Scientific Journal for Publishing in Health Research and Technology

Volume 2, Issue 2, 2026, Pages: 102-113

Journal homepage: https://sjphrt.com.ly/index.php/sjphrt/en/index

Synthesis of some aliphatic amines using TEA-CO2 laser

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تخليق بعض الأمينات الأليفاتية باستخدام ليزر ***TEA-CO_2***

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Received: March 19, 2026	Accepted: April 11, 2026	Published: April 27, 2026

Abstract:

This study presents a catalyst-free approach for the synthesis of high-purity aliphatic amines via laser-induced alkylation of ammonia using a TEA-CO_2 laser in an optoacoustic cell. Infrared multiphoton absorption (IRMPA) enables the activation of ammonia and alcohol molecules, leading to the formation of reactive radical intermediates. Mass spectrometric analysis confirmed the formation of eight types of primary amines with high selectivity. The laser-driven process effectively suppresses the formation of secondary, tertiary, and quaternary amines, resulting in the preferential production of monoamines. The observed reaction behavior demonstrates that product yield and selectivity strongly depend on molecular structure and absorption characteristics. This study highlights the potential of laser-assisted synthesis as a clean and efficient alternative to conventional catalytic methods.

Keywords: TEA-CO_2 laser, alkylamine, mass spectrometric analysis, optoacoustic.

الملخص

تقدم هذه الدراسة منهجاً خالياً من المحفزات لتحضير أمينات أليفاتية عالية النقاوة، وذلك عبر عملية ألكلة الأمونيا المستحثة بالليزر باستخدام ليزر ثاني أكسيد الكربون النبضي (TEA-CO2) داخل خلية كهرومغناطيسية صوتية (Optoacoustic cell). يتيح الامتصاص متعدد الفوتونات للأشعة تحت الحمراء (IRMPA) تنشيط جزيئات الأمونيا والكحول، مما يؤدي إلى تكوين وسائط جذرية نشطة (reactive radical intermediates). وقد أكد تحليل طيف الكتلة تكون ثمانية أنواع من الأمينات الأولية بانتقائية عالية. وتعمل هذه العملية المدفوعة بالليزر بشكل فعال على كبح تكوين الأمينات الثانوية، والثالثية، والرباعية، مما ينتج عنه تفضيل في إنتاج الأمينات الأحادية (monoamines). ويوضح سلوك التفاعل المرصود أن محصول المنتج وانتقائيته يعتمدان بقوة على التركيب الجزيئي وخصائص الامتصاص. تسلط هذه الدراسة الضوء على إمكانات التصنيع بمساعدة الليزر كبديل نظيف وفعال للطرق التحفيزية التقليدية.

الكلمات المفتاحية: ليزر ثنائي اوكسيد الكاربون، الكيل أمين، تحليل مطيافية الكتلة، التقنية الصوتية الضوئية.

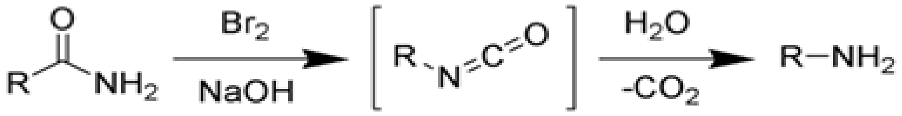
Introduction

Aliphatic amines belong to the essential intermediaries of the chemical industries. It is estimated that the annual production of amines worldwide is in the hundreds of thousands of tonnes. Methylamine production accounts for about half of this figure. Approximately 35 to 40 percent of the remaining half are ethyl amines [1]. The most significant consideration will be given to these two groups of amines. The following are some of the most important applications for methylamines and ethyl amines. Mono methylamine (MMA) is primarily utilized as an intermediary in synthesizing a variety of herbicides, pesticides, insecticides, and the solvent methyl-2-pyrrolidone and several medicines [2]. MEA is primarily used to make a variety of triazine herbicides by reacting it with cyanuric chloride and making plasticizers [3].

In 1909, the first report of the amination of alcohols in the gas phase was published [4]. Methylamines were first commercially produced in the 1920s for use in the tanning business for dehairing animal skins by the commercial solvents corporation in Terra Haute, Indiana [5]. The used and present processes are methanol gas and ammonia interactions with dehydrating catalysts (e.g., silica-alumina). The items are gathered and separated [1-8]. In the case of higher aliphatic amines, the catalytic hydrogenation and dehydrogenation properties have also become important [9].

Last four decades, many applications of laser photochemistry have been investigated [10]; one such application is that some chemical reactions are triggered by a multiphoton absorption process [11]. In 1982, Cong Meng Xiong reported on the organic synthesis of methylamine by multiphoton dissociation using the TEA_CO2 laser; Chen and Wang obtained mono-methylamine based on methanol and ammonia using a CW-CO2 laser, in which they demonstrated selectivity [12]. A successful synthesis of ethylamine with CW-CO2 laser was reported in 1988 [13]. The preparation of aliphatic amines can be carried out according to the following methods [14-16]:

The treatment of an amide with sodium hypobromite or sodium hypochlorite solution leads to producing an amine with one less carbon atom.

