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HYDROFORMYLATION OF METHYL ACRYLATE USING A PALLADIUM SCHIFF BASE CATALYST UNDER SYNGAS SOURCE

D. Prakash[1], B. Pant[1] and P. Sagar[2]
[1]Department of Chemistry, Kumaun University Nainital, 263001, Uttarakhand, India
[2]Department of Chemistry, Soban Singh Jeena Campus Almora, Almora Univerity 263601, India
✉Corresponding Author: sagarpriyanka2006@gmail.com

Hydroformylation of methyl acrylate can be carried out in a short time and without the use of syngas under microwave dielectric heating. We show that a Palladium Schiff base catalyst can control regioselectivity in heterogenous hydroformylation. Microwave irradiation, which produces greater yields in less reaction time and uses less energy than conventional heating systems, may carry out the hydroformylation reactions of the Methyl acrylate with greater efficiency and sustainability without using the CO and H_2 cylinder. This method offers a hopeful prospect for a more sustainable future in chemical synthesis. Hydroformylation of Methyl acrylate using $(PdL_2)Cl_2$) (where L= N-(diphynylmethylide) Aniline (LA) and (E)-1-(2-methoxyphenyl)-N-phenylmethanimine (LB), as a catalyst at 120 °C for 20 minutes in the microwave and at 200 °C, 5 h in the conventional heating. This work demonstrates that methyl acrylates can be hydroformed in glyoxylic acid using a palladium catalyst system, producing the intended products, aldehydes, in outstanding yields and selectivities. Moreover, solventless synthesis using specific catalyst systems has improved catalytic performance compared to solvent-based reactions, attributed to higher reactant concentrations. Palladium complexes PdLA and PdLB gave excellent aldehyde yields in the microwave, 89 % (l/b ratio 96:4) and 86 % (95:5), respectively, over the conventional heating, which were analyzed by 1HNMR and GCMS spectroscopic techniques.

Keywords: Microwave Assisted, Methyl Acrylate, Glyoxylic acid, Alternative Source, Schiff base, Green Chemistry.
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INTRODUCTION

Alkenes are hydroformylated with carbon monoxide and hydrogen in the presence of a transition metal catalyst to produce aldehydes.[1,2] Otto Roelen developed the technique of hydroformylation in 1938.[3–7] When carbon dioxide and carbon monoxide are introduced to an alkene simultaneously, transition metal catalysts stimulate the formation of two new carbon-carbon and carbon-hydrogen bonds. Homogeneous catalytic hydroformylation eight has become one of the most widely used commercial procedures for producing over 10 million tonnes of oxo chemicals annually.[8-10] Hydroformylation reactions can be efficiently conducted under microwave dielectric heating, enabling rapid transformations without gaseous H_2 and CO.[11] This method allows for synthesizing various heterocycles from unsaturated alcohols, amines, and amides through domino hydroformylation cyclization reactions.[12,13] Conventional heating allows versatile hydroformylation but is substrate-sensitive. It's advantageous for specific reactions but may require longer times and yield substrate-dependent results.[14,15] The alkene is hydroformylated with palladium metal while being cooked in a microwave to avoid this laborious procedure. In comparison to the traditional heating method, the hydroformylation with microwave heating combination showed a number of advantages, such as a notable decrease in reaction time and temperature as well as sporadic increases in selectivity.[16–18]

The industrial application of the hydroformylation reaction is significant for synthesizing aldehydes from olefins using transition metal catalysts.[19] This process is widely employed due to its versatility in converting various alkenes into valuable aldehyde products. Researchers have explored different strategies to enhance the efficiency of hydroformylation reactions, such as utilizing novel catalytic systems, improving catalyst recyclability, and developing regioselective approaches.[20-22]

The hydroformylation reaction can occur in solventless conditions and various media, including benzene, hexane, and toluene. We also describe the palladium Schiff base as a precursor for hydroformylation

catalysts and the environmentally beneficial, solvent-free hydroformylation process.[23-27] Alternative sources for syngas in catalytic hydroformylation include using formaldehyde as a surrogate for syngas, known as asymmetric transfer hydroformylation.[28,29]

