as a rhodium source. Triphenylphosphine was used as a phosphorus-containing ligand. In the case of hydroaminomethylation of nonene-1 catalyzed by  $Rh(acac)(CO)_2$  with large excess PPh<sub>3</sub>, the complete conversion of the substrate is observed even at 80°C (Table 1). Aldehydes, isomeric *n*-alkenes, and nitrogen compounds, i.e., enamines and tertiary amines with a branched and linear alkyl substituent, are formed during the reaction. The amount of unreacted aldehydes in the amination hardly depends on the syngas pressure at this temperature. The predominance of enamine in the nitrogencontaining products is apparently attributed to a low rate of hydrogenation of the internal double bond in its molecule under the experimental conditions.

A significant increase in the yield of amines is observed at 130°C: the reaction products have almost no aldehydes after 6 h of the process under 2.0 MPa. The maximum yield of amines (73%) was recorded when the pressure was increased to 4.0 MPa; in this case, the selectivity for *n*-decyldimethylamine was 58%, and that for the products formed from *n*-aldehyde was 61%.

A further increase in temperature leads to an increase in the olefin-to-amine conversion rate; at 170°C, the yield is 53% for *n*-decyldimethylamine and 20% for isoamines within 3 h (Fig. 1). In addition, enamines are almost absent from the mixture as well as aldehydes. The amount of the product nonane significantly increases at  $150-170^{\circ}$ C.

A study of the dependence of the yields of hydroaminomethylation products on the reaction time at 150°C and a pressure of 2.0 MPa showed that under these conditions, the main amount of amines is formed within 1 h and an increase in the experiment time has almost no effect on the ratio of enamines and amines (Table 2). Apparently, the hydrogenation of enamines can be considered the rate-determining step of the process. An increase in the hydrogen concentration up to a ratio of  $H_2 : CO = 2$  makes it possible to significantly increase the reaction rate; in this case, the

Pressure, MPa	Time h	Conver- sion, %	Yield, wt %								
	Time, n		aldehydes	1	enamines	2	amines	3	olefins		
				80	°C						
0.6		99	57	47	22	22	2	2	19		
2	3	98	57	41	27	27	5	5	11		
4		98	51	33	32	32	5	5	12		
	130°C										
0.6	3	97	12	8	15	12	27	27	54		
	1	98	24	13	11	10	48	44	17		
2	3	99	16	9	22	16	51	45	11		
	6	99	1	—	19	—	69	51	11		
4	3	99	7	4	12	2	73	58	8		

**Table 1.** Hydroaminomethylation of nonene-1 in the presence of a Rh catalyst system ( $H_2/CO = 1$ , [Rh] = 2.8 mmol/L, substrate/catalyst = 160, [PPh<sub>3</sub>]/[Rh] = 214)

Note: (1) n-decanal; (2) decene-1-yl-dimethylamine; and (3) n-decyldimethylamine.

yield of amines is 80%, and the selectivity for decyldimethylamine remains the same (81%).

It should be noted that all these results were obtained under conditions of excess triphenylphosphine. In the absence of a phosphorus-containing ligand at 80°C, the reaction does not occur; at 150°C, the conversion is 35% and the main products are isononenes (16%) and nonane (17%).

An increase in the P/Rh ratio leads to an increase in the substrate conversion and to a change in the chemoselectivity of the process: the yield of amines increases. This is most clearly evident at 150°C (Table 3). Apparently, at low triphenylphosphine concentrations, the solution mostly contains rhodium complexes with dimethylamine, which do not exhibit activity in hydroformylation. An increase in the phosphorus ligand concentration leads to a shift in the equilibrium in the solution in the direction of phosphine-containing complexes which are active species.

The hydroaminomethylation of nonene-1 also occurs in the presence of a rhodium catalyst system with tri(o-tolyl)phosphine, tricyclohexylphosphine, and triphenyl phosphite (Fig. 2). In the case of excess triphenylphosphine, an almost complete conversion of the substrate was observed; however, large amounts of the byproducts isononenes (27%) and nonane (16%) are formed along with amines (39%). The cata-



Fig. 1. Hydroaminomethylation of nonene-1 at different temperatures ([Rh] = 2.8 mmol/L;  $[PPh_3]/[Rh] = 214.2$  MPa;  $H_2/CO = 1.3$  h).