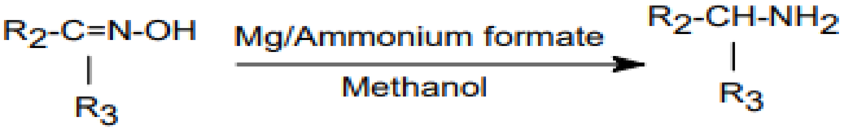


.............(1)

The reduction of nitriles with molten sodium and absolute ethyl alcohol.

$$CH_3(CH_2)_3CN \xrightarrow{\text{Ethanol / Na}} CH_3(CH_2)_3CH_2NH_2 \quad ....(2)$$

The reduction of oximes with Magnesium and methyl alcohol.



$$\begin{array}{c} R_2\text{-}C{=}N\text{-}OH \\ | \\ R_3 \end{array} \xrightarrow[\text{Methanol}]{\text{Mg/Ammonium formate}} \begin{array}{c} R_2\text{-}CH\text{-}NH_2 \\ | \\ R_3 \end{array} \quad ....(3)$$

The hydrolysis of di alkyl cyanamides with dilute sulfuric acid.

$$(C_4H_9)_2NCN + 2H_2O \xrightarrow{\text{sulphuric acid}} (C_4H_9)_2NH + CO_2 + NH_3 \quad ....(4)$$

This study concentrated on producing alkyl amines by irradiating ammonia and alcohols (as raw materials) using a TEA-CO2 laser. In addition, the optoacoustic technique has been used to study the absorption spectrum of ammonia and alcohols. This technique is also used to follow the dissociation process of the raw materials and the formation of amines.

2- Experimental

As shown in (Figure1), the irradiation system consists of LUMONICS TEA CO2 laser, tuned at 971.81 cm-1 (10R14 branch), at which ammonia and alcohols have a strong absorption band, where alcohols are methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, sec-butanol, tert-butanol, and cyclopentanone. The laser energy is 1 J for spectroscopic study and 3 j for the amination process with a 100-sec pulse duration. The laser beam is focused at the center of the optoacoustic cell with a 10 cm ZnSe lens. The spot size of the laser beam is about 5 mm, whereas the st. the st optoacoustic cell has 25 mm diameter and 200 mm length with NaCl window, the cell evacuated using a rotary vacuum pump.

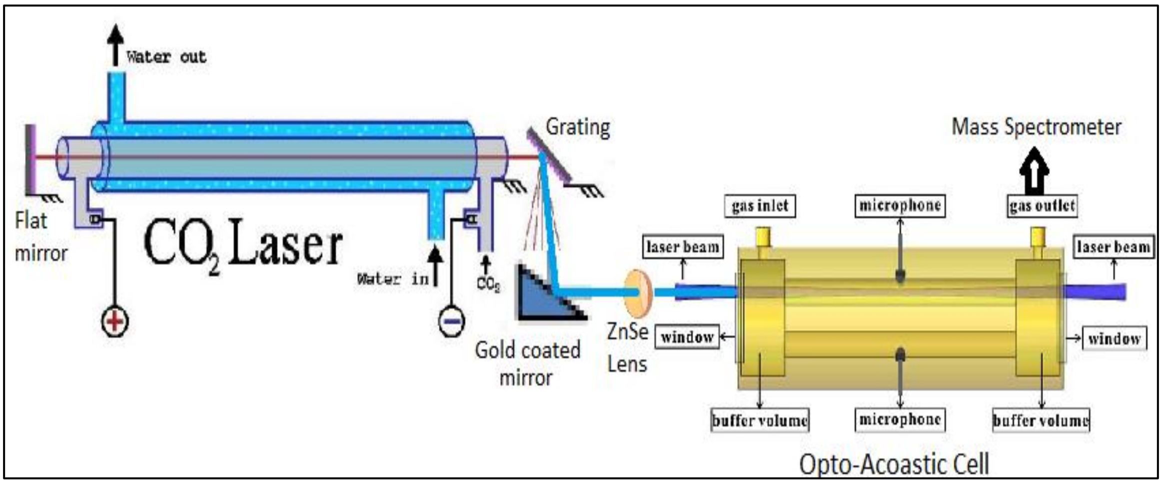


Fig. 1: Irradiation system for synthesizing aliphatic amines**.**

Multiphoton absorption was measured opto- acoustically; the microphone used for the optoacoustic measurements was a general radio model 1961-9611. Alcohol vapor and ammonia were mixed in a mixer connected to the cell. All experiments were carried out at a pressure of 5 bar. The partial pressure ratio of ammonia and alcohol was 1:1. Samples had been analyzed by mass spectrometry techniques before and immediately after irradiation using BALZERS QMG511 mass spectrometer.

3- Results and discussion

The advantage of the laser process in the preparation of alkyl amine from ammonia and alcohols is the elimination of byproducts: secondary, tertiary, and even quaternary amines.

3.1-Proposed Reaction Mechanism

The amination reaction proceeds via an infrared multiphoton absorption (IRMPA) mechanism induced by TEA-CO_2 laser irradiation. Both ammonia and alcohol molecules absorb laser energy at the selected wavelength (10R14), leading to vibrational excitation followed by dissociation into reactive radical species.

Alcohol molecules undergo photodissociation to generate alkyl radicals (R•) and hydroxyl radicals (•OH), while ammonia decomposes into amino radicals (NH_2•) and hydrogen atoms (H•). The recombination of alkyl radicals with amino radicals results in the formation of primary amines (RNH_2).

The formation of water molecules occurs through recombination of hydroxyl and hydrogen radicals, which also affects the absorption characteristics of the system. The absence of secondary and tertiary amines can be attributed to the short reaction time, selective excitation of reactants, and the low probability of further alkylation under the applied laser conditions.

This mechanism is consistent with the experimental observations and provides a rational explanation for the high selectivity toward primary amines under the applied laser conditions. The dominance of radical recombination pathways, combined with selective excitation and short interaction time, effectively suppresses further alkylation reactions.

Therefore, pure monoamine can be obtained without significant excess of ammonia or any catalyst except laser energy. An optoacoustic study was done to select the suitable laser line for the alkylation reactions of ammonia by alcohols. As it is known, primary alkyl amines absorb IR in the range of 9R and 9P bands, therefore these two bands are not suitable for the alkylation [17]. As shown in figures 2-10, we found that ammonia absorbs only 5, 3, 5, and 3 lines from the 9R, 9P, 10R, and 10P respectively. While the absorption lines of alcohol are more than that of ammonia.

$$ROH + NH_3 \xrightarrow[10R14]{TEA-CO_2\ laser} R^{\bullet} + NH_2^{\bullet} + H^{\bullet} + OH^{\bullet} \rightarrow RNH_2 + H_2O \ldots(5)$$

Proposed mechanism for TEA-CO_2 laser-induced amination of alcohols via IR multiphoton dissociation.