Furthermore, syngas can be derived from various sources like formic acid, methanol, methyl formate, and glyoxylic acid, which provide a sustainable and diverse range of feedstocks for hydroformylation processes.[30-31]These alternative syngas sources offer flexibility and potential environmental benefits in producing valuable compounds through catalytic hydroformylation reactions. The research paper addresses utilizing glyoxylic acid as a CO and H_2 source in solvent-free microwave-assisted hydroformylation, offering a safer and more efficient alternative to traditional syngas cylinders. Hydroformylation of methyl acrylate using Palladium Schiff base catalysts showed excellent regioselectivity and high yields with the glyoxylic acid as a source of the syngas under microwave dielectric heating.[32] Using specific catalyst systems in solventless synthesis improved catalytic performance compared to solvent-based reactions. Microwave-assisted hydroformylation reactions of methyl acrylate with PdLA and PdLB complexes yielded higher product yields in a shorter time than conventional methods.[33]

EXPERIMENTAL

Material and Methods

Palladium dichloride ($PdCl_2$. H_2O) was obtained from CDH (New Delhi, India), Aniline, 4- Amino phenol, 4-nitrobenzaldehyde, methyl acrylate, Butyl acrylate, and phenyl acrylate was procured from Sigma Aldrich (Mumbai, India). Sigma Aldrich (Bengaluru, India) received Glyoxylic acid, formaldehyde, formic acid, methyl formate, and DMF. Bruker Avance 400 or 600 MHz spectrometers recorded ^1H and ^{13}C NMR spectra at room temperature. Chemical changes are linked to the internal standard tetramethylsilane and reported in parts per million (ppm).[34]

Instrumentation

Utilizing Bruker 400 or 600 spectrometers, the ^1H- and ^{13}CNMR spectra of compounds in DMSO-d6 solutions were obtained; TMS was used as the internal standard for the ^1H-NMR experiments. A mass spectrometer called Sciex Esi was used to record electrospray mass spectra or ESMS. An FTIR-600 FTIR spectrometer and GCMS analysis using ethyl acetate as an internal standard were used to acquire FT-IR spectra as KBr discs in the 4000-400 cm^{-1} range. Quartz cells of (1.0) cm in length and a concentration of 10^{-3} mol L^{-1} of materials in DMSO were used to capture the electronic spectra at room temperature using a Shimadzu UV-Vis 1800 range of 11000–200 nm. Melting point measurements were made with an electrothermal Stuart instrument (type SMP40).

Preparation of N-(diphenyl methylidene)aniline (LA)

Aniline (15 ml, 0.1634 mol) and benzophenone (29.77 ml, 0.1634 mol) were dissolved in methanol (12 ml) in an equimolar ratio. The mixture was stirred occasionally and allowed to reflux for an hour. The most intriguing part was the color transformation, from a dark yellow to a surprising white after refluxing. Under low pressure, the resultant mixture was distilled. Isolated from the concentrated solution, N-(diphylmethylidene) aniline is a greenish-yellow crystal. These crystals underwent vacuum drying after being cleaned, recrystallized, and washed with methanol. The same method was used to generate a Ligand, (E)-1-(2-methoxyphenyl)-N-phenylmethanimine (LB), using the necessary anilines and aldehydes or ketones.

Preparation of "di-μ-chloro-bis(benzylideneaniline-)) Palladium (II) Complex

Palladium chloride (2.44 mmol; 0.4330 gm) and Schiff base (4.88 mmol; 0.8844 gm) were added dropwise to the methanolic solution while stirring continuously at 100 ºC in 15 milliliters of methanol. An extra hour was spent stirring the mixture once the LA had been completely integrated. The greenish-yellow precipitate of the subject chemical gradually became visible. Palladium complexes that were filtered were repeatedly washed with methanol. The chemical was then vacuum-dried. The second palladium complexes $[Pd_2(LB)_2Cl_2]$, {where LB = (E)-1-(2-methoxyphenyl)-N-phenylmethanimine, were prepared following the same procedure.

Characterization

N-(diphenylmethylidene)aniline (LA)

Yield: 80%, m.p.: 250°C decomp, color: greenish yellow. IR (KBr, ν_{max}, cm^{-1}) : 1682(C = C), 1784 (C = N), 1492 (C-N), 762, 724 (C-H benzene out of the plane), ^{1}H NMR (400MHz, $CDCl_3$)δ, ppm: 8.6(s, 1H),7.6 − 7.9(m, 5H),7.10 − 7.12 (m, 5H).