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	1										
Time, h	Conver- sion, %	Reaction mixture composition, wt %									
		aldehydes	1	enamines	2	amines	3	isononenes	nonane		
0.5	73	21	15	17	17	17	16	7	11		
1	93	5	2	17	5	53	40	7	11		
2	95	6	2	15	6	55	42	8	11		
3	95	5	2	14	3	57	46	8	11		
6	99	2	2	17	3	58	47	8	14		
3*	99	_	—	4	—	80	65	7	8		
				1							

**Table 2.** Effect of reaction time on the composition of nonene-1 hydroaminomethylation products ( $H_2/CO = 1.2$  MPa; 150°C; [Rh] = 2.8 mmol/L; substrate/catalyst = 160; [PPh<sub>3</sub>]/[Rh] = 214)

Note: (1) n-decanal; (2) decene-1-yl-dimethylamine; and (3) n-decyldimethylamine.

**Table 3.** Hydroaminomethylation of nonene-1 at different  $[PPh_3]/[Rh]$  ratios  $(H_2/CO = 1.2 \text{ MPa}; 3 \text{ h}; [Rh] = 2.8 \text{ mmol/L};$  substrate/catalyst = 160)

No.	P/Rh	Conver- sion, %	Reaction mixture composition, wt %							
	1 / Kii		aldehydes	1	enamines	2	amines	3	isononenes	nonane
80°C										
1	0	1	_	_	_	_	_	_	_	1
2	20	3	—	—	1	1	1	1	-	1
3	214	98	57	41	27	27	5	5	7	2
150°C										
4	0	35	_	_	_	_	2	2	16	17
5	5	51	—	—	3	—	34	25	5	9
6	20	71	_	—	2	_	58	43	4	7
7	214	95	5	2	14	3	57	46	8	11

Note: (1) n-decanal; (2) decene-1-yl-dimethylamine; and (3) n-decyldimethylamine.

lyst system with triphenyl phosphite exhibited a low activity; this can be attributed to a partial hydrolysis of the ligand under the reaction conditions.

## Hydroaminomethylation Mediated by Mixed Rhodium–Ruthenium Catalyst Systems

An alternative to an increase in the hydrogen pressure relative to carbon monoxide for increasing the hydrogenation rate of enamines can be doping the system with metal complexes that are more active in hydrogenation in the presence of amines than rhodium compounds. Published data [12–14] show that one of the most promising components of a catalyst system can be ruthenium; its compounds with donor nitrogen-containing ligands are known catalysts for the hydrogenation of functional compounds. We selected Ru<sub>3</sub>(CO)<sub>12</sub> as a source of ruthenium. Our data

(Table 4) show that at 80°C, the introduction of a ruthenium compound into the catalyst system has little effect on the results of hydroaminomethylation; only the yield of enamines increases from 27 to 38% within a reaction time of 3 h (Table 4, rows 1, 6). At the same time, both the total yield of amines and the selectivity for the normal product significantly increase at 150°C. The predominant formation of amines with the selectivity for *n*-decyldimethylamine of 80–86% is observed even for 1 h (Table 4, rows 9– 14). Experiments with additional hydrogen supply (Table 4, rows 10, 11) showed that the maximum selectivity for *n*-amine (86%) in this case was observed under a pressure of 2.0 MPa, and the yield of amine increased to 92% under 4.0 MPa (selectivity of 80%). The admixture of water to the reaction system led to a decrease in the yield of amines, whereas the selectivity



Fig. 2. Hydroaminomethylation of nonene-1 in the presence of different ligands ([Rh] = 2.8 mmol/L; [PPh<sub>3</sub>]/[Rh] = 214.2 MPa; H<sub>2</sub>/CO = 1.3 h).

did not decrease (Table 4, rows 12, 9). Thus, ruthenium additives in this system give the possibility to significantly increase the rate of formation of amine.