As mentioned above, there are eight absorption lines in the 10R and 10P branches, which are common between ammonia and alcohols; we select line 10R14 because the reactants have the strongest absorption at these lines compared to others. Mixtures of ammonia and alcohols show different behaviors when they react with CO2 laser.

Figure 11 shows the variation in optoacoustic signals with a number of pulses as a function of the dissociation rates of the reactants. In figure 11 methanol-ammonia system dissociated rapidly with about 195 pulses (15 min) to give methylamine, after another 130 pulses it seems to be stable because of the decrease in the absorbent amount substituted by the formation of water as shown in the reaction (6):

$$CH_3\text{-}OH + NH_3 \longrightarrow CH_3\text{-}NH_2 + H_2O \ldots\ldots\ldots\ldots (6)$$

Water is an excellent absorber to this line. It will absorb the same amount of laser photons that the irradiated reactants might be absorbed; this causes stability in the optoacoustic signal, and still, the water vapor condenses on the cooled surfaces in the reaction cell.

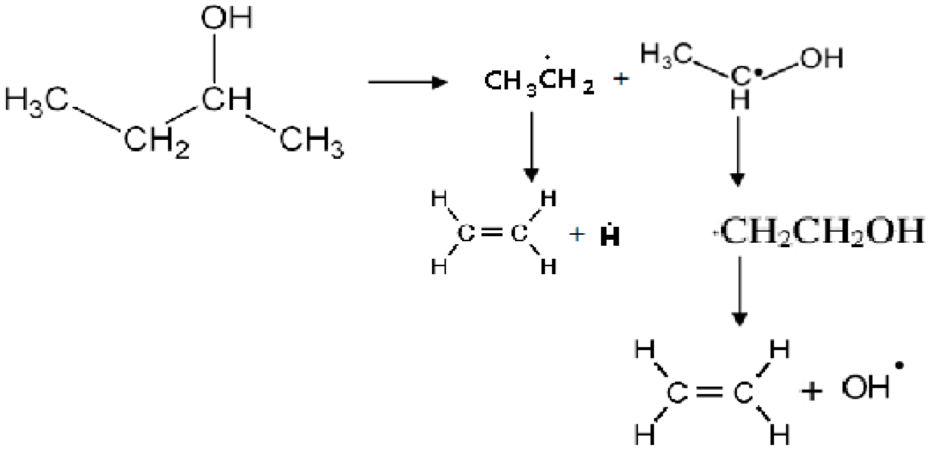
Figure 11 for the ethanol-ammonia system shows five stable stages in the dissociation curve. The same reason is that in the methanol-ammonia system, methanol and ethanol have nearly the same absorption coefficient as the line 10R14 of the CO2 laser. On the other hand, the increasing of the optoacoustic signal at the beginning of the dissociation curve was due to the formation of ethylene molecules (reaction (7) which appears in the mass spectrometry analysis of the product, ethylene has a higher absorption coefficient for the line 10R14 than ethanol [18].

$$CH_3\text{–}CH_2OH \rightarrow CH_2{=}CH_2 + H_2O \qquad \ldots\ldots\ldots\ldots (7)$$

After 500 pulses (40 min), ethylene formation will be less than the dissociation of ethanol to form a mine.

Figure 11 shows the dissociation of the 1-propanol-ammonia system and 2-propanol-ammonia system, respectively. They have no stable stage because the absorption coefficient of propanol is much higher than that of methanol and ethanol (figures 2-5). Therefore, there is a rapid decrease in the optoacoustic curves of the two systems.

We can see in the same figure the dissociation curve of the n-butanol-ammonia system, it behaves like a propanol-ammonia system, but the sec-butanol-ammonia system shows reversible behaviors compared with that of the n-butanol-ammonia system, this is due to the formation of a large number of ethylene molecules from the dissociation process of sec-butanol by irradiation:



……..(8)

The above reactions mean that one molecule of sec-butanol gives two molecules of ethylene: this will increase the amount of the absorbed photons, increasing the height of the optoacoustic signal.

Also, figure 11 shows the dissociation curve of the tert-butanol-ammonia system. It has a stable stage at the beginning of the curve, due to the formation of water. After that, the reactants dissociate rapidly to form the amine. The rapid production of amine caused by the (OH) position in the molecule gives the high possibility of dissociation process.

The cyclo-pentanol molecule. (OH) the group bonded to a carbon atom in the cycle, which gives it a very high possibility to dissociate. This appeared in the steep portion of the dissociation curve of the cyclo-pentanol-ammonia system in figure 11.

Reaction products of all systems were analyzed using mass spectrometry techniques. We found that all reactions gave only primary amines with different yields. We calculate the yield, by comparison, the ratio of the base peak in the mass spectrum of amine and alcohol before irradiation (B) to the ratio after irradiation (A).

Table 1: ratio of the base peak in the mass spectrum before and after irradiation**.**

System	A/B
Methanol-ammonia	2.0
Ethanol-ammonia	5.5
1-Propanol-ammonia	10.0
2-Propanol-ammonia	11.0
n-Butanol-ammonia	29.0
Sec-Butanol-ammonia	15.0
tert-Butanol-ammonia	2.4
Cyclo-Pentanol-ammonia	3.0

From table 1, we conclude that increasing the number of carbon atoms in the normal alcohols will increase the yield of amines, while circularization of the molecule decreases the yield.