(E)-1-(2-methoxyphenyl)-N-phenylmethanimine (LB)

Yield: 80%, color: yellow; MS $\frac{m}{z(M^+)}$: 152.6. ^{1}H NMR (400MHz, DMSO, $CDCl_3$)δ8.97 (s,1H,CH=N), 8.24 − 8.18(dd, J = 7.9,1.8 Hz, 1H, Ar − H), 7.43-7.35 (ddd, J = 15.6,14.7,4.6 Hz, 3H, Ar − H),7.22 − 7.20 (m, 3H, Ar-H), 7.09 − 7.05(t, J = 7.12 Hz, 1H, Ar − H),7.04 − 6.97(d, J = 8.5 Hz, 1H, Ar − H), 3.92(s,3H,OCH_3).

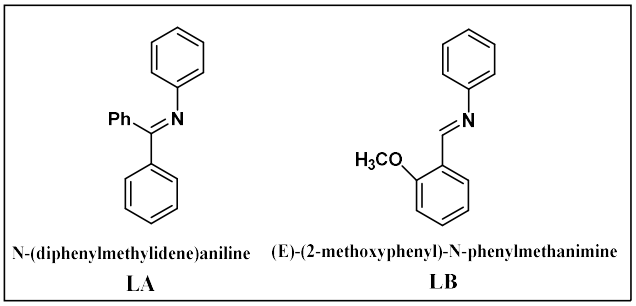


Fig.-1: Structure of the Schiff Base Ligands LA and LB

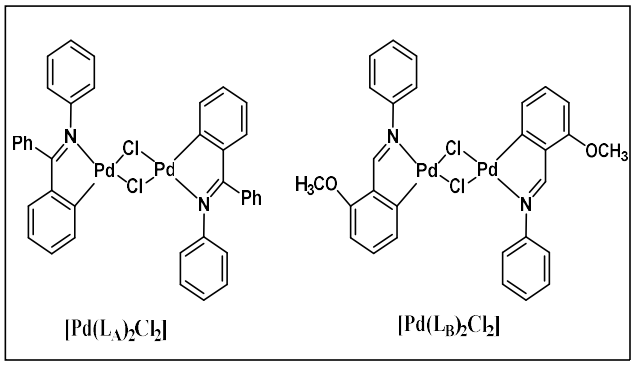


Fig.-2: Structure of the Palladium Complexes $[Pd_2(L_A)_2Cl_2]$ 1A and $[Pd_2(L_B)_2Cl_2]$ 1B

Hydroformylation Reaction in Conventional Heating

The 100 ml reaction flask was prepared for the hydroformylation of all the substrates in the glyoxylic acid medium by routinely purging and vacuum-pressurizing it with pure, dry nitrogen. The next step involved the use of conventional heating for hydroformylation. Before the glyoxylic acid-based palladium Schiff base complex catalyst solutions were added to the reaction flask, they bubbled for ten to fifteen minutes in dry, pure nitrogen. After adding the catalyst (0.004 g), 2 ml of substrate, 1-2 drops of DMF, and 10 ml of glyoxylic acid to the round bottle flask, shut off the apparatus. Position the tripod stand and the condenser within the round bottle flask. Maintaining the stand's stability and allowing heat to enter the Bunsen burner, completes the arrangement.

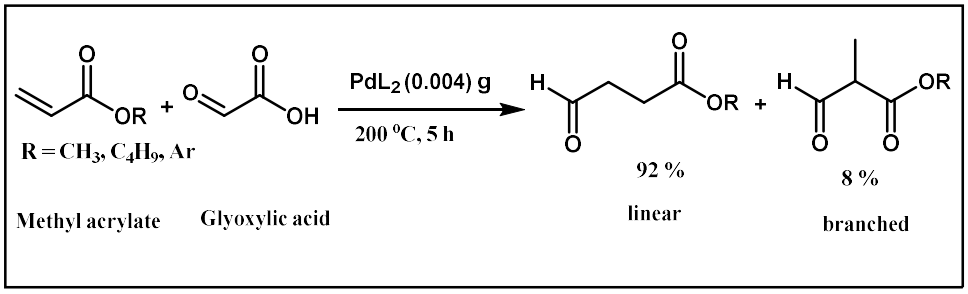
By agitating the reacting solution vigorously with a magnetic stirrer and submerging the flask in a silicon oil bath that was kept at a set temperature, the reaction's temperature was kept constant. The palladium catalyst solution turned green or greenish brown within the first five to ten minutes of being added. A color shift occurred during the response. To complete the process, the mixture was heated for five hours to 180–200 ºC. After separating the completed product into its component parts and calculating the required quantities, the product release assembly put the parts back together. Gas chromatography on an eight-fit 10% OV-17 column was used to analyze the reactants and products.. Methyl 2-methyl-3-oxopropanoate and Methyl 4-oxobutanoate products were the two aldehyde compounds that were detected by GCMS.