An increase in the total reaction rate and the prevalence of amines in the reaction products confirm the conclusion that the rate-limiting step for the overall hydroaminomethylation reaction under these conditions is the hydrogenation of enamines. Thus, an optimum combination of activity and selectivity is achieved using the Rh(acac)(CO)<sub>2</sub> + Ru<sub>3</sub>(CO)<sub>12</sub> +

**Table 4.** Hydroaminomethylation of nonene-1 in the presence of the Ru/Rh catalyst system ( $H_2/CO = 1.2$  MPa; [Rh] = 2.8 mmol/L; substrate/catalyst = 160; [PPh<sub>3</sub>]/[Rh] = 214)

No	Ru/Rh	h Time h	Conver-	Reaction mixture composition, wt %								
110.	Ku/ Kii	Time, ii	sion, %	aldehydes	1	enamines	2	amines	3	isononenes	nonane	
	80°C											
1	0	3	98	57	41	27	27	5	5	7	2	
2	0	6	99	39	19	35	34	21	16	1	2	
3		3	89	46	18	32	32	5	3	3	3	
4	6	6	97	45	25	20	20	25	23	3	4	
5		6 <sup>a</sup>	99	24	15	33	33	37	34	2	3	
6	12	3	91	41	29	38	38	7	7	2	3	
7	12	6	97	40	21	29	29	23	21	2	3	
					150	)°C						
8	0	1	93	5	2	17	5	53	40	7	11	
9	3	1	99	_	_	2	_	83	69	6	8	
10	3 <sup>a</sup>	1	99	_	_	2	—	84	72	5	8	
11	3 <sup>a,b</sup>	1	99	_	—	2	—	92	74	2	3	
12	3 <sup>c</sup>	1	99	2	2	3	—	78	65	7	9	
13	6	1	99	_	_	2	—	83	67	6	8	
14	12	1	99	_	_	3	_	83	67	5	8	
	170°C											
15	3	1	93	0		2	0	73	59	8	10	

<sup>a</sup>  $H_2/CO = 2$ ; <sup>b</sup> 4 MPa; <sup>c</sup> Experiment with the addition of water ( $H_2O/HNMe_2 = 2$ ).

Note: (1) n-decanal; (2) decene-1-yl-dimethylamine; and (3) n-decyldimethylamine.

**Table 5.** Hydroaminomethylation of linear alkenes ( $H_2/CO = 1.2 \text{ MPa}$ ; 150°C; 1 h; [Rh] = 2.8 mmol/L; substrate/cata-lyst = 160; [PPh<sub>3</sub>]/[Rh] = 214)

Alkene	Conversion, %	Yield of amines, %	S*, %
Octene-1	98	82	87
Nonene-1	99	83	83
Decene-1	99	80	85
Dodecene-1	99	91	84

\* Selectivity for *n*-alkylamines.

PPh<sub>3</sub> bimetallic system in the process at  $150^{\circ}$ C, 2 MPa (H<sub>2</sub>/CO = 2), Ru/Rh = 3, and P/Rh = 214.

High yields of amines with a linear alkyl substituent were also recorded under these conditions for some  $C_8-C_{12}$  terminal alkenes (Table 5), with the length of the hydrocarbon chain having no effect on the reaction rate.

### Hydroaminomethylation with DMF as Aminating Agent

Taking into account that DMF can be decomposed into dimethylamine and carbon monoxide in the presence of platinum group metal complexes according to published [15–17], we studied the reaction of nonene-1 with synthesis gas in a DMF medium without the addition of dimethylamine. Table 6 shows the results obtained using the Rh(acac)(CO)<sub>2</sub> + PPh<sub>3</sub> catalyst system. The formation of free amine was confirmed in experiments on the decomposition of DMF in a synthesis gas medium in the presence of  $Rh(acac)(CO)_2$ and  $Rh(acac)(CO)_2 + PPh_3$  at a temperature of 150°C: the dimethylamine concentration was 12% within 3 h.