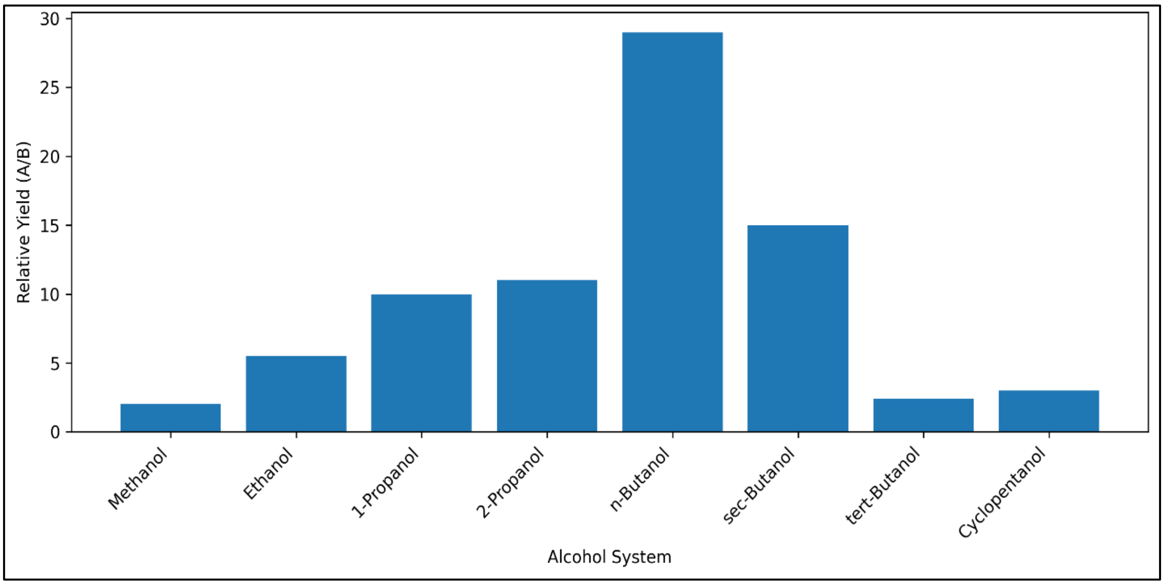


Figure 2. Variation of amine yield with alcohol structure (A/B ratio)

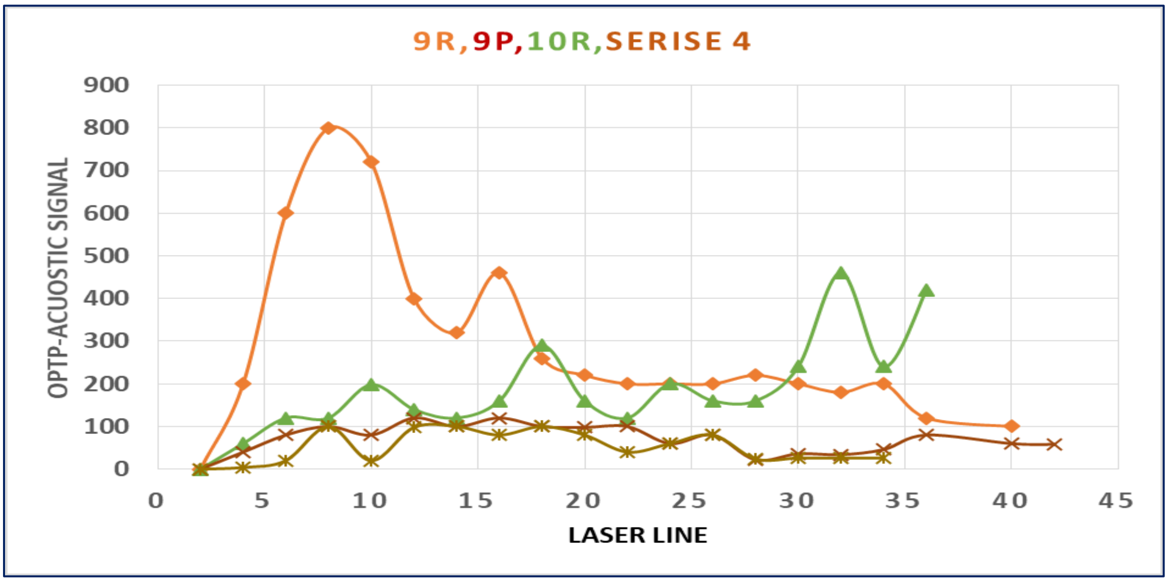


Fig. 3: Absorption spectrum of CO2 laser line by methanol using opto -acoustic technique.