Hydroformylation Reaction in Microwave Heating

The catalyst can be dissolved by adding one drop of DMF and 0.0004 g of palladium catalyst to the reaction tube. This mixture was then given a good stir after 2 milliliters of glyoxylic acid was added. It was solvent-free, thus no solvent was added. In order to allow the glyoxylic acid to break down into hydrogen and carbon monoxide, now give the entire mixture a two to three-minute blast. The substrate (one milliliter of methyl acrylate) was added to the solution once the glyoxylic acid had dissolved, and the complete apparatus was microwave-heated for twenty minutes at 120 °C. NMR and GCMS analyses of the final product were conducted after the reaction was complete. After the GC/MS analysis of the crude reaction product, the peak at m/z 116 (methyl 4-oxobutanoate or an isomer) vanished. This was a promising sign of a successful reaction. The next step involved purifying the combination using column chromatography. Once purified, NMR was used to demonstrate the production of Methyl 4-oxobutanoate. The precision of the NMR analysis ensures the accuracy of the results, providing a high level of confidence in the outcome.

RESULTS AND DISCUSSION

A methyl acrylate's hydroformylation with glyoxylic acid depends critically on the ligand, as Table-1 illustrates. Consequently, we compared the aldehyde yield and regioselectivities under standard heating conditions using representative ligands such as N-(diphenylmethylidene) aniline (LA) and E-1-(2-methoxyphenyl)-N-phenylmethanimine (LB) (Fig.-1). Glyoxylic acid content stayed about 10 ml, according to an analysis of the aldehyde compounds produced during the hydroformylation of acrylate aided by the Pd/Schiff base. The generality of the reaction was examined when the reaction conditions were optimized. Table-1 illustrates that methyl acrylate exhibited reduced reactivity regardless of conventional heating. This produced the corresponding aldehydes in less than 40% of the samples, with linear solid regioselectivities (l/b = 89/11–92/5) (table 1, entries 1-6). Using 0.004 gm Pd/Schiff base as a catalyst precursor, we first used conventional heating to select hydroformylation of 2 ml of methyl acrylate with 10 ml of glyoxylic acid at 200 °C. After screening both Schiff base ligands, it was discovered that the ligand's characteristics significantly impacted the performance of the reaction, particularly regioselectivity (Table 1 entries 1-6). Even with a linear selectivity of 92:8, a reasonable yield of 39% of C1-elongated aldehyde could be achieved with complex PdLA (Table-1, entry 1). With a yield of 35%, butyl acrylate somewhat reduces the regioselectivity (Table-1, entry 2). Phenyl acrylate (entry 3) yields the lowest percentage (34%), with a l/n ratio of 89:11, under the same reaction conditions. Methyl acrylate, butyl acrylate, and phenyl acrylate give fewer aldehyde yields with PdLB in comparison to PdLA; these yields are entry 4, 36%, entry 5, 33%, and entry 6, 32%, respectively.

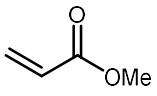
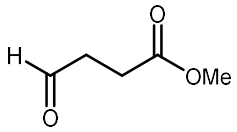
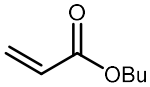
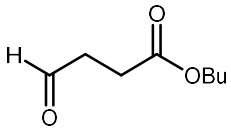
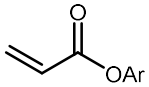
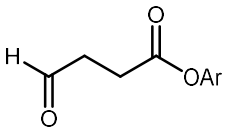
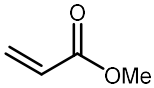
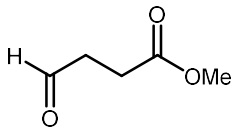
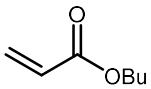
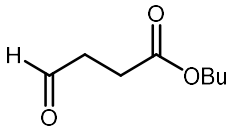
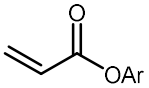
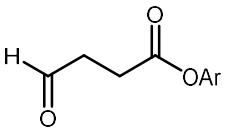