In the case of reaction conducted under 0.6 MPa at 80°C, the formation of amination products, i.e., decene-1-yl-dimethylamine and amines (*n*-decyldimethyl- and isoamines), was observed (Table 6, rows 1–3). An increase in temperature leads to an increase in their yield: at 130°C, their yields were as high as 16 and 30%, respectively, within 6 h (4 MPa) (Table 6, row 7). In the case of the Ru–Rh catalyst system, we managed to increase the yield of amines to 43% (of which *n*-decyldimethylamine made 38%) (Table 6, rows 8, 9).

Thus, it can be concluded that the combined use of a bimetallic rhodium—ruthenium catalyst system leads to a significant increase in both the rate of formation of amines and selectivity for *n*-alkyldimethylamine. It has been found that the reaction can proceed with DMF as an aminating agent without the addition of dimethylamine.

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Table 6.	Reaction of nonene-1 with synthesis	gas in a DMF medium (	$H_2/CO = 1; 150^{\circ}C; 3 h;$	[Rh] = 2.8  mmol/L;  sub-
strate/ca	$talyst = 160; [PPh_3]/[Rh] = 214)$		-	

No	Pressure,	sure, Conversion,	Yield, wt %							
100.	MPa	%	aldehydes	1	enamines	2	amines	3		
	80°C									
1	0.6	99	84	64	3	3	6	6		
2	2	99	89	65	1	1	7	7		
3	4	99	86	60	3	3	7	7		
	130°C									
4	0.6	95	21	13	11	11	20	19		
5	2	99	57	39	10	10	17	16		
6	4	98	61	35	12	12	16	14		
7	4	96 <sup>a</sup>	35	13	16	16	30	24		
150°C										
8	4	98 <sup>a</sup>	34	6	7	6	35	29		
9		99 <sup>b</sup>	20	7	16	9	43	38		

<sup>a</sup> 6 h; <sup>b</sup> 6 h, [Ru]/[Rh] = 6.

Note: (1) n-decanal; (2) decene-1-yl-dimethylamine; and (3) n-decyldimethylamine.

# REFERENCES

- 1. H. Kimura, Catal. Rev. Sci. Eng. 53, 1 (2011).
- 2. P. Eilbracht, L. Barfacker, C. Buss, et al., Chem. Rev. **99**, 3329 (1999).
- M. Ahmed, A. M. Seayad, R. Jackstell, and M. Beller, J. Am. Chem. Soc. 125, 10311 (2003).
- 4. D. Crozet, M. Urrutigoïty, and P. Kalck, Chem-CatChem 3, 1102 (2011).
- Y. Wang, C. Zhang, M. Luo, H. Chen, X. J. Li, Arkivoc 2008 (xi), 165 (2008).
- Y. Y. Wang, M. M. Luo, Y. Z. Li, H. Chen, X. J. Li, Appl. Catal. A: Gen. 272, 151 (2004).
- Y. Y. Wang, M. M. Luo, Y. Z. Li, et al., Chin. Chem. Lett. 15, 774 (2004).
- Y. Wang, J. Chen, M. Luo, et al., Catal. Commun. 7, 979 (2006).
- 9. A. Behr, M. Becker, and S. Reyer, Tetrahedron Lett. **51**, 2438 (2010).

- Yu. S. Varshavskii and T. G. Cherkasova, Zh. Neorg. Khim. 1, 1701 (1967).
- 11. Hanbuch der präporativen anorganischen Chemie, Ed. by G. Brauer, (Ferdinand Enke, Stuttgart, 1981; Mir, Moscow, 1986), p. 1944.
- 12. T. Baig, J. Molinier, and P. Kalck, J. Organometall. Chem **455**, 219 (1993).
- D. E. Fogg and E. N. Santos, Coord. Chem. Rev. 248, 2365 (2004).
- 14. K. Murata, A. Matsuda, and T. Masuda, J. Mol. Catal. 23, 121 (1984).
- 15. M. Dickmeis and H. Ritter, Macromol. Chemi. Phys. **210**, 776 (2009).
- 16. J. Uchisawa, T. Nanba, S. Masukawa, and A. Obuchi, Catal. Lett. **98**, 103 (2004).
- E. Kahrovic, P. Orioli, B. Bruni, M. Di Vaira, L. Messori, Inorg. Chim. Acta 355 (2003).