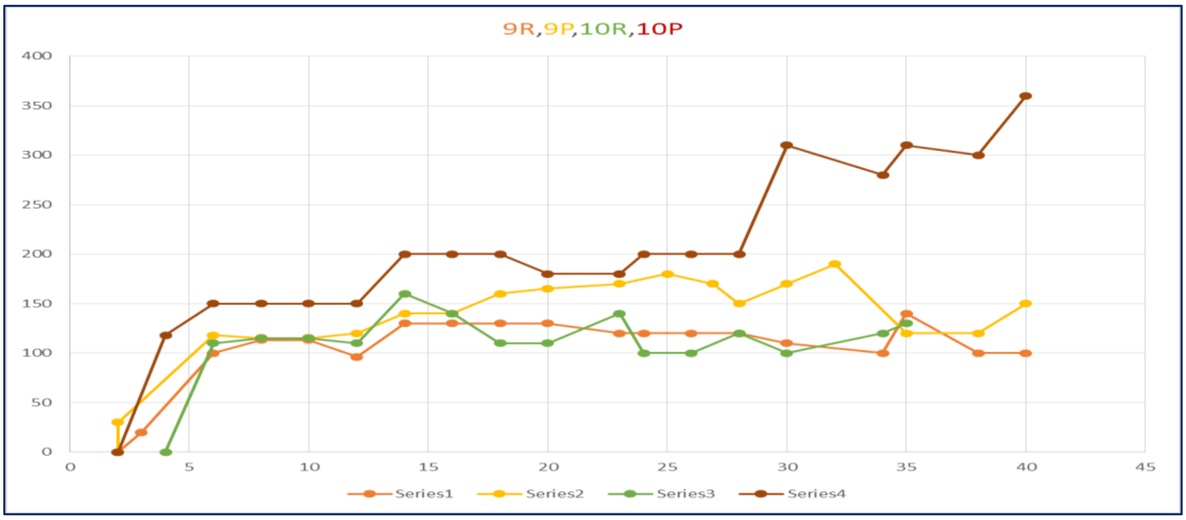


Fig. 4: Absorption spectrum of CO_2 laser line by ethanol

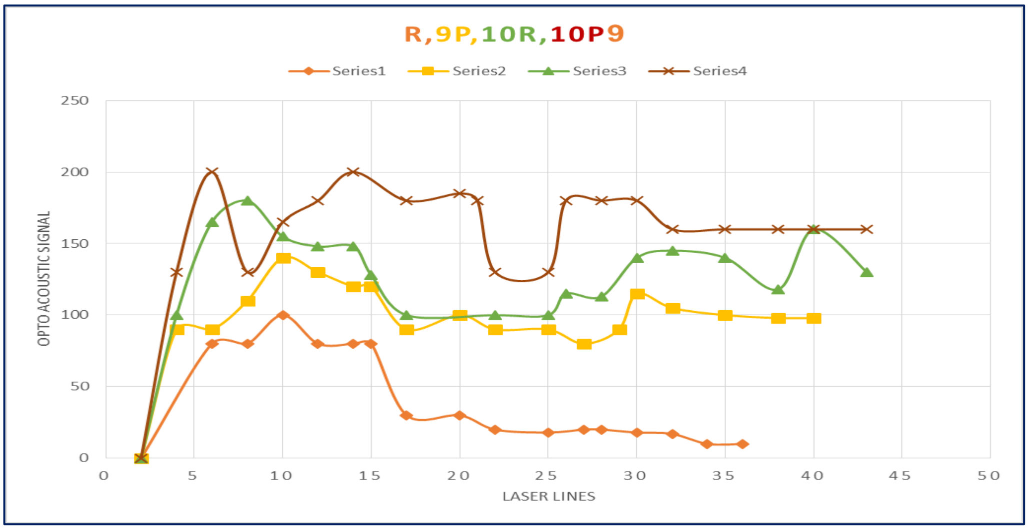


Fig 5. Absorption spectrum of CO_2 by 1-propanol by using opto-acoustic technique

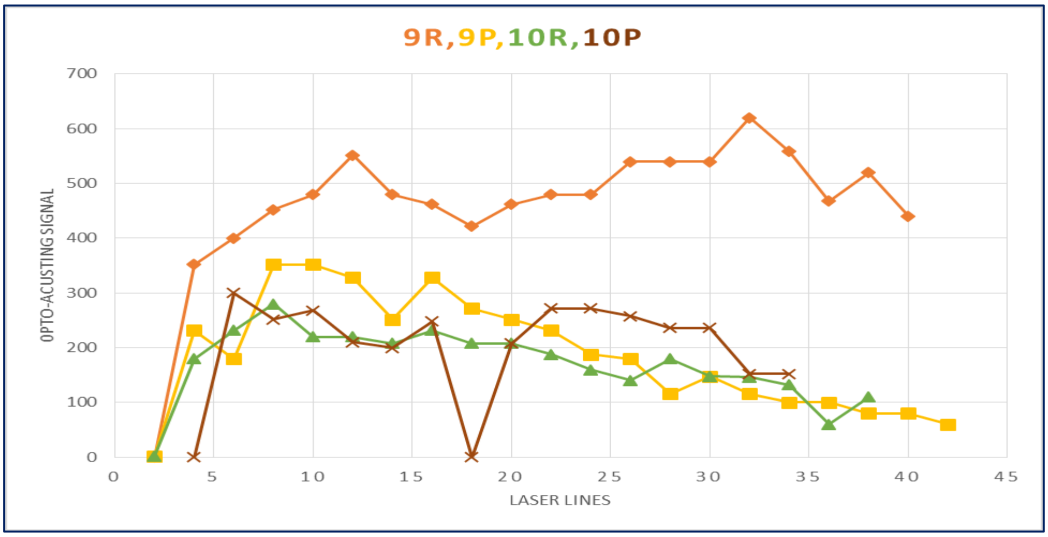


Fig. 6. Absorption spectrum of CO_2 laser lines by 2-propanol using optoacoustic technique