Scheme-1: Hydroformylation of Methyl Acrylate in Conventional Heating by Palladium Complexes

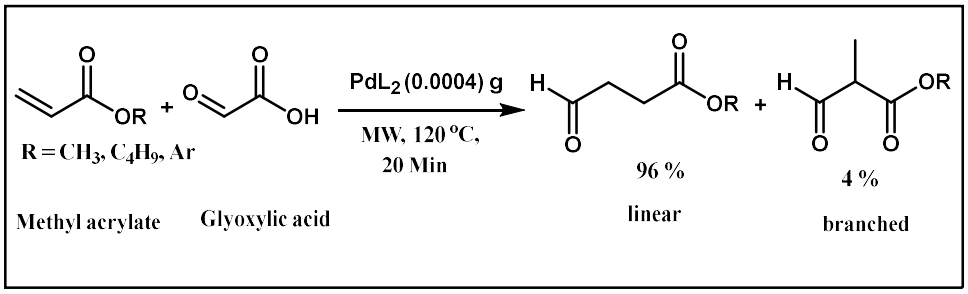
When methyl acrylate was hydroformylated, ligands LA and LB were examined (Table-2), and most demonstrated excellent branched to linear selectivity. Under these circumstances, N-(diphenyl methylidene)aniline (LA) and E-1-(2-methoxyphenyl)-N-phenylmethanimine (LB) both showed remarkable efficacy, resulting in a significantly improved conversion to linear aldehyde. N-(diphenylmethylidene)aniline (LA) has never before been used as a ligand in a hydroformylation reaction, and this outcome shows some potential for the novel catalytic system. Using Schiff base ligands, Pd-catalyzed hydroformylation of methyl acrylate under microwave in the presence of glyoxylic acid was first studied (Table-2). Regeneration of syngas could be achieved by breaking down glyoxylic acid. Aldehydes with a linear to branched ratio (l/b) of 94:6 were produced in 89% yield using the complex PdLA (Table-1, entry 1). An electron-donating group, such as MeO, in a Schiff base ligand resulted in somewhat less activity

or regioselectivity (entries 4-6). Higher concentrations of the aldehydes were obtained using the widely utilized ligands N-(diphenylmethylidene)aniline (LA) and E-1-(2-methoxyphenyl)-N-phenylmethanimine (LB), which are well known to facilitate highly regioselective hydroformylation. In neither case did hydrogenated byproducts form. An 86% aldehyde yield with a 95:5 l/b ratio was produced when the reaction was carried out using butyl acrylate (entry 2). Using phenyl acrylate resulted in a Good regioselectivity (94:6) and a reduced aldehyde yield (84%) (entry 3). It is important to note that PdLB catalytic performance is marginally less than PdLA, which produced yields and regioselectivities that were almost identical (85% with a ratio of 95:5). When employing the PdLB complex table 2, entries 4-6, the range of aldehyde product will obtain 85% to 81% with l/b (95:5) to 94/6. Methyl acrylate is more reactive towards hydroformylation than butyl acrylate and phenyl acrylate. This work shows that methyl acrylates undergo hydroformylation with high regioselectivity and excellent yield using both palladium catalyst systems. In contrast, the reaction of phenyl acrylate with Schiff base presence of $PdCl_2$ results in lower yields of the desired products. Additionally, complexes formed from $Co_2(CO)_8$ and specific phosphine ligands exhibit higher activity for the hydroformylation of methyl acrylate compared to other ligands; therefore, based on the research findings, methyl acrylate demonstrates greater reactivity towards hydroformylation compared to phenyl acrylate in both microwave and conventional method. In the same reaction carried out under "on Toluene" conditions, a decrease in the aldehyde yield with a ratio of 92:8 was noted (Table-3, entry 3). The "on toluene" hydroformylation of phenyl acrylate, catalyzed by palladium catalyst, shows a lower yield (71%) (Table-2, entry 4).

Table-1: Hydroformylation of Methyl Acrylate in conventional Heating with the Schiff Base Palladium Complexes (PdLA-PdLB)

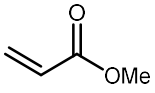
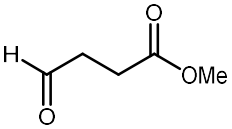
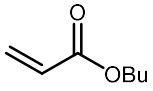
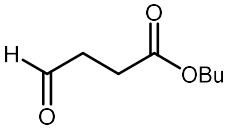
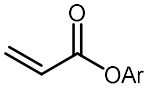
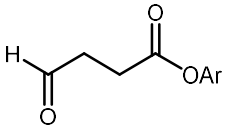
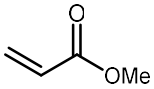
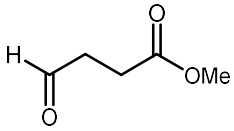
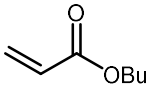
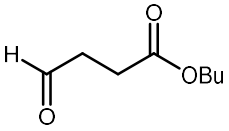
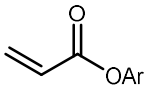
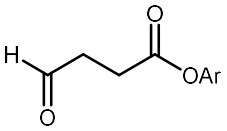
Entry	Cat.	Substrate	Main Product (%)	Yields(%)	l/b
1.	PdLA			39	92:8
2.	PdLA			35	90:10
3.	PdLA			34	89:11
4.	PdLB			36	90:10
5.	PdLB			33	89:11
6.	PdLB			35	88:12

Reaction Condition: Microwave heating, Temperature, 120 °C, time 20 min, Catalyst (0.0004 gm), Substrate 1 ml, Glyoxylic Acid, Product analyzed by ^{1}HNMR and GCMS.



Scheme-2: Hydroformylation of Methyl Acrylate in the Microwave Heating by Palladium Complexes

Table-2: Hydroformylation of Methyl Acrylate in Microwave Heating with the Schiff Base Palladium Complexes (PdLA-PdLB)

Entry	Cat.	Substrate	Main Product (%)	Yields(%)	l/b
1.	PdLA			89	96:4
2.	PdLA			86	95:5
3.	PdLA			84	94:6
4.	PdLB			85	95:5
5.	PdLB			83	94:6
6.	PdLB			81	94:6

Reaction Condition: Microwave heating, Temperature, 120 °C, time 20 min, Catalyst (0.0004 gm), Substrate 1 ml, Glyoxylic Acid, Product analyzed by ^{1}HNMR and GCMS

Consequently, the catalyst Pd/Schiff base employed in a glyoxylic acid medium enhanced regioselectivity towards the linear aldehyde. It should be emphasized that the conventional technique required around 5 hours for the same reaction, including a Pd/Schiff base catalyst. However, utilizing the palladium complexes, the microwave method only needed 20 minutes to convert methyl acrylate, utilizing the palladium complexes ultimately methyl acrylate. When the catalyst is insoluble in all solvents, the hydrophobic effect is substantially exhibited, which may account for the variation in reaction rate. In contrast, using the soluble catalyst increased the linear aldehyde's selectivity. After examining solventless and in-toluene reactions using a palladium Schiff base catalytic system (Table-3, entries 1, 2, 3, and 4), it

was determined that there are significant differences between the four systems and that the outcomes varied greatly.

Table-3: Hydroformylation Reaction of Acrylate with the Different Solvents

Entry	Substrate	Source of CO/H_2	Solvent	Yields (%)	l/b
1.	Methyl Acrylate	Glyoxylic Acid	-	89	94:6
2.	Phenyl Acrylate	Glyoxylic Acid	-	84	95:5
3.	Methyl Acrylate	Glyoxylic Acid	Toluene	72	92:8
4.	Phenyl Acrylate	Glyoxylic Acid	Toluene	71	91:9
5.	Methyl Acrylate	Glyoxylic Acid	Hexane	70	93:7
6.	Phenyl Acrylate	Glyoxylic Acid	Hexane	68	94:6
7.	Methyl Acrylate	Glyoxylic Acid	Benzene	72	94:6
8.	Phenyl Acrylate	Glyoxylic Acid	Benzene	69	92:8

Reaction Condition: Microwave heating, Temperature, 120 ºC, time 20 min, Catalyst (0.0004 gm), Solvent 2 ml, Substrate 1 ml, Glyoxylic Acid 1 ml, Product analyzed by ^{1}HNMR and GCMS

When the Pd/Schiff base catalytic system was used, the reaction occurred solventless and showed good selectivity for the formation of aldehydes. There are several benefits to carrying out hydroformylation operations without a solvent. Notably, high selectivities and conversions, a testament to the effectiveness of the solventless hydroformylation procedures, have been demonstrated.