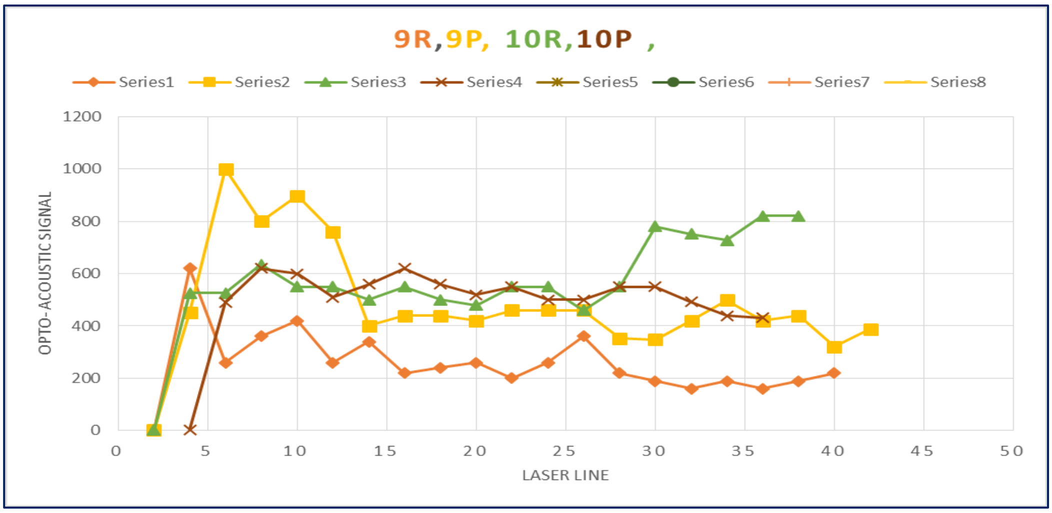


Fig. 7. Absorption spectrum of CO2 by 1-butanol by using opto-acoustic technique

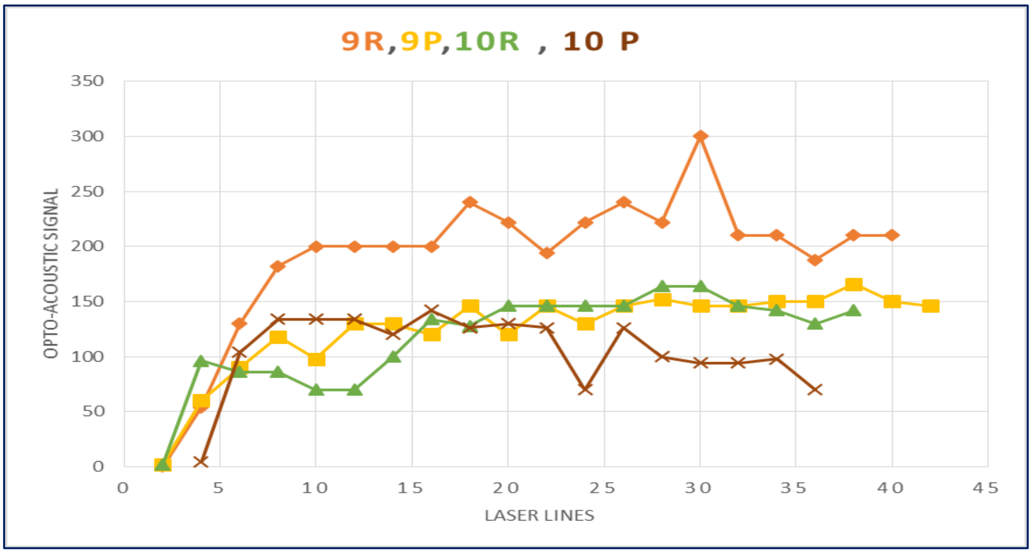


Fig 8: Absorption spectrum of CO2 laser lines by Sec-butanol using opto-acoustic technique

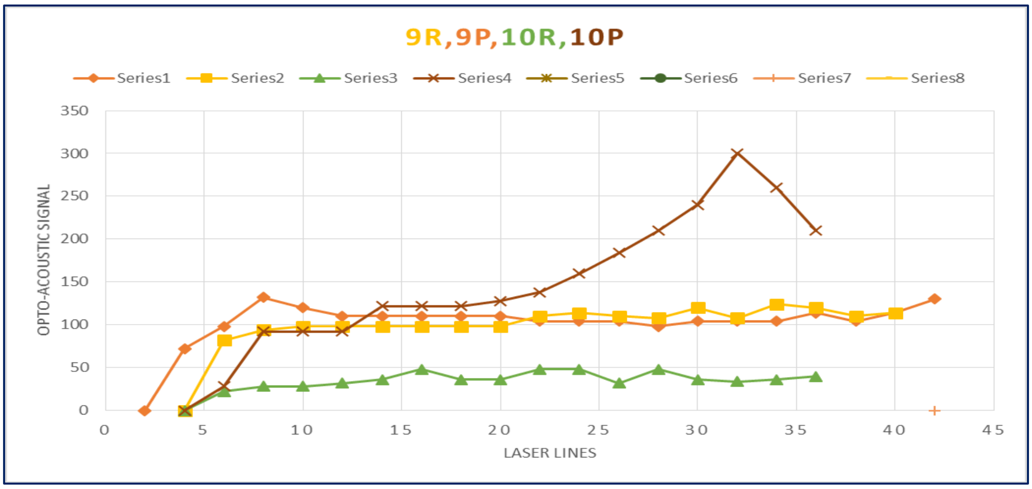


Fig 9: Absorption spectrum of CO$_2$ laser lines by Tert-butanol using opto-acoustic technique

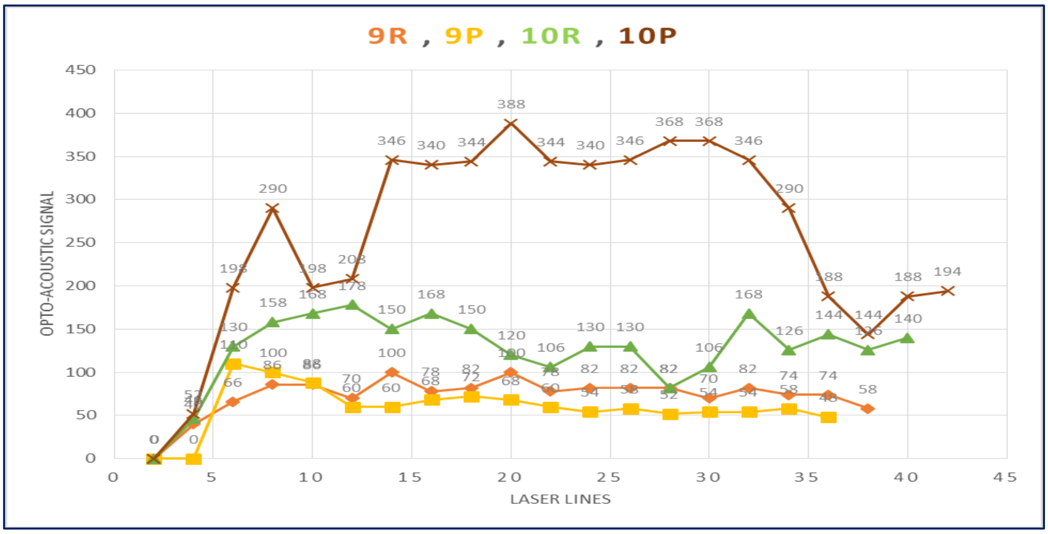


Fig 10: absorption spectrum of CO$_2$ laser lines by Cyclo-pentanol using optpacoustic technique