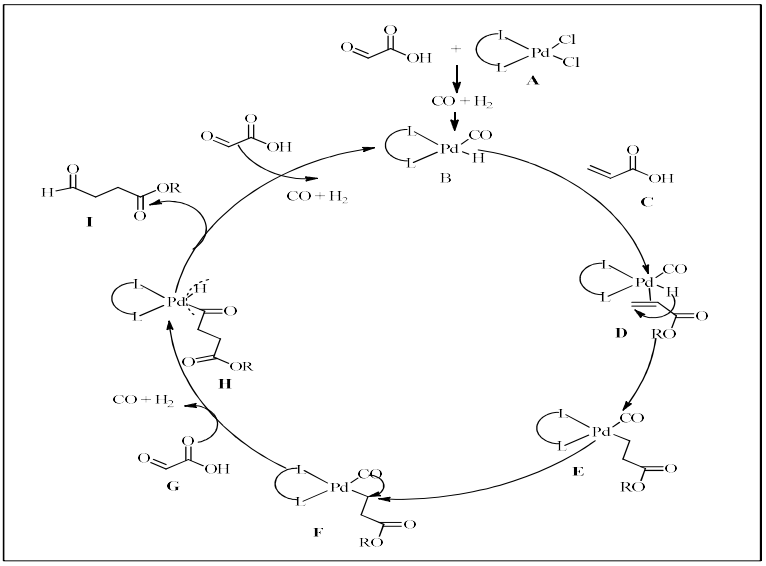
Table-4: Hydroformylation Reaction of Acrylate with Different Snygas Sources

Entry.	Substrate	Source of CO/H_2	Additive	Yields (%)	l/b
1.	Methyl Acrylate	Glyoxylic Acid	DMF	87	95:5
2.	Phenyl Acrylate	Glyoxylic Acid	DMF	85	94:6
3.	Methyl Acrylate	Methyl Formate	DMF	-	-
4.	Phenyl Acrylate	Methyl Formate	DMF	-	-
5.	Methyl Acrylate	Formaldehyde	DMF	-	-
6.	Phenyl Acrylate	Formaldehyde	DMF	-	-
7.	Methyl Acrylate	Methanol	DMF	-	-
8.	Methyl Acrylate	Methanol	DMF	-	-

Reaction Condition: Microwave heating, Temperature, 120 ºC, time 20 min, Catalyst (0.0004 gm), DMF (0.2 ml), Substrate 1 ml, Syngas source 2 ml, Product analyzed by ^{1}HNMR and GCMS

Using glyoxylic acid as the syngas surrogate, we have achieved an efficient and highly regioselective Pd-catalyzed hydroformylation of methyl acrylate. Very mild circumstances allow for easy handling of the reaction in the lab, with no need for extra caution about toxicity or reaction pressure (Schemes 1 and 2). Thus, in the presence of Schiff base ligands, methyl acrylate was subjected to a reaction with glyoxylic acid using a palladium catalyst (entry 1, Table 4), 20 minutes of heating at 120 °C resulted in an 87% yield conversion. Less than 7% of the branched aldehyde was found in the crude, according to the analysis (entries 2, Table-4). The same parameters were sadly not fulfilled while attempting to hydroformylate methyl and phenyl acrylate with methyl formate, formaldehyde, and methyl alcohol using palladium catalyst and DMF as partners (entries 3-8). Prior studies have demonstrated that alkene conversion can occur with high selectivity and yield when Rh(I) is combined with Biphep (for formalin breakdown) and Nixantphos (for hydroformylation) (Morimoto's conditions).[35] Our research, along with the work of Dmitry Gorbunov and coworkers, has opened up new possibilities for the field of hydroformylation. According to Gorbunov, methyl formate combined with water is another syngas source for the hydroformylation of unsaturated compounds with rhodium catalysts modified with phosphine ligands to produce aldehydes. Methyl formate degrades to produce carbon monoxide and methanol under specific reaction conditions.[36] There was a tube connecting the hydroformylation reaction involving styrene and the Wilkinson complex ($Rh(H)(CO)(PPh_3)_3$) to another reactor where the alcohols were degraded in the presence of the complex $[Ir(cod)Cl]_2$ and the BINAP ligand. Syngas sources include mannitol, xylitol, glycerol (which have aldehyde yields ranging from 54 to 83 %), and other polyols that can be generated through biomass processing.[37] It is worth noting that all the alternative syngas sources other than glyoxylic acid do not decompose into CO and H_2 under such conditions (Table-3, entries 3-8). Our research, in conjunction with these findings, has the potential to inspire further exploration and innovation in the field. Our proposed