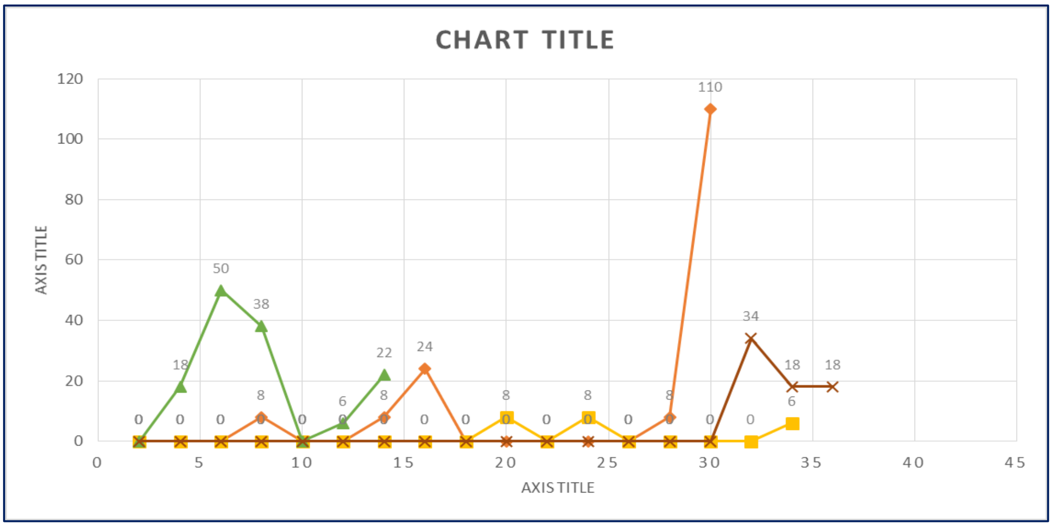


Fig 11: absorption spectrum of CO_2 laser lines by ammonia using opto-acoustic technique

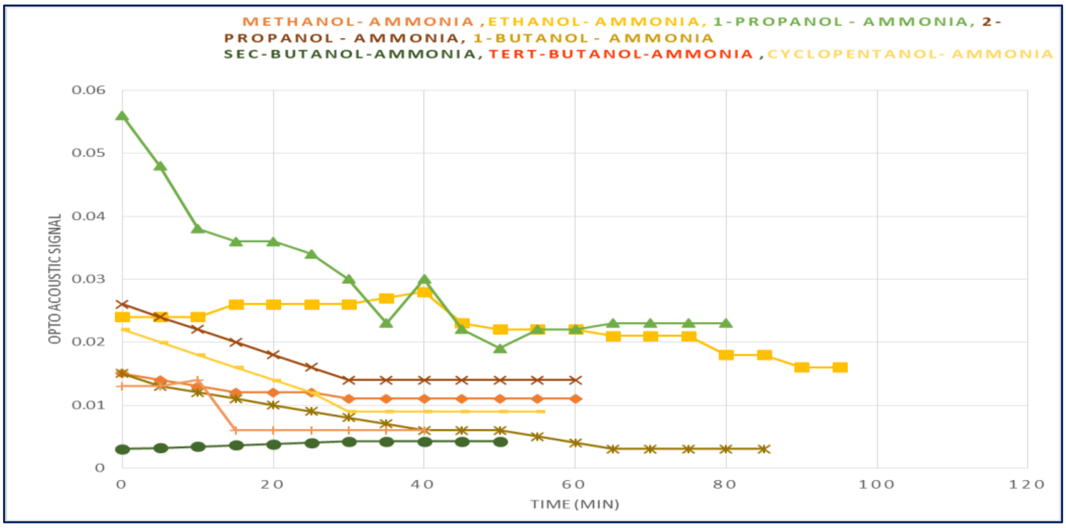


Fig 12: reaction curves of alcohols- ammonia systems with line 10R14 of TEA - CO_2 LASER

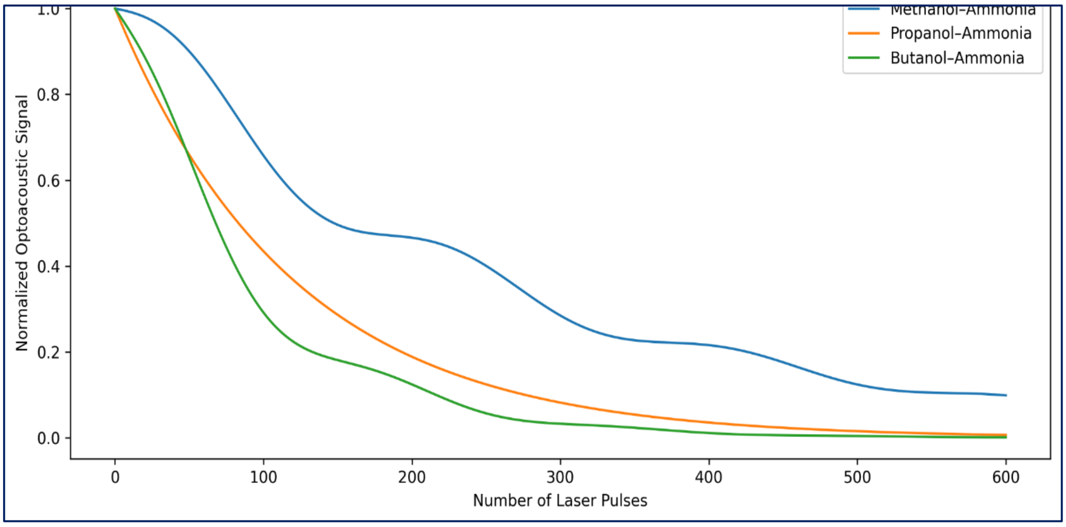


Figure 13: Representative dissociation behavior of alcohol–ammonia systems under TEA-CO_2 laser irradiation