chemical mechanism (Scheme 3) for the hydroformylation of methyl acrylate with glyoxylic acid significantly contributes to the field. In light of all of these findings, we suggest the following sequence of events. In the beginning, palladium complexes **A** break down glyoxylic acid to yield CO and H_2, which are easily coordinated with a catalyst. Pd-catalyzed microwaved hydroformylation proceeds without a hitch in the presence of H_2 and CO produced in situ. Based on our experimental findings, this proposed mechanism provides a comprehensive understanding of the reaction and paves the way for further research and development in the field.



Scheme-3: Cyclic Mechanism of the Hydroformylation Reaction by Palladium Catalyst

The sequential steps of the catalytic cycle are as follows: coordination of the alkene **D**, hydride transfer to produce the linear alkyl species **E**(as well as the isomeric branched one), coordination of CO and migratory CO insertion **F**, and finally, oxidative addition of H_2 **H** and reductive elimination of the aldehyde **I** to regenerate the active species **B**. Reductive removal of the aldehyde and simultaneous reformation of [PdL_2COH] constitute the final phase of the catalytic cycle. Bending the two Pd-H and Pd-acyl bonds in the direction of one another is the transition state of this stage.

With an estimated Pd----H---aldehyde distance of 2.008 Å, a stable intermediate **D may** be near a square pyramidal shape and interact weakly with the aldehydic hydrogen atom. Most of the transition states between the active computed species are represented by all the **D-H** intermediates in Scheme 3. Interestingly, the branched aldehyde could have a comparable catalytic cycle.

CONCLUSION

In this paper, we demonstrated that microwave irradiation, which produces greater yields in less reaction time and uses less energy than conventional heating systems, may be used to carry out the hydroformylation reactions of the Methyl acrylate with greater efficiency and sustainability. Furthermore, this ground-breaking discovery made possible the development of Palladium Schiff base catalytic systems that could primarily promote sequential hydroformylation in a microwave environment or external double-bond hydroformylation (with conventional heating). The comparison of product yields between conventional and microwave heating methods reveals significant advantages of microwave-assisted synthesis.[38] Studies show that microwave-assisted reactions generally result in higher yields (89 % and 86 %) in a shorter time than conventional methods (39 And 36%) with both PdLA and PdLB complexes, respectively. Here, we used different alternative syngas sources to hydroformylation methyl acrylate. Under normal reaction conditions, only glyoxylic acid decomposed into CO and H_2, while all other sources do not decompose; they are also good sources of the syngas for hydroformylation. Glyoxylic acid offers several advantages as an alternative syngas source for hydroformylation reactions. Firstly, it serves as an environmentally friendly and cost-effective substitute for toxic and gaseous CO, enhancing the sustainability of the process. Additionally, using glyoxylic acid in hydroformylation reactions can lead to the formation of industrially relevant

products in good to excellent yields, making it a practical choice for industrial applications. Palladium catalytic systems were used to explore the solventless hydroformylation of methyl acrylate. The primary benefit of the methods under study was the total removal of the organic solvent. We demonstrated that methyl acrylate can be hydroformylation extremely effectively in glyoxylic acid, producing the intended products, aldehydes, in outstanding yields and selectivities. Furthermore, our research revealed that solventless hydroformylation using specific catalyst systems has significantly improved catalytic performance compared to solvent-based reactions, attributed to higher reactant concentrations. This finding opens up intriguing possibilities for the future of chemical synthesis.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

D. Prakash http://orchid.org/0000-0002-4342-3674
B. Pant http://orchid.org/0000-0002-0709-7381
P. Sagar http://orchid.org/0000-0003-3584-1582

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