3.2 Optoacoustic Analysis and Reaction Behavior

An optoacoustic study was conducted to determine the optimal laser line for initiating the amination reaction. It is known that primary alkyl amines absorb strongly in the 9R and 9P bands; therefore, these bands are not suitable for selective amination. Instead, the 10R14 line was selected due to its strong absorption by both ammonia and alcohols.

As shown in Figures 2–10, ammonia exhibits limited absorption lines compared to alcohols. However, several common absorption lines exist in the 10R and 10P branches, enabling simultaneous excitation of both reactants. The selection of the 10R14 line ensures efficient energy transfer and enhances reaction selectivity.

Figure 11 illustrates the variation of optoacoustic signals as a function of laser pulses, reflecting the dissociation kinetics of the reactants. The methanol–ammonia system shows rapid dissociation within approximately 195 pulses, followed by a stabilization stage. This behavior can be attributed to the formation of water, which strongly absorbs laser radiation and competes with reactants for photon absorption.

Similarly, the ethanol–ammonia system exhibits multiple stable stages due to comparable absorption coefficients of ethanol and methanol at the selected laser line. The initial increase in signal intensity is associated with the formation of ethylene, which possesses a higher absorption coefficient than ethanol.

In contrast, propanol systems (1-propanol and 2-propanol) show no stable stages and exhibit rapid signal decay. This behavior can be attributed to their higher absorption coefficients, which result in faster multiphoton dissociation rates.

The butanol systems demonstrate more complex behavior. The n-butanol system follows a trend similar to propanol, while the sec-butanol system exhibits partial reversibility due to enhanced ethylene formation. The increased formation of ethylene leads to higher photon absorption and a corresponding increase in optoacoustic signal intensity.

The tert-butanol system displays an initial stabilization stage due to water formation, followed by rapid dissociation. This behavior is attributed to the tertiary structure of the molecule, which facilitates bond cleavage under laser irradiation. The cyclopentanol system shows a steep dissociation curve, indicating a high susceptibility to laser-induced decomposition due to its cyclic structure.

These findings demonstrate that the dissociation behavior is strongly influenced by molecular structure and infrared absorption properties. The results highlight the superiority of IRMPA-driven processes over conventional catalytic systems in achieving selective amination under controlled conditions.

3.3 Product Analysis and Yield Interpretation

The reaction products were analyzed using mass spectrometry, confirming the formation of primary amines in all investigated systems. The relative yield was estimated using the ratio of base peak intensities before and after irradiation.

As shown in Table 1, the yield increases with increasing carbon chain length in normal alcohols. This trend can be attributed to the enhanced stability of larger alkyl radicals and their higher absorption cross-sections under infrared laser irradiation.

In contrast, cyclic alcohols exhibit lower yields, which can be attributed to structural constraints that limit efficient radical formation and recombination. Additionally, steric effects may hinder the interaction between reactive intermediates.

The proposed reaction mechanism provides a consistent explanation for the observed trends in product selectivity and yield. The dominance of radical recombination pathways, combined with the short residence time and selective excitation conditions, suppresses secondary reactions and favors the formation of monoamines.

Although mass spectrometry confirms the dominant formation of primary amines, further structural characterization using complementary techniques such as NMR spectroscopy is recommended to validate the purity of the synthesized products.

These observations are in strong agreement with the proposed radical-based reaction mechanism, further supporting the dominance of IRMPA-driven pathways.

4- Conclusion

In this study, a catalyst-free and selective method for the synthesis of primary aliphatic amines was successfully demonstrated using TEA-CO_2 laser irradiation. The application of infrared multiphoton absorption enabled efficient activation of ammonia and alcohol molecules, leading to the formation of reactive radical species and subsequent production of monoamines.

The proposed reaction mechanism provides a clear interpretation of the observed selectivity toward primary amines, highlighting the dominant role of radical recombination pathways and the suppression of secondary reactions. The absence of secondary and tertiary amines can be attributed to the short interaction time, selective excitation of reactants, and the low probability of further alkylation under the applied laser conditions.

The optoacoustic analysis confirmed that the choice of laser line (10R14) plays a crucial role in controlling the dissociation behavior of reactants. Variations in absorption coefficients among different alcohols significantly influence the reaction kinetics and product yield. In particular, higher aliphatic alcohols exhibited increased yields due to enhanced radical stability and stronger absorption characteristics, whereas cyclic structures showed comparatively lower efficiency.

The results demonstrate that laser-induced amination offers a clean, controllable, and efficient alternative to conventional catalytic processes, with the advantage of minimizing byproduct formation. This approach has potential applications in green chemistry and sustainable synthesis of amines.

However, further investigations involving quantitative analytical techniques such as gas chromatography and nuclear magnetic resonance spectroscopy are recommended to provide more precise evaluation of product yield and purity.

This study provides a promising platform for future research in laser-assisted organic synthesis, particularly for developing environmentally friendly and catalyst-free chemical processes.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no conflict of interest.

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